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Crystal Structure Analysis Using the "Superposition"- and "Complementary"-Structures

by

Ernst Höhne and Leo Kutschabsky

Series Preface

The long term aim of the Commission on Crystallographic Teaching in establishing this pamphlet programme is to produce a large collection of short statements each dealing with a specific topic at a specific level. The emphasis is on a particular teaching approach and there may well, in time, be pamphlets giving alternative teaching approaches to the same topic. It is not the function of the Commission to decide on the 'best' approach but to make all available so that teachers can make their own selection. Similarly, in due course, we hope that the same topics will be covered at more than one level.

The initial selection of ten pamphlets published together represents a sample of the various levels and approaches and it is hoped that it will stimulate many more people to contribute to this scheme. It does not take very long to write a short pamphlet, but its value to someone teaching a topic for the first time can be very great.

Each pamphlet is prefaced by a statement of aims, level, necessary background, etc.

C. A. Taylor
Editor for the Commission

Teaching Aims

Broad: To illustrate and illuminate the relation between diffraction pattern and crystal structure, and to draw together direct and vector methods.

Specific: To provide a method for solving structures when standard methods fail.

Level

Postgraduate

Background

Sound understanding of the theory, combined with practical experience, of the standard methods of structure solution.

Practical Resources

Computing aid highly desirable.

Time Required

A heavy and demanding course requiring an estimated 8 hours.

Crystal Structure Analysis Using the
"Superposition"- and "Complementary"-Structures

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1. General

Quite a number of crystal structures contain parts (e.g. heavy atoms or building units) with a higher symmetry (e.g. with additional translation or pseudotranslation) compared with the whole structure. In those cases, standard methods may not lead to correct results, this is why special methods may have to be applied.

As an example let the heavy atoms (strongly reflecting atoms) have parameters x_s, y_s, z_s and x_s, y_s, $\frac{1}{2} + z_s$ (Fig. 1). Then they contribute only to the structure factors $F(hkl)$ with $1 = 2n$, since their contribution $F_s(hkl)$ is equal to

$$F_s(hkl) = f_s \{\exp[2\pi i(hx_s + ky_s + lz_s] + \exp[2\pi i(hx_s + ky_x + l(\tfrac{1}{2} + z_s))]\}$$
$$= f_s\{\exp[2\pi i(hx_s + ky_s + lz_s)][1 + (-1)^l]\}$$
$$F_s(hkl)_{l=2n+1} \equiv 0 \tag{1.1}$$

Therefore the $|F(hkl)|^2$ with $l = 2n$ are systematically strong, compared with those with $l = 2n+1$, i.e. for the mean values $\langle I(hkl)\rangle$ of the intensities within any region of σ values

$$\langle I(hkl)_{1=2n}\rangle \text{ strong,} \qquad \langle I(hkl)_{1=2n+1}\rangle \text{ weak.}$$

If such a systematic distribution of the intensities or a similar one occurs, it is useful, for methodical reasons, to regard the electron density $\rho(x, y, z)$ as the sum of two—or if necessary—of several parts.

Thus the electron density function

$$\rho(x, y, z) = \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + 1z)]$$

may for the case indicated in Fig. 1 be written

$$\rho(x, y, z) = \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + 1z)$$
$$(1 = 2n) \tag{1.2}$$

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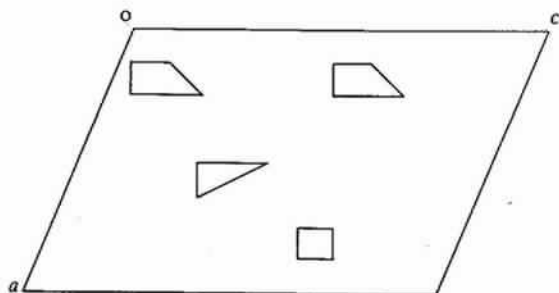
Fig. 1. Crystal structure in P1. △—symbol for the arrangement of heavy atoms, ▽ and □ remaining atoms of the structure.

$$+\sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + 1z)]$$

$$(1 = 2n + 1)$$

$$= \rho_{sup}(x, y, z) + \rho_{com}(x, y, z) \tag{1.2'}$$

where

$$\rho_{sup}(xyz) = \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + 1z)]$$

$$(1 = 2n)$$

$$\rho_{com}(xyz) = \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + 1z)]$$
$$(1 = 2n + 1)$$

$\rho_{sup}(x, y, z)$ denotes a hypothetical structure, called the superposition structure, which is related to the real structure in the following way

$$\rho_{sup}(x, y, z) = \tfrac{1}{2}[\rho(x, y, z) + \rho(x, y, \tfrac{1}{2} + z)] \tag{1.3}$$

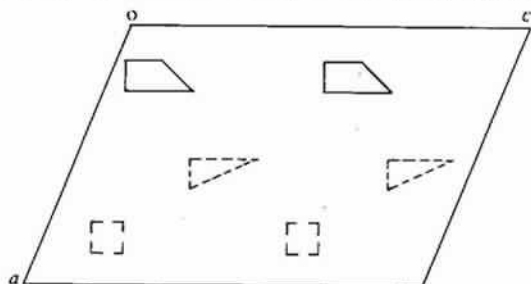In $\rho_{sup}(x, y)$ (Fig. 2) the two heavy atoms (△) appear with correct

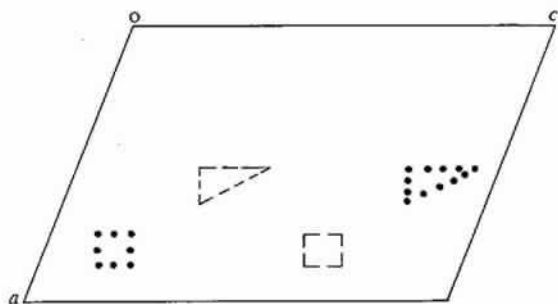Fig. 2. Superposition structure. △—heavy atoms ⟨⟩, [] —remaining atoms with half weight.

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Fig. 3. *Complementary structure.* $\square$, $\square$—*atoms with positive half weight.* $\vdots$.
$\vdots$—*atoms with negative half weight.*

weights because they are connected by a translation of $c/2$, whereas the remaining atoms (squares and triangles) appear with half their weights (marked by shaded symbols) at the original position and at a second point shifted relative to it by $c/2$.

Generally speaking, the symmetry of $\rho_{sup}(x, y, z)$ is identical with the symmetry of the arrangement of the heavy atoms (or other building units with higher symmetry) taken by themselves. This higher symmetry may either be strictly true for the heavy atoms taken by themselves, or only in approximation. In the latter case it may be useful to disregard deviations from the higher symmetry, to start with.

The symmetry of the complementary structure $\rho_{com}(x, y, z)$ follows from (1.2) and (1.3):

$$\rho_{com}(x, z, y) = \tfrac{1}{2}[\rho(x, y, z) - \rho(x, y, \tfrac{1}{2} + z)] \tag{1.4}$$

Its properties are shown in Fig. 3. Accordingly, the heavy atoms (i.e. those which occur in pairs related to a shift of $c/2$) are absent in $\rho_{com}(x, y, z)$, whereas any other atom appears with half its weight at its real position and with half negative weight at a position shifted by $c/2$ (Fig. 3). The space group symmetry of the arrangement with positive weights in $\rho_{com}(x, y, z)$ is identical with the space group of the real structure $\rho(x, y, z)$. In a similar way, the introduction of a superposition and a complementary structure may be indicated by systematically strong reflections occurring, e.g. for $h = 2n$ or $h + k = 2n$ or $h + k + 1 = 2n$ etc.

If, on the other hand, the heavy atoms (or another part of the structure, taken by itself) possesses a higher symmetry (other than translation) than the structure as a whole, the introduction of other kinds of hypothetical structures, also to be called $\rho_{sup}(x, y, z)$ and $\rho_{com}(x, y, z)$ may be of use. In this case, no systematically strong and weak reflections result.
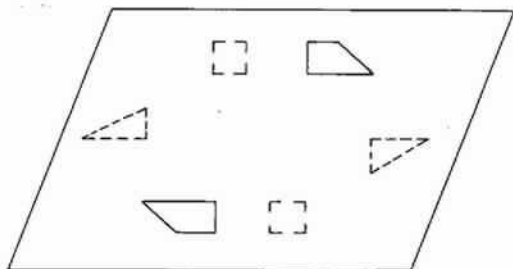
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Fig. 4. Superposition structure (centrosymmetric). $\square$—centrosymmetric arrange-
ment of heavy atoms, $\square$, $\square$—remaining atoms with half weights.

As an example, we consider a structure in $P1$ containing two heavy atoms of the same element per unit cell. The heavy atoms considered by themselves are connected by a centre of symmetry. The structure computed with phases (signs) taken from the heavy atom contribution is necessarily centrosymmetric and is related to the real structure by its superposition with its centrosymmetric image (Fig. 4). If referred to such a partial centre of symmetry as origin, the electron density distribution of the superposition structure $\rho_{sup}(x, y, z)$ may be expressed as

$$\rho_{sup}(x, y, z) = \tfrac{1}{2}[\rho(x, y, z) + \rho(\bar{x}, \bar{y}, \bar{z})] \tag{1.5}$$

The real structure or at least part of it may in many cases of this kind be obtained using well established chemical knowledge, such as atomic distances, known stereochemistry of molecules or parts of them as of coordination polyhedra etc.

2. Special Methods

2.1. Linear Structure Factor Equations

In many cases two coordinates (e.g. x_j, y_j) of any atom in the real structure are the same as those of the superposition structure. There arises the task of determining the third atomic coordinate (z_j). The method of linear structure factor equations (SFE) by Kutschabsky[2] and by Kutschabsky and Höhne[3] allows us to calculate these atomic coordinates (z_j) directly, using the reflection of the first level of the reciprocal lattice $(F(hkl))$.

The basic relation follows directly from the formula for the structure factor

$$F(\mathbf{H}) = \sum_{s=1}^{p} \sum_{j=1}^{N} (f_{sj}(\mathbf{H}) \cos 2\pi \mathbf{H}\mathbf{r}_{sj} + i f_{sj}(\mathbf{H}) \sin 2\pi \mathbf{H}\mathbf{r}_{sj}) \tag{2.1}$$

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where P is the number of equipoints in the unit cell, N is the number of symmetrically independent atoms, f_{sj} is the atomic scattering factor and $\mathbf{r}_{sj}$ is the radius vector of the centre of atom s, j.

Vector $\mathbf{H}$ is defined by $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, where $(\mathbf{a}, \mathbf{b}^*, \mathbf{c}^*)$ are the basic reciprocal vectors.

Using the symmetry matrices R_s and the translation t_s we obtain:

$$F(H) = \sum_{s=1}^{P} \sum_{j=1}^{N} f_{sj}(\mathbf{H})[\cos 2\pi H(R_s\mathbf{r}_j + \mathbf{t}_s) + i \sin 2\pi H(R_s\mathbf{r}_j + \mathbf{t}_s)] \quad (2.2)$$

The separation into the components leads to

$$F(H) = \sum_{s=1}^{P} \sum_{j=1}^{N} \gamma_{sj}(\mathbf{H})[\cos 2\pi(\alpha_s x_j + \beta_s y_j + \gamma_s z_j + \delta_s)$$
$$+ i \sin 2\pi(\alpha_s x_j + \beta_s y_j + \gamma_s z_j + \delta_s)] \quad (2.3)$$

$$F(H) = \sum_{s=1}^{P} \sum_{j=1}^{N} \gamma_{sj}(\mathbf{H})[\cos 2\pi(\alpha_s x_j + \beta_s y_j + \delta_s) \cdot \cos 2\pi\gamma_s z_j$$
$$- \sin 2\pi(\alpha_s x_j + \beta_s y_j + \delta_s) \cdot \sin 2\pi\gamma_s z_j$$
$$+ i \sin 2\pi(\alpha_s x_j + \beta_s y_j + \delta_s) \cdot \cos 2\pi\gamma_s z_j$$
$$+ i \cos 2\pi(\alpha_s x_j + \beta_s y_j + \delta_s) \sin 2\pi\gamma_s z_j \quad (2.4)$$

In the most important cases the factor γ_s depends only on l (not h or k). In those cases we obtain for structure factors $P(hkl)$ with constant L

$$F(\mathbf{H}) = \sum_{j=1}^{N} (a_j + ib_j)C_j^{(L)} + \sum_{j=1}^{N} (c_j + id_j)s_j^{(L)} \quad (2.5)$$

where the unknown variables $\cos 2\pi L z_j$ and $\sin 2\pi L z_j$ have been denoted by $C_j^{(L)}$ and $S_j^{(L)}$, respectively, and their known coefficients by a_j, b_j, c_j and d_j.

$a_j = a_j(h, k, f_j, x_j, y_j)$ etc. where the exact form of dependence on h, k, f_j, x_j and y_j may be obtained from Table 4 of International Tables for X-ray Crystallography, Vol. 1.

The $2N$ unknown variables $C_j^{(L)}$ and $S_j^{(L)}$ may be determined by a system of linear equations using $F_{obs}(\mathbf{H})$ for $F(\mathbf{H})$.

If the phases of the $F_{obs}(\mathbf{H})$ are unknown the unobserved reflections may be used to obtain a system of homogenous linear equations. Often it is of advantage to use in addition to the homogenous equations one equation belonging to a strong structure factor whose phase may be fixed arbitrarily in centrosymmetrical space groups, and in the non-centrosymmetrical space groups in which the origin may have any position in the z-direction.

Because the coefficients of these equations are inaccurate and, moreover, the structure factors are zero only approximately a more

accurate solution for the values $C_j^{(L)}$ and $S_j^{(L)}$ may be obtained by using more equations than there are variables and by minimizing the sum of the squares of the deviations $\sum |F_{obs}(\mathbf{H}) - F_{calc}(\mathbf{H})|^2$, where $F_{calc}(\mathbf{H})$ stands for the right side of equation (2.5) and $F(H)$ is to replace by $F_{obs}(\mathbf{H})$ in this relation. The $C_j^{(L)}$ and $S_j^{(L)}$ from the first calculation may be used to determine the phases of further structure factors. Taking these equations in addition to those used already, the number of equations increases and thus the accuracy of $C_j^{(L)}$ and $S_j^{(L)}$ is improved.

If the $F(hkl)$ with $L = 1$ are used, the atomic parameters z_j of all atoms resolved in the (x, y)-projection follow from $C_j^{(1)} = \cos 2\pi z_j$ and $S_j^{(1)} = \sin 2\pi z_j$ and $(C_j^{(1)})^2 + (S_j^{(1)})^2 = 1$. The accuracy of the values z_j may be further improved by using $F(hkl)$ with L larger than one.

2.2. The Application of Direct Methods to Centrosymmetric Structures Containing heavy atoms[4]

It is assumed that the positions of the heavy atoms are known and that there is a sufficient number of reflections whose signs are determined by the heavy atoms. These reflections do not obey the probability relation (2.6).

$$S_{h+h'} \sim S_h \cdot S_{h'} \qquad (2.6)$$

On subtracting the heavy atom contribution from the observed structure factors of these reflections, one obtains the sign of the light atom contributions for these reflections. Thereafter one can solve the remaining light atom structure by applying equation (2.6) to obtain the signs of the reflections that do not have contributions from the heavy atoms.

The procedure was used to solve the structure of the complex $Au[S_2C_2(CN)_2]_2 \ Au[S_2CN(C_4H_9)_2]_2$. The space group was found to be $P2_1/c$, with two formula units per unit cell. The reflections hkl ($h = 2n$, $k + 1 = 2n$) were all very strong and the gold atoms were placed at the (special) position 000, $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$. 1337 observed 'strong' reflections (with equal positive contributions from the gold atoms) and 538 observed 'weak' reflections (without any contributions from the gold atoms) were used.

The first step was a calculation of the Wilson plot. The following expressions was used:

$$\langle I \rangle_h = K_L \langle \sum_i^L f_i^2 \exp(-2B_L \sin^2 \theta/\lambda^2) \rangle_h + K_H \langle |F_H|^2 \exp(-2B_H \sin^2 \theta/\lambda^2) \rangle_h \qquad (2.7)$$

where $I = (K|F_{obs}|_i^2)$ is the observed intensity on a relative scale, $K = K_L = K_H$ is the scale factor, $\sum^L$ denotes a summation over all light atoms in the unit cell, F_H is the heavy atom contribution to the structure factor and B_L and B_H are the overall temperature factor parameters of the light

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and heavy atoms respectively. The average is taken over reflections h within a given $\sin \theta$ interval.

For the 'weak' reflections ($F_H = 0$) the second term in equation (2.7) vanishes and a Wilson plot for these reflections gave the scale factor K_L (1.29) and the value of B_L (3.24 Å²). On substituting these results in equation (2.7) a Wilson plot for the 'strong' reflections gave the scale factor K_H (1.26) and the value of B_H (2.91 Å²). A small difference in K_L and K_H will not affect the following steps.

The second step is the calculation of the normalized structure factors E. The formulae normally used for the calculation of E values do not make sense for a structure containing heavy atoms. For the corresponding light atom structure the E values, E_L, are defined by:

$$E_L = F_L (\varepsilon \sum_i^L f_i^2)^{-1/2} \exp (B_L \sin^2 \theta/\lambda^2) \qquad (2.8)$$

where F_L is the light atom contribution to the structure factor and, for space group $P2_1/c$, $\varepsilon = 2$ for $h01$ and $0k0$ reflections and $\varepsilon = 1$ for all other reflections.[6]

The 'strong' reflections have positive structure factors and we have $F_1 = F_{obs} - F_H$; the magnitude and the sign of the E_L value is obtained by equation (2.8). This resulted in 365 signed E_L values, with $|E_L| > 1.3$. For the 'weak' reflections we have $|F_L| = |F_{obs}|$ and only the magnitude of the E_L value is obtained. This resulted in 270 reflections with $|E_L| > 1.3$.

The third step is the application of equation (2.6) to obtain the signs of the 'weak' reflections. When several interactions of the type $(h + h') = (h) + (h')$ occur for $|E_L| > 1.3$, where both S_h and $S_{h'}$ are known, several predictions of the sign $S_{h+h'}$ are obtained by application of (2.6). These predictions should be reasonably consistent before $S_{h+h'}$ is considered to be determined and singly occurring interactions should never be trusted. We have followed a procedure similar to the sign correlation procedure. The origin is partly fixed by the choice of the gold atom positions and further determined by assigning arbitrary signs to two 'weak' reflections: 221 ($|E_L| = 4.0$) and $34\bar{8}$ ($|E_L| = 2.9$). We define the following sets of reflections, all $|E_L| > 2.0$:

h_1 are 'strong' reflections, $hkl(h = 2n, k + 1 = 2n)$.
h_2 are the two origin determining choices.
h_3 are the reflections $h_1 + h_2$ and $h_2 + h_2'$.
h_4 are the reflections $h_1 + h_3$, $h_2 + h_3$ and $h_3 + h_3'$.

The application of the equation (2.6) on only reflections h_1 cannot give new signs; together with the reflections h_2 probable signs for 36 reflections h_3 were calculated. Upon entering h_3 in equation (2.6), many reflections take part in the calculations and consequently the sign of one reflection h_4 will often be found from several independent sign relations

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(2.6). Signs were calculated for 48 reflections h_4; of these the signs of 24 reflections were determined by at least five consistent relations (2.6) and accepted to be correct. Although some of the signs for reflections h_3 may be incorrectly determined, it is highly improbable that all reflections h_3 used for the signs determination of one reflection h_4 are incorrect. The intermediate results for h_3 and the rest of h_4 were rejected.

Continued application of equation (2.6) on 365 'strong' reflections, 2 reflections h_2 and 24 reflections h_4 resulted in the sign determination of 158 more 'weak' reflections with $|E_L| > 1.3$. A Fourier synthesis revealed the positions of all of the light atoms, except the hydrogen atoms.

The above described procedure may be generalized for heavy atoms on general positions. In this case there also exist reflections with intermediate heavy atom contributions. For these reflections $|F_L| = \|F_{obs}| \pm |F_H\|$ and the lowest F_L value is taken to avoid incorrect sign indications. In our opinion this procedure is well suited to an automatic solution of structures containing heavy atoms.

3. Steps of Structure Determination

1. Determine the space group and unit cell of the real structure
2. Test for systematically strong intensities
3. Determine the space group of the superposition structure (see examples)
4. Determine the superposition structure $\rho_{sup}(x, y, z)$ or at least the heavy atom position(s) in $\rho_{sup}(x, y, z)$
5. Determine the complementary structure $\rho_{com}(x, y, z)$ or the real structure
   5.1. Compute and discuss the Patterson function of the complementary structure, if this corresponds to the systematically weak reflection
   5.2. Apply "Direct methods" (see above)
   5.3. Apply the method of "linear structure factor equations"
   5.4. Resolve the ambiguity of the superposition structure using chemical knowledge, such as minimum distance between atoms, knowledge of groups, coordination polyhedra etc.

4. Examples

A. Demissidine hydroiodide[8]

Crystal data: $C_{27}H_{45}NO \cdot HI \cdot \frac{1}{2}C_2H_5OH$
orthorhombic: $P2_12_12_1$; $a = 23.0$ Å $b = 7.6$ Å $c = 16.0$ Å
   $Z = 4$
Observed systematic intensity distribution:

$\langle I(hkl)_{1=2n} \rangle$ strong; $\langle I(hkl)_{l=2n+1} \rangle$ weak.

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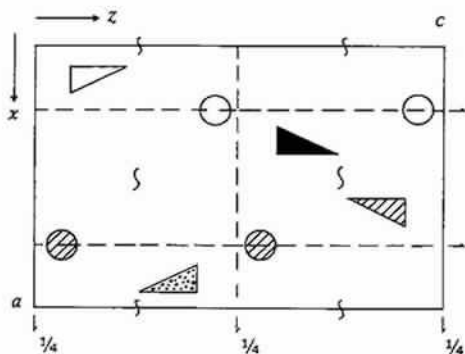Fig. 5. (a) Space group symmetry of (a) real structure-$P2_12_12_1$ ▷ building unit in y, ◤ in $\bar{y}$, ◤ in $1/2-y$, ◤ in $1/2+y$; the heavy atoms marked by circles.

According to the chemical formula and number of molecules per unit cell there are 4 heavy atoms per unit cell, i.e. one per asymmetric unit. Thus the 2 heavy atoms related by a shift of $c/2$ (on account of systematic intensity distribution) must necessarily belong to the same set of equipoints. This results if and only if the atoms lie on screw dyads parallel to c (see Fig. 5), thus the set of equipoints in $P2_12_12_1$

$$x, y, z; \tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z; \tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z}; \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z$$

specializes to

$$(000, 00\tfrac{1}{2}) + \tfrac{1}{4}, 0, z; \tfrac{3}{4}, \tfrac{1}{2}, \bar{z}$$

With $z' = 2z$ this corresponds within the unit cell $a' = a$, $b' = b$, $c' = c/2$ of
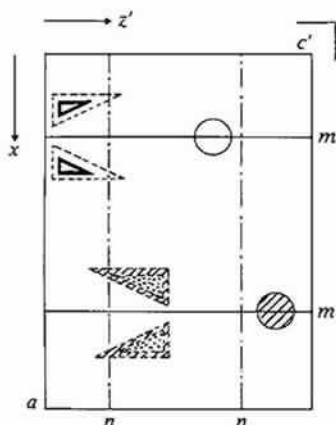
(b) superposition structure—$Pmmn$, derived from $P2_12_12_1$; the reduced weights of all building units in general position (triangles) to a quarter compared with the weight of the heavy atoms (circles) is symbolized by dashed lines.

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the superposition structure, to the equipoints

$$\tfrac{1}{4}, 0, z'; \tfrac{3}{4}, \tfrac{1}{2}, \bar{z}'$$

Obviously (Fig. 5), any of these two points lies on mirror planes perpendicular to a' and b' and are related by an n-glide plane perpendicular to c'. Thus the space group of the superposition structure is $Pmmn$.

The same result could have been obtained by scanning the orthorhombic higher symmetry space group for such equipoints. Then the set of special positions (a) $00z, \tfrac{1}{2}\tfrac{1}{2} z$ would be found for $Pmmn$, which corresponds to the set found, after a shift of the origin by $a'/4$.

The space group for the superposition structure thus obtained may now be tested with the usual space group tests, and indeed, the $hk0$-reflections with $h + k = 2n + 1$ are weak (corresponding to the n-glide plane). The superposition structure thus contains for each of 4 symmetry related atoms (x, y, z) etc., of the real structure the following sets of 4 atoms.

$$(x, y, z), (x, y, \tfrac{1}{2}+z), (\tfrac{1}{2}-x, y, z), (\tfrac{1}{2}-x, y, \tfrac{1}{2}+z)$$

i.e. 4 atoms to any atom of the real structures. This superposition structure would be obtained, if the usual heavy atom technique could be applied, and would certainly be difficult to interpret.

The Patterson function gave, however, not only the z-coordinate of the heavy atom but also hinted that it may not lie exactly on the dyad screw, but only approximately so; this was confirmed by the Patterson of the complementary structure, obtained from the reflections with $1 = 2n + 1$.

This indicated a deviation of x_j from $\tfrac{1}{4}$, and this deviation results in contribution of reflections with high values of h which even determine their phases.

The iodine parameters were refined and with the resulting phases a first Fourier synthesis of the complementary structure was obtained in space group $P2_12_12_1$.

This result was compared with the known part of the model and thus a part of the structure deduced and used as a starting point for the final determination of the real structure.

B. Piperidino-acet-m-bromo-anilide[9]

Crystal data: $C_{13}H_{17}N_2OBr$
orthorhombic: $Pbca$; $a = 23.65$ Å, $b = 12.66$ Å, $c = 9.37$ Å;
$Z = 8$
Observed systematic intensity distribution:
$\langle I(hkl)_{h=2n} \rangle$ strong; $\langle I(hkl)_{h=2n+1} \rangle$ weak
Space group of $\rho_{sup}(x, y, z)$: $Pbcm$ with lattice parameters

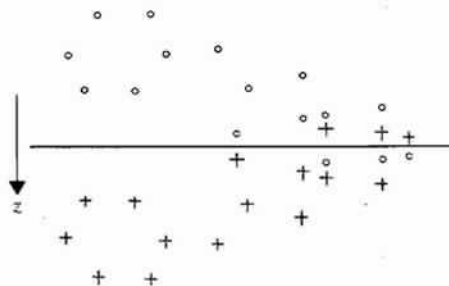$$a' = \frac{a}{2}, \ b' = b, \ c' = c.$$

Fig. 6. (y, z)-projection of the superposition structure with the pseudo-mirror-plane.

The 3-dimensional Patterson function explained the systematic distribution in the intensities by the particular position of the bromine-atom on the a-glide plane with the fractional coordinates $x = 0.159$, $y = 0.193$, $z = 0.25$. With the known position of the bromine atom (refined by least squares methods) the signs of most of the $F_{obs}(hkl)_{h=2n}$ but not of the $F_{obs}(hkl)_{h=2n+1}$ were determined.

With $F_{obs}(hkl)_{h=2n}$ a 3-dimensional Fourier synthesis of the superposition structure was calculated. This $\rho_{sup}(x, y, z)$ involves perpendicular to c an additional mirror plane, not existing in the real structure, through the bromine atom. That is why each maximum in the synthesis has a corresponding reflected one (Fig. 6). But only one of these pairs corresponds to an atom in the real structure. In addition many maxima occurred in the Fourier synthesis which do not refer to atoms. Therefore the interpretation of the synthesis by the model of the molecule failed.

To preclude the spurious peaks in the Fourier synthesis a spatial minimum function $M_4(x, y, z)^{10}$ was derived from the Patterson function by using the known bromine-bromine vectors.

The comparison of Fourier synthesis and minimum function revealed to which of the pairs of peaks connected by the mirror plane atoms could be assigned. These peaks of the superposition structure are shown in Fig. 7. Its (x, y)-projection is identical with the projection of the real structure. A model of the molecule enabled us to determine the z-coordinates of the atoms by eliminating the ambiguity in the Fourier synthesis.

C. Acetamide hemihydrobromide[11,12]

Crystal data: $(CH_3CONH_2)_2 \cdot HBr$
monoclinic: $P2_1/c$, $a = 6.51$ Å, $b = 8.64$ Å, $c = 8.24$ Å, $\beta = 113.1°$, $Z = 2$.

$\langle I(hkl)_{k+1=2n} \rangle$, strong, $\langle I(hkl)_{k+1=2n+1} \rangle$ weak.

From $Z = 2$ and $P2_1/c$ it follows that the bromine atom lies at the centre of symmetry forming, taken by themselves, an A-centred lattice. The
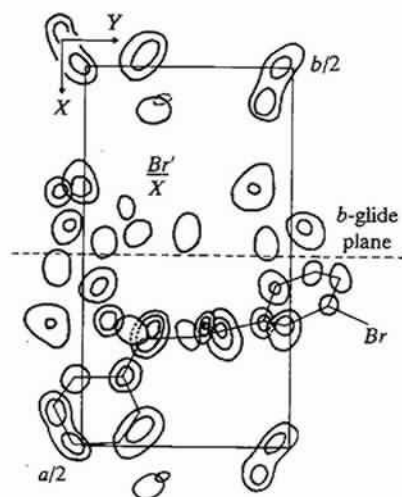
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Fig. 7. *Peak coinciding in Fourier synthesis and minimum function.*

$F_{obs}(hkl)_{k+l=2n}$ correspond to a superposition structure with the space group $A\ 2/m$, which has a mirror plane perpendicular b in addition to the space group of the real structure.

The (x, z)-projection of the superposition structure is identical to the corresponding projection of the real structure. This projection, calculated with $F_{obs}(h01)$ revealed the position of all atoms. Although the determination of the real structure in 3 dimensions with the help of a model did not seem feasible, due to the poor data available, it was possible to determine approximate y-coordinates of the atoms by means of two independent systems of linear structure factor equations:

$$F(h1l)_{l=2n+1} = K \sum_j 4f_j \cos 2\pi(hx_j + lz_j) \cos 2\pi y_j \qquad (4.1)$$

and

$$F(h1l)_{l=2n} = -K \sum_j 4f_j \sin 2\pi(hx_j + lz_j) \sin 2\pi y_j \qquad (4.2)$$

where K is the scaling factor. The expressions $4f_j \cos 2\pi(hx_j + lz_j) = a_j$ and $-4f_j \sin 2\pi(hx_j + lz_j) = b_j$ may be calculated because x_j and z_j are known, whereas $K \cos 2\pi y_j = C'_j$ and $K \sin 2\pi y_j = S'_j$ are the unknown values. From the known position of the heavy atom (bromine) most of the signs of the $F(h1l)_{1=2n+1}$ could be determined and a system of equations (4.1) with a twelvefold overdetermination could be set up

$$F(h1l)_{1=2n+1} = \sum_j a_j(h1l)C'_j. \qquad (4.1)$$

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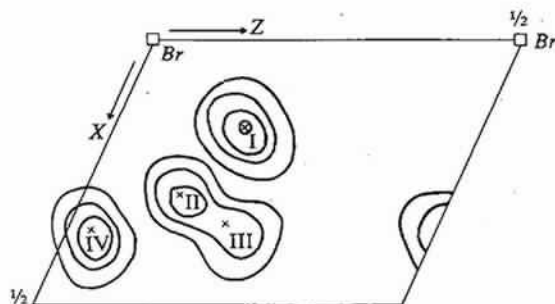
Fig. 8. Electron density projection ρ (x, z) of acetamide hemi-hydrobromide.

This system of equations was solved by least squares technique. Because the $F(h1l)$ are on a relative scale the solutions C'_j were multiplied with a constant $(1/K)$ so that $(1/K)C'_{Br} = 1$ is valid.

Two values $y_j = y_{jo}$ and $y_j = 1 - y_{jo}$ are in keeping with the solutions $C_j = (1/K)C'(y_{jo})$ obtained. To find out which of these two values is correct, equations of the type (4.2):

$$F(h1l)_{1=2n} = \sum_j b_j(h1l)S'_j \qquad (4.2)$$

were used. The bromine atoms do not contribute to the $F(h11)_{j=2n}$. The signs of these structure factors were unknown. Therefore the unobserved reflections $F(h1l)_{1=2n}$ and one strong reflection $F(h1l)_{1=2n}$ were used for setting up a system of inhomogeneous equations. The $S_j = (1/k)S'_j$ were less accurate than the C_j because this system of equations had only a twofold overdetermination. That is why the absolute values of the y-coordinates were calculated from the C_j, but the ambiguity was eliminated by the S_j. The results are shown in Fig. 9. Structure refinement proved these approximate values to be correct.
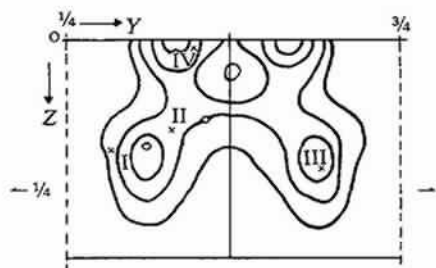

Fig. 9. The average structure ρ(yz) of acetamide hemihydrobromide calculated only with $F_{obs}(0k1)$ for $k+1 = 2n$. Atomic position obtained with the help of SFE are marked by crosses, the refined positions are marked by squares.

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D. α-Calciumtetraborate-hydrate[13]

Crystal data: $CaB_2O_4 \cdot 4\,H_2O$

Monoclinic: Pc or $P2/c$, $a = 5.86$ Å, $b = 6.93$ Å, $c = 7.78$ Å, $\beta = 94°$; $Z = 2$

Observed systematic intensity distribution:

$\langle I(hkl)_{1=2n} \rangle$ strong, $\langle I(hkl)_{1=2n+1} \rangle$ weak

The intensity statistic of Howells, Phillips and Rogers[14] using the $I(hkl)$ showed that the real structure has the centrosymmetric space group $P2/c$.

The Patterson function showed in agreement with $Z = 2$ and $P/2c$ that the calcium atom occupies a special position on the twofold rotation axis with parameters $x_{Ca} = 0$, $z_{Ca} = \frac{1}{4}$ and y_{Ca} approximately zero. This position is near the c-glide plane and thus explains why the reflections $I(hkl)_{1=2n+1}$ are systematically weak.

On the other hand the calcium atom determined most of the signs of the $F(hk0)$. The Fourier projection $\rho(x, y)$ gave the positions of the oxygen and boron atoms. Because the signs of the $F(hkl)$ with $1 = 2n + 1$ were not determined by the contribution of the calcium atom the z-parameters of the atoms could not be derived from a Fourier synthesis based on the contributions of the calcium atom to the sign of the $F(hkl)$. But with the SFE-method the approximate z-coordinates were easily obtained.

From the structure factor formula follows

with
$$F(hkl) = \sum_j (a_j^{(L)} C_j^{(L)} + b_j^{(L)} S_j^{(L)}) \quad \text{for} \quad L = 1, 2$$

$$a_j^{(1)} = -4f_j \sin 2\pi h x_j \sin 2\pi k y_j$$
$$b_j^{(1)} = -4f_j \cos 2\pi h x_j \sin 2\pi k y_j$$
$$a_j^{(2)} = 4f_j \cos 2\pi h x_j \cos 2\pi k y_j$$
$$b_j^{(2)} = -4f_j \sin 2\pi h x_j \cos 2\pi k y_j$$
$$C_j^{(L)} = \cos 2\pi L z_j, \; S_j^{(L)} = \sin 2\pi L z_j$$

Two systems of equations were set up. For the first system $F(hkl)$ and for the second $F(hk2)$ were used. In each case the unobserved structure factors and one strong structure factor with arbitrary sign was used. These systems of equations gave approximate values for $C_j^{(L)}$ and $S_j^{(L)}$, by which $F_c(hkl)$ were calculated.

By comparing the $F_c(hkl)$ with the $F_o(hkl)$ the signs of more structure factors could be determined. The corresponding equations were added to the previous systems of equations. In this way the overdetermination of the systems of equations was increased and the accuracy of the results improved. The final results obtained after several cycles are listed in

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the Table. The last column contains the refined parameter for comparison.

Atom	$C_j^{(1)}$	$S_j^{(1)}$	$C_j^{(2)}$	$S_j^{(2)}$	z_j	z_j refined
Ca	—	1.00	−1.000	—	0.250	0.25
O_1	—	0.20	0.872	—	0.036	0.0359
O_2	1.00	0.51	0.703	0.756	0.070	0.0588
O_3	0.68	0.44	0.111	0.923	0.106	0.1042
O_4	0.66	−0.74	−0.338	0.680	0.842	0.8193

E. Dimethylaminomethylpinene[12,15]

Crystal data: $C_{13}H_{24}NBr$
monoclinic: $P2_1$, $a = 11.37$ Å, $b = 8.62$ Å, $c = 7.48$ Å, $\beta = 97.4$; $Z = 2$

The x- and z-parameters of the bromine atom were determined from the Patterson synthesis and refined by Fourier methods. The y coordinate was chosen arbitrarily as $y_{Br} = \frac{1}{4}$. The 3-dimensional Fourier synthesis based on the phases of the $F_{obs}(hkl)$ derived from the bromine contributions is a superposition structure with the space group $P2_1/m$ with an additional mirror plane at $y = \frac{1}{4}$. For the calculation of this synthesis only $F_o(hkl)$ for $0k4$ were available because the crystals were very small. The Fourier synthesis revealed the positions of all non-hydrogen atoms, most of them resolved in the x and z directions. Nearly all these atoms are, however, located so closely to the pseudo mirror plane that the peak corresponding to one atom and its mirror image were not separated but formed an elliptical maximum with its peak on the mirror plane (Fig. 10).

The main problem of the structure determination was to determine the small deviations of the light atoms from this pseudo mirror plane.
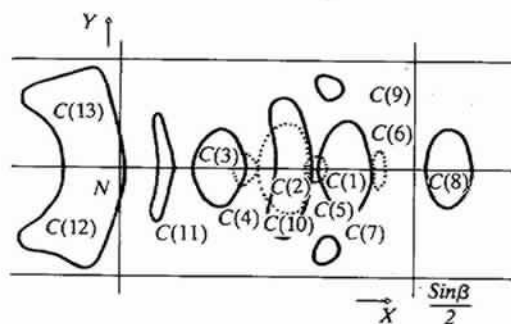

Fig. 10. Comparison of the composite three dimensional electron density projected along 001 (only one full or dashed contour of the same height at arbitrary level is drawn) of atomic positions obtained by SFE (results from F(h21) are marked by open circles, from F(h31) by open squares, average values solid) and of the positions obtained by least-squares refinement marked by crosses.

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Analysis of the peak shape resulted in rather inaccurate values of the deviations from the mirror plane. Better values were obtained by the SFE method. To start with, the positions of all atoms in (x, z)-projection were refined by difference Fourier synthesis to an R value of 0.16. Using the formulae

$$A_o(h21) = K_1 \sum_j 2f_j \cos 2\pi(hx_j + 1z_j) \cos 2\pi 2y_j$$

and

$$A_o(h31) = K_2 \sum_j -2f_j \sin 2\pi(hx_j + 1z_j) \sin 2\pi 3y_j$$

where K_1 and K_2 are the scaling factors, two systems of equations were obtained taking $A_o(hkl)$ equal to $F_o(hkl)$. This may be done without creating large errors since the $B_o(hkl)$, to which the bromine atoms do not contribute, are expected to be small. In these systems of equations only those $A_o(hkl)$ were used whose signs could be deduced from the contributions $F_{Br}(hkl)$ of the bromine atoms:

With the abbreviations

$$a_j = 2f_j \cos 2\pi(hx_j + 1z_j) \qquad C_j^{(2)\prime} = K_1 \cos 2\pi 2y$$
$$b_j = -2f_j \sin 2\pi(hx_j + 1z_j) \qquad S_j^{(3)\prime} = K_2 \sin 2\pi 3y_j$$

the systems of the equations have the form

$$F_o(h21) = \sum_j a_j C_j^{(2)\prime}$$

$$F_o(h31) = \sum_j b_j S_j^{(3)\prime}.$$

The structure factors $F_0(h21)$ and $F_o(h31)$ are on a relative scale. The scaling factors K_1 and K_2 were given such values that $(1/K_1)C_{Br}^{(2)} = (1/K_2)S_{Br}^{(3)} = 1$. Four values for the coordinate y_j of any atom are in keeping with

$$C_j^{(2)} = (1/K_1)C_j^{(2)}(y_{jo}) \qquad \text{namely} \qquad y_j = \pm y_{jo}, y_j = \pm y_{jo} + \tfrac{1}{2}.$$

Two of these values for any atom could be excluded by comparison with the Fourier synthesis of the superposition structure (see above). From the two remaining values one could be precluded for most of the atoms by using a model of the molecule (Fig. 10). The accuracy of the y coordinates obtained from the $C_j^{(2)}$ was improved using the results obtained from $S_j^{(3)}$. The coordinates thus obtained were sufficiently accurate for a starting set for a least squares refinement of the real structure.

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