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TWINNING OF CRYOLITE*

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The immensely successful development of the atomic structure of minerals (Bragg, 1937) has made this subject a rich repository of exemplifications of structural principles. An attempt has long been under way to obtain clues to the structures of the native proteins from a study of their crystals (Wrinch, 1948). Even the comparatively few crystalline proteins which have been studied by classical or x-ray methods focus attention on two striking characteristics: a prevalence of crystals with high symmetry or pseudosymmetry, and a prevalence of twins and intergrowths. There can be little doubt that these two characteristics, possessed by few if any other types of organic materials, are highly significant. However, if any serious attempt is to be made to discover wherein this significance consists, a first line of enquiry is the answer to the parallel question for the many minerals (albeit a minority of all minerals so far investigated) which also share these characteristics.

Accordingly, the study of a number of such minerals is in progress and a general viewpoint is emerging. Minerals are selected whose atomic patterns are already known by x-ray structure analyses: in this way, we can test the viewpoint, step by step and see, without delay, whether it leads to useful conclusions. According to this viewpoint, the high symmetry or pseudosymmetry of certain crystals and the laws according to which they twin are regarded jointly as direct pointers to and direct indications of the nature of their crystal structure. On a previous occasion (Wrinch 1947), the viewpoint has been applied to staurolite and its pseudosymmetry and twinnings have been interpreted in terms of the (slightly disturbed) face-centered cubic oxygen network. From the standpoint of mineralogy, the point of interest was the way in which a classification of the twin laws of staurolite emerged to make, with the pseudosymmetry of the crystal, a simple and unified picture, directly indicating the nature of the atomic pattern.

The monoclinic mineral cryolite Na_3AlF_6, which is also pseudocubic, has long been a focus of attention for studies of twins (Friedel, 1905, 1926; Böggild, 1912); it exhibits at least 13 twin laws (Dana, 1951). It

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was therefore thought to be of interest to treat it as staurolite was treated, particularly as an x-ray structure analysis (Náray-Szabó and Sasvári, 1938) has yielded the crystal structure, though in it little interest is evinced in the pseudosymmetry or the twin laws.

MORPHOLOGICAL DATA

According to Krenner (Dana, 1892), cryolite is monoclinic $(2/m)$ with $\beta = 90°11'$ and

$$a{:}b{:}c = 0.966{:}1{:}1.388.$$

Twin laws given in the new Dana (1951) based upon a statement by Donnay are as follows:

(1) By a 90° or 270° rotation on [110], penetration, common.
(2) By a 180° rotation on [110], rhombic section $(1\bar{1}0)$, repeated, less common.
(3) By a 120° rotation on [021], composition surface irregular: common, especially in granular cryolite, as fine lamellae and probably always secondary.
(4) By a 180° rotation on $[\bar{1}11]$, rhombic section near (110), repeated; rare, never found in granular cryolite.
(5) On (001) or by a 180° rotation on [100], composition plane (001).
(6) On (100) or by a 180° rotation on [001], composition plane (100).
(7) On (112), composition plane (112).
(8) On $(\bar{1}12)$, composition plane $(\bar{1}12)$.
(9) On (110), composition plane (110).
(10) By a 180° rotation on [111], rhombic section near $(1\bar{1}0)$.
(11) On (211).
(12) By a 90° rotation on [001].
(13) By a 120° rotation on [201].
(14) By a 120° rotation on $[\bar{2}01]$.

Study of the data

The description of the unit cell shows that it closely approaches and yet deviates measurably from a cell with β a right angle and axial ratio $\sqrt{2}{:}\sqrt{2}{:}2$, a cell which can have all its vertices on a simple cubic lattice with k as cube edge, provided that k is chosen to be in the range $a/\sqrt{2}$, $c/2$, $b/\sqrt{2}$. These facts suggest that the crystal, which is not cubic, may yet in some sense have a cubic character, a view of which is implicit in much of Böggild's great Memoir (1912). We then have to find out how this statement can be interpreted.

As before (Wrinch, 1947), we introduce this new cell, which may be called a compound cubic cell since all its vertices can lie at nodes of a single simple cubic lattice, as companion cell to the actual cell. We reformulate the coordinates xyz of the actual cell by introducing cubic coordinates $x_cy_cz_c$ which are fractions of k, as follows:

$$[100] = [110]_c, \qquad [010] = [\bar{1}10]_c, \qquad [001] = [002]_c;$$

so that

$$x_c = x - y, \qquad y_c = x + y, \qquad z_c = 2z; \qquad 2x = x_c + y_c, \qquad 2y = y_c - x_c, \qquad 2z = z_c.$$

We may then reformulate xyz planes in the cubic system $x_cy_cz_c$ and vice versa thus:

$$\begin{array}{lll} (200) = (110)_c, & (020) = (\bar{1}10)_c, & (002) = (001)_c, \\ (100)_c = (1\bar{1}0), & (010)_c = (110), & (001)_c = (002) \end{array}$$

Here the first relation expresses the fact that the plane $x=1$ is also the plane $x_c+y_c=2$, and so on. This companion cell yields a multiple lattice of the k cube lattice, to which the actual lattice of the crystal is a close approximation, since k has been chosen appropriately. Its volume is $4k^3$. We remark that the $(2/m)$ symmetry of the actual crystal is now associated with the cube face diagonal $[\bar{1}10]$.

Proceeding as before we study the formulation, in the $x_cy_cz_c$ system of the companion cell, of the cubic forms of its embedded cubes, (x) denoting $(100)_c$, (s) and (t) denoting $(110)_c$ and $(111)_c$ and $[x]$, $[s]$ and $[t]$ denoting the normals to the planes; in terms of these planes and lines all the symmetry elements of the cubic system can be expressed.

$$\begin{array}{rlll} (x) \equiv & (002)_c, & (200)_c, & (020)_c, \\ = & (001), & (2\bar{2}0), & (220) \end{array}$$

yielding two forms, the pinacoid (001) and the rhombic prism (110).

$$\begin{array}{rllllll} (s) \equiv & (110)_c, & (\bar{1}10)_c, & (011)_c, & (101)_c, & (0\bar{1}1)_c, & (\bar{1}01)_c, \\ & (200), & (020), & (112), & (1\bar{1}2), & (\bar{1}\bar{1}2), & (\bar{1}12), \end{array}$$

yielding 4 forms, two pinacoids (100) and (010) and two rhombic prisms (112) and $(\bar{1}12)$.

$$\begin{array}{rllll} (t) \equiv & (111)_c, & (11\bar{1})_c, & (\bar{1}11)_c, & (1\bar{1}1)_c, \\ & (202), & (20\bar{2}), & (022), & (0\bar{2}2), \end{array}$$

yielding 3 forms, two pinacoids, (101) and $(10\bar{1})$ and one rhombic prism (011).

We may proceed in the same manner with the directions normal to the planes of the various forms, putting together the axes which are symmetric for the crystal:

$$\begin{array}{rlllllll} [x] \equiv & [002]_c, & [200]_c & \text{and} & [020]_c, & & & \\ = & [001], & [1\bar{1}0] & \text{and} & [110], & & & \\ [s] \equiv & [110]_c, & [\bar{1}10]_c, & [022]_c & \text{and} & [202]_c, & [02\bar{2}]_c & \text{and} \quad [20\bar{2}]_c, \\ = & [100], & [010], & [111] & \text{and} & [1\bar{1}1], & [11\bar{1}] & \text{and} \quad [1\bar{1}\bar{1}], \\ [t] \equiv & [111]_c, & [11\bar{1}]_c, & [\bar{1}11]_c & \text{and} & [1\bar{1}1]_c, & & \\ = & [201], & [20\bar{1}], & [021] & \text{and} & [0\bar{2}1]. & & \end{array}$$

In these results we observe the characteristic way in which single cubic forms correspond, for our compound cubic cell which does not have cubic symmetry, to two or more separate forms (Wrinch, 1947). If we refer to the forms observed for cryolite crystals (Dana, 1951), we remark the occurrence of all these forms.

Let us now examine the twin laws recorded, for any support which they can afford to the suggestion of some cubic character in the non-cubic crystal. This may be done, in a routine manner, by reformulating the planes and the axes occurring in the twin laws in terms of the $x_cy_cz_c$ coordinates of the companion cell. We may subdivide the twin laws, now in the two formulations, into a series of subsets:

A. Rotations of 180° and of 90° about the following axes:
  Laws (6) and (12) $[001]=[001]_c$,
  Laws (2) and (1) $[110]=[100]_c$ and $[010]_c$.
B. Rotations of 180° only about the following axes:
  Law (5) $[100]=[110]_c$,
  Law (10) $[111]=[011]_c$ and $[101]_c$,
  Law (4) $[\bar{1}11]=[\bar{1}01]_c$ and $[0\bar{1}1]_c$.
C. Rotations of 120° about the following axes:
  Law (13) $[201]=[111]_c$,
  Law (14) $[\bar{2}01]=[\bar{1}\bar{1}1]_c$,
  Law (3) $[021]=[\bar{1}11]_c$ and $[1\bar{1}1]_c$.
D. Mirrors in the following planes:
  Law (5) $(001)=(001)_c$.
  Law (9) $(110)=(010)_c$ and $(100)_c$,
  Law (6) $(100)=(110)_c$,
  Law (7) $(112)=(011)_c$ and $(101)_c$,
  Law (8) $(\bar{1}12)=(\bar{1}01)_c$ and $(0\bar{1}1)_c$,
  Law (11) $(211)=(131)_c$ and $(311)_c$.

We notice in this series of twin laws some remarkable features. The symmetry elements in *A* comprise the $\frac{1}{2}x$ and $\frac{1}{4}x$ rotations of the symmetry O_h. Those in *B* comprise correspondingly the $\frac{1}{2}s$ rotations of the symmetry O_h, except for the 180° rotation about the *s* line $[\bar{1}10]$, which is a symmetry element of the crystal itself. The symmetry elements in *C*, we notice, comprise the four $\frac{1}{3}t$ rotations of O_h. Thus all the rotational symmetry elements of O_h are now accounted for. The interpretation of the mirror twins is equally interesting. The crystal itself has an *s* mirror, the mirror in the *s* plane $(\bar{1}10)$. In virtue of this fact, it follows that one of the $\frac{1}{2}x$ symmetry elements, $\frac{1}{2}[001]$, is equivalent to an *s* mirror, $(110)_m$, that one of the $\frac{1}{2}s$ symmetry elements, $\frac{1}{2}[110]$, is equivalent to an *x* mirror, $(001)_m$. We duly observe these alternative formulations of law (6) and of law (5) in the subset *D*. In this subset we further remark the presence of the remaining *x* mirror, in law (9) and of two other *s* mirrors which, with the *s* mirror belonging to the crystal, complete all the symmetry elements involving mirrors belonging to O_h. The crystal itself has a center of symmetry. Already all the twin laws except (11) have been discussed. As we have, in fact, demonstrated in studying the twin laws, there are 13 and only 13 independent symmetry elements which, for our monoclinic crystal of symmetry $(2/m)$ associated with a cube face diagonal, are required to complete the symmetry O_h. The remarkable fact has now emerged that the 13 twin laws on the list, excluding law (11), provide just these symmetry elements. In a clear and useful sense, we may call the twins covered by these 13 laws "cubic" twins and the result may be expressed in the statement that, for the cryolite crystal, all possible "cubic" twins have been recorded. Only the twin law (11) lies outside this scheme.

There are two consequences of this analysis, one a matter of description, the other a question of interpretation. On the one hand we can now give a description of 13 of the twin laws, which shows that they constitute a coherent system, with no missing members: the 13 symmetry elements are those which, combined with the 2 symmetry elements of the crystal, give the symmetry O_h. That the 13 twin laws, for which no interrelations are suggested in the literature, can be so described is a fact of some interest, in and for itself. On the other hand, with the present viewpoint, an interpretation of this striking fact is readily forthcoming. The analysis was undertaken in response to the question of what support, if any, the twin laws can give to the hypothesis of some cubic character in the crystal. The answer is that there is complete support for the hypothesis, since every "cubic" twin law which can exist has been shown to occur.

If these striking facts have any significance, it must reside in the positions in the unit cell of the crystal of the known complement of $3Na+Al+6F$ ions or some multiple thereof. In the case of staurolite, sites for complements of atoms on nodes of cubic lattices associated with the companion cell were immediately suggested, and it was recognized that assigning the atoms to positions at or associated with such sites, such sites being subsequently transferred to the actual cell, would give a ready interpretation of the cubic quality of the crystal.

Proceeding after the same manner for the cryolite crystal, we remark that there are only 4 nodes of the simple cubic lattice of metric k in the companion cell to contrast with 10 ions in the elementary composite of cryolite. This k lattice is, of course, merely the coarsest of the possible cubic lattices on which the companion cell can place all its vertices and it is evident that it is too coarse for our purpose. We therefore proceed one step further, to cubic lattices depending on a $\frac{1}{2}k$ metric. Introducing the $\frac{1}{2}k$ simple-cubic lattice, we should get 32 nodes: there are also the intermediate cases, of a body-centered cubic lattice with 8 nodes and a face-centered cubic lattice with 16, all the nodes lying on the $\frac{1}{2}k$ lattice.

Actually the three types of cubic lattice involve superpositions. Thus, begin with 4 points of the k-lattice and supplement with the 8 points and the 16 points and there emerge only 20 points. These may be described as the nodes of the body-centered cubic lattice (at vertices and body-centers of the k cubes) plus only 12 nodes of the face centered cubic lattice: these 12 lie either at face-centers of k cubes (the vertices being already tenanted) or at mid-edges of k cubes (the body-centers being already tenanted). Furthermore, we may, if we wish, subdivide the body centered cubic lattice into two simple cubic lattices, with nodes at vertices of k-cubes and at body-centers of these cubes. Thus there are alternative formulations

$$20 = 8 + 12, \qquad 20 = 4 + 4 + 12.$$

The comparison with the composition of cryolite involving 10 ions is now very interesting. The first hypothesis for consideration is that there are two equivalents in the unit cell, with the 12F ions in positions associated with the 12 nodes of the (incomplete) face-centered cubic lattice in one or other of its expressions: there then remain, for 4Na ions positions associated with one or other of the simple cubic lattices, for the remaining 2Na+2Al positions associated with the nodes of the other. It is to be remarked that the subdivision among different ions of sets of nodes which form single equivalent sets for the cubic system is to be regarded, on the present viewpoint, as the meaning of the subdivision of a single cubic crystal form for the companion cell into two or more monoclinic forms of the actual crystal.

It is to be emphasized that the hypothesis just formulated is to be regarded simply as the first hypothesis to consider. Other hypotheses may be formulated, but only if still finer lattices involving smaller metrics than $\frac{1}{2}k$ are considered. Thus it would be possible to put in order a whole set of such hypotheses, each being of interest only if the preceding hypotheses have been shown to be untenable. One example may be given. In scrutinizing the composition of cryolite, the possibility of a face centered cubic lattice for the 3Na and Al ions early presents itself for consideration. But we readily see that this idea requires the introduction of lattices with a metric finer than $\frac{1}{2}k$. For giving the 3Na and Al ions positions associated with the nodes of even the coarsest face-centered cubic lattice in the cell, we are accommodating 4 such sets. There are then only 16 of the 32 positions with the $\frac{1}{2}k$ metric left, these are insufficient for the accompanying 24F ions. It is therefore necessary to proceed to a finer metric. Thus quite apart from any assessment of prior probability which may be given to this hypothesis for extraneous reasons, it is to be considered only if the preceding hypothesis involving only the $\frac{1}{2}k$ metric is discarded.

The actual crystal structure

We may now turn to the structure analysis which is given in the literature (Náray-Szabó and Sasvári, 1938). The findings are as follows:

Space group $P2_1/n$. $a = 5.46$ Å, $b = 5.61$ Å, $c = 7.80$ Å, $\beta \sim 90°$. Cell contents $2(\mathrm{Na_3AlF_6})$

2Al	$000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$;	4F	0.065, 0.06, 0.22, etc.
2Na	$00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$;	4F	0.71, 0.16, 0.03, etc.
4Na	0.50, 0.945, 0.24, etc.	4F	0.15, 0.28, 0.94, etc.

The hypothesis suggested is therefore correct in the number of equivalents per cell. Furthermore, the 2Na+2Al ions do indeed lie on one of the two simple cubic lattices—at vertices of *k* cubes. We should then, on our hypothesis, have the 4Na ions at the body centers of the *k* cubes, at $\frac{1}{2}0\frac{1}{4}$ etc., giving positions less than 0.4 Å from the positions actually found in the structure analysis. For the F positions, taking midedges of cubes, our hypothesis gives 4F at $00\frac{1}{4}$, etc., 4F at $\frac{\bar{1}}{4}\frac{1}{4}0$, etc., 4F at $\frac{1}{4}\frac{1}{4}0$, etc., which represent deviations from the actual positions which are about twice as great.

CONCLUSIONS

We may now assess the value of the approach to the crystal structure of cryolite which has been developed on the basis of the morphological data. The first of the hypotheses suggested, indeed the only hypothesis based upon the coarsest cubic lattice with sufficient sites to accommodate the 10 ions in the composition of the crystal, is essentially on the right lines. We see, in fact, that all the ions do indeed have positions associated with cubic sites. This means that, now in a precise sense, the statement can be made that cryolite, while not cubic, yet has a cubic character. It has also been shown how this interpretation of the cubic quality of this crystal affords a method of approach to possible sites with which the various ions of the crystal are associated. The part played by the twin laws in developing this argument perhaps needs emphasis. For most minerals, a twin law, like the twin law (11) in the present case, proves interpretable only after the crystal structure analysis has been completed. The remarkable feature in the present case is that there are 13 twin laws which are not only interpretable, as forming a coherent whole with the symmetry elements of the crystal, but serve as direct pointers to the nature of the crystal structure. Certainly the close approach of the shape of the unit cell to that of a compound cubic cell is very suggestive: however the set of 13 separate twin laws provide a much more detailed clue to the crystal. Together they constitute, as it were, the complete case which morphological data can present for a cubic quality in the crystal, with every symmetry element of O_h accounted for, either in the crystal or in the twin laws.

In scrutinizing the relations between the actual atomic positions in the unit cell of the crystal and the suggested cubic sites in the companion cells, two contrasting facts are worthy of comment. We remark the close approach of the positions of the 6Na and 2Al ions to points of a cubic space group—and the fact that positions associated with nodes of a *body-centered* cubic lattice might not have suggested themselves for these ions without the line of argument developed in this communication, makes it perhaps all the more remarkable—and we notice also the implications of this fact in relation to the symmetry elements of the 13 twin laws. But equally interesting is the extent of the deviation of the positions of the F ions from the nodes of the (incomplete) face-centered cubic lattice, with which, nevertheless, they can properly be said to be associated. Naturally we can make no estimate, *a priori*, as to the extent of the deviations of actual atomic positions from available cubic sites in a crystal of unknown structure in which both the shape of the unit cell and the nature of the twin laws combine to suggest some cubic character in the crystal structure. In the case of cryolite, we have the opportunity to study the inescapable manner in which the cubic character of a non-cubic crystal can demonstrate its presence, even when the deviation for a majority of the atoms is of considerable magnitude, through the morphology of the crystal and the morphology of its twins.

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