CHAPTER 11

The Growing Field of Mineral Structures

by F. Laves

11.1. General Remarks

Minerals are substances of either 'inorganic' or 'metallic' character. From a purely crystallographic point of view it would appear unscientific to prefer minerals to other substances as objects for structure determination, as minerals are only a chance selection of possible compounds. Thus, it was to be expected that major progress in 'crystallography' would be made by people, who did not care whether the object of investigation was a mineral or not. The fact that many mineralogists of influence were hesitant to consider structural work on non-minerals as belonging to the realm of mineralogy may be in part responsible for the present situation, in which crystallography can no longer be considered a part of mineralogy, as it was before 1912. Crystallography is now a science in its own right with many facets and roots, mineralogy being only one of many others, among them mathematics, physics, chemistry and biology. Previously it was desirable for physicists, chemists and biologists to know mineralogy, for it included an education in crystallography. This situation is well demonstrated by some sentences von Laue (1943) wrote commemorating the 100th birthday of P. von Groth who was Professor of Mineralogy and Crystallography at Munich at the time when von Laue conceived his idea:

'Mit Entdeckungen ist es in der Physik—diese im weitesten Sinne verstanden—eine eigene Sache. In dieser 300 Jahre alten Wissenschaft ist jeder Entdecker ein Erbe, ein Erbe des geistigen Gutes welches viele Generationen geschaffen und gemehrt haben. Paul von Groth hat sich neben vielen anderen grossen Verdiensten auch das erworben, dass er die mehr als 100-jährige, anderswo in Deutschland kaum noch vorhandene Tradition der Raumgitterhypothese in München durch seine Lehrtätigkeit lebendig erhalten und so eine der Voraussetzungen geschaffen hat, ohne welche die Auffindung der Röntgenstrahlinterferenzen rein Glückssache, ihre Deutung ganz unmöglich gewesen wäre.' Today crystallography is nearly equally needed by mineralogy, physics and chemistry; conversely mineralogists, physicists and chemists join in the effort to promote the new science of modern crystallography. From this point of view the last fifty years have been very fateful ones for mineralogy in two respects as far as crystallography is concerned. Mineralogy lost the field of crystallography as its 'dominated colony', but it gained from the new possibilities of solving problems of central interest to mineralogy.

Before going into details of a structural character it should be mentioned that mineralogy and petrography obtained great advantage from Laue's discovery through using the powder method. invented by the physicists Debye and Scherrer in 1916, for the identification of minerals. Thus it became possible to investigate natural processes of mineral formation, even in those cases where the products were badly crystallized or microcrystalline. In addition, in many cases it turned out that substances which were thought to be different minerals proved to be identical from a structural point of view and vice versa. This is impressively shown in the book by Strunz Mineralogische Tabellen (1959, 3rd edition). Another application of the powder method of steadily increasing importance is the identification, or at least the characterization, of substances produced in experiments carried out to compare the conditions under which minerals can be formed in the laboratory with those under which minerals may have formed in nature.

Two highlights in this respect may be mentioned: (a) the first artificial production of diamond in 1955; (b) the production of a previously unknown high-pressure form of SiO_2 by Coes in 1953, later named coesite. The last mentioned discovery is of a unique mineralogic and cosmic interest: after the material was produced in the laboratory it was looked for in nature and was found as a mineral on the earth's surface where giant meteorites had collided with the earth. The crystal structure of coesite was determined by Zoltai and Buerger in 1959.

Other important problems are questions of nomenclature and of the classification of minerals. Crystal structure, structural types and the rules of crystal chemistry became leading principles. P. Niggli's textbooks of mineralogy (1920, 1924) are milestones in this respect; they educated and fascinated a generation of mineralogists.

175

11.2. Highlights of Structure Determination

Some highlights in determining the important structure types occurring in minerals shall be mentioned now, regardless of whether the determinations were done by physicists, chemists or mineralogists.

- 1913: The first structure determinations (W. H. and W. L. Bragg) were done on the minerals zincblende, diamond and NaCl. It still appears miraculous to the writer how fortunate and ingenious the Braggs were in chosing these 'easy' substances, considering how many much more complex structures could have been picked.
- 1914: Copper (W. L. Bragg); CaF_2 (W. L. Bragg); FeS_2 (W. L. Bragg).
- 1915: Spinel (W. H. Bragg, independently Nishikawa); calcite (W. H. Bragg).
- 1916: Graphite (Debye and Scherrer; independently Hull in 1917); rutile and anatase (Vegard).
- 1919: $Mg(OH)_2 = CdJ_2$ -type (Aminoff).
- 1920: Wurtzite (W. L. Bragg).
- 1923: NiAs (Aminoff).
- 1924: The first silicate, garnet (Menzer).
- 1925/1926: SiO₂ structures (W. H. Bragg and Gibbs; Wyckoff; Seljakow, Strebinski and Krasnikow).
- 1923-1926: V. M. Goldschmidt's famous rules of Crystal Chemistry and the determination of the size of atoms and ions. The main rule may be quoted here in the original formulation (*Geochemische Verteilungsgesetze der Elemente*, VII, pg. 9):

'Die Kristallstruktur eines Stoffes ist bedingt durch Grösse und Polarisationseigenschaften seiner Komponenten; als Komponenten sind Atome (respective Ionen) und Atomgruppen zu bezeichnen.'

The rules were drawn from the results of a large amount of experimental work gained in cooperation with his coworkers, mainly Zachariasen and Barth. The initial purpose of the work was to get information on the rules which govern the behaviour of matter with respect to isomorphism, isomorphous exchange, polymorphism and morphotropism. This would be a basis for investigating the petrological problem of the rules which govern the distribution of the elements within the earth and in its crust. The influences of V. M. Goldschmidt's work on the development of mineralogy and crystallography cannot be overestimated.

- 1926–1930: Bragg and coworkers (mainly Warren, West and Taylor), Zachariasen, and Pauling established the principles of silicate structures and their dependence on the Si/O ratio (Si₄O₁₆ leading to tetrahedral groups; Si₄O₁₂ leading to rings or chains; Si₄O₁₁ leading to bands; Si₄O₁₀ leading to sheets; Si₄O₈ leading to frameworks).
- 1928: Machatschki recognized that in silicate structures Al can replace Si; he was able to predict important features of the feldspar structures.
- 1929: Pauling formulated some very valuable rules for the crystal chemistry of compounds of predominantly ionic character. Whereas these rules are covered in principle by those given by V. M. Goldschmidt (1926), some of them formulate additional and very important aspects in a precise way. Two are quoted here in the original:

'IInd rule, electrostatic valence principle: In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedron of which it forms a corner; that is, for each anion $\zeta = \Sigma_i s_i$.' [ζ = charge of the anion; $s = z/\nu$; z = charge of the cation; $\nu =$ coordination number of the cation.]

'IIIrd rule: The presence of shared edges, and particularly of shared faces, in a coordinated structure decreases its stability; this effect is large for cations with large valence and small coordination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.' [The limit of stability had been worked out already by V. M. Goldschmidt in 1926].

- 1928: In agreement with the rules mentioned before Pauling and Sturdivant succeeded in an ingenious way in determining the crystal structure of brookite, the orthorhombic modification of TiO_2 . In addition they were able to give reasons for the sequence of stability of the three TiO_2 -modifications (rutilebrookite-anatase).
- 1933: Stibnite, Sb_2S_3 , and bismuthinite, Bi_2S_3 (W. Hofmann). General rules regarding the crystal chemistry of sulpho salts were given later by Hellner (1958).
- 1933: W. H. Taylor's determination of the structure of feldspars (refinements are still in progress in the Cavendish Laboratory, Cambridge, England) may be considered as a most importana

step in structural mineralogy, which brought the first period in this field to a close. An impressive account of this period has been given by W. L. Bragg (1937) in a book *Atomic structures of minerals*. Additional ideas have been put forward by Belov (1960).

This first period was one in which a large number of key structure types were worked out; these still form the foundations and the framework of the edifice of structural mineralogy as far as structural types are concerned. It is a large edifice with much room for many research workers to put walls and windows in the right places and to decorate the rooms with the beauty of further research results in structural mineralogy.

In one respect this 'edifice' seems to be different from those accomodating the results of structure research on substances produced artificially. In structural mineralogy the architectural style is restricted by the fairly small number of building stones offered in nature. In the fields of inorganic and organic chemistry, however, the human spirit may continuously produce new materials under varying conditions differing from those in nature. Thus in these other fields the style may be changed to adjust itself to new developments in building materials from year to year.

This simile should not be taken as indicating that in the writer's opinion structural mineralogy is doomed to reach a state of stagnation. The opposite is the case due to the fact that no crystal is perfect. The degree of perfection (respectively imperfection) can differ both in different mineral species and in different specimens of the same species. The kind and degree of imperfection may be rather significant for the question of mineral and rock genesis. Therefore, the study of mineral imperfections is not only fascinating as a research object of crystallography, but the results of such studies will be important for general mineralogy and petrology.

Some examples may be discussed in this respect following a historical order.

11.3. Point Defect

Minerals are usually formed from solutions (magmatic or hydrous) containing many elements which are not needed for the mineral formation, but which become incorporated in the crystal. The question of how this incorporation can occur (and mostly does occur) was already answered by Vegard in 1917. He found random distribution of different kinds of atoms on identical lattice points and a change of lattice constants nearly proportional to the amount of incorporated material ('Vegard's law'). Deviations of this 'Law' are of special interest nowadays. V. M. Goldschmidt (1926, pg. 83) investigated the question of how different the sizes of atoms or ions may be so that substitution can still occur. He gave the empirical rule:

'Isomorphe Mischbarkeit in erheblichem Ausmasse und bei Temperaturen, welche nicht sehr nahe dem Schmelzniveau liegen, tritt ein, wenn die Radien der betreffenden Bausteine um nicht mehr als etwa 15% (in Prozenten des kleinsten Radius) voneinander verschieden sind.' (For more details on this statement see the original paper.)

Hume-Rothery and coworkers (1934) showed that a similar rule holds for solid solutions in metals.

Another kind of more or less randomly distributed point defect (now called 'Leerstelle' or 'vacancy') was first described by Laves (1930) to explain the 'excess' of sulphur usually found in natural 'FeS'. He proposed the formula $Fe_{n-1}S_n$ instead of Fe_nS_{n+1} . Barth and Posnjak (1931) introduced the concept of 'variate atom equipoints' in discussing the imperfections in spinel and other structures, and Hägg (1933) distinguished between 'substitution, addition and subtraction mixed crystals'.

11.4. Feldspars

This concept led Barth (1934) to a hypothesis which turned out to be one of the most important ideas in the advance of mineralogy and petrology, if feldspars are considered as important minerals. He explained the different symmetries of potassium or K-feldspars (optically monoclinic sanidine and optically triclinic microcline) on the assumption that Al and Si may be disordered (as 'variate atom equipoints') in sanidine and ordered in microcline. This new hypothesis contradicted an older one advanced by Mallard (1876), who considered optically monoclinic K-feldspar to be the same 'phase' as triclinic microcline; the true symmetry of the latter would not be recognizable optically owing to submicroscopical twinning. The decision between these hypotheses was not possible, however, as long as the triclinic character of microcline had not been established by X-rays. In those days (Barth, 1928) no differences in geometry

between the two lattices had been observed. The problem was taken up again in 1950 and 1952 by Laves. It could be shown that (a) many microclines have a small but significant deviation from monoclinic geometry, $\alpha = 90.5^{\circ}$ and $\gamma = 92.5^{\circ}$, later called 'maximum microcline': (b) microcline is usually twinned polysynthetically after a combination of two twin laws, which fact is understandable if microcline was once monoclinic; (c) some optically monoclinic K-feldspars show the same kind of microcline twinning when X-rayed: (d) there are states with deviations from monoclinic symmetry which lie between those of maximum microcline and $\alpha = \gamma = 90^{\circ}$, later called 'intermediate microcline': (e) many hkl and hkl reflections show significant differences in intensity, the differences being larger for maximum microcline than for material with intermediate deviations from monoclinic geometry; (f) there are optically monoclinic Kfeldspars with sharp reflections in monoclinic positions plus diffuse tails which have shapes and intensity distributions which can best be explained by the submicroscopical twinning of domains of triclinic character with atomic arrangements approaching those of intermediate or maximum microcline. Such material was called 'orthoclase' to distinguish it from sanidine which does not show these tails and which appears to be truly monoclinic-not only optically but also when investigated by X-rays; (g) in addition to the tails mentioned in (f) many 'orthoclases' show diffuse reflections in positions not consistent with the feldspar lattice proposed by Taylor (1933). A gualitative model explaining these reflections was given in 1961 (Laves and Goldsmith; I. V. Smith).

With these observations (a-f) it could be proved that there are at least two K-feldspar modifications: monoclinic sanidine and triclinic microcline, thus supporting Barth's (1934) hypothesis; that there are optically monoclinic K-feldspars with a structural appearance supporting Mallard's hypothesis (1876); and that there are K-feldspar states, which may not be considered as stable phases in the sense of Gibbs, which are neither sanidine nor microcline but something in between. Such material was called common or normal orthoclase or just 'orthoclase'. There is still much discussion nowadays between crystallographers and mineralogists on the significance and characterization of such K-feldspar states which can be considered neither as sanidine nor as microcline as a consequence of structural imperfections which show themselves in X-ray photographs as described above in (f) and (g). The present situation is expressed in a paper given by Laves and Goldsmith at a feldspar symposium sponsored by the International Mineralogical Association in Copenhagen in 1960 entitled 'Polymorphism, order, disorder, diffusion and confusion in the feldspars'. Other papers and discussions on the subject by R. B. Ferguson, J. B. Jones, W. S. Mackenzie, A. S. Marfunin, H. D. Megaw, J. V. Smith, W. H. Taylor are compiled in the Proceedings of this meeting (*Cursillos y Conferencias* Vol. ϑ , September 1961, Instituto 'Lucas Mallada', Madrid), which in addition contains many other important papers by Megaw and coworkers on structural features of the plagioclases which will not be discussed here in detail. The papers of this Conference show in an impressive way the lively activity of crystallographers and mineralogists in using X-rays for the solution of the problems and puzzles which nature has offered through the production of feldspars. Much has been done but more is needed in order to understand the complexities involved.

The feldspars are treated here in great detail for three reasons: (1) The problems involved are typical of the difficulties mineralogy has to put up with. These difficulties are such that it appears to be impossible to reproduce in the laboratory the conditions under which some minerals were formed, because we may vary in the laboratory the pressure and temperature and the chemical compositions of our reaction products but we cannot compete with the time nature had available. All attempts to synthesize the ordered low-temperature modifications of K-feldspar (microcline) and Na-feldspar (albite) failed. The products have been always disordered high-temperature modifications. On the other hand it is easy to produce disordered high-temperature modifications by heating the ordered low-temperature modifications to near the melting point. (2) The feldspars offer an excellent example of the central question in mineralogy and crystallography: What is a mineral, what is a single crystal, a question which is not only one of semantics but involves interesting problems of the nature of the condensed state currently discussed. (3) Besides quartz the feldspars are the most frequent minerals as together they make up approximately 65% of the earth's crust.

Returning to Barth's Al/Si order/disorder hypothesis the question arises of how can it be proved? The scattering powers of Al and Si are so similar that it is impossible to decide by X-rays whether a particular site is occupied by Al or Si except perhaps by methods not yet easily feasable. For this reason Taylor gave in 1933 only the sites where Al or Si are located. Therefore, other methods had to be tried for information on the Al/Si order and disorder. They are summed up in short. (a) By diffusion experiments near the melting point the Na of an albite could

be replaced by K leading to microcline (Laves, 1951). This indicated that the alkali ions are not responsible for the differences between the high and low-temperature forms and that the differences must lie in the AlSi₃O₈ framework. It was proved further that the Al/Si distribution of albite and microcline are identical. Very accurate structure determinations of albite and maximum microcline are now at hand (unpublished work by S. W. Bailey, personal communication) which are in line with this. (b) It can be shown theoretically that mechanical twinning cannot take place if the Al/Si distribution is ordered but it may take place if it is disordered. Experiments to twin albite mechanically failed (Mügge and Heide, 1931) even under extreme conditions, but mechanical twinning can easily be performed at room temperature (Laves, 1952) with Na-rich feldspars if they are in a high-temperature state. (c) Results of crystal chemistry gained from substances other than feldspar suggested that the size of (Al,Si)O4 tetrahedra should be approximately proportional to the probability of an Al sitting in the tetrahedra (I. V. Smith, 1954). A refined structure determination of a halfway intermediate microcline (Bailey and Taylor, 1955) revealed significant differences in size between the four tetrahedral sites. (These results should be compared with those of a structure determination of an 'orthoclase' carried out by Jones and Taylor in 1961.) The same was true in a refined structure determination of albite (Ferguson, Traill and Taylor, 1958). The refined structure determination of NaAlSi₃O₈ in a high-temperature state, carried out with the same accuracy by the same authors did not reveal any differences in the sizes of the tetrahedra. (d) The difference in the sharpness of infrared absorption bands between low and hightemperature forms strongly indicates differences in the degree of Al/Si order (Laves and Hafner, 1956 and 1957). (e) Finally, measurements of the nuclear magnetic resonance of KAlSi₃O₈ and NaAlSi₃O₈ in the low and high-temperature state leave no doubt, that the Al/Si order is practically complete in microcline and albite, whereas it is practically zero in the corresponding high-temperature states (Brun, Hafner, Hartmann and Laves, 1960).

The account given above shows that sometimes the combination of different approaches—field evidence, good ideas (Barth), accurate structure determinations (Taylor and coworkers) and physical methods other than X-ray investigations—is necessary if problems are to be solved which are of pertinent interest to mineralogy and petrology.

11.5. One-dimensional Disorder (Stacking Faults) and Polytypism

In the above section some diffuse reflections were mentioned which occur in X-ray photographs of feldspars; these have not yet been explained rigorously by mathematical treatment. Thus, there is still much to be done in the future. However, somewhat similar effects have been observed in other minerals which could be treated mathematically in a more rigorous way: stacking faults. The first observation of this kind was published in 1927 by Mauguin who observed 'streaks' corresponding to rows in reciprocal space in X-ray photographs of micaceous minerals. Similar effects were observed by Nieuwenkamp and Laves (1935) in X-ray photographs of maucherite, Ni₃As₂, and of SiO₂. Hendricks and Teller (1942) added much to the theoretical interpretation of these effects in the case of the mica minerals and A. J. C. Wilson (1942) in the case of metals and alloys. Jagodzinski and Laves (1949) introduced the concept of 'eindimensionale Fehlordnung' (one-dimensional disorder) having observed similar effects in single crystals of graphite and ZnS. The most general theoretical treatment of the observed X-ray effects has been given by Jagodzinski (1949); he considered the influence of the position of a given laver on the position of other layers up to four layers away. As unidirectional stress can change the order-disorder relations (for example, it is possible experimentally to produce 'rhombohedral graphite' domains within a single crystal of hexagonal graphite) applications of such investigations to the geological history of mica and other sheet minerals in rocks may become important for future studies of rock metamorphism.

An important example for such polymorphism or polytypism which is chemically simple and has mineralogical interest is 'tridymite', a 'polymorph' of SiO₂. If we consider the tridymite structure as it is given in textbooks it can be described in some analogy to the hexagonal close-packed structure with a sequence of layers ABAB... If we call this a 2-layer sequence, structural work has shown that no tridymites are known yet which have such an ideal 2-layer sequence. Mistakes occur which necessitate the consideration of an additional C position in such a way that ABC-sequences must be present. Buerger and Lukesh (1942) observed natural tridymites with n-layer sequences with n = 10 or 20. Flörke (1955) found the same sequences in tridymites produced synthetically; other kinds of stacking disorder within single crystals were found by him too. Whereas some correlations between layer sequence and impurities could be worked out, the reasons for the preference for 10- and 20-layer sequences are still obscure. Several authors discussed similar structural anomalies observed in SiC where n-layer sequences up to n = 594 and more are reported in the literature (Mitchell, 1958). For a discussion of the reasons for such large periodicities perpendicular to the layer plane a paper by Jagodzinski and Arnold (1960) may be quoted. Jagodzinski rejects the opinions advanced by such authors as Bhidde, Verma and Mitchell suggesting that the polytypes are caused by screw dislocations and proposes that the influence of entropy terms may be more important. However, his concluding sentence reads 'A great deal of effort is needed to solve these problems'.

11.6. What is a Mineral? What is a Crystal?

The writer as a professor of mineralogy has frequently been asked 'What is mineralogy?' An answer like 'it is the science which deals with minerals' can easily be given; some people however, are not content with such an answer and want to know 'What are minerals?' At this point it is better to leave the room, for there is no satisfactory answer to such a question. Here are the problems.

Looking into textbooks of mineralogy one finds (neglecting such 'minerals' as amber and others) that a mineral is an inorganic substance produced by natural processes, implying in this context that processes in which men are involved are considered unnatural. Furthermore 'homogeneity' is one of the properties which belongs to a mineral.

However, what does 'homogeneous' mean? This question could not be answered in a satisfactory way before 1912, nor can it be answered today as we shall see. Thus it may appear that the new tool available since Laue's discovery has not helped us to answer this basic question of mineralogy. In a strict sense this is true. However, in many special cases X-rays can tell us that substances previously thought to be homogeneous are actually mixtures of different substances; in other cases X-rays have revealed structural features in 'minerals' which are fascinating and which add considerably to the liveliness of the present day research in structural mineralogy.

One example may be given for illustration. Moonstone, a gemstone with beautiful blue schiller belonging to the feldspar group, can be considered as 'really' being homogeneous when in a high-temperature state, i.e. for example when formed under magmatic conditions. However, when we pick up such a feldspar in nature it usually has a low temperature and may have changed considerably in its atomic arrangement during the millions of years which may have elapsed since it was formed.

Neglecting minor impurities always present in each 'pure' substance the chemical composition of the feldspars can be expressed as a mixture of three 'molecules' $Or = KAlSi_3O_8$, $Ab = NaAlSi_3O_8$, $An = CaAl_2Si_2O_8$. Moonstone, an alkali feldspar, is a mixture of the molecules Or and Ab and usually appears 'homogeneous' when investigated with a microscope.

X-ray photographs, however, give results which can be interpreted as a single-crystal pattern of 'orthoclase' or sanidine (KAlSi₃O₈) plus oriented reflections, more or less diffuse, in positions which correspond approximately to those positions which a pure but twinned NaAlSi₃O₈ would show when X-rayed alone (either in the low-temperature form albite or in the high-temperature form analbite or in an intermediate state between albite and analbite).

The conclusion may be that moonstone is not a mineral but a mixture of minerals. Considering that the K and Na-rich areas cannot be discriminated by microscopic investigation but that their existence can be shown by X-rays, and considering that the size and shape of these areas changes from specimen to specimen (as revealed by the varying diffuseness and position of the Na-feldspar reflections) the question 'mineral' or 'not-mineral' finally boils down to a question similar to 'has a Texas Grapefruit a yellow or an orange colour?'

Thus, trying to answer the question 'What is a mineral' leads to the question 'What does homogeneous mean?' Through trying to answer this question, theoretical problems of high importance arise which are of general interest not only for mineralogy but also for the theory of the condensed state in its broadest sense. The problems involved have not yet been solved, but X-ray investigations of minerals offer excellent examples for future discussion of the kinetics and thermodynamics of solid-state reactions.

As one of these examples moonstone has been mentioned already. For further discussion it is chosen again for several reasons. It belongs to the group of feldspars which are a major component of the earth (appr. 65%). Thus, it occurs in many localities and there is a good opportunity to study and to compare samples of different origin on the one hand, and to compare the structural states (there is no *one* state characteristic of *the* moonstone) of moonstones with the structural states of other feldspars which are chemically alike.

185

As a result of such investigations we now know that feldspars with moonstone composition can exist in an infinite number of different states. These states lie between two extremes. (1) An ideal homogeneous mineral in which the alkali sites of the crystal structure are randomly occupied by K and Na ions and in which structural sites exist which are occupied nearly at random by Al and Si ions. (2) An ideal mixture (called perthite) of two ideal homogeneous minerals, namely microcline and albite, both having structural sites which are occupied either by Al or by Si ions. In microcline the alkali sites are occupied only by K ions, in albite only by Na ions. Thus, after the crystallization of a feldspar with moonstone composition processes may take place concurrently during geological times within a morphological unit: (a) separation into areas of different K/Na ratio, (b) change of the original Al-Si disorder into states of higher order, (c) enlargement of the Na-rich and K-rich areas by a process of 'recrystallization' into areas of a visible size.

Whether the state, stable at room temperature (microcline plus albite), is fully reached by these processes or only partly approached may depend on several factors, some among them of geological character. Thus a morphological unit of *one* typical mineral (sanidine) may change continuously into a material of *two* typical minerals (microcline and albite) which can easily be separared mechanically. At which stage does such a morphological unit cease to be *one* mineral and become a mixture of *two* minerals? There is no satisfactory answer to this question.

Another feldspar example may be chosen to elucidate the question 'What is a single crystal?' Na-feldspar in its most disordered state (monalbite) has monoclinic symmetry like sanidine. However the monoclinic states are stable only at high temperatures; at low temperatures a triclinic form is stable. Two kinds of phase transformation can occur leading to 'crystals' that appear to be monoclinic when investigated optically. One transformation (diffusive in the sense of Laves, 1952) is due to a change in Al/Si distribution needing geological times at low temperature, whereas the other transformation (displacive in the sense of Buerger, 1948) takes place without a change in Al/Si distribution and cannot be suppressed either by quenching or rapid heating. In both cases 'microcline twinning' is produced which is frequently on a submicroscopical scale and then detectable only by means of X-rays. As a matter of fact the displacive transformation of monalbite into analbite (the disordered triclinic form of NaAlSi₃O₈ in contrast to the ordered triclinic form, albite) has hitherto always led

to an optically monoclinic material which is submicroscopically twinned.

Before 1912 such material would have been called in good faith a single crystal. Trouble now arises because we have X-rays. Again we may expect a continuous series of states between two extreme cases (and we find it in nature in the case of microcline): (1) a real single crystal in which the 'twinning' is expressed by the symmetry of a space group somewhat different from the one the transformed phase has; (2) a morphological unit in which the twinned domains are so large that they can be 'seen' and which can be cut into small pieces of real single crystal character. At which stage does such a morphological unit cease to be *one* single crystal and becomes a twinned aggregate of *more* than one single crystal? There is no satisfactory answer to this question.

The difficulties involved in answering the questions 'What is a mineral?' and 'What is a crystal?' are closely related to the question 'What is a phase?' A discussion of this last question is not only important for mineralogists but for all people who are interested in the condensed state. A very valuable contribution to this problem has been given by Jagodzinski (1959).

11.7. Concluding Remarks

The preceding sections have shown how large the variation of the structural state of even *one* mineral can be as revealed by X-rays. Laue's discovery in 1912 provided the tools for recognizing this variation and for using it in attempts to reconstruct the conditions under which minerals in their various structural states were formed in nature. In some cases reproduction can be achieved by experimental synthesis in the laboratory; in other cases where the times involved are available to nature but not to men, intelligent thinking is needed to explain the facts offered by nature.

Unfortunately, only a few topics of structural mineralogy could be discussed in enough detail to give an impression of the development of such problems during the last 50 years and the present-day state of their solution. Many other topics might have been chosen equally well, but the selection given here should illustrate not only the impact Laue's discovery had on the growing field of structural mineralogy, but should also show the importance of this field for problems of general mineralogy, petrology, geology, chemistry and physics.

References

- References of papers cited in the text (see also Strukturbericht and Structure Reports for additional references):
- S. W. Bailey and W. H. Taylor (1955), The structure of a triclinic potassium feldspar; Acta Cryst. 8, 621-632.
- T. F. W. Barth (1928), Die Symmetrie der Kalifeldspäte; Fortschr. d. Min. 13, 31–35; (1934) Polymorphic phenomena and crystal structure; Am. J. Sci. 27, 273–286.
- T. F. W. Barth and E. Posnjak (1931), The spinel structure: an example of variate atom equipoints; *7. Wash. Acad. Sci. 21*, 255-258.
- N. V. Belov (1960, short survey in English), Chapter B of the Crystal Chemistry of Silicates; Fortschr. d. Mineralogie 38, 4-6.
- W. L. Bragg (1937), Atomic structure of minerals; Cornell University Press, Ithaca, N.Y.; 292 p.
- E. Brun, St. Hafner, P. Hartmann, F. Laves und H. H. Staub (1960), Magnetische Kernresonanz zur Beobachtung des Al, Si-Ordnungs/Unordnungsgrades in einigen Feldspäten; Z. Kristallogr. 113, 65-76.
- M. J. Buerger (1948), The role of temperature in mineralogy; Am. Mineralogist 33, 101-121.
- M. J. Buerger and J. Lukesh (1942), The tridymite problem; Science 95, 20-21.
- F. P. Bundy, H. T. Hall, H. M. Strong and R. H. Wentorf (1955), Man-made diamonds; *Nature 176*, 51-55.
- L. Coes (1953), A new dense crystalline silica; Science 118, 131.
- 'R. B. Ferguson, R. J. Traill and W. H. Taylor (1958), The crystal structure of low-temperature and high-temperature albites; Acta Cryst. 11, 331–348.
- O. W. Flörke (1955), Strukturanomalien bei Tridymit und Cristobalit; Ber. D. Keram. Ges. 32, 369–381.
- General Electric Research Laboratory (Marshall, Bundy, Hall, Strong, Nerad) 1955: Manmade diamonds; Research information services, The Knolls, Schenectady, New York, 25 p.
- V. M. Goldschmidt (1926), Geochemische Verteilungsgesetze, VII: Die Gesetze der Krystallochemie (nach Untersuchungen gemeinsam mit T. Barth, G. Lunde, W. Zachariasen); *Skrifter Norsk. Vid. Akademie*, Oslo, *Mat. Nat. Kl.* 1926. No. 2; See in addition VIII: Untersuchungen über Bau und Eigenschaften von Krystallen, l.c. No. 8.
- St. Hafner und F. Laves (1956, 1957), Ordnung/Unordnung und Ultrarotabsorption I, (Al, Si)-Verteilung in Feldspäten; II, Zur Struktur von Orthoklas und Adular; Z. Kristallogr. 107, 196-201 and 109, 204-225.
- G. Hägg und I. Sucksdorff (1933), Die Kristallstruktur von Troilit und Magnetkies; Z. phs. Chem. B, 22, 444–452.
- E. Hellner (1958), A structural scheme for the sulfide minerals; J. Geology 66, 503-525.
- St. Hendricks and E. Teller (1942), X-ray interference in partially ordered layer lattices; *J. Chem. Physics 10*, 147-167.
- W. Hume-Rothery, G. W. Mabbott and K. M. Channel-Evans (1934), The freezing points, melting points, and solid solubility limits of the alloys of silver and copper with the elements of the B sub-groups; *Phil. Trans. R. S.* London, A, 233, 1–97.
- H. Jagodzinski (1949), Eindimensionale Fehlordnung in Kristallen und ihr Einfluss auf die Röntgeninterferenzen; Acta Cryst. 2, 201–207; 208–214; 298–304; (1959) Strukturund Phasenbegriff in Mischkristallen; in Beiträge zur Physik und Chemie des 20. Jahrhunderts, Vieweg-Verlag, Braunschweig, p. 188–209.
- H. Jagodzinski and H. Arnold (1960), Anomalous silicon carbide structure, in Silicon Carbide, Pergamon Press, London, p. 136–146.
- H. Jagodzinski and F. Laves (1948), Eindimensional fehlgeordnete Kristallgitter; Schweiz. Min. Petr. Mitt. 28, 456–467.
- J. B. Jones and W. H. Taylor (1961), The structure of orthoclase; Acta Cryst. 14, 443-446.
- M. v. Laue (1943), Zu P. v. Groths 100. Geburtstage; Z. Kristallogr. 105, 81.

- F. Laves (1930), Die Bau-Zusammenhänge innerhalb der Kristallstrukturen; Z. Kristallogr. 73, 202-265, 275-324; (1950) The lattice and twinning of microcline and other potash feldspars; J. Geology 58, 548-571; (1951) Artificial preparation of microcline; J. Geology 59, 511-512; (1952) Phase relations of the alkali feldspars; J. Geology 60, 436-450, 549-574; see in addition Al/Si Verteilungen, Phasentransformationen und Namen der Alkalifeldspäte; Z. Kristallogr. 113 (1960) 265-296; (1952) Ueber den Einfluss von Ordnung und Unordnung auf mechanische Zwillingsbildung; Naturwissenschaften 39, 546.—Mechanische Zwillingsbildung in Feldspäten in Abhängigkeit von Ordnung-Unordnung der Si/Al-Verteilung innerhalb des (Si, Al)₄O₈—Gerüstes; l.c. 546-547.
- F. Laves and J. R. Goldsmith (1961), Polymorphism, order, disorder, diffusion and confusion in the feldspars; *Cursillos y Conferencias*, Madrid, 8, 71-80.
- F. Machatschki (1928), Zur Frage der Struktur und Konstitution der Feldspäte (Gleichzeitig vorläufige Mitteilung über die Prinzipien des Baues der Silikate); Zentralbl. f. Min. 1928, 97-100.
- F. Mallard (1876), Explications des phénomènes optiques anomaux, que présentent un grand nombre de substances cristallisées; Annales des Mines 10, 187-240; reviewed in Z. Kristallogr. 1 (1877) 309-320.
- Ch. Mauguin (1928), Les rayons X ne donnent pas toujours la véritable maille des cristaux; C. R. Paris 187, 303-304.
- R. S. Mitchell (1957), A correlation between theoretical screw dislocations and the known polytypes of silicon carbide; *Z. Kristallogr. 109*, 1–28.
- O. Mügge und F. Heide (1931), Einfache Schiebungen am Anorthit; Neues Jahrb. f. Min., Beilage Band A 64, 163-170.
- W. Nieuwenkamp (1935), Zweidimensionale Cristobalitkristalle; Z. Kristallogr. 90, 370–380; see in addition l.c. 273–278 and 279–282.
- P. Niggli (1920, 1924; 1st and 2nd edition), Lehrbuch der Mineralogie; Verlag Borntraeger, Berlin.
- L. Pauling (1929), The principles determining the structure of complex ionic crystals; Am. Chem. Soc. 51, 1010-1026.
- L. Pauling and J. H. Sturdivant (1928), The crystal structure of brookite; Z. Kristallogr. 68, 239-256.
- J. V. Smith (1954), A review of the Al-O and Si-O distances; Acta Cryst. 7, 479-483.
- J. V. Smith and W. S. MacKenzie (1961), Atomic, chemical and physical factors that control the stability of alkali feldspars; *Cursillos y Conferencias*, Madrid, 8, 39–52.
- H. Strunz (1941, 1949, 1957, 1st-3d edition), Mineralogische Tabellen; Akademische Verlagsgesellschaft, Leipzig, 448 p.
- W. H. Taylor (1933), The structure of sanidine and other feldspars; Z. Kristallogr. 85, 425-442.
- L. Vegard und H. Schjelderup (1917), Die Konstitution der Mischkristalle; Phys. Zeitschrift 18, 93–96. See in addition L. Vegard (1921): Die Konstitution der Mischkristalle und die Raumerfüllung der Atome; Vidensk. Skrifter, Mat. Nat. Kl., Kristiania 1921. No. 6, 36 p.
- A. J. C. Wilson (1942), Imperfection in the structure of cobalt, II. Mathematical treatment of proposed structure; Proc. R. Soc. London A 180, 277-285.
- T. Zoltai and M. J. Buerger (1959), The crystal structure of coesite, the dense, high-pressure form of silica; Z. Kristallogr. 111, 129-141.