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Computing Newsletter No. 10 / Teaching Newsletter No. 3, November 2009

Teaching Addendum (A) to :

Age Concern

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(This issue's editor: Lachlan Cranswick)

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Following historical teaching material as a separate addendum PDF file to this issue

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Practical Aspects of Direct Phase Determination

(presented at the Erice School: Direct Methods for Solving Crystal Structures, 27 March to 9 April 1978)

by Isabella L. Karle

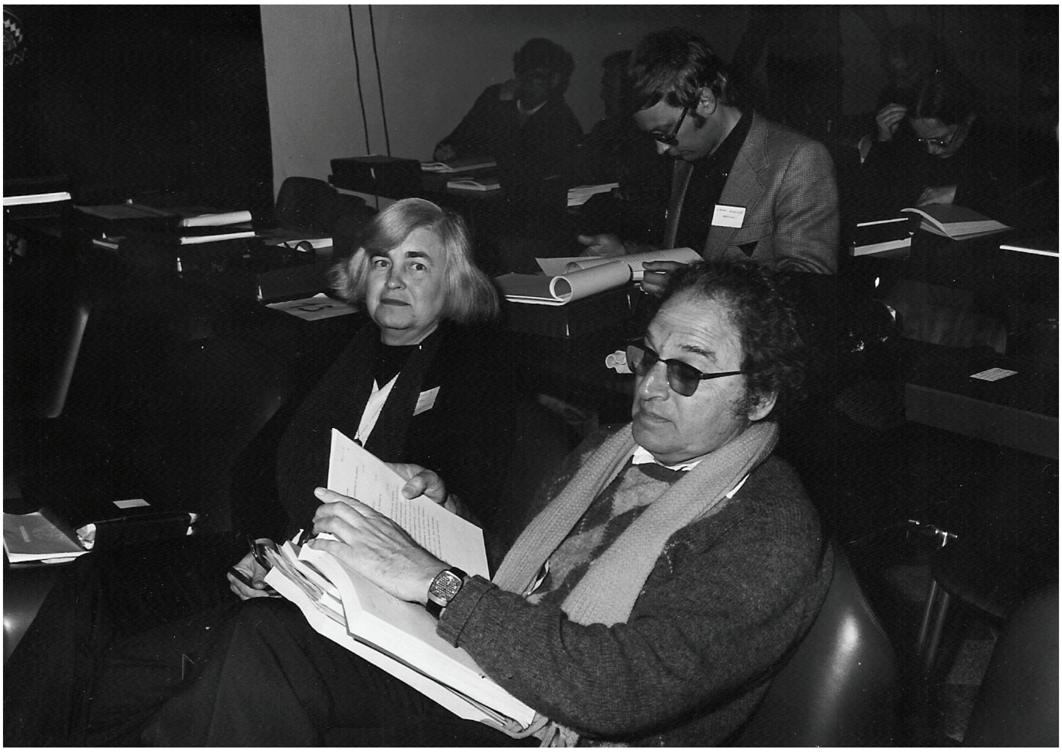

Fig. 1: *Isabella Karle and Herbert Hauptman at the Erice School: Direct Methods for Solving Crystal Structures, 27 March to 9 April 1978. Photo courtesy of Lodovico Riva.*

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XVII

PRACTICAL ASPECTS OF DIRECT PHASE DETERMINATION

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The structures of many hundreds of crystals containing only light atoms have been solved by direct phase determination. The required phases associated with the reflections obtained from x-ray diffraction of single crystals can be determined from a knowledge of the experimental structure factor magnitudes. The only requirement is that a sufficient number of data be available. Although a number of different relationships between phases and magnitudes have been derived, the most useful relationships for the practical solution of crystal structures are the following. For centrosymmetric crystals where all phases are either 0 or π, or equivalently the signs of the structure factors are either + or -, the $\sum_2$ formula applies (Karle and Hauptman, 1950; Hauptman and Karle, 1953),

$$s\,E_{\underset{\sim}{h}} \sim s\,E_{\underset{\sim}{k}}\,E_{\underset{\sim}{h}-\underset{\sim}{k}}\,, \tag{1}$$

or for several contributors,

$$s\,E_{\underset{\sim}{h}} \sim s\sum E_{\underset{\sim}{k}}\,E_{\underset{\sim}{h}-\underset{\sim}{k}}\,, \tag{2}$$

where the symbol s means the "the sign of", $E_{\underset{\sim}{h}}$ is a normalized structure factor and $\underset{\sim}{h} \equiv (h,k,l)$ is a vector whose components are the Miller indices. At the beginning of the phase determination, single terms, Eq. 1, determine the sign of $E_{\underset{\sim}{h}}$. As the phase determination progresses, more terms are available for determining the sign of a particular $E_{\underset{\sim}{h}}$. Since, initially, the process is dependent upon the sequential determination of phases, each step in the chain of events must be correct. In order to insure the greatest probability that a sign or phase is correct, the following expression for the probability that $E_{\mathbf{h}}$ is positive is used with Eq.(1) or (2) (Hauptman and Karle, 1953; Woolfson, 1954):

$$P_{+}(E_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{\sigma_3 \, |E_{\mathbf{h}}| \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}}{\sigma_2^{3/2}} \qquad (3)$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$, Z_j is the atomic number of the jth atom and N is the total number of atoms in the unit cell. The quantity $\sigma_3/\sigma_2^{3/2} = N^{-\frac{1}{2}}$ for an equal atom crystal. The larger the magnitudes of $E_{\mathbf{h}}$, $E_{\mathbf{k}}$ and $E_{\mathbf{h}-\mathbf{k}}$ are, the higher will be the probability of a correct sign assignment. Therefore, a phase determination should be initiated with reflections with the largest E magnitudes.

For noncentrosymmetric space groups where the phase of a structure factor, ϕ, can assume values from $-\pi$ to $+\pi$, the following phase relationships are most useful (Karle and Hauptman, 1950; Karle and Karle, 1964a; 1966):

$$\phi_{\mathbf{h}} \sim \langle \phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_r} \qquad (4)$$

(where $\mathbf{k}_r$ refers to a set of data restricted to the largest magnitudes) and (Karle and Hauptman, 1956)

$$\tan \phi_{\underset{\sim}{h}} = \frac{\sum_{\underset{\sim}{k}} E_{\underset{\sim}{k}} E_{\underset{\sim}{h}-\underset{\sim}{k}} \quad \sin(\phi_{\underset{\sim}{k}} + \phi_{\underset{\sim}{h}-\underset{\sim}{k}})}{\sum_{\underset{\sim}{k}} E_{\underset{\sim}{k}} E_{\underset{\sim}{h}-\underset{\sim}{k}} \quad \cos(\phi_{\underset{\sim}{k}} + \phi_{\underset{\sim}{h}-\underset{\sim}{k}})} \tag{5}$$

The variance associated with the determination of ϕ_h can be derived from a probability formula of Cochran (1955) and is given by (Karle and Karle, 1966)

$$V = \frac{\pi^2}{3} + \left[I_o(\alpha)\right]^{-1} \sum_{n=1}^{\infty} \frac{I_{2n}(\alpha)}{n^2} - 4\left[I_o(\alpha)\right]^{-1} \sum_{n=0}^{\infty} \frac{I_{2n+1}(\alpha)}{(2n+1)^2} \tag{6}$$

where

$$\alpha = \left\{ \left[\sum 2\sigma_3 \, \sigma_2^{-3/2} \left| E_{\underset{\sim}{h}} E_{\underset{\sim}{k}} E_{\underset{\sim}{h}-\underset{\sim}{k}} \right| \; \cos(\phi_{\underset{\sim}{k}} + \phi_{\underset{\sim}{h}-\underset{\sim}{k}}) \right]^2 + \left[\sum 2\sigma_3 \, \sigma_2^{-3/2} \left| E_{\underset{\sim}{h}} E_{\underset{\sim}{k}} E_{\underset{\sim}{h}-\underset{\sim}{k}} \right| \; \sin(\phi_{\underset{\sim}{k}} + \phi_{\underset{\sim}{h}-\underset{\sim}{k}}) \right]^2 \right\}^{1/2} . \tag{7}$$

The I_n are Bessel functions of imaginary argument. The variance as a function of α is shown in Fig. 1. For noncentrosymmetric space groups, the larger magnitudes of E lead to smaller variances of the determined phases, a situation comparable to the higher reliability of sign determination associated with the larger magnitudes of E, in centrosymmetric crystals.

In addition to Eqs.(1), (2), ~~(4) and~~ (5), several other phase relationships are useful at times. Examples are the $\sum_1$, $\sum_3$ and $B_{3,0}$ formulas (Karle and Hauptman, 1958; Karle, 1970) and are often referred to as auxiliary formulas. The $\sum_1$ and $\sum_3$ formulas

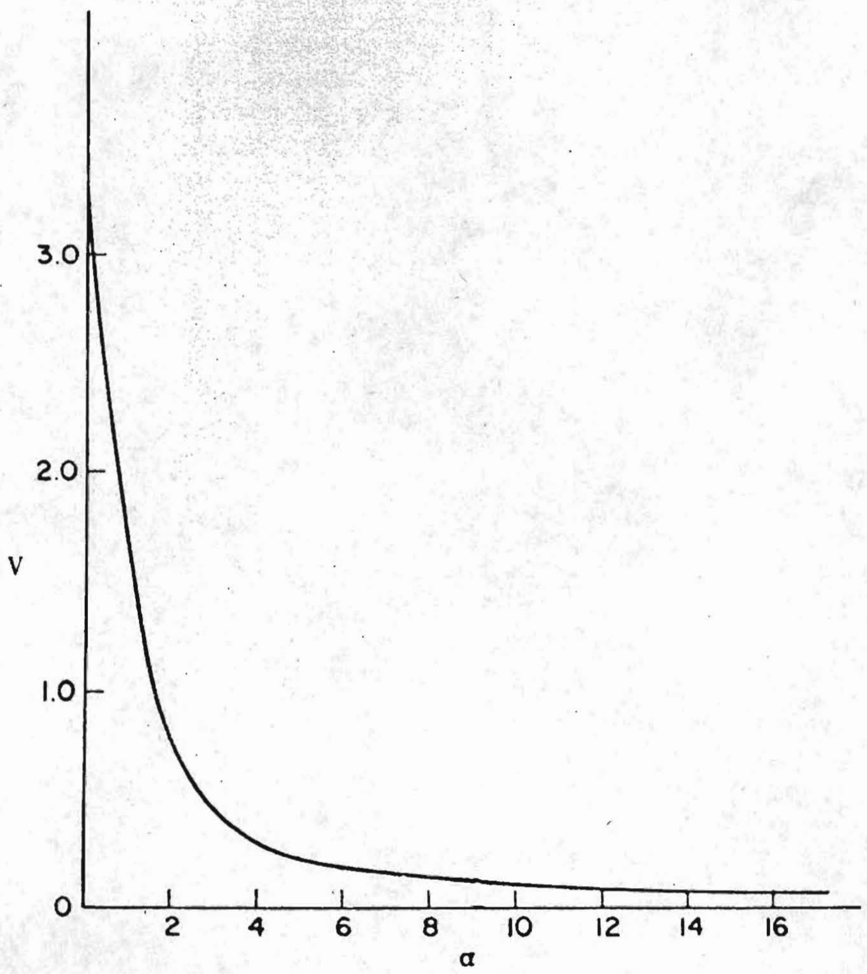


Fig. 1. Curve showing the variance, V (in radians squared), of a phase angle determined from known values of other phase angles. The variance is expressed as a function of α (Karle and Karle, 1966).

(Hauptman and Karle, 1953) are space group dependent and will be illustrated in the examples for particular space groups.

The normalized structure factors $E_{\underset{\sim}{h}}$ are defined by (Hauptman and Karle, 1953)

$$E_{\underset{\sim}{h}} = F_{\underset{\sim}{h}} \Big/ \left(\varepsilon \sum_{j=1}^{N} f_{j\underset{\sim}{h}}^{2} \right)^{\frac{1}{2}} \qquad (8)$$

where $f_{j\underset{\sim}{h}}$ is the scattering factor for the jth atom, N is the total number of atoms in a unit cell, and ε is a small integer that is space group dependent (see e.g. Karle, 1969). If, for example, we were to start with the observed magnitudes, $|F_{\underset{\sim}{h}}|_{obs}$, for the structure factors where

$$F_{\underset{\sim}{h}\,obs} = \sum_{j=1}^{N} f_{j\underset{\sim}{h}} \, e^{-B_j s^2} \exp(2\Pi i \underset{\sim}{h} \cdot \underset{\sim}{r}_j) \quad , \qquad (9)$$

by use of a data reduction procedure to be described below we obtain through (8) a set of normalized structure factor magnitudes $|E_{\underset{\sim}{h}}|$ where

$$E_{\underset{\sim}{h}} \simeq \frac{1}{(\varepsilon \sum_{j} Z_j^2)^{\frac{1}{2}}} \sum_{j=1}^{N} Z_j \exp(2\Pi i \underset{\sim}{h} \cdot \underset{\sim}{r}_j) \quad . \qquad (10)$$

and Z_j is the atomic number of the jth atom. Note that the effect of vibrational motion is eliminated in the procedure for obtaining the $|E|$ values. Furthermore, the $E_{\underset{\sim}{h}}$ are independent of scattering angle since each $f_{j\underset{\sim}{h}}$ that varies with $\sin\Theta/\lambda$ is replaced with a constant $Z_j/(\varepsilon \sum Z_j^2)^{\frac{1}{2}}$. To see why this is approximately so, it may be assumed that the atomic scattering factors for all atoms involved have essentially the same shape, so that $f_{j\underset{\sim}{h}} \simeq Z_j f_{\underset{\sim}{h}}$ where $f_{\underset{\sim}{h}}$ is a shape factor. Employing Eq.(8) yields the factor $f_{j\underset{\sim}{h}} / (\varepsilon \sum_j f^2_{j\underset{\sim}{h}})^{\frac{1}{2}} = Z_j f_{\underset{\sim}{h}} / (\varepsilon \sum_j Z_j^2 f_{\underset{\sim}{h}}^2)^{\frac{1}{2}} = Z_j / (\varepsilon \sum_j Z_j^2)^{\frac{1}{2}}$. This operation, in addition to the elimination of the vibrational factor in Eq.(9), accounts for the form of Eq.(10). We therefore may conclude from Eq.(10) that the normalized structure factors represent to a good approximation scattering from stationary point atoms. For equal atom structures, this is exactly true.

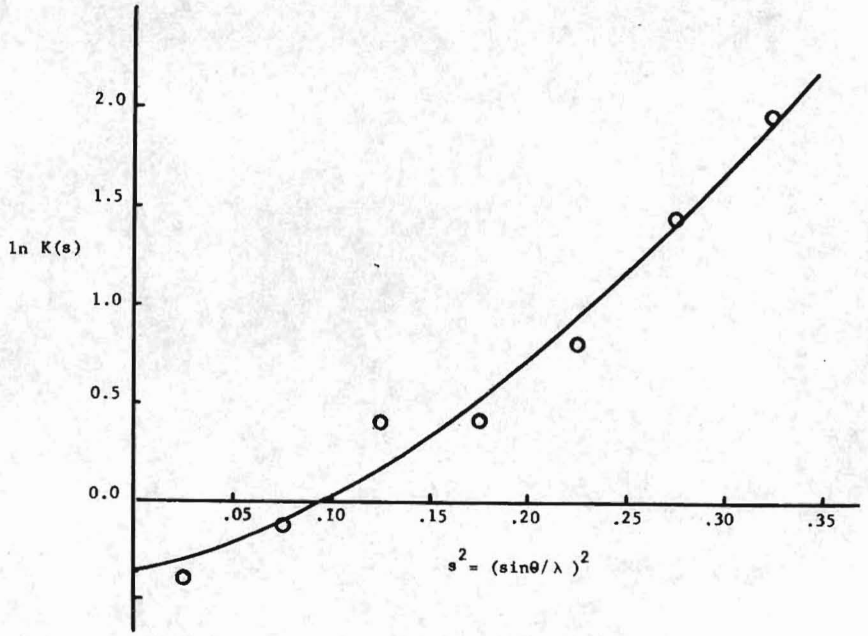
$|E_{\underset{\sim}{h}}|^2$ values are obtained from the observed intensities, I_{obs}, corrected for Lorentz and polarization factors, in two steps. First the observed intensities are corrected for the effects of thermal motion and are placed on an absolute scale by means of a K-curve. The K-curve is constructed by dividing the range of s^2 (where $s = \sin\theta/\lambda$) into a number of equal segments. For the midpoint of each interval of s^2, the value of K is computed where

$$K(s_{mid}) = \frac{\sum \varepsilon \sum_{j=1}^{N} f_j^2(s)}{\sum I_{obs}(s)} \tag{11}$$

and the sum is made over all the I_{obs} occurring in the particular interval and also over the values of the scattering factors f_j occurring in that same interval. Figure 2 shows a typical K-curve for data from an organic compound. In the example, each interval of s^2 contains 200-300 data. A least-squares procedure is used to fit a best smooth analytic function to the experimental points. Usually the function used is $K = \exp(A + Bs^c)$

Fig. 2. K-curve for the observed data from a cyclic tetrapeptide

$$\ln K = A + Bs^{c} = -0.35 + 12.23s^{3}$$



or $\ln K = A + Bs^c$. If the exponent $\underline{c}$ is 2.0, then the expression is the same as Wilson's curve (1942). For crystals of many organic materials, such as the one illustrated in Fig. 2, the exponent $\underline{c}$ is > 2.0. It is important to fit the K-curve well in order to obtain meaningful $|E|$ values. The $|F_h|^2$ corrected for scale and thermal motion are obtained from

$$I_{obs}(s)K(s) = |F_h|^2 \tag{12}$$

and expression (8) is used to calculate the $|E_h|^2$.

The normalized structure factors $|E_h|$ have definite statistical properties, independent of chemical composition, which are useful in distinguishing between centrosymmetric and noncentrosymmetric space groups (see e.g. Karle, 1969). Some of these properties are associated with various averages: e.g.

Average	Centric	Acentric
$\langle \lvert E_{\underset{\sim}{h}}\rvert^2 \rangle$	1.0	1.0
$\langle \lvert E_{\underset{\sim}{h}}\rvert \rangle$	0.798	0.886
$\langle \lvert \lvert E_{\underset{\sim}{h}}^2\rvert -1\rvert \rangle$	0.968	0.736

For acentric space groups, the reflections should be divided into two groups: Those structure factors which are real or pure imaginary, as determined by the space group symmetry, have averages corresponding to the centrosymmetric case. The remainder of the structure factors having general values for the phases have averages corresponding to the acentric case. Other properties are associated with the distribution of $|E_{\underset{\sim}{h}}|$ values:

	Centric	Acentric
$\|E_{\underset{\smile}{h}}\| > 1$	32%	37%
$\|E_{\underset{\smile}{h}}\| > 2$	5%	2%
$\|E_{\underset{\smile}{h}}\| > 3$	0.3%	0.1%

Experimental values are found to be close to the theoretical values.

Details for phase determination in several commonly occurring space groups will be presented now.

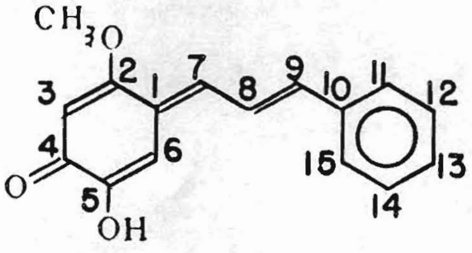
Space Group $P2_1/a$

Phase determination in centrosymmetric space groups is quite routine. The first example will illustrate the complete phase determination for obtusaquinone, crystallizing in space group $P2_1/a$ (Karle, 1975). Tables 1-8 contain the reflection data, details of phase determination and the structure. The statistical averages in Table 3 show that the theoretical value for $\langle |E| \rangle$ for centrosymmetric crystals, is lower than the theoretical value for noncentrosymmetric crystals and that the experimental value is even lower. Conversely, the theoretical value for $\langle ||E|^2-1| \rangle$ is higher for centrosymmetric crystals than for the noncentrosymmetric case, and that the experimental value is even higher. The deviations of the experimental values from ideal values for centrosymmetric crystals indicate a hypercentering in the cell. And indeed, the structure analysis shows that the two independent molecules in the asymmetric unit are nearly related by a non-crystallographic center.

The $\sum_2$ relationship, formulas (1) and (2), requires that some

Table 1. OBTUSAQUINONE

Karle, Bultman and Jurd,
Acta Cryst. B32, 1963(1976).



Two molecules plus solvent  in asymmetric unit ≡ 44 carbon and oxygen atoms in asymmetric unit.

Space group $P2_1/a$

a = 19.66 A, b = 9.72 A, c = 16.52 A, β = 97.8°

Table 2. Listing of strongest |E| for obtusaquinone

G	G	G	|E|	U	G	G	|E|	G	U	G	|E|	U	U	G	|E|
4	0	-4	7,0888	11	-2	10	3,5230	16	-1	4	3,7969	5	-1	6	3,7900
10	-6	2	4,2796	11	-6	2	3,3382	8	-7	0	3,1062	1	-5	0	3,5887
6	-6	6	4,1713	9	-6	4	3,1909	2	-3	-10	3,0801	5	-5	-4	3,5614
8	0	-8	3,8950	7	-2	12	3,1767	4	-1	-4	2,9339	9	-1	2	3,3967
4	-6	6	3,6798	7	-8	2	2,7777	4	-7	4	2,8406	5	-7	2	2,9090
10	-6	4	3,6361	7	-6	6	2,6951	6	-3	4	2,8178	9	-7	-2	2,8456
8	-2	10	3,5986	5	-8	4	2,6449	10	-7	-2	2,7746	3	-3	4	2,4929
8	0	10	3,3057	5	-6	8	2,5753	6	-1	-8	2,5936	1	-3	-8	2,3933
4	-8	4	3,2292	3	-2	0	2,3529	10	-3	0	2,4164	11	-1	4	2,3634
8	-6	2	3,1750	11	-6	0	2,2937	2	-1	-10	2,3159	15	-1	6	2,2572
4	0	14	2,9968	13	-6	0	2,2411	6	-7	2	2,3052	1	-1	10	2,1277
6	0	-2	2,9938	1	-2	8	2,0786	2	-3	6	2,2203	13	-1	-2	2,0618
0	-6	10	2,7284	9	-2	10	1,9953	12	-1	-10	2,1821	3	-5	-4	2,0014
6	-6	8	2,6775	3	-4	6	1,9378	6	-3	0	2,1649	1	-5	-4	1,9939
8	0	-6	2,6416	1	-2	-4	1,9272	4	-1	-2	2,1642	7	-3	0	1,9637
2	-6	10	2,5815	5	-2	4	1,8563	14	-1	6	2,1357	11	-7	0	1,8548
0	-2	0	2,5571	1	-8	6	1,8422	12	-3	8	2,0522	5	-7	-2	1,8002
12	0	-12	2,4449	1	-8	-6	1,8404	10	-7	-4	1,9664	11	-3	-4	1,7420
6	-8	2	2,4438	11	-2	8	1,8402	2	-3	4	1,9219	15	-1	4	1,7132
2	0	-4	2,3477	15	-2	4	1,8302	6	-3	2	1,8798	7	-7	6	1,7026
2	-8	-6	2,3446	5	-6	-4	1,7418	2	-5	-2	1,8762	9	-5	-8	1,7016
12	-6	0	2,3389	1	-6	0	1,7209	10	-1	-12	1,8283	15	-1	0	1,6522
12	-2	6	2,3297	7	-2	-4	1,6712	2	-1	-4	1,7970	1	-7	6	1,6317
12	-6	-2	2,3199	3	-6	-4	1,6501	12	-1	8	1,7968	3	-7	0	1,5747
4	-4	-4	2,1999	1	-8	4	1,6422	14	-3	6	1,7696	5	-3	0	1,5356
8	-6	4	2,0903	7	-6	4	1,6240	0	-1	6	1,7636	1	-7	-4	1,5321
16	-2	2	1,9520	3	-2	-2	1,5731	10	-1	-6	1,7233	1	-3	6	1,5038
2	-8	6	1,8811	1	-4	8	1,5462	10	-3	10	1,7227	9	-7	-6	1,4921
16	0	4	1,8771	7	-4	6	1,5403	10	-3	-4	1,7099	7	-5	-2	1,4840
8	-6	6	1,8432	7	-8	-2	1,4885	2	-7	6	1,6731	11	-1	8	1,4553
6	-2	-14	1,8195	9	-4	-8	1,4710	10	-1	0	1,6458	1	-3	4	1,4453
2	-6	4	1,8112	7	-2	-6	1,4634	8	-5	-6	1,6047	5	-5	10	1,4219
12	0	8	1,7970	1	-2	-14	1,4041	2	-1	2	1,5991	1	-5	2	1,4038
10	-2	0	1,7926	5	-4	4	1,3982	6	-7	0	1,5980	7	-1	8	1,4025
14	-2	-4	1,7393	3	-8	2	1,3870	0	-7	8	1,5944	7	-7	0	1,3833
0	-8	4	1,7281	9	-6	-8	1,3678	4	-5	-6	1,5852	5	-5	4	1,3795
6	-2	12	1,6375	5	-4	-2	1,3527	4	-1	14	1,5748	7	-1	12	1,3530
0	-4	0	1,6216	3	-4	-2	1,3450	10	-3	-2	1,5556	7	-5	-8	1,2959
2	-2	2	1,6201	5	-8	2	1,3065	0	-5	2	1,5531	1	-7	2	1,2727
4	-6	10	1,5952	1	-2	-2	1,2999	4	-5	-2	1,4858	5	-5	-8	1,2597

Table 2. (Continued)

G	G	U	|E|	U	G	U	|E|	G	U	U	|E|	U	U	U	|E|
8	0	-7	5,1876	3	-6	-3	3,7055	12	-1	7	6,1696	11	-1	9	4,6651
2	-2	7	3,8080	3	-6	9	3,1911	4	-1	-3	6,0999	7	-7	3	3,4375
6	-6	7	3,5738	1	-6	-1	3,1080	8	-1	11	5,5726	1	-7	7	3,4237
4	0	-3	3,5397	5	-8	1	2,7624	16	-1	3	3,4638	15	-1	5	3,3851
6	-8	-1	3,3012	1	-8	5	2,5026	8	-1	-7	3,3474	1	-7	5	2,7606
6	-2	3	3,2114	7	-2	7	2,0789	2	-7	5	3,1431	11	-3	9	2,6427
4	-6	5	3,0005	3	-4	-3	2,0543	8	-7	3	3,1107	3	-7	-3	2,5734
10	-6	3	2,8766	7	-6	-7	2,0214	2	-7	-9	2,8865	9	-7	1	2,4277
12	0	-11	2,6959	5	-6	-5	2,0164	6	-7	1	2,7838	5	-7	5	2,3595
16	0	3	2,6025	3	-8	3	1,9764	6	-3	1	2,5701	11	-7	-1	2,3483
2	-8	3	2,5302	7	-6	5	1,8844	10	-1	11	2,5084	1	-7	1	2,1952
12	-2	7	2,2597	7	-8	-1	1,8801	0	-7	7	2,4608	1	-7	-9	2,1913
12	0	7	2,2137	1	-2	-3	1,8662	2	-1	1	2,2380	5	-7	1	2,1659
4	0	-5	2,1940	1	-4	1	1,7965	0	-5	1	2,1984	3	-5	-5	2,1515
16	-2	3	2,1216	9	-2	3	1,7260	4	-7	7	2,1879	9	-3	1	2,1506
2	-4	-3	1,9562	5	-4	5	1,7198	4	-1	13	2,1157	3	-7	7	2,1204
0	-4	3	1,9244	5	-6	7	1,7179	10	-1	-5	2,0170	5	-3	1	2,1168
2	0	-5	1,8973	11	-4	-1	1,6393	2	-3	5	1,9802	7	-3	1	2,0843
4	-8	3	1,8357	1	-4	-1	1,5926	4	-7	3	1,8751	13	-3	7	2,0821
4	-2	-9	1,8061	3	-8	1	1,5830	2	-5	-3	1,8720	3	-5	9	2,0286
0	0	5	1,7615	11	-2	7	1,5687	2	-1	-3	1,8638	5	-7	-3	1,9669
0	-2	1	1,7462	13	-2	-1	1,5395	14	-5	-1	1,7575	1	-7	-7	1,9274
12	0	1	1,7390	11	-2	3	1,5304	0	-5	9	1,7437	3	-3	5	1,8601
6	-2	-3	1,7337	7	-4	11	1,5274	12	-1	-9	1,7230	5	-1	11	1,8293
6	-6	1	1,7274	9	-6	3	1,4948	4	-5	-3	1,7200	7	-5	5	1,8237
2	-2	-11	1,7197	9	-6	7	1,4407	8	-3	-3	1,5787	3	-7	-9	1,8116
10	-4	3	1,6950	1	-4	9	1,4402	4	-5	-1	1,5490	5	-3	5	1,8063
2	-4	7	1,6813	5	-6	5	1,4313	4	-1	3	1,5443	5	-7	3	1,8058
0	-2	3	1,6755	1	-2	-1	1,4150	0	-3	7	1,5195	7	-1	-7	1,7032
12	-2	9	1,6144	11	-4	7	1,3864	0	-1	1	1,4977	13	-1	-1	1,6999
10	-2	1	1,6127	15	-2	3	1,3670	4	-5	5	1,4517	9	-3	-3	1,6258
12	-2	1	1,6062	5	-8	3	1,3634	10	-7	-3	1,4327	7	-3	3	1,6098
14	-2	7	1,5644	15	-2	5	1,3417	2	-7	3	1,4260	7	-5	-9	1,5889
2	-6	9	1,5595	11	-6	1	1,3083	8	-7	-1	1,4196	3	-7	-5	1,5755
14	0	-9	1,5569	7	-8	1	1,3022	16	-1	-3	1,4115	3	-1	11	1,5676
4	-6	5	1,5541	3	-4	-5	1,2756	6	-7	5	1,3896	7	-1	7	1,5626
4	-6	7	1,5384	3	-2	-11	1,2700	6	-5	-5	1,3741	9	-1	3	1,5537
6	-4	-3	1,5132	1	-2	-9	1,1812	10	-1	-7	1,3718	7	-5	9	1,5278
6	0	-3	1,5116	13	-6	-1	1,1745	8	-5	3	1,3695	1	-1	9	1,5271
8	0	-9	1,4942	9	-2	9	1,1575	2	-3	-7	1,3669	9	-5	-7	1,5176
8	-4	-7	1,4592	7	-4	3	1,1327	2	-5	3	1,3665	9	-3	7	1,5173

Table 3. Statistical averages for obtusaquinone.

	Experimental	Centrosym.	Non-centrosym.
$\langle \lvert E \rvert \rangle$	0.720	0.798	0.886
$\langle \lvert E^2-1 \rvert \rangle$	1.135	0.968	0.736
$\langle \lvert E \rvert^2 \rangle$	1.007	1.000	1.000

Table 4 . Phase assignments for specifying the origin and implementing the $\sum_2$ relation for obtusaquinone.

$\vec{h}$	$\lvert E_{\vec{h}} \rvert$	$\phi_{\vec{h}}$	
$5\ \bar{1}\ 6$	3.79	0	origin
$11\ \bar{2}\ 10$	3.52	0	
$8\ 0\ \bar{7}$	5.19	0	
$4\ 0\ \bar{4}$	7.09	a	
$3\ \bar{6}\ \bar{3}$	3.70	b	
$8\ \bar{1}\ 11$	5.57	c	
$7\ \bar{7}\ 3$	3.43	d	

Table 5. Space group $P2_1/a$

$x, y, z;\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ z$ (b axis unique)
$\bar{x}, \bar{y}, \bar{z};\ \tfrac{1}{2}-x,\ \tfrac{1}{2}+y,\ \bar{z}$

$$\left.\begin{array}{ll} h+k \text{ even:} & \alpha(h\,k\,l) = \alpha(h\,\bar{k}\,l) \\ & \alpha(\bar{h}\,k\,l) = \alpha(h\,k\,\bar{l}) \\ & \\ h+k \text{ odd:} & \alpha(h\,k\,l) = \pi + \alpha(h\,\bar{k}\,l) \\ & \alpha(\bar{h}\,k\,l) = \pi + \alpha(h\,k\,\bar{l}) \end{array}\right\} \begin{array}{c} F(h\,k\,l) \neq F(\bar{h}\,k\,l) \\ \alpha = 0 \text{ or } \pi \end{array}$$

$$\varepsilon = 2 \left\{\begin{array}{l} g\,0\,l \\ 0\,g\,0 \end{array}\right. ;\quad \varepsilon = 1 \text{ for all other } hkl.$$

Table 6.

BASIC VECTOR H 4 -1 -3 E= 6.100

NUMBER OF INTERACTIONS(H-K-L) = 56

	K		EK		L		EL	EH*EK*EL
-12	-2	-7	2.260	16	1	4	3.797	52.345
-12	-2	-6	2.330	16	1	3	3.464	49.234
-12	-1	-7	6.170	16	0	4	1.877	70.645
-12	-0	-7	2.214	16	-1	4	3.797	51.280
-11	-2	-8	1.840	15	1	5	3.385	37.993
-9	2	-10	1.995	13	-3	7	2.082	25.337
-8	-7	-3	3.111	12	6	0	2.339	44.387
-8	-2	-10	3.599	12	1	7	6.170	135.456
-8	-0	-10	3.306	12	-1	7	6.170	124.428
-8	-0	7	5.188	12	-1	-10	2.182	69.053
-7	-8	-2	2.778	11	7	-1	2.348	39.789
-7	-7	-3	3.437	11	6	0	2.294	48.095
-7	-2	-12	3.177	11	1	9	4.665	90.406
-7	-2	-7	2.079	11	1	4	2.363	29.967
-7	2	-12	3.177	11	-3	9	2.643	51.221
-7	5	-5	1.824	11	-6	2	3.338	37.140
-6	-8	1	3.301	10	7	-4	1.966	39.588
-6	-0	2	2.994	10	-1	-5	2.017	36.837
-6	2	-3	3.211	10	-3	0	2.416	47.322
-5	-8	-4	2.645	9	7	1	2.428	39.175
-5	-8	-1	2.762	9	7	-2	2.866	48.287
-5	2	-4	1.856	9	-3	1	2.151	24.353
-4	-8	-3	1.836	8	7	0	3.106	34.786
-4	-7	-7	2.188	8	6	4	2.090	27.895
-4	-1	-13	2.116	8	0	10	3.306	42.673
-4	-1	3	6.100	8	0	-6	2.642	98.309
-4	-1	4	2.934	8	0	-7	5.188	92.852
-4	-0	-14	2.997	8	-1	11	5.573	101.884
-4	-0	4	7.089	8	-1	-7	3.347	144.734
-4	1	-13	2.116	8	-2	10	3.599	46.454
-4	6	-6	3.680	8	-7	3	3.111	69.836
-3	5	-9	2.029	7	-6	6	2.695	33.356
-3	5	4	2.001	7	-6	-7	2.021	24.669
-2	-8	-4	1.811	6	7	1	2.784	30.755
-2	-3	-6	2.220	6	2	3	3.211	43.483
-2	-1	-1	2.238	6	0	-2	2.994	40.873
-2	-0	5	1.897	6	-1	-8	2.594	30.017
-2	2	-7	3.808	6	-3	4	2.818	65.459
-2	7	-5	3.143	6	-8	2	2.444	46.857
-1	-8	-6	1.842	5	7	3	1.806	20.293
-1	-8	-5	2.503	5	7	2	2.909	44.415
-1	-6	1	3.108	5	5	-4	3.561	67.512
-1	2	-8	2.079	5	-3	5	1.806	22.904
-1	7	-7	3.424	5	-8	4	2.645	55.245
0	-5	1	2.198	4	4	-4	2.200	29.497
0	-2	0	2.557	4	1	-3	6.100	95.146
-0	6	-10	2.728	4	-7	7	2.188	36.410
-0	7	-7	2.461	4	-8	4	3.229	48.474
1	-8	-6	1.840	3	7	3	2.573	28.879
1	-8	6	1.842	3	7	-9	1.812	20.360
1	-5	0	3.589	3	4	-3	2.054	44.968
1	5	0	3.589	3	-6	-3	3.705	81.113

Table 7 . Use of $\sum_2$ for phase determination in $P2_1/a$.

(1)	$4\ 0\ \bar{4}$	a	
	$8\ \bar{1}\ 11$	c	㉔3
	$12\ \bar{1}\ 7$	a+c	
(2)	$12\ \bar{1}\ 7$	a+c	
	$4\ 0\ \bar{4}$	a	(151)
	$16\ \bar{1}\ 3$	c	
(3)	$8\ 0\ \bar{7}$	0	
	$8\ \bar{1}\ 11$	c	(110)
	$16\ \bar{1}\ 4$	c	
(4)	$5\ \bar{1}\ 6$	0	
	$4\ 0\ \bar{4}$	a	(91)
	$9\ \bar{1}\ 2$	a	
(5)	$\overline{12}\ 1\ \bar{7}$	a+c	
	$16\ \bar{1}\ 4$	c	(82)
	$4\ 0\ \bar{3}$	a	
	$\bar{4}\ 0\ 4$	a	
	$8\ 0\ \bar{7}$	0	(130)
	$4\ 0\ \bar{3}$	a	
(6)	$\bar{3}\ \bar{6}\ 3$	π+b	
	$4\ 0\ \bar{4}$	a	(81)
	$1\ \bar{6}\ \bar{1}$	π+a+b	
(7)	$\bar{8}\ 1\ \overline{11}$	c	
	$16\ \bar{1}\ 3$	c	(75)
	$8\ 0\ \bar{8}$	0	
	$4\ 0\ \bar{4}$	a	
	$4\ 0\ \bar{4}$	a	(195)
	$8\ 0\ \bar{8}$	0	
(8)	$7\ \bar{7}\ 3$	d	
	$4\ 0\ \bar{4}$	a	(57)
	$11\ \bar{7}\ \bar{1}$	a+d	
(9)	$5\ \bar{1}\ 6$	0	
	$\bar{4}\ 0\ 4$	a	(57)
	$1\ \bar{1}\ 10$	a	
(10)	$12\ \bar{1}\ 7$	a+c	
	$\bar{7}\ \bar{7}\ \bar{3}$	d	(56)
	$5\ \bar{8}\ 4$	a+c+d	
(11)	$3\ \bar{6}\ \bar{3}$	b	
	$4\ 0\ \bar{4}$	a	(53)
	$7\ \bar{6}\ \bar{7}$	a+b	
(12)	$7\ \bar{7}\ 3$	d	
	$\bar{4}\ 0\ 4$	a	(57)
	$3\ \bar{7}\ 7$	a+d	
(13)	$9\ \bar{1}\ 2$	a	
	$4\ 0\ \bar{4}$	a	(49)
	$13\ \bar{1}\ \bar{2}$	0	
(14)	$16\ \bar{1}\ 4$	c	
	$\bar{4}\ 0\ 4$	a	(48)
	$12\ \bar{1}\ 8$	a+c	
(15)	$1\ \bar{6}\ \bar{1}$	π+a+b	
	$4\ 0\ \bar{4}$	a	(44)
	$5\ \bar{6}\ \bar{5}$	π+b	
(16)	$3\ \bar{6}\ \bar{3}$	b	
	$5\ \bar{1}\ 6$	0	(43)
	$8\ \bar{7}\ 3$	b	
(17)	$\bar{8}\ \bar{7}\ \bar{3}$	π+b	
	$12\ \bar{1}\ 7$	a+c	(62)
	$4\ \bar{8}\ 4$	π+a+b+c	
(18)	$8\ \bar{7}\ 3$	b	
	$\bar{4}\ 0\ 4$	a	(48)
	$4\ \bar{7}\ 7$	a+b	
	$\bar{4}\ \bar{8}\ \bar{4}$	π+a+b+c	
	$8\ 1\ 11$	π+c	(39)
	$4\ \bar{7}\ 7$	a+b	
(19)	$11\ 2\ 10$	π	
	$\bar{5}\ \bar{8}\ \bar{4}$	π+a+c+d	
	$6\ \bar{6}\ 6$	a+c+d	
(20)	$6\ \bar{6}\ 6$	a+c+	
	$4\ 0\ \bar{4}$	a	
	$10\ \bar{6}\ 2$	c+d	
(21)	$\overline{10}\ \bar{6}\ \bar{2}$	c+d	
	$12\ \bar{1}\ 7$	a+c	
	$2\ \bar{7}\ 5$	a+d	
(22)	$\bar{6}\ \bar{6}\ \bar{6}$	a+c+	
	$8\ \bar{1}\ 11$	c	
	$2\ \bar{7}\ 5$	a+d	
(23)	$6\ \bar{6}\ 6$	a+c+	
	$\bar{4}\ 0\ 4$	a	
	$2\ \bar{6}\ 10$	c+d	
(24)	$\bar{6}\ \bar{6}\ \bar{6}$	a+c+d	
	$12\ \bar{1}\ 7$	a+c	
	$6\ \bar{7}\ 1$	d	
	$2\ \bar{7}\ 5$	a+d	
	$4\ 0\ \bar{4}$	a	
	$6\ \bar{7}\ \bar{1}$	d	
(25)	$10\ \bar{6}\ 2$	c+d	
	$\bar{8}\ \bar{1}\ \overline{11}$	π+c	
	$2\ \bar{7}\ \bar{9}$	π+d	
	$\bar{2}\ \bar{7}\ 5$	π+a+d	
	$4\ 0\ \bar{4}$	a	
	$2\ \bar{7}\ \bar{9}$	π+d	
(26)	$10\ \bar{6}\ 2$	c+d	
	$\bar{5}\ 1\ \bar{6}$	0	
	$5\ \bar{5}\ \bar{4}$	c+d	
(27)	$5\ \bar{5}\ \bar{4}$	c+d	
	$\bar{4}\ 0\ 4$	a	
	$1\ \bar{5}\ 0$	a+c+d	

The numbers within the circles represent the $E_hE_kE_{h-k}$ product.

Table 7. (Continued)

$$\begin{array}{rrrc} 1 & 5 & 0 & a+c+d \\ 3 & \bar{6} & \bar{3} & b \\ \hline 4 & \bar{1} & \bar{3} & a+b+c+d \end{array} \quad (81)$$

$$\begin{array}{rrrc} 5 & 5 & \bar{4} & c+d \\ \bar{1} & \bar{6} & 1 & a+b \\ \hline 4 & \bar{1} & \bar{3} & a+b+c+d \end{array} \quad (67)$$

$$\begin{array}{rrrc} 4 & \bar{1} & \bar{3} & a+b+c+d \\ 4 & 0 & \bar{4} & a \\ \hline 8 & \bar{1} & \bar{7} & b+c+d \end{array} \quad (144)$$

$$\begin{array}{rrrc} \bar{4} & \bar{1} & 3 & a+b+c+d+\pi \\ 2 & \bar{1} & 7 & a+c \\ \hline 8 & \bar{2} & 10 & \pi+b+d \end{array} \quad (135)$$

$$\begin{array}{rrrc} \bar{4} & 1 & 3 & a+b+c+d \\ 2 & \bar{1} & 7 & a+c \\ \hline 8 & 0 & 10 & b+d \end{array} \quad (124)$$

$$\begin{array}{rrrc} \bar{4} & 1 & 3 & a+b+c+d \\ 8 & \bar{1} & 11 & c \\ \hline 4 & 0 & 14 & a+b+d \end{array} \quad (101)$$

$$\begin{array}{rrrc} 4 & \bar{1} & \bar{3} & a+b+c+d \\ 4 & 1 & \bar{3} & \pi+a+b+c+d \\ \hline 8 & 0 & \bar{6} & \pi \end{array} \quad (98)$$

$$\begin{array}{rrrc} \bar{4} & \bar{1} & 3 & \pi+a+b+c+d \\ 8 & 0 & \bar{7} & 0 \\ \hline 4 & \bar{1} & \bar{4} & \pi+a+b+c+d \end{array} \quad (92)$$

$$\begin{array}{rrrc} \bar{4} & 0 & 3 & a \\ 8 & \bar{1} & \bar{7} & b+c+d \\ \hline 4 & \bar{1} & \bar{4} & a+b+c+d \end{array} \quad ㉞$$

X

$$\begin{array}{rrrc} 4 & 1 & \bar{3} & \pi+a+b+c+d \\ 2 & \bar{1} & 7 & a+c \\ \hline 6 & 0 & 4 & \pi+b+d \end{array} \quad (70)$$

$$\begin{array}{rrrc} \bar{4} & 1 & 3 & a+b+c+d \\ 8 & \bar{7} & 3 & b \\ \hline & \bar{6} & 6 & a+c+d \end{array} \quad (69)$$

$$\begin{array}{rrrc} & \bar{6} & 6 & a+c+d \\ & 0 & \bar{4} & a \\ \hline & \bar{6} & 2 & c+d \end{array} \quad (82)$$

(38) $$\begin{array}{rrrc} 4 & \bar{6} & 6 & a+c+d \\ \bar{4} & 0 & 4 & a \\ \hline 0 & 6 & 10 & c+d \end{array} \quad (71)$$

(39) $$\begin{array}{rrrc} 4 & \bar{1} & \bar{3} & a+b+c+d \\ 8 & 0 & \bar{7} & 0 \\ \hline 12 & \bar{1} & \overline{10} & a+b+c+d \end{array} \quad (69)$$

(40) $$\begin{array}{rrrc} 4 & \bar{1} & \bar{3} & a+b+c+d \\ 8 & 1 & 11 & \pi+c \\ \hline 12 & 0 & 8 & \pi+a+b+d \end{array} \quad (61)$$

(41) $$\begin{array}{rrrc} 8 & \bar{2} & 10 & \pi+b+d \\ 4 & 0 & \bar{4} & a \\ \hline 12 & \bar{2} & 6 & \pi+a+b+d \end{array} \quad (59)$$

(42) $$\begin{array}{rrrc} 4 & 6 & 6 & a+c+d \\ 7 & \bar{7} & 3 & d \\ \hline 11 & \bar{1} & 9 & a+c \end{array} \quad (59)$$

(43) $$\begin{array}{rrrc} 11 & \bar{1} & 9 & a+c \\ 4 & 0 & \bar{4} & a \\ \hline 15 & \bar{1} & 5 & c \end{array} \quad (111)$$

(44) $$\begin{array}{rrrc} \bar{4} & \bar{1} & 3 & \pi+a+b+c+d \\ 11 & \bar{1} & 9 & a+c \\ \hline 7 & \bar{2} & 12 & \pi+b+d \end{array} \quad (90)$$

(45) $$\left\{ \begin{array}{rrrcl} \overline{10} & \bar{6} & \bar{2} & c+d & \\ 11 & \bar{1} & 9 & a+c & (68) \\ \hline 1 & \bar{7} & 7 & a+d & \\ & & & & \\ 5 & \bar{8} & 4 & a+c+d & \\ \bar{4} & 1 & 3 & a+b+c+d & (55) \\ \hline 1 & \bar{7} & 7 & b & \end{array} \right.$$

a+b+d=0

(46) $$\begin{array}{rrrc} \bar{9} & \bar{1} & \bar{2} & a \\ 11 & \bar{1} & 9 & a+c \\ \hline 2 & \bar{2} & 7 & c \end{array} \quad (60)$$

(47) $$\left\{ \begin{array}{rrrcl} 2 & \bar{2} & 7 & c & \\ 4 & 0 & \bar{4} & a & (86) \\ \hline 6 & \bar{2} & 3 & a+c & \\ & & & & \\ \bar{5} & \bar{1} & \bar{6} & 0 & \\ 11 & \bar{1} & 9 & a+c & (56) \\ \hline 6 & \bar{2} & 3 & a+c & \end{array} \right.$$

(48) $$\begin{array}{rrrc} 4 & \bar{1} & \bar{3} & a+b+c+d \\ \bar{2} & \bar{2} & \bar{7} & c \\ \hline 2 & \bar{3} & \overline{10} & a+b+d \end{array} \quad (71)$$

(49) $$\left\{ \begin{array}{rrrcl} 4 & \bar{1} & \bar{3} & a+b+c+d & \\ 2 & \bar{2} & 7 & c & (65) \\ \hline 6 & \bar{3} & 4 & a+b+d & \\ & & & & \\ 8 & \bar{1} & 11 & c & \\ \bar{2} & \bar{2} & \bar{7} & c & (59) \\ \hline 6 & \bar{3} & 4 & 0 & \\ & & & & \\ \bar{6} & \bar{2} & \bar{3} & a+c & \\ 12 & \bar{1} & 7 & a+c & (55) \\ \hline 6 & \bar{3} & 4 & 0 & \end{array} \right.$$

a+b+d=0

(50) $$\left\{ \begin{array}{rrrcl} \bar{2} & \bar{2} & \bar{7} & c & \\ 12 & \bar{1} & 7 & a+c & (56) \\ \hline 10 & \bar{3} & 0 & a & \\ & & & & \\ 6 & \bar{3} & 4 & 0 & \\ 4 & 0 & \bar{4} & a & ㊽ \\ \hline 10 & \bar{3} & 0 & a & \end{array} \right.$$

(51) $$\begin{array}{rrrc} \bar{2} & \bar{2} & \bar{7} & c \\ 4 & 1 & \bar{3} & \pi+a+b+c+d \\ \hline 2 & \bar{1} & \overline{10} & \pi+a+b+d \end{array} \quad (71)$$

(52) $$\left\{ \begin{array}{rrrcl} \bar{1} & \bar{7} & \bar{7} & a+d & \\ 12 & 1 & 7 & \pi+a+c & ㊽ \\ \hline 11 & \bar{6} & 0 & \pi+c+d & \\ & & & & \\ 7 & \bar{7} & 3 & d & \\ 4 & 1 & \bar{3} & \pi+a+b+c+d & ㊽ \\ \hline 11 & \bar{6} & 0 & \pi+a+b+c & \end{array} \right.$$

a+b+d=0

Table 7. (Continued)

(53)
$$\left\{\begin{array}{rrrcll}
12 & 1 & 7 & \pi+a+c & & \\
\bar{12} & 1 & \bar{7} & a+c & & \textcircled{97} \\ \hline
0 & 2 & 0 & \pi & & \\[1em]
8 & 1 & 11 & \pi+c & & \\
\bar{8} & 1 & \bar{11} & c & & \textcircled{79} \\ \hline
0 & 2 & 0 & \pi & & \\[1em]
4 & \bar{1} & \bar{3} & a+b+c+d & & \\
\bar{4} & \bar{1} & 3 & \pi+a+b+c+d & & \textcircled{95} \\ \hline
0 & \bar{2} & 0 & \pi & & \\[1em]
11 & \bar{1} & 9 & a+c & & \\
\bar{11} & \bar{1} & \bar{9} & a+c & \times & \textcircled{55} \\ \hline
0 & \bar{2} & 0 & 0 & & \\[1em]
5 & \bar{1} & 6 & 0 & & \\
\bar{5} & \bar{1} & \bar{6} & 0 & \times & \textcircled{36} \\ \hline
0 & \bar{2} & 0 & 0 & &
\end{array}\right.$$

(54)
$$\begin{array}{rrrcl}
4 & \bar{8} & 4 & \pi+a+b+c & \\
\bar{4} & 1 & 3 & a+b+c+d & \textcircled{48} \\ \hline
0 & \bar{7} & 7 & \pi+d &
\end{array}$$

(55)
$$\begin{array}{rrrcl}
4 & 0 & \bar{3} & a & \\
6 & \bar{6} & 6 & a+c+d & \textcircled{42} \\ \hline
10 & \bar{6} & 3 & c+d &
\end{array}$$

(56)
$$\begin{array}{rrrcl}
10 & \bar{6} & 3 & c+d & \\
\bar{4} & 0 & 4 & a & \textcircled{72} \\ \hline
6 & \bar{6} & 7 & a+c+d &
\end{array}$$

(57)
$$\begin{array}{rrrcl}
\bar{6} & \bar{6} & \bar{7} & a+c+d & \\
11 & \bar{1} & 9 & a+c & \textcircled{48} \\ \hline
5 & \bar{7} & 2 & d &
\end{array}$$

(58)
$$\begin{array}{rrrcl}
5 & \bar{7} & 2 & d & \\
4 & 0 & \bar{4} & a & \textcircled{59} \\ \hline
9 & \bar{7} & \bar{2} & a+d &
\end{array}$$

(59)
$$\begin{array}{rrrcl}
\bar{9} & \bar{7} & 2 & a+d & \\
12 & 1 & 7 & \pi+a+c & \textcircled{56} \\ \hline
3 & \bar{6} & 9 & \pi+c+d &
\end{array}$$

(60)
$$\left\{\begin{array}{rrrcl}
\bar{3} & \bar{6} & \bar{9} & c+d & \\
11 & \bar{1} & 9 & a+c & \textcircled{46} \\ \hline
8 & \bar{7} & 0 & a+d & \\[1em]
 & & & & a = \pi \\[1em]
0 & \bar{7} & 7 & \pi+d & \\
8 & 0 & \bar{7} & 0 & \\ \hline
8 & \bar{7} & 0 & \pi+d &
\end{array}\right.$$

(61)
$$\begin{array}{rrrcl}
3 & \bar{6} & 9 & \pi+c+d & \\
8 & 0 & \bar{7} & 0 & \textcircled{55} \\ \hline
11 & \bar{6} & 2 & \pi+c+d &
\end{array}$$

(62)
$$\left\{\begin{array}{rrrcl}
11 & \bar{6} & 2 & \pi+c+d & \\
\bar{4} & 0 & 4 & a & \textcircled{63} \\ \hline
7 & \bar{6} & 6 & \pi+a+c+d & \\[1em]
 & & & & \pi = b+d \\[1em]
\bar{4} & \bar{8} & \bar{4} & \pi+a+b+c & \\
11 & 2 & 10 & \pi & \textcircled{30} \\ \hline
7 & \bar{6} & 6 & a+b+c &
\end{array}\right.$$

and continue
with additional phase
determinations.

Strong indications:

$$\left\{\begin{array}{r}
a + b + d = 0 \\
b + d = \Pi \\
a = \Pi
\end{array}\right.$$

Four possibilities:

	1	2	3	4
b	Π	Π	0	0
c	0	Π	0	Π
d	0	0	Π	Π

↑
correct solution

EXAMPLE OF MULTIPLE SOLUTION

Table 8. Obtusaquinone

	E-map				Refined Coordinates			
	x	y	z	Peak height	B	x	y	z
C(1A)	.370	.770	.253	417	3.4	.372	.770	.249
C(3A)	.269	.804	.145	395	3.4	.268	.816	.147
O(2A)	.334	.999	.214	372	4.6	.340	.998	.211
C(6B)	-.038	.706	.079	340	3.9	-.040	.701	.074
C(7B)	.016	.906	.145	337	3.3	.018	.905	.143
C(5A)	.304	.580	.188	333	4.0	.306	.579	.191
O(5B)	-.104	.514	.006	322	4.6	-.105	.520	.002
C(3B)	-.134	.894	-.018	320	3.3	-.137	.901	-.009
O(2B)	-.069	1.081	.062	315	4.2	-.070	1.077	.060
C(2B)	-.079	.935	.044	305	3.4	-.083	.940	.044
O(4B)	-.201	.702	-.071	298	4.5	-.197	.703	-.067
O(4A)	.203	.622	.095	284	5.3	.208	.619	.097
C(15B)	.169	.699	.320	274	4.8	.172	.691	.319
C(10A)	.563	.774	.485	266	4.0	.565	.769	.480
C(7A)	.424	.820	.303	262	3.3	.425	.829	.302
C(9B)	.118	.901	.254	261	3.9	.114	.899	.250
C(8A)	.470	.754	.364	247	3.5	.472	.753	.359
C(6A)	.363	.627	.245	246	3.3	.360	.622	.240
C(2A)	.324	.852	.204	245	3.6	.324	.857	.198
C(4B)	-.139	.747	-.034	227	2.9	-.145	.751	-.022
C(8B)	.070	.826	.196	218	3.2	.068	.825	.198
O(5A)	.292	.439	.181	210	4.0	.292	.437	.179
C(5B)	-.094	.662	.023	208	3.6	-.093	.657	.020
C(13B)	.265	.733	.436	206	5.4	.261	.724	.436
C(1B)	-.031	.848	.089	195	2.4	-.032	.850	.088
C(10B)	.168	.838	.308	194	4.2	.166	.833	.310
C(12A)	.655	.807	.602	190	5.3	.648	.812	.604
C(11B)	.208	.930	.365	186	4.6	.208	.924	.365
C(16A)	.285	1.095	.168	172	5.4	.295	1.101	.164
C(4A)	.261	.669	.136	170	4.0	.257	.668	.141
C(9A)	.516	.822	.419	162	4.3	.517	.831	.414
C(12B)	.261	.863	.425	160	5.4	.259	.863	.427
C(14A)	.625	.579	.557	159	5.7	.619	.577	.561
C(16B)	-.122	1.178	.016	152	3.7	-.118	1.183	.021
C(14B)	.224	.632	.382	150	5.4	.219	.638	.381
C(11A)	.605	.862	.539	149	5.2	.602	.864	.536
C(13A)	.659	.679	.617	105	4.6	.654	.677	.615
C(15A)	.567	.650	.483	98	4.5	.574	.626	.492
C(1S)	solvent molecule				9.2	.083	.257	.360
C(2S)					7.9	.016	.242	.318
C(3S)					8.9	.005	.293	.238
C(4S)					9.5	.083	.351	.208
C(5S)					8.2	.129	.326	.264
C(6S)					13.3	.145	.299	.347

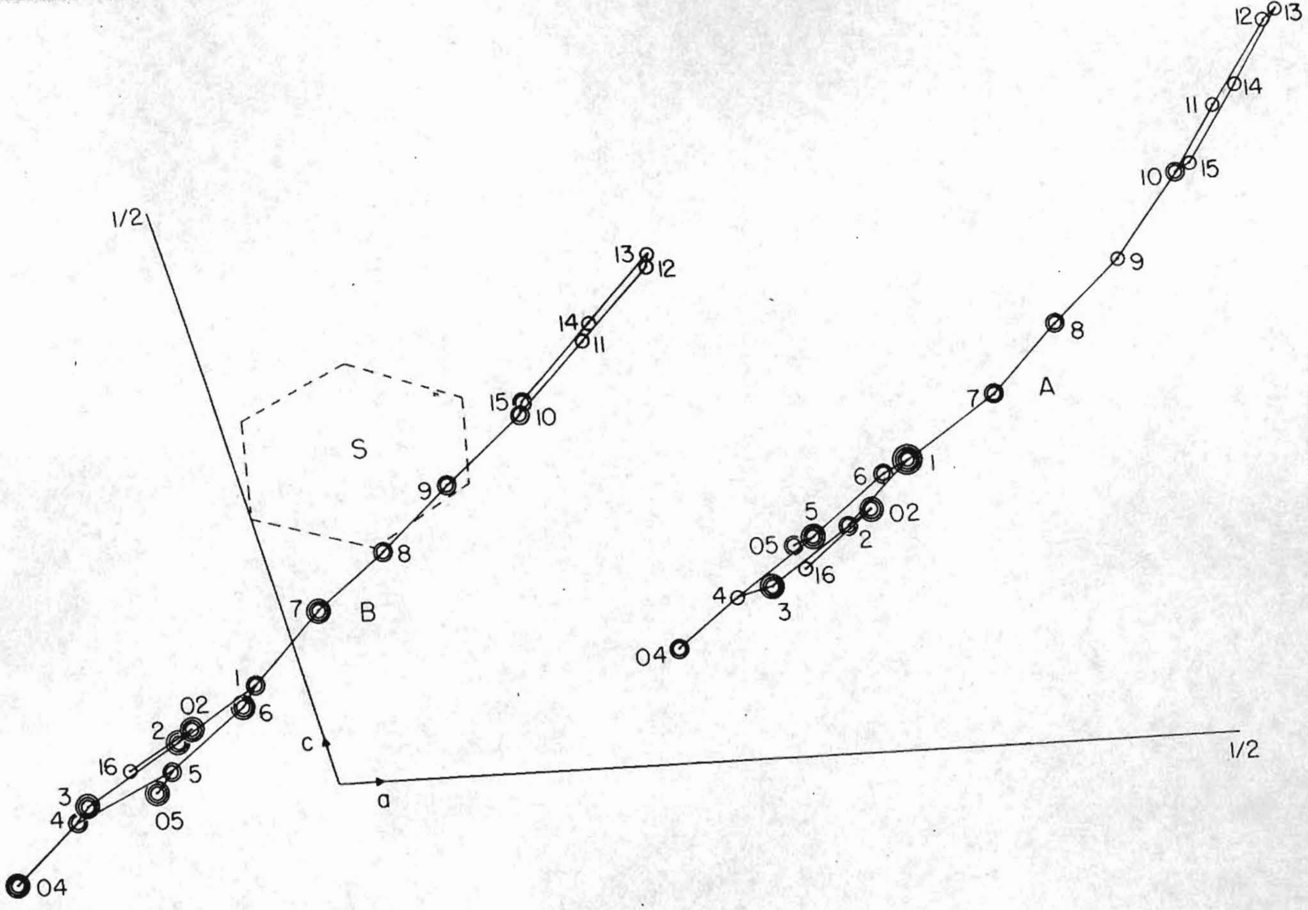


Fig. 3. E-map for the asymmetric unit for obtusaquinone computed with 364 terms with |E| > 1.1 using the phases determined by the symbolic addition procedure. Molecules A and B are independent molecules. The heights of the maxima in the E-map are proportional to the number of concentric circles. Atomic positions for the solvent molecule S were subsequently found in a difference map. High thermal factors are associated with the atoms in the solvent molecule.

phases (or signs) be known before other phases can be determined. For $P2_1/a$, three phases are known immediately by specifying the origin in the cell. In addition to following the prescribed rules for origin specification (Karle, 1974), reflections for specifying the origin should have large $|E|$ values and have many interactions for applying the $\sum_2$ formula. In space group $P2_1/a$, three reflections for the origin are chosen from parity groups other than ggg(g = even, u = odd). If a uug and a ugg are selected, for example, then the phases of reflections in gug are known, in principle, and the third reflection for specifying the origin must be chosen from one of the four remaining parity groups.

Usually the assignment of the origin does not supply enough known phases to proceed with the $\sum_2$ formula, and phases for additional reflections are assigned as symbols, see Table 4. The discovery that very few unknown symbols are needed on which to base an entire phase determination has made the direct method practical. Again, the reflections to which symbols are assigned should have large $|E|$ and should interact with many other reflections having large $|E|$. To facilitate the application of the $\sum_2$ relationship, a listing is made of all pairs of reflections, $\underset{\sim}{k}$ and $\underset{\sim}{h} - \underset{\sim}{k}$ with $|E| > 1.8$ that can be used to determine the phase of reflection $\underset{\sim}{h}$. Table 6 shows such a listing for one reflection, $4\ \bar{1}\ \bar{3}$. This listing also contains the $E_{\underset{\sim}{h}}\ E_{\underset{\sim}{k}}\ E_{\underset{\sim}{h}-\underset{\sim}{k}}$ products which are directly related to the probability, Eq.(3). For this crystal, a triple product of 30 corresponds to $P_+ = 98.9\%$ while a triple product of 21 corresponds to $P_+ = 95\%$. For a probability level of 95%, it should be remembered that 1 out of 20 indications will be in error.

The sequential application of the $\sum_2$ formula is shown in Table 7. Indices are added and phases are added since they are expressed as 0 or π.

It should be remembered that 2x, where x is any symbol, equals 0 for centrosymmetric space groups. An alternative procedure for centrosymmetric space groups is to use + and - signs, instead of 0 and π, in which case the signs and unknown symbols are multiplied. At the beginning, phases are determined by single indications. It is very important to use only those reflections with the strongest $|E|$ values and the strongest triples to assure that the probability that the phase is correct is at least 99%. Several triples in Table 7, in entries (34) and (53), marked with an X, indicate an erroneous phase. The triples marked with an X have a considerably lower triple product than other triples in the same entry that indicate the phase correctly.

When the phase for reflection hkl is determined in space group $P2_1/a$, then the phases for $h\bar{k}l$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}\bar{l}$ are also known by applying the symmetry relationships as shown in Table 5. The symmetry relationships for all space groups are listed in Vol.I of the International Tables for X-Ray Crystallography. For example, in entry (6) of Table 7, the $\bar{3}6\bar{3}$ reflection that had been assigned the symbol $\underline{b}$ is used as $\bar{3}\bar{6}3$ and the phase must be changed to $\pi + b$.

After a number of phases are determined, there are multiple indications for new phases. These indications may contain different symbols and, in that manner, relationships among the symbols are discovered. In this example, the first relationship among the symbols occurred at entry (45) where it appears that a + d = b or a + b + d = 0. The same relationship is also indicated at entries (49) and (52). Since all the triple $E_{\underline{h}} E_{\underline{k}} E_{\underline{h}-\underline{k}}$ products involved are very strong, it is very probable that the relationship a + b + d = 0 is correct. At entries (60) and (62), it appears that $a = \pi$ and $b + d = \pi$. Taken together, these indications are consistent with the indication that $a + b + d = 0$. A continuation of the phase determination beyond that shown in Table 7 did not produce any other reliable relationships among the symbols. Four symbols were assigned initially, two independent relations among the symbols were found, hence four possibilities remained, as shown at the end of Table 7. For centrosymmetric space groups, the number of possibilities is equal to 2^n where n is the number of unknown symbols. In this determination, the first possibility was the correct one.

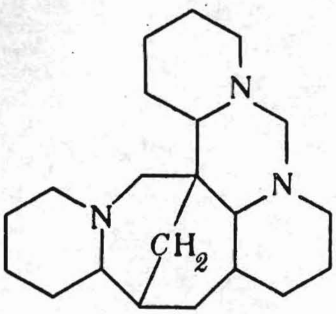
After the assignment of the symbols, phases for additional reflections were determined by computer and an E-map was computed using 364 terms with $|E| > 1.1$. An E-map (Karle, Hauptman, Karle and Wing, 1958) is a Fourier map in which the F values are replaced with E values. The resulting map has peaks that are much sharper than in the conventional Fourier. The coordinates of the atoms as inidcated by the initial E-map, Fig. 3, are sufficiently good to use directly in a least-squares refinement. Table 8 contains the coordinates of the 38 atoms of the two independent molecules as read from the initial E-map, the peak height, the isotropic thermal factor B, and the coordinates after least-squares refinement. A comparison of the coordinates shows the accuracy of position as indicated by the E-map. The peak heights for similar atomic specie are ranked roughly inversely proportional to the thermal paramters. This is particularly noticeable for the solvent molecule (the last six atoms listed in Table 8) where the peaks for the atoms were almost non-existent in the E-map and the B values ranged from 8 to 13. The solvent molecule was found subsequently in a difference map using all the $(F_o - F_c)$ data.

Space Group $P\bar{1}$

Phase determination in space group $P\bar{1}$ occasionally presents some difficulties owing to the small number of equivalent reflections. Because $F(hkl)$ is related only to $F(\bar{h}\bar{k}\bar{l})$, there are fewer combinations of $E_{\mathbf{k}}\, E_{\mathbf{h}-\mathbf{k}}$ for each $E_{\mathbf{h}}$ in the $\sum_2$ relation, Eq.(1) or (2). As a consequence, among those reflections available for $\sum_2$, the $E_{\mathbf{h}}\, E_{\mathbf{k}}\, E_{\mathbf{h}-\mathbf{k}}$ products are usually not as high as in space groups containing more symmetry, and, therefore, the probabilities, Eq.(3) are somewhat lower. Hence, it is even more important to use phase relationships based on the highest triple products.

The details for phase determination for jamine (Karle and Karle, 1964b) are shown in Tables 9-16. The statistical averages in Table 11 show that the space group is $P\bar{1}$ rather than $P1$. In Table 10 the data have been divided into the eight parity groups for hkl and listed in decreasing values of $|E|$ in each group. The origin specification and the additional reflections to which a symbol has been assigned for implementing the $\sum_2$ formula are listed in Table 12. The reflections to which a symbol has been assigned to represent the phase were chosen one at a time, as needed, to proceed with the $\sum_2$ formula and maintain very high probability values. The sequential application of the $\sum_2$ formula is shown in Table 14. Symbol d was introduced at entry (25) while symbol g was introduced sometime after entry (64) because there still remained a number of reflections with high $|E|$ values for which phases were not yet determined. For this crystal containing 48 atoms in the unit cell, a

Table 9. JAMINE
I.L. Karle and J. Karle (1964),
Acta Cryst. 17, 1356.



Space group P$\bar{1}$

a = 6.79 A
b = 10.61 A
c = 13.41 A
α = 95.0°
β = 97.3°
γ = 103.9°

Z = 2

Final fractional coordinates

Atom	x	y	z
C(1)	0.1382	0.3760	0.3810
N(2)	0.0436	0.2501	0.4104
C(3)	0.9407	0.2645	0.4999
C(4)	0.1060	0.3114	0.6007
C(5)	0.2397	0.2179	0.6134
C(6)	0.3522	0.2030	0.5180
C(7)	0.1747	0.1605	0.4231
C(8)	0.4181	0.0593	0.3307
C(9)	0.2622	0.1396	0.3210
C(10)	0.3588	0.2739	0.2888
N(11)	0.2141	0.3592	0.2825
C(12)	0.3126	0.4906	0.2606
C(13)	0.3955	0.4852	0.1572
C(14)	0.5445	0.3937	0.1591
C(15)	0.4348	0.2581	0.1854
C(16)	0.5723	0.1628	0.1871
C(17)	0.4761	0.0307	0.2219
C(18)	0.2726	0.9525	0.1517
C(19)	0.3038	0.8145	0.1156
C(20)	0.1005	0.7322	0.0461
C(21)	0.9186	0.7254	0.0979
C(22)	0.9011	0.8656	0.1342
N(23)	0.0959	0.9365	0.2012
C(24)	0.0672	0.0648	0.2420

Table 10. Listing of strongest |E| for jamine.

G	G	G	|E|	U	G	G	|E|	G	U	G	|E|	U	U	G	|E|
2	4	-10	2.98845	1	4	-2	3.35682	2	1	4	6.88787	3	5	2	4.74511
4	6	2	2.95572	3	8	8	3.26305	2	-1	-6	3.66796	3	3	-8	4.44610
4	-4	-6	2.89561	3	0	-6	3.24035	4	-5	-6	3.27584	1	-9	2	3.14582
0	2	10	2.63352	1	0	-6	3.21171	2	-5	0	2.68191	1	-7	2	3.14179
4	-4	-8	2.46907	3	-4	0	3.06949	4	5	-6	2.57634	1	3	10	2.97252
2	-8	2	2.46121	1	-2	-16	2.91243	2	5	-2	2.52550	1	1	10	2.75013
0	2	-2	2.30045	1	8	2	2.76269	2	3	2	2.21237	3	1	-6	2.67800
2	4	-8	2.12985	3	-6	-10	2.70740	2	5	8	2.17930	3	3	-10	2.52560
2	0	-6	2.09591	3	-2	10	2.63967	2	3	14	2.05262	3	-1	8	2.47227
0	10	8	2.05781	3	0	6	2.61823	4	5	2	1.90050	1	7	4	2.43441
2	-8	4	2.02879	1	2	-12	2.51943	2	-1	6	1.86843	3	5	0	2.38327
2	-6	-10	1.67600	3	2	-8	2.22297	2	-5	-10	1.86070	3	7	8	2.37423
2	6	0	1.66314	1	-2	-8	2.19172	0	9	0	1.82400	3	-5	-8	2.36622
2	2	2	1.60948	1	6	6	2.17742	0	13	-4	1.81960	1	-1	2	2.21353
4	8	2	1.60242	3	-2	8	2.12938	2	5	6	1.80676	1	-11	-8	2.01435
4	-6	-4	1.59259	1	0	-8	2.10105	2	-3	0	1.79379	3	-3	10	1.98492
2	4	0	1.52700	3	-10	-4	2.05163	2	-9	-6	1.77213	3	-1	-4	1.95951
0	4	-4	1.52119	1	6	4	2.04271	2	-9	4	1.71100	3	1	2	1.82278
4	-6	-8	1.45132	1	-4	-14	2.01014	2	7	8	1.68467	1	-5	0	1.73907
4	2	-8	1.43689	1	-4	-2	1.98956	2	1	-6	1.63110	3	5	-8	1.70154
4	8	-4	1.42307	1	-2	-6	1.97439	4	9	-2	1.56102	3	-7	-8	1.68114
2	-4	-14	1.39484	1	10	2	1.92817	4	9	-4	1.55791	3	5	12	1.65095
4	6	-8	1.37993	3	8	-10	1.89283	2	1	2	1.45349	1	-7	12	1.59002
2	0	4	1.37750	1	0	2	1.88627	2	5	0	1.44974	3	9	6	1.55891
2	2	10	1.37152	3	-4	-8	1.80650	4	9	0	1.44105	3	-9	-4	1.55690

Table 10. (Continued)

G	G	U	|E|	U	G	G	|E|	G	U	U	|E|	U	U	U	|E|
2	-8	3	2.86377	3	6	1	4.82261	2	3	-9	3.34460	1	-1	-7	3.76101
4	6	3	2.85483	3	2	5	3.40391	2	-1	-5	2.73673	3	5	-7	3.07064
2	0	-5	2.80413	3	0	5	2.96864	2	5	-1	2.72372	1	-11	-7	2.96535
4	4	-7	2.56368	1	2	11	2.96670	2	-3	-3	2.37064	3	1	3	2.65483
2	2	-7	2.25133	1	6	7	2.94427	0	1	9	2.28453	1	-1	-9	2.44412
2	-4	-1	2.18283	3	-4	1	2.88254	4	5	3	2.18223	1	1	3	2.44005
4	4	-5	2.13271	3	4	1	2.73296	2	5	1	1.85816	3	1	5	2.41630
0	2	-13	1.85565	3	6	11	2.53510	4	-5	-5	1.81479	1	5	7	2.38126
4	10	-1	1.84269	3	-4	-7	2.49537	2	3	-11	1.78853	1	1	1	2.33991
0	2	9	1.81094	1	-10	-7	2.21634	0	1	-3	1.78516	1	5	-3	2.29387
2	2	3	1.78695	1	4	-11	2.21227	2	1	-7	1.74122	3	1	-9	2.05173
2	2	1	1.78146	3	-6	-9	2.17405	4	5	1	1.72009	3	9	-3	2.00917
2	-2	9	1.76507	3	2	3	2.16288	4	-5	-7	1.71597	1	3	9	1.97273
2	-6	-9	1.75301	3	10	-5	2.04576	0	1	-11	1.67982	3	5	3	1.94639
2	0	7	1.71469	1	-10	-9	1.99302	2	7	9	1.66045	1	3	-11	1.87360
4	8	-11	1.62146	1	-8	1	1.94225	4	-3	3	1.63941	3	7	3	1.82274
4	8	-1	1.61391	3	10	-3	1.93018	2	7	11	1.60388	1	-1	1	1.79460
4	-4	-9	1.56104	3	4	-9	1.92682	4	9	-9	1.59328	1	-5	-11	1.79334
2	-10	-7	1.52697	1	4	9	1.90857	2	5	13	1.57256	3	7	-1	1.74582
4	-6	-5	1.52559	1	0	1	1.88750	0	9	1	1.50140	3	-9	-5	1.69625
2	-6	1	1.51307	1	0	3	1.87664	2	1	7	1.44760	1	-5	-3	1.67806
2	2	-11	1.49911	1	-2	-9	1.87328	2	-7	-9	1.40969	1	9	1	1.66145
2	-4	-3	1.48257	3	4	-7	1.87206	2	-3	-15	1.36020	3	3	-7	1.65256
2	4	-1	1.47795	1	0	-11	1.86325	4	-9	-3	1.34718	3	7	1	1.64918
2	4	-11	1.44923	3	-10	-3	1.82453	4	-7	7	1.34463	3	-5	-1	1.62847

Table 11. Statistical averages for jamine.

	Experimental	Centrosym.	Non-centrosym.
$\langle \lvert E \rvert \rangle$	0.728	0.798	0.886
$\langle \lvert E^2-1 \rvert \rangle$	1.083	0.968	0.736
$\langle \lvert E \rvert^2 \rangle$	0.994	1.000	1.000

Table 12. Phase assignments for specifying the origin and implementing the $\sum_2$ relation in jamine.

$\vec{h}$	$\phi_{\vec{h}}$	$\lvert E_{\vec{h}} \rvert$	
$1\ \bar{1}\ \bar{7}$	+	3.76	origin
$2\ 1\ 4$	+	6.88	
$3\ 5\ 2$	+	4.74	
$0\ 2\ 10$	a	2.63	
$3\ 6\ 1$	b	4.82	
$0\ 1\ 9$	c	2.28	
$1\ \bar{9}\ 2$	d	3.14	
$0\ 2\ \bar{2}$	g	2.30	

Table 13. Space group $P\bar{1}$.

$x, y, z;\ \bar{x}, \bar{y}, \bar{z}$

$F(h\ k\ l) = F(\bar{h}\ \bar{k}\ \bar{l}) \neq F(\bar{h}\ k\ l) \neq F(h\ \bar{k}\ l) \neq F(h\ k\ \bar{l})$

$\varepsilon = 1$ for all hkl.

Table 14 . Application of $\sum_2$ in space group P$\bar{1}$.

)
$$\begin{array}{cccc} 2 & 1 & 4 & + \\ 0 & \bar{2} & \overline{10} & \underline{a} \\ \hline 2 & \bar{1} & \bar{6} & a \end{array}$$

)
$$\begin{array}{cccc} 2 & 1 & 4 & + \\ \bar{1} & 1 & 7 & \underline{+} \\ \hline 1 & 2 & 11 & + \end{array}$$

)
$$\begin{array}{cccc} \bar{2} & \bar{1} & \bar{4} & + \\ 3 & 5 & 2 & \underline{+} \\ \hline 1 & 4 & \bar{2} & + \end{array}$$

)
$$\begin{array}{cccc} 1 & \bar{1} & \bar{7} & + \\ 3 & 5 & 2 & \underline{+} \\ \hline 4 & 4 & \bar{5} & + \end{array}$$

)
$$\begin{array}{cccc} 1 & \bar{1} & \bar{7} & + \\ 1 & 4 & \bar{2} & \underline{+} \\ \hline 2 & 3 & \bar{9} & + \end{array}$$

)
$$\left\{\begin{array}{l} \begin{array}{cccc} 3 & 5 & 2 & + \\ 0 & \bar{2} & \overline{10} & \underline{a} \\ \hline 3 & 3 & \bar{8} & a \end{array} \\ \\ \begin{array}{cccc} 2 & \bar{1} & \bar{6} & a \\ 1 & 4 & \bar{2} & \underline{+} \\ \hline 3 & 3 & \bar{8} & a \end{array} \end{array}\right.$$

)
$$\begin{array}{cccc} 1 & 4 & \bar{2} & + \\ 0 & \bar{2} & \overline{10} & \underline{a} \\ \hline 1 & 2 & \overline{12} & a \end{array}$$

)
$$\left\{\begin{array}{l} \begin{array}{cccc} 1 & \bar{1} & \bar{7} & + \\ 0 & 2 & 10 & \underline{a} \\ \hline 1 & 1 & 3 & a \end{array} \\ \\ \begin{array}{cccc} 4 & 4 & \bar{5} & + \\ \bar{3} & \bar{3} & 8 & \underline{a} \\ \hline 1 & 1 & 3 & a \end{array} \\ \\ \begin{array}{cccc} 2 & 3 & \bar{9} & + \\ \bar{1} & \bar{2} & 12 & \underline{a} \\ \hline 1 & 1 & 3 & a \end{array} \end{array}\right.$$

(9)
$$\begin{array}{cccc} 3 & 6 & 1 & b \\ 1 & \bar{1} & \bar{7} & \underline{+} \\ \hline 4 & 5 & \bar{6} & b \end{array}$$

(10)
$$\left\{\begin{array}{l} \begin{array}{cccc} \bar{2} & \bar{1} & \bar{4} & + \\ 4 & 5 & \bar{6} & \underline{b} \\ \hline 2 & 4 & \overline{10} & b \end{array} \\ \\ \begin{array}{cccc} 3 & 6 & 1 & b \\ \bar{1} & \bar{2} & \overline{11} & \underline{+} \\ \hline 2 & 4 & \overline{10} & b \end{array} \end{array}\right.$$

(11)
$$\left\{\begin{array}{l} \begin{array}{cccc} 2 & 4 & \overline{10} & b \\ \bar{1} & 1 & 7 & \underline{+} \\ \hline 1 & 5 & \bar{3} & b \end{array} \\ \\ \begin{array}{cccc} 3 & 6 & 1 & b \\ \bar{2} & \bar{1} & \bar{4} & \underline{+} \\ \hline 1 & 5 & \bar{3} & b \end{array} \end{array}\right.$$

(12)
$$\begin{array}{cccc} 0 & 1 & 9 & c \\ 3 & 5 & 2 & \underline{+} \\ \hline 3 & 6 & 11 & c \end{array}$$

(13)
$$\begin{array}{cccc} 0 & \bar{1} & \bar{9} & c \\ 2 & 1 & 4 & \underline{+} \\ \hline 2 & 0 & \bar{5} & c \end{array}$$

(14)
$$\left\{\begin{array}{l} \begin{array}{cccc} 3 & 5 & 2 & + \\ \bar{2} & 0 & 5 & \underline{c} \\ \hline 1 & 5 & 7 & c \end{array} \\ \\ \begin{array}{cccc} 0 & 1 & 9 & c \\ 1 & 4 & \bar{2} & \underline{+} \\ \hline 1 & 5 & 7 & c \end{array} \\ \\ \begin{array}{cccc} \bar{2} & \bar{1} & \bar{4} & + \\ 3 & 6 & 11 & \underline{c} \\ \hline 1 & 5 & 7 & c \end{array} \end{array}\right.$$

(15)
$$\left\{\begin{array}{l} \begin{array}{cccc} \bar{1} & \bar{2} & \overline{11} & + \\ 2 & 0 & \bar{5} & \underline{c} \\ \hline 1 & \bar{2} & \overline{16} & c \end{array} \\ \\ \begin{array}{cccc} \bar{3} & \bar{6} & \overline{11} & c \\ 4 & 4 & \bar{5} & \underline{+} \\ \hline 1 & \bar{2} & \overline{16} & c \end{array} \\ \\ \begin{array}{cccc} \bar{1} & \bar{5} & \bar{7} & c \\ 2 & 3 & \bar{9} & \underline{+} \\ \hline 1 & \bar{2} & \overline{16} & c \end{array} \end{array}\right.$$

(16)
$$\left\{\begin{array}{l} \begin{array}{cccc} 0 & 2 & 10 & a \\ 1 & \bar{2} & \overline{16} & \underline{c} \\ \hline 1 & 0 & \bar{6} & ac \end{array} \\ \\ \begin{array}{cccc} 1 & 1 & 3 & a \\ 0 & \bar{1} & \bar{9} & \underline{c} \\ \hline 1 & 0 & \bar{6} & ac \end{array} \end{array}\right.$$

(17)
$$\left\{\begin{array}{l} \begin{array}{cccc} \bar{1} & 0 & 6 & ac \\ 2 & 1 & 4 & \underline{+} \\ \hline 1 & 1 & 10 & ac \end{array} \\ \\ \begin{array}{cccc} 2 & \bar{1} & \bar{6} & a \\ \bar{1} & 2 & 16 & \underline{c} \\ \hline 1 & 1 & 10 & ac \end{array} \end{array}\right.$$

(18)
$$\left\{\begin{array}{l} \begin{array}{cccc} 4 & 4 & \bar{5} & + \\ \bar{1} & 0 & 6 & \underline{ac} \\ \hline 3 & 4 & 1 & ac \end{array} \\ \\ \begin{array}{cccc} 1 & 5 & 7 & c \\ 2 & \bar{1} & \bar{6} & \underline{a} \\ \hline 3 & 4 & 1 & ac \end{array} \\ \\ \begin{array}{cccc} 2 & 3 & \bar{9} & + \\ 1 & 1 & 10 & \underline{ac} \\ \hline 3 & 4 & 1 & ac \end{array} \end{array}\right.$$

$$(19)\left\{\begin{array}{ll} 4\;5\;\bar{6} & \mathrm{b} \\ \underline{\bar{1}\;0\;6} & \underline{\mathrm{ac}} \\ 3\;5\;0 & \mathrm{abc} \\ & \\ 1\;1\;10 & \mathrm{ac} \\ \underline{2\;4\;\overline{10}} & \underline{\mathrm{b}} \\ 3\;5\;0 & \mathrm{abc} \end{array}\right.$$

$$(20)\left\{\begin{array}{ll} 1\;4\;\bar{2} & + \\ \underline{1\;0\;\bar{6}} & \underline{\mathrm{ac}} \\ 2\;4\;\bar{8} & \mathrm{ac} \\ & \\ \bar{1}\;\bar{1}\;\overline{10} & \mathrm{ac} \\ \underline{3\;5\;2} & \underline{+} \\ 2\;4\;\bar{8} & \mathrm{ac} \end{array}\right.$$

$$(21)\left\{\begin{array}{ll} 1\;4\;\bar{2} & + \\ \underline{1\;1\;10} & \underline{\mathrm{ac}} \\ 2\;5\;8 & \mathrm{ac} \\ & \\ 3\;6\;11 & \mathrm{c} \\ \underline{\bar{1}\;\bar{1}\;\bar{3}} & \underline{\mathrm{a}} \\ 2\;5\;8 & \mathrm{ac} \\ & \\ 3\;4\;1 & \mathrm{ac} \\ \underline{\bar{1}\;1\;7} & \underline{+} \\ 2\;5\;8 & \mathrm{ac} \end{array}\right.$$

$$(22)\left\{\begin{array}{ll} 2\;5\;8 & \mathrm{ac} \\ \underline{2\;3\;\bar{9}} & \underline{+} \\ 4\;8\;\bar{1} & \mathrm{ac} \\ & \\ 1\;4\;\bar{2} & + \\ \underline{3\;4\;1} & \underline{\mathrm{ac}} \\ 4 & \mathrm{ac} \end{array}\right.$$

$$(23)\left\{\begin{array}{ll} \bar{2}\;1\;6 & \mathrm{a} \\ \underline{3\;5\;0} & \underline{\mathrm{abc}} \\ 1\;6\;6 & \mathrm{bc} \\ & \\ 3\;6\;1 & \mathrm{b} \\ \underline{\bar{2}\;0\;5} & \underline{\mathrm{c}} \\ 1\;6\;6 & \mathrm{bc} \end{array}\right.$$

$$(24)\left\{\begin{array}{ll} \bar{2}\;\bar{5}\;\bar{8} & \mathrm{ac} \\ \underline{3\;5\;0} & \underline{\mathrm{abc}} \\ 1\;0\;\bar{8} & \mathrm{b} \\ & \\ 2\;4\;\overline{10} & \mathrm{b} \\ \underline{\bar{1}\;\bar{4}\;2} & \underline{+} \\ 1\;0\;\bar{8} & \mathrm{b} \\ & \\ 4\;5\;\bar{6} & \mathrm{b} \\ \underline{\bar{3}\;\bar{5}\;\bar{2}} & \underline{+} \\ 1\;0\;\bar{8} & \mathrm{b} \end{array}\right.$$

$$(25)\quad\begin{array}{ll} 1\;\bar{9}\;2 & \mathrm{d} \\ \underline{2\;4\;\overline{10}} & \underline{\mathrm{b}} \\ 3\;\bar{5}\;\bar{8} & \mathrm{bd} \end{array}$$

$$(26)\left\{\begin{array}{ll} \bar{3}\;5\;8 & \mathrm{bd} \\ \underline{3\;5\;0} & \underline{\mathrm{abc}} \\ 0\;10\;8 & \mathrm{acd} \\ & \\ \bar{1}\;9\;\bar{2} & \mathrm{d} \\ \underline{1\;1\;10} & \underline{\mathrm{ac}} \\ 0\;10\;8 & \mathrm{acd} \end{array}\right.$$

$$(27)\left\{\begin{array}{ll} 3\;\bar{5}\;\bar{8} & \mathrm{bd} \\ \underline{1\;2\;11} & \underline{+} \\ 4\;\bar{3}\;3 & \mathrm{bd} \\ & \\ 3\;6\;1 & \mathrm{b} \\ \underline{1\;\bar{9}\;2} & \underline{\mathrm{d}} \\ 4\;\bar{3}\;3 & \mathrm{bd} \end{array}\right.$$

$$(28)\left\{\begin{array}{l} \bar{1}\;1\;7 \\ \underline{3\;\bar{5}\;\bar{8}} \\ 2\;\bar{4}\;\bar{1} \\ \\ 1\;\bar{9}\;2 \\ \underline{1\;5\;\bar{3}} \\ 2\;\bar{4}\;\bar{1} \\ \\ 4\;\bar{3}\;3 \\ \underline{\bar{2}\;\bar{1}\;\bar{4}} \\ 2\;\bar{4}\;\bar{1} \end{array}\right.$$

$$(29)\left\{\begin{array}{l} 1\;0\;\bar{6} \\ \underline{0\;10\;8} \\ 1\;10\;2 \\ \\ \bar{1}\;9\;\bar{2} \\ \underline{2\;1\;4} \\ 1\;10\;2 \\ \\ 3\;6\;1 \\ \underline{\bar{2}\;4\;1} \\ 1\;10\;2 \end{array}\right.$$

$$(30)\left\{\begin{array}{l} 3\;\bar{5}\;\bar{8} \\ \underline{\bar{1}\;0\;8} \\ 2\;\bar{5}\;0 \\ \\ 1\;\bar{9}\;2 \\ \underline{1\;4\;\bar{2}} \\ 2\;\bar{5}\;0 \\ \\ \bar{1}\;\overline{10}\;\bar{2} \\ \underline{3\;5\;2} \\ 2\;\bar{5}\;0 \end{array}\right.$$

$$(31)\left\{\begin{array}{l} 1\;0\;\bar{6} \\ \underline{2\;\bar{4}\;\bar{1}} \\ 3\;\bar{4}\;\bar{7} \\ \\ 0\;\overline{10}\;\bar{8} \\ \underline{3\;6\;1} \\ 3\;\bar{4}\;\bar{7} \end{array}\right.$$

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$\varepsilon = 1$ for all hkl.

$$(32)\quad\left\{\begin{array}{rrrl} 0 & \bar{2} & \overline{10} & \mathrm{a} \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \hline 4 & \bar{5} & \bar{7} & \mathrm{abd} \\ \\ 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 2 & \bar{1} & \bar{6} & \mathrm{a} \\ \hline 4 & \bar{5} & \bar{7} & \mathrm{abd} \end{array}\right.$$

$$(33)\quad\left\{\begin{array}{rrrl} \bar{1} & \bar{1} & \bar{3} & \mathrm{a} \\ 3 & \bar{4} & \bar{7} & \mathrm{abcd} \\ \hline 2 & \bar{5} & \overline{10} & \mathrm{bcd} \\ \\ 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 0 & \bar{1} & \bar{9} & \mathrm{c} \\ \hline 2 & \bar{5} & \overline{10} & \mathrm{bcd} \end{array}\right.$$

$$(34)\quad\left\{\begin{array}{rrrl} 4 & 4 & \bar{5} & + \\ \bar{3} & 4 & 7 & \mathrm{abcd} \\ \hline 1 & 8 & 2 & \mathrm{abcd} \\ \\ 3 & 4 & 1 & \mathrm{ac} \\ \bar{2} & 4 & 1 & \mathrm{bd} \\ \hline 1 & 8 & 2 & \mathrm{abcd} \\ \\ \bar{2} & 5 & 10 & \mathrm{bcd} \\ 3 & 3 & \bar{8} & \mathrm{a} \\ \hline 1 & 8 & 2 & \mathrm{abcd} \end{array}\right.$$

$$(35)\quad\left\{\begin{array}{rrrl} \bar{2} & 1 & 6 & \mathrm{a} \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \hline 2 & \bar{2} & 9 & \mathrm{abd} \\ \\ 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 0 & 2 & 10 & \mathrm{a} \\ \hline 2 & \bar{2} & 9 & \mathrm{abd} \\ \\ \bar{1} & \bar{8} & \bar{2} & \mathrm{abcd} \\ 3 & 6 & 11 & \mathrm{c} \\ \hline 2 & \bar{2} & 9 & \mathrm{abd} \end{array}\right.$$

$$(36)\quad\left\{\begin{array}{rrrl} 0 & \bar{1} & \bar{9} & \mathrm{c} \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \hline 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ \\ 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 2 & 0 & \bar{5} & \mathrm{c} \\ \hline 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ \\ 2 & \bar{5} & \overline{10} & \mathrm{bcd} \\ 2 & 1 & 4 & + \\ \hline 4 & \bar{4} & \bar{6} & \mathrm{bcd} \end{array}\right.$$

$$(37)\quad\left\{\begin{array}{rrrl} 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ \bar{3} & \bar{3} & 8 & \mathrm{a} \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \\ \\ \bar{1} & \bar{5} & \bar{7} & \mathrm{c} \\ 2 & \bar{2} & 9 & \mathrm{abd} \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \\ \\ 2 & 1 & 4 & + \\ \bar{1} & \bar{8} & \bar{2} & \mathrm{abcd} \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \\ \\ 2 & \bar{5} & \overline{10} & \mathrm{bcd} \\ \bar{1} & \bar{2} & 12 & \mathrm{a} \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \\ \\ 3 & \bar{4} & \bar{7} & \mathrm{abcd} \\ \bar{2} & \bar{3} & 9 & + \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \\ \\ \bar{3} & \bar{4} & \bar{1} & \mathrm{ac} \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \hline 1 & \bar{7} & 2 & \mathrm{abcd} \end{array}\right.$$

$$(38)\quad\left\{\begin{array}{rrrl} 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ \bar{1} & 2 & 16 & \mathrm{c} \\ \hline 3 & \bar{2} & 10 & \mathrm{bd} \\ \\ \bar{1} & 1 & 7 & + \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \hline 3 & \bar{2} & 10 & \mathrm{bd} \\ \\ 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 1 & 2 & 11 & + \\ \hline 3 & \bar{2} & 10 & \mathrm{bd} \\ \\ 2 & 5 & 8 & \mathrm{ac} \\ 1 & \bar{7} & 2 & \mathrm{abcd} \\ \hline 3 & \bar{2} & 10 & \mathrm{bd} \end{array}\right.$$

$$(39)\quad\left\{\begin{array}{rrrl} 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ \bar{1} & 0 & 6 & \mathrm{ac} \\ \hline 3 & \bar{4} & 0 & \mathrm{abd} \\ \\ 3 & \bar{2} & \overline{10} & \mathrm{a} \\ 3 & \bar{2} & 10 & \mathrm{bd} \\ \hline 3 & \bar{4} & 0 & \mathrm{abd} \\ \\ 4 & \bar{5} & \bar{7} & \mathrm{abd} \\ \bar{1} & 1 & 7 & + \\ \hline 3 & \bar{4} & 0 & \mathrm{abd} \\ \\ 4 & \bar{3} & 3 & \mathrm{bd} \\ \bar{1} & \bar{1} & \bar{3} & \mathrm{a} \\ \hline 3 & \bar{4} & 0 & \mathrm{abd} \\ \\ 2 & \bar{5} & \overline{10} & \mathrm{bcd} \\ 1 & 1 & 10 & \mathrm{ac} \\ \hline 3 & \bar{4} & 0 & \mathrm{abd} \end{array}\right.$$

$$(40)\quad\left\{\begin{array}{rrrl} 4 & \bar{4} & \bar{6} & \mathrm{bcd} \\ 0 & 10 & 8 & \mathrm{acd} \\ \hline 4 & 6 & 2 & \mathrm{ab} \\ \\ 3 & \bar{4} & 0 & \mathrm{abd} \\ 1 & 10 & 2 & \mathrm{d} \\ \hline 4 & 6 & 2 & \mathrm{ab} \end{array}\right.$$

$$(41)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 3 & \bar{4} & 0 & \mathrm{abd} \\ \bar{1} & 9 & 2 & \mathrm{d} \\ \hline 2 & 5 & \bar{2} & \mathrm{ab} \end{array} \\[2ex]
\begin{array}{rrrl} 3 & 6 & 1 & \mathrm{b} \\ \bar{1} & \bar{1} & \bar{3} & \mathrm{a} \\ \hline 2 & 5 & \bar{2} & \mathrm{ab} \end{array} \\[2ex]
\begin{array}{rrrl} \bar{2} & \bar{1} & \bar{4} & + \\ 4 & 6 & 2 & \mathrm{ab} \\ \hline 2 & 5 & \bar{2} & \mathrm{ab} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & \bar{5} & \overline{10} & \mathrm{bcd} \\ 0 & 10 & 8 & \mathrm{acd} \\ \hline 2 & 5 & \bar{2} & \mathrm{ab} \end{array}
\end{array}\right.$$

$$(42)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} \bar{2} & 5 & 0 & \mathrm{d} \\ 3 & \bar{2} & 10 & \mathrm{bd} \\ \hline 1 & 3 & 10 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & 5 & \bar{2} & \mathrm{ab} \\ \bar{1} & \bar{2} & 12 & \mathrm{a} \\ \hline 1 & 3 & 10 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 3 & 6 & 1 & \mathrm{b} \\ \bar{2} & \bar{3} & 9 & + \\ \hline 1 & 3 & 10 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} \bar{3} & \bar{3} & 8 & \mathrm{a} \\ 4 & 6 & 2 & \mathrm{ab} \\ \hline 1 & 3 & 10 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & \bar{7} & 2 & \mathrm{abcd} \\ 1 & 10 & 8 & \mathrm{acd} \\ \hline 1 & 3 & 10 & \mathrm{b} \end{array}
\end{array}\right.$$

$$(43)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 1 & 3 & 10 & \mathrm{b} \\ 1 & 4 & \bar{2} & + \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 3 & \bar{2} & 10 & \mathrm{bd} \\ \bar{1} & 9 & \bar{2} & \mathrm{d} \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 4 & 6 & 2 & \mathrm{ab} \\ \bar{2} & 1 & 6 & \mathrm{a} \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & 5 & \bar{2} & \mathrm{ab} \\ 0 & 2 & 10 & \mathrm{a} \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 3 & 6 & 1 & \mathrm{b} \\ \bar{1} & 1 & 7 & + \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & 2 & 11 & + \\ 1 & 5 & \bar{3} & \mathrm{b} \\ \hline 2 & 7 & 8 & \mathrm{b} \end{array}
\end{array}\right.$$

$$(44)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 4 & 6 & 2 & \mathrm{ab} \\ \bar{1} & \bar{5} & 3 & \mathrm{b} \\ \hline 3 & 1 & 5 & \mathrm{a} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & 1 & 10 & \mathrm{ac} \\ 2 & 0 & \bar{5} & \mathrm{c} \\ \hline 3 & 1 & 5 & \mathrm{a} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & 2 & 11 & + \\ 2 & \bar{1} & \bar{6} & \mathrm{a} \\ \hline 3 & 1 & 5 & \mathrm{a} \end{array}
\end{array}\right.$$

$$(45)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} \bar{1} & \bar{4} & 2 & + \\ 3 & \bar{5} & \bar{8} & \mathrm{bd} \\ \hline 2 & \bar{9} & \bar{6} & \mathrm{bd} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & 0 & \bar{8} & \mathrm{b} \\ 1 & \bar{9} & 2 & \mathrm{d} \\ \hline 2 & \bar{9} & \bar{6} & \mathrm{bd} \end{array}
\end{array}\right.$$

$$(46)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 2 & \bar{9} & \bar{6} & \mathrm{bd} \\ 2 & 5 & \bar{2} & \mathrm{ab} \\ \hline 4 & \bar{4} & \bar{8} & \mathrm{ad} \end{array} \\[2ex]
\begin{array}{rrrl} 1 & 0 & \bar{8} & \mathrm{b} \\ 3 & \bar{4} & 0 & \mathrm{abd} \\ \hline 4 & \bar{4} & \bar{8} & \mathrm{ad} \end{array}
\end{array}\right.$$

$$(47)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 2 & \bar{9} & \bar{6} & \mathrm{bd} \\ 1 & 5 & 7 & \mathrm{c} \\ \hline 3 & \bar{4} & 1 & \mathrm{bcd} \end{array} \\[2ex]
\begin{array}{rrrl} 0 & 1 & 9 & \mathrm{c} \\ 3 & \bar{5} & \bar{8} & \mathrm{bd} \\ \hline 3 & \bar{4} & 1 & \mathrm{bcd} \end{array}
\end{array}\right.$$

$$(48)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 3 & \bar{4} & 1 & \mathrm{bcd} \\ \bar{1} & \bar{4} & 2 & + \\ \hline 2 & \bar{8} & 3 & \mathrm{bcd} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & \bar{9} & \bar{6} & \mathrm{bd} \\ 0 & 1 & 9 & \mathrm{c} \\ \hline 2 & \bar{8} & 3 & \mathrm{bcd} \end{array}
\end{array}\right.$$

$$(49)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} \bar{2} & 5 & 0 & \mathrm{d} \\ 3 & \bar{4} & 1 & \mathrm{bcd} \\ \hline 1 & 1 & 1 & \mathrm{bc} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & \bar{8} & 3 & \mathrm{bcd} \\ \bar{1} & 9 & \bar{2} & \mathrm{d} \\ \hline 1 & 1 & 1 & \mathrm{bc} \end{array}
\end{array}\right.$$

$$(50)\quad\left\{\begin{array}{l}
\begin{array}{rrrl} 2 & 1 & 4 & + \\ 1 & 1 & 1 & \mathrm{bc} \\ \hline 3 & 2 & 5 & \mathrm{bc} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & \bar{8} & 3 & \mathrm{bcd} \\ 1 & 10 & 2 & \mathrm{d} \\ \hline 3 & 2 & 5 & \mathrm{bc} \end{array} \\[2ex]
\begin{array}{rrrl} 2 & \bar{4} & \bar{1} & \mathrm{bd} \\ 1 & 6 & 6 & \mathrm{bc} \\ \hline 3 & 2 & 5 & \mathrm{cd} \end{array}
\end{array}\right.$$

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$$(51)\left\{\begin{array}{rrrl}
1 & 1 & 1 & \text{bc}\\
3 & 3 & \bar{8} & \text{a}\\ \hline
4 & 4 & \bar{7} & \text{abc}\\[2ex]
3 & 5 & 0 & \text{abc}\\
1 & \bar{1} & \bar{7} & +\\ \hline
4 & 4 & \bar{7} & \text{abc}\\[2ex]
3 & 4 & 1 & \text{ac}\\
1 & 0 & \bar{8} & \text{b}\\ \hline
4 & 4 & \bar{7} & \text{abc}
\end{array}\right.$$

$$(52)\left\{\begin{array}{rrrl}
4 & 4 & \bar{7} & \text{abc}\\
\bar{2} & 1 & 6 & \text{a}\\ \hline
2 & 5 & \bar{1} & \text{bc}\\[2ex]
\bar{2} & 0 & 5 & \text{c}\\
4 & 5 & \bar{6} & \text{b}\\ \hline
2 & 5 & \bar{1} & \text{bc}\\[2ex]
3 & \bar{4} & 1 & \text{bcd}\\
\bar{1} & 9 & \bar{2} & \text{d}\\ \hline
2 & 5 & \bar{1} & \text{bc}
\end{array}\right.$$

$$(53)\left\{\begin{array}{rrrl}
2 & 7 & 8 & \text{b}\\
\bar{2} & \bar{5} & 1 & \text{bc}\\ \hline
0 & 2 & 9 & \text{c}\\[2ex]
3 & \bar{2} & 10 & \text{bd}\\
\bar{3} & 4 & \bar{1} & \text{bcd}\\ \hline
0 & 2 & 9 & \text{c}\\[2ex]
\bar{4} & \bar{4} & 7 & \text{abc}\\
4 & 6 & 2 & \text{ab}\\ \hline
0 & 2 & 9 & \text{c}\\[2ex]
1 & 3 & 10 & \text{b}\\
\bar{1} & \bar{1} & \bar{1} & \text{bc}\\ \hline
0 & 2 & 9 & \text{c}
\end{array}\right.$$

$$(54)\left\{\begin{array}{rrrl}
1 & 4 & \bar{2} & +\\
0 & 2 & 9 & \text{c}\\ \hline
1 & 6 & 7 & \text{c}\\[2ex]
3 & \bar{2} & 10 & \text{bd}\\
\bar{2} & 8 & \bar{3} & \text{bcd}\\ \hline
1 & 6 & 7 & \text{c}\\[2ex]
2 & 7 & 8 & \text{b}\\
\bar{1} & \bar{1} & \bar{1} & \text{bc}\\ \hline
1 & 6 & 7 & \text{c}
\end{array}\right.$$

$$(55)\left\{\begin{array}{rrrl}
\bar{1} & \bar{3} & \overline{10} & \text{b}\\
2 & \bar{8} & 3 & \text{bcd}\\ \hline
1 & \overline{11} & \bar{7} & \text{cd}\\[2ex]
0 & \bar{2} & \bar{9} & \text{c}\\
1 & \bar{9} & 2 & \text{d}\\ \hline
1 & \overline{11} & \bar{7} & \text{cd}\\[2ex]
2 & \bar{5} & 0 & \text{d}\\
\bar{1} & \bar{6} & \bar{7} & \text{c}\\ \hline
1 & \overline{11} & \bar{7} & \text{cd}\\[2ex]
\bar{2} & \bar{7} & \bar{8} & \text{b}\\
3 & \bar{4} & 1 & \text{bcd}\\ \hline
1 & \overline{11} & \bar{7} & \text{cd}
\end{array}\right.$$

$$(56)\left\{\begin{array}{rrrl}
3 & \bar{4} & 1 & \text{bcd}\\
1 & \bar{1} & \bar{7} & +\\ \hline
4 & \bar{5} & \bar{6} & \text{bcd}\\[2ex]
3 & 6 & 1 & \text{b}\\
1 & \overline{11} & \bar{7} & \text{cd}\\ \hline
4 & \bar{5} & \bar{6} & \text{bcd}\\[2ex]
2 & 3 & \bar{9} & +\\
2 & \bar{8} & 3 & \text{bcd}\\ \hline
4 & \bar{5} & \bar{6} & \text{bcd}\\[2ex]
4 & \bar{3} & 3 & \text{bd}\\
0 & \bar{2} & \bar{9} & \text{c}\\ \hline
4 & \bar{5} & \bar{6} & \text{bcd}
\end{array}\right.$$

$$(57)\left\{\begin{array}{rrrl}
4 & \bar{5} & \bar{6} & \text{bcd}\\
\bar{2} & 5 & 0 & \text{d}\\ \hline
2 & 0 & \bar{6} & \text{bc}\\[2ex]
3 & 6 & 1 & \text{b}\\
\bar{1} & \bar{6} & \bar{7} & \text{c}\\ \hline
2 & 0 & \bar{6} & \text{bc}\\[2ex]
1 & \bar{1} & \bar{7} & +\\
1 & 1 & 1 & \text{bc}\\ \hline
2 & 0 & \bar{6} & \text{bc}
\end{array}\right.$$

$$(58)\left\{\begin{array}{rrrl}
1 & 1 & 1 & \text{bc}\\
0 & \bar{2} & \overline{10} & \text{a}\\ \hline
1 & \bar{1} & \bar{9} & \text{abc}\\[2ex]
\bar{1} & \bar{1} & \bar{3} & \text{a}\\
2 & 0 & \bar{6} & \text{bc}\\ \hline
1 & \bar{1} & \bar{9} & \text{abc}\\[2ex]
4 & 4 & \bar{7} & \text{abc}\\
\bar{3} & \bar{5} & \bar{2} & +\\ \hline
1 & \bar{1} & \bar{9} & \text{abc}\\[2ex]
\bar{1} & \bar{6} & \bar{7} & \text{c}\\
2 & 5 & \bar{2} & \text{ab}\\ \hline
1 & \bar{1} & \bar{9} & \text{abc}
\end{array}\right.$$

$$(59)\left\{\begin{array}{rrrl}
1 & 5 & \bar{3} & \text{b}\\
1 & \overline{11} & \bar{7} & \text{cd}\\ \hline
2 & \bar{6} & \overline{10} & \text{bcd}\\[2ex]
\bar{2} & \bar{1} & \bar{4} & +\\
4 & \bar{5} & \bar{6} & \text{bcd}\\ \hline
2 & \bar{6} & \overline{10} & \text{bcd}\\[2ex]
3 & \bar{4} & 1 & \text{bcd}\\
\bar{1} & \bar{2} & \overline{11} & +\\ \hline
2 & \bar{6} & \overline{10} & \text{bcd}\\[2ex]
2 & \bar{4} & \bar{1} & \text{bd}\\
0 & \bar{2} & \bar{9} & \text{c}\\ \hline
2 & \bar{6} & \overline{10} & \text{bcd}
\end{array}\right.$$

$$(60)\ \left\{\begin{array}{ccc l}
\overline{2} & 0 & 6 & \text{bc} \\
2 & 4 & \overline{10} & \text{b} \\ \hline
0 & 4 & \overline{4} & \text{c} \\
 & & & \\
\overline{1} & \overline{1} & \overline{1} & \text{bc} \\
1 & 5 & \overline{3} & \text{b} \\ \hline
0 & 4 & \overline{4} & \text{c} \\
 & & & \\
1 & 10 & 2 & \text{d} \\
\overline{1} & \overline{6} & \overline{6} & \text{bc} \\ \hline
0 & 4 & \overline{4} & \text{bcd} \\
 & & & \\
\overline{2} & 8 & \overline{3} & \text{bcd} \\
2 & \overline{4} & \overline{1} & \text{bd} \\ \hline
0 & 4 & \overline{4} & \text{c} \\
 & & & \\
2 & \overline{5} & \overline{10} & \text{bcd} \\
\overline{2} & 9 & 6 & \text{bd} \\ \hline
0 & 4 & \overline{4} & \text{c} \\
 & & & \\
1 & 6 & 7 & \text{c} \\
\overline{1} & \overline{2} & \overline{11} & + \\ \hline
0 & 4 & \overline{4} & \text{c}
\end{array}\right.$$

$$\boxed{\text{bd} = +}$$

$$(61)\ \left\{\begin{array}{ccc l}
4 & \overline{5} & \overline{6} & \text{bcd} \\
0 & 10 & 8 & \text{acd} \\ \hline
4 & 5 & 2 & \text{ab} \\
 & & & \\
2 & 5 & 8 & \text{ac} \\
2 & 0 & \overline{6} & \text{bc} \\ \hline
4 & 5 & 2 & \text{ab} \\
 & & & \\
3 & 6 & 11 & \text{c} \\
1 & \overline{1} & \overline{9} & \text{abc} \\ \hline
4 & 5 & 2 & \text{ab} \\
 & & & \\
3 & 4 & 1 & \text{ac} \\
1 & 1 & 1 & \text{bc} \\ \hline
3 & 5 & 2 & \text{ab} \\
 & & & \\
4 & 4 & \overline{7} & \text{abc} \\
0 & 1 & 9 & \text{c} \\ \hline
4 & 5 & 2 & \text{ab}
\end{array}\right.$$

$$(62)\ \left\{\begin{array}{ccc l}
2 & 3 & \overline{9} & + \\
0 & \overline{4} & 4 & \text{c} \\ \hline
2 & \overline{1} & \overline{5} & \text{c} \\
 & & & \\
1 & \overline{11} & \overline{7} & \text{cd} \\
1 & 10 & 2 & \text{d} \\ \hline
2 & \overline{1} & \overline{5} & \text{c} \\
 & & & \\
4 & 4 & \overline{7} & \text{abc} \\
\overline{2} & \overline{5} & 2 & \text{ab} \\ \hline
2 & \overline{1} & \overline{5} & \text{c} \\
 & & & \\
4 & \overline{5} & \overline{6} & \text{bcd} \\
\overline{2} & 4 & 1 & \text{bd} \\ \hline
2 & \overline{1} & \overline{5} & \text{c} \\
 & & & \\
2 & 1 & 4 & + \\
0 & \overline{2} & \overline{9} & \text{c} \\ \hline
2 & \overline{1} & \overline{5} & \text{c} \\
 & & & \\
3 & 5 & 2 & + \\
\overline{1} & \overline{6} & \overline{7} & \text{c} \\ \hline
2 & \overline{1} & \overline{5} & \text{c}
\end{array}\right.$$

$$(63)\ \left\{\begin{array}{ccc l}
0 & \overline{4} & 4 & \text{c} \\
3 & 4 & 1 & \text{ac} \\ \hline
3 & 0 & 5 & \text{a} \\
 & & & \\
\overline{1} & \overline{5} & 3 & \text{b} \\
4 & 5 & 2 & \text{ab} \\ \hline
3 & 0 & 5 & \text{a} \\
 & & & \\
1 & 8 & 2 & \text{abcd} \\
2 & \overline{8} & 3 & \text{bcd} \\ \hline
3 & 0 & 5 & \text{a} \\
 & & & \\
1 & 1 & 10 & \text{ac} \\
2 & \overline{1} & \overline{5} & \text{c} \\ \hline
3 & 0 & 5 & \text{a}
\end{array}\right.$$

$$(64)\ \left\{\begin{array}{ccc l}
\overline{2} & 8 & \overline{3} & \text{bcd} \\
2 & \overline{6} & \overline{10} & \text{bcd} \\ \hline
0 & 2 & \overline{13} & + \\
 & & & \\
0 & \overline{2} & \overline{9} & \text{c} \\
0 & 4 & \overline{4} & \text{c} \\ \hline
0 & 2 & \overline{13} & + \\
 & & & \\
3 & 3 & \overline{8} & \text{a} \\
\overline{3} & \overline{1} & \overline{5} & \text{a} \\ \hline
0 & 2 & \overline{13} & + \\
 & & & \\
\overline{1} & \overline{3} & \overline{10} & \text{b} \\
1 & 5 & \overline{3} & \text{b} \\ \hline
0 & 2 & \overline{13} & + \\
 & & & \\
2 & 3 & \overline{9} & + \\
\overline{2} & \overline{1} & \overline{4} & + \\ \hline
0 & 2 & \overline{13} & + \\
 & & & \\
1 & 4 & \overline{2} & + \\
\overline{1} & \overline{2} & \overline{11} & + \\ \hline
0 & 2 & \overline{13} & +
\end{array}\right.$$

Table 15. Application of $\sum_1$ in $P\bar{1}$

$$sE_{2\vec{h}} \approx s(E_{\vec{h}}^2-1)$$

$$P_+(E_{2\vec{h}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh \frac{\sigma_3 \left|E_{2\vec{h}}\right| (E_{\vec{h}}^2-1)}{2\sigma_2^{3/2}}$$

$sE_{2\vec{h}} \approx s(E_{\vec{h}}^2-1)$		
$0\ 4\ \bar{4}$	$\lvert E\rvert = 1.52$	$P_+(0\ 4\ \bar{4}) = 0.72$ (correct sign)
$0\ 2\ \bar{2}$	$(E^2-1) = 4.29$	
$4\ \bar{8}\ \bar{2}$	$\lvert E\rvert = 1.36$	$P_+(4\ \bar{8}\ \bar{2}) = 0.68$ (incorrect sign)
$2\ \bar{4}\ \bar{1}$	$(E^2-1) = 3.75$	

Table 16. *Sets of possible phases based on the four unknowns, a, b, d and g*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
a	−	+	+	−	+	−	+	−	−	+	+	−	−	+	+	−
b	−	−	−	−	+	+	+	+	−	−	−	−	+	+	+	+
d	−	−	−	−	+	+	+	+	+	+	+	+	−	−	−	−
g	+	+	−	−	+	+	−	−	+	−	+	−	+	−	+	−
No. positive	105		94		203			92	94	90					124	86
No. negative	98		93		0			94	98	101					68	106
No. indeterminate	0	37	16	40	0	35	40	17	11	12	40	34	40	34	11	11

EXAMPLE OF MULTIPLE SOLUTION

$E_{\underset{\sim}{h}} E_{\underset{\sim}{k}} E_{\underset{\sim}{h}-\underset{\sim}{k}}$ product of 11 will give a P_+ value of 95% while a triple product of 16 corresponds to $P_+ = 99\%$.

It should be noted that in space group $P\bar{1}$, negative signs cannot be obtained from symmetry equivalent reflections, as in space group $P2_1/a$, for example. Therefore, at least one symbol must be assigned to the phase determination which will have a negative sign. If the origin is specified by assigning negative signs, rather than three positive signs, merely the origin will be shifted by ½ in the a, b and/or c directions, but there is still a need to obtain negative signs by assigning symbols to one or more reflections.

In this example, signs of the structure factors, + or -, are used rather than the phases 0 or π. Accordingly, in the sign determination, the indices are added and the signs or symbols are multiplied. For any symbol x, $x^2 \equiv +$ for centrosymmetric space groups. In the entries shown in Table 14, for many phases, there are multiple terms indicating the same symbol; however, there are only two relationships between symbols. Both of these relationships indicate that b = d with $P_+ = 0.99$ and 0.86, and it will be seen that this relationship is incorrect. Sign determination for additional reflections not listed in Table 14 yielded other relationships among symbols with relatively low probabilities.

In an attempt to reduce the number of unknowns, the $\sum_1$ formula for space group $P\bar{1}$ (Hauptman and Karle, 1953) was applied to two reflections. The details are shown in Table 15. In each case the probability that the sign be + is rather low. The $\sum_1$ indication that the sign of $04\bar{4}$ is + and the $\sum_2$ result that the sign of $04\bar{4}$ is c, i.e. c = +, proved to be correct. On the other hand, the $\sum_1$ and $\sum_2$ indications for $4\bar{8}\bar{2}$ showing that bd = + or b = d, proved to be incorrect.

Table 16 shows the sixteen sets of possible phases based on the unknowns a, b, d and g. Symbol c was assumed to be +. Two hundred and three reflections for which signs in terms of unknown symbols had been assigned were considered. At the bottom of the table are listed the number of reflections with positive signs, the number with negative signs and the number of reflections whose signs were indeterminate because multiple indications disagreed with each other for particular assignments of a, b, d and g. Eight of the sets in Table 16 had 34 or more indeterminate phases as compared with 17 or less for the other eight sets and therefore were eliminated immediately. Furthermore set 5, having all positive signs, and set 15, having a predominance of positive signs, were not considered because an atom was not expected at the origin.

Set 1 had a completely consistent set of phases, which is an unusual occurrence. The E-map based on signs from set 1 was completely meaningless. This is an illustration of a pitfall of depending entirely upon consistency in phase determination. Set 16 was the correct assignment for the unknown symbols and yielded the E-map shown in Fig. 4. Although set 16 did not represent the most consistent set of phases, it was among the sets of phases with a high degree of consistency.

Set 10 produced a map very similar to set 16, except that the whole molecule was translated too close to a center of symmetry. Procedures for obtaining the true position of a misplaced molecule will be discussed in some of the following articles.

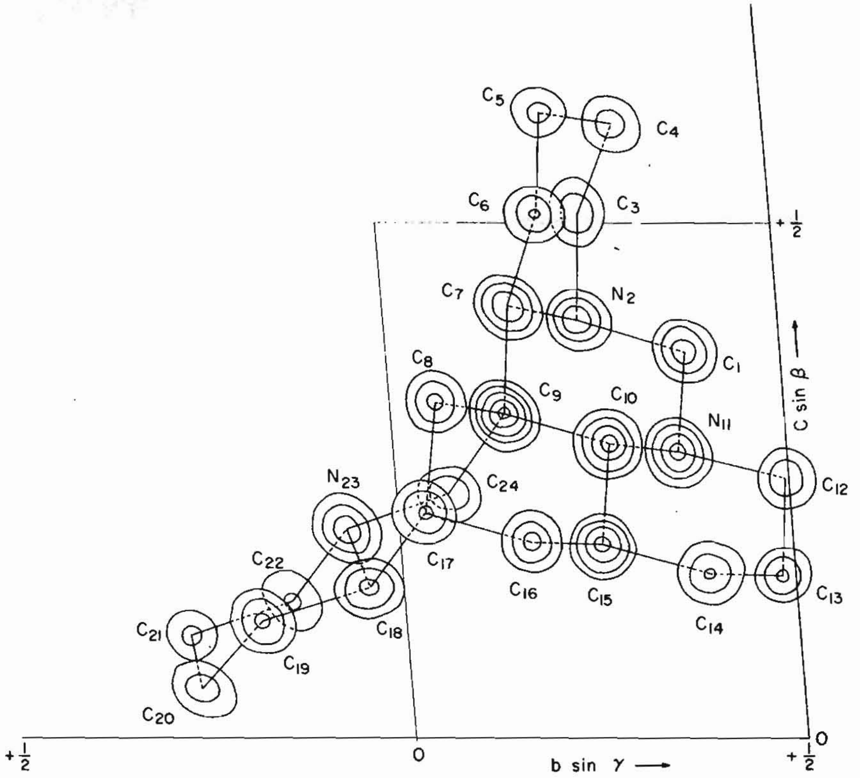


Fig. 4. Sections from a three-dimensional E-map for jamine computed with 286 terms with $|E| > 1.36$ and the phase determined by the symbolic addition procedure.
Contours are at equally spaced, arbitrary levels.

In many structure determinations in space group $P\bar{1}$, as well as other space groups, it was possible to evaluate all the symbols from multiple indications for the phases and only one E-map needed to be computed. Examples in the literature are, for example, the structure of a thymine-thymine adduct (Karle, 1969) and a thymine trimer (Flippen and Karle, 1971). The procedure described above has been used to solve a number of structures in space group $P\bar{1}$ in which there were four independent molecules in the asymmetric unit containing from 64 to over 100 C, O and/or N atoms per asymmetric unit (see e.g. Karle and Fratini, 1970; Karle, J.M. and Karle, 1972; and Karle and Karle, 1963). The latter reference, to cyclohexaglycyl with four independent molecules in the asymmetric unit, describes the first application of the symbolic addition procedure.

Space Group $P2_12_12_1$

Many materials crystallize in the acentric space group $P2_12_12_1$. The example chosen for discussion is the phase determination for L-arginine dihydrate (Karle and Karle, 1964a). This was the first acentric crystal solved by the direct method of phase determination. The many points emphasized in the structure analysis are as valid today as they were ten years ago. Tables 17-21 contain the normalized structure factors, the initial steps in the phase determination and the final coordinates. The $|E_{\underset{\sim}{h}}|$ were derived from the experimental intensities and were arranged in parity groups of hkl. Triples were formed from sets of $\underset{\sim}{k}$ and $\underset{\sim}{h}-\underset{\sim}{k}$ associated with a given $\underset{\sim}{h}$ for these reflections with the largest $|E|$ values. Listings were made in the same manner as for centrosymmetric space groups.

Table 17. **L-Arginine·$2H_2O$**

I.L. Karle and J. Karle (1964),
Acta Cryst. 17, 835.

$^{+}(H_2N)_2CNH(CH_2)_3CH(NH_2)COO^{-}$

Space group $P2_12_12_1$

a = 5.68 ± .01 A

b = 11.87 ± .02

c = 15.74 ± .02

Z = 4

Final fractional coordinates

Atom	x	y	z
O(1)	0.3022	0.4036	0.3231
O(2)	0.3340	0.5832	0.2830
C(3)	0.2353	0.5047	0.3220
C(4)	0.0072	0.5293	0.3724
N(5)	-0.0839	0.6432	0.3524
C(6)	0.0622	0.5186	0.4680
C(7)	0.2546	0.5995	0.5002
C(8)	0.3822	0.5478	0.5753
N(9)	0.5532	0.6274	0.6118
C(10)	0.7315	0.5955	0.6633
N(11)	0.7796	0.4862	0.6760
N(12)	0.8579	0.6739	0.7016
W(1)	0.5506	0.2790	0.6214
W(2)	0.6222	0.2871	0.4356

Table 18. Reflection data with $|E| > 1.5$ for L-Arginine·$2H_2O$.

g	g	g	|E|	Ø	g	g	u	|E|	Ø
*2	12	0	3.20	p					
0	8	14	3.07	p	2	0	5	2.15	$-\pi/2+m$
2	0	12	3.05	$\pi-2a$	2	0	3	2.04	$-\pi/2$
0	2	20	2.77	$\pi+p+s$	0	8	7	1.98	$\pi+a$
2	0	8	2.59	$\pi+m$	4	0	9	1.83	$+\pi/2$
*4	0	14	2.56	m	4	0	13	1.83	$+\pi/2$
0	12	8	2.52	p	4	0	15	1.73	$+\pi/2$
2	0	18	2.50	π	0	6	15	1.73	
6	8	0	2.46						
2	0	6	2.40	π	2	12	9	1.73	
*2	10	0	2.31	s	0	6	11	1.70	
0	12	6	2.20	$\pi+p$	6	0	1	1.69	$+\pi/2$
0	12	2	2.14	p	4	12	5	1.68	$+\pi/2+p$
4	0	6	2.08	0	2	8	13	1.65	0
2	10	6	2.07	s	2	6	11	1.62	
0	10	6	2.04	$\pi+s$	2	10	9	1.60	$+\pi/2+s$
4	10	0	1.99	$\pi+s$					
0	6	18	1.96	0	4	6	1	1.58	
					0	4	11	1.58	p
4	0	16	1.96	0	2	6	7	1.56	$-\pi/2$
0	10	14	1.92	s	2	14	3	1.56	
6	0	6	1.91		4	0	1	1.54	$-\pi/2$
6	4	8	1.91	$-\pi/2+p$	0	14	1	1.55	
0	12	4	1.90		0	14	3	1.55	
2	8	6	1.87	$+\pi/2-a$	4	8	1	1.51	π
2	0	4	1.86		2	2	7	1.50	s
2	2	18	1.85	$\pi+p+s$					
6	2	8	1.83	$-\pi/2+s$, p+s					
2	2	12	1.80	$\pi+p+s$					
2	10	12	1.77	s					
0	4	18	1.74						
4	8	10	1.69	$-\pi/2$					
4	2	16	1.68	$-\pi/2+s$, p+s					
2	0	2	1.66	0					
4	6	2	1.63						

Table 18. (Continued)

u g g	|E|	Ø
*3 0 10	3.46	0
1 0 4	2.62	m
1 0 16	2.24	π
1 14 0	2.21	
5 0 12	2.19	0
5 0 2	2.03	0
1 10 10	2.03	s
3 0 14	2.01	π
3 0 12	1.95	π
1 12 4	1.92	p
1 0 12	1.90	0
3 2 18	1.87	$\pi+p+s, +\pi/2+s$
1 6 12	1.83	
3 8 4	1.81	
1 10 2	1.80	$\pi+s$
3 0 18	1.80	π
7 0 2	1.78	π
1 12 6	1.76	$\pi+p$
1 12 2	1.72	$\pi+p$
3 8 10	1.71	
3 10 4	1.67	$\pi+s$
1 0 2	1.66	0
3 2 10	1.64	$p+s$
7 0 4	1.64	
3 10 12	1.63	s
3 0 4	1.59	0
1 2 16	1.58	$\pi+p+s$
3 2 4	1.57	$p+s$
3 10 10	1.57	$\pi+s$
5 8 6	1.56	$-\pi/2$
5 2 12	1.55	$p+s, -\pi/2+s$

u g u	|E|	Ø
*3 0 1	2.76	$+\pi/2$
*3 8 3	2.31	a
1 0 3	2.06	$+\pi/2\pm 2a$
1 8 9	2.05	
1 0 9	2.04	$+\pi/2$
5 0 13	1.93	$-\pi/2$
3 12 9	1.90	$+\pi/2+p$
1 12 1	1.82	$+\pi/2+p$
3 0 11	1.82	$+\pi/2$
1 2 3	1.77	$\pi+s$
3 2 9	1.66	s
1 8 15	1.64	π
3 12 3	1.56	$+\pi/2+p$
3 4 17	1.55	
5 8 5	1.54	0
1 0 5	1.54	
1 8 11	1.53	0
1 0 7	1.52	$-\pi/2$
5 8 7	1.51	π

Table 18. (Continued)

g u g	|E|	ϕ
0 9 6	2.13	
0 1 20	2.09	
4 3 12	2.00	$-\pi/2$
6 3 0	1.97	
0 5 4	1.86	
0 3 10	1.85	$+\pi/2$
2 3 14	1.74	$-\pi/2$
2 1 0	1.69	
2 1 14	1.67	s
2 1 8	1.67	
4 3 6	1.63	$-\pi/2$
2 11 0	1.63	0
0 3 12	1.58	$-\pi/2$
0 7 6	1.50	$+\pi/2+s$

g u u	|E|	ϕ
6 3 1	2.06	0
4 9 9	2.04	$\pi+p$
2 3 13	2.01	$\pi+m$
4 3 7	1.94	π, m
0 3 1	1.86	
2 5 1	1.85	
6 1 7	1.81	
6 5 7	1.74	
4 11 1	1.73	$+\pi/2$
4 7 13	1.68	s
4 7 11	1.66	$\pi+s$
2 3 19	1.61	0
6 3 7	1.54	0
2 9 1	1.52	$\pi+p$
4 7 1	1.50	s

u u g	|E|	ϕ
*3 3 0	2.17	$-\pi/2$
5 3 14	2.12	$-\pi/2+m$
3 11 4	2.08	$\pi-a$
3 3 10	2.05	$-\pi/2$
3 11 10	1.74	π
3 1 16	1.68	
1 9 10	1.66	$-\pi/2+p$
3 1 10	1.63	s
1 3 6	1.59	$+\pi/2$
5 7 10	1.56	$-\pi/2+s$
5 3 8	1.52	
1 9 2	1.52	$+\pi/2+p$
5 1 12	1.51	
1 5 0	1.51	

u u u	|E|	ϕ
5 3 3	2.15	m
3 3 11	2.04	π
5 1 13	2.04	
3 3 15	1.91	0
1 3 17	1.89	0
3 5 5	1.70	
3 5 3	1.70	$-\pi/2$
3 3 9	1.59	0
5 5 3	1.55	$-\pi/2, \pi+p+s$

Table 19. Phase relations in $P2_12_12_1$.

	h k l	$\bar{h}$ k l	h $\bar{k}$ l	h k $\bar{l}$
g g g u u u	α	$-\alpha$	$-\alpha$	$-\alpha$
g g u u u g	α	$-\alpha$	$\pi-\alpha$	$\pi-\alpha$
g u g u g u	α	$\pi-\alpha$	$\pi-\alpha$	$-\alpha$
g u u u g g	α	$\pi-\alpha$	$-\alpha$	$\pi-\alpha$

0 g g	0,π	g 0 g	0,π	g g 0	0,π
0 u u	$\pm\pi/2$	u 0 g	0,π	u g 0	$\pm\pi/2$
0 u g	$\pm\pi/2$	g 0 u	$\pm\pi/2$	g u 0	0,π
0 g u	0,π	u 0 u	$\pm\pi/2$	u u 0	$\pm\pi/2$

Table 20. Phase assignments for specifying the origin and implementing the sum of angles formula.

$\vec{h}$	|E|	ϕ	
3 0 10	3.46	0	
3 3 0	2.17	$-\pi/2$	
3 0 1	2.77	$+\pi/2$	
2 12 0	3.21	p	must be 0 or π
2 10 0	2.31	s	
4 0 14	2.56	m	
3 8 3	2.31	a	

$$\mathcal{E} = 2 \begin{cases} 0\ k\ 0 \\ 0\ 0\ l \\ h\ 0\ 0 \end{cases}$$

$\mathcal{E} = 1$ for all others

Table 21. The application of Eq. 4.

$$(1)\quad \begin{array}{rrr} 3&0&1\\ 3&3&0\\ \hline 6&3&1 \end{array} \qquad \begin{array}{c} +\pi/2\\ -\pi/2\\ \hline 0 \end{array}$$

$$(2)\quad \begin{array}{rrr} \bar{3}&0&10\\ 6&3&1\\ \hline 3&3&11 \end{array} \qquad \begin{array}{c} \pi\\ 0\\ \hline \pi \end{array}$$

$$(3)\quad \begin{array}{rrr} \bar{4}&0&14\\ 6&3&\bar{1}\\ \hline 2&3&13 \end{array} \qquad \begin{array}{c} m\\ \pi\\ \hline \pi+m \end{array}$$

$$(4)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} \bar{3}&0&\bar{1}\\ 3&3&11\\ \hline 0&3&10 \end{array} & \begin{array}{c} -\pi/2\\ \pi\\ \hline +\pi/2 \end{array} \\ \\ \begin{array}{rrr} 3&3&0\\ \bar{3}&0&10\\ \hline 0&3&10 \end{array} & \begin{array}{c} -\pi/2\\ \pi\\ \hline +\pi/2 \end{array} \end{array} \right.$$

$$(5)\quad \begin{array}{rrr} 3&0&\overline{10}\\ 2&3&13\\ \hline 5&3&3 \end{array} \qquad \begin{array}{c} \pi\\ \pi+m\\ \hline m \end{array}$$

$$(6)\quad \begin{array}{rrr} 3&0&1\\ 2&3&13\\ \hline 5&3&14 \end{array} \qquad \begin{array}{c} +\pi/2\\ \pi+m\\ \hline -\pi/2+m \end{array}$$

$$(7)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} 6&3&1\\ \bar{5}&\bar{3}&3\\ \hline 1&0&4 \end{array} & \begin{array}{c} 0\\ m\\ \hline m \end{array} \\ \\ \begin{array}{rrr} \bar{3}&0&\overline{10}\\ 4&0&14\\ \hline 1&0&4 \end{array} & \begin{array}{c} 0\\ m\\ \hline m \end{array} \end{array} \right.$$

$$(8)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} 5&3&\bar{3}\\ \bar{3}&\bar{3}&11\\ \hline 2&0&8 \end{array} & \begin{array}{c} m\\ \pi\\ \hline \pi+m \end{array} \\ \\ \begin{array}{rrr} 1&0&4\\ 1&0&4\\ \hline 2&0&8 \end{array} & \begin{array}{c} m\\ m\\ \hline 0 \end{array} \end{array} \right. \qquad m=\pi$$

$$(9)\quad \begin{array}{rrr} 5&3&3\\ \bar{4}&0&14\\ \hline 1&3&17 \end{array} \qquad \begin{array}{c} m\\ m\\ \hline 0 \end{array}$$

$$(10)\quad \begin{array}{rrr} 3&0&1\\ \bar{1}&0&4\\ \hline 2&0&5 \end{array} \qquad \begin{array}{c} +\pi/2\\ \pi+m\\ \hline \end{array}$$

$$(11)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} 2&0&5\\ \bar{1}&0&4\\ \hline 1&0&9 \end{array} & \begin{array}{c} -\pi/2+m\\ \pi+m\\ \hline +\pi/2 \end{array} \\ \\ \begin{array}{rrr} 3&0&1\\ \bar{2}&0&8\\ \hline 1&0&9 \end{array} & \begin{array}{c} +\pi/2\\ \pi+m\\ \hline -\pi/2+m \end{array} \end{array} \right. \qquad m=\pi$$

$$(12)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} 3&0&\overline{10}\\ 1&3&17\\ \hline 4&3&7 \end{array} & \begin{array}{c} \pi\\ 0\\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} \bar{1}&0&4\\ 5&3&3\\ \hline 4&3&7 \end{array} & \begin{array}{c} \pi-m\\ m\\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} 1&0&\bar{4}\\ 3&3&11\\ \hline 4&3&7 \end{array} & \begin{array}{c} \pi+m\\ \pi\\ \hline m \end{array} \\ \\ \begin{array}{rrr} \bar{2}&0&8\\ 6&3&\bar{1}\\ \hline 4&3&7 \end{array} & \begin{array}{c} \pi+m\\ \pi\\ \hline m \end{array} \end{array} \right. \qquad m=\pi$$

$$(13)\quad \begin{array}{rrr} 2&12&0\\ 1&0&9\\ \hline 3&12&9 \end{array} \qquad \begin{array}{c} p\\ +\pi/2\\ \hline \pi/2+p \end{array}$$

$$(14)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} \bar{2}&12&0\\ 3&0&1\\ \hline 1&12&1 \end{array} & \begin{array}{c} p\\ +\pi/2\\ \hline \pi/2+p \end{array} \\ \\ \begin{array}{rrr} 3&12&9\\ \bar{2}&0&\bar{8}\\ \hline 1&12&1 \end{array} & \begin{array}{c} \pi/2+p\\ 0\\ \hline \pi/2+p \end{array} \end{array} \right.$$

$$(15)\quad \left\{ \begin{array}{ll} \begin{array}{rrr} 2&12&1\\ \bar{1}&0&4\\ \hline 1&12&4 \end{array} & \begin{array}{c} p\\ 0\\ \hline p \end{array} \\ \\ \begin{array}{rrr} \bar{1}&12&\bar{1}\\ 2&0&5\\ \hline 1&12&4 \end{array} & \begin{array}{c} \pi+\pi/2+p\\ +\pi/2\\ \hline p \end{array} \\ \\ \begin{array}{rrr} 3&12&9\\ \bar{2}&0&\bar{5}\\ \hline 1&12&4 \end{array} & \begin{array}{c} \pi/2+p\\ -\pi/2\\ \hline p \end{array} \end{array} \right.$$

$$(16)\quad \left\{\begin{array}{ccc@{\qquad}c}
2 & 12 & 0 & p \\
\bar{2} & 0 & 8 & 0 \\ \hline
0 & 12 & 8 & p \\[2ex]
3 & 12 & 9 & \pi/2+p \\
\bar{3} & 0 & \bar{1} & -\pi/2 \\ \hline
0 & 12 & 8 & p \\[2ex]
\bar{1} & 12 & \bar{1} & \pi+\pi/2+p \\
1 & 0 & 9 & +\pi/2 \\ \hline
0 & 12 & 8 & p \\[2ex]
1 & 12 & 4 & p \\
\bar{1} & 0 & 4 & 0 \\ \hline
0 & 12 & 8 & p
\end{array}\right.$$

$$(17)\quad \left\{\begin{array}{ccc@{\qquad}c}
\bar{1} & 0 & 4 & 0 \\
3 & 0 & \bar{1} & -\pi/2 \\ \hline
2 & 0 & 3 & -\pi/2 \\[2ex]
\bar{3} & \bar{3} & 0 & \pi/2 \\
5 & 3 & 3 & \pi \\ \hline
2 & 0 & 3 & -\pi/2 \\[2ex]
5 & 3 & 14 & \pi/2 \\
\bar{3} & \bar{3} & \overline{11} & \pi \\ \hline
2 & 0 & 3 & -\pi/2
\end{array}\right.$$

$$\left\{\begin{array}{ccc@{\qquad}c}
3 & 0 & 10 & 0 \\
2 & 0 & \bar{8} & 0 \\ \hline
5 & 0 & 2 & 0 \\[2ex]
3 & 0 & \bar{1} & -\pi/2 \\
2 & 0 & 3 & -\pi/2 \\ \hline
5 & 0 & 2 & \pi \\[2ex]
3 & \bar{3} & \overline{11} & \pi \\
2 & 3 & 13 & 0 \\ \hline
5 & 0 & 2 & \pi
\end{array}\right.$$

$$(18)\quad \left\{\begin{array}{ccc@{\qquad}c}
3 & 0 & 10 & 0 \\
\bar{1} & 0 & \bar{4} & \pi \\ \hline
2 & 0 & 6 & \pi \\[2ex]
4 & 0 & 14 & \pi \\
\bar{2} & 0 & \bar{8} & 0 \\ \hline
2 & 0 & 6 & \pi \\[2ex]
6 & \bar{3} & \bar{1} & \pi \\
\bar{4} & 3 & 7 & 0 \\ \hline
2 & 0 & 6 & \pi \\[2ex]
3 & \bar{3} & \overline{11} & \pi \\
\bar{1} & 3 & 17 & 0 \\ \hline
2 & 0 & 6 & \pi \\[2ex]
\bar{2} & \bar{3} & 13 & \pi \\
4 & 3 & \bar{7} & 0 \\ \hline
2 & 0 & 6 & \pi
\end{array}\right.$$

$$(19)\quad \begin{array}{ccc@{\qquad}c}
3 & 8 & 3 & a \\
\bar{2} & 0 & 6 & \pi \\ \hline
1 & 8 & 9 & \pi+a
\end{array}$$

$$(20)\quad \left\{\begin{array}{ccc@{\qquad}c}
\bar{3} & 8 & 3 & \pi-a \\
6 & 3 & 1 & 0 \\ \hline
3 & 11 & 4 & \pi-a \\[2ex]
1 & 8 & \bar{9} & \pi-a \\
2 & 3 & 13 & 0 \\ \hline
3 & 11 & 4 & \pi-a
\end{array}\right.$$

$$(21)\quad \begin{array}{ccc@{\qquad}c}
3 & 8 & \bar{3} & -a \\
\bar{1} & 0 & 9 & \pi/2 \\ \hline
2 & 8 & 6 & \pi/2-a
\end{array}$$

$$(22)\quad \begin{array}{ccc@{\qquad}c}
2 & 12 & 0 & p \\
\bar{2} & 0 & 6 & \pi \\ \hline
0 & 12 & 6 & \pi+p
\end{array}$$

$$\left\{\begin{array}{l}
\begin{array}{rrr}3&0&10\\1&0&\bar{4}\\\hline 3&0&6\end{array}\qquad\begin{array}{c}0\\0\\\hline 0\end{array}\\[2ex]
\begin{array}{rrr}3&8&\bar{3}\\1&\bar{8}&9\\\hline 4&0&6\end{array}\qquad\begin{array}{c}-a\\-a\\\hline -2a\end{array}\qquad\times\\[2ex]
\begin{array}{rrr}3&3&\overline{11}\\1&\bar{3}&17\\\hline 4&0&6\end{array}\qquad\begin{array}{c}\pi\\0\\\hline \pi\end{array}\\[2ex]
\begin{array}{rrr}2&0&3\\2&0&3\\\hline 4&0&6\end{array}\qquad\begin{array}{c}-\pi/2\\-\pi/2\\\hline \pi\end{array}
\end{array}\right.$$

$$(23)\ \left\{\begin{array}{l}
\begin{array}{rrr}2&0&\bar{6}\\\bar{1}&0&9\\\hline 1&0&3\end{array}\qquad\begin{array}{c}\pi\\+\pi/2\\\hline -\pi/2\end{array}\qquad\times\\[2ex]
\begin{array}{rrr}3&\bar{8}&\bar{3}\\\bar{2}&8&6\\\hline 1&0&3\end{array}\qquad\begin{array}{c}\pi+a\\-\pi/2+a\\\hline \pi/2+2a\end{array}\qquad 2a=0,\pi\\[2ex]
\begin{array}{rrr}\bar{1}&8&9\\2&\bar{8}&\bar{6}\\\hline 1&0&3\end{array}\qquad\begin{array}{c}-a\\\pi/2-a\\\hline \pi/2-2a\end{array}\\[2ex]
\begin{array}{rrr}2&0&12\\\bar{1}&0&\bar{9}\\\hline 1&0&3\end{array}\qquad\begin{array}{c}\pi-2a\\-\pi/2\\\hline \pi/2-2a\end{array}
\end{array}\right.$$

$$(24)\quad\begin{array}{rrr}\bar{1}&8&9\\3&\bar{8}&3\\\hline 2&0&12\end{array}\qquad\begin{array}{c}-a\\\pi-a\\\hline \pi-2a\end{array}$$

$$(25)\quad\begin{array}{rrr}\bar{2}&10&0\\3&0&10\\\hline 1&10&10\end{array}\qquad\begin{array}{c}s\\0\\\hline s\end{array}$$

$$(26)\quad\begin{array}{rrr}1&10&10\\3&0&\overline{10}\\\hline 4&10&0\end{array}\qquad\begin{array}{c}s\\\pi\\\hline \pi+s\end{array}$$

$$(27)\ \left\{\begin{array}{l}
\begin{array}{rrr}1&10&10\\1&0&\bar{4}\\\hline 2&10&6\end{array}\qquad\begin{array}{c}s\\0\\\hline s\end{array}\\[2ex]
\begin{array}{rrr}4&10&0\\\bar{2}&0&6\\\hline 2&10&6\end{array}\qquad\begin{array}{c}\pi+s\\\pi\\\hline s\end{array}
\end{array}\right.$$

$$(28)\ \left\{\begin{array}{l}
\begin{array}{rrr}1&10&10\\\bar{1}&0&\bar{4}\\\hline 0&10&6\end{array}\qquad\begin{array}{c}s\\\pi\\\hline \pi+s\end{array}\\[2ex]
\begin{array}{rrr}\bar{2}&10&\bar{6}\\2&0&12\\\hline 0&10&6\end{array}\qquad\begin{array}{c}s\\\pi-2a\\\hline \pi+s-2a\end{array}\qquad a=0,\pi\\[2ex]
\begin{array}{rrr}2&10&0\\\bar{2}&0&6\\\hline 0&10&6\end{array}\qquad\begin{array}{c}s\\\pi\\\hline \pi+s\end{array}
\end{array}\right.$$

$$(29)\ \left\{\begin{array}{l}
\begin{array}{rrr}\bar{1}&0&4\\1&10&10\\\hline 0&10&14\end{array}\qquad\begin{array}{c}0\\s\\\hline s\end{array}\\[2ex]
\begin{array}{rrr}2&10&6\\\bar{2}&0&8\\\hline 0&10&14\end{array}\qquad\begin{array}{c}s\\0\\\hline s\end{array}\\[2ex]
\begin{array}{rrr}4&10&0\\\bar{4}&0&14\\\hline 0&10&14\end{array}\qquad\begin{array}{c}\pi+s\\\pi\\\hline s\end{array}
\end{array}\right.$$

$$(30)\ \left\{\begin{array}{l}
\begin{array}{rrr}\bar{1}&10&10\\2&0&\bar{8}\\\hline 1&10&2\end{array}\qquad\begin{array}{c}\pi+s\\0\\\hline \pi+s\end{array}\\[2ex]
\begin{array}{rrr}2&10&6\\\bar{1}&0&\bar{4}\\\hline 1&10&2\end{array}\qquad\begin{array}{c}s\\\pi\\\hline \pi+s\end{array}\\[2ex]
\begin{array}{rrr}0&10&6\\1&0&\bar{4}\\\hline 1&10&2\end{array}\qquad\begin{array}{c}\pi+s\\0\\\hline \pi+s\end{array}
\end{array}\right.$$

$$(31)\ \left\{\begin{array}{l}
\begin{array}{rrr}\bar{3}&0&10\\3&8&\bar{3}\\\hline 0&8&7\end{array}\qquad\begin{array}{c}\pi\\-a\\\hline \pi-a\end{array}\\[2ex]
\begin{array}{rrr}3&11&\bar{4}\\\bar{3}&\bar{3}&11\\\hline 0&8&7\end{array}\qquad\begin{array}{c}a\\\pi\\\hline \pi+a\end{array}
\end{array}\right.$$

Let a=0
det'm
enantio

$$(32)\left\{\begin{array}{ccc@{\qquad}c}
3 & 0 & 10 & 0\\
2 & 0 & 3 & -\pi/2\\ \hline
5 & 0 & 13 & -\pi/2\\[2ex]
2 & 0 & 12 & \pi\\
3 & 0 & 1 & +\pi/2\\ \hline
5 & 0 & 13 & -\pi/2\\[2ex]
3 & 3 & 0 & -\pi/2\\
2 & \bar{3} & 13 & 0\\ \hline
5 & 0 & 13 & -\pi/2\\[2ex]
5 & \bar{3} & 3 & \pi\\
0 & 3 & 10 & +\pi/2\\ \hline
5 & 0 & 13 & -\pi/2
\end{array}\right.$$

$$(33)\quad\begin{array}{ccc@{\qquad}c}
\bar{2} & 0 & 12 & \pi\\
5 & 3 & 3 & \pi\\ \hline
3 & 3 & 15 & 0
\end{array}$$

$$(34)\left\{\begin{array}{ccc@{\qquad}c}
\bar{1} & 0 & 4 & 0\\
2 & 0 & 8 & 0\\ \hline
1 & 0 & 12 & 0\\[2ex]
0 & 12 & 8 & p\\
1 & \bar{12} & 4 & -p\\ \hline
1 & 0 & 12 & 0\\[2ex]
\bar{1} & 0 & 9 & \pi/2\\
2 & 0 & 3 & -\pi/2\\ \hline
1 & 0 & 12 & 0\\[2ex]
0 & \bar{10} & 14 & s\\
1 & 10 & \bar{2} & -s\\ \hline
1 & 0 & 12 & 0
\end{array}\right.$$

$$\left\{\begin{array}{ccc@{\qquad}c}
\bar{3} & 0 & \bar{10} & 0\\
3 & 3 & 11 & \pi\\ \hline
0 & 3 & 1 & \pi\\[2ex]
\bar{2} & 0 & \bar{12} & \pi\\
2 & 3 & 13 & 0\\ \hline
0 & 3 & 1 & \pi\\[2ex]
3 & 0 & 1 & +\pi/2\\
\bar{3} & 3 & 0 & +\pi/2\\ \hline
0 & 3 & 1 & \pi\\[2ex]
\bar{3} & \bar{8} & \bar{3} & 0\\
3 & 11 & 4 & \pi\\ \hline
0 & 3 & 1 & \pi
\end{array}\right.$$

should be ± $\pi/2$

$$(35)\left\{\begin{array}{ccc@{\qquad}c}
2 & 0 & 12 & \pi\\
2 & 0 & \bar{3} & -\pi/2\\ \hline
4 & 0 & 9 & +\pi/2\\[2ex]
\bar{1} & 0 & \bar{4} & \pi\\
5 & 0 & 13 & -\pi/2\\ \hline
4 & 0 & 9 & +\pi/2\\[2ex]
2 & 0 & 6 & \pi\\
2 & 0 & 3 & -\pi/2\\ \hline
4 & 0 & 9 & +\pi/2
\end{array}\right.$$

$$(36)\left\{\begin{array}{ccc@{\qquad}c}
3 & 0 & 10 & 0\\
1 & 0 & 3 & +\pi/2\\ \hline
4 & 0 & 13 & +\pi/2\\[2ex]
3 & 0 & 1 & +\pi/2\\
1 & 0 & 12 & 0\\ \hline
4 & 0 & 13 & +\pi/2\\[2ex]
2 & 0 & 8 & 0\\
2 & 0 & 5 & +\pi/2\\ \hline
4 & 0 & 13 & +\pi/2\\[2ex]
1 & \bar{12} & 4 & p\\
3 & 12 & 9 & \pi/2+p\\ \hline
4 & 0 & 13 & +\pi/2
\end{array}\right.$$

$$(37)\left\{\begin{array}{ccc@{\qquad}c}
2 & 0 & 8 & 0\\
1 & 0 & 3 & +\pi/2\\ \hline
3 & 0 & 11 & +\pi/2\\[2ex]
4 & 0 & 14 & \pi\\
\bar{1} & 0 & \bar{3} & -\pi/2\\ \hline
3 & 0 & 11 & +\pi/2
\end{array}\right.$$

$$\left\{\begin{array}{ccc@{\qquad}c}
2 & 0 & \bar{5} & \pi/2\\
1 & 8 & 9 & \pi\\ \hline
3 & 8 & 4 & -\pi/2\\[2ex]
\bar{1} & 8 & \bar{9} & 0\\
4 & 0 & 13 & \pi/2\\ \hline
3 & 8 & 4 & +\pi/2\\[2ex]
0 & 8 & \bar{7} & 0\\
3 & 0 & 11 & +\pi/2\\ \hline
3 & 8 & 4 & +\pi/2
\end{array}\right.$$

$$\left\{\begin{array}{ccc@{\qquad}c}
0 & 12 & 6 & \pi+p\\
2 & \bar{10} & 6 & s\\ \hline
2 & 2 & 12 & \pi+p+s\\[2ex]
0 & 10 & 6 & \pi+s\\
2 & \bar{8} & 6 & -\pi/2\\ \hline
2 & 2 & 12 & \pi/2+s
\end{array}\right.$$

$$\left\{\begin{array}{rrrcl} \bar{2} & 0 & 8 & \quad & 0 \\ 2 & 8 & 6 & & \pi/2 \\ \hline 0 & 8 & 14 & & \pi/2 \end{array}\right.$$

X should be 0 or π

$$\begin{array}{rrrcl} 3 & 8 & 3 & \quad & 0 \\ \bar{3} & 0 & 11 & & \pi/2 \\ \hline 0 & 8 & 14 & & \pi/2 \end{array}$$

(38)

$$\begin{array}{rrrcl} 0 & 12 & 6 & \quad & \pi+p \\ 0 & \overline{10} & 14 & & s \\ \hline 0 & 2 & 20 & & \pi+p+s \end{array}$$

(39)

$$\left\{\begin{array}{rrrcl} 5 & 3 & 3 & \quad & \pi \\ \bar{3} & \bar{3} & 15 & & 0 \\ \hline 2 & 0 & 18 & & \pi \end{array}\right.$$

$$\begin{array}{rrrcl} \bar{2} & 0 & 5 & \quad & -\pi/2 \\ 4 & 0 & 13 & & +\pi/2 \\ \hline 2 & 0 & 18 & & 0 \end{array}$$

X

$$\begin{array}{rrrcl} 1 & 8 & 9 & \quad & \pi \\ 1 & \bar{8} & 9 & & 0 \\ \hline 2 & 0 & 18 & & \pi \end{array}$$

$$\begin{array}{rrrcl} 1 & 0 & 9 & \quad & +\pi/2 \\ 1 & 0 & 9 & & +\pi/2 \\ \hline 2 & 0 & 18 & & \pi \end{array}$$

(40)

$$\left\{\begin{array}{rrrcl} 3 & 0 & 10 & \quad & 0 \\ \bar{2} & 0 & 6 & & \pi \\ \hline 1 & 0 & 16 & & \pi \end{array}\right.$$

$$\begin{array}{rrrcl} 2 & 0 & 12 & \quad & \pi \\ \bar{1} & 0 & 4 & & 0 \\ \hline 1 & 0 & 16 & & \pi \end{array}$$

$$\begin{array}{rrrcl} \bar{2} & 0 & 5 & \quad & -\pi/2 \\ 3 & 0 & 11 & & +\pi/2 \\ \hline 1 & 0 & 16 & & 0 \end{array}$$

X

$$\begin{array}{rrrcl} 2 & \overline{10} & 6 & \quad & s \\ \bar{1} & 10 & 10 & & \pi+s \\ \hline 1 & 0 & 16 & & \pi \end{array}$$

$$\begin{array}{rrrcl} 1 & 8 & 9 & \quad & \pi \\ 0 & \bar{8} & 7 & & 0 \\ \hline 1 & 0 & 16 & & \pi \end{array}$$

$$\begin{array}{rrrcl} 0 & \overline{10} & 6 & \quad & \pi+s \\ 1 & 10 & 10 & & s \\ \hline 1 & 0 & 16 & & \pi \end{array}$$

(41)

$$\left\{\begin{array}{rrrcl} 1 & 0 & 3 & \quad & +\pi/2 \\ \bar{1} & 12 & \bar{1} & & -\pi/2+p \\ \hline 0 & 12 & 2 & & p \end{array}\right.$$

$$\begin{array}{rrrcl} \bar{3} & 12 & \bar{9} & \quad & -\pi/2+p \\ 3 & 0 & 11 & & +\pi/2 \\ \hline 0 & 12 & 2 & & p \end{array}$$

(42)

$$\left\{\begin{array}{rrrcl} 1 & 0 & \bar{3} & \quad & -\pi/2 \\ 2 & 3 & 13 & & 0 \\ \hline 3 & 3 & 10 & & -\pi/2 \end{array}\right.$$

$$\begin{array}{rrrcl} \bar{1} & 0 & 3 & \quad & \pi/2 \\ 4 & 3 & 7 & & \pi \\ \hline 3 & 3 & 10 & & -\pi/2 \end{array}$$

$$\begin{array}{rrrcl} 6 & 3 & \bar{1} & \quad & \pi \\ \bar{3} & 0 & 11 & & \pi/2 \\ \hline 3 & 3 & 10 & & -\pi/2 \end{array}$$

(43)

$$\left\{\begin{array}{rrrcl} 0 & 12 & 2 & \quad & p \\ 4 & \bar{3} & 7 & & \pi \\ \hline 4 & 9 & 9 & & \pi+p \end{array}\right.$$

$$\begin{array}{rrrcl} 3 & \bar{3} & 10 & \quad & -\pi/2 \\ 1 & 12 & \bar{1} & & -\pi/2+p \\ \hline 4 & 9 & 9 & & \pi+p \end{array}$$

$$
\left\{\begin{array}{rrrc}
3 & 0 & \overline{10} & \pi \\
2 & 0 & 12 & \pi \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & 0 \\[1em]
3 & 0 & 10 & 0 \\
2 & 0 & \bar{8} & 0 \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & 0 \\[1em]
3 & 0 & \bar{1} & -\pi/2 \\
2 & 0 & 3 & -\pi/2 \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & \pi \\[1em]
4 & 0 & \overline{14} & \pi \\
1 & 0 & 16 & \pi \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & 0 \\[1em]
4 & 0 & 14 & \pi \\
1 & 0 & \overline{12} & \pi \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & 0 \\[1em]
3 & 3 & \overline{11} & \pi \\
2 & \bar{3} & 13 & 0 \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & \pi \\[1em]
2 & 3 & \overline{13} & \pi \\
3 & \bar{3} & 15 & 0 \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & \pi \\[1em]
4 & 10 & 0 & \pi+s \\
1 & \overline{10} & 2 & \pi+s \\ \cline{1-3}\cline{4-4}
5 & 0 & 2 & 0
\end{array}\right.
$$

$$
(44)\quad\left\{\begin{array}{rrrc}
1 & 0 & \bar{4} & 0 \\
2 & 0 & 18 & \pi \\ \cline{1-3}\cline{4-4}
3 & 0 & 14 & \pi \\[1em]
2 & 0 & 5 & +\pi/2 \\
1 & 0 & 9 & +\pi/2 \\ \cline{1-3}\cline{4-4}
3 & 0 & 14 & \pi \\[1em]
6 & 3 & \bar{1} & \pi \\
\bar{3} & \bar{3} & 15 & 0 \\ \cline{1-3}\cline{4-4}
3 & 0 & 14 & \pi
\end{array}\right.
$$

$$
(45)\quad\left\{\begin{array}{rrrc}
3 & 3 & 0 & -\pi/2 \\
1 & 0 & 12 & 0 \\ \cline{1-3}\cline{4-4}
4 & 3 & 12 & -\pi/2 \\[1em]
5 & 3 & 3 & \pi \\
\bar{1} & 0 & 9 & \pi/2 \\ \cline{1-3}\cline{4-4}
4 & 3 & 12 & -\pi/2 \\[1em]
1 & 0 & \bar{3} & -\pi/2 \\
3 & 3 & 15 & 0 \\ \cline{1-3}\cline{4-4}
4 & 3 & 12 & -\pi/2
\end{array}\right.
$$

$$
\left\{\begin{array}{rrrc}
3 & 0 & 10 & 0 \\
3 & 3 & \overline{10} & \pi/2 \\ \cline{1-3}\cline{4-4}
6 & 3 & 0 & \pi/2 \\[1em]
2 & 0 & 12 & \pi \\
4 & 3 & \overline{12} & \pi/2 \\ \cline{1-3}\cline{4-4}
6 & 3 & 0 & -\pi/2 \\[1em]
5 & 3 & 3 & \pi \\
1 & 0 & \bar{3} & -\pi/2 \\ \cline{1-3}\cline{4-4}
6 & 3 & 0 & \pi/2 \\[1em]
3 & 3 & 11 & \pi \\
3 & 0 & \overline{11} & -\pi/2 \\ \cline{1-3}\cline{4-4}
6 & 3 & 0 & \pi/2
\end{array}\right.
$$

$$
(46)\quad\left\{\begin{array}{rrrc}
2 & 0 & 8 & 0 \\
2 & 0 & 8 & 0 \\ \cline{1-3}\cline{4-4}
4 & 0 & 16 & 0 \\[1em]
\bar{1} & 0 & 3 & \pi/2 \\
5 & 0 & 13 & -\pi/2 \\ \cline{1-3}\cline{4-4}
4 & 0 & 16 & 0
\end{array}\right.
$$

47)

should be

$$\begin{array}{rrr} 6 & \bar{3} & 1 \\ \bar{3} & 3 & 11 \\ \hline 3 & 0 & 12 \end{array} \qquad \begin{array}{c} 0 \\ \pi \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} 1 & 0 & 9 \\ 2 & 0 & 3 \\ \hline 3 & 0 & 12 \end{array} \qquad \begin{array}{c} \pi/2 \\ -\pi/2 \\ \hline 0 \end{array} \qquad X$$

$$\begin{array}{rrr} 1 & 0 & 4 \\ 2 & 0 & 8 \\ \hline 3 & 0 & 12 \end{array} \qquad \begin{array}{c} \pi \\ 0 \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} \bar{1} & 0 & \bar{4} \\ 4 & 0 & 16 \\ \hline 3 & 0 & 12 \end{array} \qquad \begin{array}{c} \pi \\ 0 \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} \bar{1} & 0 & 3 \\ 4 & 0 & 9 \\ \hline 3 & 0 & 12 \end{array} \qquad \begin{array}{c} \pi/2 \\ \pi/2 \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} 2 & 0 & \bar{8} \\ 4 & 0 & 14 \\ \hline 6 & 0 & 6 \end{array} \qquad \begin{array}{c} 0 \\ \pi \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} 3 & 8 & 3 \\ 3 & \bar{8} & 3 \\ \hline 6 & 0 & 6 \end{array} \qquad \begin{array}{c} 0 \\ \pi \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} 2 & 10 & 6 \\ 4 & \overline{10} & 0 \\ \hline 6 & 0 & 6 \end{array} \qquad \begin{array}{c} s \\ \pi+s \\ \hline \pi \end{array}$$

$$\begin{array}{rrr} 2 & 0 & \bar{3} \\ 4 & 0 & 9 \\ \hline 6 & 0 & 6 \end{array} \qquad \begin{array}{c} -\pi/2 \\ +\pi/2 \\ \hline 0 \end{array}$$

$$\begin{array}{rrr} 2 & \bar{3} & 13 \\ 4 & 3 & 7 \\ \hline 6 & 0 & 6 \end{array} \qquad \begin{array}{c} 0 \\ 0 \\ \hline 0 \end{array}$$

$$\left\{ \begin{array}{ll} \begin{array}{rrr} \bar{2} & 0 & \overline{12} \\ 4 & 0 & 16 \\ \hline 2 & 0 & 4 \end{array} & \begin{array}{c} \pi \\ 0 \\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} 3 & 0 & 1 \\ \bar{1} & 0 & 3 \\ \hline 2 & 0 & 4 \end{array} & \begin{array}{c} +\pi/2 \\ +\pi/2 \\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} 4 & 0 & \overline{14} \\ \bar{2} & 0 & 18 \\ \hline 2 & 0 & 4 \end{array} & \begin{array}{c} \pi \\ \pi \\ \hline 0 \end{array} \\ \\ \begin{array}{rrr} \bar{1} & 0 & 16 \\ 3 & 0 & \overline{12} \\ \hline 2 & 0 & 4 \end{array} & \begin{array}{c} 0 \\ 0 \\ \hline 0 \end{array} \\ \\ \begin{array}{rrr} 1 & 0 & 16 \\ 1 & 0 & \overline{12} \\ \hline 2 & 0 & 4 \end{array} & \begin{array}{c} \pi \\ \pi \\ \hline 0 \end{array} \end{array} \right.$$

$$\left\{ \begin{array}{ll} \begin{array}{rrr} \bar{3} & 3 & 0 \\ 4 & 3 & 12 \\ \hline 1 & 6 & 12 \end{array} & \begin{array}{c} +\pi/2 \\ -\pi/2 \\ \hline 0 \end{array} \\ \\ \begin{array}{rrr} 5 & \bar{3} & 3 \\ \bar{4} & 9 & 9 \\ \hline 1 & 6 & 12 \end{array} & \begin{array}{c} \pi \\ p \\ \hline \pi+p \end{array} \end{array} \right. \qquad p=\pi$$

$$(48) \quad \left\{ \begin{array}{ll} \begin{array}{rrr} \bar{1} & 0 & 4 \\ 4 & 0 & 14 \\ \hline 3 & 0 & 18 \end{array} & \begin{array}{c} 0 \\ \pi \\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} 2 & 0 & 6 \\ 1 & 0 & 12 \\ \hline 3 & 0 & 18 \end{array} & \begin{array}{c} \pi \\ 0 \\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} \bar{2} & 0 & 5 \\ 5 & 0 & 13 \\ \hline 3 & 0 & 18 \end{array} & \begin{array}{c} -\pi/2 \\ -\pi/2 \\ \hline \pi \end{array} \\ \\ \begin{array}{rrr} \bar{1} & 0 & 9 \\ 4 & 0 & 9 \\ \hline 3 & 0 & 18 \end{array} & \begin{array}{c} +\pi/2 \\ +\pi/2 \\ \hline \pi \end{array} \end{array} \right.$$

$$(49) \quad \left\{ \begin{array}{lll} \begin{array}{rrr} 4 & 0 & 14 \\ 3 & 0 & \overline{12} \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} \pi \\ 0 \\ \hline \pi \end{array} & \\ \\ \begin{array}{rrr} 3 & 3 & \overline{10} \\ 4 & \bar{3} & 12 \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} -\pi/2 \\ -\pi/2 \\ \hline \pi \end{array} & \\ \\ \begin{array}{rrr} 3 & 0 & \overline{14} \\ 4 & 0 & 16 \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} 0 \\ 0 \\ \hline 0 \end{array} & X \\ \\ \begin{array}{rrr} 4 & 0 & \overline{16} \\ 3 & 0 & 18 \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} 0 \\ \pi \\ \hline \pi \end{array} & \\ \\ \begin{array}{rrr} 4 & 0 & \bar{9} \\ 3 & 0 & 11 \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} \pi/2 \\ \pi/2 \\ \hline \pi \end{array} & \\ \\ \begin{array}{rrr} 4 & 0 & 13 \\ 3 & 0 & \overline{11} \\ \hline 7 & 0 & 2 \end{array} & \begin{array}{c} \pi/2 \\ -\pi/2 \\ \hline 0 \end{array} & X \end{array} \right.$$

$$(50) \quad \left\{ \begin{array}{ll} \begin{array}{rrr} 3 & 0 & 10 \\ \bar{1} & 10 & 2 \\ \hline 2 & 10 & 12 \end{array} & \begin{array}{c} 0 \\ s \\ \hline s \end{array} \\ \\ \begin{array}{rrr} \bar{2} & 0 & 12 \\ 4 & 10 & 0 \\ \hline 2 & 10 & 12 \end{array} & \begin{array}{c} \pi \\ \pi+s \\ \hline s \end{array} \\ \\ \begin{array}{rrr} 2 & 0 & 18 \\ 0 & 10 & \bar{6} \\ \hline 2 & 10 & 12 \end{array} & \begin{array}{c} \pi \\ \pi+s \\ \hline s \end{array} \\ \\ \begin{array}{rrr} 2 & 0 & 6 \\ 0 & 10 & 6 \\ \hline 2 & 10 & 12 \end{array} & \begin{array}{c} \pi \\ \pi+s \\ \hline s \end{array} \end{array} \right.$$

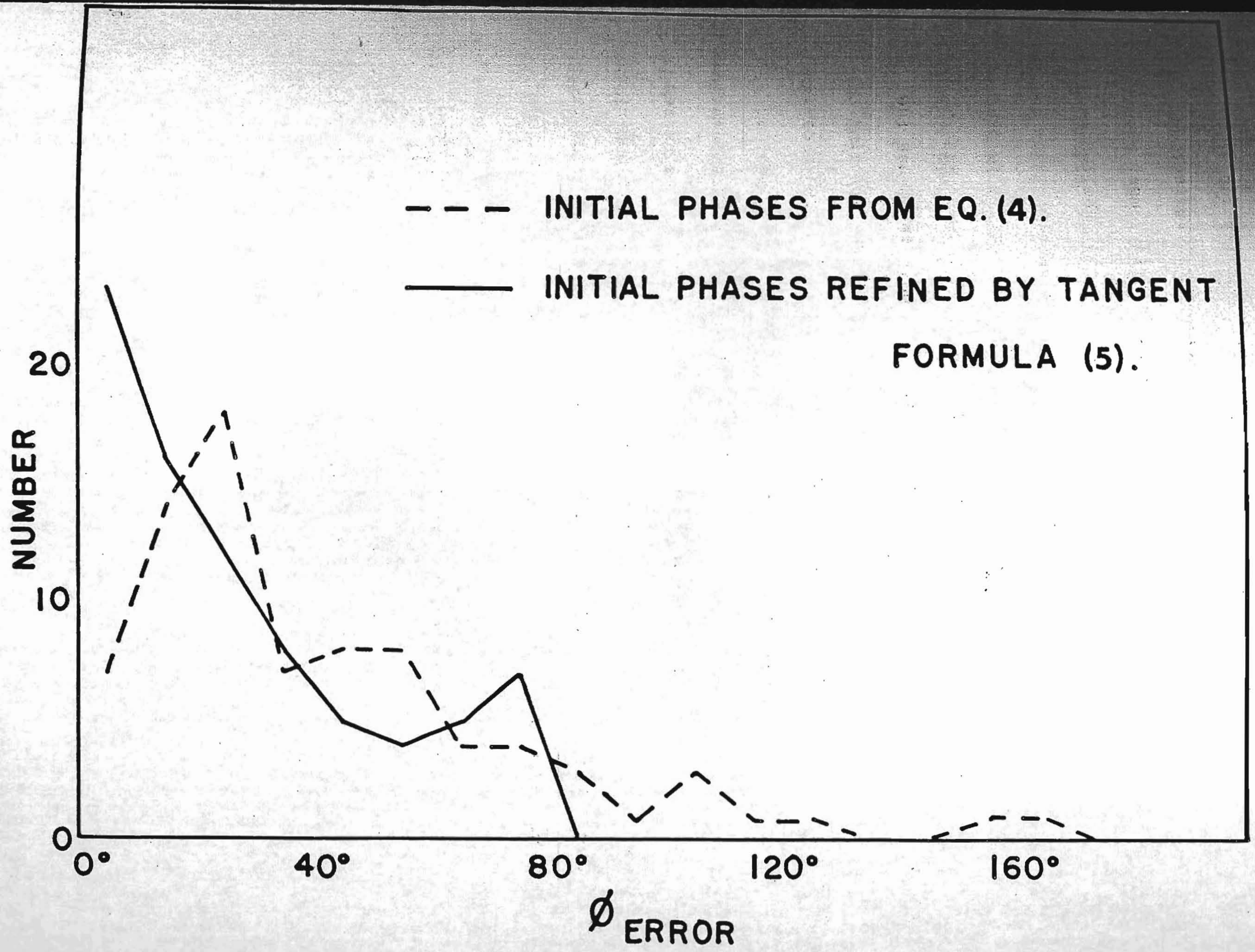
$$(51)\quad \left\{ \begin{array}{l}
\begin{array}{rrr} 3 & \bar{8} & 3 \\ \bar{2} & 10 & 0 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} \pi \\ s \\ \hline \pi+s \end{array} \\[1em]
\begin{array}{rrr} 3 & \bar{8} & \bar{3} \\ \bar{2} & 10 & 6 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} \pi \\ s \\ \hline \pi+s \end{array} \\[1em]
\begin{array}{rrr} \bar{3} & \bar{8} & 3 \\ 4 & 10 & 0 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} 0 \\ \pi+s \\ \hline \pi+s \end{array} \\[1em]
\begin{array}{rrr} 2 & 10 & \bar{6} \\ \bar{1} & \bar{8} & 9 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} s \\ \pi \\ \hline \pi+s \end{array} \\[1em]
\begin{array}{rrr} \bar{2} & \overline{10} & \bar{6} \\ 3 & 12 & 9 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} s \\ \pi/2+p \\ \hline \pi/2+p+s \end{array} \\[1em]
\begin{array}{rrr} \bar{1} & \bar{8} & \bar{9} \\ 2 & 10 & 12 \\ \hline 1 & 2 & 3 \end{array} \qquad \begin{array}{c} \pi \\ s \\ \hline \pi+s \end{array}
\end{array} \right.$$

$$(52)\quad \left\{ \begin{array}{l}
\begin{array}{rrr} 1 & 0 & 4 \\ 0 & 12 & 2 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} \pi \\ p \\ \hline \pi+p \end{array} \\[1em]
\begin{array}{rrr} 0 & 12 & \bar{6} \\ 1 & 0 & 12 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} \pi+p \\ 0 \\ \hline \pi+p \end{array} \\[1em]
\begin{array}{rrr} 5 & 3 & \bar{3} \\ \bar{4} & 9 & 9 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} \pi \\ p \\ \hline \pi+p \end{array} \\[1em]
\begin{array}{rrr} 2 & 0 & 5 \\ \bar{1} & 12 & 1 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} +\pi/2 \\ \pi/2+p \\ \hline \pi+p \end{array} \\[1em]
\begin{array}{rrr} 4 & 9 & \bar{9} \\ \bar{3} & 3 & 15 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} p \\ 0 \\ \hline p \end{array} \\[1em]
\begin{array}{rrr} \bar{2} & 0 & \bar{3} \\ 3 & 12 & 9 \\ \hline 1 & 12 & 6 \end{array} \qquad \begin{array}{c} \pi/2 \\ \pi/2+p \\ \hline \pi+p \end{array}
\end{array} \right.$$

And so forth

Table 22. An application of the Σ_1 formula

$2\vec{h}$	symbol	Σ_1	$P_+(E_{2\vec{h}})$
2 12 0	p	-	0.14
2 10 0	s	-	0.15
4 8 0	Π +p	+	0.72
0 12 8	p	-	0.27
0 10 14	s	-	0.28


- - - INITIAL PHASES FROM EQ. (4).
——— INITIAL PHASES REFINED BY TANGENT FORMULA (5).
NUMBER
0
10
20
0°
40°
80°
120°
160°
Ø ERROR

In space group $P2_12_12_1$ it is most convenient to specify the origin (Karle, 1974) by assigning phases to three two-dimensional reflections as shown in Table 20. In addition to the origin specification, most acentric space groups require another specification to choose one of the two enantiomorphs and/or axis direction. Often, the enantiomorph specification can be made at the beginning. However, at times it is more convenient to proceed with several reflections whose phases are assigned symbols and when the symbols are evaluated, one of them, in effect, will serve to choose the enantiomorph. In order to proceed with the phase determination using the reflections with the largest $|E|$ values, it was found necessary to assign symbols to four reflections, Table 20. Three of the assigned symbols, p, s and m, can have only 0 or π as their values. These symbols were assigned to reflections of the type gg0 and g0g. In this space group, the phases of these types of reflections are invariants, i.e. they are independent of origin selection. The fourth symbol $\underline{a}$ is assigned to reflection 383 which is a general reflection whose phase may have any value between 0 and 2π. We shall see later that the symbol $\underline{a}$ will serve to select the enantiomorph.

The phase determination is initiated with the use of formula (4). The indices of the reflections are added and the phase values are added. Again, it is imperative that the strongest reflections are used initially to insure the best values for the phases. Since the phases are used in a step-wise fashion, an error near the beginning can generate a whole subgroup of incorrect phases. Table 21 shows how the initial phases were used to obtain other phases of reflections with large $|E|$ values. Entry (2) uses a symmetry equivalent, $\bar{3}$ 0 10, of an origin specifying reflection, 3 0 10. Relationships between symmetry equivalents for $P2_12_12_1$ are shown in Table 19. Entries (8), (11) and (12) have multiple indications for the same phase and show that $\underline{m}$ probably has the value π.

The phase indications for a number of reflections were inconclusive. For example, for reflection 5 0 2, after entry (17), and for reflection 4 0 6, after entry (22), both 0 and π were indicated and thus the phase was not determined at this point. It has been found from experience that triples formed from three two-dimensional phases from the same zone which are pure real or pure imaginary, e.g.

$$\begin{array}{ccc} h_1 & k_1 & 0 \\ h_2 & k_2 & 0 \\ \hline h_{1+2} & k_{1+2} & 0 \end{array}$$

very often indicate an erroneous phase even though each reflection has a large $|E|$ value. It is best to avoid these types of combinations whenever possible in using Eqs.(1), (2) and (4), or at least to use them cautiously, for all space groups except $P\bar{1}$ and $P1$.

The phase of reflection 0 3 1, after entry (34), also was not determined at this point since all indications were π, whereas the space group requires that the value be $\pm\pi/2$. Similarly for the phase of 0 8 14, after entry (37), which should have the value 0 or π and was indicated as $\pm\pi/2$. Later in the phase determination, the phase of 0 8 14 was shown to be $\underline{p}$ which must have a value of 0 or π.

The enantiomorph was effectively selected by choosing a value of 0 instead of π for the symbol $\underline{a}$. This seemingly odd statement is based on the consideration that the phase of the refleltion 0 8 7 is determined by a choice of the value for a. If the reflection 0 8 7 having a prescribed value is combined with the originally chosen ones, 3 0 10, 3 3 0 and 3 0 1, whose values were specified, we have the 0 8 7 and the first two to specify the origin and the 3 0 1 reflection to specify the enantiomorph. In this context, a value could have been assigned to the 0 8 7 reflection initially, however the sequence that was used was selected because $|E_{087}|$ is somewhat small and forms relatively few interactions as defined in Eq.(4). An examination of the phase values in the parity groups in Table 18 shows that in each group the phases are mostly 0 or π with few $\pm\pi/2$ values or they are mostly $\pm\pi/2$ with few 0 or π values. This condition indicates that among the reflections with the stronger $|E|$ values, the enantiomorph does not control many phases in this particular structure. Nevertheless, the structure could not have been solved without an enantiomorph specification.

The values of symbols p and s have not been indicated with any certainty in the application of Eq.(4). One alternative would be to continue the structure determination with four different sets of phases based on p = 0 and π and s = 0 and π . With large computers this is no problem. However, there are other relationships which define phases in terms of structure factor magnitudes which may indicate the values of p and s. The forms of the $\sum_1$ relationship of interest to $P2_12_12_1$ are:

$$S\ E_{2h2k0} \sim S \sum_{\ell} (-1)^{\ell+h} (|E^2_{hkl}| - 1) \qquad (13)$$

$$S\ E_{02k2\ell} \sim S \sum_{h} (-1)^{h+k} (|E^2_{hkl}| - 1) \qquad (14)$$

and

$$S\ E_{2h02\ell} \sim S \sum_{k} (-1)^{k+\ell} (|E^2_{hkl}| - 1) \qquad (15)$$

with the associated probability:

$$P_{+}(E_{2\underset{\sim}{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{\sigma_3 |E_{2\underset{\sim}{h}}| \sum_1}{2\sigma_2^{3/2}} \qquad (16)$$

In this structure, it was possible to apply the $\sum_1$ formula to several reflections with the results shown in Table 22. In space group $P2_12_12_1$, the $\sum_1$ relations can indicate either + or - signs for the two-dimensional reflections, in contrast to space group $P\bar{1}$ where $\sum_1$ can have a large probability only for + sign indications. Although the probability in each determination is not very high, the over-all probability, taking into consideration three determinations for p and two for s, is considerably higher. Hence it appears that both p and s have the value π.

The phases as listed in Table 18 were then given numerical values on the basis that $p = s = m = \pi$ and $a = 0$. Most of the values are $0, \pi$ and $\pm \pi/2$. In several instances, the phase indications were mixed, e.g. ($-\pi/2+s$ and $p+s$). When such a mixed indication occurs near the beginning of a phase determination, both values are assigned to the reflection and both are used for determining additional phases. When the time comes to assign numerical values to the symbols, mixed indications like ($-\pi/2 + s$; $p + s$) are averaged; i.e. if $p = s = \pi$, then the phase value is

$$\left[(-\pi/2 + \pi) + (\pi + \pi)\right]/2 \longrightarrow \left[+\pi/2 + 0\right]/2 \longrightarrow +\pi/4,$$

remembering that $2\pi \equiv 0$. (Each indication is evaluated first, the numerical values are reset to be in the range $-\pi$ to $+\pi$, and then the numerical values are averaged.)

These approximate phase values were then used as input values into the tangent formula, Eq. 5, for the purpose of refining the initial phases and for extending the phase determination to other reflections. Two cycles of the tangent formula were performed on the initial set of phases. Reflections were eliminated if (1) the number of contributors was less than 3, (2) if the phase changed by more than 2.0 radians or (3) if the $|E|$ calculated from the tangent formula was less than some minimum value such as 0.5. Reflections which are eliminated from any cycle in the application of the tangent formula are reintroduced into the next cycle with unknown phases.

After the initial phases are refined by the tangent formula, phases for additional reflections are derived. The reflections are added in groups of ~100 in order of decreasing $|E|$ and one iteration is made for each addition. The addition of new reflections in decreasing order of $|E|$ values has the effect of weighting in which the stronger reflections have a greater influence on phase determination than those with moderate $|E|$ values. In general, for those reflections which must have special phase values, i.e. $0, \pi$ or $\pm \pi/2$, the computer program resets the calculated value to the nearest special value. Two pages reproduced from the computer print-out of a phase expansion by the tangent formula are contained in the Appendix.

The effect of the number of reflections on the E-map is shown in Fig. 5. Although the E-map computed with $|E|_{min} = 1.4$ contains all the peaks for the molecule, the extraneous peaks cause confusion.

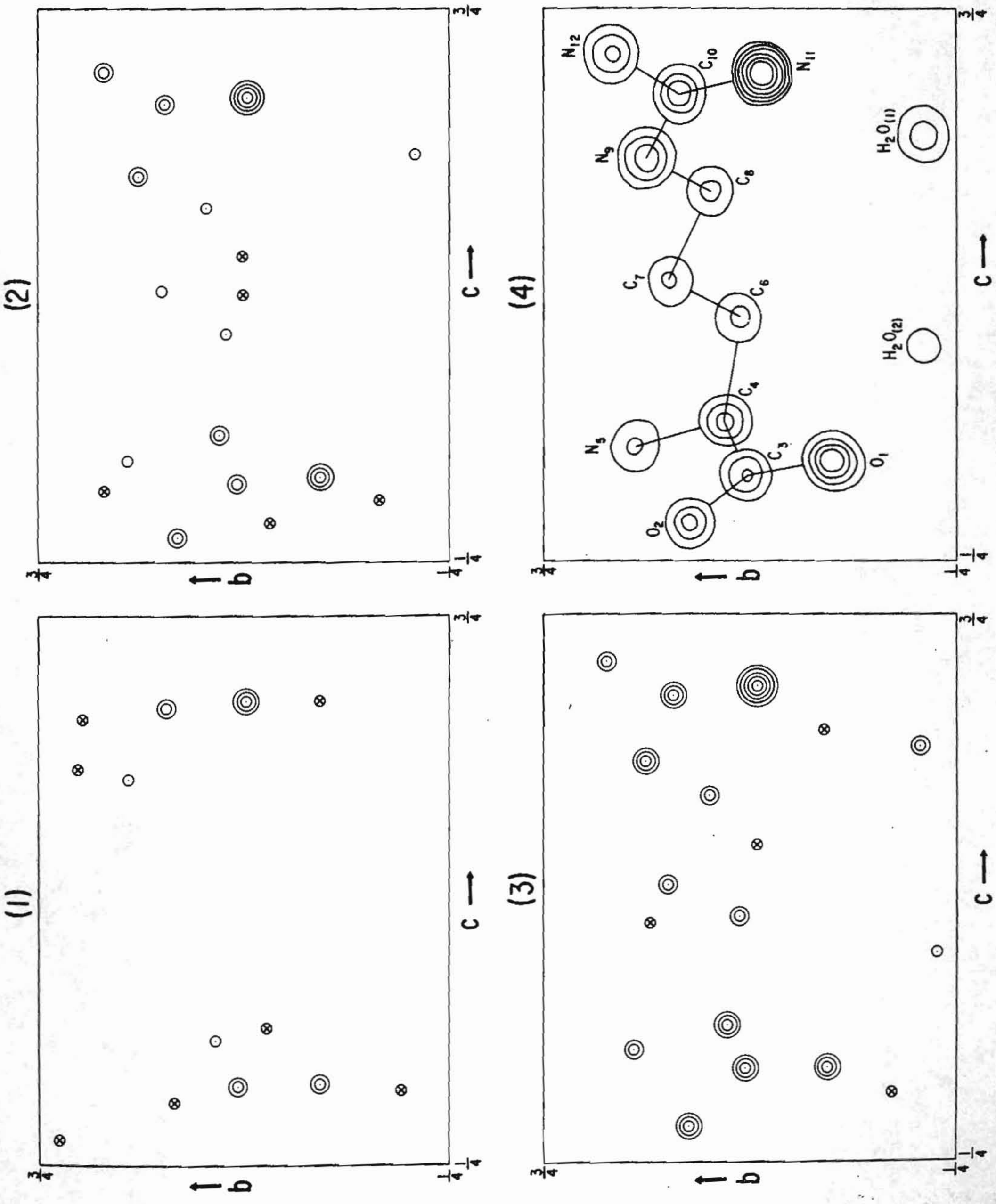


Fig. 5. Three dimensional E-maps for L-arginine·$2H_2O$ that were computed with normalized structure factors, E_h, as coefficients. The phases were derived with the symbolic addition procedure. (1) 137 data with $|E|_{min}$ = 1.50, (2) 200 data with $|E|_{min}$ = 1.40, (3) 300 data with $|E|_{min}$ = 1.15, and (4) 400 data with $|E|_{min}$ = 1.00. The peaks marked with crosses are extraneous.

Additional data eliminates or minimizes extraneous peaks. Maps with $|E|_{min}$ near 1.1 or 1.0 are quite adequate.

The procedure described for space group $P2_12_12_1$ can be applied to most other acentric space groups with minor modifications. Details for phase determination for other structures in $P2_12_12_1$, $P4_12_12$, and Aba2 have been published (see e.g. Karle, 1970; Karle, Ottenheym and Witkop, 1974; Karle and Karle, 1970).

Space Group $P2_1$

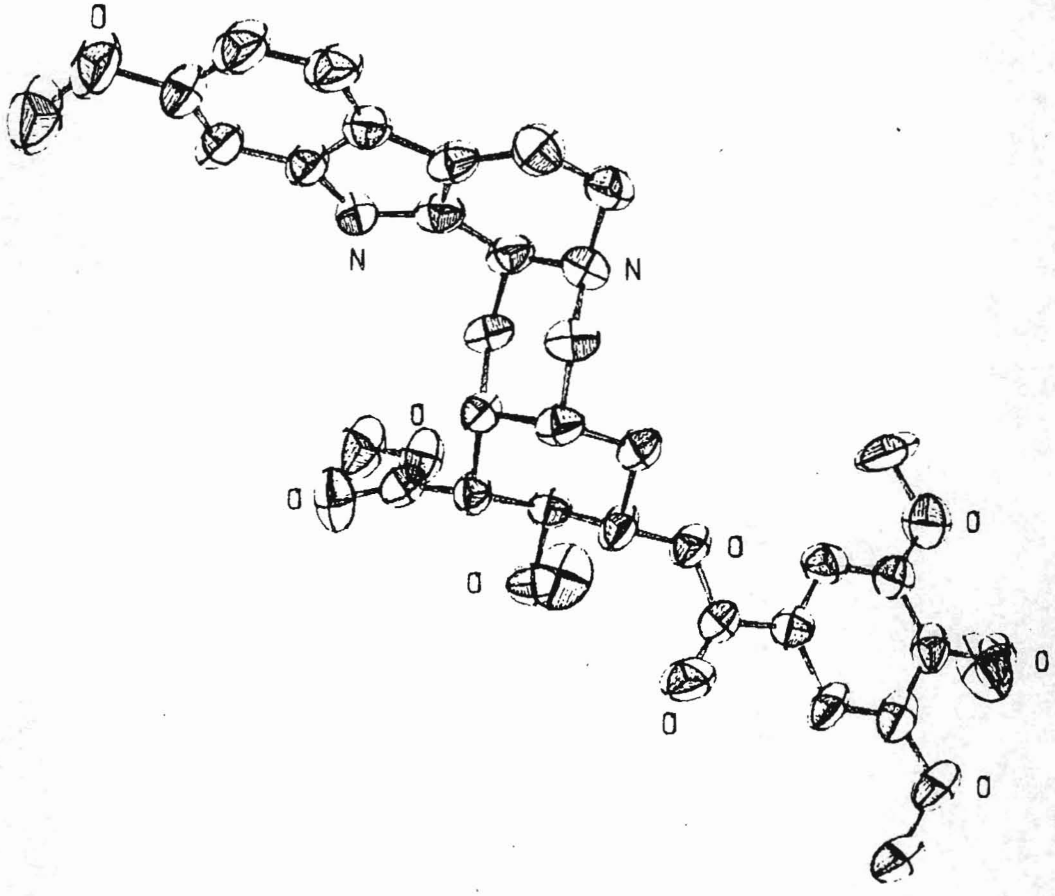
The specification of the enantiomorph in $P2_1$ (or the axial direction in a space group like Aba2) cannot be made directly at the beginning of the phase determination. In space group $P2_1$, the origin is specified by assigning the value 0 to two reflections from g0u, u0g or u0u and to one reflection of the type $h1\ell$. In order to develop the phase determination by means of the sum of angles formula, Eq. 4, one or more symbols will need to be assigned. The enantiomorph will be determined by one of the symbols representing a phase different than 0 or π, preferably near $\pi/2$. In the example for reserpine (Karle and Karle, 1968), four symbols were assigned, one at a time, as needed, to implement the sum of angles formula, see Tables 23-27. Symbols a and b were assigned to $h0\ell$ type of reflections and therefore could have only the values 0 or π. There were numerous relationships indicating that $a = \pi$ and $b = 0$, as shown in Table 26. Symbols p and s were assigned to $hk\ell$ type of reflections and could have any value from

Table 23

RESERPINE, $C_{33}H_{40}N_{2}O_{9}$

I. L. Karle and J. Karle, Acta Cryst. B24, 81(1968).

Laboratory for the Structure of Matter
Naval Research Laboratory, Washington, D.C.



sp.gr.	$P2_1$
a	14.45
b	8.98
c	13.37
β	115.2°
Z	2

Table 24. Space group $P2_1$

$x, y, z; \ \bar{x}, \tfrac{1}{2} + y, \bar{z}$ (b axis unique)

$$\left.\begin{array}{ll} \text{k even:} & \alpha(h\,k\,l) = -\alpha(h\,\bar{k}\,l) \\ & \alpha(\bar{h}\,k\,l) = \alpha(h\,k\,\bar{l}) \\ & \\ \text{k odd:} & \alpha(h\,k\,l) = \pi - \alpha(h\,\bar{k}\,l) \\ & \alpha(\bar{h}\,k\,l) = \pi + \alpha(h\,k\,\bar{l}) \end{array}\right\} \ \alpha(h\,k\,l) \neq \alpha(\bar{h}\,k\,l)$$

Table 25. Phase assignments.

$\vec{h}$	$\lvert E_{\vec{h}} \rvert$	$\phi_{\vec{h}}$	
0 0 3	2.07	0	origin
1 0 2	3.12	π *	
$\overline{12}$ 1 8	4.46	0	
$\overline{12}$ 0 4	2.90	a $(0,\pi)$	
1 0 3	2.94	b $(0,\pi)$	
$\bar{6}$ 7 2	2.38	p	
$\overline{11}$ 1 1	2.69	s	

* In specifying an origin the value of zero is ordinarily employed instead of π. The value π was inserted here in retrospect because it improves the placement of the molecule in the unit cell.

Table 26. Application of $\phi_{\vec{h}} \approx \langle \phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}} \rangle_{\vec{k}_r}$ to reserpine data.

$$\begin{array}{rrrl} 0&0&3&0\\ \bar{12}&0&4&a\\ \hline \bar{12}&0&7&a \end{array}$$

$$\begin{array}{rrrl} \bar{1}&0&\bar{2}&\pi\\ \bar{12}&0&7&a\\ \hline \bar{13}&0&5&\pi+a \end{array}$$

$$\begin{array}{rrrl} 6&7&\bar{2}&\pi+p\\ \bar{12}&\bar{1}&8&\pi\\ \hline \bar{6}&6&6&p \end{array}$$

$$\begin{array}{rrrl} \bar{6}&7&2&p\\ 1&0&2&\pi\\ \hline \bar{5}&7&4&\pi+p \end{array}$$

$$\begin{array}{rrrl} 1&0&3&b\\ \bar{12}&0&7&a\\ \hline \bar{11}&0&10&a+b \end{array}$$

$$\begin{array}{rrrl} \bar{12}&1&8&0\\ \bar{1}&0&\bar{3}&b\\ \hline \bar{13}&1&5&b \end{array}$$

$$\begin{array}{rrrl} \bar{13}&1&5&b\\ 0&0&\bar{3}&0\\ \hline \bar{13}&1&2&b \end{array}$$

$$\begin{array}{rrrl} 13&\bar{1}&\bar{5}&b\\ \bar{6}&6&6&p\\ \hline 7&5&1&b+p \end{array}$$

$$(9)\left\{\begin{array}{rrrl} \bar{13}&1&2&b\\ 7&5&1&b+p\\ \hline \bar{6}&6&3&p\\ &&&\\ \bar{6}&6&6&p\\ 0&0&\bar{3}&0\\ \hline \bar{6}&6&3&p \end{array}\right.$$

$$(10)\left\{\begin{array}{rrrl} \bar{12}&1&8&0\\ 6&6&\bar{3}&p\\ \hline \bar{6}&7&5&p\\ &&&\\ \bar{6}&7&2&p\\ 0&0&3&0\\ \hline \bar{6}&7&5&p\\ &&&\\ \bar{12}&0&7&a\\ 6&7&\bar{2}&\pi+p\\ \hline \bar{6}&7&5&\pi+a+p \end{array}\right.$$

$$\boxed{\pi = a}$$

$$(11)\quad\begin{array}{rrrl} \bar{6}&6&3&p\\ \bar{1}&0&\bar{2}&\pi\\ \hline \bar{7}&6&1&\pi+p \end{array}$$

$$(12)\left\{\begin{array}{rrrl} \bar{6}&7&5&p\\ 6&\bar{6}&\bar{3}&-p\\ \hline 0&1&2&0\\ &&&\\ &&&b = 0\\ 7&\bar{5}&1&\pi+b-p\\ \bar{7}&6&1&\pi+p\\ \hline 0&1&2&b \end{array}\right.$$

$$(13)\left\{\begin{array}{rrrl} \bar{6}&7&5&p\\ 1&0&2&\pi\\ \hline \bar{5}&7&7&\pi+p\\ &&&\\ \bar{12}&1&8&0\\ 7&6&\bar{1}&\pi+p\\ \hline \bar{5}&7&7&\pi+p\\ &&&\\ \bar{5}&7&4&\pi+p\\ 0&0&3&0\\ \hline \bar{5}&7&7&\pi+p \end{array}\right.$$

$$(14)\left\{\begin{array}{rrrl} \bar{6}&7&2&p\\ \bar{7}&\bar{6}&1&\pi-p\\ \hline \bar{13}&1&3&\pi\\ &&&\\ 0&1&\bar{2}&\pi,\ \pi+b\\ \bar{13}&0&5&\pi+a\\ \hline \bar{13}&1&3&a,\ a+b \end{array}\right.$$

$$\boxed{a = \pi}$$

$$(15)\left\{\begin{array}{rrrl} \bar{12}&1&8&0\\ 13&\bar{1}&\bar{3}&\pi\\ \hline 1&0&5&\pi\\ &&&\\ 1&0&2&\pi\\ 0&0&3&0\\ \hline 1&0&5&\pi\\ &&&\\ 7&\bar{6}&\bar{1}&\pi-p\\ \bar{6}&6&6&p\\ \hline 1&0&5&\pi\\ &&&\\ \bar{5}&7&7&\pi+p\\ 6&\bar{7}&\bar{2}&-p\\ \hline 1&0&5&\pi \end{array}\right.$$

$$(16)\quad \begin{array}{rrrl} \overline{12} & 1 & 8 & 0 \\ 12 & 0 & \overline{7} & a \\ \hline 0 & 1 & 1 & a \end{array}$$

$$(17)\quad \begin{array}{rrrl} \overline{11} & 1 & 1 & s \\ 0 & 1 & 1 & a \\ \hline \overline{11} & 2 & 2 & a+s \end{array}$$

$$(18)\quad \begin{array}{rrrl} \overline{13} & 1 & 2 & b \\ 11 & 1 & \overline{1} & \pi+s \\ \hline \overline{2} & 2 & 1 & \pi+b+s \end{array}$$

$$(19)\quad \left\{ \begin{array}{rrrl} 0 & 1 & 1 & a \\ 7 & 5 & 1 & b+p \\ \hline 7 & 6 & 2 & a+b+p \\ & & & \boxed{a+b = \pi} \\ 7 & 6 & \overline{1} & \pi+p \\ 0 & 0 & 3 & 0 \\ \hline 7 & 6 & 2 & \pi+p \\ \\ 6 & 6 & \overline{3} & p \\ 1 & 0 & 5 & \pi \\ \hline 7 & 6 & 2 & \pi+p \\ \\ \overline{6} & 7 & 5 & p \\ 13 & \overline{1} & \overline{3} & \pi \\ \hline 7 & 6 & 2 & \pi+p \end{array} \right.$$

$$(20)\quad \left\{ \begin{array}{rrrl} \overline{12} & 1 & 8 & 0 \\ 0 & \overline{1} & 2 & \pi \\ \hline \overline{12} & 0 & 10 & \pi \\ & & & \boxed{a = \pi} \\ 0 & 0 & 3 & 0 \\ \overline{12} & 0 & 7 & a \\ \hline \overline{12} & 0 & 10 & a \\ \\ \overline{13} & 0 & 5 & \pi+a \\ 1 & 0 & 5 & a \\ \hline \overline{12} & 0 & 10 & \pi \\ \\ \overline{6} & 7 & 5 & p \\ \overline{6} & \overline{7} & 5 & \pi-p \\ \hline \overline{12} & 0 & 10 & \pi \end{array} \right.$$

$$(21)\quad \left\{ \begin{array}{rrrl} \overline{12} & 1 & 8 & 0 \\ 0 & \overline{1} & 1 & \pi+a \\ \hline \overline{12} & 0 & 9 & \pi+a \\ & & & \boxed{a = \pi} \\ \overline{6} & 6 & 6 & +p \\ \overline{6} & \overline{6} & 3 & -p \\ \hline \overline{12} & 0 & 9 & 0 \end{array} \right.$$

$$(22)\quad \left\{ \begin{array}{rrrl} 7 & 6 & 2 & \pi+p \\ \overline{11} & 1 & 1 & s \\ \hline \overline{4} & 7 & 3 & \pi+p+s \\ & & & \boxed{a+b = \pi} \\ \overline{11} & 2 & 2 & a+s \\ 7 & 5 & 1 & b+p \\ \hline \overline{4} & 7 & 3 & a+b+p+s \end{array} \right.$$

$$(23)\quad \left\{ \begin{array}{rrrl} \overline{12} & 1 & 8 & 0 \\ 7 & 5 & 1 & b+p \\ \hline \overline{5} & 6 & 9 & b+p \\ \\ \overline{12} & 0 & 7 & a \\ 7 & 6 & 2 & \pi+p \\ \hline \overline{5} & 6 & 9 & \pi+a+p \\ & & & \boxed{a+} \\ \overline{6} & 6 & 6 & p \\ 1 & 0 & 3 & b \\ \hline \overline{5} & 6 & 9 & b+p \\ & & & \boxed{b} \\ \overline{12} & 0 & 10 & \pi \\ 7 & 6 & \overline{1} & \pi+p \\ \hline \overline{5} & 6 & 9 & p \end{array} \right.$$

$$(24)\quad \left\{ \begin{array}{rrrl} 7 & 5 & 1 & b+p \\ 1 & 0 & 5 & \pi \\ \hline 8 & 5 & 6 & \pi+b+p \\ \\ 13 & \overline{1} & \overline{3} & \pi \\ \overline{5} & 6 & 9 & b+p \\ \hline 8 & 5 & 6 & \pi+b+p \end{array} \right.$$

$$(25)\left\{\begin{array}{l}
\begin{array}{rrrl}
\overline{13} & 1 & 2 & b \\
13 & 1 & \overline{2} & \pi+b \\ \hline
0 & 2 & 0 & \pi
\end{array} \\
\qquad\qquad \boxed{2s = 0} \\
\begin{array}{rrrl}
\overline{11} & 1 & 1 & s \\
11 & 1 & \overline{1} & \pi+s \\ \hline
0 & 2 & 0 & \pi+2s
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{13} & 1 & 5 & b \\
13 & 1 & \overline{5} & \pi+b \\ \hline
0 & 2 & 0 & \pi
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{13} & 1 & 3 & \pi \\
13 & 1 & \overline{3} & 0 \\ \hline
0 & 2 & 0 & \pi
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{12} & 1 & 8 & 0 \\
12 & 1 & \overline{8} & \pi \\ \hline
0 & 2 & 0 & \pi
\end{array} \\[2ex]
\begin{array}{rrrl}
0 & 1 & 2 & 0 \\
0 & 1 & \overline{2} & \pi \\ \hline
0 & 2 & 0 & \pi
\end{array} \\[2ex]
\begin{array}{rrrl}
0 & 1 & 1 & a \\
0 & 1 & \overline{1} & \pi+a \\ \hline
0 & 2 & 0 & \pi
\end{array}
\end{array}\right.$$

$$(25)\quad \begin{array}{rrrl}
\overline{12} & 0 & 4 & a \\
1 & 0 & 3 & b \\ \hline
\overline{11} & 0 & 7 & a+b
\end{array}$$

$$(26)\quad \begin{array}{rrrl}
\overline{11} & 0 & 7 & a+b \\
1 & 0 & 3 & b \\ \hline
\overline{10} & 0 & 10 & a
\end{array}$$

$$(27)\quad \begin{array}{rrrl}
\overline{10} & 0 & 10 & a \\
\overline{1} & 0 & \overline{5} & \pi \\ \hline
\overline{11} & 0 & 5 & \pi+a
\end{array}$$

$$(28)\left\{\begin{array}{l}
\begin{array}{rrrl}
\overline{11} & 0 & 7 & a+b \\
13 & 1 & \overline{5} & \pi+b \\ \hline
2 & 1 & 2 & \pi+a
\end{array} \\[2ex]
\begin{array}{rrrl}
12 & 1 & \overline{8} & \pi \\
\overline{10} & 0 & 10 & a \\ \hline
2 & 1 & 2 & \pi+a
\end{array} \\[2ex]
\begin{array}{rrrl}
13 & 1 & \overline{3} & 0 \\
\overline{11} & 0 & 5 & \pi+a \\ \hline
2 & 1 & 2 & \pi+a
\end{array}
\end{array}\right.$$

$$(29)\left\{\begin{array}{l}
\begin{array}{rrrl}
7 & 6 & 2 & \pi+p \\
\overline{11} & 0 & 5 & \pi+a \\ \hline
\overline{4} & 6 & 7 & a+p
\end{array} \\[2ex]
\begin{array}{rrrl}
6 & 6 & \overline{3} & p \\
\overline{10} & 0 & 10 & a \\ \hline
\overline{4} & 6 & 7 & a+p
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{6} & 7 & 5 & p \\
2 & \overline{1} & 2 & a \\ \hline
\overline{4} & 6 & 7 & a+p
\end{array}
\end{array}\right.$$

$$(30)\left\{\begin{array}{l}
\begin{array}{rrrl}
\overline{12} & 1 & 8 & 0 \\
2 & 1 & 2 & \pi+a \\ \hline
\overline{10} & 2 & 10 & \pi+a
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{10} & 0 & 10 & a \\
0 & 2 & 0 & \pi \\ \hline
\overline{10} & 2 & 10 & \pi+a
\end{array}
\end{array}\right.$$

$$(31)\left\{\begin{array}{l}
\begin{array}{rrrl}
1 & 0 & 3 & b \\
0 & 1 & \overline{2} & \pi+b \\ \hline
1 & 1 & 1 & \pi
\end{array} \\[2ex]
\begin{array}{rrrl}
1 & 0 & 2 & \pi \\
0 & 1 & \overline{1} & \pi+a \\ \hline
1 & 1 & 1 & a
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{5} & 7 & 4 & \pi+p \\
6 & \overline{6} & \overline{3} & -p \\ \hline
1 & 1 & 1 & \pi
\end{array} \\
\qquad\qquad\qquad \boxed{a = \pi} \\
\begin{array}{rrrl}
13 & 1 & \overline{3} & 0 \\
\overline{12} & 0 & 4 & a \\ \hline
1 & 1 & 1 & a
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{5} & 7 & 7 & \pi+p \\
6 & \overline{6} & \overline{6} & -p \\ \hline
1 & 1 & 1 & \pi
\end{array}
\end{array}\right.$$

$$\left\{\begin{array}{l}
\begin{array}{rrrl}
\overline{11} & 0 & 5 & \pi+a \\
\overline{1} & 0 & \overline{2} & \pi \\ \hline
\overline{12} & 0 & 3 & a
\end{array} \\[2ex]
\begin{array}{rrrl}
\overline{13} & 1 & 2 & b \\
1 & \overline{1} & 1 & 0 \\ \hline
\overline{12} & 0 & 3 & b
\end{array}
\end{array}\right.$$

$$(32)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{10} & 2 & 10 \\ 0 & \bar{1} & 1 \\ \hline \overline{10} & 1 & 11 \end{array} \quad \begin{array}{c} \pi+a \\ \pi+a \\ \hline 0 \end{array} \\[2em]
\begin{array}{ccc} \overline{10} & 0 & 10 \\ 0 & 1 & 1 \\ \hline \overline{10} & 1 & 11 \end{array} \quad \begin{array}{c} a \\ a \\ \hline 0 \end{array} \\[2em]
\begin{array}{ccc} \overline{12} & 0 & 9 \\ 2 & 1 & 2 \\ \hline \overline{10} & 1 & 11 \end{array} \quad \begin{array}{c} 0,\ \pi+a \\ +a \\ \hline \pi+a,\ 0 \end{array}
\end{array}\right.$$

$$(33)\quad \left\{\begin{array}{l}
\begin{array}{ccc} 13 & 1 & \bar{3} \\ \overline{11} & 0 & 10 \\ \hline 2 & 1 & 7 \end{array} \quad \begin{array}{c} 0 \\ a+b \\ \hline a+b \end{array} \\
\qquad\qquad\qquad \boxed{b = 0} \\
\begin{array}{ccc} 12 & 0 & \bar{4} \\ \overline{10} & 1 & 11 \\ \hline 2 & 1 & 7 \end{array} \quad \begin{array}{c} a \\ 0 \\ \hline a \end{array}
\end{array}\right.$$

$$(34)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{10} & 1 & 11 \\ 13 & 1 & \bar{3} \\ \hline 3 & 2 & 8 \end{array} \quad \begin{array}{c} 0 \\ 0 \\ \hline 0 \end{array} \\[2em]
\begin{array}{ccc} 2 & 1 & 7 \\ 1 & 1 & 1 \\ \hline 3 & 2 & 8 \end{array} \quad \begin{array}{c} a \\ a \\ \hline 0 \end{array}
\end{array}\right.$$

$$(35)\quad \left\{\begin{array}{l}
\begin{array}{ccc} 2 & 1 & 7 \\ 1 & 0 & 2 \\ \hline 3 & 1 & 9 \end{array} \quad \begin{array}{c} a \\ \pi \\ \hline \pi+a \end{array} \\[2em]
\begin{array}{ccc} 3 & 2 & 8 \\ 0 & \bar{1} & 1 \\ \hline 3 & 1 & 9 \end{array} \quad \begin{array}{c} 0 \\ \pi+a \\ \hline \pi+a \end{array}
\end{array}\right.$$

$$(36)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{10} & 2 & 10 \\ 1 & 0 & 2 \\ \hline \bar{9} & 2 & 12 \end{array} \quad \begin{array}{c} \pi+a \\ \pi \\ \hline a \end{array} \\[2em]
\begin{array}{ccc} \overline{12} & 0 & 4 \\ 3 & 2 & 8 \\ \hline \bar{9} & 2 & 12 \end{array} \quad \begin{array}{c} a \\ 0 \\ \hline a \end{array}
\end{array}\right.$$

$$(37)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{12} & 0 & 7 \\ 2 & 1 & 2 \\ \hline \overline{10} & 1 & 9 \end{array} \quad \begin{array}{c} a \\ \pi+a \\ \hline \pi \end{array} \\
\qquad\qquad\qquad \boxed{\pi = a} \\
\begin{array}{ccc} \bar{4} & \bar{6} & 7 \\ \bar{6} & 7 & 2 \\ \hline \overline{10} & 1 & 9 \end{array} \quad \begin{array}{c} a-p \\ p \\ \hline a \end{array} \\
\qquad\qquad\qquad \boxed{s = 0} \\
\begin{array}{ccc} \bar{4} & 7 & 3 \\ \bar{6} & \bar{6} & 6 \\ \hline \overline{10} & 1 & 9 \end{array} \quad \begin{array}{c} \pi+p+s \\ -p \\ \hline \pi+s \end{array}
\end{array}\right.$$

$$(38)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{11} & 0 & 7 \\ \bar{1} & 0 & \bar{5} \\ \hline \overline{12} & 0 & 2 \end{array} \quad \begin{array}{c} a+b \\ \pi \\ \hline \pi+a+b \end{array} \\[2em]
\begin{array}{ccc} \overline{11} & 0 & 5 \\ \bar{1} & 0 & \bar{3} \\ \hline \overline{12} & 0 & 2 \end{array} \quad \begin{array}{c} \pi+a \\ b \\ \hline \pi+a+b \end{array} \\
\qquad\qquad\qquad \boxed{a = \pi} \\
\begin{array}{ccc} \overline{10} & 1 & 9 \\ \bar{2} & \bar{1} & \bar{7} \\ \hline \overline{12} & 0 & 2 \end{array} \quad \begin{array}{c} a \\ a+b \\ \hline b \end{array}
\end{array}\right.$$

$$(39)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{13} & \bar{1} & 3 \\ 1 & 2 & \bar{2} \\ \hline \overline{12} & 1 & 1 \end{array} \quad \begin{array}{c} 0 \\ a+s \\ \hline a+s \end{array} \\
\qquad\qquad\qquad \boxed{s = \pi+b} \\
\begin{array}{ccc} \bar{8} & \bar{5} & \bar{6} \\ \bar{4} & 6 & 7 \\ \hline \overline{12} & 1 & 1 \end{array} \quad \begin{array}{c} \pi+b-p \\ a+p \\ \hline \pi+a+b \end{array} \\[2em]
\begin{array}{ccc} \overline{12} & 0 & 2 \\ 0 & 1 & \bar{1} \\ \hline 12 & 1 & 1 \end{array} \quad \begin{array}{c} \pi+a+b \\ \pi+a \\ \hline b \end{array}
\end{array}\right.$$

$$(40)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \overline{12} & 1 & 1 \\ 7 & 6 & 2 \\ \hline \bar{5} & 7 & 3 \end{array} \quad \begin{array}{c} b \\ \pi+p \\ \hline \pi+b+p \end{array} \\
\qquad\qquad\qquad \boxed{a = \pi} \\
\begin{array}{ccc} 6 & 7, & \bar{2} \\ \overline{11} & 0 & 5 \\ \hline \bar{5} & 7 & 3 \end{array} \quad \begin{array}{c} \pi+p \\ \pi+a \\ \hline a+p \end{array} \\[2em]
\begin{array}{ccc} 2 & 1 & 2 \\ \bar{7} & 6 & 1 \\ \hline \bar{5} & 7 & 3 \end{array} \quad \begin{array}{c} \pi+a \\ \pi+p \\ \hline a+p \end{array} \\
\qquad\qquad\qquad \boxed{b =} \\
\begin{array}{ccc} 5 & 7 & \bar{7} \\ \overline{10} & 0 & 10 \\ \hline \bar{5} & 7 & 3 \end{array} \quad \begin{array}{c} p \\ a+b \\ \hline a+b+p \end{array}
\end{array}\right.$$

$$(41)\quad \left\{\begin{array}{l}
\begin{array}{ccc} \bar{6} & 7 & 2 \\ 12 & \bar{1} & \bar{1} \\ \hline 6 & 6 & 1 \end{array} \quad \begin{array}{c} p \\ b \\ \hline b+p \end{array} \\
\qquad\qquad\qquad a = \\
\begin{array}{ccc} 12 & 0 & \bar{2} \\ \bar{6} & 6 & 3 \\ \hline 6 & 6 & 1 \end{array} \quad \begin{array}{c} \pi+a+b \\ p \\ \hline \pi+a+b+p \end{array}
\end{array}\right.$$

$$\left\{\begin{array}{rrrl}
1 & \bar{2} & \bar{2} & a-s \\
\bar{9} & 2 & 12 & a \\ \hline
8 & 0 & 10 & -s \quad \times \\[3ex]
\overline{11} & 1 & 1 & s \\
3 & \bar{1} & 9 & a \\ \hline
\bar{8} & 0 & 10 & a+s
\end{array}\right.$$

$$2)\left\{\begin{array}{rrrl}
\bar{5} & 7 & 3 & a+p \\
0 & 2 & 0 & \pi \\ \hline
\bar{5} & 9 & 3 & \pi+a+p \\[3ex]
\overline{10} & 2 & 10 & \pi+a \\
5 & 7 & \bar{7} & p \\ \hline
\bar{5} & 9 & 3 & \pi+a+p \\[3ex]
\bar{6} & 7 & 5 & p \\
1 & 2 & \bar{2} & a+s \\ \hline
\bar{5} & 9 & 3 & a+p+s
\end{array}\right.$$

$$\boxed{s = \pi}$$

$$)\left\{\begin{array}{rrrl}
\overline{10} & 2 & 10 & \pi+a \\
0 & 0 & 3 & 0 \\ \hline
\overline{10} & 2 & 13 & \pi+a \\[3ex]
\overline{10} & 1 & 11 & 0 \\
0 & 1 & 2 & 0 \\ \hline
\overline{10} & 2 & 13 & 0 \\[3ex]
3 & 2 & 8 & 0 \\
\overline{13} & 0 & 5 & \pi+a \\ \hline
\overline{10} & 2 & 13 & \pi+a
\end{array}\right.$$

$$\boxed{a = \pi}$$

$$(44)\left\{\begin{array}{rrrl}
\overline{10} & 1 & 9 & \pi \\
1 & 0 & 3 & 0 \\ \hline
\bar{9} & 1 & 12 & \pi \\[3ex]
\overline{11} & 0 & 5 & \pi+a \\
2 & 1 & 7 & a \\ \hline
\bar{9} & 1 & 12 & \pi \\[3ex]
\bar{5} & \bar{6} & 9 & \pi+a-p \\
\bar{4} & 7 & 3 & \pi+s+p \\ \hline
\bar{9} & 1 & 12 & a+s
\end{array}\right.$$

$$\boxed{s = \pi+a\,(=0)}$$

$$(45)\left\{\begin{array}{rrrl}
\overline{10} & 1 & 9 & \pi \\
0 & 0 & 3 & 0 \\ \hline
\overline{10} & 1 & 12 & \pi \\[3ex]
\overline{10} & 2 & 10 & \pi+a \\
0 & \bar{1} & 2 & \pi \\ \hline
\overline{10} & 1 & 12 & a \\[3ex]
\overline{10} & 0 & 10 & a \\
0 & 1 & 2 & 0 \\ \hline
\overline{10} & 1 & 12 & a \\[3ex]
\bar{5} & 7 & 3 & a+p \\
\bar{5} & \bar{6} & 9 & \pi+a-p \\ \hline
\overline{10} & 1 & 12 & \pi \\[3ex]
\overline{12} & 0 & 10 & \pi \\
2 & 1 & 2 & \pi+a \\ \hline
\overline{10} & 1 & 12 & a \\[3ex]
\bar{4} & \bar{6} & 7 & a-p \\
\bar{6} & 7 & 5 & p \\ \hline
\overline{10} & 1 & 12 & a
\end{array}\right.$$

$$\boxed{a = \pi}$$

$$(46)\left\{\begin{array}{rrrl}
\bar{5} & 7 & 3 & a+p \\
\bar{5} & \bar{7} & 4 & -p \\ \hline
\overline{10} & 0 & 7 & a \\[3ex]
\overline{11} & 0 & 5 & \pi+a \\
1 & 0 & 2 & \pi \\ \hline
\overline{10} & 0 & 7 & a \\[3ex]
\overline{10} & 1 & 9 & \pi \\
0 & \bar{1} & \bar{2} & 0 \\ \hline
\overline{10} & 0 & 7 & \pi
\end{array}\right.$$

$$(47)\left\{\begin{array}{rrrl}
\overline{12} & 0 & 2 & \pi+a+b \\
0 & 0 & 3 & 0 \\ \hline
\overline{12} & 0 & 5 & \pi+a+b \\[3ex]
\overline{11} & 0 & 7 & a+b \\
\bar{1} & 0 & \bar{2} & \pi \\ \hline
\overline{12} & 0 & 5 & \pi+a+b \\[3ex]
\bar{6} & 6 & 6 & p \\
\bar{6} & \bar{6} & \bar{1} & b-p \\ \hline
\overline{12} & 0 & 5 & b \\[3ex]
\overline{10} & 1 & 12 & a \\
\bar{2} & \bar{1} & \bar{7} & a \\ \hline
\overline{12} & 0 & 5 & 0
\end{array}\right.$$

$$\boxed{\begin{array}{l} b = 0 \\ a = \pi \end{array}}$$

(48)

$$\begin{array}{rrrl} \bar{11} & 0 & 7 & a+b \\ 0 & 1 & 2 & 0 \\ \hline \bar{11} & 1 & 9 & a+b \end{array}$$

$\boxed{b = 0}$

$$\begin{array}{rrrl} \bar{10} & 1 & 11 & 0 \\ \bar{1} & 0 & \bar{2} & \pi \\ \hline \bar{11} & 1 & 9 & \pi \end{array}$$

$\boxed{a = \pi}$

$$\begin{array}{rrrl} \bar{6} & \bar{6} & 6 & -p \\ \bar{5} & 7 & 3 & a+p \\ \hline \bar{11} & 1 & 9 & a \end{array}$$

$$\begin{array}{rrrl} \bar{10} & 1 & 12 & a \\ \bar{1} & 0 & \bar{3} & 0 \\ \hline \bar{11} & 1 & 9 & a \end{array}$$

(49)

$$\begin{array}{rrrl} \bar{10} & \bar{1} & 11 & \pi \\ 4 & 7 & \bar{3} & p+s \\ \hline \bar{6} & 6 & 8 & \pi+p+s \end{array}$$

$\boxed{s = 0}$

$$\begin{array}{rrrl} \bar{12} & 0 & 7 & a \\ 6 & 6 & 1 & b+p \\ \hline \bar{6} & 6 & 8 & a+b+p \end{array}$$

(50)

$$\begin{array}{rrrl} \bar{10} & 1 & 11 & 0 \\ 13 & 1 & \bar{2} & \pi+b \\ \hline 3 & 2 & 9 & \pi+b \end{array}$$

$$\begin{array}{rrrl} 8 & \bar{5} & 6 & b-p \\ \bar{5} & 7 & 3 & a+p \\ \hline 3 & 2 & 9 & a+b \end{array}$$

$\boxed{\begin{array}{l} b = 0 \\ \pi = a \end{array}}$

$$\begin{array}{rrrl} \bar{10} & 1 & 12 & a \\ 13 & 1 & \bar{13} & 0 \\ \hline 3 & 2 & 9 & a \end{array}$$

(51)

$$\begin{array}{rrrl} 2 & 1 & 2 & \pi+a \\ \bar{11} & 1 & 9 & a \\ \hline \bar{9} & 2 & 11 & \pi \end{array}$$

$$\begin{array}{rrrl} 3 & 2 & 9 & a+b \\ \bar{12} & 0 & 2 & \pi+a+b \\ \hline \bar{9} & 2 & 11 & \pi \end{array}$$

$$\begin{array}{rrrl} \bar{9} & 2 & 11 & \pi \\ \bar{3} & \bar{2} & \bar{8} & 0 \\ \hline \bar{12} & 0 & 3 & \pi \end{array}$$

$$\begin{array}{rrrl} \bar{12} & 1 & 1 & b \\ 0 & \bar{1} & 2 & \pi \\ \hline \bar{12} & 0 & 3 & \pi+b \end{array}$$

$$\begin{array}{rrrl} \bar{11} & 0 & 5 & \pi+a \\ \bar{1} & 0 & \bar{2} & \pi \\ \hline \bar{12} & 0 & 3 & a \end{array}$$

?

$$\begin{array}{rrrl} \bar{13} & 1 & 2 & b \\ 1 & \bar{1} & 1 & 0 \\ \hline \bar{12} & 0 & 3 & b \end{array}$$

$$\begin{array}{rrrl} \bar{9} & 1 & 12 & \pi \\ \bar{3} & \bar{1} & \bar{9} & \pi+a \\ \hline \bar{12} & 0 & 3 & a \end{array}$$

$$\begin{array}{rrrl} \bar{9} & 2 & 12 & a \\ \bar{3} & \bar{2} & \bar{9} & a+b \\ \hline \bar{12} & 0 & 3 & b \end{array}$$

(52)

$$\begin{array}{rrrl} \bar{11} & 1 & 1 & s \\ 0 & 1 & 1 & a \\ \hline \bar{11} & 2 & 2 & a+s \end{array}$$

$$\begin{array}{rrrl} \bar{7} & \bar{5} & \bar{1} & b-p \\ \bar{4} & 7 & 3 & \pi+s+p \\ \hline \bar{11} & 2 & 2 & \pi+b+s \end{array}$$

$$\begin{array}{rrrl} \bar{12} & 0 & 4 & a \\ 1 & 2 & \bar{2} & a+s \\ \hline \bar{11} & 2 & 2 & s \end{array}$$

X

(53)

$$\begin{array}{rrrl} 11 & 2 & \bar{2} & a+s \\ \bar{9} & 2 & 11 & \pi \\ \hline 2 & 4 & 9 & \pi+a+s \end{array}$$

$$\begin{array}{rrrl} \bar{13} & 1 & 2 & b \\ 12 & 1 & \bar{1} & \pi+b \\ \hline \bar{1} & 2 & 1 & \pi \end{array}$$

s = a(

$$\begin{array}{rrrl} 2 & 4 & 9 & \pi+a+s \\ \bar{3} & \bar{2} & \bar{8} & 0 \\ \hline \bar{1} & 2 & 1 & \pi+a+s \end{array}$$

Correct set of phases:

$a = \pi$
$b = 0$
$p = +\pi/2$ (enantiomorph
$s = \pi$

Table 27. List of |E| for reserpine.

G	G	G	E	PHASE	U	G	G	E	PHASE	G	U	G	E	PHASE	U	U	G	E	PHASE
-12	0	4	2.8980		1	0	2	3.1218		-12	1	8	4.4655		-11	9	6	2.8527	
-12	0	10	2.8864		-5	2	4	2.5113		-16	5	6	2.9203		-9	3	10	2.7584	
-8	0	10	2.6004		7	6	2	2.4927		2	1	8	2.5175		-5	7	4	2.5540	
-14	4	8	2.5423		9	0	6	2.4188		-8	3	10	2.4807		-13	1	2	2.4260	
-10	2	10	2.4283		-9	6	4	2.2766		0	1	2	2.4438		-3	7	2	2.1686	
0	2	0	2.3189		-1	2	2	2.2452		-6	7	2	2.3845		-7	3	10	2.0775	
-10	0	10	2.2679		-11	2	2	2.2215		-8	5	6	2.3329		-7	1	10	2.0536	
8	4	4	2.2321		1	2	0	2.1761		-14	1	8	2.3194		-3	3	12	1.9601	
-6	6	6	2.2118		-11	0	10	2.1585		4	1	2	2.2056		-17	3	6	1.9559	
-10	0	16	2.1855		3	2	8	2.0724		2	1	2	2.0521		-9	5	6	1.9075	
-8	8	4	2.1510		-3	0	4	2.0247		-4	7	2	1.9599		-5	9	4	1.8772	
-12	0	2	2.1372		-9	2	12	1.9713		-14	3	8	1.9540		-9	1	12	1.8624	
-18	0	8	2.1211		-13	0	6	1.9451		-10	1	12	1.9414		-3	1	6	1.8499	
4	0	8	2.0747		9	0	2	1.9192		-4	1	8	1.9262		3	1	4	1.8318	
-4	0	2	2.0503		-13	4	2	1.8662		-4	5	12	1.8797		-5	7	2	1.7740	
-12	4	8	2.0241		-1	0	6	1.8365		-6	1	10	1.8632		7	5	4	1.7558	
2	0	2	2.0023		-15	4	8	1.7810		-12	1	4	1.8486		-17	1	12	1.7340	
-4	2	6	1.9943		9	2	4	1.7667		8	5	4	1.7280		-15	3	12	1.7335	
-10	6	8	1.9585		-9	0	0	1.7423		-2	3	12	1.7262		-9	1	16	1.7008	
-10	4	8	1.9412		-11	0	14	1.7401		-6	3	4	1.7050		-9	1	10	1.6987	
-12	4	2	1.8777		-11	0	4	1.7195		-4	5	8	1.7043		-3	3	6	1.6832	
-8	2	10	1.8765		-17	2	8	1.7087		8	1	10	1.6862		-13	1	6	1.6712	
-6	6	8	1.8481		1	0	8	1.6904		-14	5	8	1.6791		-17	1	8	1.6471	
0	0	10	1.8226		-3	4	12	1.6834		6	5	2	1.6765		3	1	8	1.6470	
6	0	2	1.8163		5	2	2	1.6770		-18	1	6	1.6713		-3	5	2	1.5976	
8	6	2	1.8086		-7	4	10	1.6757		-10	3	16	1.6630		-13	3	2	1.5916	
-8	6	6	1.7897		-7	8	4	1.6703		-10	9	6	1.6623		9	3	4	1.5788	
-4	6	8	1.7673		7	8	2	1.6611		-4	7	6	1.6568		1	1	4	1.5706	
-4	4	8	1.7296		-11	4	2	1.6304		-8	5	8	1.6512		-3	1	12	1.5549	
0	4	2	1.6848		1	6	0	1.5947		-4	1	6	1.6234		-11	1	8	1.5498	
-8	4	10	1.6807		-11	4	8	1.5562		-2	5	2	1.6200		5	5	2	1.5203	
-18	2	8	1.6787		-1	6	10	1.5468		-12	3	8	1.6136		7	7	2	1.5187	
-10	0	12	1.6563		-11	6	6	1.5327		-12	1	16	1.6049		1	1	10	1.4914	
8	8	0	1.6467		-13	0	2	1.5116		-8	1	14	1.6002		-1	3	6	1.4801	
2	8	4	1.5981		-5	10	6	1.4993		-4	9	8	1.5794		5	1	2	1.4764	
2	2	8	1.5863		-5	6	2	1.4889		0	7	10	1.5794		5	7	2	1.4685	
8	0	4	1.5838		9	4	0	1.4749		-10	3	10	1.5770		-1	9	6	1.4591	
-14	0	6	1.5731		-9	4	6	1.4736		0	3	12	1.5694		3	5	8	1.4523	
-10	6	6	1.5692		-7	8	6	1.4689		10	7	4	1.5581		-9	5	10	1.4198	
-6	2	4	1.5138		3	0	6	1.4686		-8	1	10	1.5470		15	1	0	1.4033	
6	2	2	1.4596		5	0	8	1.4555		4	7	2	1.5292		-7	3	4	1.4020	
-8	2	4	1.4593		7	8	6	1.4508		-14	3	4	1.4995		-13	1	8	1.3959	
-12	8	4	1.4331		-1	0	8	1.4344		-4	5	10	1.4983		-13	1	4	1.3918	
-6	2	10	1.4329		-5	6	6	1.4065		14	1	0	1.4963		-3	5	12	1.3904	
-12	0	12	1.4313		5	0	6	1.4060		8	1	4	1.4886		-11	1	10	1.3716	
4	0	4	1.4087		1	4	4	1.4056		16	1	0	1.4762		7	7	0	1.3645	
2	2	4	1.4081		-13	2	2	1.3967		-18	1	8	1.4762		-9	5	6	1.3598	
10	6	4	1.4066		-13	2	10	1.3691		-8	1	12	1.4690		-1	7	2	1.3508	
6	2	6	1.3940		-5	6	8	1.3682		2	5	0	1.4672		-1	1	2	1.3438	
4	0	0	1.3842		-15	2	14	1.3638		-12	3	2	1.4520		15	3	0	1.3326	
0	6	6	1.3764		-13	2	14	1.3534		-6	9	4	1.4438		-5	7	10	1.3272	
2	10	4	1.3559		7	4	6	1.3441		-4	9	4	1.4246		-3	7	6	1.3159	
6	0	6	1.3543		-1	8	2	1.3426		8	3	2	1.4120		7	5	6	1.3149	
-16	2	10	1.3518		7	2	6	1.3365		6	7	0	1.3931		-15	3	8	1.3136	
-10	2	12	1.3313		-5	4	8	1.3335		-4	7	4	1.3929		-9	3	2	1.3114	
0	2	6	1.3308		-13	4	10	1.3283		-14	1	12	1.3848		-7	5	10	1.3096	
12	0	0	1.3219		-5	6	10	1.3219		-4	3	12	1.3772		3	5	0	1.3067	
-18	0	6	1.3171		-3	8	10	1.3089		8	3	4	1.3750		-15	1	6	1.2914	
-2	6	10	1.3170		-3	6	6	1.3077		-10	3	8	1.3708		-11	1	12	1.2899	
-6	2	8	1.3002		-15	0	4	1.2940		-4	7	8	1.3583		-5	1	6	1.2866	
-14	6	8	1.2963		13	2	2	1.2822		-10	1	10	1.3527		-13	1	10	1.2782	
-12	0	8	1.2887		-1	6	4	1.2800		6	5	6	1.3214		-11	3	10	1.2728	

Table 27. (continued)

G	G	U	E	PHASE	U	G	U	E	PHASE	G	U	U	E	PHASE	U	U	U	E	PHASE
-12	0	7	3.2102		-11	0	7	3.5244		**$\overline{8}$**	**3**	**7**	**3.62**		-5	7	3	2.9161	
-14	4	13	3.0107		1	0	3	2.9449		**$\overline{10}$**	**1**	**11**	**3.02**		3	1	9	2.7784	
-12	0	9	2.9751		-13	0	5	2.8956		**$\overline{14}$**	**3**	**9**	**2.58**		-11	1	1	2.6883	
16	0	1	2.5758		-11	0	11	2.6909		**$\overline{10}$**	**1**	**9**	**2.45**		7	5	1	2.6248	
2	4	9	2.5754		-9	2	11	2.5662		**2**	**1**	**7**	**2.41**		-9	7	1	2.5947	
-4	0	11	2.5381		1	0	5	2.4408		**$\overline{4}$**	**7**	**3**	**2.28**		-13	1	5	2.5289	
-12	0	3	2.5238		9	4	5	2.3288		**$\overline{12}$**	**1**	**1**	**2.18**		-5	7	7	2.4553	
-10	4	11	2.4070		-13	4	13	2.3126		**$\overline{6}$**	**7**	**5**	**2.06**		-13	1	9	2.4223	
-4	6	7	2.3785		-11	0	5	2.2729		-10	7	1	1.9943		-13	1	3	2.3358	
6	6	1	2.3649		1	4	9	2.1720		-14	5	9	1.9886		-11	1	9	2.1108	
-10	0	9	2.3619		-5	6	9	2.1555		-2	5	1	1.9554		-5	9	3	2.0915	
-6	6	3	2.3518		-1	2	1	2.1093		-18	1	5	1.9414		-1	1	11	2.0643	
-14	4	9	2.2280		-9	0	1	2.0849		-12	1	9	1.9399		-15	3	9	1.9965	
-10	0	7	2.2162		-13	0	9	2.0769		-18	1	9	1.9348		-1	5	1	1.9887	
-6	2	1	2.1461		15	0	1	2.0760		-4	9	3	1.8889		-3	7	3	1.9509	
-12	0	5	2.1395		-7	6	1	2.0500		0	1	1	1.8428		-13	1	7	1.9218	
-2	4	1	2.0996		3	2	9	2.0042		-12	1	1	1.8354		-15	3	7	1.8871	
0	0	3	2.0673		-13	4	7	1.9576		0	3	11	1.8225		9	1	5	1.8688	
-6	2	3	2.0494		-15	0	5	1.9435		-16	3	5	1.7967		-5	1	3	1.7609	
-10	2	13	2.0017		-3	8	11	1.9095		-10	1	13	1.7946		-9	3	3	1.7264	
6	6	3	1.9499		-5	6	7	1.9080		-12	3	3	1.7791		-3	3	13	1.7257	
-12	8	9	1.9219		-11	4	7	1.8816		-16	5	5	1.7476		1	1	1	1.6780	
-2	6	7	1.8865		9	0	3	1.8470		-8	7	5	1.7287		-3	1	7	1.6531	
4	0	9	1.8630		-13	0	7	1.8284		-10	3	13	1.6029		1	1	5	1.6449	
-2	2	1	1.8049		15	2	1	1.7339		8	5	3	1.5819		-11	1	7	1.6440	
-18	0	7	1.7764		-7	8	5	1.7293		-14	1	3	1.5766		1	1	7	1.6438	
-12	4	9	1.7445		1	6	9	1.7164		4	3	7	1.5729		3	3	7	1.6417	
-8	0	3	1.7350		-9	0	17	1.7122		-8	3	1	1.5405		-3	5	3	1.6238	
8	6	1	1.7321		1	2	9	1.6930		-12	1	5	1.5216		-7	7	5	1.6181	
-14	2	9	1.7308		-1	8	5	1.6756		-2	3	13	1.5214		-15	1	9	1.6122	
0	8	5	1.7307		9	2	5	1.6723		-4	5	7	1.5197		-3	1	3	1.5878	
-10	4	9	1.7302		1	2	1	1.6656		-10	1	1	1.5000		1	1	3	1.5751	
-10	2	9	1.6863		7	6	5	1.6211		8	3	5	1.4997		7	7	5	1.5611	
-12	0	11	1.6819		-9	0	9	1.6156		-8	9	5	1.4960		-7	7	7	1.5445	
-2	0	13	1.6707		3	6	7	1.6092		-10	3	11	1.4609		-3	3	7	1.5378	
-8	4	9	1.6596		3	2	11	1.6059		-4	3	11	1.4595		-13	3	9	1.5308	
-6	6	5	1.6365		-13	2	1	1.5983		-10	9	7	1.4546		9	5	1	1.5012	
2	0	7	1.6175		-11	2	7	1.5961		-10	9	1	1.4188		-7	3	11	1.4950	
-4	8	9	1.6149		5	6	7	1.5936		-2	5	7	1.4146		-5	7	3	1.4901	
-10	2	15	1.6055		-7	2	5	1.5782		-10	1	7	1.4107		-3	5	7	1.4873	
4	0	1	1.5863		3	4	9	1.5332		-4	5	9	1.3984		-7	5	9	1.4783	
-8	6	5	1.5777		-11	8	7	1.5313		-8	5	1	1.3885		3	1	3	1.4611	
2	2	5	1.5658		5	0	1	1.5297		14	1	1	1.3869		-11	3	1	1.4468	
-6	4	3	1.5554		-17	2	11	1.5252		-10	3	7	1.3853		-7	1	9	1.4360	
-4	4	7	1.5530		7	6	1	1.5018		-18	1	7	1.3556		-15	1	13	1.4360	
8	2	5	1.5465		13	0	3	1.5004		-4	1	7	1.3488		-3	5	13	1.4263	
0	4	9	1.5440		-3	6	11	1.4920		-4	5	3	1.3463		7	7	1	1.4225	
-8	0	9	1.4616		-15	2	9	1.4844		-14	3	1	1.3371		-15	3	11	1.4210	
10	0	9	1.4536		7	2	1	1.4787		-4	7	7	1.3244		-15	3	1	1.4190	
-14	6	7	1.4518		-3	6	7	1.4571		0	7	5	1.2909		-15	3	5	1.4044	
0	0	7	1.3985		-3	4	11	1.4527		2	3	7	1.2800		-13	1	1	1.3842	
-8	2	9	1.3718		-9	0	13	1.4520		4	1	9	1.2716		1	9	3	1.3806	
-14	0	7	1.3700		7	8	1	1.4499		-12	5	5	1.2708		-7	7	3	1.3774	
-18	2	7	1.3682		5	6	9	1.4485		-16	5	7	1.2673		-11	1	5	1.3578	
-4	0	15	1.3643		-7	8	9	1.4464		-6	3	3	1.2671		-5	7	9	1.3571	
-18	2	5	1.3600		-7	0	3	1.4463		0	9	5	1.2608		-5	5	5	1.3395	
8	8	5	1.3582		-11	0	3	1.4338		-4	7	5	1.2598		-3	3	11	1.3209	
-4	8	7	1.3519		-13	2	3	1.4337		-12	1	11	1.2595		-17	1	9	1.3124	
-12	2	3	1.3380		-13	6	7	1.4028		-14	3	7	1.2569		3	5	7	1.3083	
12	2	3	1.3374		1	8	3	1.4026		-12	1	7	1.2557		7	1	1	1.3053	
6	8	5	1.3288		-9	0	11	1.3938		6	9	5	1.2532		-11	1	3	1.2945	
-10	2	1	1.3197		-13	0	3	1.3915		10	1	1	1.2262		5	5	5	1.2895	

$-\pi$ to $+\pi$. Symbol s appeared to have a value of 0 or π from several indications that were contradictory. There were no indications for symbol p; therefore it was arbitrarily assigned the value $+\pi/2$. This assignment arbitrarily chose one of the enantiomorphs and introduced phase values other than 0 or π. From experience with a number of structures in space group $P2_1$ (b axis unique), a symbol assigned to an hkl reflection where k is considerably different than zero, i.e. $k = 4 \rightarrow 8$, usually has a value near $\pm\pi/2$ and can be used for enantiomorph specification. Refinement of the phases, and determination of phases for additional reflections with the use of the tangent formula, Eq.5, was performed for the two possibilities with $s = 0$ and $s = \pi$. E-maps for both possibilities showed that the latter choice was correct.

An E-map computed with phases determined directly from the structure factor magnitudes does not always reveal the complete structure in non-centrosymmetric space groups. The phases in the acetric case take on values between 0 and 2π and are not as accurately determined as in the centrosymmetric case where the phases must be either 0 or π. In the determination of reserpine, Fig. 6, the largest peaks in the initial E-map corresponded to the 16 atoms depicted by the solid circles. To derive the remainder of the structure, the tangent formula, Eq. 5 , was used with phases based on the known partial structure (Karle, 1968). Phases were accepted for those reflections with $|E| > 1.5$ and $|F_{calc}| > k\,|F_{obs}|$ where k is approximately equal to the fraction of known atoms. These phases were used as input into the tangent formula and refined by reiterating the calculation for two cycles. Subsequently, the initial phases were held constant while phases for additional reflections

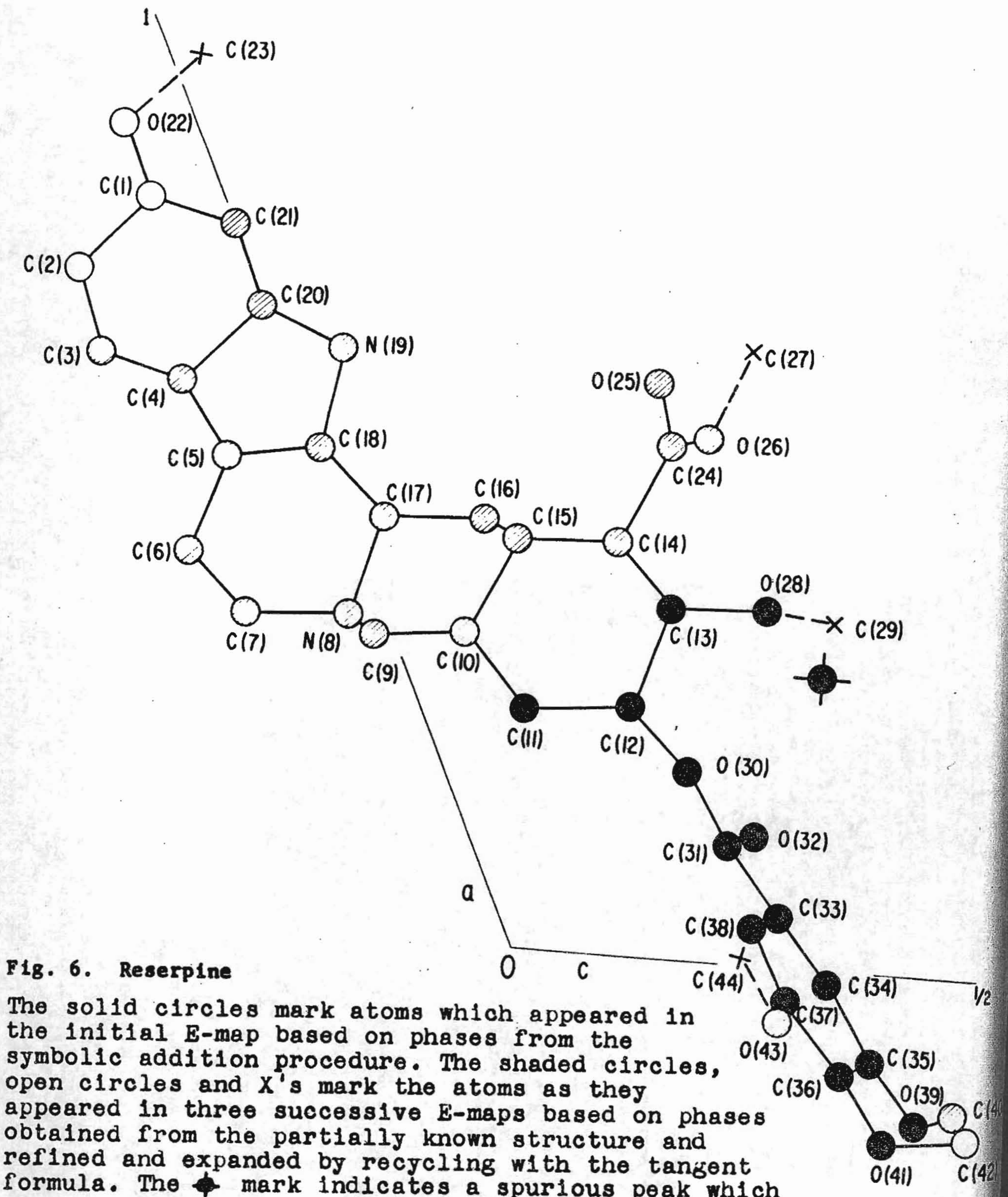


Fig. 6. Reserpine

The solid circles mark atoms which appeared in the initial E-map based on phases from the symbolic addition procedure. The shaded circles, open circles and X's mark the atoms as they appeared in three successive E-maps based on phases obtained from the partially known structure and refined and expanded by recycling with the tangent formula. The ✦ mark indicates a spurious peak which disappeared in the later E-maps.

were determined. New reflections were added in four groups in order of decreasing $|E|$ values. The first addition had about the same number of reflections with unknown phases as the number of initially known phases. Subsequent additions each doubled the number of unknowns. One cycle of tangent formula was run for each group. Those phases with a sufficient number of contributors ($N > 3$) and a large enough $|E_{calc}|$ (greater than 0.5) were accepted and added to the known phases for use with the subsequent group having lower $|E|$ values. Phases were determined for reflections with $|E| > 1.0$ and a new E-map was computed which showed 34 atoms of the molecule. The remaining 10 atoms were found in two more rounds of partial structure calculations. When 34 atoms were known, a conventional difference map may have been as effective in locating the remaining atoms.

Many structures in $P2_1$ have been solved in a similar manner, for example, strophanthidin with 59 atoms in the asymmetric unit (Gilardi and Flippen, 1973).

Summary

A period of more than ten years elapsed between the publication of the inequalities (Karle and Hauptman, 1950), from which the phase relationships derive, and the advent of the symbolic addition procedure. Among the problems in applying the theory to practice were the dearth of definitive indications from the $\sum_1$, $\sum_3$ and $B_{3,0}$ formulas, as indicated by the probability measures, and the inaccuracies imposed on these formulas by regularities in the distributions of atoms in real crystals. The realization that phase determination for a crystal could be pursued with the $\sum_2$ relation by use of a small number of symbols representing key phases, with careful application of the appropriate probability measures, was the basis for the development of modern direct crystal structure analysis.

With the assignment of phases specifying the origin, and the enantiomorph and/or axis directions as required, it has been found in practice that no more than five symbols in all representing unknown phases are needed to implement the phase determination. These symbols are assigned as needed in the $\sum_2$ or sum of angles formulas, Eqs. 1,2 and 4, consistent with high probabilities or low variance, Eqs. 3 and 6. During the phase determination, relationships develop among the symbols, allowing some of them to be defined in terms of others. Usually some of the symbols, and, at times, all of the symbols can be assigned definite numerical values. For those symbols for which a specific numerical value could not thus be determined, there exists a multisolution condition. Symbols representing phases that can have only two values, such as 0 or π in centrosymmetric space groups or $\pm\pi/2$ in space groups such as $P2_12_12_1$, for example, yield 2^n possible sets of phases where n is the number of symbols. On the other hand, it has been found from experience, that four values such as $0, \pi$, $\pm\pi/2$ or $\pm\pi/4$, $\pm 3/4\pi$, are usually sufficient to represent the numerical possibilities of symbols assigned to reflections that can assume any value between $-\pi$ and $+\pi$. Therefore such symbols give rise to 4^n possible sets of phases.

Various criteria have been developed to assist in evaluating the multiple sets of phases as being the most probable, or at least among the more probable, to yield the correct E-map. Some of these criteria are:

1. Consistency: The correct set of phases will be among the most consistent sets but will not necessarily be the most consistent set, as has been illustrated by the structure of jamine in the example described for space group $P\bar{1}$.

2. Distribution of phases: In centric space groups, the phases should not be predominantly 0 (unless there is an atom at the origin) and in acentric space groups, the phases should not be all 0 and π. It should be borne in mind, that in centric space groups like $P\bar{1}$ and $R\bar{3}$, e.g., at least one symbol must be assigned a negative value in order to introduce negative signs. Similarly, in acentric space groups like $P2_1$ and Aba2, e.g. at least one symbol must be assigned a value other than 0 or π, preferably near $\pm\pi/2$, in order to specify the enantiomorph and/or axial direction and to introduce phases other than 0 and π.

3. The reliability factor R: After using the tangent formula, Eq.5, calculated $|E_{\underset{\sim}{h}}|$ values can be obtained for all $\underset{\sim}{h}$ by taking the square root of the sum of the squares of the numerator and denominator of the tangent formula. That is,

$$\left\{\left(\sum_{\kappa}|E_{\underset{\sim}{k}}\,E_{\underset{\sim}{h}-\underset{\sim}{k}}|\sin(\phi_{\underset{\sim}{k}}+\phi_{\underset{\sim}{h}-\underset{\sim}{k}})\right)^2 + \left(\sum_{\kappa}|E_{\underset{\sim}{k}}\,E_{\underset{\sim}{h}-\underset{\sim}{k}}|\cos(\phi_{\underset{\sim}{k}}+\phi_{\underset{\sim}{h}-\underset{\sim}{k}})\right)^2\right\}^{\frac{1}{2}} = K\,|E_{\underset{\sim}{h}}|^2_{calc} \qquad (13)$$

and the $|E_{\underset{\sim}{h}}|_{calc}$ values are normalized by

$$K = \frac{\sum |E_{\underset{\sim}{h}}|^2_{obs}}{\sum |E_{\underset{\sim}{h}}|^2_{calc}} \qquad (14)$$

The residual R = $$\frac{\sum \left| |E_{\underset{\sim}{h}}|_{calc} - |E_{h}|_{obs} \right|}{\sum |E_{\underset{\sim}{h}}|_{obs}} \qquad (15)$$

often has the minimum value for the correct set of phases.

4. Auxiliary formulas: Phase values for some reflections may be indicated by formulas such as $\sum_1$, $\sum_3$ and $B_{3.0}$, among others. These indications may be helpful in choosing the correct set of phases, or at least, in eliminating sets of phases with a low probability of being correct.

5. Packing considerations: At times, it is obvious from the size of the molecule and the shape of the cell that certain low order reflections must have particular phases. For example, in space group $P2_1$ (b axis unique), if the b axis is short, and either the 200 or 002 reflections has a large $|E|$ value, the phase must be π so that the molecules do not approach each other too closely around the 2-fold screw axis.

In the examples described in this paper, the initial phase determination was performed manually. Most of the ideas presented in the manual application of the phase determining procedure have been incorporated into computer programs. Some of these programs will be described in detail in the succeeding papers. Some of the computer programs retain the use of symbols. Other computer programs replace the unknown symbols by multiple values, usually four values for general phases; hence 4^n (where n is the number of reflections whose phases are represented by the equivalent of unknown symbols) sets of phases are developed. In the numerical procedures, schemes similar to ones described here are used to reduce the number of possibilities which need to be

Appendix A. Refinement of initial phases with tangent formula for 3,4-dihydroxy-L-proline[/] (Space group $P2_12_12_1$).

H	K	L	OBS R	CALC R	OBS E	CALC E	N
0	4	10	3,140	3,142	2,690	2.776	4,000
5	4	3	-1,570	-1,572	2,610	2.530	5,000
3	0	2	0,000	0,000	2,520	2.717	14,000
1	3	7	1,570	1,570	2,420	2.181	12,000
2	0	8	0,000	0,000	2,340	2.464	9,000
0	0	10	0,000	0,000	2,320	0.371	12,000
4	3	5	-1,570	-1,494	2,270	2.700	11,000
3	6	5	0,000	0,470	2,250	1.941	5,000
7	3	0	1,570	1,571	2,190	2.666	4,000
4	2	2	3,140	-3,141	2,180	2.125	12,000
3	3	1	-1,570	-1,484	2,160	1.748	15,000
0	5	3	1,570	1,571	2,120	2.497	10,000
6	1	3	-1,570	-1,712	2,060	2,317	7,000
9	1	5	-1,570	-1,992	2,030	1.250	5,000
1	1	8	0,000	0,518	2,030	1.582	6,000
2	1	1	-1,570	-1,486	2,010	2,216	13,000
6	3	0	3,140	3,142	2,010	1.795	8,000
4	5	5	1,570	1,373	1,990	1.580	7,000
5	0	2	3,140	3,142	1,970	2.723	9,000
1	3	5	1,570	-0,259	1,930	0.304	7,000
6	4	4	3,140	3,019	1,920	2.273	7,000
3	2	4	3,140	3,141	1,910	2.682	6,000
2	1	10	0,000	0,000	1,880	2.541	2,000*
3	4	8	0,000	-0,001	1,820	2.158	7,000
7	1	3	1,570	1,571	1,790	2.550	11,000
9	2	4	0,000	0,178	1,780	2.019	5,000
0	2	3	3,140	3,142	1,750	1.161	14,000
8	0	0	0,000	0,000	1,740	2.261	16,000
5	2	0	1,570	1,571	1,740	0.594	10,000
1	2	4	0,000	0,101	1,730	1.966	11,000
8	1	2	3,140	-3,139	1,730	0.973	3,000
1	0	6	3,140	3,142	1,720	2.750	9,000
4	5	3	1,570	1,654	1,720	1.747	7,000
4	0	6	0,000	0,000	1,710	1.199	8,000
4	3	0	3,140	0,000	1,710	1.490	11,000*
3	1	5	1,570	1,571	1,700	2.014	9,000
7	0	7	1,570	1,571	1,640	2.901	3,000
9	0	1	-1,570	-1,571	1,590	1.633	6,000
5	0	7	-1,570	-1,571	1,530	1.813	11,000

R-FACTORS FOR CALCULATED VALUES- E, 0.2524

* These reflections were rejected because $N<3$, $|E|_{calc} < 0.5$, or ϕ changed by more than 1.6 radians. They were added to the succeeding cycle with unknown phases.

[/] Karle (1970).

Note: For reflections that have special values for phases, such as 0 or π, the calculated phase values are reset

Appendix B. **Expansion of phase determination with tangent formula: First addition to initial phases.**

H	K	L	OBS R	CALC R	OBS E	CALC E	N
0	4	10	3,142	3,142	2,690	2.430	4,000
5	4	3	-1,550	-1,550	2,610	2.140	5,000
3	0	2	0,000	0,000	2,520	2.392	12,000
1	3	7	1,556	1,556	2,420	2.211	11,000
2	0	8	0,000	0,000	2,340	2.112	9,000
0	0	10	0,000	0,000	2,320	0.881	12,000
4	3	5	-1,518	-1,518	2,270	2.369	11,000
3	6	5	0,009	0,009	2,250	2.092	4,000
7	3	0	1,571	1,571	2,190	2.123	4,000
4	2	2	-3,115	-3,115	2,180	2.173	11,000
3	3	1	-1,357	-1,357	2,160	1.728	15,000
0	5	3	1,571	1,571	2,120	2.179	10,000
6	1	3	-1,839	-1,839	2,060	2.042	7,000
9	1	5	-2,242	-2,242	2,030	1.358	5,000
1	1	8	0,235	0,235	2,030	2.373	4,000
2	1	1	-1,379	-1,379	2,010	1.593	13,000
6	3	0	3,142	3,142	2,010	1.643	8,000
4	5	5	1,485	1,485	1,990	1.554	7,000
5	0	2	3,142	3,142	1,970	2.370	9,000
1	3	5	0,560	0,560	1,930	1.282	6,000
6	4	4	2,930	2,930	1,920	2.022	7,000
3	2	4	2,912	2,912	1,910	1.964	6,000
3	4	8	0,098	0,098	1,820	2.494	6,000
7	1	3	1,698	1,698	1,790	2.277	10,000
9	2	4	0,281	0,281	1,780	1.794	5,000
0	2	3	3,142	3,142	1,750	1.510	12,000
8	0	0	0,000	0,000	1,740	2.189	15,000
5	2	0	1,571	1,571	1,740	1.324	10,000
1	2	4	0,339	0,339	1,730	1.557	11,000
1	0	6	3,142	3,142	1,720	2.393	9,000
4	5	3	1,666	1,666	1,720	2.147	6,000
4	0	6	0,000	0,000	1,710	1.835	8,000
3	1	5	1,531	1,531	1,700	1.760	9,000
7	0	7	1,571	1,571	1,640	2.539	3,000
9	0	1	-1,571	-1,571	1,590	1.530	6,000
5	0	7	-1,571	-1,571	1,530	2.620	7,000
4	3	0	0,000	0,000	1,710	1.720	10,000
6	5	0	0,000	0,000	2,240	0.726	4,000
5	0	9	0,000	1,571	2,100	0.000	0,000 *
1	0	8	0,000	3,142	1,980	1.864	2,000 *
6	2	4	0,000	0,209	1,680	1.798	6,000
3	6	0	0,000	-1,571	1,670	0.857	9,000
3	3	7	0,000	-1,337	1,650	1.647	5,000
2	3	1	0,000	1,929	1,650	1.584	8,000
8	1	1	0,000	2,818	1,640	1.087	6,000
1	0	7	0,000	1,571	1,630	1.585	7,000
2	4	2	0,000	-3,082	1,610	2.003	8,000
2	2	2	0,000	-0,484	1,610	1.622	10,000
1	1	5	0,000	-2,252	1,600	1.510	9,000

```
 1   1   9   0,000  -1,747   1,600   2.105    1,000 *
 0   2   6   0,000   0,000   1,590   1.259    6,000
 3   2   5   0,000  -2,930   1,570   1.458    7,000
 5   6   3   0,000   0,759   1,560   1.335    2,000 *
 1   1   1   0,000   1,564   1,550   1.033    5,000
 5   4   8   0.000  -2,974   1,540   1.223    6.000
 5   5   3   0,000  -2,226   1,520   1,556    2,000 *
 7   4   1   0,000   0,000   1,520   0.000    0,000 *
 2   3   2   0,000   1,834   1,520   1,694    4,000
 2   5   4   0,000  -1,289   1,520   1,892    1,000 *
 7   3   7   0,000  -1,466   1,520   2,000    7,000
 2   3   7   0,000  -0,819   1,510   1,555    4,000
 3   1   9   0,000   1,743   1,510   2,170    4,000
 3   2   7   0,000  -1,527   1,510   1,981    1,000 *
 2   5   5   0,000   1,504   1,500   2,055    3,000
10   1   1   0,000  -1,488   1,500   1,730   10,000
 3   2   9   0,000  -0,834   1,500   1,403    3,000
 2   6   2   0,000   0,427   1,500   1,597    6,000
 4   2   6   0,000   0,381   1,490   1,398    4,000
 7   0   6   0,000   0,000   1,490   1,977    8,000
 4   6   8   0,000   0,080   1,490   2,675    2,000 *
 4   1   8   0,000  -1,356   1,490   1,936    4,000
 9   3   1   0,000   1,563   1,490   1,734    3,000
 9   2   3   0,000   0,000   1,490   0.000    0,000 *
 9   2   1   0,000   2,444   1,490   1,862    3,000
 4   4   4   0,000  -3,121   1,480   1,526    6,000
 2   1   4   0,000  -2,564   1,480   1,195    8,000
 7   4   2   0,000  -0,178   1,470   1,598    5,000
 1   1   3   0,000  -1,718   1,470   1,967   13,000
 5   1   6   0,000  -0,048   1,470   2,113    3,000
 2   1   3   0,000  -1,070   1,470   1,591   10,000
10   2   2   0,000  -0,461   1,460   1,709    7,000
 0   5   7   0,000   1,571   1,450   2,205    5,000
 5   3   1   0,000   1,085   1,440   0,840   10,000
 3   1   3   0,000   2,824   1,440   0,688    5,000
 1   4   6   0,000  -2,927   1,430   1,727    4,000
 2   4   9   0,000  -2,152   1,430   1,659    2,000 *
 0   3   1   0,000  -1,571   1,430   1,777   16,000
 1   2  10   0,000   0,024   1,430   1,955    4,000
 5   5   8   0,000   0,000   1,420   0.000    0,000 *
 3   5   5   0,000   1,611   1,420   2,293    4,000
 8   2   2   0,000   2,366   1,420   1.737    8,000
 5   5   7   0,000  -2,143   1,400   1,724    2,000 *
 3   6   3   0,000   1,422   1,400   1,961    1,000 *
 7   2   8   0,000   1,804   1,400   0,942    4,000
 8   5   3   0,000   1,427   1,400   1,890    5,000
 6   6   4   0,000  -0,274   1,380   1,354    5,000
 4   6   1   0,000   3,033   1,380   1.399    4,000
 7   6   1   0,000  -0,667   1,380   1.430    2,000 *
 8   1   2  -3,083  -3,031   1,730   1,923    3,000
 2   1  10  -0,339  -0,109   1,880   1,878    2,000 *

R-FACTORS FOR CALCULATED VALUES- E,  0,2793
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* These reflections were rejected because N < 3 or $|E|_{calc} < 0.5$. They were added to the next cycle with unknown phases.

References

COCHRAN, W. (1955). Acta Cryst. 8, 473

FLIPPEN, J.L. & KARLE I.L. (1971). J. Amer. Chem. Soc. 93, 2762

GILARDI R.D. & FLIPPEN, J.L. (1973). Acta Cryst. B29, 1842

HAUPTMAN H. & KARLE J. (1953). Solution of the Phase Problem. I. The Centrosymmetric Crystal. A.C.A. Monograph 3. Pittsburgh: Polycrystal Book Service

KARLE I.L. (1969) Acta Cryst. B25, 2119

KARLE I.L. (1970). Crystallographic Computing, pp. 19-25. Edited by F.R. Ahmed, S.R. Hall & C.P. Huber. Copenhagen, Munskgaard.

KARLE I.L. (1975). Acta Cryst. (to be published)

KARLE I.L. & FRATINI A.V. (1970). Acta Cryst. B26, 596

KARLE I.L., HAUPTMAN H., KARLE J. & WING A.B. (1958). Acta Cryst. 11, 257

KARLE I.L. & KARLE J. (1963). Acta Cryst. 16, 969

KARLE I.L. & KARLE J. (1964a). Acta Cryst. 17, 835

KARLE I.L. & KARLE J. (1964b). Acta Cryst. 17, 1356

KARLE I.L. & KARLE J. (1968). Acta Cryst. B24, 81

KARLE I.L. & KARLE J. (1970). Acta Cryst. B26, 1276

KARLE I.L., OTTENHEYM H.C.J. & WITKOP B. (1974). J. Amer. Chem. Soc. 96, 539

KARLE Jean M. & KARLE I.L. (1972). J. Amer. CHem. Soc. 94, 9182

KARLE J. (1968). Acta Cryst. B24, 182

KARLE J. (1969). Advanced Chemical Physics, Edited by I. Prigogine & S.A. Rice. Vol. XVI, p. 131. New York-London : Interscience.

KARLE J. (1970) Acta Cryst. B26, 1614

KARLE J. (1974). In International Tables for X-Ray Crystallography, Edited by J. Ibers & W. Hamilton. Vol. IV, p. 345. Birmingham : The Kynoch Press

KARLE J. & HAUPTMAN H. (1950). Acta Cryst. 3, 181

KARLE J. & HAUPTMAN H. (1956). Acta Cryst. 9, 635

KARLE J. & HAUPTMAN H. (1958). Acta Cryst. 11, 264

KARLE J. & KARLE I.L. (1966). Acta Cryst. 21, 849

WILSON A.J.C (1942). Nature 150, 151

WOOLFSON M.M. (1954). Acta Cryst. 7, 61

PROBLEMS IN PHASE DETERMINATION

1. Determine the phases in terms of symbols.
2. Evaluate symbols, if possible.
3. Determine the number of possible phase sets (and E-maps).

EXAMPLE I
(Centrosymmetric)

DIANIN'S CLATHRATE

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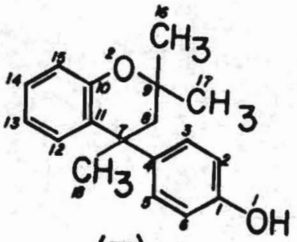
J. Am. Chem. Soc. 92, 3749(1970).

Naval Research Laboratory, Washington, D.C.



(I)

Space group	R $\bar{3}$
a	26.969 ± .003
c	10.990 ± .002
γ	120°

Atom	x	y	z
O(1)	0.0644	0.1202	0.9817
O(2)	0.0869	0.2611	0.3746
C(1)	0.0883	0.1614	0.8912
C(2)	0.1407	0.1753	0.8375
C(3)	0.1621	0.2157	0.7444
C(4)	0.1328	0.2436	0.7040
C(5)	0.0819	0.2296	0.7617
C(6)	0.0595	0.1887	0.8547
C(7)	0.1577	0.2868	0.5991
C(8)	0.1647	0.2593	0.4814
C(9)	0.1104	0.2239	0.4080
C(10)	0.0874	0.2982	0.4620
C(11)	0.1197	0.3124	0.5682
C(12)	0.1178	0.3530	0.6441
C(13)	0.0845	0.3768	0.6177
C(14)	0.0522	0.3613	0.5110
C(15)	0.0537	0.3221	0.4329
C(16)	0.0643	0.1717	0.4718
C(17)	0.1260	0.2085	0.2849
C(18)	0.2183	0.3355	0.6350

Table A. List of |E|

G	E	PHASE	U	G	G	E	PHASE	G	U	G	E	PHASE	U	U	G	E	PHASE
6	3.4930		7	10	6	2.8600		2	9	8	3,3610		3	7	8	2.9380	
-4	3.4080		21	4	2	2.7700		14	3	8	2,9700		1	11	8	2.8780	
0	3.2580		13	4	-6	2.5960		12	9	-6	2,5790		1	13	6	2.6650	
4	2.4280		15	12	0	2.5590		6	17	4	2,4820		1	3	-2	2.4450	
8	2.3700		7	18	-2	2.4790		2	21	-4	2,2210		23	5	0	2.3930	
-2	2.2940		3	12	6	2.4450		0	13	8	2,2020		17	1	-8	2.3070	
2	2.2730		11	10	4	2.3860		6	5	-2	2,1730		17	1	4	2.1210	
-12	2.2400		5	14	6	2.3070		4	13	6	2,1330		5	9	-10	2.1140	
-2	2.2260		3	8	10	2.2700		0	9	-12	2,1300		11	13	-2	2.0850	
-12	2.2130		13	0	-8	2.2100		4	17	-4	2,1270		9	7	-10	2.0840	
-2	2.1910		5	12	8	2.1700		0	19	-4	2,1220		5	17	-6	2.0720	
-2	2.1700		13	12	4	2.1310		8	3	-10	2,1120		1	17	-4	2.0510	
-8	2.1650		13	12	-8	2.1110		12	7	-10	2,0040		5	19	4	2.0080	
-4	2.1060		9	20	4	2.0380		2	9	2	1,9600		5	15	8	1.9970	
10	2.0910		7	4	0	2.0270		12	9	6	1,9580		3	3	0	1.9790	
2	2.0180		7	8	-4	2.0250		4	13	0	1,9560		19	3	4	1.9730	
10	2.0020		9	18	6	2.0050		2	3	2	1,8760		15	5	4	1.9720	
4	1.9940		3	2	10	1.9690		0	19	2	1,8240		17	11	0	1.9690	
-10	1.9890		13	10	0	1.9520		4	5	2	1,8210		9	13	-4	1.9610	
-10	1.9840		9	14	4	1.9400		8	11	0	1,8160		5	11	6	1.9430	
6	1.9620		1	4	12	1.8900		18	7	2	1,8040		23	7	-2	1.9350	
-2	1.9420		13	8	-4	1.8860		0	7	8	1,7760		25	1	0	1.8850	
-4	1.9020		7	4	-12	1.8770		6	5	-8	1,7700		7	21	4	1.8220	
2	1.9000		13	6	4	1.8660		2	1	10	1,7400		15	7	2	1.8190	
0	1.8260		9	2	-2	1.8540		8	1	4	1,7390		7	3	4	1.8090	
2	1.8250		19	0	-2	1.8260		12	11	-2	1,7150		23	1	4	1.7660	
6	1.7350		7	12	-2	1.7900		6	1	-10	1,7010		9	19	-4	1.7640	
6	1.7340		11	14	-6	1.7850		4	11	-10	1,6930		1	3	10	1.7640	
-6	1.7080		7	0	-8	1.7800		4	7	12	1,6770		3	5	-2	1.7560	
6	1.7030		1	18	-2	1.7360		8	11	6	1,6400		17	7	4	1.7490	
-2	1.6890		3	10	-4	1.7340		12	19	2	1,6310		3	17	-2	1.7400	
-2	1.6840		13	12	-2	1.7310		6	5	4	1,6220		9	9	0	1.7400	
2	1.6420		13	8	2	1.7250		20	3	8	1,6190		5	19	-2	1.6940	
2	1.6400		11	6	-10	1.7180		8	7	-2	1,6180		13	15	4	1.6930	
-2	1.6330		9	8	4	1.7110		20	5	-6	1,5920		11	17	6	1.6850	
-2	1.5990		9	4	-10	1.6940		4	15	4	1,5900		11	7	10	1.6710	
4	1.5890		5	16	-2	1.6700		10	13	-6	1,5860		15	9	-6	1.6680	
0	1.5660		1	10	0	1.6440		0	11	4	1,5800		1	23	-4	1.6370	
4	1.5610		1	22	-6	1.6380		16	13	0	1,5800		5	13	10	1.6360	
-10	1.5290		3	6	12	1.5990		18	9	-6	1,5750		1	13	-6	1.6350	
4	1.5270		17	14	0	1.5870		12	13	8	1,5690		19	11	2	1.6270	
-6	1.4980		17	10	4	1.5810		20	3	2	1,5650		9	1	-4	1.5590	
4	1.4680		11	0	-4	1.5790		20	1	-2	1,5240		5	1	-8	1.5490	
-2	1.4680		9	10	-10	1.5730		10	5	2	1,4960		19	9	4	1.5470	
-2	1.4630		3	20	-2	1.5650		12	15	0	1,4930		19	7	0	1.5330	
-6	1.4490		5	4	-8	1.5620		6	1	2	1,4750		17	9	-4	1.5260	
0	1.4410		5	2	0	1.5570		2	1	-2	1,4520		1	7	12	1.4720	
2	1.4150		5	4	10	1.5300		0	21	0	1,4480		3	5	10	1.4660	
-8	1.4110		9	14	-2	1.4980		0	11	10	1,4470		9	7	8	1.4590	
6	1.4000		5	18	-4	1.4820		6	5	10	1,4440		7	19	-6	1.4570	
8	1.3940		21	0	0	1.4720		4	3	-2	1,4340		11	3	8	1.4530	
4	1.3870		15	4	2	1.4500		20	11	0	1,4310		5	1	10	1.4460	
-4	1.3810		5	14	-6	1.4500		6	15	-6	1,4120		17	9	2	1.4450	
-2	1.3680		1	14	8	1.4480		14	17	0	1,4080		3	1	2	1.4210	
-4	1.3660		11	0	-10	1.4470		8	13	4	1,4050		25	3	-2	1.4100	
-4	1.3600		1	6	-2	1.4240		12	11	-8	1,3780		13	15	-2	1.4060	
-4	1.3420		11	6	2	1.4120		22	7	0	1,3770		13	5	2	1.3640	
2	1.3350		7	6	-2	1.4120		12	15	6	1,3750		15	9	0	1.3570	

Table A. (continued)

G	G	U	E	PHASE	U	G	L	F	PHASE	G	U	U	E	PHASE	U	U	U	E	PH
14	10	1	2.6500		17	10	1	2.8180		6	15	-3	3,7340		11	7	-5	3,2240	
18	8	1	2.4940		1	24	-5	2.5700		20	7	1	3,2120		11	11	-3	3,1800	
6	6	-3	2.4530		3	4	11	2.5450		14	7	-5	3,1580		3	11	7	2,9380	
10	14	-1	2.4490		13	12	7	2.4550		10	9	-5	3,1000		5	3	11	2,8790	
10	4	-3	2.4100		7	4	3	2.3750		10	5	-7	3,0350		3	7	11	2,5890	
14	8	9	2.2950		5	8	3	2.3370		12	19	-1	2,7020		17	5	3	2,5590	
4	16	-3	2.2790		7	18	7	2.2620		14	3	-7	2,6660		1	9	-5	2,2980	
22	8	-1	2.2680		5	10	7	2.2430		4	1	-9	2,5380		11	15	-7	2,2290	
12	14	7	2.2490		17	12	-1	2.1620		4	7	-3	2,4590		1	7	9	2,2210	
12	14	-5	2.1880		11	0	-7	2.1280		18	11	-5	2,3590		11	3	-1	2,2040	
4	6	-11	2.1320		1	10	9	2.1120		12	13	-1	2,3480		9	13	5	2,0040	
12	14	1	2.0810		23	6	-1	2.1090		6	21	-3	2,3230		13	9	1	1,9720	
2	12	11	2.0600		15	0	-9	2.0670		6	7	11	2,2680		9	9	9	1,9700	
6	8	-11	2.0320		15	6	9	2.0530		24	3	-3	2,2580		13	11	5	1,9510	
6	14	7	1.9700		1	12	1	2.0350		4	3	-5	2,2050		1	3	1	1,9220	
20	4	-5	1.9580		3	18	-3	1.9770		24	1	5	2,1810		9	7	5	1,8990	
4	2	-1	1.9540		15	4	5	1.9700		14	13	1	2,1750		1	21	-5	1,8770	
4	22	-3	1.9510		5	8	-3	1.9440		2	23	-3	2,1440		11	13	1	1,8740	
24	2	-5	1.9320		25	2	-1	1.9250		10	19	3	2,1400		1	7	-3	1,8390	
0	18	-3	1.9290		11	18	-1	1.8930		10	3	1	2,1310		19	9	1	1,8210	
4	6	-5	1.8150		11	4	1	1.8360		0	5	-5	2,0890		17	9	-1	1,8160	
2	24	-1	1.8010		3	8	1	1.8200		2	17	-3	2,0660		9	5	-11	1,7880	
12	0	-9	1.7660		7	14	-1	1.7740		0	15	9	2,0510		3	5	-11	1,7190	
4	2	5	1.7570		7	0	-5	1.7550		8	5	-3	2,0260		15	13	-1	1,6970	
0	12	9	1.7530		3	8	-11	1.7510		8	15	5	1,9870		19	11	-1	1,6530	
0	10	5	1.7240		15	10	-7	1.7420		0	11	7	1,9720		13	5	-7	1,6490	
10	0	-5	1.7220		9	16	-1	1.7250		8	15	-1	1,9530		11	5	9	1,6160	
4	12	7	1.7220		5	20	-3	1.6860		2	15	-1	1,9340		7	17	5	1,6150	
2	8	-9	1.6960		7	2	-7	1.6520		6	19	-7	1,9160		1	9	7	1,6120	
0	12	-3	1.6760		15	16	-1	1.6450		4	21	1	1,9030		7	5	11	1,5990	
20	4	1	1.6710		17	4	1	1.6450		10	1	3	1,8860		7	13	-3	1,5860	
8	8	9	1.6610		7	12	-5	1.6410		0	9	-3	1,8740		9	19	5	1,5850	
12	12	-3	1.5930		11	18	5	1.6330		12	3	-9	1,8710		17	1	-5	1,5700	
18	12	-3	1.5780		15	6	3	1.6150		2	23	3	1,8550		15	9	3	1,5630	
2	24	5	1.5760		1	12	7	1.5880		12	7	-1	1,8320		1	13	-9	1,5390	
14	14	3	1.5730		1	16	-3	1.5790		4	3	7	1,8290		5	3	-1	1,5190	
0	14	1	1.5680		1	6	-5	1.5680		4	5	-1	1,8030		7	21	-5	1,4800	
14	0	-1	1.5620		13	10	3	1.5170		6	7	5	1,7810		21	1	-7	1,4720	
24	4	-1	1.5580		5	6	11	1.5150		0	7	5	1,7640		3	3	9	1,4700	
14	4	-5	1.5490		1	22	3	1.5130		4	9	1	1,7600		17	9	-7	1,4560	
14	12	-7	1.5420		5	14	9	1.4970		8	11	-3	1,7420		13	3	1	1,4490	
2	2	-3	1.5370		3	2	1	1.4930		12	11	-5	1,7010		3	21	-3	1,4430	
12	18	3	1.5280		7	4	-3	1.4910		6	3	-3	1,6430		3	9	-3	1,4370	
10	6	-5	1.5150		3	6	-3	1.4830		2	3	-1	1,6420		15	3	-9	1,4360	
2	6	5	1.5010		9	14	-5	1.4800		14	7	1	1,6320		9	1	11	1,4080	
16	6	1	1.4890		1	20	-1	1.4780		0	11	-5	1,6260		7	21	1	1,3840	
12	10	5	1.4800		9	18	3	1.4640		2	7	1	1,6140		9	9	-9	1,3670	
16	12	1	1.4740		3	14	7	1.4330		2	17	9	1,6100		3	19	-1	1,3280	
6	12	-3	1.4730		7	22	-3	1.4320		4	17	-1	1,5730		7	5	-7	1,3240	
18	6	-3	1.4690		3	16	-7	1.3920		2	9	5	1,5710		11	13	7	1,3140	
16	6	-5	1.4630		3	4	-1	1.3750		4	9	7	1,5540		17	11	-3	1,3110	
4	18	-5	1.4630		21	6	-3	1.3220		6	9	9	1,5510		11	1	7	1,3100	
0	20	-5	1.4600		23	0	-7	1.3190		4	1	3	1,5290		1	19	-3	1,3070	
6	10	-1	1.4560		5	18	5	1.3170		12	11	7	1,5240		13	11	-7	1,2850	
4	8	11	1.4510		5	2	-3	1.3140		2	7	-5	1,5100		11	17	3	1,2840	
8	8	3	1.4340		5	22	-5	1.3080		20	7	-5	1,4950		15	3	9	1,2800	
0	8	-5	1.4230		5	16	1	1.2850		8	3	-7	1,4880		19	3	7	1,2750	
10	10	9	1.4100		19	2	5	1.2790		14	15	5	1,4800		5	7	7	1,2720	

Table B Relationships in space group $R\bar{3}$ (hexagonal).

$$F(h\,k\,l) = F(\bar{h}\,\bar{k}\,\bar{l}) = F(k\,i\,l) = F(i\,h\,l) \neq F(h\,k\,\bar{l})$$

$$F(h\,k\,\bar{l}) = F(k\,i\,\bar{l}) = F(i\,h\,\bar{l})$$

where $i = -(h + k)$

(0, 0, 0; 1/3, 2/3, 2/3; 2/3, 1/3, 1/3) +

$x, y, z;\ \bar{y}, x-y, z;\ y-x, \bar{x}, z;\ \bar{x}, \bar{y}, \bar{z};\ y, y-x, \bar{z};\ x-y, x, \bar{z}.$

Table C . Assignments used to implement $\sum_2$.

h k l	$\lvert E_{\vec{h}} \rvert$	Sign	
$6\ 15\ \bar{3}$ $15\ \overline{21}\ \bar{3}$ $\overline{21}\ 6\ \bar{3}$	3.73	+	origin specification; l must be odd.
$10\ 8\ \bar{4}$ $8\ \overline{18}\ \bar{4}$ $\overline{18}\ 10\ \bar{4}$	3.41	a	
$10\ 16\ 6$ $\overline{26}\ 10\ 6$ $16\ \overline{26}\ 6$	3.26	b	
$11\ 7\ \bar{5}$ $\overline{18}\ 11\ \bar{5}$ $7\ \overline{18}\ \bar{5}$	3.22	c	

Table D. Use of $\sum_2$ for phase determination.

(1)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ \bar{18} & 10 & \bar{4} \\ \hline \bar{12} & 25 & \bar{7} \end{array}$$

(eq to 13 12 7)

(2)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ 8 & \bar{18} & \bar{4} \\ \hline 14 & \bar{3} & \bar{7} \end{array}$$

(eq to 3 11 7)

(3)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ 16 & \bar{26} & 6 \\ \hline 22 & \bar{11} & 3 \end{array}$$

(eq to 11 11 $\bar{3}$)

(4)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ \bar{11} & \bar{7} & 5 \\ \hline 5 & 8 & 2 \end{array}$$

(5)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ 11 & \bar{22} & \bar{3} \\ \hline 17 & \bar{7} & \bar{6} \end{array}$$

(6)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ 11 & \bar{14} & 7 \\ \hline 17 & 1 & 4 \end{array}$$

(7)
$$\begin{array}{rrr} \bar{10} & \bar{8} & 4 \\ 10 & 16 & 6 \\ \hline 0 & 8 & 10 \end{array}$$

(8)
$$\begin{array}{rrr} \bar{10} & \bar{8} & 4 \\ 11 & 11 & \bar{3} \\ \hline 1 & 3 & 1 \end{array}$$

(9)
$$\begin{array}{rrr} 10 & 8 & \bar{4} \\ 4 & \bar{1} & \bar{1} \\ \hline 14 & 7 & \bar{5} \end{array}$$

(10)
$$\left\{ \begin{array}{rrr} \bar{10} & \bar{8} & 4 \\ 13 & 12 & 7 \\ \hline 3 & 4 & 11 \\ \\ \bar{8} & 18 & 4 \\ 11 & \bar{14} & 7 \\ \hline 3 & 4 & 11 \\ \\ 10 & \bar{17} & 6 \\ \bar{7} & 21 & 5 \\ \hline 3 & 4 & 11 \end{array} \right.$$

(11)
$$\begin{array}{rrr} 10 & 16 & 6 \\ 7 & \bar{18} & \bar{5} \\ \hline 17 & \bar{2} & 1 \end{array}$$

(12)
$$\left\{ \begin{array}{rrr} 10 & 16 & 6 \\ \bar{11} & \bar{11} & 3 \\ \hline \bar{1} & 5 & 9 \\ \\ \bar{7} & \bar{10} & \bar{6} \\ 11 & 11 & \bar{3} \\ \hline 4 & 1 & \bar{9} \end{array} \right.$$

(13)
$$\begin{array}{rrr} \bar{11} & \bar{7} & 5 \\ 11 & 11 & \bar{3} \\ \hline 0 & 4 & 2 \end{array}$$

(14)
$$\begin{array}{rrr} 14 & 7 & \bar{5} \\ \bar{11} & \bar{11} & 3 \\ \hline 3 & \bar{4} & \bar{2} \end{array}$$

(15)
$$\begin{array}{rrr} 14 & 7 & \bar{5} \\ 11 & \bar{14} & 7 \\ \hline 25 & \bar{7} & 2 \end{array}$$

(16)
$$\left\{ \begin{array}{rrr} 14 & 7 & \bar{5} \\ 10 & \bar{17} & 6 \\ \hline 24 & \bar{10} & 1 \\ \\ 6 & 15 & \bar{3} \\ 4 & \bar{1} & 2 \\ \hline 10 & 14 & \bar{1} \end{array} \right.$$

(17)
$$\begin{array}{rrr} 6 & 15 & \bar{3} \\ \bar{7} & 3 & 11 \\ \hline \bar{1} & 18 & 8 \end{array}$$

(18)
$$\begin{array}{rrr} \bar{4} & \bar{1} & 9 \\ 6 & 15 & \bar{3} \\ \hline 2 & 14 & 6 \end{array}$$

(19)
$$\begin{array}{rrr} 10 & 8 & \bar{4} \\ 14 & \bar{16} & 6 \\ \hline 24 & \bar{8} & 2 \end{array}$$

(20)
$$\begin{array}{rrr} 2 & 14 & 6 \\ 11 & \bar{22} & \bar{3} \\ \hline 13 & \bar{8} & 3 \end{array}$$

$$\begin{array}{rrr} 2 & 14 & 6 \\ 7 & \overline{18} & \overline{5} \\ \hline 9 & \overline{4} & 1 \end{array}$$

$$\begin{array}{rrr} 2 & 14 & 6 \\ \overline{1} & \overline{3} & 2 \\ \hline 1 & 11 & 8 \end{array}$$

$$\begin{array}{rrr} 10 & 8 & \overline{4} \\ 11 & \overline{12} & 8 \\ \hline 21 & \overline{4} & 4 \end{array}$$

$$\begin{array}{rrr} 10 & 8 & \overline{4} \\ 3 & \overline{4} & \overline{2} \\ \hline 13 & 4 & \overline{6} \end{array}$$

$$\begin{array}{rrr} 11 & 7 & \overline{5} \\ 3 & \overline{4} & \overline{2} \\ \hline 14 & 3 & \overline{7} \end{array}$$

$$\begin{array}{rrr} \overline{14} & \overline{3} & 7 \\ \overline{10} & 17 & \overline{6} \\ \hline \overline{24} & 14 & 1 \end{array}$$

$$\begin{array}{rrr} 6 & 15 & \overline{3} \\ \overline{13} & \overline{4} & 6 \\ \hline \overline{7} & 11 & 3 \end{array}$$

$$\begin{array}{rrr} 10 & 8 & \overline{4} \\ 17 & \overline{14} & 7 \\ \hline 27 & \overline{6} & 3 \end{array}$$

(29) $$\begin{array}{rrr} 10 & 16 & 6 \\ 7 & \overline{11} & \overline{3} \\ \hline 17 & 5 & 3 \end{array}$$

(30) $$\begin{array}{rrr} 6 & 15 & \overline{3} \\ 5 & \overline{22} & 3 \\ \hline 11 & \overline{7} & 0 \end{array}$$

(31) $$\begin{array}{rrr} 11 & 7 & \overline{5} \\ 14 & \overline{16} & 6 \\ \hline 25 & \overline{9} & 1 \end{array}$$

(32) $$\begin{array}{rrr} 2 & 14 & 6 \\ \overline{11} & 14 & \overline{7} \\ \hline \overline{9} & 28 & \overline{1} \end{array}$$

(33) $$\begin{array}{rrr} 2 & 14 & 6 \\ 5 & \overline{22} & 3 \\ \hline 7 & 8 & 9 \end{array}$$

(34) $$\left\{ \begin{array}{rrr} \overline{16} & 26 & \overline{6} \\ \overline{1} & \overline{3} & 2 \\ \hline \overline{17} & 23 & \overline{4} \\ \\ 10 & 16 & 6 \\ \overline{4} & 1 & \overline{2} \\ \hline 6 & 17 & 4 \end{array} \right.$$

(35) $$\left\{ \begin{array}{rrr} 11 & 11 & \overline{3} \\ \overline{7} & 3 & 11 \\ \hline 4 & 14 & 8 \\ \\ 11 & \overline{4} & 3 \\ \overline{7} & 18 & 5 \\ \hline 4 & 14 & 8 \end{array} \right.$$

(36) $$\begin{array}{rrr} 11 & 7 & \overline{5} \\ \overline{1} & \overline{3} & 2 \\ \hline 10 & 4 & \overline{3} \end{array}$$

(37) $$\begin{array}{rrr} 11 & 11 & \overline{3} \\ 4 & \overline{14} & \overline{3} \\ \hline 15 & \overline{3} & \overline{6} \end{array}$$

(38) $$\begin{array}{rrr} 7 & \overline{3} & \overline{11} \\ 3 & 12 & 6 \\ \hline 10 & 9 & \overline{5} \end{array}$$

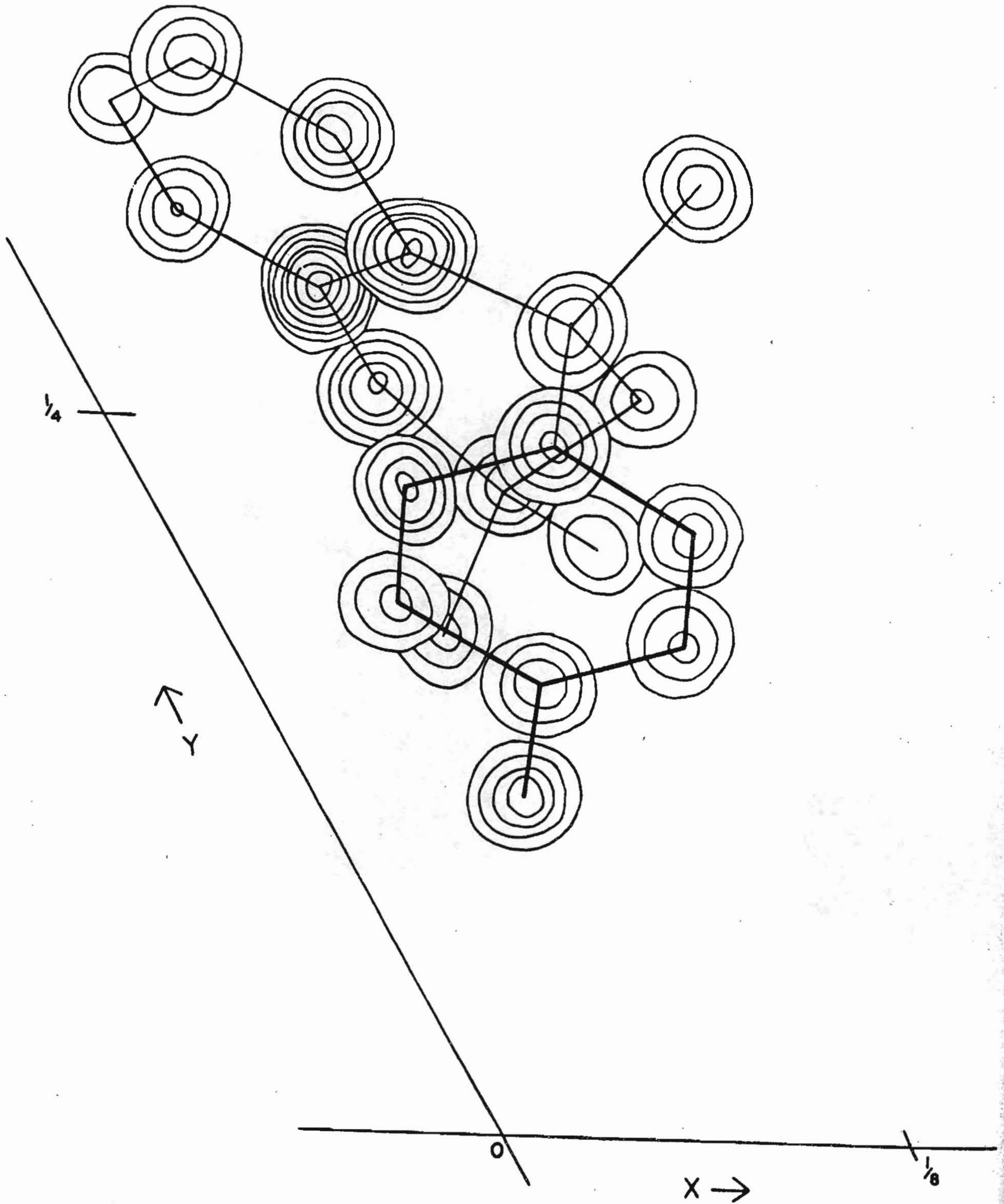
(39) $$\left\{ \begin{array}{rrr} \overline{9} & 19 & 5 \\ 14 & \overline{16} & 6 \\ \hline 5 & 3 & 11 \\ \\ \overline{1} & 18 & 5 \\ 12 & \overline{15} & 6 \\ \hline 5 & 3 & 11 \end{array} \right.$$

(40) $$\begin{array}{rrr} 10 & 8 & \overline{4} \\ \overline{19} & 10 & \overline{5} \\ \hline \overline{9} & 18 & \overline{9} \end{array}$$

(41) $$\begin{array}{rrr} 10 & 8 & \overline{4} \\ 17 & \overline{23} & 4 \\ \hline 27 & \overline{15} & 0 \end{array}$$

(42) $$\left\{ \begin{array}{rrr} \overline{5} & \overline{3} & \overline{11} \\ \overline{4} & 14 & 3 \\ \hline \overline{9} & 11 & \overline{8} \\ \\ \overline{27} & 15 & 0 \\ 18 & \overline{4} & \overline{8} \\ \hline \overline{9} & 11 & \overline{8} \\ \\ \overline{12} & 15 & \overline{6} \end{array} \right.$$

(43) $$\left\{ \begin{array}{rrr} \overline{4} & 14 & 3 \\ 18 & \overline{11} & 5 \\ \hline 14 & 3 & 8 \\ \\ 11 & 11 & \overline{3} \\ 3 & \overline{8} & 11 \\ \hline 14 & 3 & 8 \\ \\ 19 & \overline{10} & 5 \end{array} \right.$$



Dianin's clathrate.

Sections from a 3-dimensional E-map computed with 550 reflections with $|E| > 1.0$. The contours are evenly spaced on an arbitrary scale.

EXAMPLE II
(Noncentrosymmetric)
3,4-Dihydroxy Proline in Space Group $P2_12_12_1$

I.L. Karle, Acta Cryst. B26, 765 (1970)

Table I. Reflection data with $|E| > 1.5$ for $C_5H_9NO_4$

g	g	g	$\|E\|$
0	4	10	2,69
2	0	8	2.34
0	0	10	2.32
4	2	2	2.18
6	4	4	1.92
8	0	0	1.74
4	0	6	1.71
6	2	4	1.68
2	4	2	1.61
2	2	2	1.61
0	2	6	1.59
2	6	2	1.50

u	g	g	$\|E\|$
3	0	2	2.52
1	0	8	1.98
5	0	2	1.97
3	2	4	1.91
3	4	8	1.82
9	2	4	1.78
5	2	0	1.74
1	2	4	1.73
1	0	6	1.72
3	6	0	1.67
5	4	8	1.54

g	u	g	$\|E\|$
6	5	0	2.24
6	3	0	2.01
2	1	10	1.88
8	1	2	1.73
4	3	0	1.71
2	3	2	1.52
2	5	4	1.52

u	u	g	$\|E\|$
7	3	0	2.19
1	1	8	2.03

g	g	u	$\|E\|$
0	2	3	1.75

u	g	u	$\|E\|$
5	4	3	2.61
3	6	5	2.25
5	0	9	2.10
7	0	7	1.64
1	0	7	1.63
9	0	1	1.59
3	2	5	1.57
5	6	3	1.56
5	0	7	1.53
7	4	1	1.52
3	2	7	1.51
3	2	9	1.50

g	u	u	$\|E\|$
4	3	5	2.27
0	5	3	2.12
6	1	3	2.06
2	1	1	2.01
4	5	5	2.00
4	5	3	1.72
2	3	1	1.65
8	1	1	1.64
2	3	7	1.51
2	5	5	1.50
10	1	1	1.50

u	u	u	$\|E\|$
1	3	7	2.42
3	3	1	2.16
9	1	5	2.03
1	3	5	1,93
7	1	3	1.79
3	1	5	1.70
3	3	7	1.65
1	1	5	1.60
1	1	9	1.60
1	1	1	1.55
5	5	3	1.53
7	3	7	1.52
3	1	9	1.51

Table II

h	$\|E\|$	φ	
3 0 2	2,52	0	origin specification
7 3 0	2,19	$+\pi/2$	
0 5 3	2.12	$+\pi/2$	
7 0 7	1.64	$+\pi/2$	enantiomorph
2 0 8	2.34	a	(0 or π)
1 3 7	2.42	p	
5 4 3	2.61	q	

Table III. Phase relations in $P2_12_12_1$

	hkl	$\bar{h}kl$	$h\bar{k}l$	$hk\bar{l}$
ggg uuu	α	$-\alpha$	$-\alpha$	$-\alpha$
ggu uug	α	$-\alpha$	$\pi-\alpha$	$\pi-\alpha$
gug ugu	α	$\pi-\alpha$	$\pi-\alpha$	$-\alpha$
guu ugg	α	$\pi-\alpha$	$-\alpha$	$\pi-\alpha$

0gg	$0,\pi$	g0g	$0,\pi$	gg0	$0,\pi$
0uu	$\pm\pi/2$	u0g	$0,\pi$	ug0	$\pm\pi/2$
0ug	$\pm\pi/2$	g0u	$\pm\pi/2$	gu0	$0,\pi$
0gu	$0,\pi$	u0u	$\pm\pi/2$	uu0	$\pm\pi/2$

Table IV. The application of Eq. 3

$$(1)\quad \begin{array}{rrr} 3&0&-2\\ 1&3&7\\ \hline 4&3&5 \end{array}$$

$$(2)\quad \begin{array}{rrr} 2&0&8\\ 1&3&-7\\ \hline 3&3&1 \end{array}$$

$$(3)\quad \begin{array}{rrr} 7&3&0\\ -4&3&5\\ \hline 3&6&5 \end{array}$$

$$(4)\quad \begin{array}{rrr} 4&-3&5\\ 0&5&-3\\ \hline 4&2&2 \end{array}$$

$$(5)\quad \left\{\begin{array}{rrr} 4&3&5\\ -4&-3&5\\ \hline 0&0&10\\ \\ 3&6&5\\ -3&-6&5\\ \hline 0&0&10 \end{array}\right.$$

$$(6)\quad \begin{array}{rrr} 3&-3&1\\ 0&5&3\\ \hline 3&2&4 \end{array}$$

$$(7)\quad \begin{array}{rrr} 3&3&-1\\ 3&-2&4\\ \hline 6&1&3 \end{array}$$

$$(8)\quad \left\{\begin{array}{rrr} 0&5&-3\\ 1&-3&7\\ \hline 1&2&4\\ \\ 4&2&2\\ -3&0&2\\ \hline 1&2&4\\ \\ -2&0&8\\ 3&2&-4\\ \hline 1&2&4 \end{array}\right.$$

$$(9)\quad \begin{array}{rrr} 3&0&2\\ 6&1&3\\ \hline 9&1&5 \end{array}$$

$$(10)\quad \begin{array}{rrr} 6&-1&3\\ -4&2&-2\\ \hline 2&1&1 \end{array}$$

$$(11)\quad \begin{array}{rrr} 9&-1&-5\\ -3&6&5\\ \hline 6&5&0 \end{array}$$

$$(12)\quad \left\{\begin{array}{rrr} 9&1&5\\ -3&3&-1\\ \hline 6&4&4\\ \\ 2&1&-1\\ 4&3&5\\ \hline 6&4&4 \end{array}\right.$$

$$\left\{\begin{array}{rrr} 2&1&1\\ 2&1&1\\ \hline 4&2&2 \end{array}\right.$$

$$\left\{\begin{array}{rrr} 9&1&5\\ -9&-1&5\\ \hline 0&0&10 \end{array}\right.$$

$$(13)\quad \left\{\begin{array}{rrr} 9&-1&-5\\ -4&3&5\\ \hline 5&2&0\\ \\ 2&-1&-1\\ 3&3&1\\ \hline 5&2&0 \end{array}\right.$$

$$(14)\quad \begin{array}{rrr} 2&1&1\\ 1&3&7\\ \hline 3&4&8 \end{array}$$

$$(15)\quad \begin{array}{rrr} 3&4&8\\ -3&0&2\\ \hline 0&4&10 \end{array}$$

$$(16)\quad \begin{array}{rrr} 7&0&7\\ -1&3&-7\\ \hline 6&3&0 \end{array}$$

$$(17)\quad \left\{\begin{array}{rrr} 6&3&0\\ 3&-3&1\\ \hline 9&0&1\\ \\ 7&0&-7\\ 2&0&8\\ \hline 9&0&1 \end{array}\right.$$

$$(18)\quad \begin{array}{rrr} 5&4&3\\ -4&-3&5\\ \hline 1&1&8 \end{array}$$

$$(19)\quad \left\{\begin{array}{rrr} -2&1&1\\ 6&4&4\\ \hline 4&5&5\\ \\ -1&1&8\\ 5&4&-3\\ \hline 4&5&5 \end{array}\right.$$

$$(20)\quad \left\{\begin{array}{rrr} 5&-4&-3\\ 0&4&10\\ \hline 5&0&7\\ \\ 6&3&0\\ -1&-3&7\\ \hline 5&0&7 \end{array}\right.$$

$$(21)\quad \left\{\begin{array}{rrr} 1&3&7\\ 4&-3&-5\\ \hline 5&0&2\\ \\ 1&2&4\\ 4&-2&-2\\ \hline 5&0&2 \end{array}\right.$$

$$(22)\quad \left\{\begin{array}{rrr} -2&1&1\\ 3&2&4\\ \hline 1&3&5\\ \\ 2&1&1\\ -1&2&4\\ \hline 1&3&5 \end{array}\right.$$

$$(23)\quad \begin{array}{rrr} -1&1&8\\ 3&0&2\\ \hline 2&1&10 \end{array}$$

(24)
$$\left\{\begin{array}{rrr}
-2 & 0 & 8\\
9 & 1 & -5\\ \hline
7 & 1 & 3\\
\\
1 & -3 & 7\\
6 & 4 & -4\\ \hline
7 & 1 & 3\\
\\
2 & 1 & 1\\
5 & 0 & 2\\ \hline
7 & 1 & 3\\
\\
3 & -4 & 8\\
4 & 5 & -5\\ \hline
7 & 1 & 3\\
\\
3 & 3 & 1\\
4 & -2 & 2\\ \hline
7 & 1 & 3\\
\\
4 & -3 & -5\\
3 & 4 & 8\\ \hline
7 & 1 & 3
\end{array}\right.$$

(25)
$$\left\{\begin{array}{rrr}
2 & 1 & 1\\
7 & 1 & 3\\ \hline
9 & 2 & 4\\
\\
3 & 3 & 1\\
6 & -1 & 3\\ \hline
9 & 2 & 4\\
\\
4 & 2 & 2\\
5 & 0 & 2\\ \hline
9 & 2 & 4
\end{array}\right.$$

(26)
$$\left\{\begin{array}{rrr}
7 & 3 & 0\\
-7 & -1 & 3\\ \hline
0 & 2 & 3\\
\\
6 & 3 & 0\\
-6 & -1 & 3\\ \hline
0 & 2 & 3\\
\\
-3 & -4 & 8\\
3 & 6 & 5\\ \hline
0 & 2 & 3\\
\\
1 & -1 & 8\\
-1 & 3 & -5\\ \hline
0 & 2 & 3
\end{array}\right.$$

(27)
$$\left\{\begin{array}{rrr}
9 & 2 & 4\\
-1 & -2 & -4\\ \hline
8 & 0 & 0\\
\\
5 & 0 & 2\\
3 & 0 & -2\\ \hline
8 & 0 & 0\\
\\
4 & 5 & 5\\
4 & -5 & -5\\ \hline
8 & 0 & 0\\
\\
4 & 3 & 5\\
4 & -3 & -5\\ \hline
8 & 0 & 0\\
\\
4 & 2 & 2\\
4 & -2 & -2\\ \hline
8 & 0 & 0
\end{array}\right.$$

(28)
$$\begin{array}{rrr}
0 & -2 & -3\\
5 & 4 & 3\\ \hline
5 & 2 & 0
\end{array}$$

(29)
$$\begin{array}{rrr}
3 & -3 & -1\\
5 & 4 & 3\\ \hline
8 & 1 & 2
\end{array}$$

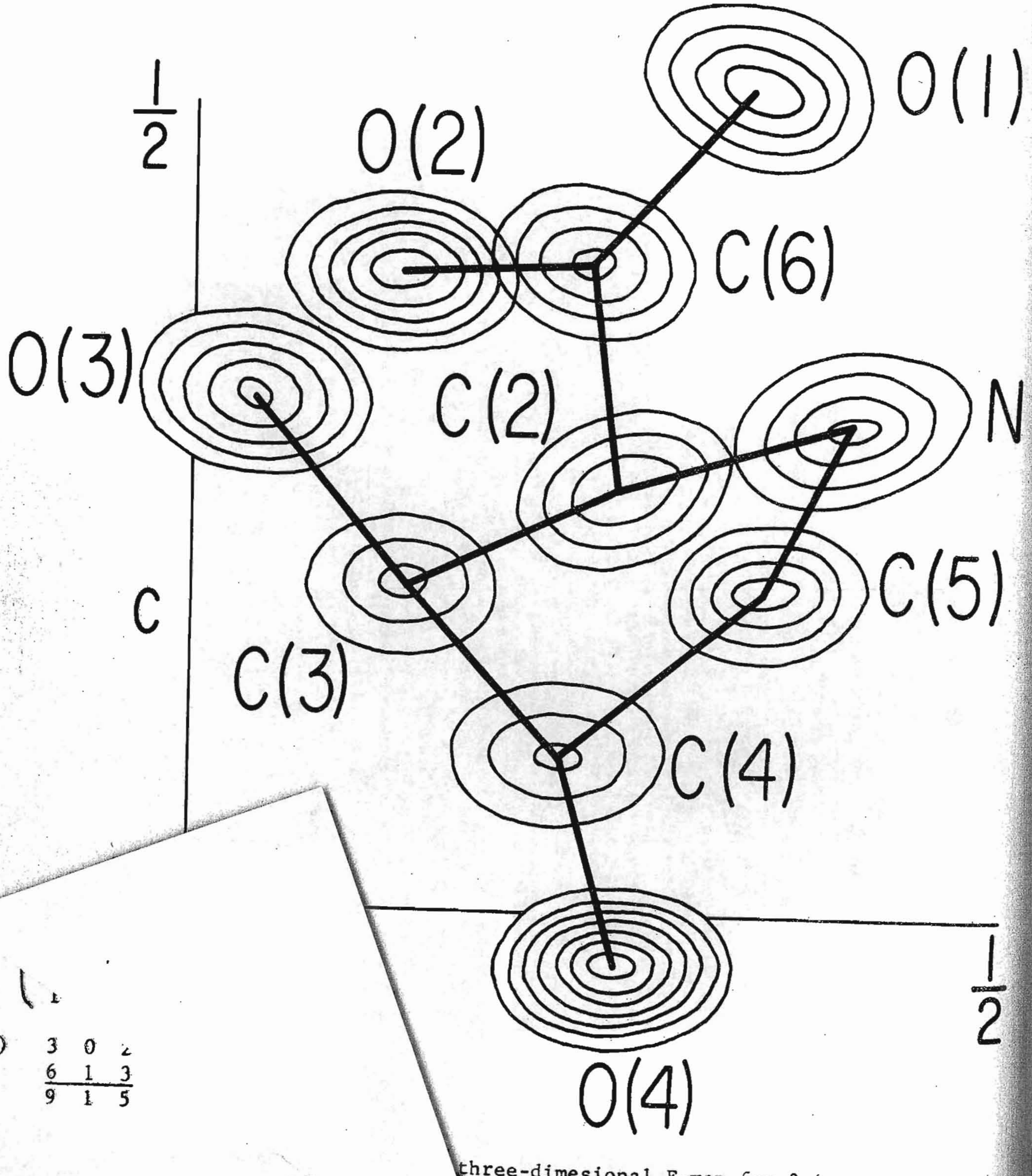
(30)
$$\left\{\begin{array}{rrr}
-6 & 1 & 3\\
7 & -1 & 3\\ \hline
1 & 0 & 6\\
\\
-3 & -3 & 1\\
4 & 3 & 5\\ \hline
1 & 0 & 6\\
\\
-3 & 2 & 4\\
4 & -2 & 2\\ \hline
1 & 0 & 6\\
\\
-2 & 0 & 8\\
3 & 0 & -2\\ \hline
1 & 0 & 6
\end{array}\right.$$

(31)
$$\left\{\begin{array}{rrr}
-2 & 1 & -1\\
6 & 4 & 4\\ \hline
4 & 5 & 3\\
\\
1 & -1 & 8\\
3 & 6 & -5\\ \hline
4 & 5 & 3\\
\\
1 & 2 & 4\\
3 & 3 & -1\\ \hline
4 & 5 & 3\\
\\
1 & 3 & 7\\
3 & 2 & -4
\end{array}\right.$$

(32)
$$\left\{\begin{array}{rrr}
-5 & 0 & 7\\
9 & 0 & -1\\ \hline
4 & 0 & 6\\
\\
0 & -5 & 3\\
4 & 5 & 3\\ \hline
4 & 0 & 6\\
\\
1 & -3 & 5\\
3 & 3 & 1\\ \hline
4 & 0 & 6\\
\\
1 & 3 & 7\\
3 & -3 & -1\\ \hline
4 & 0 & 6
\end{array}\right.$$

(33)
$$\left\{\begin{array}{rrr}
-4 & 2 & -2\\
8 & 1 & 2\\ \hline
4 & 3 & 0\\
\\
1 & -1 & -8\\
3 & 4 & 8\\ \hline
4 & 3 & 0
\end{array}\right.$$

(34)
$$\left\{\begin{array}{rrr}
-4 & 2 & 2\\
7 & -1 & 3\\ \hline
3 & 1 & 5\\
\\
-3 & -3 & 1\\
6 & 4 & 4\\ \hline
3 & 1 & 5\\
\\
-3 & 0 & 2\\
6 & 1 & 3\\ \hline
3 & 1 & 5\\
\\
-1 & 3 & -7\\
4 & -2 & -2\\ \hline
3 & 1 & 5\\
\\
0 & 5 & -3\\
3 & -4 & 8\\ \hline
3 & 1 & 5\\
\\
2 & 1 & -1\\
1 & 0 & 6\\ \hline
3 & 1 & 5\\
\\
2 & -1 & 1\\
1 & 2 & 4\\ \hline
3 & 1 & 5
\end{array}\right.$$



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(9) 3 0 2
6 1 3
9 1 5

three-dimesional E-map for 3,4-
ne computed with 214 reflections
e phases were determined directly
factor magnitudes.

EXAMPLE III
(Noncentrosymmetric)

CYCLOPHOSPHAMIDE
IN SPACE GROUP R3

I. L. Karle et al, J. Amer. Chem. Soc. <u>99</u>, 4803 (1977)

Table 1. Equivalent points:

x y z; y z x; z x y

Table 2. All $\varepsilon = 1$.

Table 3. Phase relationships:

$$\alpha(h\ k\ l) = \alpha(k\ l\ h) = \alpha(l\ h\ k)$$

$$\alpha(h\ k\ l) = -\alpha(\bar{h}\ \bar{k}\ \bar{l})$$

For origin assign <u>phase</u> to u u u.

For enantiomorph choose <u>sign</u> for phase near ± 90°.

Table 4. Assignments:

$\vec{h}$	$\lvert E_{\vec{h}} \rvert$	phase	
7 -1 1	2.71	0	origin
0 2 -2	2.75	a	
-7 6 3	2.46	b	
-4 0 9	2.01	c	

Reprint copy courtesy of Lodovico Riva (Dip. di Scienze della Terra e Geologico-Ambientali, Università di Bologna, Piazza di Porta S. Donato 1, I-40126, Bologna. E-mail: lodovico.riva@unibo.it):

Partial Structures and use of the Tangent Formula

(presented at the Erice School: Direct Methods for Solving Crystal Structures, 27 March to 9 April 1978)

by Isabella L. Karle

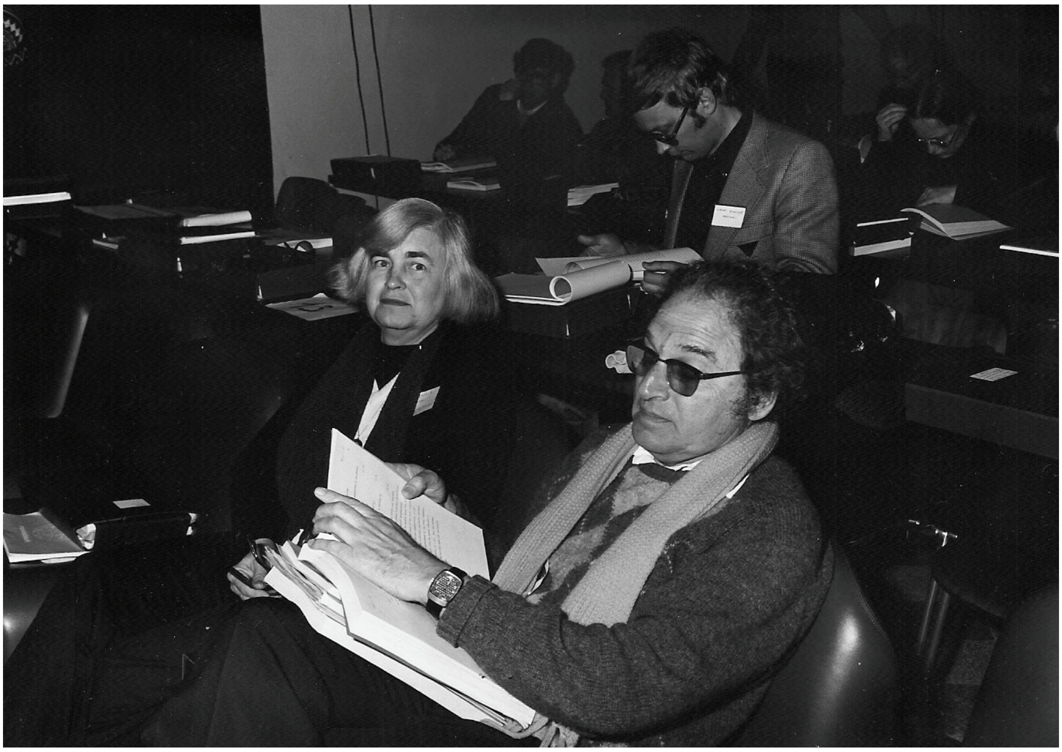

Fig. 1: *Isabella Karle and Herbert Hauptman at the Erice School: Direct Methods for Solving Crystal Structures, 27 March to 9 April 1978. Photo courtesy of Lodovico Riva.*

Place holder page. Teaching material starts on following page.

IX

PARTIAL STRUCTURES AND USE OF THE TANGENT FORMULA

I.L. Karle

Difference structures

Karle J., Acta Cryst B28, 820 (1972)

Tollin P, Acta Cryst. ~~B~~ 21, 613 (1966)

Rossmann, Acta Cryst ~~B~~17, 338 (1964)

Partial Structures and Use of the Tangent Formula

ISABELLA KARLE

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Phase determination procedures often result in partial structures, rather than complete structures. This is particularly the case for noncentrosymmetric crystals. The partial structures are properly oriented and usually correctly located with respect to a proper origin for the space group. At times the partial structure is properly oriented but not correctly placed. One of the ways that the correct location can be found is by use of translation functions. In view of the common occurrence of properly oriented structural fragments, a number of procedures have been proposed for readily developing the partial structure into a complete one. The tangent formula offers the basis for such a procedure (Karle, 1968). The partial structure can consist of a light atom fragment or it can involve a heavy atom which may have been located by use of the Patterson function. In the case of a fragment containing a heavy atom, special precautions are required to avoid obtaining phases which correspond only to the heavy atom position.

The tangent formula (Karle & Hauptman, 1956) is

$$\tan\varphi_{\mathbf{h}} \simeq \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})} \qquad (1)$$

where $\varphi_{\mathbf{h}}$ is the phase associated with the normalised structure factor $E_{\mathbf{h}}$. Use of Eq. (1) in developing a complete structure is implemented by the computation of structure factors from the partial structure and the selection of an appropriate subset for extension by Eq. (1). The extended set of phases so obtained is employed in the computation of a Fourier map of the structure. When the partial structure contains a heavy atom, this procedure is clearly distinguished from the usual heavy atom method by the interposition of a calculation with the tangent formula before proceeding with the Fourier series.

A relatively small structural fragment can generate phases which are sufficiently accurate for use with Eq. (1). However, only certain of the phases computed from the partial structure are suitable for use. These phases are selected by means of an acceptance criterion which is based on the amplitudes of the diffracted rays and the corresponding amplitudes computed from the structural fragment. A phase computed from a partial structure is accepted if $|F_{\mathbf{h}}|_{\text{calc}} \geqslant p|F_{\mathbf{h}}|_{\text{obs}}$ where p is the fraction of the total scattering power contained in the fragment and where $|F_{\mathbf{h}}|$ is associated with an $|E_{\mathbf{h}}|_{\text{obs}} \geqslant 1{\cdot}5$. The quantity $|F_{\mathbf{h}}|_{\text{calc}}$ is the value of the structure factor amplitude computed from the partial structure and $|F_{\mathbf{h}}|_{\text{obs}}$ is the experimentally observed amplitude. As a working rule, if $p < 0{\cdot}25$, it is replaced by 0·25 or, at least, a number somewhat larger than p. If $p > 0{\cdot}6$, it is replaced by 0·6.

Phases obtained by use of the acceptance criterion do not change very much throughout the structure development procedure as more and more atoms are added to the initial partial structure (Karle, 1968). It was found in studies starting with about 20% of the structure that the average change in the values of the phases was about 0·7 radians. It was also found that

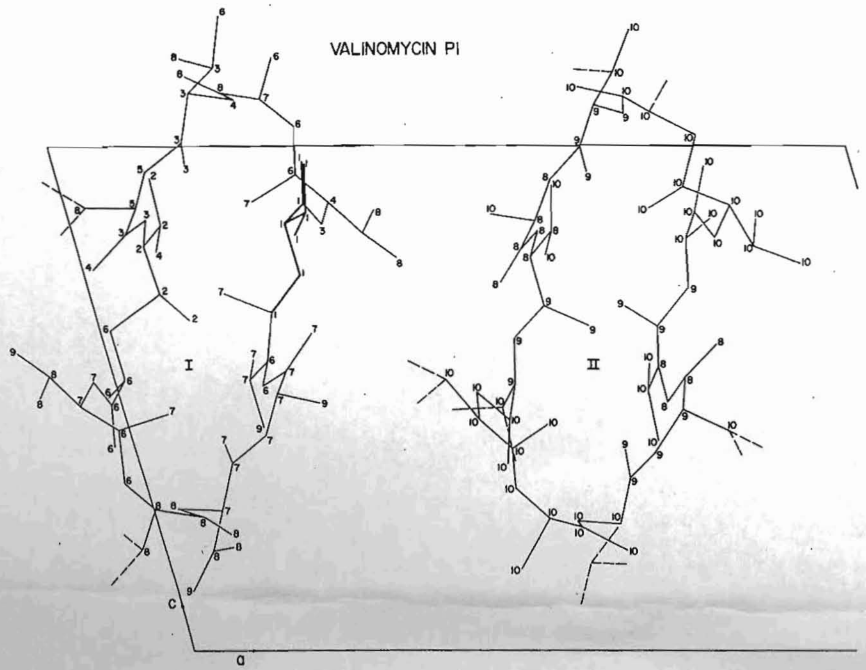

Fig. 1. The development of the structure of valinomycin from a structural fragment by means of the tangent formula. Atoms labeled 1, 2, ..., n *were used in the* n*th cycle to produce atoms labeled* n + 1.

atomic positions for the partial structure changed very little, generally much less than 0·02 of a cell edge, in the course of the development of the complete structure. Incorrect atomic locations will disappear in the successive cycles. The limited variation of the initial phases and atomic positions as the structure development progresses and the disappearance of incorrect atomic positions account for the usefulness of the tangent formula in the procedure.

A number of examples of the development of partial structures into complete ones by means of the tangent formula have been reviewed previously (Karle, 1968, 1970). Two examples will be discussed in some detail here. One is valinomycin (Karle, 1975a) which is composed of atoms having almost equal atomic numbers, except for the hydrogen atoms, and the second is a lithium antamanide complex for which the counter ion is bromine (Karle, 1974).

The form of valinomycin to be discussed crystallizes in space group P1 with two molecules (156 nonhydrogen atoms) in the unit cell. To illustrate the capabilities of the method, the recycling procedure was initiated with only 9 atomic positions, although about half the atoms were actually available initially from the phase determination by the symbolic addition procedure. These 9 atoms however form a chemically sensible cluster of atoms. It is worthwhile to start with a good chemical unit even though this may mean using fewer atoms than are indicated by a phase determination. Although 9 atoms represented about 0·06 of the structure, the value of p in the acceptance criterion was set at a value of 0·10. As the number of atoms increased, p was correspondingly increased to a maximum value of 0·6. With a start based on only 0·06 of the structure, it required 9 cycles and a final difference map to complete the development. The number of atoms employed at each step of the application of the tangent formula were 9, 13, 20, 25, 29, 36, 81 and 99. The last cycle produced 141 atoms. The remaining 15 atoms can be readily obtained from a difference map. This process is illustrated in Fig. 1 where the numbers

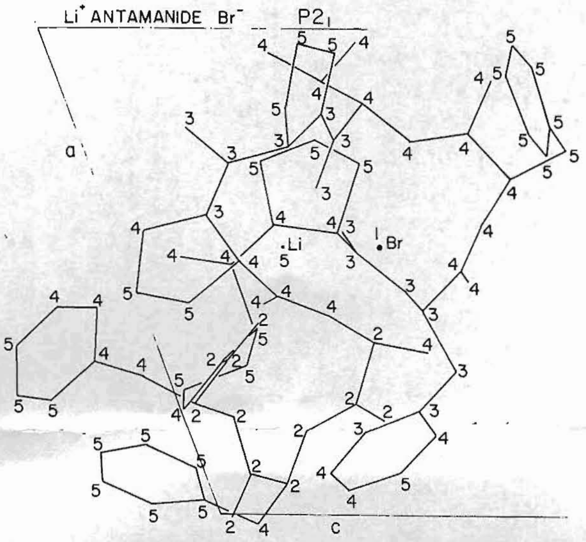

Fig. 2. The development of the structure of Li$^+$ *Antamanide*-Br$^-$ *from a structural fragment by means of the tangent formula. Atoms labeled* 1, 2, ..., n *were used in the* nth *cycle to produce atoms labeled* n + 1.

next to the atoms represent the cycle in which they were employed together with those obtained previously. Atoms labeled 1, 2, ..., n were used in the nth cycle to produce atoms labeled n + 1.

Phases were selected for $|E| \geqslant 1{\cdot}5$, were refined twice using the tangent formula and were then used as a basic set for proceeding with the determination of new ones. In our tangent formula program new phases are added in a stepwise fashion, each time roughly doubling the number of phases which were used as the known set in each cycle of calculation. Once new phases are determined, they are used in the succeeding cycles without further refinement. This process is continued with sets of unknown phases corresponding to $|E|$ values of continually decreasing magnitude until some lower limit is reached. In this calculation the lowest value considered was $|E| = 1{\cdot}3$. Ordinarily the lowest value would be about 1·0, but computing capacity was a factor to be considered for this large structure. The 9 cycles of partial structure refinement are more than have been otherwise required for any structure in our laboratory by more than a factor of 2. This number might well have been cut down had the lower limit on $|E|$ been set at 1·0 instead of 1·3.

The lithium ion complex of antamanide associated with a bromine ion crystallizes in space group $P2_1$ with 95 atoms in the asymmetric unit (Karle, 1974). This includes three molecules of acetonitrile. The development of the structure, which was initiated with the location of the bromine ion with the aid of the Patterson function, is shown in Fig. 2. The bromine ion represents 0·31 of the total scattering and this number was used for p in using the acceptance criterion for new phases based on this ion. The new phases were used as input to the tangent formula for the computation of additional phases in the stepwise fashion described above for the remaining $|E| > 1{\cdot}1$. In space group $P2_1$, phases based on one atom result in a map which contains atoms for both enantiomorphs. Fourteen atomic positions were chosen which seemed to form a good fragment of one polypeptide chain and were used along with the bromine ion for the next cycle of development. With a heavy atom present it is most important not to recycle with the tangent formula for the purpose of refinement of the initial phases selected by means of the acceptance criterion. These phases would, in fact, not refine but instead, with a heavy atom present, the contribution from the light atoms would be lost and the phases would converge to those which would be obtained from the heavy atom alone. Of the 14 light atom positions selected, two were incorrect in that their mirror images across a $y=\frac{1}{4}$ plane should have been selected instead. This was corrected in the next cycle when 14 more light atoms were obtained to make 28 in all. Pairs of atoms corresponding to both enantiomorphs still appeared in the resulting *E* map, but they were of unequal weight with the correct one usually the stronger. Choosing only the stronger of the pair and making sure that a good structural fragment ensued avoided errors of selection. At the next stage a total of 54 light atoms were located and finally in the last stage, the *E* map revealed all 95 atoms in the asymmetric unit including the three molecules of the solvent, acetonitrile.

Valinomycin and antamanide are examples of some of the more complicated partial structure developments which have been pursued. With the equal atom structures previously developed, the starting partial structures consisted of 25% or more of the atoms, and the total number of atoms was considerably fewer than for valinomycin. Often, the complete structure was obtained in one or two cycles of partial structure development. The same has been found to hold for the heavy atom structures. Some tests with equal atom structures (Karle, 1970) have shown that it is possible at times to start with a partial structure possessing only two atoms.

FLIPPEN-ANDERSON,J., GILARDI,R. and KONNERT,J.H. (1983). Program RESLSQ. NRL Memorandum Report 5042, Naval Research Laboratory,Washington,D.C. 20375, USA.

KARLE,I.L. (1974). J. Amer.Chem. Soc. <u>96</u>, 4000-4006.

KARLE,I.L. (1975a). J. Amer.Chem.Soc. <u>97</u>, 4397-4386.

KARLE,I.L., GILARDI, R.D., FRATINI,A.V. & KARLE, J. (1969). Acta Cryst. <u>B25</u>, 1469-1479.

KARLE,J. (1968). Acta Cryst. <u>B24</u>, 182.

KARLE,J. (1969). <u>Advances in Chemical Physics</u>, Vol. XVI, edited by I. Prigogine & S.A.Rice, pp. 131-222, New York: Interscience.

KARLE,J. (1970). Partial Structures and the Tangent Formula, in <u>Crystallographic Computing</u>, ed. F. R. Ahmed, S.R. Hall and C.P.Huber. Copenhagen: Munksgaard

KARLE,J.& HAUPTMAN,H. (1956). Acta. Cryst. <u>9</u>, 635.

KARLE,J. & KARLE,I.L. (1966). Acta Cryst. <u>21</u>, 849-859.

KONNERT,J.H. (1976). Acta Cryst. <u>A32</u>, 614-617.

KONNERT,J.H. & HENDRICKSON,W.A. (1980). Acta Cryst. <u>A36</u>, 344-350.

Proc. Natl. Acad. Sci. USA
Vol. 78, No. 2, pp. 681–685, February 1981
Chemistry

(EXCERPT)

Conformation of cyclo(Gly-L-Pro-L-Pro-Gly-L-Pro-L-Pro)$_2$Mg^{2+} complex crystallized from C^{2}H$_3$CN solution

(x-ray analysis/magnesium–oxygen ligands/sandwich complex/solvent channels/tangent formula)

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Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375

Contributed by Isabella L. Karle, October 29, 1980

ABSTRACT The cyclic hexapeptides (Gly-L-Pro-L-Pro-Gly-L-Pro-L-Pro) in the (peptide–Mg–peptide)$^{2+}$ complex have nearly identical asymmetric conformations. Each has two *cis* Pro-Pro linkages and lacks any intraring hydrogen bonds. The Mg^{2+} ion forms six ligands in a regular octahedral array with the carbonyl oxygen atoms of the two Gly residues and one Pro residue of each peptide. The "sandwich" complex has an approximate 2-fold rotation axis through the Mg^{2+} relating the two peptide moieties. Cyclo(Gly-Pro-Pro-Gly-Pro-Pro)$_2$Mg(ClO$_4$)$_2$·4C^{2}H$_3$CN crystallizes in space group P3$_1$ with $a = b = 15.744(4)$ Å, $c = 24.002(6)$ Å, $\gamma = 120°$, and Z = 3. A highlight of the structure determination is the ready location of the Mg self-vector in a Harker section and the development of the entire structure by use of the tangent formula starting with the known position of the Mg atom.

Cyclic peptides complex with alkali metal and alkaline earth ions in several different modes—e.g., encapsulation, infinite sandwiches, and discrete sandwiches. Crystal structure analyses show that encapsulation occurs in the Li$^+$ and Na$^+$ complexes with antamanide (1), a decapeptide, and in the K$^+$ complex with valinomycin (2, 3), a dodecadepsipeptide. The formation of complexes with smaller cyclic peptides results in sandwiches rather than encapsulation, such as the infinite sandwich of a stack of alternating Rb$^+$ ions and the L,D,L,L,D,L stereoisomer of enniatin (4). Discrete sandwiches have been found for the complex of beauvericin and barium picrate with the sequence [beauvericin–Ba(picrate)$_3$Ba–beauvericin]$^+$ (5) and also for cyclo(L-Pro-Gly)$_4$ with Rb$^+$ in a (peptide–Rb$_2$–peptide)$^{2+}$ complex (6). Recently, Kartha *et al.* (7) showed that cyclo(L-Pro-Gly)$_3$ and Ca^{2+} form a (peptide–Ca–peptide)$^{2+}$ sandwich that has 3-fold rotation symmetry and cyclo(L-Pro-Gly)$_3$ and Mg^{2+} form a (peptide–Mg·3H$_2$O)$^{2+}$ complex that has approximate 3-fold rotation symmetry.

In this paper, we present the crystal structure of the 2:1 complex of cyclo(Gly-L-Pro-L-Pro-Gly-L-Pro-L-Pro) and Mg^{2+}. Radics and Hollosi (8) have shown by NMR spectroscopy that, in C^{2}H$_3$CN solution, the peptides in this complex assume two *cis* Pro-Pro linkages and two *trans* Gly-Pro linkages and that the number of resonances attests to the lack of overall symmetry.

EXPERIMENTAL

Crystals grown from a C^{2}H$_3$CN solution of cyclo(Gly-L-Pro-L-Pro)$_2$ and Mg(ClO$_4$)$_2$ were supplied by L. Radics of the Central Research Institute of Chemistry, Budapest. The crystal used for data collection was a clear colorless rhomb having dimensions of 0.4 mm on each side and the *c* axis along the body diagonal. The crystal was sealed in a thin glass capillary with a drop of mother liquor. The space group is P3$_1$ and has dimensions $a = b = 15.744(4)$Å, $c = 24.002(6)$Å, $\gamma = 120°$, and $V = 5153.5$ Å^3, and there are three formula units in the unit cell. For the composition C$_{48}$H$_{68}$N$_{12}$O$_{12}$Mg·2ClO$_4$·4C^{2}H$_3$CN, the calculated density is 1.358 g cm^{-3}. Reflections were scanned with Ni-filtered Cu radiation to a scattering angle of $2\theta = 112°$. A four-circle automatic diffractometer was used in the θ–2θ scan mode to collect 4600 independent reflections. Lorentz and polarization corrections were made and normalized structure factors, $|E_h|$, were obtained with the aid of a K curve.

An $(|E_h|^2 - 1)$ Patterson map showed one major peak in the Harker section. It proved to be the Mg-Mg vector from which the entire structure was derived, even though Mg represents only 3.0% of the total scattering. In retrospect, it is clear why the Mg-Mg vector was prominent although the Cl-Cl vectors were not apparent. The analysis showed that the thermal factor for the Mg atom, $B = 2.7$ Å^2, implies a rigidly held atom of concentrated electron density, whereas the thermal factors for the Cl atoms, $B = 7$ and 10 Å^2, imply considerable positional disorder.

Two hundred fifty-five phases based on the coordinates of the Mg atom alone that satisfied the criteria that $|E_h| > 1.5$ and $|F_h|_{\text{calc}} > k|F_h|_{\text{obs}}$, where $k = 0.20$, were used as input to the tangent formula (9, 10) to compute the phases for the remaining $|E_h| > 1.1$. Only those phases for which $|E_h|_{\text{calc}} > 0.5$ in the tangent formula extension were used in the initial E map, which showed the positions of four O atoms at ≈2.1 Å from the Mg and arranged in a square. In four additional rounds of phase extension by the tangent formula, in which the input phases were based on the Mg atom plus any additional atoms located in the intervening E maps and the value of k was raised successively to a maximum of 0.5, the coordinates of 75 atoms were determined. The tangent formula was used only for phase extension, not phase refinement. A series of cycles of least-squares refinement on the coordinates and thermal factors of the known atoms interspersed with difference maps yielded approximate coordinates for eight highly disordered O atoms in the two ClO$_4^-$ anions and for 12 atoms in four C^{2}H$_3$CN solvent molecules, also highly disordered.

Two different procedures for refining the values of the coordinates and anisotropic thermal factors were used. One procedure was the conventional full-matrix least-squares refinement (11) in which parameters for 95 nonhydrogen atoms were varied and parameters for 68 hydrogen atoms were held constant. Two passes were required for each cycle of refinement because the capacity of the program was restricted to 500 variables. Refinement was terminated at $R = 8.8\%$ and $R_w = 7.5\%$ for all the 4543 observed data points. Although the changes in the coordinates for the complex itself were minimal at this point in the refinement, the large thermal values for the ClO$_4^-$ ions and the C^{2}H$_3$CN solvent molecules, which suggested large positional disorders, precluded the determination of good values for the coordinates of these moieties. Our present interest

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(EXCERPT)

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[Leu^5]enkephalin: Four Cocrystallizing Conformers with Extended Backbones that Form an Antiparallel β-Sheet

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Abstract

[Leu^5]enkephalin (Tyr-Gly-Gly-Phe-Leu) grown from *N,N*-dimethylformamide(DMFA)/water crystallizes with four quite different conformers side-by-side in the asymmetric unit. The four conformers with extended backbones form an infinite antiparallel β-sheet. β-sheets related by the twofold screw axis are separated by a 12 Å spacing. Side groups protrude above and below the β-sheets and are entirely immersed in a thick layer of solvent occupying the volume between β-sheets. The crystal, stable only in contact with its mother liquor, appears to be a hybrid consisting of rather rigid sheets of peptide molecules separated by spaces filled with mobile solvent, thus having some resemblance to molecules in solution. Many solvent molecules are completely disordered and may be fluid. The space group is $P2_1$ with $a = 18{\cdot}720\,(4)$, $b = 24{\cdot}732\,(6)$, $c = 20{\cdot}311\,(5)$ Å, $\beta = 115{\cdot}86\,(1)^\circ$, $V = 8462$ Å^3. Composition of the asymmetric unit includes four enkephalin molecules, eight water molecules, eight DMFA molecules, plus an unknown number of disordered solvent molecules: $4C_{28}H_{37}N_5O_7.8H_2O.8C_3H_7NO.X$. The R factor from a restrained least-squares refinement (with six-parameter thermal factors) is 11·9% for 8155 data with $|F_o| > 0$. The procedure used for phase determination and structure analysis is described. Parameters for an extensive antiparallel β-sheet are presented.

Introduction

Endogenous enkephalin, a linear pentapeptide functioning as a natural analgesic with opiate-like activity, occurs in the brain as [Leu^5]enkephalin and [Met^5]-enkephalin in varying proportions, depending upon the species (Hughes, Smith, Kosterlitz, Fothergill, Morgan & Morris, 1975). The extreme flexibility of peptides, as compared to the more rigid molecules of morphine and other opiates, necessitates the delineation of probable conformations for the peptide to facilitate structure–activity studies. In the present study of the crystal structure of [Leu^5]enkephalin, the serendipitous occurrence of four molecules of the peptide, each having a different conformation, and a large amount of solvent surrounding the peptide may give good indications for the preferred conformations in solution.

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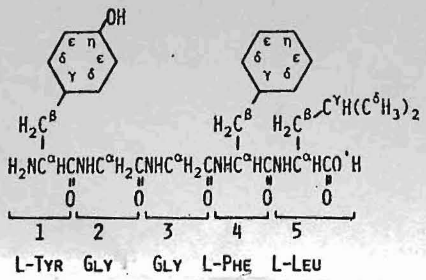
[Leu^5]ENKEPHALIN: FOUR COCRYSTALLIZING CONFORMERS

The structure contains more than 210 independent C, N and O atoms in space group $P2_1$. It provides an excellent vehicle for the application of formulas and techniques for direct phase determination and demonstrates that the practical limit with respect to size of a structure containing only light atoms has not been reached. This particular structure lies in an area intermediate between small-molecule crystallography and protein analysis. Small structures are normally considered to be those that have about 100 or fewer non-hydrogen atoms in the asymmetric unit. The intermediate range is an area in which few structure analyses have been reported.

In this paper, the procedures for determining the peptide will be described. In addition, the use of restrained least-squares refinement and the location of the solvent molecules will be discussed. The solvent, consisting of H_2O and *N,N*-dimethylformamide molecules (DMFA), comprises about 25% of the total content of the cell. Many of the solvent molecules are moderately well-ordered while others, occurring in special regions, are grossly disordered. It is conceivable that some of the disorder may be resolved by further study of the data. The low thermal factors for the atoms in the peptide molecules indicate that the peptide conformations are well established.

The labelling of atoms in an individual enkephalin molecule is as follows:



Experimental procedure

Leucine-enkephalin ($C_{28}H_{37}N_5O_7$) was crystallized from a mixture of DMFA and water maintained at a temperature of 318 K. Upon standing in air the crystals lose solvent of crystallization and their diffraction pattern changes to powder rings. Consequently, for collection of X-ray photographs and diffractometer intensity data, a single crystal was sealed in a capillary tube along with some mother liquor. X-ray data indicated space group $P2_1$ with unit-cell dimensions as in the *Abstract*. The density of the crystals was not measured but calculations assuming a reasonable density for such a molecule suggested that the asymmetric unit consisted of four enkephalin pentapeptide molecules plus 40–50 solvent atoms, a total of over 200 non-hydrogen atoms. X-ray intensities were collected on a Picker four-circle diffractometer with a θ–2θ scan to a resolution of $2\theta = 110°$ with Cu radiation on a crystal measuring approximately 0·6 × 0·2 × 0·1 mm. A total of 10942 independent reflections were measured of which 5965 had intensity greater than $2\sigma_I$. Three standard reflections monitored periodically during data collection indicated no measurable crystal deterioration. Absorption corrections, based on the variation in intensity of a reflection on the φ axis as a function of φ angle and ranging from 1·01 to 1·42, were applied to the data.

Normalized structure factors $|E|$ were obtained from the measured intensities by means of a *K*-curve where the *K*-curve was fit analytically by the exponential function $k\exp(Bs^c)$ (Karle, 1976). For the enkephalin data, $B = 13{\cdot}6$ and $c = 2{\cdot}7$. A value of 2·0 for c is equivalent to the Wilson plot.

Peptide structure determination

Phase determination

Since the asymmetric unit contained more than 200 C, O and N atoms with no heavier atom present, solving the crystal structure was not a routine procedure. Attempts utilizing several computerized direct-phasing multiple-solution methods were uniformly unsuccessful. The successful structure determination, although somewhat circuitous, made use of a combination of several approaches.

An immediately obvious departure from a usual distribution of $|E|$ values was the large number of reflections, 83 with unusually high $|E|$ values ranging from 3·0 to 8·3, that indicated a considerable regularity in the structure. In addition to the direct phase determination employing the Symbolic Addition Procedure, a Patterson map using ($|E|^2 - 1$) values for coefficients was calculated employing a special set of only 55 reflections with high $|E|$ values. The particular reflections chosen were those that occurred in sets with varying k indices such as $\overline{17},k,8$ ($0 \le k \le 7$) and $\overline{16},k,4$ ($0 \le k \le 6$), all with $|E| > 2{\cdot}4$, in order to determine the implications of these sets concerning the structure. The peaks in this vector map, Fig. 1, were consistent with a β-sheet structure. When all the observed data were included in the ($|E|^2 - 1$) map, the vectors defining the β-sheet were sufficiently masked by vectors from other parts of the structure to make the analysis of the implications of the map much more uncertain. It is possible that in other structures such an abbreviated ($|E|^2 - 1$) map derived from only special sets of reflections may give indications of characteristic features of the structure.

Direct phase determination by the Symbolic Addition Procedure (Karle & Karle, 1966, 1968) proceeded in

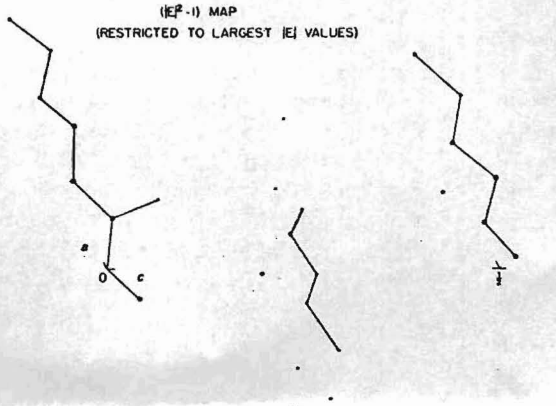


Fig. 1. The highest peaks in a Patterson function computed with $(|E_h^2| - 1)$ values for coefficients. A special set of only 55 reflections were used, each with $|E| > 2{\cdot}4$. The vectors indicated by the abbreviated $(|E^2| - 1)$ map are consistent with a β-sheet structure.

the usual fashion for space group $P2_1$.* An origin was selected by assigning a phase value of zero to reflections $\overline{10},0,19$, $\overline{17},0,12$ and 014. The phases of reflections 020 and 060 were readily determined to be π in the initial stages. Four other symbolic assignments, *a*, *b*, *c*, and *d*, were required for the phase determination to proceed. They were assigned to $\overline{16},0,4$, 7,1,13, 170 and $\bar{3}35$, respectively. All assignments were made to reflections with $|E| > 4{\cdot}0$. From the application of the Σ_2 relationship and examination of the values from multiple phase indications, it was not possible to make an unambiguous evaluation of any of the symbols. At this point, the Σ_3 relationship for non-centrosymmetric crystals† (Karle, 1969), proved to be useful in evaluating symbols *a*, *b* and *c* as π, π and 0, while symbol *d* remained indeterminate. Accordingly, since up to this point all phases would have values of 0 or π, as in a centrosymmetric crystal, symbol *d* was chosen to be $+\pi/2$, a choice that effectively selected the enantiomorph. In the resulting *E* map the strongest peaks represented segments of four parallel chains. The atoms, although near $y \sim \frac{1}{4}$, were not coplanar but showed the characteristic pleats of a pleated sheet. With the aid of the indications from the restricted $(|E|^2 - 1)$ map, forty peaks in the *E* map, calculated with ~1800 reflections, were selected consistent with an antiparallel β-sheet. Phases for reflections with $|E| > 1{\cdot}5$ calculated from this partial structure, and accepted if $|F_{\text{calc}}| > 0{\cdot}18|F_{\text{obs}}|$, were used for phase extension by the tangent formula for reflections with $|E| > 1{\cdot}2$. The phase values were *not* recycled in the attempt to refine their values, since in space group $P2_1$, particularly if a heavier atom is present, or, as in this example, where many atoms lie near a plane parallel to (010), recycling has the tendency to shift the phases toward centrosymmetric values (Karle, Gilardi, Fratini & Karle, 1969; Karle, 1974). The 84 atoms in the backbones of the four conformers were found in two stages of partial-structure development by use of the tangent formula and calculation of *E* maps.

The satisfactory appearance of the β-sheet, the many hydrogen bonds that were indicated and the relatively low *R* factor of 46% for the initial stages of phase extension by the tangent formula suggested that the structure could be correct up to this point. The location of the 76 atoms in the side chains was very difficult, however, since the partial-structure technique did not give any further information. From the known sequence of the [Leu^5]enkephalin, it was possible to place the twelve C$^\beta$ atoms fairly accurately. From difference maps and models, the positions of most of the atoms in the side chains were eked out. Cycles of restrained least-squares refinement (Konnert, 1976; Konnert & Hendrickson, 1980) were interspersed with difference maps that showed possible water molecules separated by distances appropriate to hydrogen-bond separations. The *R* factor, however, could not be reduced below 29% for the 190 to 210 atoms that were included in the refinement process and this high value, in fact, indicated that the structure was incorrectly placed with respect to a proper origin.

At this point it was decided to relax the space group to *P*1 (Karle & Karle, 1971). The data base was doubled with $|E_{hkl}| = |E_{h\bar{k}l}|$ and $|E_{\bar{h}kl}| = |E_{\bar{h}\bar{k}l}|$. About 150 atoms comprising the backbones and most of the side chains in the apparently misplaced structure determined above were used as the partial structure for computation of the initial phases in *P*1. Refinement and extensions of phases with the tangent formula and calculation of an *E* map based on the derived phases, with $|E|_{\min} = 1{\cdot}2$, yielded peaks that reproduced the original backbones but not the side chains. Thirty peaks in the other half of the cell, *i.e.* near $y = \frac{3}{4}$, were assigned to the backbones of additional enkephalin molecules potentially related to the original molecules by a symmetry operation. With these additional atoms, the twofold screw operation, for the original space group $P2_1$, could be satisfied either by the original position of the origin, or by a new position shifted by $x - 0{\cdot}068$ and $z - 0{\cdot}135$, or by another new position shifted by $x - 0{\cdot}096$ and $z - 0{\cdot}257$, or even largely satisfied by origins in several other locations. Another round of the partial-structure development in *P*1, with the addition of the 30 new peaks, yielded another 30 or so new atomic positions that could be more definitely related to the original backbone atoms by a twofold screw placed at $x - 0{\cdot}096$ and $z - 0{\cdot}257$ with respect to the original location.

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* The Symbolic Addition Procedure is programmed for interactive use on a computer (program *SAPPI*; R. Gilardi, Naval Research Laboratory, Washington, DC).

† See Appendix.

The next step involved the return to space group $P2_1$ with a shift to the new origin and a partial structure development based initially only on the backbone atoms. Since some of the side-chain atoms in the original structure may have been in error, they were omitted at this stage so as not to prejudice the calculation. This time, with the correct placement of the atoms for the backbone with respect to an appropriate origin, use of the tangent formula only for phase extension and not for phase refinement produced atomic positions for the side chains quite rapidly. After three cycles of partial structure development, positions were obtained for 156 of the 160 atoms in the four peptide molecules and seven atoms in solvent molecules.

The initial incorrect placement of the enkephalin chains with respect to an origin may have been caused by a subset of phases derived from reflection $\overline{16},3,4$ ($|E| = 3{\cdot}4$). The phase of $\overline{16},3,4$ was accepted from two strong Σ_2 triplets, each of which indicated an erroneous phase displaced by nearly π from the correct value. Under such circumstances, when a large subset of phases is inconsistent with the remainder of the phases, there is no combination of values for the symbolic phases that will produce a correct E map. The best map may be displaced from a correct origin.

Refinement

Several cycles of restrained least-squares refinement were computed with the newest version of the program *RESLSQ* (Flippen-Anderson, Gilardi & Konnert, 1983) that included a six-parameter thermal refinement. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Cycles of refinement were interspersed with difference

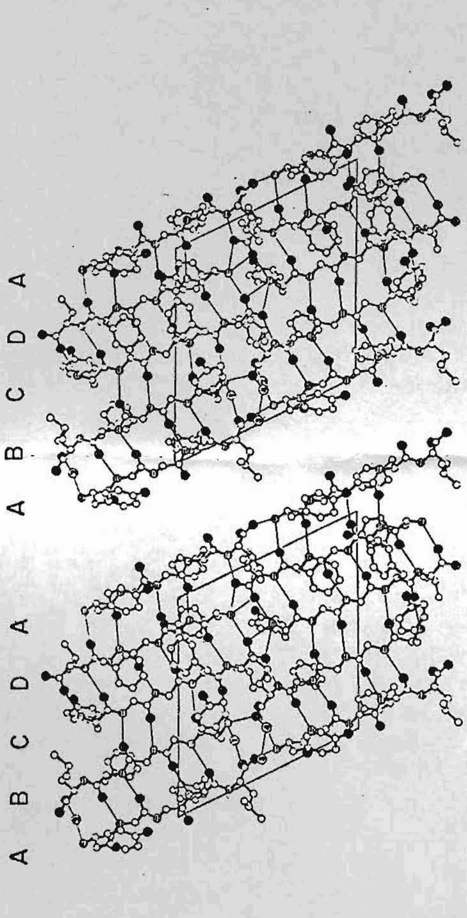

Fig. 2. Four independent molecules of enkephalin, labelled A, B, C and D, each with a different conformation, form an infinite antiparallel β-sheet in the crystal. The layer of hydrogen-bonded molecules near $y \sim \frac{1}{4}$ is shown in the stereodiagram. The axial directions are a ↖ and c →. Four water molecules are labelled 1–4, O atoms are indicated by filled circles and N atoms by hatched circles. See Fig. 3 for the schematic representation. There may be an additional hydrogen bond between $W(1)\cdots W(2)$.

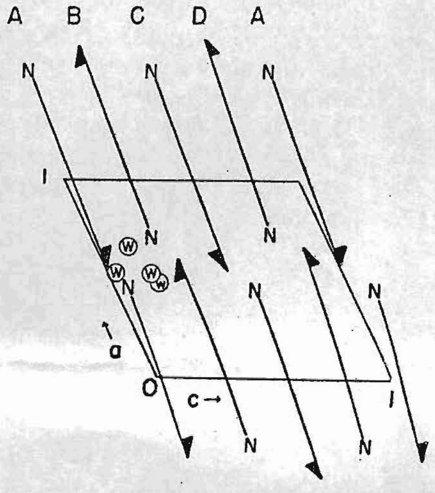

Fig. 3. A schematic representation of the orientation of the independent enkephalin conformers A–D that form the parallel β-sheet in Fig. 2. The semi-arrowheads represen carboxyl termini. The backbone of molecule C is flipped ov compared to A and similarly the backbone of molecule flipped over as compared to B. Four water molecules represented by W.

As suggested by Massimo Nespolo (CRM2 UMR - CNRS 7036, Institut Jean Barriol, FR 2843, Faculté des Sciences et Techniques, Nancy Université, BP 70239, Boulevard des Aiguillettes, F54506 Vandoeuvre-lès-Nancy cedex, France. E-mail: massimo.nespolo@crm2.uhp-nancy.fr):

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The Analytical Theory of Point Systems

(written in 1923)

by John Desmond Bernal (1901-1971)

with Introductions by Alan Mackay and Rolph Schwarzenberger

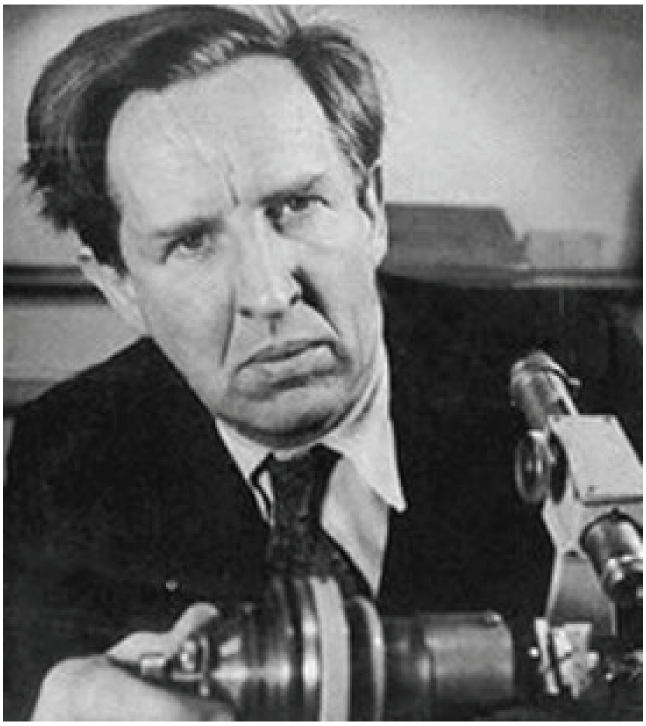

Fig. 1: *John Desmond Bernal (1901-1971). Photo from* *http://en.wikipedia.org/wiki/John_Desmond_Bernal*

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The
Analytic Theory
of
Point Systems

by

J.D.Bernal

1923

DR. ALAN L. MACKAY,
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"NOTHING EXISTS EXCEPT ATOMS AND EMPTY SPACE-
ALL ELSE IS OPINION" - DEMOCRITOS

OCCASIONAL PAPER No.1

from the

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Corrections! -
Prof. 3.

The
Analytic Theory
of
Point Systems

by

J. D. Bernal

1923

PREFACE

In 1923, Sir William Bragg received the following letter from the mineralogist, Arthur Hutchinson in Cambridge:

> Dear Sir William Bragg 25th June 1923
>
> I am venturing to write to you on behalf of a pupil of mine, Bernal by name, whose work on point systems has, I think, been sent to you - Bernal is I think quite a remarkable person; he is a shy, diffident, retiring kind of creature, but something of a genius. He attended my course on Elementary Crystallography and I realized that he was interested and was taking things in quickly. I did not however realize (and he never let on) that he had got so keen that he spent the whole of his next vacation in developing a method of dealing with point systems in the hope that it might be useful in X-ray work! When therefore, he suddenly appeared and deposited on my table a thick type-written MS., rather with the air of a dog bringing a poached rabbit to his master's feet, I was quite amazed - of course I make no pretence of being able to appraise its merit or even its usefulness - still it seemed to me a remarkable effort for an undergraduate in his third year - and Professor H.F.Baker was much interested in it and I believe thinks well of it...
> .....

This paper was thus written by John Desmond Bernal (1901-1971) when he was 21. It was submitted as a prize essay to Emmanuel College, Cambridge where Bernal was an undergraduate and earned him the Sudbury Hardyman prize of £30, but it also got him a post with Sir William Bragg and set him on a career in crystallography. The paper was then presented to the Cambridge Philosophical Society on 7th July 1923 as "The Analytic Theory of Crystals" but, although it was accepted, the paper was, on account of its length, never published. One manuscript copy, typed, we believe, by Mrs Eileen Bernal, has circulated in this department for many years, surviving precariously, but we now hasten to publish it in facsimile to avoid further danger of its loss.

Some of the circumstances of the production of this paper are described at length by Professor Dorothy Hodgkin, O.M., F.R.S., who was the earliest of Bernal's students and co-workers during his period in the crystallographic laboratory at Cambridge, in her biographical notice of Bernal (Biographical Memoirs of Fellows of the Royal Society, 26, (1980) which we quote for Prof. Hutchinson's letter and to which reference should be made for details of Bernal's scientific career.

The accompanying article, "X-rays and Crystal Structure" was written by Bernal in 1929 for the 14th Edition of the Encyclopaedia Britannica (and is here reproduced by kind permission of the copyright holders). It clearly follows from Bernal's essay. Bernal also wrote the corresponding article for the 1953 edition of the Encyclopaedia (Vol. 6, pp. 809-829. It ends with the sentences:

"The beating out of metal under the hammer, the brittleness of glass and the cleavage of mica, the plasticity of clay, the lightness of ice, the greasiness of oil, the elasticity of rubber, the contraction of muscle, the waving of hair and the hardening of a boiled egg are among the hundreds of phenomena that had already been completely or partially explained. They were an earnest of the millions of others, old or new, that still had to be explained."

In the period Bernal prepared a further version for the succeeding edition but, regrettably, this was not published because it was too long and had too many illustrations. Evidently the successes of crystallography in explaining the material world and Bernal's enthusiam had outrun commercial prudence!

J.D.Bernal was elected a Fellow of the Royal Society in 1938 for his work on the elucidation of the structures of biological molecules by the methods of X-ray crystallography and in the same year he succeeded P.M.S.Blackett as Professor of Physics here at Birkbeck College in the University of London. Almost immediately Bernal was drawn into the war but in 1946 the Birkbeck College Research Laboratory for bio-molecular structure was founded in two old houses at 21/22 Torrington Square (now the site of the library of the School of Oriental and African Studies). This was formally opened by Sir Lawrence Bragg on 1 July 1948 for which occasion Bernal wrote: "the central theme of the laboratory is the application of physical methods to the understanding of the structures and reactions of molecules in biological systems". The formal teaching of crystallography (M.Sc. by examination) began at Birkbeck also in 1948 and has continued ever since. In 1964 the Laboratory became the Department of Crystallography (moving into the new extension building and separating from the Department of physics) with Bernal as its first Head and first Professor of Crystallography, bur in the same year Bernal suffered the first of a series of strokes. On his retirement in 1968 he was succeeded by C.H.Carlisle and in

1978 by T.L.Blundell, the present occupant of the established chair of crystallography and Head of the Department.

We have invited Professor Rolph Schwarzenberger of Warwick University to give an assessment of this, Bernal's first paper, which, by accident, has remained hitherto unpublished, and we are most grateful for his note which puts the paper into perspective and explains quaternions.

We believe that nothing could be more appropriate as Occasional Paper No.1 from the Department of Crystallograhy which Bernal founded to continue the studies which he himself had advanced so much.

Alan Mackay

July 1981

INTRODUCTORY NOTE

R.L.E. Schwarzenberger
Science Education Department
University of Warwick

One way to assess the novelty of Bernal's manuscript is to place it side by side with the two books which he himself used:

H.HILTON. Mathematical Crystallography and the theory of groups of movement, Clarendon Press,Oxford 1903.

P.NIGGLI. Geometrische Kristollographie des Diskontinuums, Borntraeger, Leipzig 1919.

The two books have in common that they include the listing of the 230 space groups as it was published by Schönflies* in 1891 (Niggli copies Schönflies exactly whereas Hilton changes some nomenclature in translation and alters the order in which the crystal systems occur. Bernal follows Hilton). They differ in that Hilton attempts to give a full proof that there are precisely 230 possibilities whereas Niggli gives proofs of general results, listings of groups and much additional information about each group (along the lines of the future International Tables). Hilton is more interested in group theory than in crystallography and uses geometrical methods which stem directly from those of Schönflies, whereas Niggli uses algebra more and deals also with crystal form and with deformations of structure.

It is worth recalling that neither Schönflies nor Fedorov nor Barlow succeeded in getting the number of distinct groups correct at their first attempt: the list of 230 space groups was achieved only as a result of mutual checking between Schönflies and Fedorov. I do not believe that Hilton would have done better, had he not been writing with the list of Schönflies in front of him, because his method is not guaranteed to catch every possible special case of existence or equivalence. Thus Bernal was inspired by Niggli's more analytic approach to try to make more precise the "simple and geometric" qualitative proof contained in Hilton's book. In this approach Bernal was following very closely in the footsteps of Fedorov who had written over 30 years earlier:

---

*Kristallsysteme und Krystallstruktur, B.G.Teubner, Leipzig, 1891.
The second revised edition appeared as Theorie der Kristallstruktur-ein Lehrbuch, Borntraeger, Berlin, 1923.
There is no evidence in the manuscript of Bernal having consulted Schonflies directly - in any case Hilton is considerably clearer.

"...here, for the first time, the symmetry of figures is expressed in analytical terms and in this way the theory of symmetry is itself introduced into the realm of analytic geometry. Originally I intended to find analytic terms for the symmetry of finite regular systems. I was prompted to do this by the difficulty of interpreting Sohncke's derivations.......an error which remained unnoticed for a long time by the author himself........this could hardly have happened if these systems had been expressed in analytical terms"

(E.S.Fedorov "Symmetry of Finite Figures" 1889
translated by D.Harker 1971)

Similarly Bernal realised that more precise and analytic methods were required for the qualitative listing (Sohncke, Schönflies, Barlow, Hilton) to become useful in the new crystallographic applications. In the remainder of this note I would like to draw attention to three ways in which Bernal notably achieved this aim.

The first important improvement made to Hilton's proof is the decision to work in vector space (i.e. with fixed origin) rather than in affine space. Hilton follows Schönflies in writing, for example, $A(\alpha)$ to denote a rotation through angle α about an axis A, or $S(t)$ to denote a glide transformation with translation component t lying in the plane of reflection S. But the axis A and the plane S need not pass through the origin, which is good for nice qualitative pictures of crystals but bad for precise analytic proofs of the mathematics. Bernal chooses an origin and assigns each affine transformation

$$X \longmapsto \varrho X + c$$

its linear part ϱ and its translation component c. The importance of this change for the development of mathematical crystallography is in no way diminished by the fact that, under the steadily increasing influence of modern algebra, many other mathematicians did the same thing quite naturally and most crystallographers do so today.

This leads to the most striking aspects of the manuscript: the influence of modern algebra in the discussion of quadratic forms (in Chapters II and III the symbol SXY is the scalarproduct of X and Y) and in the use of quaternions throughout. In crystallography the linear part of a symmetry is, of course, a 3×3 matrix determined by coefficients. The fact that ϱ preserves lengths and angles imposes 6 conditions so only 3 degrees of freedom are left for ϱ . Clearly a more precise analytic approach would benefit from a more economic method of presentation of 3 parameters. It was fairly well known among theoretical physicists and mathematicians that all such linear parts arise from transformations of the form

$$\mathbf{X} \longmapsto \pm q \mathbf{X} q^{-1}$$

where q is a unit quaternion (the correspondence between unit quaternions and linear parts is actually not one-one, because -q determines the same transformation as q ; this does not cause any confusion in practice). Most readers of this note will be familiar with this fact but, for those who are not, a brief note on quaternions is appended which covers those facts assumed without comment by Bernal in Chapters II and III. Note that the quaternion notation - unlike matrix notation - allows angles of rotation, axis of rotation, plane of rotation to be read off immediately. This is a great advantage when trying to decide whether two groups are or are not equivalent.

The third important improvement is the explicit mention of specialisation : no doubt influenced by the algebraic geometry of the time. This is merely the very simple observation that, for example, a tetragonal lattice is a special case of a orthorhombic lattice. This observation is present but less explicit in Hilton, and explains why Hilton (and so also Bernal) deals with the tetragonal system immediately after the orthorhombic system (Schönflies has the rhombohedral system in between, presumably on the ground that 12 is between 8 and 16).

The effect of these three improvements is that far more facts can be established as general theorems applicable to many crystal systems. Here Bernal is following the example set by Niggli in contrast to Hilton's insistence on a separate discussion for each crystal system. It follows too that the listing of space groups becomes essentially a listing of the relevent translation components which can be handled algebraically. In modern language, Bernal is listing the relevant cocycles to determine a first cohomology group.

In summary, Bernal has rewritten the proof (Sohncke, Schönflies) which he found in Hilton but has brought to it the more analytic attitudes of a quite different crystallographic tradition (Möbius, Fedorov, Niggli). His excellent knowledge of current mathematics yields an improvement upon the treatment of Hilton, 20 years earlier, and comes close to foreshadowing the cohomological work of Zassenhaus, 20 years later.

Rolph Schwarzenberger
April 1981

NOTE ON QUATERNIONS

Any set of 4 real numbers a, b, c, d can be displayed conveniently as a single quaternion $a+bi+cj+dk$. The chief advantage of the notation is the ability to multiply using the idenitities $i^2=j^2=k^2=-1$ and $ij=-ji=k$. Many properties are analogous to those of complex numbers; for example if $q=a+bi+cj+dk$ then the conjugate $\bar{q}=a-bi-cj-dk$ satisfies $\bar{q}q = a^2+b^2+c^2+d^2$.

For present purposes we need to consider two very special kinds of quaternion q : those for which $\bar{q}=-q$ (pure quaternions so called because they must necessarily have the form $q=xi+yj+zk$) and those for which $\bar{q}=q^{-1}$ (unit quaternions so called because if $q=a+bi+cj+dk$ then necessarily $a^2+b^2+c^2+d^2=1$). Note that a pure quaternion $xi+yj+zk$ may be identified with a point $X=(x,y,z)$ in ordinary three dimensional space, while a unit quaternion $q=a+bi+jc+kd$ can also be writeen in the form $q = \cos\alpha + \sin\alpha\,(b'i+c'j+d'k$ for some angle α where $b'^2+c'^2+d'^2=1$. We assume this form for q in what follows.

If X is a pure quaternion then the transformation

$$\rho : \quad X \longmapsto qXq^{-1}$$

sends X to another pure quaternion because

$$\overline{qXq^{-1}} = \bar{q}^{-1}\bar{X}\bar{q} = q\bar{X}q^{-1} = -qXq^{-1}$$

Moreover it is easily shown to preserve lengths and angles. The vector X is fixed under the transformation if and only if $qX=Xq$. Inspection shows that this happens if and only if X is a multiple of $b'i+c'j+d'k$. Thus ρ is a rotation about the axis (b', c', d'), and it can be checked that the angle of rotation is 2α.

Similarly the transformation

$$-\rho : \quad X \longmapsto -qXq^{-1}$$

is a combination of a reflection and a rotation, that is a symmetry of the second kind.

The power of this notation can be seen when considering composition. If the rotation $X \longmapsto q_1Xq_1{}^{-1}$ is preceded by the rotation $X \longmapsto q_2Xq_2{}^{-1}$ then the composite rotation may be represented by the transformation

$$X \longmapsto q_2Xq_2{}^{-1} \longmapsto q_1(q_2Xq_2{}^{-1})q_1{}^{-1}$$

or precisely the transformation $X \longmapsto q_3Xq_3{}^{-1}$ where $q_3 = q_1q_2$. This is a very much simpler formula for the composition of two rotations than that of Euler and Rodrigues quoted by Hilton.

Preface

I was led to the subject of the present paper by a consideration of the X-ray analysis of crystals. The general uncoordinated and tentative aspect of the methods used seemed to point to an unsuitable geometric groundwork. When Schoenflies, Von Fedorof and Barlow solved the final problem of the 230 types of homogeneous structures there conclusions were purely geometric and there seemed no immediate prospect of applying them to actual crystal structure. As it was only necessary to distinguish one such structure from another, a qualitative basis was sufficient. But this qualitative basis did not meet the needs of X-ray analysis of crystal structure, and the pioneers in this field consequently fell back upon simple and geometric methods which they evolved in the course of their work.

What was wanted, it seemed to me, was an analytic theory in which the structure of a crystal could be represented by a quantitative formula, and the analysis of this structure could be reduced to the solution of certain equations. It occurred to me that the application of simple vector and quaternion calculus would supply the need of experimentalists while at the same time providing yet another solution to the problem of homogeneous structures.

This solution occupies the first six chapters of the paper. It is given in extremely condensed form, and the absence of examples and diagrams may make it difficult to follow the geometric meaning of the various expressions. In this connection references under the heads of Classes and Systems should be made to Hilton's Mathematical Crystallography. Chapters VII and VIII are deductions from the theory which lead to Chapter IX on the X-ray analysis.

Circumstances prevented this Chapter from being as full as was originally intended, especially with respect to the lack of examples and the scant attention paid to the Laue and Hull methods, deficiencies which I intend to make good at a later date.

As the theoretical part has been written independently the absence of references will be understood: the only works to which I am indebted are Hilton (ibid) and Niggli, Analytische Geometrie der Discontinuums, from which I have takensome of the proofs in Chapter III. In Chapter IX I have relied almost entirely on Bragg's X-rays and Crystal Structure, and in view of the forthcoming appearance of the 2nd edition of this work, the elementary nature of the Chapter is perhaps not unfortunate.

CHAPTER I

POINT SYSTEMS

1.1 Point Systems

Consider a system of points in an n dimensional continuum. The position of any point is determined by the vector X representing the line drawn from an arbitrary origin 0 (not necessarily a point of the system) to the point. This point is called the point X. The whole system is determined when the origin 0 and the vectors corresponding to all the points are given. Thus the system is completely determined by

$$X_1, X_2, X_3, \quad X_r \text{ written for short } /X_r$$

$/X_r$ is called the aspect of the system from 0.

.2 If n independent vectors are chosen. i.e. if $A_1, A_2, \ldots\ldots A_n$. can be chosen such that

$$x_1A_1+x_2A_2+x_3A_3+\ldots\ldots\; x_nA_n \neq 0 \text{ unless } x_1=x_2=\ldots\ldots=x_n=0$$

then X_r can always be written

$$x_{11}A_1 + x_{21}A_2 + x_{31}A_3 + \ldots\ldots + x_{n1}A_n \;.$$

and the aspect of the system represented by

$$/x_{1r}A_1 + x_{2r}A_2 + \ldots\ldots\ldots\ldots x_{nr}A_n$$

The vectors $A_1, A_2, \ldots\ldots\ldots A_n$. are called the coordinate system or reference vectors.

The scalar coefficients $x_{11}, x_{21}, \ldots\ldots\ldots x_{n1}$. are called the coordinates of the point X_1 and are often used to denote the point X_1.

Discontinuous Systems.

If for two points of the system $x_1, x_2, \ldots\ldots x_n$. $x'_1, x'_2, \ldots\ldots x'_n$. all the positive scalar differences

$$x_1 \sim x'_1 ;\; x'_2 \sim x_2 ;\ldots\ldots\ldots\ldots x'_n \sim x_n ;$$

are either $=0$ or e, when e is a finite positive scalar, the system is said to be discontinuous. In everything that follows all systems are assumed to be discontinuous.

Homogeneous Systems.

If there exists at least n points whose vectors are independent and from which the aspect of the system is the same, i.e. for which $/X_r$ represents the aspect of the system; then the system is called homogeneous.

Let the points

$$\begin{array}{l} B_1 = b_{11}A_1 + b_{21}A_2 + \ldots\ldots\ldots\ldots b_{n1}A_n . \\ B_2 = b_{12}A_1 + b_{22}A_2 + \ldots\ldots\ldots\ldots b_{n2}A_n . \\ \cdot \quad \cdots\cdots\cdots\cdots \\ B_n = b_{1n}A_1 + b_{2n}A_2 + \ldots\ldots\ldots\ldots b_{nn}A_n . \end{array}$$

be such a set of points then since the system has the same aspect from $B_1, B_2,$ B_n. as it has from 0 there is corresponding to any point $x_1, x_2, \ldots x_n$. the points

$$\begin{array}{l} x_1 + b_{11}, \; x_2 + b_{21}, \ldots\ldots\ldots x_n + b_{n1} . \\ x_1 + b_{12}, \; x_2 + b_{22}, \ldots\ldots\ldots x_n + b_{n2} . \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ x_1 + b_{1n}, \; x_2 + b_{2n}, \ldots\ldots\ldots x_n + b_{nn} . \end{array}$$

Corresponding to these again are the points

$$x_1 + 2b_{11}, \; x_2 + 2b_{21}, \ldots\ldots x_n + 2b_{n1}. \text{ etc.}$$

also the points $x_1 + b_{11} + b_{12}$, $x_2 + b_{21} + b_{22}$, $\ldots\ldots\ldots x_n + b_{n1} + b_{n2}$. etc.

in general all the points

$$x_1 + n_{11}b_{11} + n_{12}b_{12} + \ldots + n_{1n}b_{1n}, \; x_2 + n_{21}b_{21} + n_{22}b_{22} + \ldots + n_{2n}b_{2n}, \; \ldots\ldots x_n + n_{n1}b_{n1} + n_{n2}b_{n2} + \ldots + n_{nn}b_{nn}$$

where $/n_{rs}$ can have integral values positive or negative

.41 Further, the coordinates of any point $x_1, x_2, x_3, \ldots\ldots x_n$, become if the point $n_{11}b_{11}+n_{12}b_{12}+\ldots+n_{1n}b_{1n}$, $n_{21}b_{21}+n_{22}b_{22}+\ldots+n_{2n}b_{2n}, \ldots\ldots$ be chosen as origin

$$x_1-n_{11}b_{11}-n_{12}b_{12}-\ldots-n_{1n}b_{1n},\ x_2-n_{21}b_{21}-n_{22}b_{22}-\ldots-n_{2n}b_{2n},\ldots\ldots$$

and since there is a point with the same coordinates referred to the old origin, the system must have the same aspect from all the points

$$/\ n_{11}b_{11}+n_{12}b_{12}+\ldots+n_{1n}b_{1n},\ n_{21}b_{21}+n_{22}b_{22}+\ldots+n_{2n}b_{2n},\ldots\ldots\ n_{n1}b_{n1}+n_{n2}b_{n2}+\ldots+n_{nn}b_{nn}$$

These points form a point system inside tthe given one and as the origin was chosen arbitrarily in the first place a set with the same aspect can be found for any origin.

These systems have the property of having the same aspect from every point of the system. Such systems are called lattices. All lattices can be written in the form

$$/n_{1r}A_1+n_{2r}A_2+\ldots\ldots+n_{nr}A_n.$$

when $/n_{sr}$ are integers and $A_1, A_2, \ldots\ldots A_n$ a set of properly chosen vectors.

.5 Returning to the original system; now suppose there is another point $b_{1\,n+1}, b_{2\,n+1}, \ldots\ldots b_{n\,n+1}$ isognomic with the origin i.e. such that the system has the same aspect when viewed from these two points; then the point $x_1+n_{1\,n+1}b_{1\,n+1}+n_{11}b_{11}+\ldots+n_{1n}b_{1n}$, $x_2+n_{2\,n+1}b_{2\,n+1}+n_{21}b_{22}+\ldots+n_{2n}b_{2n}, \ldots\ldots$ and the point $x_1+n_{11}b_{11}+n_{12}b_{12}+\ldots+n_{1n}b_{1n}$, $x_2+n_{21}b_{21}+n_{22}b_{22}+\ldots+n_{2n}b_{2n}, \ldots\ldots$ are points of the system. Subtracting, we have the difference of coordinates $n_{1\,n+1}b_{1\,n+1}-n_{11}b_{11}$, $n_{2\,n+1}b_{2\,n+1}-n_{21}b_{21}, \ldots\ldots$

Now none of these must be infinitensimal and this can only happen for all integral values of n_{rs} if $\frac{\cancel{n}\ b_{1\,n+1}}{b_{11}}$ is commensurate, extending we have $\angle\frac{b_{r\,n+1}}{b_{rs}}$ commensurate.

Therefore all points isognomic with 0 may be written in the form

$$p_{11}b_{11}+p_{12}b_{12}+..+p_{1n}b_{1n}, \quad p_{21}b_{21}+p_{22}b_{22}+..+p_{2n}b_{2n}, \ldots\ldots$$

where $/p_{rs}$ are rational fractions

.6 All the isognomic points of the system may be written

$$/p_{1r}B_1+p_{2r}B_2+\ldots\ldots+p_{nr}B_n.$$

p_r can always be written $l_r+\frac{m_r}{n_r}$ where l_r, m_r, n_r are all integers and $n > m \geq 0$ ~~Now since B ?B, — B, are isognomic points~~

The points $\frac{m_1}{n_1}, \frac{m_2}{n_2} \ldots\ldots \frac{m_r}{n_n}$ must belong to the system and there must be a finite number k of such points. Of these n independent points may be chosen as reference vectors (If $k<n$ some of the points $B_1 B_2 \quad B_n$ can be taken as well) The number of isognomic points with pure fractional coefficients referred to these vectors must be less than before, ~~and~~ continuing the process we must arrive after a finite number of operations to a set of reference vectors in which there is only one point with fractional coefficients and this is the point 0?0,.....0. Such a set ~~system~~ is called a primitive.

.61 All the isognomic points referred to a primitive set of vectors $A_1, A_2, \ldots\ldots A_n$. can be expressed in the form

$$/l_{1r}A_1+l_{2r}A_2+\ldots\ldots+l_{nr}A_n.$$

where $/l_{rs}$ take all integral values positive or negative.

This lattice which includes allthe isognomic points of the system with respect to the origin O is called the skelstal lattice of the ~~sys~~ system.

.7 The choice of an primitive ~~elementary~~ set is not unique. There are except for the case (n=0) an infinite number of such sets.

If
$$A'_1 = l_{11}A_1 + l_{21}A_2 + \dots\dots\dots l_{n1}A_n \ .$$
$$A'_2 = l_{12}A_1 + l_{22}A_2 + \dots\dots\dots l_{n2}A_n \ .$$
$$\dots\dots\dots\dots\dots\dots\dots\dots$$
$$A'_n = l_{1n}A_1 + l_{2n}A_2 + \dots\dots\dots l_{nn}A_n \ .$$
is such another set it must be possible to express A_1 in the form
$$A_1 = l'_{11}A'_1 + l'_{21}A'_2 + \dots\dots\dots l'_{n1}A'_n \ .$$
etc. Where $/l'_{rs}$ are integers

Now the condition for this is

$$\begin{vmatrix} l_{11} & l_{21} & l_{31} & & l_{n1} \\ l_{12} & l_{22} & l_{32} & & l_{n2} \\ l_{13} & l_{23} & l_{33} & & l_{n3} \\ \cdot & \cdot & \cdot & \cdot & \cdot\cdot \\ l_{1n} & l_{2n} & l_{3n} & \cdot & \cdot\cdot \end{vmatrix} = \pm 1$$

so that this relation must hold good for the coordinates of any primitive set expressed in terms of any other.

By an extension of this proof it can be seen that if the determinant $(l_{11} \dots l_{nn}) = \pm m$ the set of referrence vectors $A'_1, A'_2, \dots A'_n$. is of the m th order, that is the number of proper fractional points is m and the highest value of any denominator must also be m.

.8 Component Set.

The general expression for a homogeneous system may now be written
$$/(x_{11}+l_{11})A_1 + (x_{21}+l_{21})A_2 + \dots\dots\dots (x_{n1}+l_{n1})A \ .$$
$$/(x_{12}+l_{12})A_1 + (x_{22}+l_{22})A_2 + \dots\dots\dots (x_{n2}+l_{n2})A \ .$$
$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$
$$/(x_{1n}+l_{1n})A_1 + (x_{2n}+l_{2n})A_2 + \dots\dots\dots (x_{nn}+l_{nn})A \ .$$
where $/A_r$ is a primitive set. This expression represents every point of the system once and once only if $/(x_{rs}-x_{r1})$ are not all integers for all values of r(s constant) and of s. ~~We~~ Each point $x_{1s} x_{2s} x_{3s} \quad x_{rs}$ is seen to to be accompanied by a lattice of equivalent points; ~~and the number of such lattices m is called the~~

Since there are m of such lattices the system is called an m lattice or m point system. The set of points $x_{1s}A_1 + x_{2s}A_2 + \ldots\ldots + x_{ns}A_n$. is called a component set of the system. One component set corresponds to each point of the skeletal lattice. Instead of $/x_{1s}, x_{2s}, x_{3s} \quad x_{ns}$ $/(x_{1s}+l_{1r}), (x_{2s}+l_{2s}), \ldots\ldots(x_{ns}+l_{ns})$ might have been chosen as one of the component set, it is consequently possible and sometimes useful to limit the values of the coordinates of the points in a component set. The limits most often employed are (A) $0 \leq X < 1$ and (B) $-\frac{1}{2} < x \leq \frac{1}{2}$ (A) avoids negative coordinates, (B) is more symmetrical.

CHAPTER II.

SYMMETRY

2.1 Characteristics of a Vector set

For every set of n independent vectors there exists $\frac{n(n+1)}{2}$ symmetrical ~~of the type~~ quadratic forms of the type $Q(X)$ $Q(XY)$ these forms are called the characteristics of the set.

.2 Congruence

Two sets of vectors $/A_r$ and $/A_r'$ are said to be congruent if

$$Q(A_r) = Q(A_r)' \text{ and } Q(A_r A_s) = Q(A_r' A_s')$$

for all values of r and s

Taking these vectors as reference vectors, we have

$$Q(x_1A_1 + x_2A_2 + \ldots + x_nA_n) \equiv Q(x_1A_1' + x_2A_2' + \ldots\ldots + x_nA_n')$$

and $Q(x_1A_1 + x_2A_2 + \ldots + x_nA_n)(x_1'A_1 + x_2'A_2 + \ldots\ldots + x_n'A_n)$

$$\equiv Q(x_1A_1' + x_2A_2' + \ldots\ldots + x_nA_n')(x_1'A_1' + x_2'A_2' + \ldots\ldots + x_n'A_n')$$

for all values of $/x_r$. From this it follows that if in two systems with congruent reference vectors, there corresponds to every point $x_1 x_2 \ldots\ldots x_n$ in one ~~there~~ a point $x_1 x_2 \ldots\ldots x_n$ in the other, then the two systems are congruent and conversely.

.3 Symmetry

If a system is such that two or more aspects of it are congruent though not in general identical, it is said to be symmetrical.
If O, C, C' .... are the points from which the system has ~~the same~~ congruent aspects then for any two points X and Y there are corresponding points $C + X', C + Y'$; $C' + X'', C' + Y''$;.......
where X, Y ; X', Y' ;..... are connected by the equations

$$Q(X) = Q(X') \quad \ldots\ldots$$

$$Q(XY) = Q(X'Y') \quad \ldots\ldots$$

Now X' must obviously be some vector function of X consistent with the above conditions. Writing $X' = f(X)$ then ~~we have~~ if Y is the point corresponding to X, i.e. if $Y = X' + C$ we may write as the general form of the ~~mx~~ condition of symmetry the identity,

$$Y \equiv f(X)+C.$$

.4 Symmetry in three dimensions.

Leaving at this point the study of point systems in n dimensions we may examine the form which the symmetry function f(X) takes up ~~wh~~ where n = 3 that is in the ordinary space of three dimensions. In this case we may write $Q(X) = X^2$ and $Q(XY) \ne S.XY$ and the conditions which f(X) must satisfy become

$$f(X)^2 = X^2 \text{ and } Sf(X)f(Y) = SXY$$

One form of f(X) which satisfies both these conditions is the quaternion transformation

$$f(X) = qXq^{-1} \quad \text{where q is a quaternion}$$

another is the negative quaternion transformation

$$f(X) = -qXq^{-1}.$$

There are no other forms which can satisfy the conditions; for since $f(X)^2 = X^2$, q can always be found such that $f(X) = qXq^{-1}$ and similarly q' can always be found such that $f(X') = q'X'q'^{-1}$,

then $S\,f(X)f(X') = SqXq^{-1}q'X'q'^{-1} = S\,XX'$ if and only if $q' = q$

.5 Thus the general condition of symmetry must always take one or other of the forms $Y \equiv qXq^{-1}+C$ $Y \equiv -qXq +C$. These identities are known as symmetry relations of the first and second sort respectively

.6 The symmetry relation $Y \equiv \pm qXq^{-1}+C$ may always be written in the inverse form $X \equiv \pm q^{-1}Yq \mp C$ where $C' \equiv q^{-1}Cq$ Multiplying both of these expressions by q adding them and dividing the sum by two we arrive at the symmetry relation in its most symmetrical shape,

$$(Y-\frac{C}{2})q - q(X+\frac{C}{2}) \equiv 0$$

or $(Y-\frac{C}{2})q + q(X-\frac{C}{2}) \equiv 0$ for relations of the first and second sort respectively, or more simply still

$$\underline{(Y-C)q-q(X+D) \equiv 0}$$

$\underline{(Y-C)q+q(X-D) \equiv 0}$ where $Cq-qD=0$

In the important particular case in which $C=0$ the relation takes the simplest form of all

$$\underline{Yq \mp qX \equiv 0}.$$

The unsymmetrical forms are in general more easy to deal with because they involve only one constant vector, and they will be used in all the subsequent work. The other forms were only introduced to show the essential symmetry of the relations.

.7 Combinations and Transformations of Symmetry Relations.

If a system posesses two symmetry relations

(1) $Y \equiv (-1)^{v}qXq^{-1}+C$

(2) $Y' \equiv (-1)^{v'}q'X'q'^{-1}+C'$ where v is an integer odd or even

and in (1) we put $X \equiv Y'$, we have

.71 (12) $Y \equiv (-1)^{v'}q'\{(-1)^{v}qXq^{-1}+C\}q'^{-1}+C'$

which reduces to

(12) $Y \equiv (-1)^{v+v'}q'qXq^{-1}q'^{-1}+(-1)^{v}q'Cq'^{-1}+C'$

and since $q'q$ is a quaternion whose reciprocal is $q^{-1}q'^{-1}$ this is equivalent to another symmetry relation.

This new relation is called the combined relation (12).

The combined relation (21)

(21) $Y \equiv (-1)^{\nu+\nu'} q q' X q^{-1} q'^{-1} + (-1)^{\nu} q C' q^{-1} + C'$

is in general not the same.

It should be noticed that if (1) and (2) be both relations of the first or both of the second sort their combination is a relation of the first sort; whereas if one is of the first and the other of the second sort their combination is of the second sort.

.72 The combination of one relation with it self n times will always be a relation of the system so that the relation

$Y \equiv (-1)^{\nu} q X q + C$ always implies the further relations

$Y \equiv (-1)^{n\nu} q^{n} X q^{-n} + nC$

where n may have all integral values positive or negative.

.73 The combination (-121)

(-121) $Y \equiv (-1)^{\nu'} q q' q^{-1} X q q'^{-1} q^{-1} - (-1)^{\nu'} q q' q^{-1} C q q'^{-1} q^{-1} + q C' q^{-1} + C$

is called the transformation of (2) by (1)

.8 Reduced Symmetry Relations

In any point system we can always write

$X = X_{lmn} + X'$; $Y = Y_{lmn} + Y'$ where $X_{lmn} = lA + mB + nC$, A, B, C being primitive reference vectors, and l, m, n integers; while $X' = pA + qB + rC$ where p, q, r are proper fractions though not necessarily rational: similarly for Y_{lmn} and Y'. The general symmetry relation now takes the form

$Y_{l'm'n'} + Y' \equiv (-1)^{\nu} q (X_{lmn} + X') q^{-1} + D$ (writing D for C to avoid confusion)

l', m', n' are the integers corresponding to l, m, n.

For the skeletal lattice that includes the origin $X' = Y' = 0$

The relation can therefore be considered as the sum of the two rel-

relations

$$Y_{lmn} = (-1)^{\nu} q X_{lmn} q^{-1} + D_1,$$

$$Y' = (-1)^{\nu} q X' q^{-1} + D_2 \quad \text{where } D_1 + D_2 = D$$

If l,m,n be put = 0 it can be seen from the first relation that $D = lA+mB+nC$ where l,m,n are integers, now putting $Y'_{lmn}+D_1$ instead of Y we have $Y'_{lmn} = (-1)qX_{lmn}q^{-1}$ In the same way D_2 can be made to take the form $pA+qB+rC$ where $0 \leq p,q,r < 1$. Thus every symmetry relation implies a relation of the type

$\underline{Y \equiv (-1)^{\nu} q X q^{-1}}$ for the skeletal lattice, and of the type $\underline{Y \equiv (-1)^{\nu} q X q^{-1} + pA+qB+rC}$ for a component set, or for the whole system. If in addition the system has no relation of the type

$$Y \equiv (-1) q' X q'^{-1} + D' \quad \text{where } q'^{n} = q$$

the above relations are called the reduced symmetry relations of the skeletal lattice and of the system respectively.

Equivalent Points, Simple and multiple Systems.

A point system possesses in general m distinct reduced symmetry relations, m being always finite or there would be an infinite number of points in each component set. Of these m relations n only will be independent all the others can be derived from these m by combining them in different ways. To any point X there correspond the points $X_1, X_2, \ldots\ldots X_m$ to which it is related by the m relations, also the points $X_{m+1}, X_{m+2}, \ldots X_n$ derived from X by the m relations applied 2,3,...k times each(the values of k will be explained subsequently,) All the points $X_1, X_2, X_3,$ X_n. belong tp the same component set, they are called equivalent points.

If these are all the points in each component set, the point system is called simple. If there are other groups of equivalent points $/Y_r$ $/Z_r$ etc the system is called multiple. The groups $/X_r$, $/Y_r$ etc may have more but cannot have fewer symmetry elements than the system

. The group with the fewest symmetry elements determines the symmetry of the system. If $/X_r$ is such a group the other groups $/Y_r$, $/Z_r$ can be split up into partial groups $/_1Y_r$, $/_2Y_r$ etc. each with the symmetry of /X and derivable from each other by relations not included in the symmetry of $/X_r$. The whole system is now expressible as: the points X, $_1Y$, $_2Y$, ..., $_1Z$, $_2Z$, and their equivalent points making up a component set; and the points corresponding to all these points. The points X, $_1Y$, $_2Y$, ..., $_1Z$, $_2Z$, ... may be infinite in number and taken together make up a geometrical figure which is in genefal asymmetrical. For most purposes however it is sufficient to consider simple systems remembering that every point may represent an asymmetrical figure.

CHAPTER III

ROTATIONS

3.1 Symmetry of System and of Skeletal lattice.

It has been shown already that if a system has a symmetry relation $Y=(-1)^{v}qXq^{-1}+D$ the skeletal lattice has the relation $Y=(-1)^{v}qXq^{-1}$. Such relations not involving any constant vector are called rotations. They are in fact representable geometrically by a rotation of the whole system about the axis of q through twice its angle. Further we must have if $/\,Y=(-1)^{v_r}q_rXq_r^{-1}+D_r$ is the symmetry group of the system that the skeletal lattice possesses the group of rotations $/\,Y=(-1)^{v_r}q_rXq_r^{-1}$. We must therefore examine all the possible classes of groups of rotation that lattices can possess.

.2 Possible Rotations.

To begin with we need only consider the form $Y=qXq^{-1}$ for since the relation $Y\equiv -X$ holds for all lattices $Y=qXq^{-1}$ always implies $Y\equiv -qXq^{-1}$ and only those relations of the second kind which correspond to possible relations of the first can exist.

Writing q in the form A^{h} where A is a vector and h a scalar the general rotation becomes,

$$Y\equiv A^{h}XA^{-h}$$

The vector A is called the axis of the rotation.

This relation implies $Y=A^{mh}XA^{-mh}$ where m is an integer

But $Y\equiv A^{2n}XA^{-2n}$ i.e. $Y\equiv X$ is always a relation of the lattice.

Combining we have $Y = A^{mh+2n} X A^{-mh-2n}$

Now $\overline{mh+2n} \geq c$ where c is a finite positive scalar or $(X - Y)$ would not be a finite vector; h must therefore be rational

Writing h in the form $\frac{2}{k_1 + \frac{m}{n}}$ where k, m, n are integers and $n > m$

then $$k_1 h = \frac{2k_1}{k_1 + \frac{m}{n}} = 2 - \frac{2\frac{m}{n}}{k_1 + \frac{m}{n}}$$

$$2 - k_1 h = \frac{2}{\frac{k_1 n}{m} + 1} = \frac{2}{k_2 + 1 + \frac{m}{p}}$$ where p is an integer $> m$

and this must be a possible value of the index of A. Continuing the process we must arrive ultimately at a value $\frac{2}{k}$ since the value $\frac{2}{\infty}$ is inadmissible. The ~~symmetry~~ reduced general rotation now takes the form

$$\underline{Y = A^{\frac{1}{k}} X A^{-\frac{1}{k}}}$$

Such a rotation is called a k fold axis of symmetry because repeated k times it leaves the aspect of the lattice as it was to begin with.

.3 <u>Possible values of A and k.</u>

.31 From the conditions of symmetry we have

$$S.AY = S.AX$$
$$S.A(Y-X) = 0$$

but $(Y - X)$ must be a point of the lattice for all corresponding values of Y and X. This shows that in a plane through any point of the lattice perpendicular to any axis of symmetry there is a net of points of the
the lattice.

.32 Further let
$$X_1 = A^{\frac{1}{k}} X A^{-\frac{1}{k}}$$
$$X_2 = A^{\frac{2}{k}} X A^{-\frac{2}{k}}$$
$$\cdots\cdots\cdots$$
$$X_n = A^{\frac{n}{k}} X A^{-\frac{n}{k}}$$
$$X_r = A^{\frac{r}{k}} X A^{-\frac{r}{k}}$$

adding $$\Sigma X = A^{\frac{1}{k}} \Sigma X_r A^{-\frac{1}{k}}$$

this is only possible if $\Sigma X_r = pA$, but as the value of the tensor of A does not affect the symmetry relation, and ΣX_r is a point of the lattice A can always be chosen as a point of the lattice.

.33 Let X_1, X_2, X_3 be three points of the lattice satisfying the conditions $S.AX = S.AX = S.AX = 0$

$$X_2 = A^{\frac{2}{k}} X_1 A^{-\frac{2}{k}} \quad : \quad X_3 = A^{\frac{4}{k}} X A^{-\frac{4}{k}}$$

Rational values of p;q;r can always be found such that

$$pX_1 + qX_2 + rX_3 = 0$$

Multiplying throughout by X_2 and taking scalar products

$$pS.X_1X_2 + qX_2^2 + rS.X_3X_2 = 0$$

$$(p+r)X_2^2 \cos\frac{2\pi}{k} + qX_2^2 = 0 \quad \text{since } S.X_1X_2 = S.X_3X_2 = X_2^2 \cos\frac{2\pi}{k}$$

$$\cos\frac{2\pi}{k} = \frac{-q}{p+R}$$

$\cos\frac{2\pi}{k}$ is rational, it can only have the values

$-1, -\frac{1}{2}, 0, \frac{1}{2}, 1$ corresponding to the values

$2, 3, 4, 6, \infty$ of k, and these must be the only values that k can have. Excluding the identical relation $k = \infty$ we have the following theorem.

IN any lattice or point system there can only be axes of 2, 3, 4 or 6 fold symmetry. Such axes are known as diad, triad, tetrad and hexad axes respectively. The general rotatinn must now take one of the particular forms

$k = 2 \qquad Y = AXA^{-1}$

$\;\;= 3 \qquad Y = A^{\frac{2}{3}} X A^{-\frac{2}{3}}$

$\;\;= 4 \qquad Y = A^{\frac{1}{2}} X A^{-\frac{1}{2}}$

$\;\;= 6 \qquad Y = A^{\frac{1}{3}} X A^{-\frac{1}{3}}$

.4 Combinations of Rotations

We will first establish some trigonometrical formulae connecting angles between axes and their angles of rotation i.e. the angles $\frac{2\pi}{k}$

.41 Transform a rotation $Y = B^{\frac{1}{k}}XB^{-\frac{1}{k}}$ by the rotation $Y = A^{\frac{1}{k}}XA^{-\frac{1}{k}}$ this gives $Y = A^{\frac{1}{k}}B^{\frac{1}{k}}A^{-\frac{1}{k}}XA^{\frac{1}{k}}B^{-\frac{1}{k}}A^{-\frac{1}{k}} = (A^{\frac{1}{k}}BA^{-\frac{1}{k}})^{\frac{1}{k}}X(A^{\frac{1}{k}}BA^{-\frac{1}{k}})^{-\frac{1}{k}} = B'^{\frac{1}{k}}XB'^{-\frac{1}{k}}$

$B' = A^{\frac{1}{k}}BA^{-\frac{1}{k}}$ is called an axis equivalent to B. The angle between B And B′ is given by $\cos\theta = S.\bar{B}\bar{B}' = S.\bar{B}A^{\frac{1}{k}}\bar{B}A^{-\frac{1}{k}} = S.\bar{B}(\cos\frac{\pi}{k} + \bar{A}\sin\frac{\pi}{k})\bar{B}(\cos\frac{\pi}{k} + \bar{A}\sin\frac{\pi}{k})$ (where $\bar{A}, \bar{B}$ stands for versor A B) $= \cos^2\frac{\pi}{k} + \cos 2\phi\sin^2\frac{\pi}{k}$

$$\underline{\sin\frac{\theta}{2} = \sin\frac{\pi}{k}\sin\phi}$$

where ϕ is the angle AB

.42 Combining the two relations $Y = A^{\frac{1}{l}}XA^{-\frac{1}{l}}$ and $Y = B^{\frac{1}{m}}XB^{-\frac{1}{m}}$ we have $Y = A^{\frac{1}{l}}B^{\frac{1}{m}}XB^{-\frac{1}{m}}A^{-\frac{1}{l}} = C^{\frac{1}{n}}XC^{-\frac{1}{n}}$ where $C^{\frac{1}{n}} = A^{\frac{1}{l}}B^{\frac{1}{m}}$, writing the quaternions in full

$$(\cos\frac{\pi}{n} + \bar{C}\sin\frac{\pi}{n}) = (\cos\frac{\pi}{l} + \bar{A}\sin\frac{\pi}{l})(\cos\frac{\pi}{m} + \bar{B}\sin\frac{\pi}{m})$$

$$\underline{\cos\frac{\pi}{n} = \cos\frac{\pi}{l}\cos\frac{\pi}{m} + \cos\theta\sin\frac{\pi}{l}\sin\frac{\pi}{m}}$$ Where θ is the angle A

.43 Consider the two equivalent rotations $Y = A^{\frac{1}{n}}XA^{-\frac{1}{n}}$, $Y = B^{\frac{1}{n}}XB^{-\frac{1}{n}}$ Transforming the second by the first gives $Y = B'^{\frac{1}{n}}XB'^{-\frac{1}{n}}$ where $B' = A^{\frac{1}{n}}BA^{-\frac{1}{n}}$ A rotation $C^{\frac{1}{m}}$ may exist that transforms B′ into A and A into B.

Then $B' = C^{\frac{1}{m}}AC^{-\frac{1}{m}}$ and $B = C^{-\frac{1}{m}}AC^{\frac{1}{m}}$. From these we have

$B'-A = C^{\frac{1}{m}}(A-B)C^{-\frac{1}{m}}$

The angle between $(B'-A)$ and $(A-B) = \frac{2\pi}{m}$

$$\cos\frac{2\pi}{m} = \frac{-S(B'-A)(A-B)}{S(B'-A)S(A-B)}$$

$$= \frac{SA - SAB - SBA + SBB'}{S(A-B)}$$

$$= \frac{-1 + 2\cos\theta - \cos^2\frac{\pi}{n} - \cos 2\theta\sin^2\frac{\pi}{n}}{-2 + 2\cos}$$ where θ is the angle between A and B.

$$= 1 - \sin^2\frac{\pi}{n}(1 + \cos\theta)$$

That is $\sin\frac{\pi}{m} = \sin\frac{\pi}{n}\cos\frac{\theta}{2}$ or $\cos\frac{\theta}{2} = \frac{\sin\frac{\pi}{m}}{\sin\frac{\pi}{n}}$.

Giving m and n all allowable values for which $m > n$ we obtain all the possible values of $\cos\frac{\theta}{2}$ which are shown in the following table

	n=6	4	3	2	
m=6	1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{2}$	
4		1	$\frac{\sqrt{2}}{\sqrt{3}}$	$\frac{1}{\sqrt{2}}$	
3			1	$\frac{3}{4}$	
2				1	

from this we see that

6 fold axes cannot exist in different directions

4 fold axes must be at right angles

3 fold axes must intersect at angles of $\cos^{-1}\frac{\sqrt{2}}{\sqrt{3}}$ or the complementary a angle of $\cos^{-1}\frac{1}{\sqrt{3}}$

2 fold axes when equivalent must intersect at angles of $\frac{2\pi}{3}$ $\frac{\pi}{2}$ $\frac{\pi}{3}$

.5 Classes of Rotation groups; First Sort.

We are now in a position to consider the various classes into which groups of rotations of the first sort may be divided. These c classes will be designated for convenience of reference, by their Schoenflies symbols.

.51 Groups containing one rotation only. General type $Y \equiv A^{\frac{2}{k}} X A^{\frac{1}{k}}$

There are four classes $k = 2 \quad 3 \quad 4 \quad 6$

symbol $C_2 \quad C_3 \quad C_4 \quad C_6$

.52 Groups with one k fold and 2 fold axes only.

General type $Y = A^{\frac{1}{k}} X A^{-\frac{1}{k}}$ B_1, B_2 ? are equivalent axes. Any two

$Y = B_1 X B_1^{-1}$ of the axes A? B_1, B_2 B_k. canbe taken

$Y = B_2 X B_2^{-1}$ as the independent rotations of the

$Y \doteq B_k X B_k^{-1}$ group.

~~We have by substituting in~~ Transforming A by B we must obtain -A or they would be two k fold axes which is inadmissible in this type The angle ϕ between A and B must be $\frac{\pi}{2}$, and substituting in 3·41 we have $\sin\frac{\theta}{2} = \sin\frac{\pi}{n}$ $\theta = \frac{2\pi}{n}$

If k is of the form 2h, $B_{n+h} = -B_h$ there are only h distinct axes equivalent to B. In this case also the combined relations $A^{\frac{2}{k}}B$ give rise to h diad axes ~~distinct~~ $B'_1\ B'_2\ B'_h$ distinct from B_1 ?B_2 B_h

Now $A^{\frac{1}{k}}B'_1 = A^{\frac{2}{k}}B_1 = B_1$ so that B'_1 can be put in the form $B+B_1$

If k = 3 the combined relation $A^{\frac{1}{3}}B_1 = B_3$ so that there are only three equivalent diad axes and no more.

Here again there are four classes: $n = 2$ 3 4 6

symbol $D_2 = Q$ D_3 D_4 D_6

Q	Rotations	$Y \equiv AXA^{-1}$ $Y \equiv BXB^{-1}$ $Y \equiv CXC^{-1}$	With the conditions	$S.BC = S.CA = S.AB = 0$ $S.\overline{ABC} = -1$
D_4	"	$Y \equiv A^{\frac{1}{2}}XA^{-\frac{1}{2}}$ $Y \equiv BXB^{-1}$ $Y \equiv CXC^{-1}$ $Y \equiv (B+C)X(B+C)^{-1}$ $Y \equiv (B-C)X(B-C)^{-1}$	" " "	$S.AB = S.AC = S.BC = 0$ $B^2 = C^2$
D_3	"	$Y \equiv A^{\frac{2}{3}}XA^{-\frac{2}{3}}$ $Y \equiv BXB^{-1}$ $Y \equiv CXC^{-1}$ $Y \equiv DXD^{-1}$	" " "	$S.AB = S.AC = S.AD = 0$ $S.\overline{CD} = S.\overline{DB} = S.\overline{BC} = -\frac{1}{2}$ $B^2 = C^2 = D^2$ $B+C+D = 0$
D_6.	"	$Y \equiv A^{\frac{1}{3}}XA^{-\frac{1}{3}}$ $Y \equiv BXB^{-1}$ $Y \equiv CXC^{-1}$ $Y \equiv DXD^{-1}$ $Y \equiv (C+D)X(C+D)^{-1}$ $Y \equiv (D+B)X(D+B)^{-1}$ $Y \equiv (B+C)X(B+C)^{-1}$	" " "	Same asD

.53 More than one k fold axes ($k > 2$) . There are two classes: T with triad and diad axes; 0 with tetrad, triad and diad axes. Both have a set of four triad axes T_1, T_2, T_3, T_4 which are all equivalent and must by 343 and considerations of symmetry fulfil the conditions $S\bar{T}_1\bar{T}_2 = S\bar{T}_3\bar{T}_4 = S\bar{T}_1\bar{T}_3 = S\bar{T}_2\bar{T}_4 = S\bar{T}_1\bar{T}_4 = S\bar{T}_2\bar{T}_3 = -\frac{\sqrt{2}}{\sqrt{3}}$: $T_1^2 = T_2^2 = T_3^2 = T_4^2$: $T_1 + T_2 + T_3 + T_4 = 0$

In class T there are in addition only the three diad axes A, B, C related to T_1, T_2, T_3 ?T_4 by the rotations (written in their symmetrical form)

$$AT_1 - T_2A = AT_3 - T_4A = BT_1 - T_3B = BT_2 - T_4B = CT_1 - T_4C = CT_2 - T_3C = 0$$

$$T_1^{\frac{2}{3}}B - BT_1^{\frac{2}{3}} = T_1^{\frac{2}{3}}C - AT_1^{\frac{2}{3}} = T_1^{\frac{2}{3}}A - BT_1^{\frac{2}{3}} = T_2^{\frac{2}{3}}B - CT_2^{\frac{2}{3}} \quad T_2^{\frac{2}{3}}C + AT_2^{\frac{2}{3}} = T_2^{\frac{2}{3}}A + BT_2^{\frac{2}{3}} = 0$$

similarly for T_3 and T_4, from these we find $S.BC = S.CA = S.AB = 0$ $A^2 = B^2 = C^2$ also $T_1 = A+B+C$; $T_2 = A-B-C$; $T_3 = -A+B-C$; $T_4 = -A-B+C$. We have therefore for

T Rotations
$Y \equiv AXA^{-1}$
$Y \equiv BXB^{-1}$
$Y \equiv CXC^{-1}$
$Y \equiv (A+B+C)^{\frac{2}{3}}X(A+B+C)^{-\frac{2}{3}}$
$Y \equiv (A\ B\ C)^{\frac{2}{3}}X(A\ B\ C)^{-\frac{2}{3}}$
$Y \equiv (A+B\ C)^{\frac{2}{3}}X(A+B\ C)^{-\frac{2}{3}}$
$Y \equiv (A\ B+C)^{\frac{2}{3}}X(A\ B+C)^{-\frac{2}{3}}$

Class O differs by having A,B,C as tetrad axes and in consequenc has four more triad axes which by virtue of the relations $T_3 = A^{\frac{1}{4}} T_1 A^{-\frac{1}{4}}$ are the inverses of the original four. Also for the same reasons as D_4 it has three pairs of diad axes of the type B+C or $T_1 - T_2$ In all there are thirteen rotations any two of which may be chosen as independent if they are of different kinds.

$$
\begin{aligned}
Y &= A^{\frac{1}{4}} X A^{-\frac{1}{4}} \\
Y &= B^{\frac{1}{4}} X B^{-\frac{1}{4}} \\
Y &= C^{\frac{1}{4}} X C^{-\frac{1}{4}} \\
Y &= (A+B+C)^{\frac{1}{3}} X (A+B+C)^{-\frac{1}{3}} \\
Y &= (A+B+C)^{\frac{1}{3}} X (A\ B\ C)^{-\frac{1}{3}} \\
Y &= (A+B\ C)^{\frac{1}{3}} X (A+B\ C)^{-\frac{1}{3}} \\
Y &= (A\ B+C)^{\frac{1}{3}} X (A\ B+C)^{-\frac{1}{3}} \\
Y &= (B+C) X (B+C)^{-1} \\
Y &= (B-C) X (B-C)^{-1} \\
Y &= (C+A) X (C+A)^{-1} \\
Y &= (C-A) X (C-A)^{-1} \\
Y &= (A+B) X (A+B)^{-1} \\
Y &= (A-B) X (A-B)^{-1}
\end{aligned}
$$

There are no other classes of rotation groups of the first sort By 3.43 there are no other arrangements of triad and tetrad axes possibl than those of T and O and a lattice can only posses one hexad axis.

.6 Classes of Rotation groups: Second sort

The general rotation of the second sort is

$$Y \equiv A^{\frac{2}{k}} X A^{-\frac{2}{k}}$$

Combined with another relation of the second sort it gives fise to one of the first sort, so we need only consider classes containing second sort operations only, or those formed by combining with one of the classes of the first sort one rotation of the second sort. Further since the effect of combining $Y \equiv A^{\frac{2}{j}} X A^{-\frac{2}{j}}$ and $Y \equiv -A^{\frac{2}{k}} X A^{-\frac{2}{k}}$ to form $Y \equiv -A^{\frac{3}{k}} X A^{-\frac{3}{k}}$ is the same as that of combining $Y \equiv A^{\frac{2}{k}} X A^{-\frac{2}{k}}$ and $Y \equiv -X$ we need only consider the combinations of $Y \equiv -X$ with classes of the first sort ~~and~~, the combinations of $Y \equiv -A^{\frac{2}{k}} X A^{-\frac{2}{k}}$ with classes of the first sort which have no axis in the direction A . $Y \equiv -AXA^{-1}$ is the only second sort rotation which can be combined in this way because allt the others include a rotation of the first sort.*

.61 Second sort operations alone . General type . $Y \equiv -A^{\frac{2}{k}} X A^{-\frac{2}{k}}$

There are five classes	$k = \infty$	2	3	4	6
Symbol	C_i	C_s	C_{3i}	C_4'	C_{3h}

C_i	Rotations	$Y \equiv -X$	This is called a centre of symmetry.
C_s	"	$Y \equiv -AXA^{-1}$	" " " a plane of symmetry.
C_{3i}	"	$Y \equiv -A^{\frac{2}{3}} X A^{-\frac{2}{3}}$ $Y \equiv -X$ $Y \equiv A^{\frac{2}{3}} X A^{-\frac{2}{3}}$	
C_4'	"	$Y \equiv -A^{\frac{1}{2}} X A^{-\frac{1}{2}}$ $Y \equiv AXA^{-1}$	
C_{3h}	"	$Y \equiv -A^{\frac{1}{3}} X A^{-\frac{1}{3}}$ $Y \equiv -AXA^{-1}$ $Y \equiv A^{\frac{2}{3}} X A^{-\frac{2}{3}}$	

---

*Except in the case where the axis to which A is perpendicular is a diad axis. We have therefore also to consider the results of combining second class ~~operat~~ rotations with perpendicular diad axes.

.62 Combination of $Y \equiv -X$ with first sort, classes

Ten classes corresponding to C_2 C_3 C_4 C_6 Q D_2 D_4 D_6 T O

Symbol C_{2i} C_{3i} C_{4i} C_{6i} Q_i D_{3i} D_{4i} D_{6i} T_i O_i

One of these C_{3i} belongs also to the last set so that their are really only nine classes.

C_{2i}	Relations in addition to those of	C_2	$Y \equiv -X$ $Y \equiv -AXA^{-1}$
	Conditions as for C_n		
C_{3i}	" " "	C_3	$Y \equiv -X$ $Y \equiv A^{2/3}XA^{-2/3}$
C_{4i}	" " "	C_4	$Y \equiv -X$ $Y \equiv -AXA^{-1}$ $Y \equiv -A^{1/2}XA^{-1/2}$
C_{6i}	" " "	C_6	$Y \equiv -X$ $Y \equiv -AXA^{-1}$ $Y \equiv -A^{2/3}XA^{-2/3}$ $Y \equiv -A^{1/3}XA^{-1/3}$
Q_i	" " "	Q	$Y \equiv -X$ $Y \equiv -AXA^{-1}$ $Y \equiv -BXB^{-1}$ $Y \equiv -CXC^{-1}$
D_{3i}	" " "	D_3	$Y \equiv -X$ $Y \equiv -A^{2/3}XA^{-2/3}$ $Y \equiv -BXB^{-1}$ $Y \equiv -CXC^{-1}$ $Y \equiv -DXD^{-1}$
D_{4i}	" " "	D_4	$Y \equiv -X$ $Y \equiv -AXA^{-1}$ $Y \equiv -A^{1/2}XA^{-1/2}$ $Y \equiv -BXB^{-1}$ $Y \equiv -CXC^{-1}$ $Y \equiv -(B+C)X(B+C)^{-1}$ $Y \equiv -(B\ C)X(B\ C)^{-1}$
D_{6i}	" " "	D_6	$Y \equiv -X$ $Y \equiv -AXA^{-1}$ $Y \equiv -A^{2/3}XA^{-2/3}$ $Y \equiv -A^{1/3}XA^{-1/3}$ $Y \equiv -BXB^{-1}$ $Y \equiv CXC^{-1}$ $Y \equiv DXD^{-1}$ $Y \equiv (C+D)X(C+D)^{-1}$ $Y \equiv (D+B)X(D+B)^{-1}$ $Y \equiv (B+C)X(B+C)^{-1}$

T_h Relations in addition to those of T
conditions as for T

$Y \equiv -X$
$Y \equiv -AXA^{-1}$
$Y \equiv -BXB^{-1}$
$Y \equiv -CXC^{-1}$
$Y \equiv -(A+B+C)^{\frac{1}{3}}X(A+B+C)^{\frac{1}{3}}$ ETC.

O_h " " " " " " O

$Y \equiv -X$
$Y \equiv -AXA^{-1}$
$Y \equiv -BXB^{-1}$
$Y \equiv -CXC^{-1}$
$Y \equiv -(B+C)X(B+C)^{-1}$ ETC.

$Y \equiv -A^{\frac{1}{2}}XA^{-\frac{1}{2}}$ ETC.

$Y \equiv -(A+B+C)^{\frac{1}{3}}X(A+B+C)^{-\frac{1}{3}}$ ETC.

.63 Combination of Y BXB with rotations Y of the first sort

Four classes corresponding to C_2 C_3 C_4 C_6

Symbol C_{2v} C_{3v} C_{4v} C_{6v}

C_{2v} Relations inaddition to those of C_2

$Y \equiv -BXB^{-1}$
$Y \equiv -CXC^{-1}$

C_{3v} " " " " " C_3

$Y \equiv -BXB^{-1}$
$Y \equiv -CXC^{-1}$
$Y \equiv -DXD^{-1}$

C_{6v} " " " " " C_6

$Y \equiv -BXB^{-1}$
$Y \equiv -CXC^{-1}$
$Y \equiv -DXD^{-1}$
$Y \equiv -(C+D)X(C+D)^{-1}$
$Y \equiv -(D+B)X(D+B)^{-1}$
$Y \equiv -(B+C)X(B+C)^{-1}$

C_{4v} " " " " " C_4

$Y \equiv -BXB^{-1}$
$YY \equiv -CXC^{-1}$
$Y \equiv -(B+C)X(B+C)^{-1}$
$Y \equiv -(B-C)X(B-C)^{-1}$

The only other class of the first sort with no axes perpendicular to a k fold axis $(k > 2)$ is T. From this we have therefore one class T_d Relations in addition to Thoseof T

$Y \equiv -(B+C)X(B+C)^{-1}$
$Y \equiv -(B-C)X(B-C)^{-1}$
$Y \equiv -(C+A)X(C+A)^{-1}$
$Y \equiv -(C-A)X(C-A)^{-1}$
$Y \equiv -(A+B)X(A+B)^{-1}$
$Y \equiv -(A-B)X(A-B)^{-1}$

.64 Lastly we have to consider the classes which are the result of combining a diad axis $Y \equiv BXB^{-1}$ with with a rotation of the second sort $Y \equiv -A^{\frac{2}{k}}XA^{-\frac{2}{k}}$ where $S.AB = 0$ and $k > 2$. There are three classes

$k = 3 \quad 4 \quad 6$ AS $Y \equiv -A^{\frac{2}{3}}XA^{-\frac{2}{3}}$ itself possesses a centre of sym-

symbol $D_{3d} \quad D_{2d} \quad D_{3h}$ metry D_{3d} must have one and we have already dealt with it. There remain two new classes

D_{2d} whose rotations are

$$
\begin{aligned}
Y &\equiv -A^{\frac{1}{2}}XA^{-\frac{1}{2}} \\
Y &\equiv AXA^{-1} \\
Y &\equiv BXB^{-1} \\
Y &\equiv CXC^{-1} \\
Y &\equiv -(B+C)X(B+C)^{-1} \\
Y &\equiv -(B\ C)X(B\ C)^{-1}
\end{aligned}
$$

with the conditions

$$S.AB = S.AC = S.BC = 0$$

$$B^2 = C^2$$

D_{3h} " " "

$$
\begin{aligned}
Y &\equiv -A^{\frac{1}{3}}XA^{-\frac{1}{3}} \\
Y &\equiv A^{\frac{2}{3}}XA^{-\frac{2}{3}} \\
Y &\equiv BXB^{-1} \\
Y &\equiv CXC^{-1} \\
Y &\equiv DXD^{-1} \\
Y &\equiv -(C+D)X(C+D)^{-1} \\
Y &\equiv -(D+B)X(D+B)^{-1} \\
Y &\equiv -(B+C)X(B+C)^{-1}
\end{aligned}
$$

$$S.AB = S.AC = S.AD = 0$$

$$S.\overline{CD} = S.\overline{DB} = S.\overline{BC} = -\tfrac{1}{2}$$

$$B^2 = C^2 = D^2$$

$$B+C+D = 0$$

IN both these cases can be expressed alternatively with rotations $Y = -AXA^{-1}$ etc and $Y = (B+C)X(B+C)^{-1}$ etc . This is of some importance subsequently.

.7 We have now derived all the classes of both sorts into which groups of rotations can be divided. There are thirty two in all, if we include that class with no rotation but the identity relation $Y = X$ They are divided for reasons that will appear later into five "systems"

I. Triclinic system	C_1 , C_i
II. Monoclinic system	C_s , C_2 , C_{2h}
III. Orthorhombic system	C_{2v} , D_2 , D_{2h} or $Q + Q_h$
IV. Tetragonal system (a) tetrad axis 1st sort	C_4 , C_{4v} , C_{4h} , D_4 , D_{4h} .
(b) " " 2nd "	C_4' , D_{2d} .
V. Rhombohedral system	C_3 , C_{3i} , C_{3v} , D_3 , D_{3d} .

VI. Hexagonal system (a) Hexad axis 1st sort C_6, C_{6h}, C_{6v}, D_6, D_h .
(b) " " 2nd " C_{3h}, D_{3h} .

VII. Regular system T, T_h, T_d, O, O_h .

The classes C_i, C_{2h}, Q_h, D_{4h}, D_{3d}, D_{6h} O_h are called holohedral. Holohedral classes have all the rotations of both sorts that are in the other classes of the same system.

The classes C_2, Q, D_3, D_4, D_6, O . are called holoaxial . They c contain all the rotations of the first sort that are in the system.

The classes C_2, C_3, C_4, C_6, C_{2v}, C_{3v}, C_{4v}, C_{6v}, T, T_d and D_3 . are called hemimorphic . They all contain one sided axes, that is axes such as A, to which there corresponds no axis -A.

CHAPTER IV.

LATTICES

0 Types of symmetrical lattices.

We are now in a position to examine the number of types to to one of which any lattice must correspond. The symmetry of any lattice must be that of one of the thirty two classes, but the following considerations show that the choice of these is limited.

.01 In a lattice containing a K fold axis A, $(k > 2)$ let B be a primitive vector perpendicular to A such that no vector B also perpendicular to A exists making $B^2 > B'^2$. Then if $B_1 = A^{\frac{1}{k}} B A^{-\frac{1}{k}}$, $B_{-1} = A^{-\frac{1}{k}} B A^{\frac{1}{k}}$ the pairs B, B_1 and B_{-1}, B must be primitive vectors for the net perpendicular to A. Also since $B_1 = B\, B_{-1} B^{-1}\, B$ and likewise B_1 and B_{-1} must be diad axes for the net, further A, B, B_1 and $-A, B, B_{-1}$ are congruent reference systems which are related by a rotation about B so that B must be a diad axis of the lattice. From this we have the theorem
There are diad axes perpendicular to every triad, tetrad, and hexad axis of a lattice.

.02 Every lattice has a centre of symmetry $Y = -I$. Combining this with the symmetry axes of the lattice we have the theorem.
Perpendicular to every diad, tetrad, and hexad axis of a lattice there is a plane of symmetry and every triad axis is an axis of the second sort. From these two theorems we can see that the only classes of symmetry to which lattices can belong are the holohedral classes C_i, C_{2h}, Q_h, D_{4h}, D_{3d}, D_{6h}, O_h.

1 .C Let us begin with lattices whose class of symmetry is that of C_i This is the most general type and the choice of a suitable reference set is arbitrary so that we can always choose three primitive vectors a ,b ,c and write the formula of the lattice

$$\Gamma_{tr} \qquad \underline{/\ la + mb + nc}$$

Here and in the subsequent work the small letters a,b,c (d) are used exclusively to denote reference vectors; capitals A,B, being used in the general expressions for axes. The letters l,m,n,(o) will always represent integers, while p,q,r,(s) and u,v,w,(t) stand for rational fractions. The rotations of the various lattices are not given here , they are those of the class of symmetry to which the lattice belongs.

.2 C_{2h}

a can here be chosen to be the one diad axis while b and c can be chosen arbitrarily so as to be primitive vectors in the net perpendicular to a . The formula of the lattice is now /pa+qb+rc as a,b,c are not necessarily primitive vectors for the lattice. Now if p,q,r is a point of the lattice the rotation $Y = aXa^{-1}$ gives p,-q,-r, as an equivalent point. By subtraction we find that 2p,0,0 and 0,2q,2r must be points of the lattice. But by the choice of the reference set 1,0,0 and 0,m,n are points of the lattice. p,q,r, therefore must have the form $\frac{l}{2},\frac{m}{2},\frac{n}{2}$, When l is odd m and n cannot both be even, Now as b and c wre chosen arbitrarily in the first place we can always choose them so that either l,m,n are always even or so thatm is always even and l and m both even or both odd. Thus there are two types of lattice whose formulae may be written.

.21 $\Gamma_m \qquad /la + mb + nc$

.22 $\Gamma_m' \qquad /\frac{(l+m)}{2}a + \frac{(l-m)}{2}b + nc$

.3 Q_h a, b, c are here chosen along the three diad axes. Writing the formula of the lattice in the first place as / la+mb+nc. we can show exactly as in the previous case that the points 2pa , 2qb , 2rc belong to the lattice p, q, r, must have the form $\frac{l}{2}, \frac{m}{2}, \frac{n}{2}$. Here however as a, b, c are geometrically indistinguishable, there are four types $\Gamma_o, \Gamma_o', \Gamma_o'', \Gamma_o'''$ according as Γ_o, l, m, n are always even; Γ_o', l(say) is always even and m and n are both odd or both even; Γ_o'', two of the numbers are odd and the other is even or they are all even; Γ_o''' l, m, n are all odd or all even. The formulae of these are written

.31 Γ_o / $la + mb + nc$ With the conditions S.bc = S.ca = S.ab =

.32 Γ_o' / $la + \frac{m+n}{2}b + \frac{m-n}{2}c$

.33 Γ_o''' / $\frac{-l+m+n}{2}a + \frac{l-m+n}{2}b + \frac{l+m-n}{2}c$

.34 Γ_o'' / $\frac{m+n}{2}a + \frac{n+l}{2}b + \frac{l+m}{2}c$

.4 D_{4h} a is chosen along, the tetrad aaxs b and c along diad axes then either b and c are primitives or (b+c) and (b-c) are, but as these are also diad axes b and c can always be chosen as primitives. Since a is also a diad axis this is only a special case of Q_h but here there can be no types corresponding to Γ_o' and Γ_o'' because when l is even m and n must also be even, so that there are only two types: Γ_t l, m, n always even; Γ_t' l, m, n all odd or all even. their formulae are written as before

.41 Γ_t / $la + mb + nc$. with the conditions

S.ab = S.ac = S.bc = 0

.42 Γ_t' / $\frac{-lam+n}{2}a + \frac{l-m+N}{2}b + \frac{l+m-n}{2}c$ $b^2 = c^2$

.5 O_h a, b, c are chosen along the three tetrad axes, and since all three are diad axes as well, the case is similar tothat of Q_h except that in this case symmetry makes Γ_c' the same as Γ_c'' so that in this class there are three types only

.51 Γ_r / $la + mb + nc$. With the conditions

.52 Γ_r' / $\frac{m+n}{2}a + \frac{n+l}{2}b + \frac{l+m}{2}c$ $\quad S.bc = S.ca = S.ab = 0$

$a^2 = b^2 = c^2$

.53 Γ_r'' / $\frac{-l+m+n}{2}a + \frac{l-m+n}{2}b + \frac{l+m-n}{2}c$

.6 D_{3d} In this and the succeedimg class four reference vectors will be chosen , this is not strictly necessary but it exhibits the symmetry of the lattices. Whenever four vectors are taken the linear relation between them of the type $pA+qB+rC+sD=0$ imposes a relation of the type $tp+uq+vr+ws = 0$ upon the coordinates of any point If the coordinates satisfy such a relation there can be no ambiguity about them .

a is taken along the triad axis, b, c, d along the diad axes perpendicular to it. The formulae of the lattices can then be written Γ / $Pa+qb+rc4sd$ with the condition $q+r+s=0$. Inthe net /$qb+rc+sd$ any pair of b, c, d are primitives. Any point of the net is $mb+nc$ but to satisfy the condition we must add $t(a+b+c)=0$ so that $m+t+n+t+t=0$, 3t must be an integer. The most symmetrical expression that satisfies these conditions for points in the net is

$$/ \frac{2l-m-n}{3}b + \frac{-l+2m-n}{3}c + \frac{-l-m+2n}{3}d$$

with the condition $l+m+n=0$ Now by the rotation about a, there are the three corresponding points of the lattice p, q, r, s; p, s, q, r and p, r, s, q hence we must have the point 3p, (q+s+r), (r+q+s), (s+r+q) that is the point 3p, 0, 0, 0. Therefore $3p = 1$ an integer also by rotation about b there are the corresponding points

p,q,r,s, and $-p,q,r,s$; hence the point $0, 2q, (r+s), (s+r)$ and similarly the points $0,(s+q),2r,(q+s)$ and $0,(q+r),(r+q),2s$ and since these must be points of the net $/(2l-m-n)b/3 +$ q,r,s must be of the form $l/3, m/3, n/3$. Now ~~if~~ since $p+q+r+s0$ 0
$(2m-n-o)/3, (-m+2n-o)/3, (-m-n+2o)/3$
we may write q,r,s either as integers or as $(m-n)/3, (n-l)/3, (l-m)/$
This leads to two lattices: Γ_h written

.61 $$/la+(2m-n-o)b/3+(-m+2n-o)c/3+(-m-n+2o)d/3$$

For l must be an integer as the remainderof the expression is the formula of the net $l=0$;and Γ_{rh} written

.62 $$/(l+m+n)a/3+(m-n)b/3+(n-l)c/3+(l-m)d/3$$

.7 D_{6h} Every lattice with a hexad axis also has a triad oneso that the only type of lattice that can correspond to D_{6h} must be one of those corresponding to D_{3d} namely Γ_h and Γ_{rh} .Now in the class D_{6h} there are corresponding points p,q,r,s and $-p,q,r,s$; and hence the point $2p,0,0,0$. p must be of the form $1/2$ but p cannot at the same time be of the form $1/3$ unless p is an integer, and this is only thee case for Γ_h so that there is only one type of hexad latti

.8 This completes the number of possible lattices. There are fourteen in all and every lattice can be reduced to one of these.

CHAPTER V.

GENERAL SYMMETRY RELATIONS

.0 **Possible forms of the General Symmetry relation.**

Returning to the general symmetry relation which we may write

$$Y \equiv (-1)^{\nu} A^{\frac{1}{k}} X A^{-\frac{1}{k}} + C \quad \text{Where } k = \underset{\wedge}{\overset{\infty}{\,}}2, 3, 4 \text{ or } 6$$

we are now in a position to examine the possible values of the constant vector C and their significance.

.1 **Screw and Rotation Axes.**

Consider the the most general relation of the first sort written in the form $Y \equiv a^{\frac{1}{k}} X a^{-\frac{1}{k}} + ua + vb + wc$ where a, b, c are primitive vectors of the skeletal lattice. If the origin is on the axis a it can only be related to the points pa and consequently $v = w = 0$ and the relation takes the form

$$Y \equiv a^{\frac{1}{k}} X a^{-\frac{1}{k}} + ua$$

Repeating this k times we obtain

$$Y \equiv X + kua$$

u has one of the values $\frac{n}{k}$; but u must also have the value $m + \frac{n}{k}$ so that the value of n may always be made to lie between such limits as (i) $0 < n < k$ or (ii) $-\frac{k}{2} < 0 < \frac{k}{2}$

As it is always possible to chose one of the primitive vectors along any axis of the system the same argument applies to all axes, ~~and~~ ~~in general if if~~ so that we may write the general relation of the first sort in the form

$$Y \equiv (pa+qb+rc)^{\frac{1}{k}} X (pa+qb+rc)^{-\frac{1}{k}} + \frac{h}{k}(pa+qb+rc) + ua+vb+wc$$

where abc are the reference vectors of one of the 14 lattices h is an integer and $S.(pa+qb+rc)(ua+vb+wc) = 0$

.11 When h is not 0 such a relation is called a screw; if $h=0$ it is called as before a rotation. Consider the two screws $Y = a^{\frac{\ell}{k}}Xa^{\frac{\ell}{k}} + \frac{h}{k}a$ and $Y = a^{\frac{\ell}{k}}Xa^{-\frac{\ell}{k}} - \frac{h}{k}a$ where $h < \frac{k}{2}$. The second may be writte in the inverse form $Y = a^{-\frac{\ell}{k}}Xa^{\frac{\ell}{k}} + \frac{h}{k}a$ which shows that it differs from th first only in the sense of its rotation, if the sense of one is that a right handed screw the second is left handed, and vice versa. If however $k=2$ or $2h=k$ right and left handed screws are indistinguiable.

.12 When h is a factor of k the screw reduces to $Y = a^{\frac{\ell}{k}}Xa^{-\frac{\ell}{k}} + \frac{a}{k'}$, where $k'h = k$ Repeating k times we have $Y = a^{\frac{\ell}{h}}Xa^{-\frac{\ell}{h}} + a$, ther is a rotation $Y = a^{\ell}Xa^{-\frac{\ell}{k}}$.

The possible types of screws and rotations are given in the table[5] They are expressed as if the axis passed through the origin and with a primitive vector a as axis but this is only for convenience ssake.

.13 Types of screws and rotations.

General form $Y = a^{\frac{2}{k}} X a^{-\frac{2}{k}} + \frac{h}{k}a$

Particular forms

$k = 2$	$h = 0$		$Y = aXa^{-1}$					
	1		$Y = aXa^{-1} + a/2$					
		or	$Y = aXa^{-1} - a/2$					
$k = 3$	$h = 0$		$Y = a^{\frac{2}{3}}Xa^{-\frac{2}{3}}$					
	1		$Y = a^{\frac{2}{3}}Xa^{-\frac{2}{3}} + a/3$					
	2		$Y = a^{\frac{2}{3}}Xa^{-\frac{2}{3}} + 2a/3$					
		or	$Y = a^{\frac{2}{3}}Xa^{-\frac{2}{3}} - a/3$					
		or	$Y = a^{-\frac{2}{3}}Xa^{\frac{2}{3}} + a/3$					
$k = 4$	$h = 0$		$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}}$	Including	the	diad	axis	$Y = aXa^{-1}$
	1		$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}} + a/4$	"	"	"	screw	$Y = aXa^{-1} + a/2$
	2		$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}} + a/2$	"	"	"	axis	$Y = aXa^{-1}$
		or	$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}} - a/2$					
	3		$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}} + 3a/4$	"	"	"	screw	$Y = a\ Xa^{-1} + a/2$
		or	$Y = a^{\frac{1}{2}}Xa^{-\frac{1}{2}} - a/4$					
		or	$Y = a^{-\frac{1}{2}}Xa^{\frac{1}{2}} + a/4$					
$k = 6$	$h = 0$		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}}$	"	"	" triad	axis "	$Y = a\ Xa$
	1		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + a/6$	" diad	&	"	screws	$Y = a\ Xa + a/3$
	2		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + a/3$	diad axis	&	"	screw	$Y = a\ Xa + 2a/3$
	3		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + a/2$	" screw	&	"	axis	$y = a\ Xa$
		or	$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} - a/2$					
	4		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + 2a/3$	" axis	&	"	screw	$Y = a\ Xa + a/3$
		or	$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} - a/3$					
		or	$Y = a^{-\frac{1}{3}}Xa^{\frac{1}{3}} + a/3$					
	5		$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + 5a/6$	" screw	&	"	"	$Y = a\ Xa + 2a/3$
		or	$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} - a/6$					
		or	$Y = a^{-\frac{1}{3}}Xa^{\frac{1}{3}} + a/6$					

.2 Axes not throught the origin

We may now write tthe general relation of symmetry of the first sort in the form $Y \equiv A^{\frac{t}{k}}XA^{-\frac{t}{k}} + pA + B$ where $S.AB = 0$

Let us change the origin to a point C where $S.AC = 0$ If X and Y are the new values of X and Y then $X = X' + C$; $Y = Y' + C$ and the relation becomes

$$Y' + C \equiv A^{\frac{t}{k}}(X' + C)A^{-\frac{t}{k}} + pA + B$$

$$Y \equiv A^{\frac{t}{k}}XA^{-\frac{t}{k}} + pA\,A^{\frac{t}{k}}CA^{-\frac{t}{k}} - C + B$$

The axis passes throughthe new origin if

$$A^{\frac{t}{k}}CA^{-\frac{t}{k}} - C + B = 0$$

This equation gives the the position of any screw or rotation axis in terms of the constants of its symmetry relation.

An important particular case is when A is the reference vector a, and B takes the form $vb + wc$ $S.ba = S.ca = 0$

If also $a^{\frac{t}{k}}ba^{-\frac{t}{k}} = f_1b + g_1c$ $a^{\frac{t}{k}}ca^{-\frac{t}{k}} = f_2b + g_2c$ the equation for a point $xb + yc$ on the axi takes the form $x(f_1b + g_1c) + y(f_2b + g_2c) - xb - yc + vb + wc = 0$

which gives for x and y

$$(1 - f_1)x - fy = v$$
$$-g_1x + (1 - g_2)y = w$$

.3 Relations of the second sort

As before we may write the general relation of the second sort in the form

$$Y \equiv -A^{\frac{t}{k}}XA^{-\frac{t}{k}} + pA + B \qquad \text{where } S.AB = 0$$

Transferring the origin to the point $\frac{pA}{2} + B'$ $S.AB' = 0$

we have $$Y \equiv -A^{\frac{t}{k}}XA^{-\frac{t}{k}} - A^{\frac{t}{k}}BA^{-\frac{t}{k}} - B' + B$$

and if B′ is chosen to satisfy $A^{\frac{t}{k}}B'A^{\frac{t}{k}} + B' - B = 0$ this reduces to

$$Y \equiv -A^{\frac{t}{k}}XA^{-\frac{t}{k}}$$

Thus the general relation of the second sort, except in the particular case $k = 2$ reduces to a rotation of the second sort. whose centre is in general not the origin. In particular the general inversion $Y \equiv -X + B$ is a centre of symmetry at the point $\frac{B}{2}$

.31 Reflections and glide planes

In the case k = 2 the equation for the centre becomes

$$A B' A'^{-1} + B' - B = 0$$

$$-B' + B' + B = 0$$

From this equation we see that $B = \omega'$ and that in general the equation cannot be reduced any further than

$$Y \equiv -A X A^{-1} + B$$

This relation repeated once gives

$$Y \equiv X + 2B$$

B must take the form $\frac{1}{2}(pa+qb+rc)$ where $pa+qb+rc$ is a vector of the skeletal lattice, this may always be reduced to one of the forms $0,0,0$; $\frac{1}{2},0,0$ etc ; $\frac{1}{2},\frac{1}{2},0$ etc ; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$;or if p,q,r are of the form $\frac{l}{2}\ \frac{m}{2}\ \frac{n}{2}$ or $\frac{l}{3}\ \frac{m}{3}\ \frac{n}{3}$, to $\frac{1}{4},0,0$ etc or $\frac{1}{6},0\ ,0$ etc

If the ~~plane~~ relation can be reduced to the form $Y \equiv -AXA + \frac{1}{2}pA$ $\boxed{\text{where } S.AB = 0}$ it is called a plane reflection; if it reduces tothe form $Y\ -AXA + pA + B$ it is called a gliding-reflection; in either case the plane passes through the point $\frac{1}{2}pA$.

.4 Parameters of the general symmetry relation.

If the general relation be written in the form

$$Y \equiv (-1)^{v} A^{\frac{h}{k}} X A^{-\frac{h}{k}} + ua + vb + wc$$

u, v, w are called the parameters of the relation, they fix the type of the relation when the axis and rotation are given. The origin can always be chosen either to be on the axis of rotation or in the plane of rotation, which allows u, v, w to be given any desired values subject to certain restrictions; one for an axis, two for a plane, none for a centre of symmetry.

The symmetry of a point system is completely determined when the rotations and parameters of its symmetry relations are known i.e. if $/_r Y \equiv (1)^{v_r} A_r^{\frac{1}{k_r}} X A_r^{-\frac{1}{k_r}} + u_r a + v_r b + w_r c$ are known ~~choice of~~ the same origin being taken for all of them. A change of origin will give different values for the parameters but there are some invaria relations between them. Two particular cases are of special importance

.41 If three of the relations are of the form

$$Y \equiv a^{\frac{1}{k_1}} X a^{-\frac{1}{k_1}} + u_1 a + v_1 b + w_1 c \qquad \text{Where} \quad S.bc = S.ca = S.ab = 0$$
$$Y \equiv b^{\frac{1}{k_2}} X b^{-\frac{1}{k_2}} + u_2 a + v_2 b + w_2 c$$
$$Y \equiv c^{\frac{1}{k_3}} X c^{-\frac{1}{k_3}} + u_3 a + v_3 b + w_3 c .$$

Here it is easily seen that change of origin does not alter the values of the three quantities $u_2 - u_3$, $v_3 - v_1$, $w_1 - w_2$; and that any three parameters, one chosen from each of the pairs u_2, u_3; v_3, v_1; w_1, w_2 can be given any desired value.

.42 If the class of symmetry is hemimorphic and it has relations

$$Y \equiv a^{\frac{1}{k}} X a^{-\frac{1}{k}} + u_1 a + v_1 b + w_1 c \qquad \text{Where} \quad S.ab = S.ac = 0$$
$$Y \equiv -bXb^{-1} + u_2 a + v_2 b + w_2 c$$
$$Y \equiv -cXc^{-1} + u_3 a + v_3 b + w_3 c$$

here only $v_1 - v_2$ and $w_1 - w_3$ are unaltered by change of origin and only two of v_1, v_2; w_1, w_3; can be given any desired value.

.5 Relations between parameters

In general the set of parameters in any class of symmetry are not all independent, they are connected by relations and can be determined when some of them; usually one, two or three are known. As these can only have some few fractional values the number of of types of symmetry in any class is always finite. It is the purpose of the next ~~section~~ chapter to derive all these types, but itis first necessary to obtain in their most general form some of the relations connecting the parameters of different symmetry relations.

5 Relations with the same rotation

51 Parallel axes

Consider the symmetry relations

$$Y \equiv A^{\frac{s}{k}} X A^{-\frac{s}{k}} + hA/k + B \qquad \text{Where} \quad S.AB = S.AB' = 0$$
$$Y \equiv A^{\frac{s}{k}} X A^{-\frac{s}{k}} + h'A/k + B'$$

Subtracting we have $Y - Y = \left(\frac{h'-h}{k}\right)A + B' - B$. $\therefore$ $\left(\frac{h-h}{k}\right)A + B' - B$ must be a point of the skeletal lattice. In general $A = p_0a + q_0b + r_0c$ $\begin{array}{l} B = ua + vb + wc \\ B' = u'a + v'b + w'c \end{array}$

with the conditions $\begin{array}{l} \Sigma u p_0 a^2 + \Sigma (vr + wq) S.bc = 0 \\ \Sigma u' p_0 a^2 + \Sigma (v'r + w'q) S.bc = 0 \end{array}$

then if $pa+qb+rc$ represents a vector of the lattice, we have

$$\frac{h'-h}{k}(p_0a + q_0b + r_0c) + (u'-u)a + (v'-v)b + (w'-w)c = pa + qb + rc$$

which gives the three conditions

$$\frac{h'-h}{k}p_0 + u'-u = p \; ; \; \frac{h'-h}{k}q_0 + v'-v = q \; ; \; \frac{h'-h}{k}r_0 + w'-w = r \; .$$

An important particular case $p_0 = 1; q_0 = 0; r_0 = 0$: $S.ab = S.ac = 0$
$u' - u = 0$

$$\frac{h'-h}{k} = p \; ; \; v'-v = q \; ; \; w'-w = r \; ;$$

If p,q,r take the form l,m,n $h'-h = kl$; all parallel screw axes must have the same pitch.

.62 Parallel planes

Consider the planes

$Y \equiv -AXA^{-1} + ua + vb + wc$; $Y' \equiv -AXA^{-1} + u'a + v'b + w'c$. Subtracting and equating to a vector of the lattice we obtain

$$u'-u = p \; ; v'-v = q \; ; \; w'-w = r$$

In the particular case where $A = a$ and p,q,r. are l,m,n we see that parallel planes are all reflection or all glide planes and that they are placed at distances $\frac{1}{2}l$ apart.

.61 Centres of symmetry

Consider the two centres $Y \equiv -X + ua + vb + wc$; $Y \equiv -X + u'a + v'b + w'c$

subtracting and equating to a vector of the lattice we obtain

$$u' - u = p \; ; \; v' - v = q \; ; w' - w = r$$

there are centres of symmetry at all the points

$$/\tfrac{1}{2}(u+p)a + \tfrac{1}{2}(v+q)b + \tfrac{1}{2}(w+r)c$$

.7 Relations with different rotations

.71 Perpendicular axes

Consider the relations

$$Y \equiv a^{\frac{l}{k}} X a^{-\frac{l}{k}} + ha/k \qquad \text{Where } Sab = S.ac = 0$$

$$Y \equiv (qb+rc)X(qb+rc)^{-1} + ua + vb + wc$$

Transforming the first by the second we obtain

$$Y = a^{\frac{l}{k}} X a^{-\frac{l}{k}} + ha/k - a^{\frac{l}{k}}(vb+wc)a^{-\frac{l}{k}} + vb + wc.$$

subtracting the original relation and equating to a point of the latti

$$a^{\frac{l}{k}}(vb+wc)a^{-\frac{l}{k}} - vb - wc = pa + qb + rc$$

And if $a^{\frac{l}{k}} b a^{-\frac{l}{k}} = f_1 b + g_1 c$; $a^{\frac{l}{k}} c a^{-\frac{l}{k}} = f_2 b + g_2 c$ we have

$$v(f_1 - 1) + w f_2 = q$$
$$v g_1 + w(g_2 - 1) = r$$

.72 Axis and parallel plane

Consider the relations

$$Y = a^{\frac{l}{k}} X a^{-\frac{l}{k}} + ha/k$$

$$Y = -(qb+rc)X(qb+rc)^{-1} + ua + vb + wc \; .$$

transforming the first by the second we obtain

$$Y = a^{\frac{l}{k}} X a^{-\frac{l}{k}} - ha/k - a^{\frac{l}{k}}(vb+wc)a^{-\frac{l}{k}} + vb + wc$$

This is seen to be an screw of opposite pitch. Subtracting from the original relation and equating we have

$$2ha/k + a^{\frac{l}{k}}(vb+wc)a^{-\frac{l}{k}} - vb - wc = pa + qb + rc$$

If as before $a^{\frac{t}{k}}ba^{-\frac{t}{k}}=f_1b+g_1c$; $a^{\frac{t}{k}}ca^{-\frac{t}{k}}=f_2b+g_2c$ we have

$$2h=kp \ ; \ v(f_1-1)+wf_2=q \ ; \ vg_1+w(g_2-1)=r \ .$$

73 Axis and Centre of Symmetry.

Consider the relations

$$Y=a^{\frac{t}{k}}Xa^{-\frac{t}{k}}+ha/k+v_1b+w_1c \quad \text{where } S.ab=S.ac=0$$

$$Y=-X+u_2a+v_2b+w_2c$$

transforming the first by the second we obtain

$$Y=a^{\frac{t}{k}}Xa^{-\frac{t}{k}}-ha/k-a^{\frac{t}{k}}(v_2b+w_2c)a^{-\frac{t}{k}}+(v_2-v_1)b+(w_2-w_1)c$$

a screw of opposite pitch . subtracting and equating as before

$$2ha/k+(2v_1-v_2)b+(2w_1-w_2)c+a^{\frac{t}{k}}(v_2b+w_2c)a^{-\frac{t}{k}}=pa+qb+rc$$

as above this gives

$$2h=kp \ ; \ 2v_1+(g_1-1)v_2+f_2w_2=q \ ; \ 2w_1+g_1v+(g-1)w_2=r$$

In this and in the previous case if p is of the form 1 , h ½k

There

CHAPTER VI

TYPES OF POINT SYSTEMS

6.0 We are now in a position to to derive the possible types of symmetry of point systems in three dimensions. The plan adopted in the work is as follows.

The symmetry relations of every class are given in their general form. Where, however, any class is derived from another by the addition of symmetry relations, only these relations are given. The conditions connecting the parameters are then found, the origin is chosen and the possible reduced values of sugh parameters as are chosen to be independent determined. Corresponding to each permutation of these there is a type of symmetry but some of these types may be shown to be geometrially indistinguishable, and will not count as separate types. In general there are several lattices which include any class of symmetry. The types of symmetry corrseponding to these lattices will be derived in turn. The lattice whose formula may be written /la+mb+nc where a, b, c are axes of symmetry is dealt with first, to every type of symmetry which it gives rise to, there corresponds one for the other lattices of the same class, but here they are not all distinct.

The types are designated by their Schoenflies symbols even when the order of their derivation would suggest different notation.

In some cases the position and nature of axes and planes are given but these can always be obtained by   from the parameters The formulae of the various types of symmetry are reserved for a later chapter.

.1 **Triclinic Types**

Two classes C_1 and C_i one lattice Γ_{tr}

.11 C_1 only the identity relation $Y \equiv X+ua+vb+wc$ u, v, w always reducible to 0, 0, 0 . only one type C_1'

.12 C_i only the centre $Y \equiv -X+ua+vb+wc$ u, v, w always reducible to 0, 0, 0 . only one type C_i'

.2 **Monoclinic Types**

Three classes C_2, C_s, C_{2h}. Two lattices Γ_m and Γ_m'

.21 C_2 the axis $Y \equiv aXa^{-1}+ua+vb+wc$ The origin can always be chosen to make $v = w = 0$ By 5.1 $u = 0$ or $\frac{1}{2}$; 561 shows that for Γ_m $u = 0$ and $u = \frac{1}{2}$ give distinct types but that for Γ_m' $u = 0$ implies u $\frac{1}{2}$ so that there is only one type. In all there are the three types

C_2'	skeletal lattice	Γ_m	, parameters	0, 0, 0
C_2^2	"	" Γ_m	"	$\frac{1}{2}$, 0, 0
C_2^3	"	" Γ_m'	"	0, 0, 0, and $\frac{1}{2}$, 0, 0.

.22 C_s The plane Y -aXa +ua+vb+wc The origin can always be chosen to make μ 0 . v and w can have the values 0 or $\frac{1}{2}$. In band c have been chosen arbitrarily so that the values for v, w $\frac{1}{2}$, 0 ; 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$ are geometrically indistinguishable so that there are only two distinct types. In by 562 the values 0, 0 imply $\frac{1}{2}$, 0 but there are still two types since b and c are no longer arbitrary, and the values 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$ are distinct from the former pair. In all th ere are the four types

C_s'	skeletal lattice	Γ_m	, parameters	0, 0, 0
C_s^2	"	" Γ_m	"	0, $\frac{1}{2}$, 0
C_s^3	"	" Γ_m'	"	0, 0, 0 and 0, $\frac{1}{2}$, 0
C_s^4	"	" Γ_m'	"	0, 0, $\frac{1}{2}$ and 0, $\frac{1}{2}$, $\frac{1}{2}$

.23 C_{2h} Derived from C_2 by the addition of the centre

$Y \equiv -X+ua+vb+wc$ The origin can still be chosen so that $u=0$

By 5B we have for Γ_m $2v=1$; $2w=m$; and for Γ_m' $2u=\frac{1+m}{2}$; $2v=\frac{1-m}{2}$; $2w=n$ but since u cannot $=\frac{1}{4}$ these both give the same possible values for the parameters namely $0,0,0$; $0,\frac{1}{2},0$; $0,0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$. For Γ_m the last three are geometrically indistinguishable, for Γ_m' the first two and the last two imply each other. In all there are six types

C_{2h}^1	skeletal lattice	Γ_m,	derived from	C_2^1,	parameters	$0,0,0$
C_{2h}^4	"	"	"	C_2^1	"	$0,\frac{1}{2},0$
C_{2h}^2	"	"	"	C_2^2	"	$0,0,0$
C_{2h}^5	"	"	"	C_2^2	"	$0,\frac{1}{2},0$
C_{2h}^3	"	"	"	C_2^3	"	$0,0,0$ and $0,\frac{1}{2},0$
C_{2h}^6	"	"	"	C_2^3	"	$0,0,\frac{1}{2}$ " $0,\frac{1}{2},\frac{1}{2}$

.3 Orthorhombic Types.

Three classes Q, C_{2v}, Q_h ; four lattices

.31 Q Three axes $Y \equiv aXa^{-1}+ua+vb+wc$

$Y \equiv bXb^{-1}+ua+vb+wc$

$Y \equiv cXc^{-1}+ua+vb+wc$

Combining the three we obtain $Y \equiv abcXc^{-1}b^{-1}a^{-1}+(u_1+u_2-u_3)a+(v_1-v_2-v_3)b+(w_1-w_2+w_3)c$

and since $Uabc=-1$ we have

for	Γ_o	Γ_o'	Γ_o'''	Γ_o''
$u_1+u_2-u_3=$	1	1	$\frac{-1+m+n}{2}$	$\frac{m+n}{2}$
$-v_1+v_2+v_3=$	m	$\frac{m+n}{2}$	$\frac{1-m+n}{2}$	$\frac{n+1}{2}$
$w_1-w_2+w_3=$	n	$\frac{m-n}{2}$	$\frac{1+m-n}{2}$	$\frac{1+m}{2}$

we can always choose the origin to make $u_3=v_1=w_2=0$

u_1, v_2, w_3, can take the values 0 or $\frac{1}{2}$; here a,b,c are geometrically indistinguishable this leads to four types for Γ_o , for Γ_o' these reduce to two since the values 0,0,0 for u_1, v_2, w_3, implies the values 0,½,½ and the values ½,0,0 implies ½,½,½; for Γ_o'' allthe types reduce to one; for Γ_o''' there are again two types 0,0,0 implying ½,½,½, and ½,0,0 0,½,½, so that there are altogether nine types.

Q^1 skeletal lattice Γ_o, parameters $\begin{matrix}0, & 0, & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{matrix}$

Q^2 " " Γ_o " $\begin{matrix}\frac{1}{2} & 0 & 0\\ 0 & 0 & 0\\ \frac{1}{2} & 0 & 0\end{matrix}$

Q^3 " " Γ_o " $\begin{matrix}0 & \frac{1}{2}0 & 0\\ 0 & \frac{1}{2} & \frac{1}{2}\\ 0 & 0 & \frac{1}{2}\end{matrix}$

Q^4 " " Γ_o " $\begin{matrix}\frac{1}{2} & 0 & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & 0\\ 0 & \frac{1}{2} & \frac{1}{2}\end{matrix}$

Q^6 " " Γ_o' " $\begin{matrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{matrix}$ $\begin{matrix}\text{and}\\ \text{"}\\ \text{"}\end{matrix}$ $\begin{matrix}0 & \frac{1}{2} & \frac{1}{2}\\ 0 & \frac{1}{2} & \frac{1}{2}\\ 0 & \frac{1}{2} & \frac{1}{2}\end{matrix}$

Q^5 " " Γ_o' " $\begin{matrix}\frac{1}{2} & 0 & 0\\ 0 & 0 & 0\\ \frac{1}{2} & 0 & 0\end{matrix}$ $\begin{matrix}\text{"}\\ \text{"}\\ \text{"}\end{matrix}$ $\begin{matrix}\frac{1}{2} & \frac{1}{2} & \frac{1}{2}\\ 0 & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{matrix}$

Q^7 " " Γ_o'' " $\begin{matrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{matrix}$ $\begin{matrix}0 & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & 0 & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & 0\end{matrix}$ $\begin{matrix}\frac{1}{2} & 0 & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & 0\\ 0 & \frac{1}{2} & \frac{1}{2}\end{matrix}$ $\begin{matrix}\frac{1}{2} & \frac{1}{2} & 0\\ 0 & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & 0 & \frac{1}{2}\end{matrix}$

Q^8 " " Γ_o''' " $\begin{matrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{matrix}$ $\begin{matrix}\text{and}\\ \text{"}\\ \text{"}\end{matrix}$ $\begin{matrix}\frac{1}{2} & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{matrix}$

Q^9 " " Γ_o''' " $\begin{matrix}0 & 0 & \frac{1}{2}\\ \frac{1}{2} & 0 & 0\\ 0 & \frac{1}{2} & 0\end{matrix}$ $\begin{matrix}\text{"}\\ \text{"}\\ \text{"}\end{matrix}$ $\begin{matrix}\frac{1}{2} & \frac{1}{2} & 0\\ 0 & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & 0 & \frac{1}{2}\end{matrix}$

From these parameters we can see that

Q^1 has three intersecting diad axes; Q^2 has one diad screw meeting both of two non intersecting diad axes; Q^3 has one diad axis passing through the centres of the ~~squares~~ rectangles formed by two intersecting diad screws; Q^4 hasthree non intersecting diad screws; Q^5 is a combination of Q^1 and Q

Q^6 of Q^1 and Q^3; Q^7 combines all the types $Q^1.Q^2,Q^3,Q^4$; Q^8 combines Q^1 and Q^5 Q^9, Q^2 and Q^4.

.32 C_{2v} An axis and two planes

$$Y = aXa^{-1}+u_1a+v_1b+w_1c$$

$$Y = -bXb^{-1}+u_2a+v_2b+w_2c$$

$$Y = -cXc^{-1}+u_3a+v_3b+w_3c$$

Combining the three we obtain $Y = abcXc^{-1}b^{-1}a^{-1}+(u_1+u_2+u_3)a+(v_1-v_2+v_3)b+(w_1+w_2-w_3)c$ and since $Uabc=-1$ we have ; for

	Γ_o	Γ_o'	Γ_o''	Γ_o'''	$\Gamma_{o\beta}'$
$u_1+u_2+u_3$	L	l	$\frac{m+n}{2}$	$\frac{-l+m4n}{2}$	$\frac{l+n}{2}$
$v_1-v_2+v_3$	m	$\frac{m+n}{2}$	$\frac{n+l}{2}$	$\frac{l-m+n}{2}$	m
$w_1+w_2-w_3$	n	$\frac{m-n}{2}$	$\frac{l+m}{2}$	$\frac{l+m-n}{2}$	$\frac{l-n}{2}$

we can always choose the origin to make $u_1=w_1=0$

u_2,u_3,w_2,v_3; can take the values 0 or $\frac{1}{2}$. For Γ_o permutations of these lead to 16 types but since b and c are indistinguishable 6 pairs of t these types are likewise, leaving only 10 distinct types . For Γ_o' as a, b and c are no longer indistinguishable there are two divisions according as we write Γ_o as $/la+\frac{m+n}{2}b+\frac{m-n}{2}c$ or as $\overset{\Gamma_{o\beta}'}{\wedge}$ $/\frac{l+n}{2}a+mb+\frac{l-n}{2}c$. In each of these divisions several sets of types corresponding to the 10 above imply each other which reduces the number to 3 in the first and 4 in the second division. For Γ_o'' the number is reduced to two and for Γ_o''' to three types. In all there are 22 types which are set forth, with their parameters in the following table.

				u	v	w				
C_{2v}^{1}	lattice	Γ_o,	parameters	0	0	0				
				0	0	0				
				0	0	0				
C_{2v}^{2}	"	"	"	½	0	0				
				½	0	0				
				0	0	0				
C_{2v}^{3}	"	"	"	0	0	0				
				½	0	0				
				½	0	0				
C_{2v}^{4}	"	"	"	0	0	0				
				0	½	0				
				0	½	0				
C_{2v}^{7}	"	"	"	½	0	0				
				½	½	0				
				0	½	0				
C_{2v}^{5}	"	"	"	½	0	0				
				½	0	½				
				0	0	½				
C_{2v}^{6}	"	"	"	0	0	0				
				½	½	0				
				½	½	0				
C_{2v}^{8}	"	"	"	0	0	0				
				0	½	½				
				0	½	½				
C_{2v}^{9}	"	"	"	½	0	0				
				½	½	½				
				0	½	½				
C_{2v}^{10}	"	"	"	0	0	0				
				½	½	½				
				½	½	½				
C_{2v}^{11}	"	Γ_o'	"	0	0	0	and	0	½	½
				0	0	0	"	0	½	½
				0	0	0	"	0	½	½
C_{2v}^{12}	"	"	"	½	0	0	"	½	½	½
				½	0	0	"	½	½	½
				0	0	0	"	0	½	½.
C_{2v}^{13}	"	"	"	0	0	0	"	0	½	½
				½	0	0	"	½	½	½
				½	0	0	"	½	½	½

C_{2v}^{14}	lattice	$\Gamma_{o\rho}'$	parameters	0 0 0 and ½ 0 ½ 0 0 0 " 0 0 0 0 0 0 " ½ 0 ½
C_{2v}^{15}	"	$\Gamma_{o\rho}'$	"	0 0 0 " ½ 0 ½ ½ 0 0 " ½ 0 0 ½ 0 0 " 0 0 ½
C_{2v}^{16}	"	$\Gamma_{o\rho}'$	"	0 0 0 " ½ 0 ½ 0 ½ 0 " 0 0 0 0 ½ 0 " ½ ½ ½
C_{2v}^{17}	"	$\Gamma_{o\rho}'$	"	0 0 0 " ½ 0 ½ ½ ½ 0 " ½ ½ 0 ½ ½ 0 " 0 ½ ½
C_{2v}^{18}	"	Γ_a''	"	0 0 0 " 0 ½ ½ and ½ 0 ½ and ½ ½ 0 0 0 0 " ½ 0 ½ 0 0 0 " ½ ½ 0
C_{2v}^{19}	"	Γ_o''	"	0 0 0 " 0 ½ ½ " ½ 0 ½ " ½ ½ 0 ¼ ¼ ¼ ¼ ¾ ¾ " ¼ ¾ ¼ " ¼ ¼ ¾
C_{2v}^{20}	"	Γ_o''	"	0 0 0 " ½ ½ ½ 0 0 0 " ½ ½ ½ 0 0 0 " ½ ½ ½
C_{2v}^{21}	"	Γ_o''	"	0 0 0 " ½ ½ ½ ½ 0 0 " 0 ½ ½ ½ 0 0 " 0 ½ ½
C_{2v}^{22}	"	Γ_o''	"	0 0 0 " ½ ½ ½ 0 ½ 0 " ½ 0 ½ 0 ½ 0 " ½ 0 ½

.33 Q_h Derived from Q by the addition of the centre of symmetry

$$Y = -X + ua + vb + wc$$

By 5·73 we have the possible values of u.v.w are 0,0,0;½,0,0;0,½,0;0,0,½; 0,½,½;½,0,½;½,½,0;½,½,½. Except in types derived from Q_7 For Q' since a,b,c are equivalent this reduces to four types. For Q^2 ~~0,0?0 & 0,½,½,~~ 0,0,0, & ½,0,0, ; 0,½,0 & ½,0,½ ; 0,0,½ & ½,½,0 ; 0,½,½ & ½,½,½ give rise to indististinguishable types leaving four.

For Q^3 0,½,0 & 0,0,½ and ½,½,0 & ½,0,½ do the same leaving six types.

For Q^4 0,0,0 & ½,½,½ and ½,0,0 ....0,½,½ give rise to indistinguishable types leaving only two.

For Q^5 and Q^6 by 5·63 0,0,0 implies 0,½,½ ; ½,0,0 ½,½,½ ; 0,½,0 0,0,½ and ½,½,0 ½,0,½ also in Q^5 0,0,0 & ½,0,0 and 0,½,0 & ½,½,0 give rise to indistinguishable types but they do not do so in Q^6 so that four types correspond to the ~~former~~ latter and only two to the former.

For Q^7 by 5·63 0,0,0, imply 0,¼,½ ;¼,0,¼ ;¼,¼,0 and ¼,¼,¼;¼,0,0 ;0,¼,0;0,0,¼ so that there are only two types.

For Q^8 and Q^9 by 5·63 0,0,0 implies ½,½,½ ; ½,0,0 0,½,½ ; etc and as the last three give rise to indistinguishable types these are only two types corresponding to each of Q^8 and Q^9.

Inall there are 28 types

Q_h^1	lattice	Γ_o	derived	from	Q^1	parameters	0 0 0
Q_h^2	"	"	"	"	Q^1	"	½ ½ ½
Q_h^3	"	"	"	"	Q^1	Q	½ 0 0
Q_h^4	"	"	"	"	Q^1	"	0 ½ ½
Q_h^5	"	"	"	"	Q^2	"	0 0 0
Q_h^6	"	"	"	"	Q^2	"	½ ½ ½
Q_h^7	"	"	"	"	Q^2	"	0 ½ 0
Q_h^8	"	"	"	"	Q^2	"	0 0½½

Q_h^9	lattice	Γ_o	derived	from	Q^3	parameters	0 0 0
Q_h^{10}	"	"	"	"	Q^3	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
Q_h^{11}	"	"	"	"	Q^3	"	$\frac{1}{2}$ 0 0
Q_h^{12}	"	"	"	"	Q^3	"	0 $\frac{1}{2}$ 0
Q_h^{13}	"	"	"	"	Q^3	"	0 $\frac{1}{2}$ $\frac{1}{2}$
Q_h^{14}	"	"	"	"	Q^3	"	$\frac{1}{2}$ $\frac{1}{2}$ 0
Q_h^{15}	"	"	"	"	Q^4	"	0 0 0
Q_h^{16}	"	"	"	"	Q^4	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
Q_h^{17}	"	Γ_o'	"	"	Q^5	"	0 0 0
Q_h^{18}	"	"	"	"	Q^5	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
Q_h^{19}	"	"	"	"	Q^6	"	0 0 0
Q_h^{20}	"	"	"	"	Q^6	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
Q_h^{21}	"	"	"	"	Q^6	"	0 $\frac{1}{2}$ 0
Q_h^{22}	"	"	"	"	Q^6	"	$\frac{1}{2}$ 0 $\frac{1}{2}$
Q_h^{23}	"	Γ_o''	"	"	Q^7	"	0 0 0
Q_h^{24}	"	"	"	"	Q^7	"	$\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$
Q_h^{25}	"	Γ_o'''	"	"	Q^8	"	0 0 0
Q_h^{26}	"	"	"	"	Q^8	"	$\frac{1}{2}$ 0 0
Q_h^{27}	"	"	"	"	Q^9	"	0 0 0
Q_h^{28}	"	"	"	"	Q^9	"	$\frac{1}{2}$ 0 0

.4 Tetragonal Types

Seven classes $C_4, C_4', C_{4h}, D_4, D_4', C_{4v}, D_{4h}$. Two lattices Γ_t and Γ_t'.

.41 C_4 The axis $Y \equiv a^t X a^{-t} + ua + vb + wc$. The origin can always be chosen to make $v = w = 0$. u can have the values $0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ (the relations they represent are called tetrad axis, right, neutral, and left tetrad screws respectively) By 5·6 we have for Γ_t $u' - u = 1$ for Γ_t' $u' - u = \frac{1}{2}$ so that for Γ_t there are four classes and for Γ_t' two. The position of the tetrad axes are given by 5·2, here $f_1 = g_2 = 0$ $g_1 = 1$ $f_2 = -1$ so that the coordinates of a point on the axis are given by $x + y = v$; $x - y = w$ for Γ_t this gives $x = \frac{M+n}{2}$ $y = \frac{m-n}{2}$; for Γ_t' $x = \frac{1}{2}m$ $y = \frac{1}{2}n$ but here if m and n are both odd or even, the pitch of the axis differs by $\frac{1}{2}$ from that which passes throug a point where one is odd and the other even. The tetrad axis implies the diad axis $Y \equiv aXa^{-1} + 2ua$ and we have from 5·2 that these must pass through the points $\frac{1}{2}m, \frac{1}{2}n$ for Γ_t and $\frac{m+n}{4}, \frac{m-n}{4}$ for Γ_t'; being all of the same kind in the first case and alternately rotation or screw axes in the second

In all there are six types

C_4^1	lattice	Γ_t	parameters	0 0 0	
C_4^2	"	"	"	$\frac{1}{4}$ 0 0	
C_4^3	"	"	"	$\frac{1}{2}$ 0 0	
C_4^4	"	"	"	$\frac{3}{4}$ 0 0	
C_4^5	"	Γ_t'	"	0 0 0	and $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
C_4^6	"	"	"	$\frac{1}{4}$ 0 0	" $\frac{3}{4}$ $\frac{1}{2}$ $\frac{1}{2}$

.42 C_4' the axis $Y \equiv -a^t X a^{-t} + ua + vb + wc$. The origin can always be chosen to make $u = v = w = 0$ so that there are only two types one derived from Γ_t and one from Γ_t'. By subtracting $Y \equiv -a^t X a^{-t}$ we have $u, v, w = l, m, n$ for Γ_t and $\frac{-L+m+n}{2}$, $\frac{l-m+n}{2}$, $\frac{l+m-n}{2}$ for Γ_t'. By §2 this shows that th centres of the set of alternating tetragonal axes are at the points $\frac{l}{2}, \frac{m+n}{2}, \frac{m-n}{2}$ in the first case and $\frac{-l+m+n}{2}$, $\frac{1}{2}$, $\frac{m-n}{2}$ in the second.

There are two types

$C_4'^1$ lattice Γ_t parameters 0 0 0

$C_4'^2$ " Γ_t' " 0 0 0 and $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

.43 C_{4h} Derived from C_4 by the addition of the centre of symmetry

$Y \equiv -X + u_1a + v_1b + w_1c$ The origin gan be chosen to make u=0 Since by §3 a centre of symmetry trans_forms right into left handed screws types of this class can only be derived from the types $C_4^1, C_4^3, C_4^5, C_4^6$ we have also the conditions: for

	Γ_t	Γ_t'
$2u_1 =$	l	$\frac{-l+m+n}{2}$
$v_1 + w_1 =$	m	$\frac{l-m+n}{2}$
$v_1 - w_1 =$	n	$\frac{l+m-n}{2}$

v and w may have the values 0,0 or $\frac{1}{2}, \frac{1}{2}$ but for C_4^5 since u is 0 or $\frac{1}{2}$ v,w can only be 0,0 while for C since u is $\frac{1}{4}$ or $\frac{3}{4}$, v,w can only be $\frac{1}{2}, \frac{1}{2}$. There are in all six types.

C_{4h}^1 lattice Γ_t derived from C_4^1, parameters 0 0 0

C_{4h}^3 " Γ_t " " C_4^1 " 0 $\frac{1}{2}$ $\frac{1}{2}$

C_{4h}^2 " Γ_t " " C_4^3 " 0 0 0

C_{4h}^4 " Γ_t " " C_4^3 " 0 $\frac{1}{2}$ $\frac{1}{2}$

C_{4h}^5 " Γ_t' " " C_4^5 " 0 0 0

C_{4h}^6 " Γ_t' " " C_4^6 " 0 $\frac{1}{2}$ $\frac{1}{2}$

4 D_4 five axes

$$\begin{array}{ll}
Y \equiv a^{\frac12}Xa^{-\frac12}+ua & 1\\
Y \equiv bXb \;+u_1a+v_1b+w_1c & 2\\
Y \equiv cXc \;+u_2a+v_2b+w_2c & 3\\
Y \equiv (b+c)x(b+c) \;+u_3a+v_3b+w_3c & 4\\
Y \equiv (b-c)X9b-c) \;+u_4a+v_4b+w_4c & 5
\end{array}$$

The parameters are connected by several conditions

Transforming 2 by 1 we obtain $Y \equiv cXc^{-1}+(2u+u_1)a-w_1b+v_1c$ but this may be the same as 3 and we have $u_2=u_1+2u$; $v_2=-w_1$; $w_2=v_1$.

similarly for 4 and 5 $u_4=u_3-2u$; $v_4=w_3$; $w_4=-v_1$

Combining 1, 2, and 4 we have since $a^{\frac12}b(b+c)X(b+c)^{-1}b^{-1}a^{-\frac12}\equiv X$

	For Γ_4	Γ_4'
$u - u_3 + u_1$	1	$\frac{-1+m4n}{2}$
$v_3+ + v_1$	m	$\frac{1-m+n}{2}$
$w_3 - w_1$	n	$\frac{1+m-n}{2}$

The equivalent parameters u_3, v_3, w_3 and u_3, v_3+1, w_3 or u_3, v_3, w_3+1 represent different axes

By 5.71 we have for Γ_4 $v = \frac{m+n}{2}$; $w = \frac{m-n}{2}$ for Γ_4' $v = \frac{1}{2}$; $w = \frac{m-n}{2}$ but by 5.61 the values 0, 0, 0 for u, v, w, imply the values $\frac12, \frac12, \frac12$ so that these can only give rise to one case. There correspond~~s~~ ~~xxx~~ two types of this class to each of the ~~classes~~ types $C_4^1, C_4^2, C_4^3, C_4^4$, and one to the types C_4^5, C_4^6; making 10 in all

D_4^1 lattice Γ_4 parameters

$$\begin{array}{cccc}
0 & 0 & 0 & 0\\
 & 0 & 0 & 0\\
 & 0 & 0 & 0\\
 & 0 & 0 & 0
\end{array}$$

D_4^2 " " "

$$\begin{array}{cccc}
0 & 0 & \frac12 & \frac12\\
 & 0 & \frac12 & \frac12\\
 & 0 & \frac12 & \frac12\\
 & 0 & \frac12 & \frac12
\end{array}$$

D_4^3 " " "

$$\begin{array}{cccc}
\frac14 & 0 & 0 & 0\\
 & \frac12 & 0 & 0\\
 & \frac14 & 0 & 0\\
 & \frac34 & 0 & 0
\end{array}$$

D_4^4 " " "

$$\begin{array}{cccc}
\frac14 & 0 & \frac12 & \frac12\\
 & \frac12 & \frac12 & \frac12\\
 & \frac14 & \frac12 & \frac12\\
 & \frac34 & \frac12 & \frac12
\end{array}$$

D_4^5 lattice Γ_t parameters $\frac{1}{2}\begin{array}{ccc}0&0&0\\0&0&0\\\frac{1}{2}&0&0\\\frac{1}{2}&0&0\end{array}$

D_4^6 " " " $\frac{1}{2}\begin{array}{ccc}0&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{array}$

D_4^7 " " " $\frac{3}{4}\begin{array}{ccc}0&0&0\\\frac{1}{2}&0&0\\\frac{3}{4}&0&0\\\frac{1}{4}&0&0\end{array}$

D_4^8 " " " $\frac{3}{4}\begin{array}{ccc}0&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{3}{4}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{4}&\frac{1}{2}&\frac{1}{2}\end{array}$

D_4^9 " Γ_t' . " $0\begin{array}{ccc}0&0&0\\0&0&0\\0&0&0\\0&0&0\end{array}\begin{array}{c}\text{and}\\''\\''\\''\end{array}\frac{1}{2}\begin{array}{ccc}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{array}$

D_4^{10} " " " $\frac{1}{4}\begin{array}{ccc}0&0&0\\\frac{1}{2}&0&0\\\frac{1}{4}&0&0\\\frac{3}{4}&0&0\end{array}\begin{array}{c}''\\''\\2\\''\end{array}\frac{3}{4}\begin{array}{ccc}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\\\frac{3}{4}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{4}&\frac{1}{2}&\frac{1}{2}\end{array}$

.45 D_{2d} three axes and two planes

$$Y = -a^{\frac{1}{2}}Xa^{-\frac{1}{2}}$$

$$\begin{aligned}Y &= bXb \quad +u_1a+v_1b+w_1c\\ Y &= cXc \quad +u_2a+v_2b+w_2c\end{aligned}$$

$$\begin{aligned}Y &= -(b+c)X(b+c) \quad +u_3a+v_3b+w_3c\\ Y &= -(b-c)X(b-c) \quad +u_4a+v_4b+w_4c\end{aligned}$$

The relations of this class can also be written ina form where diad axes and planes change places each of these ways give rise to distinct types; it is more comvenient however to consider them derived from the above relations with skeletal lattices $\Gamma_t, \Gamma_t' \Gamma_{t\beta}$ written $/la+\frac{m+n}{2}b+\frac{m-n}{2}c$ and $\Gamma_{t\beta}'$ written $/\frac{m+n}{2}a+\frac{n+l}{2}b+\frac{l+m}{2}c$.

As in D we obtain the conditions $\begin{array}{lll}u_2=-u\ ; & v_2=w_1\ ; & w_2=-v_1\\ u_4=u\ ; & v_4\ -w_3; & w_4=v_3\end{array}$

Combining 1,2,3,4 we have:

$$\begin{array}{lcccc} \text{for} & \Gamma_t & \Gamma_t^{\prime} & \Gamma_t^{\beta} & \Gamma^{\prime\beta} \\ & u_3 - u_1 = l & \frac{-l+m+n}{2} & l & \frac{m+n}{2} \\ & v_3 + v_1 = m & \frac{l-m+n}{2} & \frac{m+n}{2} & \frac{n+l}{2} \\ & w_3 - w_1 = n & \frac{l+m-n}{2} & \frac{m-n}{2} & \frac{l+m}{2} \end{array}$$

As in D_4 equivalent parameters u,v,w and u, v+1, w represent different kinds of plane. The actual arrangement of axes and planes can be seen by considering the arrangement in the corresponding types of Q and C.

By 5.71 we have:

$$\begin{array}{lcccc} \text{for} & \Gamma_t & \Gamma_t^{\prime} & \Gamma_t^{\beta} & \Gamma_t^{\prime\beta} \\ & v_1 = \frac{m+n}{2} & \frac{l}{2} & \frac{m}{2} & \frac{2l+m+n}{2} \\ & w_1 = \frac{m-n}{2} & \frac{m-n}{2} & \frac{n}{2} & \frac{m-n}{2} \end{array}$$

and by $u_1 = \frac{l}{2}$

For Γ_t Γ_t^{β} since u_1, v_1, can have the values 0,$\frac{1}{2}$ there are four types each for Γ_t the values 0,0 and $\frac{1}{2}$,$\frac{1}{2}$, 0,$\frac{1}{2}$, and $\frac{1}{2}$,0 imply each other so that there are only two, for $\Gamma_t^{\prime\beta}$ so do 0,0 and 0,$\frac{1}{2}$; $\frac{1}{2}$,0 and $\frac{1}{2}$,$\frac{1}{2}$ so that again there are only two.

In all there are twelve types (only the parameters $\begin{matrix} u_1, v_1, w_1, \\ u_3, v_3, w_3 \end{matrix}$ are given)

D_{2d}^{1} lattice Γ_t corresponding to $Q^{1}\,C_{2v}^{11}$ parameters $\begin{matrix}0&0&0\\0&0&0\end{matrix}$

D_{2d}^{2} " " " $Q^{1}\,C_{2v}^{13}$ " $\begin{matrix}\frac{1}{2}&0&0\\\frac{1}{2}&0&0\end{matrix}$

D_{2d}^{3} " " " $Q^{3}\,C_{2v}^{11}$ " $\begin{matrix}0&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\end{matrix}$

D_{2d}^{4} " " " $Q^{3}\,C_{2v}^{13}$ " $\begin{matrix}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$

D_{2d}^{5} " Γ_t^{β} " $Q^{6}\,C_{2v}^{1}$ " $\begin{matrix}0&0&0\\0&0&0\end{matrix}$ and $0\ \frac{1}{2}\ \frac{1}{2}$

D_{2d}^{6}	lattice	Γ_t^{β}	corresponding to	$Q^{6}C_{2v}^{3}$	parameters	½ 0 0 ½ 0 0	and	½ ½ ½
D_{2d}^{7}	"	"	"	$Q^{6}C_{2v}^{8}$	"	0 0 0 0 ½ ½		0 ½ ½
D_{2d}^{8}	"	"	"	$Q^{6}C_{2v}^{10}$	"	½ 0 0 ½ ½ ½		½ ½ ½
D_{2d}^{11}	"	Γ_t'	"	$Q^{8}C_{2v}^{18}$	"	0 0 0 0 0 0		½ ½ ½ ½ ½ ½
D_{2d}^{12}	"	"	"	$Q^{9}C_{2v}^{9}$	"	½ 0 0 ½ 0 0		0 ½ ½ 0 ½ ½
D_{2d}^{9}	"	$\Gamma_t'^{\beta}$	"	$Q^{7}C_{2v}^{20}$	"	0 0 0 0 0 0		0 ½ ½ 0 ½ ½
D_{2d}^{10}	"		"	$Q^{7}C_{2v}^{21}$	"	½ 0 0 ½ 0 0		½ ½ ½ ½ ½ ½

.46 $C_{4\sigma}$ one axis and four planes

$$Y = a^{\frac{1}{2}} X a^{-\frac{1}{2}} + ua$$
$$Y = -bXb^{-1} + u_1 a + v_1 b + w_1 c$$
$$Y = -cXc^{-1} + u_2 a + v_2 b + w_2 c$$
$$Y = -(b+c)X(b+c)^{-1} + u_3 a + v_3 b + w_3 c$$
$$Y = -(b-c)X(b-c)^{-1} + u_4 a + v_4 b + w_4 c$$

~~Ex~~ As in D_4 we have the conditions $u_2 = u_1$; $v_2 = -w_1$; $w_2 = v_1$
$u_4 = u_3$; $v_4 = w_3$; $w_4 = -v_3$

Combining 1,2,4 we have :	for	Γ_4	Γ_4'
	$u+u_3+u_1$	1	$\frac{-1+m+n}{2}$
	v_3-v_1	m	$\frac{1-m+n}{2}$
	w_3+w_1	n	$\frac{1+m-n}{2}$
By we have	$u-u$	$\frac{1}{2}$	$\frac{-1+m+n}{4}$
	v_1	$\frac{m+n}{2}$	$\frac{1}{2}$
	w_1	$\frac{m-n}{2}$	$\frac{m-n}{2}$

Fow Γ_4 since u can only have the values 0, ½ and v_1, w_1 can only have 0, 0 or ½½ there are 8 types. For Γ_4' u can have the values 0 ¼ ½ ¾ but 0 implies ½ and ¼, ¾, further, in the first case the value of v_1, w_1 are limited to 0?0 and ½, ½ and these imply each other; while in in the second the values are limited to ½, 0 and 0, ½ which also imply each other, so that in each of these cases there are only two types. In all there are twelve t types whose parameters are shown on the following table. (Only the va reduced values of the parameters u u_1, v_1, w_1 are shown the others may rea-
u_3, v_3, w_3
dily be calculated by the equations above.

C_{4v}^{1}	lattice	Γ_t	parameters	$0\ \begin{matrix}0&0&0\\0&0&0\end{matrix}$		
C_{4v}^{2}	"	"	"	$0\ \begin{matrix}0&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\end{matrix}$		
C_{4v}^{5}	"	"	"	$0\ \begin{matrix}\frac{1}{2}&0&0\\\frac{1}{2}&0&0\end{matrix}$		
C_{4v}^{6}	"	"	"	$0\ \begin{matrix}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$		
C_{4v}^{3}	"	"	"	$\frac{1}{2}\ \begin{matrix}0&0&0\\0&0&0\end{matrix}$		
C_{4v}^{4}	"	"	"	$\frac{1}{2}\ \begin{matrix}0&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\end{matrix}$		
C_{4v}^{7}	"	"	"	$\frac{1}{2}\ \begin{matrix}\frac{1}{2}&0&0\\\frac{1}{2}&0&0\end{matrix}$		
C_{4v}^{8}	"	"	"	$\frac{1}{2}\ \begin{matrix}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$		
C_{4v}^{9}	"	Γ_t'	"	$0\ \begin{matrix}0&0&0\\0&0&0\end{matrix}$	and	$\frac{1}{2}\ \begin{matrix}0&0&0\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$
C_{4v}^{10}	"	"	"	$0\ \begin{matrix}\frac{1}{2}&0&0\\\frac{1}{2}&0&0\end{matrix}$	" "	$\frac{1}{2}\ \begin{matrix}\frac{1}{2}&0&0\\0&\frac{1}{2}&\frac{1}{2}\end{matrix}$
C_{4v}^{11}	"	"	"	$\frac{1}{4}\ \begin{matrix}0&\frac{1}{2}&0\\\frac{1}{4}&0&\frac{1}{2}\end{matrix}$	"	$\frac{3}{4}\ \begin{matrix}0&0&\frac{1}{2}\\\frac{3}{4}&0&\frac{1}{2}\end{matrix}$
C_{4v}^{12}	"	"	"	$\frac{1}{4}\ \begin{matrix}\frac{1}{2}&\frac{1}{2}&0\\\frac{1}{4}&\frac{1}{2}&0\end{matrix}$	"	$\frac{3}{4}\ \begin{matrix}\frac{1}{2}&\frac{1}{2}&0\\\frac{3}{4}&\frac{1}{2}&0\end{matrix}$

.47 D_{4h} Derkved from D_4 by the addition of a centre of symmetry

$$Y \equiv -X+u_5 a+v_5 b+w_5 c$$

As in the case of C_{4h} the omly types of D from which types of D may be derived are are those for which u =0 or ½ or wrere it =0,½ ;¼,¾ at the same time namely D_4^{1}, D_4^{2}, D_4^{5}, D_4^{6} . D_4^{9}, D_4^{10}

As in Q_h u_5, v_5, w_5 can take the values 0 and ½ but since b and c are equivalent axes there are only four values 0 ,0,0 ; 0,½,½ ; ½,0,0 ;½,½,½

Thus each of D_4^{1256} give rise to four types. For D_4^{9} uvw must be 0,0,0 or $\frac{1}{2}$,0,0 and for D_4^{10}u,v,w must either be 0,$\frac{1}{2}$,0 implying 0,0,$\frac{1}{2}$ or $\frac{1}{2}$,$\frac{1}{2}$,0 implying $\frac{1}{2}$,0,$\frac{1}{2}$. D_4^{9} and D_4^{10} give rise to two types each. In all there are 20 types.

D_{4h}^{1}	derived	from	D_4^{1}	parameters	0 0 0
D_{4h}^{5}	"	"	D_4^{2}	"	"
D_{4h}^{10}	"	"	D_4^{5}	"	"
D_{4h}^{14}	"	"	D_4^{6}	"	"
D_{4h}^{2}	"	"	D_4^{1}	"	$\frac{1}{2}$ 0 0
D_{4h}^{6}	"	"	D_4^{2}	"	"
D_{4h}^{9}	"	"	D_4^{5}	"	"
D_{4h}^{13}	"	"	D_4^{6}	"	"
D_{4h}^{3}	"	"	D_4^{1}	"	0 $\frac{1}{2}$ $\frac{1}{2}$
D_{4h}^{7}	"	"	D_4^{2}	"	"
D_{4h}^{12}	"	"	D_4^{5}	"	"
D_{4h}^{16}	"	"	D_4^{6}	"	"
D_{4h}^{4}	"	"	D_4^{1}	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
D_{4h}^{8}	"	"	D_4^{2}	"	"
D_{4h}^{11}	"	"	D_4^{5}	"	"
D_{4h}^{15}	"	"	D_4^{6}	"	"
D_{4h}^{17}	"	"	D_4^{9}	"	0 0 0
D_{4h}^{18}	"	"	D_4^{9}	"	$\frac{1}{2}$ 0 0
D_{4h}^{19}	"	"	D_4^{10}	"	0 0 $\frac{1}{2}$ and 0 $\frac{1}{2}$ 0
D_{4h}^{20}	"	"	D_4^{10}	"	$\frac{1}{2}$ 0 $\frac{1}{2}$ " $\frac{1}{2}$ $\frac{1}{2}$ 0

Thus each of D_4^{1256} give rise to four types. For D_4^9 uvw must be 0,0,0 or ½,0,0 and for D_4^{10} u,v,w must either be 0,½,0 implying 0,0,½ or ½,½,0 implying ½,0,½ . D_4^9 and D_4^{10} give rise to two types each. In all there are 20 types.

D_{4h}^1	derived	from	D_4^1	parameters	0 0 0
D_{4h}^5	"	"	D_4^2	"	"
D_{4h}^{10}	"	"	D_4^5	"	"
D_{4h}^{14}	"	"	D_4^6	"	"
D_{4h}^2	"	"	D_4^1	"	½ 0 0
D_{4h}^6	"	"	D_4^2	"	"
D_{4h}^9	"	"	D_4^5	"	"
D_{4h}^{13}	"	"	D_4^6	"	"
D_{4h}^3	"	"	D_4^1	"	0 ½ ½
D_{4h}^7	"	"	D_4^2	"	"
D_{4h}^{12}	"	"	D_4^5	"	"
D_{4h}^{16}	"	"	D_4^6	"	"
D_{4h}^4	"	"	D_4^1	"	½ ½ ½
D_{4h}^8	"	"	D_4^2	"	"
D_{4h}^{11}	"	"	D_4^5	"	"
D_{4h}^{15}	"	"	D_4^6	"	"
D_{4h}^{17}	"	"	D_4^9	"	0 0 0
D_{4h}^{18}	"	"	D_4^9	"	½ 0 0
D_{4h}^{19}	"	"	D_4^{10}	"	0 0 ½ and 0 ½ 0
D_{4h}^{20}	"	"	D_4^{10}	"	½ 0 ½ " ½ ½ 0

.5 Rhombohedral Types

Five classes $C_3, C_{3i}, D_3, C_{3v}, D_{3d}$. Two lattices Γ_h Γ_{rh}.

.51 C_3 the axis

$$Y \equiv a^{\frac{1}{3}} X a^{-\frac{1}{3}} + ua + vb + wc + td$$

The origin can always be chosen to make $v = w = t = 0$

u can have the values 0, 1/3, 2/3 For Γ_h these are independent, the positions of the similar triad axes or screws can be found by 5.2 to be $\frac{m-n}{3}, \frac{n-o}{3}, \frac{o-m}{3}$. For Γ_{rh} the values 0, 1/3, 2/3 imply each other but these di
(21-m-n)/9, etc
dissimilar axes pass through the ~~same~~ points. There are four types

C_3^1 lattice Γ_h $u = 0$; C_3^2 lattice Γ_h, $u = \frac{1}{3}$; C_3^3 lattice Γ_h, $u = \frac{2}{3}$

C_3^4 " Γ_{rh} $u = 0$ and $\frac{1}{3}$ and $\frac{2}{3}$

.52 C_{3i} Derived from 6 by the addition of a centre of symmetry

$$Y \equiv -X + u_1 a + v_1 b + w_1 c + t_1 d$$

The origin can always be chosen to make $u_1 = 0$.

As in the case of C_4 only the types C_3^1 and C_3^4 can give rise to a type of this class. By 5.73 we have: for both Γ_h Γ_{rh} $v = \frac{m-n}{3}$; $w = \frac{n-o}{3}$; $t = \frac{o-m}{3}$
m-m
so that there are only the v two types

C_{3i}^1 lattice Γ_h derived from C_3^1 parameters 0 0 0
C_{3i}^2 " Γ_{rh} " " C_3^4 " 0 0 0

.53 D_3 four axes

$$Y \equiv a^{\frac{1}{3}} X a^{-\frac{1}{3}} + ua$$

$$\begin{aligned} Y &\equiv bXb^{-1} + u_1 a + v_1 b + w_1 c + t_1 d \quad \text{or} \quad (c+d)X(c+d)^{-1} + \text{etc} \\ Y &\equiv cXc^{-1} + u_2 a + v_2 b + w_2 c + t_2 d \quad\quad\;\; (d+b)X(d+b)^{-1} + \text{"} \\ Y &\equiv dXd^{-1} + u_3 a + v_3 b + w_3 c + t_3 d \quad\quad\;\; (b+c)X(b+c)^{-1} + \text{"} \end{aligned}$$

the two ways of writing the relations depend on the fact that both b, c, d and (c+d), (d+b), (b+c) can be taken as diad axes of the lattice Γ_h though only the first can be taken for Γ_{rh}.

Transforming 2 by 1 and equating to 3, we obtain $u_2 = u_1 + 2u;\ v_2 = t_1;\ w_2 = v_1;\ t_2 = w_1$
" 3 " 2 " 2 " 4 " " $u_3 = u_2 + 2u;\ v_3 = w_2;\ w_3 = t_2;\ t_3 = v_2$

this holds for both for both forms of the relations.

By 5.71 we have $v_1 = \frac{m-n}{3}$; $w_1 = \frac{n-o}{3}$; $t_1 = \frac{o-m}{3}$ but this is of the same form as we obtained for the axial parameters in C_3 so that only one type in each form corresponds to the three types C_3^1, C_3^2, C_3^3, and only one of the first ~~sort~~ form to C_3^4. there are in all seven types.

D_3^2 lattice Γ_h parameters $\begin{matrix}0&0&0&0&0\\&0&0&0&0\end{matrix}$ Diad axes b, c, d
D_3^1 " " " $\begin{matrix}&0&0&0&0\end{matrix}$ " " (c+d), (d+b), (b+c

D_3^4 " " " $\begin{matrix}\frac{1}{3}&0&0&0&0\\&\frac{2}{3}&0&0&0\\&\frac{1}{3}&0&0&0\end{matrix}$ " " "
D_3^3 " " " " " "

D_3^6 " " " $\begin{matrix}\frac{2}{3}&0&0&0&0\\&\frac{1}{3}&0&0&0\\&\frac{2}{3}&0&0&0\end{matrix}$ " " "
D_3^5 " " " " " "

0 0 0

D_3^7 " Γ_{rh} " $\begin{matrix}0&0&0&0&0\\&0&0&0&0\\&0&0&0&0\end{matrix}$ and $\begin{matrix}\frac{1}{3}&\frac{2}{3}&0&\frac{1}{3}&\frac{1}{3}\\&\frac{2}{3}&\frac{1}{3}&0&\frac{1}{3}\\&\frac{2}{3}&\frac{1}{3}&\frac{1}{3}&0\end{matrix}$ and $\begin{matrix}\frac{2}{3}&\frac{1}{3}&0&\frac{1}{3}&\frac{1}{3}\\&\frac{1}{3}&\frac{1}{3}&0&\frac{1}{3}\\&\frac{1}{3}&\frac{1}{3}&\frac{1}{3}&0\end{matrix}$

.54 C_{3v} one axis and three planes

$$Y \equiv a^{\frac{2}{3}} X a^{-\frac{2}{3}} + ua$$

$$\begin{aligned} Y &\equiv -bXb^{-1} + u_1a + v_1b + w_1c + t_1d \quad \text{or} \quad -(c+d)X(c+d)^{-1} + \text{etc} \\ Y &\equiv -cXc^{-1} + u_2a + v_2b + w_2c + t_2d \qquad\quad -(d+b)X(d+b)^{-1} + \text{etc} \\ Y &\equiv -dXd^{-1} + u_3a + v_3b + w_3c + t_3d \qquad\quad -(b+c)X(b+c)^{-1} + \text{etc} \end{aligned}$$

Exactly as for D_3 we obtain $u_1 = u_2 = u_3;\ v_1 = w_2 = t_3;\ w_1 = t_2 = v_3;\ t_1 = v_2 = w_3$

by 5.72 $u = 0$ and by 5.81 $u_1 = 0$ or $\frac{1}{2}$. Further as for D_3 there can only one
of each sort.
set of independent values of v_1, w_1, t_1 Thus we have two types corresponding
and two of the first sort to C_3^4
to ~~each~~ of C_3^1, C, C, In all six types.

60 + 61

				u	u_1	v_1	w_1	t_1			
C_{3v}^1	lattice	Γ_h	parameters	0	0	0	0	0	planes	perpendicular to	b, c, d
C_{3v}^3	"	Γ_r	"	0	½	0	0	0	"	n"	"
C_{3v}^2	"	Γ_h	"	0	0	0	0	0	"	"	(c+d), (d+b), (b+c)
C_{3v}^4	"	Γ_h	"	0	½	0	0	0	"	"	"
C_{3v}^5	"	Γ_{rh}	"	0	0	0	0	0	"	"	b, c, d
C_{3v}^6	"	Γ_{rh}	"	0	½0	0	0	0	"	"	"

.55 D_{3d} **derived from** D_3 **by the addition of a centre of symmetry**

$$Y \equiv -X+u_4a+v_4b+w_4c+t_4d$$

Exactly as in C_{3i} we find that the only types of D_3 that can give rise to types of D_{3d} are D_3^1, D_3^2, D_3^7, also that v_4, w_4, t_4 always reduce to the same values 0, 0, 0 . but in this case u_4 can have the values 0 or ½ so that to each of D_3^1, D_3^2, D_3^7, corresponds two types, making six in all.

D_{3d}^1 corresponding to D_3^1 $u = 0$
D_{3d}^2 " D_3^1 $u = \frac{1}{2}$
D_{3d}^3 " D_3^2 $u = 0$
D_{3d}^4 " D_3^2 $u = \frac{1}{2}$
D_{3d}^5 " D_3^7 $u = 0$
D_{3d}^6 " D_3^7 $u = \frac{1}{2}$

.5 Hexagonal Types

Seven classes $C_6, C_{6h}, C_{3h}, D_{3h}, D_6, C_{6v}, D_{6h}$. One lattice

.61 C_6 the axis

$$Y \equiv a^{\frac{1}{3}} X a^{-\frac{1}{3}} + ua + vb + wc + td$$

The origin can always be chosen to make $v = w = t = 0$

u can have the values $\overset{0}{\ } 1/6, 1/3, 1/2, 2/3, 5/6,$

By 5.2 we can find the position of the hexad axes to be $\frac{2l-m-n}{3}b$+etc and as each axis is also a triad and diad axis there are such axes through the points $\frac{l-m}{3}b$+etc and $\frac{2l-m-n}{6}b$+ respectively.

There are six types $C_6^1, C_6^2, C_6^4, C_6^6, C_6^5, C_6^3$. withe the six values respectively, that are given above for u.

.52 C_{6h} derived from C_6 by the addition of a ~~axis~~ centre of symmetry

$$Y \equiv -X + ua + vb + wc + td$$

As in C_{3i} we can see that the only types of C_6 from which types of C_{6h} can be derived are C_6^1 and C_6^6, also that that u, v, w, t, always reduce to 0

Thus there are only two types: C derived from C ; C derived from C

C

.53 C_{3h} The axis

$$Y \equiv -a^{\frac{1}{3}} X a^{-\frac{1}{3}} + ua + vb + wc + td$$

The origin can always be chosen sothat u, v, w, t, 0, 0, 0, 0.

There is only one type C_{3h}^1

.64 D_{3h} The four axes, and the three planes

$$\begin{aligned}
Y &\equiv -a^{\frac{1}{3}} X a^{-\frac{1}{3}} + ua \\
Y &\equiv bXb^{-1} + u_1a + v_1b + w_1c + t_1d \quad \text{and} \quad (c+d)X(c+d)^{-1} + \text{etc} \\
Y &\equiv cXc^{-1} + u_2a + v_2b + w_2c + t_2d \\
Y &\equiv dXd^{-1} + u_3a + v_3b + w_3c + t_3d \\
Y &\equiv -(c+d)X(c+d)^{-1} + u_4a + v_4b + w_4c + t_4d \quad \text{and} \quad -bXb^{-1} + \text{etc} \\
Y &\equiv -(d+b)X(d+b)^{-1} + u_5a + v_5b + w_5c + t_5d \\
Y &\equiv -(b+c)X(b+c)^{-1} + u_6a + v_6b + w_6c + t_6d
\end{aligned}$$

The relations between the parameters are similar to those in D_3 and C_{3v}

Here however u can be 0 or $\frac{1}{2}$ so that there two types of each sort.

D^1_{3h} $u = 0$ diad axes b, c, d, D^3_{3h} $u = 0$ diad axes $(c+d), (d+b), (b+c)$

D^2_{3h} $u = \frac{1}{2}$ " " " D^4_{3h} $u = \frac{1}{2}$ " " "

65 D_6 Seven axes

$$Y = aXa + ua$$
$$Y = bXb + u_1a + v_1b + w_1c + t_1d$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$Y = (c+d)X(c+d) + u_4a + v_4b + w_4c + t_4d$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

The relations between are similar to those of D_3

There are six types D^1_6 D^2_6 D^4_6 D^6_6 D^5_6 D^3_6

$u = 0$ $\frac{1}{6}$ $\frac{1}{3}$ $\frac{1}{2}$ $\frac{2}{3}$ $\frac{5}{6}$

.66 C_{6v} Six planes and one axis

$$Y = a^{\frac{1}{3}}Xa^{-\frac{1}{3}} + ua$$
$$Y = -bXb + u_1a + v_1b + w_1c + t_1d$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$Y = -(c+d)X(c+d) + u_4a + v_4b + w_4c + t_4d$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

The relations between the parameters are similar to those of C_{3v}

$u = 0$ or $\frac{1}{2}$, U $u_1 = u_2 = u_6 = 0$ or $\frac{1}{2}$ there are four types

C^1_{6v} $u = 0$; $u = 0$. C^2_{6v} $u = 0$; $u = \frac{1}{2}$. C^3_{6v} $u = \frac{1}{2}$; $u = 0$. C^4_{6v} $u = \frac{1}{2}$; $u = \frac{1}{2}$

.67 D_{6h} Derived from D_6 by te addition of a ~~plane~~ centre of symmetry

$$Y = -X + u_7a + v_7b + w_7c + t_7d$$

As in the case of C_{6h} u, v_7, w_7, t_7 can always be reduced to 0 0 0 and u, u_1 can only have the values 0, $\frac{1}{2}$ so that again there are four types

D^1_{6h} $u = 0$; $u = 0$. D^2_{6h} $u = 0$; $u = \frac{1}{2}$. D^3_{6h} $u = \frac{1}{2}$; $u = 0$. D^4_{6h} $u = \frac{1}{2}$; $u = \frac{1}{2}$

.7 Regular Types.

Five classes T, T_h, T_d, O, O_h. Three lattices Γ_c Γ'_c Γ''_c

.71 T seven axes

$$Y = aXa^{-1}+u_1a+v_1b+w_1c$$
$$Y = bXb^{-1}+u_2a+v_2b+w_2c$$
$$Y = cXc^{-1}+u_3a+v_3b+w_3c$$

$$Y = (a+b+c)X(a+b+c)^{-1}+u_4a+v_4b+w_4c$$
$$Y = (a-b-c)X(a-b-c)^{-1}+u_5a+v_5b+w_5c$$
$$Y = (a+b-c)X(a+b-c)^{-1}+u_6a+v_6b+w_6c$$
$$Y = (a-b+c)X(a-b+c)^{-1}+u_7a+v_7b+w_7c$$

As $\Gamma_c\,\Gamma'_c\,\Gamma''_c$ may all be considered as special forms of Γ_h we must accordingly have rotation axes in the direction of each of the triad axes.

the origin may accordingly be chosen to lie on the rotation axis $a+b+c$ so that $u_4 = v_4 = w_4 = 0$ also the parameters of the other ~~rotation~~ triad axes can always be made to refer to rotation axes if $u_5-v_5-w_5$; $-u_6+v_6-w_6$; $-u_7-v_7+w_7$ respectively are made $= 0$.

Trans-forming 1 by 4 and equating to 2, and similarly for 2 and 3 we have the conditions $u_1 = v_2 = w_3$; $u = v_3 = w_1$; $u_3 = v_1 = w_2$.

Now as T may also be regarded as a special form of Q then the only types of Q to which types of T may correspond are those which satisfy the above conditions namely Q', Q^4, Q^7, Q^9 Q^9 so that there five types of T.

Transforming 4 by 1 and equating to 5 we have $u_5 = u_1+w_1$; $v_5 = v_1+u_1$; $w_5 = w_1-v_1$
" 4 2 " " 6 " $u_6 = u_2-w_2$; $v_6 = v_2+u_2$; $w_6 = w_2 \pm v_2$
" 4 3 " " 7 " $u_7 = u_3+w_3$; $v_7 = v_3-u_3$; $w_7 = w_3+v_3$

T' lattice Γ_c corresponding to Q' parameters

$$\begin{array}{ccc} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array}$$

T^4 " Γ_c " Q^4 "

$$\begin{array}{ccc} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{array}$$

T^{2} lattice Γ'_r corresponding to Q^{4} parameters

0	0	0	0	½	½	½	0	½	½	½	0
0	0	0	½	0	½	½	½	0	0	½	½
0	0	0	½	½	0	0	½	½	½	0	½
0	0	0	½	½	0	0	½	½	½	0	½
0	0	0	½	½	0	0	½	½	½	0	½
0	0	0	½	½	0	0	½	½	½	0	½
0	0	0	½	½	0	0	½	½	½	0	½

T^{3} " Γ''_r " Q^{6} "

0	0	0	½	½	½
0	0	0	½	½	½
0	0	0	½	½	½
0	0	0	½	½	½
0	0	0	½	½	½
0	0	0	½	½	½
0	0	0	½	½	½

T^{5} " Γ'''_r " Q^{7} "

0	0	½	½	½	0
½	0	0	0	½	½
0	½	0	½	0	½
0	0	0	½	½	½
½	0	½	0	½	0
½	½	0	0	0	½
0	½	½	½	0	0

.72 T_k Derived from T by the addition of a centre of symmetry

$$Y = -X + u_s a + v_s b + w_s c$$

As in the case of Q_k the only possible values for u_r, v_r, w_r are 0 or ½ but by the trigonal symmetry $u_s = v_s = w_s$ so that these reduce to two 0 0 0 and ½ ½ ½ but just as in Q^4 we have for T^4 0 0 0 and ½ ½ ½ are indistinguishable and in T^3 and T^5 they imply each other so that only T^1 and T^2 give rise to two types of T_k thus making 7 in all.

T_k^1	lattice	Γ_r	derived	from	T^1	parameters	0 0 0
T_k^2	"	Γ_r	"	"	T^1	"	½ ½ ½
T_k^6	"	Γ_r	"	"	T^4	"	0 0 0
T_k^3	"	Γ'_r	"	"	T^2	"	0 0 0
T_k^4	"	Γ'_r	"	"	T^2	"	½ ½ ½
T_k^5	"	Γ''_r	"	"	T^3	"	0 0 0 and ½ ½ ½
T_k^7	"	Γ'''_r	"	"	T^5	"	0 0 0 " ½ ½ ½

.73 T_d Derived from T by the addition of the six planes

$$Y \equiv -(b+c)X(b+c)\Gamma^{-1} + u_8 a + v_8 b + w_8 c$$
$$Y \equiv -(b-c)X(b-c)\Gamma' + u_9 a + v_9 b + w_9 c$$
$$Y \equiv -(c+a)X(c+a)\Gamma^{-1} + u_{10} a + v_{10} b + w_{10} c$$
$$Y \equiv -(c-a)X(c-a)\Gamma' + u_{11} a + v_{11} b + w_{11} c$$
$$Y \equiv -(a+b)X(a+b)\Gamma^{-1} + u_{12} a + v_{12} b + w_{12} c$$
$$Y \equiv)(a-b)X(a-b)\Gamma' + u_{13} a + v_{13} b + w_{13} c$$

This class may be considered as a special case of both D_{2d} and C_{3v}

From the first we see that as there is no type of D_{2d} corresponding to Q^4 there can be no type of T_d corresponding to T^4. From the second we see that as in C_{3v} u_1 0 or $\frac{1}{2}$ so $u_9+v_9+w_9 = 0$ or $\frac{1}{2}$ for Γ_r and Γ_r' and 0 or $\frac{1}{4}$ for Γ_r''.

Further $D_{2d}^{''}$ is the only type of D_{2d} corresponding to Q^5 and $u+v+w = 0$

also D_{2d}^{12} " " " " " D_{2d} " Q^9 " $u+v+w = \frac{1}{4}$

so that there is only one type corresponding to T^3 and T^5.

In all there are six types

T_d^1	lattice	corresponding to	$T^1 D_{2d}^1 C_{3v}^5$	parameters	0 0 0
T_d^4	"	"	$T^1 D_{2d}^3 C_{3v}^6$	"	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
T_d^2	"	"	$T^2 D_{2d}^9 C_{3v}^5$	"	0 0 0
T_d^5	"	"	$T^2 D^{10} C^6$	"	$\frac{1}{2}$ 0 0 and $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
T_d^3	"	"	$T^3 D_{2d}^{11} C_{3v}^5$	"	0 0 0
T_d^6	"	"	$T^5 D_{2d}^{12} C_{3v}^6$	"	$\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$

.74 O Derived from T by the addition of the six axes

$$Y \equiv (b+c)X(b+c) + u_8 a + v_8 b + w_8 c$$

....

$$Y \equiv (a+b)X(a+b) + u_{13} a + v_{13} b + w_{13} c$$

This class may be regarded as a particular case of D_3 the diad and triad axes must accordingly always intersect, ~~Also~~ for by we can see that there is always a diad axis i.e v+w 0. Also as O is a particular case of D we have for types corresponding to T^1 T^2 T^3 T^4 T^5

u 0 or $\frac{1}{2}$ 0 and $\frac{1}{2}$ $\frac{1}{4}$ or $\frac{3}{4}$ $\frac{1}{4}$ and $\frac{3}{4}$

There in all then eight types. As the class O has tetrad axes in the place of the diad axes of T the parameters u, v, w are given as well as u, v, w

O^1	lattice	Γ_r	corresponding to	$T^1 D_4^1$	parameters	$\begin{matrix}0&0&0\\0&0&0\\0&0&0\\0&0&0\end{matrix}$	
O^2	"	Γ_r	"	$T^1 D_4^5$	"	$\begin{matrix}\frac{1}{2}&0&0\\0&\frac{1}{2}&0\\0&0&\frac{1}{2}\\\frac{1}{2}&0&0\end{matrix}$	
O^3	"	Γ_r'	"	$T^2 D_4^9$	"	$\begin{matrix}0&0&0\\0&0&0\\0&0&0\\0&0&0\end{matrix}$	$\begin{matrix}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\0&\frac{1}{2}&\frac{1}{2}\end{matrix}$
O^4	"	Γ_r'	"	$T^2 D_4^{10}$	"	$\begin{matrix}\frac{1}{4}&0&0\\0&\frac{1}{4}&0\\0&0&\frac{1}{4}\\\frac{1}{2}&0&0\end{matrix}$	$\begin{matrix}\frac{3}{4}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{3}{4}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{3}{4}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$
O^5	"	Γ_r''	"	$T^3 D_4^9$	"	$\begin{matrix}0&0&0\\0&0&0\\0&0&0\\0&0&0\end{matrix}$	$\begin{matrix}\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{matrix}$
O^6	"	Γ_r	"	$T^4 D_4^4$	"	$\begin{matrix}\frac{1}{4}&0&0\\0&\frac{1}{4}&0\\0&0&\frac{1}{4}\\\frac{1}{4}&0&0\end{matrix}$	
O^7	"	Γ_r	"	$T^4 D_4^8$	"	$\begin{matrix}\frac{3}{4}&0&0\\0&\frac{3}{4}&0\\0&0&\frac{3}{4}\\\frac{3}{4}&0&0\end{matrix}$	
O^8	"	Γ_r''	"	$T^5 D_4^{10}$	"	$\begin{matrix}\frac{1}{4}&0&0\\0&\frac{1}{4}&0\\0&0&\frac{1}{4}\\\frac{1}{4}&0&0\end{matrix}$	$\begin{matrix}\frac{3}{4}&\frac{1}{2}&\frac{1}{2}\\\frac{1}{2}&\frac{3}{4}&\frac{1}{2}\\\frac{1}{2}&\frac{1}{2}&\frac{3}{4}\\\frac{3}{4}&\frac{1}{2}&\frac{1}{2}\end{matrix}$

.750 Derived from 0 by the addition of a centre of symmetry

$$Y = -X + ua + vb + wc$$

As in the case of D_{4h} we can only derive types of this class from classes corresponding to $D_4^1\ D_4^2\ D_4^5\ D_4^8\ D_4^9\ D_4^{10}$ namely $O^1\ O^2\ O^3\ O^4\ O^5\ O^6$. For Γ_r we have $u = v = w = 0$ or $\frac{1}{2}$ For Γ_r' $u = 0\ \frac{1}{4}\ \frac{1}{2}\ \frac{3}{4}$ but for O^3, 0 implies $\frac{1}{2}$ and $\frac{1}{4}, \frac{3}{4}$ while for O^4 u cannot have the values 0 or $\frac{1}{2}$ so that in each case only two types are derivable. For Γ_r'' $u = 0$ implies $u = \frac{1}{2}$ so that only one t type corresponds to each of O^5 and O^6. In all there are ten types

O^1	derived	from	O^1	parameters	0 0 0
O^2	"	"	O^1	"	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
O^3	"	"	O^2	"	0 0 0
O^4	"	"	O^2	"	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
O^5	"	"	O^3	"	0 0 0
O^6	"	"	O^3	"	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$
O^7	"	"	O^4	"	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$
O^8	"	"	O^4	"	$\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$
O^9	"	"	O^5	"	0 0 0
O^{10}	"	"	O^6	"	0 0 0

CHAPTER VII

COMPONENT SETS

E

.1 Equivalent points

We have already deduced all the symmetry relations of the 230 types of point systems. By means of these we can in any system write down the vectors of all the points equivalent to a given point.

If the reduced relations of any system be given by

$$Y \equiv (-1)^{V_1} A^{\frac{1}{k_1}} X A^{-\frac{1}{k_1}} + B_1$$

$$Y \equiv (-1)^{V_2} A^{\frac{1}{k_2}} X A^{-\frac{1}{k_2}} + B_2$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$Y \equiv (-1)^{V_n} A^{\frac{1}{k_n}} X A^{-\frac{1}{k_n}} + B_n$$

all the points equivalent to X are given by the relations

$$/Y \equiv (-1)^{h_r V_r} A^{\frac{2h_r}{k_r}} X A^{-\frac{2h_r}{k_r}} + B h_r$$

where h_r has all the values 1, 2, ... k_r for each of the n values of k_r

•11 The number of such equivalent points in a component set can only depend on the rotational part of the relation, so that in what follows we will deal only with this part.

Now since $Y \equiv (-1)^{k_r V_r} A^{\frac{2k_r}{k_r}} X A^{-\frac{2k_r}{k_r}}$ reduces to $Y \equiv X$ (except in the cases where $V_r = 1$ and $k_r = 1$ or 3 when it reduces to $Y \equiv -X$) and there are n relations of this type, there are in general

$\sum_{1 \to n} k_r - n$ points equivalent to any point and in all

$$\sum_{1 \to n} k_r - n + 1 \text{ points in the set.}$$

If there is a rotation of the type $Y\equiv -X$ there are

$$\sum_{1-n} k_r - n+2$$

and if there m ofmthe type $Y\equiv -A^{\frac{1}{3}}XA^{-\frac{1}{3}}$ there are

$$\sum k_r - n+5m+1 \quad \text{points in the set}$$

•12 Alternatively we may start with the independent reduced relations / $Y\equiv(-1)^{\nu_r}A^{\frac{1}{k_r}}XA^{-\frac{1}{k_r}}$

all points equivalent to X are given by::

$$Y\equiv(-1)^{\nu\sum h_r}A^{\frac{2h_1}{k_1}}A^{\frac{2h_2}{k_2}}\dots A^{\frac{2h_n}{k_n}}XA^{-\frac{2h_n}{k_n}}\dots A^{-\frac{2h_2}{k_2}}A^{-\frac{2h_1}{k_1}}$$

where h has all the values $0,1,2,\ \dots (k-1)$

The number of equivalent points is in general

$$k_1 k_2 \dots k_n$$

As before the existance of a relation $Y\equiv -X$ doubles the number of equivalent poihts; but we need not consider the effect of $Y\equiv -A^{\frac{1}{3}}XA^{-\frac{1}{3}}$ since it can always be derived from $Y\equiv -X$ and $Y\equiv A^{\frac{1}{3}}XA^{-\frac{1}{3}}$. Sometimes the first, sometimes the second method is the most convenient for deriving the equivalent points.

•13 In the following table there is given for each class of rotation the most natural way of doing this.

<u>Note</u> <u>Abbreviations used</u>

$A^{\frac{1}{k}}$	denotes	the	relation	$Y\equiv A^{\frac{1}{k}}XA^{-\frac{1}{k}}$
$-A^{\frac{1}{k}}$	"	"	"	$Y\equiv -A^{\frac{1}{k}}XA^{-\frac{1}{k}}$
1	"	"	"	$Y\equiv X$
$\pm$	"	"	"	$Y\equiv -X$

$(A_1^{\frac{1}{k_1}},A_2^{\frac{1}{k_2}},\quad A_n^{\frac{1}{k_n}})(A_1'^{\frac{1}{k_1'}},A_2'^{\frac{1}{k_2'}}?\quad .A_{n'}'^{\frac{1}{k_{n'}'}})$ signifies that every ~~pair~~ relation in the first bracket is to be combined in turn with each one in the second, and similarly for products with more than two brackets

Symbol of class	Group of rotations	Number of equivalent points
C_1	1	1
C_i	± 1	2
C_s	$1, -A$	2
C_2	$1, A$	2
C_{2h}	$\pm(1, A)$	4
C_{2v}	$1, A, -B, -C$	4
Q	$1, A, B, C$	4
Q_h	$\pm(1, A, B, C)$	8
C_4'	$1, -A^{\frac{1}{2}}, A, -A^{\frac{3}{2}}$	4
C_4	$1, A^{\frac{1}{2}}, A, A^{\frac{3}{2}}$	4
C_{4h}	$\pm(1, A^{\frac{1}{2}}, A, A^{\frac{3}{2}})$	8
D_{2d}	$(1, -A^{\frac{1}{2}}, A, -A^{\frac{3}{2}})(1, B)$	8
C_{4v}	$(1, A^{\frac{1}{2}}, A, A^{\frac{3}{2}})(1, -B)$	8
D_4	$(1, A^{\frac{1}{2}}, A, A^{\frac{3}{2}})(1, B)$	8
D_{4h}	$\pm(1, A^{\frac{1}{2}}, A, A^{\frac{3}{2}})(1, B)$	16
C_3	$1, A^{\frac{2}{3}}, A^{\frac{4}{3}}$	3
C_{3i}	$\pm(1, A^{\frac{2}{3}}, A^{\frac{4}{3}})$	6
C_{3v}	$(1, A^{\frac{2}{3}}, A^{\frac{4}{3}})(1, -B)$	6
D_3	$(1, A^{\frac{2}{3}}, A^{\frac{4}{3}})(1, B)$	6
D_{3d}	$\pm(1, A^{\frac{2}{3}}, A^{\frac{4}{3}})(1, B)$	12

Symbol of class	Group of rotations	Number of equivalent points
C_{3h}	$(1,-A)(1,A^{2/3},A^{4/3})$	6
D_{3h}	$\pm(1,-A)(1,A^{2/3},A^{4/3})$	12
C_6	$1,A^{1/3},A^{2/3},A,A^{4/3},A^{5/3}$	6
C_{6h}	$(1,A^{1/3},A^{2/3},A,A^{4/3},A^{5/3})(1,-B)$	12
D_6	$(1,A^{1/3},A^{2/3},A,A^{4/3},A^{5/3})(1,B)$	12
D_{6h}	$\pm(1,A^{1/3},A^{2/3},A,A^{4/3},A^{5/3})(1,B)$	24
T	$(1,A,B,C)(1,T^{2/3},T^{4/3})$	12
T_h	$\pm(1,A,B,C)(1,T^{2/3},T^{4/3})$	24
T_d	$(1,A,B,C)(1,T^{2/3},T^{4/3})(1,-R)$	24
O	$(1,A,B,C)(1,T^{2/3},T^{4/3})(1,R)$	24
O_h	$\pm(1,A,B,C,)(1,T^{2/3},T^{4/3})(1,R)$	48

·2 Coordinates

In general we refer the points of a system to three reference vectors, and the position of any point is given by its coordinates λ, μ, ν with respect to these vectors. (In the rhombohedral and hexagonal systems four reference vectors are employed.)

·21 If we write $X = \lambda a + \mu b + \nu c$; $Y = \lambda' a + \mu' b + \nu' c$ in the relation $Y \equiv (-1)^{\nu} A^{\frac{k}{\kappa}} X A^{-\frac{k}{\kappa}}$ it becomes

$$\lambda' a + \mu' b + \nu' c \equiv (-1)^{\nu} A^{\frac{k}{\kappa}} (\lambda a + \mu b + \nu c) A$$

$$\equiv (-1)^{\nu} A^{\frac{k}{\kappa}} a A^{-\frac{k}{\kappa}} + (-1)^{\nu} A^{\frac{k}{\kappa}} b A^{-\frac{k}{\kappa}} \; (-1)^{\nu} A^{\frac{k}{\kappa}} c A^{\frac{k}{\kappa}}$$

Now

$$(-1)^{\nu} A^{\frac{k}{\kappa}} a A^{-\frac{k}{\kappa}} = l_1 a + m_1 b + n_1 c$$

$$(-1)^{\nu} A^{\frac{k}{\kappa}} b A^{-\frac{k}{\kappa}} = l_2 a + m_2 b + n_2 c$$

$$(-1)^{\nu} A^{\frac{k}{\kappa}} c A^{-\frac{k}{\kappa}} = l_3 a + m_3 b + n_3 c$$

where l_1 l_2 l_3 etc are integers

Equating coefficients of a, b, c we have

$$\lambda' = l_1 \lambda + l_2 \mu + l_3 \nu$$

$$\mu' = m_1 \lambda + m_2 \mu + m_3 \nu$$

$$\nu' = n_1 \lambda + n_2 \mu + n_3 \nu$$

The relations between the coordinates of two points connected by a rotation can be expressed in the form of a matrix

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{pmatrix}$$

Since the inverse of a rotation is a rotation, this matrix must have the property $\begin{vmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{vmatrix} = \pm 1$

In the following table are given the matrices corresponding to a number of rotations, together with the values of $\lambda' \mu' \nu'$ in terms of $\lambda \mu \nu$.

22

Rotation	Matrix	Coordinates
1	$\begin{matrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{matrix}$	$\lambda, \mu, \nu.$
-1	$\begin{matrix}-1 & 0 & 0\\ 0 & -1 & -0\\ 0 & 0 & -1\end{matrix}$	$-\lambda, -\mu, -\nu,$
a	$\begin{matrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{matrix}$	$\lambda, -\mu, -\nu$
-a	$\begin{matrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{matrix}$	$-\lambda, \mu, \nu$
b	$\begin{matrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{matrix}$	$-\lambda, +\mu, -\nu$
-b	$\begin{matrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{matrix}$	$\lambda, -\mu, \nu$
c	$\begin{matrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{matrix}$	$-\lambda, -\mu, \nu$
-c	$\begin{matrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{matrix}$	$\lambda, \mu, -\nu$
R = [b+c]	$\begin{matrix}-1 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{matrix}$	$-\lambda, \nu, \mu$
-R = [b+c]	$\begin{matrix}1 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{matrix}$	$\lambda, -\nu, -\mu$
a^t	$\begin{matrix}1 & 0 & 0\\ 0 & 0 & -1\\ 0 & 1 & 0\end{matrix}$	$\lambda, -\nu, \mu$
$-a^t$	$\begin{matrix}-1 & 0 & 0\\ 0 & 0 & 1\\ 0 & -1 & 0\end{matrix}$	$-\lambda, \nu, -\mu$

Rotation	Matrix	Coordinates
$a^{\frac{2}{3}}$	$\begin{matrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{matrix}$	$\lambda, \rho, -\mu, \nu$
$T^{\frac{2}{3}} = [a+b+c]^{\frac{1}{3}}$	$\begin{matrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$	ν, λ, μ
$a^{\frac{1}{3}}$	$\begin{matrix} 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \end{matrix}$	$\lambda, -\nu, -\rho, -\mu$

·23 To obtain the coordinates of points equivalent to $\lambda\ \mu\ \nu$ in the most general point system we add to the coordinates of the equivalent points derived by rotations the corresponding parameters of the general relation

Here
$$\begin{aligned}\lambda' &= l_1\lambda+l_2\mu+l_3\nu+u\\ \mu' &= m_1\lambda+m_2\mu+m_3\nu+v\\ \nu' &= n_1\lambda+n_2\mu+n_3\nu+w\end{aligned}$$

and similarly for every relation of the system.

The parameters can be taken from the various tables of Ch.VI the rotations are given in table 7.13 and their matrices in table 7.22.

For example in the system Q^5. we have for equivalent points

$$\lambda, \mu, \nu\ ;\lambda, -\mu+\tfrac{1}{2}, -\nu;\ -\lambda, \mu+\tfrac{1}{2}, -\nu+\tfrac{1}{2};\ -\lambda, -\mu, \nu+\tfrac{1}{2}$$

These will appear in a more symmetrical form if we put $\mu+\frac{1}{4}$ for μ, $\nu+\frac{1}{4}$ for ν.

$$\begin{array}{lll} \lambda, & \mu+\tfrac{1}{4} & \nu+\tfrac{1}{4}\\ \lambda, & -\mu+\tfrac{1}{4} & -\nu-\tfrac{1}{4}\\ -\lambda, & \mu-\tfrac{1}{4} & -\nu+\tfrac{1}{4}\\ -\lambda, & -\mu-\tfrac{1}{4} & \nu+\tfrac{1}{4}\end{array}$$

Here $-\frac{1}{4}$ has been written for $+\frac{3}{4}$

·3 Unit cells

As has been already shown (1.8) we can always choose certain limits for the coordinates of the points in a component set. Such limits mark off a portion of space inside of which all the points of a component set may lie, such a portion is called a unit cell. There is one unit cell corresponding to every point in the skeletal lattice.

Two alternative limits were suggested (A) $0 \leq \lambda, \mu, \nu < 1$ (B) $-\frac{1}{2} < \lambda, \mu, \nu \leq \frac{1}{2}$ (B) will be used in what follows. The unit cell has thus the shape of a parallopiped whose centre is at the origin; a point of the set may lie anywhere inside this cell, on three of its faces, three of its edges and one of its angular points. This arrangement is unsymmetrical, but if we make the limits $-\frac{1}{2} \leq \lambda, \mu, \nu \leq \frac{1}{2}$ so that points may lie on all the faces, edges and corners, such points must count as $\frac{1}{2}, \frac{1}{4}$ and $\frac{1}{8}$ of a point respectively which is liable to cause confusion.

·31 The above limits for the unit cell are only useful for the lattices $\Gamma_t, \Gamma_m, \Gamma_o, \Gamma_t, \Gamma_r$. If we write the formula of any other lattice in terms of its primitive vectors and introduce these limits we obtain unit cells which do not possess the symmetry of the system.

The limits for cells satisfying this condition for each of the 14 lattices, are given with their descriptions, in the following table.

Lattice	Limits f of cell	Description of cell
Γ_{tr}	$-\frac{1}{2}<\lambda\leq\frac{1}{2}$ $-\frac{1}{2}<\mu\leq\frac{1}{2}$ $-\frac{1}{2}<\nu\leq\frac{1}{2}$	Parallelopipedon
Γ_{m}	"	Oblique rectangular prism
Γ_{o}	"	Rectangular rhombic prism
Γ_{t}	"	Tetragonal prism
Γ_{r}	"	Cube
Γ_{m}'	$-\frac{1}{2}<\lambda+\mu\leq\frac{1}{2}$ $-\frac{1}{2}<\lambda-\mu\leq\frac{1}{2}$ $-\frac{1}{2}<\nu\leq\frac{1}{2}$	Clinodomal prism and pinacoid (Oblique prism on rhombic base)
Γ_{o}'	$-\frac{1}{2}<\lambda\leq\frac{1}{2}$ $-\frac{1}{2}<\mu+\nu\leq\frac{1}{2}$ $-\frac{1}{2}<\mu-\nu\leq\frac{1}{2}$	Primary rhombic prism (Rectangular prism on rhombic base)
Γ_{o}''	$+\frac{1}{2}<\mu+\nu\leq\frac{1}{2}$ $-\frac{1}{2}<\mu-\nu\leq\frac{1}{2}$ $-\frac{1}{2}<\nu+\lambda\leq\frac{1}{2}$ $-\frac{1}{2}<\nu-\lambda\leq\frac{1}{2}$ $-\frac{1}{2}<\lambda+\mu\leq\frac{1}{2}$ $-\frac{1}{2}<\lambda-\mu\leq\frac{1}{2}$	Rhombic, macro- and brachydomal prisms; ((Elongated dodecahedron)
Γ_{r}'	"	Rhombic dodecahedron ~~Second order t~~
Γ_{o}'''	$-\frac{3}{4}<\lambda+\mu+\nu\leq\frac{3}{4}$ $-\frac{3}{4}<+\lambda-\mu-\nu\leq\frac{3}{4}$ $-\frac{3}{4}<-\lambda+\mu-\nu\leq\frac{3}{4}$ $-\frac{3}{4}<-\lambda-\mu+\nu\leq\frac{3}{4}$ $-\frac{1}{2}<\lambda\leq\frac{1}{2}$ $-\frac{1}{2}<\mu\leq\frac{1}{2}$ $-\frac{1}{2}<\nu\leq\frac{1}{2}$	Rhombic bypyramid and pinacoids (Elongated truncated octahedron)
Γ_{t}'	"	Tetragonalbipyramid second order prism and pinacoids.
Γ_{r}''	"	Octahedron and cube; (truncated octahedron)
Γ_{h}	$-\frac{1}{2}<\lambda\leq\frac{1}{2}$ $-1<2\mu-\nu-\rho\leq1$ $-1<-\mu+2\nu-\rho\leq1$ $-1<-\mu-\nu+\rho\leq1$	Hegagonal prism and pinacoids
Γ_{κ}	$-\frac{1}{2}<2\lambda-\nu+\rho\leq\frac{1}{2}$ $-\frac{1}{2}<2\lambda-\rho+\mu\leq\frac{1}{2}$ $-\frac{1}{2}<2\lambda-\mu+\nu\leq\frac{1}{2}$	RHOMBOHEDRON

·4 **Submultiple sets**

If X is such that the relation $Y \equiv (1)^{\nu} A^{\frac{t}{k}} X A^{-\frac{t}{k}} + B$ reduces to $Y \equiv X$ then the relation $A^{\frac{t}{k}}, B$ does not increase the number of points equivalent to X, derived from the other independent relations. The total number of points equivalent to X will accordingly be $1/k_1$ the number for the most general value of X Such a set of equivalent points is called a submultiple or subset. If in addition another independent relation of the set reduces to $Y \equiv X$ we have a subset, $1/k_1k_2$ the full set, and we may ultimately arrive at a sub set containing only one point.

·41 The relation $Y \equiv (1)^{\nu} A^{\frac{t}{k}} X A^{-\frac{t}{k}} + hA/k + B$ reduces to $Y \equiv X$ in the following cases. (a) If $\nu = 2$ and $h = 0$ $X = pA + C$ where $A^{\frac{t}{k}} C A^{-\frac{t}{k}} - C + B = 0$ if $B = 0$. $C = 0$. (b) If $\nu = 1$ and $k \neq 2$ $X = hA/2k + C$ " $A^{\frac{t}{k}} C A^{-\frac{t}{k}} + C - B = 0$

(c) IF $\nu = 1$ " $k = 2$ $X = hA/4 + C$ " $SAC = 0$

Expressing this in words; A sub set can be formed when, and only when, its points lie on, (a) axes of rotation, (b) centres of rotary reflections or (c) reflection planes. (see 5.2 et seq

For example: The 48 pointer full set of O_h reduces to a 24 pointer sub set when $\mu = \nu$ and when $\lambda = 0$; to a 12 when $\mu = \nu$ and $\lambda = 0$ to an 8 pointer when $\lambda = \mu = \nu$; to a 6 pointer when $\mu = \nu = 0$ and to a 1 pointer when $\lambda = \mu = \nu = 0$.

·42 Consider the case of a multiple point system containing axes of screw symmetry or glide planes which have no rotation axes or reflection planes parallel to them. If a point lie on such an axis or plane the number of points will only be reduced by a rotation included in the screw axis if any such exist.

In no case can the number of points in the sub set reduce to one. All non equivalent points in a multiple system connot lie on the same screw axes or glide plane. In this case an ~~equation~~ relation of the type $Y \equiv A^{k}XA^{-k} + hA/k$ reduces to $Y \equiv X + hA/k$ or in the case of a glide plane $Y \equiv -A\,XA^{-1} + B/2$to $Y \equiv X + B/2$ which would imply that A/k and B/2 were vectors of the skeletal lattice.

.43 In any class of symmetry a subset of one can be formed. All the points of a multiple system however can only form subsets of one in holohedral classes. Similar conditions hold for all other sub sets. If we consider simple systems only we have for each class a sub set that exhibits the symmetry of the class with the least number of points.

.44 In the following table is given a list of sub sets for every class with sub sets characteristic of it . In these classes the last sub set, and in all other classes the full set, is the least sub set. The values of λ, μ, ν for each sub set are also given.

•44

Class	Sub set	Number in sub set
C_i	$\lambda=\mu=\nu=0$	1
C_{2h}	$\lambda=0$	2
C_{2h}	$\mu=\nu=0$	2
"	$\lambda=\mu=\nu=0$	1
2_h	$\lambda=0$	4
"	$\mu=\nu=0$	2
"	$\lambda=\mu=\nu=0$	1
D_{2d}	$\mu=\nu$	4
C_{4h}	$\lambda=0$	4
D_{4h}	$\lambda=0$	8
"	$\mu=0$ or $\mu=\nu$	8
"	$\lambda=0, \mu=0$ or $\mu=\nu$	4
"	$\mu=\nu=0$	2
"	$\lambda=\mu=\nu=0$	1
T_h	$\lambda=0$	12
T_d	$\mu=\nu$	12
O_h	$\mu=\nu$	24
"	$\lambda=0$	24
"	$\mu=\nu, \lambda=0$	12
"	$\lambda=\mu=\nu$	8
"	$\mu=\nu=0$	6
"	$\lambda=\mu=\nu=0.$	1

Class	Sub set	Number in sub set
D_{3d}	$\nu=\rho$	6
"	$\nu=-\rho$	6
"	$\lambda=\mu=\nu=\rho=0$	1
C_{3h}	$\lambda=0$	3
D_{3h}	$\nu=\rho$	6
C_{6h}	$\nu=\rho$	6
D_{6h}	$\lambda=0$	12
"	$\nu=\rho$	12
"	$\lambda=0 \quad \nu=\rho$	6
"	$\mu=\nu=\rho$	2
"	$\lambda=\mu=\nu=\rho=0.$	1

·45 Available positi8ns

The points of a sub set must lie either on rotation axes or reflection planes. There are thus in every unit cell in any point system a ~~fint~~ finite number of planes, lines and points in which the points of sub sets must lie. All the poins of the component set may be located there only in those classes included. in the foregoing table. The case of one point sub sets is peculiar; in that only a limited number of such sub sets can co-exist in any system. Only a certain number of systems can reduce to one point sub sets, other systems can only reduce to two pointers and so forth.

(At this point it was hoped to be able to introduce a table showing every sub set possible in each of the 230 systems together with the available positions ~~of such~~ for the points of such sub sets.)

This Table is given in the second form of the paper. JDB.

CHAPTER VIII

PLANES

.1 **The equation to a plane**

If the variable vector X be expressed in terms of the vectors a,b,c ~~then the~~ so that $X = pa+qb+rc$; then the existance of an equation of the type

$$fp+gq+hr+J = 0$$

between the variable scalars p,q,r and the constant scalars f,g,h,j indicates that the extremity of X must always lie on a plane determined by f,g,h,j .

If X is a vector of a point system the values of p.q.r are restricted. All permissible values of p,q,r which satisfy the equation $fp+gq+hr+j = 0$ indicate points of the system lying in the plane f,g,h,j . Should any such points exist, the number of them is given by the number of permissible solutions of the above equation.

.2 **The law of rational indices**

p,q,r can always be put in the form $\big/_{r=1\cdots z}\, l+\lambda_r, m+\mu_r, n+\nu_r$; where l,m,n can take all integral values $-\frac{1}{2} < \lambda_r \leq \frac{1}{2}$ and z is finite.
If any point corresponding to $\lambda_r \mu_r \nu_r$ be on the plane we have

$$f(l+\lambda_r)+g(m+\mu_r)+h(n+\nu_r)+j = 0$$

or $$fl+gm+hn+j_r = 0 \quad \text{where } j_r = f\lambda_r+g\mu_r+h\nu_r+j$$

this is an equation which only admits of integral solutions, there will be a doubly infinite set of these if and only if f,g,h,j are all rational multiples of the same irrational number.

By multiplying by a suitable factor f,g,h may be reduced to integers with no common factor; in this form f,g,h are called the indices of the plane. In the subsequent work we are only concerned with sugh planes; the term plane will refer exclusively to planes containing a doubly infinite system of points, corresponding to a given point of the three dimensional point system. As all such points form lattices, we will in the following sections consider lattices only.

.3 Formula of a plane net

The points of the lattice $/la+mb+nc$ which lie in the plane $fl+gm+hn+j=0$ form a two dimensional net. We can obtain the formula of this net by eliminating l,m,or n from the formula of the lattice by means of the equation of the plane. The following proceedure is however more symmetrical.

Let u_1,v_1,w_1 ; u_2,v_2,w_2 be two points on the plane $fl+gm+hn=0$ and u_3,v_3,w_3 be a point on the plane $fl+gm+hn+j=0$ the general solution to the equation of the plane may now be written

$$l=su_1+tu_2+u_3$$

$$m=sv_1+tv_2+v_3$$

$$n=sw_1+tw_2+w_3$$

Introducing these values into the formula of the lattice we obtain the formula of the net

as $/(su_1+tu_2+u_3)a+(sv_1+tv_2+v_3)b+(sw_1+tw_1+w_3)c$

or $/s(u_1a+v_1b+w_1c)+t(u_2a+v_2b+w_2c)+(u_3a+v_3b+w_3c)$

writing $(u_1a+v_1b+w_1c)=e_1$; $u_2a+v_2b+w_2c=e_2$; $u_3a+v_3b+w_3c=e_3$

the formula becomes $/se_1+te_2+e_3$

If the plane passes through the origin $e_3=0$ and the formula of the net reduces to $/se_1+te_2$

e_1 and e_2 will be primitive vectors of the net if e_1 e_2 e_3 are for the system lattice. That is if

$$\begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{vmatrix} = \pm 1$$

If we substitute for the first column, that formed by multiplying the columns by f.g.h respectively and adding.

we have
$$\begin{vmatrix} 0 & v_1 & w_1 \\ 0 & v_2 & w_2 \\ -j & v_3 & w_3 \end{vmatrix} = \pm f$$

Expanding $\quad v_1 w_2 - v_2 w_1 = \pm f/j$

similarly $\quad w_1 u_2 - w_2 u_1 = \pm g/j$

$$u_1 v_2 - u_2 v_1 = \pm h/j$$

Since $/u_1$ are all integers and f,g,h have no common factor $j_1=\pm1$, but the condition that e_1 and e_2 should be primitive is independent of the value of e_3 and consequently of j: this condition is therefore
$$v_1 w_2 - v_2 w_1 = \pm f$$
$$w_1 u_2 - w_2 u_1 = \pm g$$
$$u_1 v_2 - u_2 v_1 = \pm h$$

•4 Parallel planes

Planes with the same values of f,g,h but with different values of j are parallel. If the indices are expressed in terms of primitive vectors j must be an integer and as no plane can lie between the parallel planes f,g,h,j and f,g,h,(j+1), these are called succesive planes.

·5 Distance between planes

The perpendicular distance from the origin to the plane

$$fl+gm+hn-1=0$$

may be expressed as the quotient $\dfrac{\text{Volume of //pipedon } e_1 e_2 e_3}{\text{Area of //gm } e_1 e_2}$

$$= \frac{Se_1 e_2 e_3}{TVe_1 e_2}$$

$$= \frac{S(u_1 a+v_1 b+w_1 c)(u_2 a+v_2 b+w_2 c)(u_3 A+v_3 b+w_3 c)}{TV(u_1 a+v_1 b+w_1 c)(u_2 a+v_2 b+w_2 c)}$$

$$\frac{\begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{vmatrix} Sabc}{TV\Sigma(v_1 w_2 - v_2 w_1)Vbc}$$

Now /u_1 can always be chosen so that $(u_1\ v_2\ w_3) = 1$ also $(v_1 w_2 - v_2 w_1) = f$ etc. We have therefore

Perpendicular distance $D = \dfrac{Sabc}{T(fVbc+gVca+hVab)}$

This expression may of course be derived directly from the equation of the plane and is true for all real values of f, g, h, j In its most general form it is

$$D_j = \frac{jSabc}{T(fVbc+gVca+hVab)}$$

This ~~equatia~~ expression though simple is not convenient for numerical calculation as it involves sums and products of vectors It can easily be transformed however into one that is.

.51 We make use of the formula $-(Sabc)^2 = S.VbcVcaVab$ (see Joly "Manual of Quaternions" Art. 25, Ex. 4)

$$-(Sabc)^2 = S.VbcVcaVab$$

$$= S(bc-Sbc)(ca-Sca)(ab-Sab)$$

$$= S\,bccaab-\Sigma Sbc.caab+\Sigma SbcSca.ab-SbcScaSab$$

$$= a^2b^2c^2+\Sigma a^2(Sbc)-3SbcScaSab+SbcScaSab$$

$$= a^2b^2c^2+a^2(Sbc)+b^2(Sca)+c^2(Sab)-2SbcScaSab$$

Also $\Sigma(fVbc+gVca+hVab)^2 = \Sigma f^2(Vbc)^2-2\Sigma ghS.VcaVab$

$$= \Sigma f^2(Vbc)^2-2\Sigma gh(a^2Sbc-ScaSab)$$

We have therefore

$$D_1^2 = \frac{a^2b^2c^2-\Sigma a^2(Sbc)+2SbcScaSab}{\Sigma f^2(Vbc)^2-2\Sigma gh(a^2Sbc-ScaSab)}$$

Now if we put a for the scalar Ta, cos A for S.UbUc; sinA for TV.UbUc and similarly for b and c ; B and C the expression takes a form involving scalars only

$$D_1^2 = \frac{a^2b^2c^2(1-\cos^2A-\cos^2B-\cos^2C+2\cos A\cos B\cos C)}{\Sigma f^2b^2c^2\sin^2A - 2\Sigma \underset{bc}{a^2}gh(\cos A - \cos B\cos C)}$$

Finally we obtain the familiar formula

$$D_1 = \sqrt{\frac{1-\Sigma\cos^2A+2\cos A\cos B\cos C}{\Sigma(f/a)^2\sin^2A-2\Sigma(gh/bc)(\cos A-\cos B\cos C)}}$$

This formula loses much of its complexity when applied to symmetrical lattices. It is given for each of the 14 lattices in the table on p 94.

•52 So far we have only considered lattices whose formula is written /la+mb+nc . It is not always convenient to use such a formula, For all lattices except , Γ_h, Γ_{rh} , , the formula may be written $/(\alpha_1 l+\beta_1 m+\gamma_1 N)/2+(\alpha_2 l+\beta_2 M+\gamma_2 n)b/2+(\alpha_3 l+\beta_3 m+\gamma_3 N)c/2$ (for Γ_c, Γ_m, Γ_o, Γ_t, Γ_r, $\alpha_1=2$, $\beta_2=2$, $\gamma_3=2$ and $\alpha_2=\beta_1$ &c $=0$)

The equation of the plane becomes

$$f(\alpha_1 l+\beta_1 m+\gamma_1 n)/2+g(\alpha_2 l+\beta_2 m+\gamma_2 n)/2+h(\alpha_3 l+\beta_3 m+\gamma_3 n)/2+j=0$$

f,g,h may be such that ~~each~~ the sum of the first three terms is an integer for all values of l,m,n,
In this case j is an integer and succesive planes are at the same distance as in the corresponding lattice /la+mb+nc

If ~~all~~ the sum of the first three termw do not reduce to integers j must be of the form k/2 when k is an integer and sucessive planes are half as far apart as in the corresponding lattice.

If d_{fgh} stands for the distance between succesive planes parallel to $fp+gq+hr=0$ in any lattice, and D_{fgh} for the distance in a corresponding lattice of formula /la+mb+nc , then $d_{fgh}=\delta_{fgh}D_{fgh}$ where δ_{fgh} depends both on the lattice and on f,g,h and is always 1, $\frac{1}{2}$ or in the case of Γ_{rh} 1/3. The value of δ_{fgh} for all lattices and values of f,g,h is given in the table on p 94 .

•53 The case of Γ_h and Γ_{rh} must be dealt with separately; in this case four reference vectors are used and the equation of the plane becomes $fp+gq+hr+is+j=0$ where g,h,i are connected by the relation $g+h+i \equiv 0$.

$fp+gq+hr+j=0$ is the equation of the same plane referred to the three vectors a, b, c Now applying the formula for D we have

$$D = \sqrt{\frac{\frac{3}{4}}{\frac{3}{4}(f/a)^2+(g^2+h^2+gh)/b^2}} \quad \text{since } \cos A = -\tfrac{1}{2} \quad \cos B = \cos C = 0$$

$$= 1/\sqrt{f^2/a^2+\tfrac{4}{3}\{g^2+h^2+(h+i)(g+i)\}/b^2} \quad \text{since } g+h+i \equiv 0$$

$$= 1/\sqrt{f^2/a^2+\tfrac{4}{3}(g^2+h^2+i^2+hi+ig+gh)/b^2}$$

$$1/\sqrt{f^2/a^2+\frac{\frac{2}{3}(g^2+h^2+i^2)}{b^2}} \quad \text{since } g^2+h^2+i^2+hi+ig+gh$$

$$= \tfrac{1}{2}(g+h+i)^2+\tfrac{1}{2}(g^2+h^2+i^2)$$

The formula of Γ_h is

$$= \tfrac{1}{2}(g^2+h^2+i^2)$$

$$/la+(2m-n-o)b/3+(-m+2n-o)c/3+(-m-n+2o)d/3$$

$g(2m-n-o)/3+h(-m+2n-o)/3+i(-m-n+2o)/3$ is an integer when

$m(2g-h-i)/3+n(-g+2h-i)/3+o(-g-h+2i)/3$ is an integer

that is $2g-h-i$ is divisible by 3. ~~In this case 1 and in all other cases 1/3~~ But $2g-h-i=3g$ and is therefore always divisible by 3 so that for this lattice $\delta = 1$

The formula of Γ_{rh} is

$$/(l+m+n)a/3+(m-n)b/3+(n-l)c/3+(l-m)d/3$$

by similar reasoning we can show that if $f-h+i$ is a multiple of 3 $\delta = 1$ and if not $\delta = 1/3$

·6 Forms

We now return to the most general point system.

The plane parallel to $fl+gm+hn=0$ through the point $\lambda\ \mu\ \nu$ is $fp+gq+hr+j=0$ where j (no longer necessarily an integer) is given by $f\lambda+g\mu+h\nu+j=0$

If three points $\lambda_1\mu_1\nu_1 ; \lambda_2\mu_2\nu_2 ; \lambda_3\mu_3\nu_3$; lie in the plane f,g,h,j the three points connected with them by the rotation $Y=(1)^{\nu}A^{\frac{s}{k}}XA^{-\frac{s}{k}}$ $\lambda_1'\mu_1'\nu_1' : \lambda_2'\mu_2'\nu_2' : \lambda_3'\mu_3'\nu_3'$: WILL lie in the plane f',g',h',j where $f',g',h',$ are given by the relations

$$f' = l_1'f+l_2'G+l_3'h$$
$$g' = m_1'f+m_2'g+m_3'h$$
$$h' = n_1'f+n_2'g+n_3'h$$

where l_1', l_2', l_3' etc are the minors of $l_1\ l_2\ l_3$ in th matrix $(l_1 m_2 n_3)$ of the rotation. In other words $(l_1' m_2' n_3')$ is the matrix of the inverse rotation $Y=(1)^{\nu}A^{-\frac{s}{k}}XA^{\frac{s}{k}}$. For substituting for $/\lambda'$ and $/f'$ in terms of $/\lambda$ and $/f$ we have

$$\sum_{f\lambda}^{123} l_1'f\sum l_1\lambda+\sum m_1'f\sum m_1\lambda+\sum n_1'f\sum n_1\lambda+j=0$$
$$-j\left(\sum^{123} l_1l_1'+\sum m_1m_1'+\sum n_1n_1'\right)-\sum g\nu\sum(l_2'l_3+m_2'm_3+n_2'n_3)$$
$$-\sum h\mu\sum(l_2l_3'+m_2m_3'+n_2n_3')+j=0$$

This is the case only if $\sum l_1l_1'=1$ and $\sum l_2'l_3=0$ and since $(l_1m_2n_3)=\pm1$ $l_1'=m_2n_3-m_3n_2$.

The planes $f_1g_1h_1j_1$ and f,g,h,j are said to be equivalent planes.

If the symmetry relation is of the type $Y=(1)A'^{\frac{1}{k}}XA^{-\frac{1}{k}}+ua+vb+wc$ the plane equivalent to f,g,h,j is $f',g',h',j',$ where f,g,h are as before but $j'=fu+gv+hw+j$

•61 All the planes equivalent to a given plane are said to constitute a form. A form has in general the same number of planes as the number in the full set of equivalent points of the system. For certain values of f,g,h however k planes of the form coincide, and a sub form results each of whose planes contains k equivalent points, unless these points themselves form a sub set. Such planes must be perpendicular to rotation axes or reflection (planes The same considerations that applied to the limitation of points in component sets apply to forms also, except that in this case j alone has to be limited.

•62 If the system contains no screw axes or glide planes to which there are no parallel rotation axes or reflection planes, the form is called an infinite form; otherwise it is a finite form. Infinite forms may in certain cases contain up to 6 parallel planes. Consider the case of a ~~for example the~~ plane 1,0,0,0 perpendicular to the screw axis $Y=a^{\frac{1}{k}}Xa^{-\frac{1}{k}}+a/k$. The planes contained in the form are 1,0,0,0 ;1,0,0,1/k;1,0,0,2/k; ....1,0,0,(k-1)/k all of which are parallel.

By the symmetry of the system all the planes of a form must be congruent.

•7 Densities of systems and planes

•71 The point density of a system is defined as the number of points per unit volume of the system;aor alternately as

$$\frac{\text{Number of points in unit cell}}{\text{Volume of unit cell}}$$

The number of points in a unit cell is simply the number N of points in a component set; the volume of a unit cell is Sabc when a,b,c are primitive vectors, in general however it is $\frac{1}{\Delta}$Sabc where $\Delta = \begin{vmatrix} l_1, l_2, l_3 \\ m_1 m_2 m_3 \\ n_1 n_2 n_3 \end{vmatrix}$ and /l_1 are the coordinates of a,b,c in terms of primitive vectors.

The values of Δ for each of the 14 lattices is given in the table on p 94. We have there-fore as an expression for the point density $\frac{\Delta N}{Sabc}$

•72 The point density of a plane may be defined as

$$\frac{\text{Number of points in the plane per unit cell}}{\text{Area of unit cell}}$$

If n is the number of points of a component set that lie in the plane and δ and Δ have the same meaning as in the preceeding sections; Point density $\frac{n}{Se_1e_2}$

$$= \frac{\delta \Delta n}{T(fVbc+gVca+hVab)}$$

•73 Weighted densities

In a multiple system we may attribute to each point a weight factor m_r ; m_r being the same for all equivalent and corresponding points

The weighted density of a system or plane is the weight per unit ~~area~~volume and per unit area respectively. If N_r and n_r are the number of points of the same kind in a component set of the system and the plane respectively , the weighted densities are

$$\frac{\Delta \Sigma N_r m_r}{Sabc}$$

and $$\frac{\delta \Delta \Sigma n_r m_r}{T(fVbc+gVca+hVab)}$$

6 In the following table are given a number of important constants and expressions for each of the 14 lattices. From these by the use of the formulae reproduced below we can calculate the perpendicular distance between sucessive parallel planes and the densities of systems and planes.

Distance from origin to a plane $fp+gq+hr+j=0$

$$= \frac{jSabc}{T(fVbc+gVca+hVab)}$$

Distance between sucessive planes parallel to $fl+gm+hn=0$

$$= \frac{\delta Sabc}{T(fVbc+gVca+hVab)}$$

Volume of unit cell $= \frac{1}{\Delta}Sabc$

Density of points in a system $= \frac{\Delta N}{Sabc}$

Density of points in a plane

$$= \frac{\delta \Delta n}{T(fVbc+gVca+hVab)}$$

•8

Lattice	Δ	δ		Sabc	$T(fVbc+gVca+hVab)$
Γ_{tr}	1	1		$abc\sqrt{1-\Sigma\cos^2 A+2\cos A\cos B\cos C}$	$abc\sqrt{\Sigma\frac{f^2}{a^2}\sin^2 A-\Sigma\frac{2gh}{bc}(\cos A-\cos B\cos C)}$
Γ_m	1	1		abc sin A	$abc\sqrt{\frac{f^2}{a^2}\sin^2 A+\frac{g^2}{b^2}+\frac{h^2}{c^2}-2\frac{gh}{bc}\cos A}$
Γ_m'	2	1	f+g even	〃	
		½	f+g odd		
Γ_o	1	1		abc	$abc\sqrt{\frac{f^2}{a^2}+\frac{g^2}{b^2}+\frac{h^2}{c^2}}$
Γ_o'	2	1	g+h even	〃	〃
		½	g+h odd		
Γ_o''	4	1	f, g, h all odd	〃	〃
		½	otherwise		
Γ_o'''	2	1	two of f, g, h even, one odd	〃	〃
		½	otherwise		
Γ_t	1	1		ab^2	$ab^2\sqrt{\frac{f^2}{a^2}+\frac{g^2+h^2}{b^2}}$
Γ_t'	2	1	two of f, g, h even, one odd	〃	〃
		½	otherwise		
Γ_r	1	1		a^3	$a^2\sqrt{f^2+g^2+h^2}$
Γ_r'	4	1	f, g, h all odd	〃	〃
		½	otherwise		
Γ_r''	2	1	two of f, g, h even, one odd	〃	〃
		½	otherwise		

Lattice	Δ	δ	Sabc	T(fVbc+gVca+hVab)
Γ_h	1	1	$\sqrt{3}abc/2$	$\sqrt{\frac{3}{4}\frac{f^2}{a^2}+\frac{1}{8}\frac{g^2+h^2+i^2}{b^2}}$
Γ_{rh}	3	1 f-h+i divisible by 3 $\frac{1}{3}$ otherwise	"	"

.81 We may consider Γ_{rh} to be expressed in terms of the three primitive vectors 1/3.0,1/3.-1/3 ;1/3,-1/3.0,1/3; 1/3,1/3,-1/3,0 in which case its formula becomes /la+mb+nc; $\Delta = 1$ $\delta = 1$

$$\text{Sabc} = a^3\sqrt{1-3\cos^2 A+2\cos^3 A} \qquad \text{since here } a = b = c$$

$$A = B = C$$

$$T(f\text{V}bc+g\text{V}ca+h\text{V}ab) = a^2\sqrt{(f^2+g^2+h^2)\sin^2 A+2(gh+hf+fg)(\cos^2 A-\cos A)}$$

CHAPTER IX

X-Ray analysis of Crystals

(Elementary)

•0 We may consider a crystal as in general a multiple point system in which the place of the points is taken by atoms of the different elements.

A crystal is always finite and is in general bounded by planes, but the number of atoms in even the smallest crystal is so great that these limitations need not be taken account of in considerations of internal structure.

The external symmetry of the forms of a crystal are often sufficient to determine which of the thirty-two classes of symmetry it belongs to, but cannot possibly reveal, except in Class C_1, which skeletal lattice and point system is the basis of their structure.

•1 Defraction of X-rays by crystals.

The distance between the atoms of a crystal is comparable to the wave length of X-rays which are diffracted by a crystal as from a three-dimensional grating.

Bragg has considered the effect as that of reflection from successive, equally-spaced, congruent planes of the crystal and obtains the simple grating formula

$$n\lambda = 2d \sin\theta$$

for maximum reflection where

d is the distance between successive planes

θ is the angle which the incident and reflected rays make with the plane

λ is the wave-length of the X-ray, and

n is an integer fixing the order of the reflection.

•11 If we keep λ constant and vary θ we obtain maxima of reflection when $\theta = \theta_1, \theta_2 \cdots \theta_r \cdots$ given by :

$$\sin\theta_1 = \frac{n\lambda}{2d}$$

$$\sin\theta_2 = \frac{2n\lambda}{2d}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\sin\theta_r = \frac{r n\lambda}{2d}$$

•12 On the other hand if we keep θ constant and vary λ , or what is the same thing, use "white" light, we have reflected at an angle θ rays of wave-length $\lambda_1\ \lambda_2 \cdots \lambda_r$ given by :

$$\lambda_1 = 2d \sin\theta$$

$$\lambda_2 = \frac{2d}{2}\sin\theta$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\lambda_r = \frac{2d}{r}\sin\theta$$

These two cases are the basis of the Bragg and Laue methods respectively.

.2 Distribution of Energy among orders of Reflection.

In general, however, the series of planes parallel to a given plane are not all congruent but consist of sets of different planes which are repeated regularly. Bragg has shown that the affect of this is analogous to that of the form of grating lines and leads to a different distribution of intensity among the orders of reflections than that which would result from a series of congruent, equally-spaced planes.

In the latter case the intensity of the first, second, etc. orders falls off approximately as the inverse square of their order, i.e. in the ratio: $1, \frac{1}{4}, \frac{1}{9} \cdots$

.21 The intensity of a reflection of order n, due to a distribution of planes at distances d_1 d_2 ...... d_r from an initial plane, the whole being repeated at a distance d is given by[1]

$$I_n = \frac{k}{n^2}\left(m_0 + m_1 \cos 2n\pi d_1/d + m_2 \cos 2n\pi d_2/d + ..\right)^2 +$$

$$\left(m_1 \sin 2n\pi d_1/d + m_2 \sin 2n\pi d_2/d + ..\right)^2$$

where m_0 m_1 m_2 represent the reflecting powers of the successive planes. m_r is roughly proportional to the electronic density of the plane, i.e. to the weighted density, if to each atom of the plane we attribute the number of electrons associated with it, i.e. its atomic number. As the factor k is unknown we require relative and not absoute electron densities.

·3 The Bragg X-ray Spectrometer Method.

In the Bragg method the crystal is mounted on a goniometer and a very fine beam of monochromatic X-rays directed on to one face. The intensity of the reflected beam is measured by an ionisation chamber and a sensitive electroscope. The crystal and the ionisation chamber are so placed that the latter is always at twice the angular distance from the incident beam as the crystal face. The angles of reflection and the intensities of the first few order reflections from the face are measured.

·31 Determination of skeletal lattice

Such measurements for three faces of known indices suffice, ~~fx~~ if λ is known, to determine absolutely the skeletal lattice of the system, i.e. to give both the nature of the lattice and the lengths and mutual angles of its reference vectors.

For by the formula given above we have $2d = \frac{n\lambda}{\sin\theta}$

also $d = \frac{\delta\, Sabc}{T(fVbc + gVca + hVab)}$

$$= \delta\sqrt{\frac{1 - \Sigma\cos^2 A + 2\cos A\cos B\cos C}{\Sigma f^2/a^2\sin^2 A + 2\Sigma gh/ab(\cos A - \cos B\cos C)}}$$

Now we know λ and $\sin\theta$; also from crystallographic data we know A B C and f g h.

Hence we have three equations of the type

$$a_1x^2 + b_1y^2 + c_1z^2 + f_1yz + g_1zx + h_1xy + d_1 = 0$$
$$a_2x^2 + b_2y^2 + c_2z^2 + f_2yz + g_2zx + h_2xy + d_2 = 0$$
$$a_3x + b_3y + c_3z + f_3yz + g_3zx + h_3xy + d_3 = 0$$

These are always soluble (in the most general case only by elliptic functions). Thus a b c can always be found.

In practice, however, it is found that only the planes with simple indices give good reflections and these are generally used. In this case the equations above reduce to one or two terms each and the solution is correspondingly easy.

For the factor δ (see 8·52) which depends upon the lattice and upon the values of f g h, the latter are so chosen as to afford a criterion of the particular lattice. This may necessitate measurements from more than three planes.

·311 Examples of planes which can be used for this criterion in the various crystal systems are given in the following table. For each lattice in a given system there will exist a ratio connecting the d's of the various planes. A sufficient number of planes are chosen so that no two lattices of the same system have the same ratios of their d's.

•311 Triclinic lattice Γ_{t}	d_{100}	d_{010}	d_{001}
	$\frac{a}{\sin A}\sqrt{1-\sum\cos^2 A+2\cos A\cos B\cos C}$;	$\frac{b}{\sin B}\sqrt{}$;	$\frac{c}{\sin C}\sqrt{}$

Monoclinic	d_{100}	d_{010}	d_{001}	d_{011}
	a	$b \sin A$	$c \sin A$	$\frac{bc \sin A}{\sqrt{b^2-2bc\cos A+c^2}}$
	$\frac{1}{2}a$	$\frac{1}{2}b \sin A$	$c \sin A$	$\frac{1}{2}\frac{bc \sin A}{\sqrt{b^2-2bc\cos A+c^2}}$

Orthorhombic	d_{100}	d_{010}	d_{001}	d_{011}	d_{101}	d_{111}
	a	b	c	$bc/\sqrt{b^2+c^2}$	$ca/\sqrt{c^2+a^2}$	$1/\sqrt{\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}}$
	a	$\frac{1}{2}b$	$\frac{1}{2}c$	$bc/\sqrt{b^2+c^2}$	$ca/2\sqrt{c^2+a^2}$	"
	$\frac{1}{2}a$	$\frac{1}{2}b$	$\frac{1}{2}c$	$bc/2\sqrt{b^2+c^2}$	$ca/2\sqrt{c^2+a^2}$	"
	$\frac{1}{2}a$	$\frac{1}{2}b$	$\frac{1}{2}c$	$bc/\sqrt{b^2+c^2}$	$ca/\sqrt{c^2+a^2}$	$\frac{1}{2}$ "

Tetragonal	d_{100}	d_{010}	d_{011}
	a	b	$b/\sqrt{2}$
	$\frac{1}{2}a$	$\frac{1}{2}b$	$b/\sqrt{2}$

Cubic	d_{100}	d_{011}	d_{111}
	a	$a/\sqrt{2}$	$a/\sqrt{3}$
	$\frac{1}{2}a$	$a/2\sqrt{2}$	$a/\sqrt{3}$
	$\frac{1}{2}a$	$a/\sqrt{2}$	$a/2\sqrt{3}$

Rhombohedral	d_{1000}	d_{101-1}	d_{12-1-1}
	a	$\sqrt{3}b/2$	$\frac{1}{2}b$
	$a/3$	$\sqrt{3}b/6$	$\frac{1}{2}b$

Hexagonal	d_{1000}	d_{12-1-1}
	a	$\frac{1}{2}b$

.312 Thus in the case of rock salt NaCl a cubic crystal

$$d_{100} : d_{011} : d_{111} = 1 : 1/\sqrt{2} : 2/\sqrt{3}$$

The skeletal lattice is therefore Γ_r' and $a = 2d_{100}$

It should be remembered in this connection, that except in the cubic system ~~that~~ the indices assigned to faces by crystallographers are not necessarily the same as those which are derived from the actual lattice of the crystal. As the former indices must necessarily be known first a lattice may be deduced which is not one of the 14 types. In such a case it is always possible to change the system of indices so as to reduce the lattice to a recognised form. This is well illustrat by the case of calcite, a crystal of class D_{3d} for which Bragg foun a face centered rhombohedral lattice with faces parallel to the form 101-1 . If the lattice is taken as Γ_{rh} the indices of this form become 12-1-1.

.313 Screw axes

If the reflections from planes perpendicular to screw axes are measured the value of d will be h/k its normal value where h/k is the pitch of the screw. Since screw axes can only exist perpendicular to certain planes it is always possible by choosing suitable planes to avoid any error on this score, and a the same time to determine the position and nature of all screw that exist.

Thus in the case of the diamond a cubic crystal containing only carbon atoms, $d_{100} : d_{011} ; d_{111}$ is $\frac{1}{2} : \frac{1}{\sqrt{2}} : 2/\sqrt{3}$ a ratio not characteristic of any lattice and indicating a screw axis a. The real ratio should be $1 ; \frac{1}{\sqrt{2}} ; 2/\sqrt{3}$ characteristic of Γ_r'.

·32 Number of points in a component set

Having determined the lattice abwolutely we can proceed to find the number of points in each component set by comparing the density of the crystal on the assumtion that there are N molecules per unit cell, with the observed density of the crystal.

The weight of each molecule is Mm where M is its molecular weight and m the weight of a hydrogen atom. We have therefore,

$$\text{Density} = \frac{\Delta NMm}{Sabc} \quad \text{or } N = \frac{\rho Sabc}{\Delta Mm}$$

The formula of a molecule is in general written $X_x Y_y Z_z$ .. where x,y,z .. represent the numbers of atoms of X,Y,Z respectively in the molecule. The number of atoms of each kind per unit cell is accordingly Nx,Ny,Nz ... The number Nx when x is the least of x,y,z, ... is of the greatest importance in the eleucidation of crystal structure. It at once limits the number of classes and systems that the crystal may belong to. The crystal can belong to no system whose least subset has more points per unit cell t than Nx .

Thus in the case of quartz SiO_2 a crystal of the class D_3 Measurements show thath the lattice is Γ_h with $a = 5.38 \times 10^{-8}$ cms

We have therefore for N

$$N = \frac{\sqrt{3}\, b a^2}{2Mm}\rho \qquad b = 4.89 \times 10^{-8} \text{ cms}$$

$$Mm = 0.99 \quad 10^{-22} \text{ gms}$$

$$= 2.96 \fallingdotseq 3 \qquad \rho = 2.65$$

From measurements of d_{1000} we have $d_{1010} = a/3$ and therefore there must be a screw axis. The basic system of quartz must therefore be one of D_3^3 D_3^4 D_3^5 D_3^6 with the Si atoms as a 3point sub group.

•33 Determination of class

The class of a crystal can usually be determined by crystallographic methods. In cases of crystals which only develop very simple forms the information these afford has to be supplemented by optical , electrical or other methods. By the Bragg method it is possible to detect directly all symmetry relations except those that involve a centre of symmetry.

•331 If the class of the crystal is merohedral the orders of reflection from faces which belong to the same holohedral but not to the same merohedral forms will in general give different intensity distributions. The method fails when the two faces considered belong to forms whose faces are parallel to each other. For in this case the spacing of planes differ only in the two faces in that the sequence is inverse and as can be seen from the formula ~~xx~~ 9.21 changing the signs of d_1 d_2 d_3... does not affect the reflection intensities.

Thus in the case of zinc blende ZnS which is known to belon to class T_d there is no difference in the reflections from faces of the different forms 1,1,1 and -1,-1,-1, while for pyrites FeS_2 which belongs to class T_h the reflections from the faces 210 and 120 are totally distinct.

For the final determination of class in these doubtful cases we must have recourse to the methods of the next section.

•34 Determination of atomic positions

We may write the formula of the whole crystal as

$$\sum \left\{ l+\sum_{XYZ} \left(\sum_{1}^{N} \lambda_{X1}\right)\right\} a+\left\{ m+\sum_{XYZ} \left(\sum_{1}^{N} \mu_{X1}\right)\right\} b+\left\{ n+\sum_{XYZ} \left(\sum_{1}^{N} \nu_{X1}\right)\right\} c$$

where $\lambda_{X1}\mu_{X1}\nu_{X1}$ are the coordinates of an atom of X

$\sum^{N} \lambda_{X1},\mu_{X1}\,\nu_{X1}$ are the coordinates of all equivalent atoms of X

$\sum_{XYZ}\left(\sum_{1}^{N}\lambda_{X1},\mu_{X1}\,\nu_{X1}\right)$ are the coordinates of all the atoms in a component set

~~If there are N atoms~~

There are $N\Sigma x$ atoms in a component set we have after determining the lattice, $3N\Sigma x$ unknowns to find, before the whole crystal is absolutely determined. We may have already found, however, a number of relations connecting these coordinates. If we know the symmetry class, the number of unknowns is reduced to $3N\Sigma x/k$ where k is the number of equivalent points in the class. If there is a sub set some of the unknowns may be exactly determined. We know what screw axes exist and from this and the information of the sub sets we may be able to limit the number of possible systems ~~that~~ to which the crystal may belong, to a very few. In this case, for each possible system the number of unknowns reduces to $3\Sigma x$ and may even from considerations of sub sets reduce to 0 in which case the crystal is completely determined. Whether such reductions may be effected or not the following method is applicable.

•341 Consider the series of planes parallel to $fl+gm+hn=0$. one passing through each of the points $\sum_{XYZ}\left(\sum_{1}^{N}\lambda_{X1},\mu_{X1}\,\nu_{X1}\right)$. Their point densities are all equal to the density of points in the corresponding net of the skeletal lattice, while their electron densities are simply proportional to the atomic numbers of X, Y, Z, ...

We have therefore for the value of the m_{x1} of the formula 4.21

$$m_{x1} = \frac{\delta \Delta n_x}{T(fVbc+gVca+hVab)}$$ whre n_x is the atomic number of an element X

The spacing of the planes is given by

$$d_{x1}/d = j_{x1}/\delta \quad \text{where } j_{x1} = f\lambda_{x1}+g\mu_{x1}+h\nu_{x1}$$

Substituting in the formula

$$I_m = \frac{\delta \Delta k}{nT(fVbc+gVca+hVab)}\left[\left\{\Sigma n_x \cos 2n\pi\, j_{x1}/\delta\right\}^2 + \left\{n_x \Sigma \sin 2n\, j_{x1}/\delta\right\}^2\right]$$

If we are able to measure reflections from P planes and can obtain p_r orders of reflection from ~~each~~ the r th plane we have Σp_r equations of this type. However as the equations are trancendental in j_{x1} we cannot tell how many would be needed to find the $3N\Sigma x$ unknowns. The solution of a number of such equations is except in some simple cases extremely difficult and laborious. It should not prove difficult to construct a machine somewhat similar to a harmonic analyser, which would make $\left(\lambda_{x11}^{N}\mu_{n}\nu_{n}\right)$ pass through all their possible values and select those which led to the observed values of ~~xx~~ reflection intensities. In view of the doubtful validity of the formula and the difficulties of exact measurements of intensities it is doubtful whether such a machine would justify itself at present. The method most used in practice is to reduce by means of the considerations of the last section the possible structures to a very few, and beginning with the simplest and to compare the intensities calculated from them with those observed In this tentative method, analogies drawn from already eleucidated crystals are invaluable. In this way, proceeding step by step Bragg was able to analyse rock salt, sylvine, blende, diamond, fluorite and pyrites; all cubic crystals but of sucessively increasing complexity.

The Laue method

.4 In this method a beam of "white" i.e. heterogeneous X-rays are allowed to fall on a properly oriented crystal and the rays reflected from the various planes are registered on a photographic plate placed behind the crystal.

The reflected rays are no longer white, but consist as was show in 9.12 of radiation made up of a series of wave lengths of different intensities.

.41 The position of the spots on the photographic plate indicate merely the indices of the planes producing them, but as planes of the same form give spots of the same intensity, the nature of the symmetry of the crystal can be seen. The class however cannot in general be determined unambiguously, as for the reasons explained in 9.331 it is impossible to detect the absence of a centre of symmetry.

.42 The intensities of the spots is an average effect depending partly on the spacing and densities of the planes produceing them, partly on the wave length intensity distribution in the incident beam. This renders interpretation very difficult, but when the intensity distribution in the incident beam contains only one maximum, it is possible to analyse some simple crystals.

If the crystal is a lattice, the spacing for all planes is even and the reflection for that plane which best reflects wave lengths near the maximum will be the most intense. The intensities of reflections from other planes will fall off regularly with the change of their indices. In the case of a crystal which is not a lattice however, the suppression of reflections by certain of the planes will cause the intensities to vary irregularly with their indices and these irregularities may be used to discover their structure. Even in the simplest crystals this can only be done by trying various structures and comparing the spot intensities deduced ~~from~~ with those observed.

In spite of these apparent limitations of the Laue method Ewald, Wycoff and others have devised improvements both on the experimental and theoretic sides by means of which remarkable results have been obtained.

A method which has occurred to me but which has not as far as I know been tried, would be to take a series of Laue photographs with a sourse of homogeneous X rays of regularly varying wave length such as could be obtained for instance from a rotating rock salt crystal illuminated by white rays. If the l light were strictly homogeneous, the photographs would show no spots but the central one, for all but a certain number of wave lengths for which the reflections for certain planes would flash out . If such a method were to prove practicable as full results could be obtained from it as from the Bragg method, for in this case the wave lengths being known, absolute measurements of length could be made, the absence of which, is the chief drawback of the Laue method.

.5 The Hull method

The third important method is that developed independently by Hull, and Debye and Scherrer. In this method, not one, but ala large number of crystals are used in the form of a metallic ag aggregate or coarse powder spread on a plate or in the form of a thin cylinder. A beam of homogeneous X-rays is used. The crystals being arranged at random, there will always be a certain number that present some plane of the form f,g,h at such an angle to the incident beam that one of the orders of reflection occur and such reflected beabs are detected on a photographic plate or by an ionisation chamber.

.51 The angle that such a reflected beam makes with the incident beam is 2 θ hence if we can find n, $d_{f,g,h}$ is absolutely determined. It is often possible to pick out the orders of reflections due to the same plane on account of the simple relations between the sines of half the deflection angles.

.52 The great disadvantage og the Hull method is that we have no direct means of finding f,g,h. The intensities of a reflected beam is now proportional to that of the corresponding plane in the Bragg method multiplied by the number of faces in the form or in the case of a crystal not possessing a centre of symmetry, by twice this number; for it is obvious that the expectation of a suitably inclined face belonging to any form is proportional to the number of faces in the form, and that the intensity of of reflection is proportional to this expectation.

It can be seen that the Hull method leads to a similar but more complicated set of equations as the Bragg method and with many more unknowns. These equations are practically insoluble, and the method accordingly used in practice is to choose the st strongest of the series of reflections as corresponding to the planes with simplest indices and to check the structure thus arrived at by using it to predict the positions of the other 1 reflected beams.

.53 The Hull method is most useful when applied to,metals or to substances which can only be obtained in the so called amofphous condition or in small and imperfect crystals.

.6 Tabulation of results

The results obtained in an analysis of a crystal, whether or not they are complete can all be contained in the formula given in 9.34 ,the vectors a,b,c being also supposed known both in magnitude and in relative positions.

If however we assume the formula and also the symmetry elements of the 230 point systems as given in the tables in Ch VI all the results of an analysis may be given concisely as follows

.61 (i) The symbol of the skeletal lattice

(ii) the absolute dimensions both scalar and angular when necessa

(iii) the symbol of the point system. (Strictly speaking this includes the symbol of the lattice,)

(iv) the coordinates of one of each set of equivalent atoms stipulating the element .

From the set of of constants given under these heads we can calculate by the methods of Ch VII the position of every atom of each element in the crystal, and by the methods of Ch VIII the spacing and density of every set of parallel planes.
The number N of molecules of the substance per unit cell though included in the above deserves separate statement.

.62 In the following table these structural constants are given for a number of typical crystals which have been analysed by Bragg and others.

Name	Formula	N	Lt	Sm	Coordinates	Remarks
Rock salt	NaCl	1	Γ_c''	O_h^5	Na 0 0 0 Cl $\frac{1}{2}$ 0 0	Other alkaline halides have similar structures
Zinc blende	ZnS	1	Γ_c'	T_d^2	Zn 0 0 0 S $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$	
Diamond	C	2	Γ_c'	O_h^7	C_2 0 0 0	
Fluorite	CaF_2	1	Γ_c'	O_h^5	Ca 0 0 0 F_2 $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$	
Iron pyrites	FeS_2	1	Γ_c'	T_h^6	Fe 0 0 0 S_2 $\frac{1}{4}$-x x x	X has been variously given as 1/5 and 2/9
Cuprite	Cu_2S	1	Γ_c	O_h^4	O 0 0 0 O' $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ Cu $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$	
TIN	Sn	2	Γ_t	D_{4h}^1	Sn 0 0 0 Sn_2 $\frac{1}{2}$ $\frac{1}{2}$ 0	
Rhombic alkaline sul sulphates	R_2SO_4	1	Γ_o''	Q_h^{13}	S 0 0 0	
Calcite	$CaCO_3$	1	Γ_{rh}	D_{3d}^5	Ca 0 0 0 0 C $\frac{1}{2}$ 0 0 0 O_3 $\frac{1}{2}$ 2x/3 -x/3 -x/3	Positions of atoms not given
Quartz	SiO_2	3	Γ_h	D_3^4	Si_3 0 2x/3 -x/3 -x/3 O_6 $\lambda+\mu+\nu$ $\mu-\nu$ $\nu-\lambda$ $\lambda-\mu$.	

In this table no lattice constants are given.

Appendix

A Suggestion for a natural, numerical denotation of Crystal Systems, Classes, Lattices and Point Systems.

There are many systems of denotation in use. Of these the most commonly known is that of Schoenflies which is used almost exclusively for internal structure. It is essentially a literal system and in it the letters correspond to various words used to describe the systems etc. This makes it easy to learn, but it suffers from several disadvantages.

The basis of the system is the 32 Classes each of which are indicated by a capital letter with a suffix formed in general of a number and a letter. To denote 32 Classes by a triliteral symbol is unnecessary. The 14 lattices are all denoted by the letter Γ with suffixes and dashes: here again we have a triliteral system but this one has not even the advantages of the Class notation, as the manifest analogies between the different lattices are not shown by it. In the notation for point systems the method followed is to add to the Class symbol an index consisting of a serial number indicating the order of derivation of the system in the particular Class by Schoenflies' method. This order cannot claim to be a natural order, and moreover the index gives no indication either of the skeletal lattice of the system or of its affinities to similar systems in other Classes. It is practically impossible to remember the nature of any system denoted by its Schoenflies symbol, and references to the original derivation have constantly to be made.

The system suggested is free from these disadvantages. It is entirely numerical in character, making use of one other symbol only, the decimal point, which is used to mark off the portion indicating the crystal system and class from that indicating the lattice and point system.

The symbol of a point system in its most general form consists of five numbers, two preceding the decimal point and three following. In holohedral systems, however, only one figure precedes the point and in some systems the number of figures after the decimal point often reduces to one or two. The significance of the figures is as follows:

1. The first digit from the left indicates the crystal system. The number denoting the 7 crystal systems~~s~~ are as follows:-

0	Triclinic	
1	Monoclinic	
2	Orthorhombic	
3	Trigonal	(Rhombohedral)
4	Tetragonal	
6	Hexagonal	
8	Regular	(Cubic)

It will be seen that except for the Monoclinic and Regular systems the number stands for the highest order of axes which the system possesses. We also have the convenient relation that any system is included as a special case by a system whose number is a factor of that of the first.

2. The second digit is used to distinguish the various Classes in each crystal system, so that we use a biliteral symbol for a Class.

The holohedral Classes have 0 for their second digit which can be omitted without causing confusion, thus giving the simplest symbol to the most commonly occurring Classes. The Holoaxial have 1 and so forth as shown in the table of Classes. All Classes containing only rotations of the first sort are designated by odd numbers; those with second sort rotations also by even numbers.

3. The first figure after the decimal point in conjunction with the first figure of all denotes the skeletal lattice. For normal lattices i.e. lattices with points only at the corner of rectangular parallelopipeda, this number is 0 (in the hexagonal and triclinal systems, as this is the only lattice, the figure 0 can be dropped). For centred lattices i.e. for lattices with points at the centres of rect. par. the number is 1. For face-centred lattices the number is 2. For the Orthorhombic lattice which has points at the centres of only one pair of faces of the rect. par. the number is 3. But besides these lattices, we may often consider lattices that are not distinct from those already denoted. These are Γ'_{oc} for which the number is 4 and $\Gamma'_{t\epsilon}$ and $\Gamma_{t\beta}$ which are denoted by 4·2 and 4·3 respectively.

In the order of lattices .0, .1, .2, it is easily remembered that each has twice the number of points per unit per rect. par. as the one before it (except in the trigonal system).

The hexagonal lattice may be denoted either as 3.0 or 6.0 according as it occurs in trigonal or hexagonal systems. The notation for lattices is given in the table.

4. The second figure after the decimal point is used to distinguish between different systems of the same Class and lattice. The number is chosen on the general idea that it is higher in systems of greater complexity. When it is 0 for instance, all the axes are rotation axes. In 4, 3. and 6. this number is the pitch of the screw axes: in 2. and 8. it represents the number of perpendicular axes. Systems belonging to some Classes such as Holohedral and Paramorphic which are derived from systems in other Classes are identically the same but for an additional digit. This derivative process is generally an inversion and the last digit denotes the position of the centre of inversion.

As far as possible the notation of the systems is arranged so that the numbers after the decimal point are the same in analogous systems, thus indicating in a large number of cases the sub-groupsof any system.

The notation for the 230 point systems is given in full with the corresponding Schoenflies symbols in the table below. It can be seen that in this method of denotation each symbol contains a considerable amount of information, While at the most employing five numbers (and in this not exceeding Schoenflies) it indicates all that the Schoenflies symbols indicate and more. Moreover, it is comparatively easy to learn and with a little practice it is possible to obtain an idea of the actual configuration of all but the most complicated system by the mere inspection of its symbol.

CLASSES

System	HOLOHEDRAL	Merohedral					
		Holo-~~hedral~~ axial	Hemimorphic	Alternating	Sphenoidal	Tetartohedral	Paramorphic
Triclinic (Oblique)	C_i 0	C_1 01					
MONOCLINIC	C_{2h} 1	C_2 11	C_s 12				
Ortho-~~[illegible]~~ rhombic	Q_h 2	Q 21	C_{2v} 22				
Tetragonal	D_{4h} 4	D_4 41	C_{4v} 42	C'_4 43	D_{2d} 44	C_4 45	C_{4h} 46
Trigonal (Rhombohedral)	D_{3d} 3	D_3 31	C_{3v} 32	C_{3i} 33		C_3 35	
Hexagonal	D_{6h} 6	D_6 61	C_{6v} 62	C_{3h} 63	D_{3h} 64	C_6 65	8_{6h} 66
Regular (Cubic)	O_h 8	O 81	T_h 82		T_d 84	T 85	

LATTICES

Normal	Γ_{tr} 0.0	Γ_m 1.0	Γ_o 2.0	Γ_t 4.0	Γ_c 8.0	Γ_{rh} <u>3.0</u>	Γ_h <u>6.0</u>
Centred		Γ'_m 1.1	Γ'''_o 2.1	Γ'_t 4.1	Γ''_c 8.1	Γ_{rh} 3.1	
β Face centred		~~2x2~~	Γ''_o 2.2	$\Gamma'_{t\beta}$ <u>4.2</u>	Γ'_c 8.2		
1 Face centred			Γ'_o 2.3	$\Gamma_{t\beta}$ <u>4.3</u>			

Also $\Gamma'_{o\beta}$ <u>2.4</u>

POINT SYSTEMS

Class										
C_1 01.	1 .0									
C_i 0.	1 .0									
C_2 11.	1 .00	2 .01	3 .10							
C_s 12.	1 .00	2 .01	3 .10	4 .11						
C_{2h} 2.	1 .000	2 .010	3 .100							
	4 .001	5 .011	6 .101							
C_{2v} 22.	1 .00	2 .01	3 .02	5 .03	4 .04	7 .05	6 .06	9 .07	8 .08	10 .010
	20 .10	22 .11	21 .12							
	18 .20	19 .21								
	11 .30	12 .31	13 .32							
	14 .40	15 .41			16 .44		17 .46			
Q 21.	1 .00	2 .01	3 .02	4 03						
	8 .10			9 .13						
	7 .20									
	6 .30	5 .31								
Q_h 2.	1 .000	5 .010	9 .020	15 .030						
	2 .001	7 .011								
	4 .002		13 .022							
	3 .003	6 .013	10 .023	16 .033						
			14 .024							
			12 .025							
	25 .100			27 .130						
	26 .101			28 .131						
	23 .200									
	24 .203									
	19 .300	17 .310								
	21 .301									
	22 .302									
	20 .303	18 .313								

In the first of each double column is given the Schonfleis serial index of the point system; in the second the decimal part of the proposed notation, the whole number part being given under the head of class.

Class						
C_4 45.	1 .00	2 .01	3 .02	4 .03	5 .10	6 .11
C_4' 43	1 .00				2 .20	
C_{4h} 46	1 .000 3 .002		2 .020 4 .022		5 .100	6 .112
C_{4v} 42.	1 .000 5 .001 2 .002 6 .003		3 .020 7 .021 4 .022 8 .023		9 .100 10 .102	11 .111 12 .113
D_4 41.	1 .000 2 .002	3 .010 4 .012	5 .020 6 .022	7 .030 8 .032	9 .100	10 .112
D_{4h} 4. 5 .0[illegible]	1 .0000 2 .0001 3 .0002 4 .0003 5 .0020 6 .0021 7 .0022 8 .0023		10 .0200 9 .0201 12 .0202 11 .0203 14 .0220 13 .0221 16 .0222 15 .0223		17 .1000 18 .1001	19 .1102 20 .1103
D_{2d} 44.	1 .000 2 .002 3 .020 4 .022	9 .100 10 .102	11 .200 12 .202	5 .300 6 .302 7 .320 8 .322		
T 85.	1 .00 3 .10 2 .20			4 .03 5 .13		
T_h 82.	1 .000 2 .003 5 .100 3 .200 4 .203			6 .030 7 .130		
T_d 84	1 .000 4 .001 3 .100 2 .200 5 .201			6 .131		

Class									
O	81.	1	.000						
		2	.002			6	.031		
						7	.033		
		5	.100			8	.130		
		3	.200						
		4	.202						
O_h	8.	1	.0000						
		2	.0003						
		3	.0020						
		4	.0023						
		9	.1000			10	.1300		
		5	.2000						
		6	.2001						
		7	.2022						
		8	.2023						
C_3	35.	1	.00	2	.01	3	.02	4	.10
C_{3i}	33.	1	.0					2	.1
C_{3v}	32.	1	.00	3	.01			5	.10
		2	.20	4	.21			6	.11
D_3	31.	2	.00	4	.01	6	.02	7	.10
		1	.20	3	.21	5	.22		
D_{3d}	3.	1	.00					5	.10
		2	.01					6	.11
		3	.20						
		4	.21						

C_6	65.	1	.00	2	.1	4	.2	6	.3	5	.4	3	.5
C_{6h}	66.	1	.0					2	.3				
C_{3h}	63.	1	.0										
D_{3h}	64.	1	.00					2	.03				
		3	.20					4	.23				
C_{6v}	62.	1	.00					2	.03				
		3	.20					4	.23				
D_6	61.	1	.00	2	.1	4	.2	6	.3	5	.4	3	.5
D_{6h}	6.	1	.00					3	.30				
		2	.01					4	.31				

Call for Contributions to the Next CompComm Newsletter

The next issue of the Compcomm Newsletter is expected to appear around October of 2010 with the primary theme of Age Concern relevant to Protein Crystallography and/or Powder Diffraction. If no-one is else is co-opted, the newsletter will be edited by Lachlan Cranswick.

Contributions would be also greatly appreciated on matters of general interest to the crystallographic computing community, e.g. meeting reports, future meetings, developments in software, algorithms, coding, historical articles, programming languages, techniques and other news.

Please send articles and suggestions directly to the editor.

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