CRYOLITE TWINNING

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Abstract

Thirteen twin laws are predicted by theory (Friedel); most of them are observed (Böggild). The twin operations are the operations of pseudo-symmetry of a quasi-cubic double cell, obtained from the cryolite cell by transformation $1\bar{1}0/110/001$.

Introduction

This note is intended as a preamble to Dr. Wrinch's paper, which follows it. It summarizes the status of the cryolite problem, which I studied a number of years ago at the request of Professor Charles Palache.

Friedel's treatment of twinning (1905, 1926), applied to cryolite, leads to the prediction of 13 twin laws. We may use Krenner's axial elements for cryolite,

$$a:b:c = 0.966:1:1.388, \qquad \beta = 90°11\,,$$

which have been confirmed by x-rays

$$5.46:5.61:7.80 = 0.973:1:1.390, \qquad \beta = 90°11\,, \qquad P2_1/n,$$

(Náray-Szabó and Sasvári, 1938). The condition that must be satisfied for twinning to occur is that the ratios $a^2:b^2:c^2:\text{ca} \cos \beta$ approach rational numbers. It is here obeyed, as

$$a^2:b^2:c^2:\text{ca}\cos\beta = 0.934:1:1.927:-0.004 \cong 1:1:2:0.$$

Twins are to be expected.

The twinning is controlled by the pseudo-symmetry of a double cell, which can be defined (Fig. 1) by the vectors

$$\boldsymbol{A} = \boldsymbol{a} - \boldsymbol{b}, \qquad \boldsymbol{B} = \boldsymbol{a} + \boldsymbol{b}, \qquad \boldsymbol{C} = \boldsymbol{c}.$$

This cell is a pseudo-cube, for $A = B$ is very nearly equal to C. Any operation of cubic pseudo-symmetry of this double cell can be a twin opera-

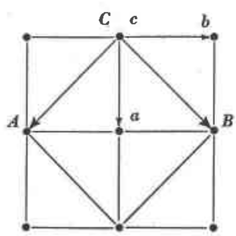

Fig. 1. Net plane (001) of the cryolite lattice showing four meshes (***ab***) and one double mesh (***AB***).

tion, unless it happens to be an operation of the monoclinic symmetry of the crystal. This is a case of "twinning by reticular pseudo-merohedry" (Friedel, 1905, 1926), that is to say, one in which a multiple lattice simulates a symmetry higher than that of the lattice. In cryolite the double cell ***ABC*** is *C*-centered. Leaving out the *C*-centering node, this cell becomes primitive and can be used to define a pseudo-cubic lattice, which is called a "double lattice" of cryolite because its cell has twice the volume of the cell in the true cryolite lattice.

To predict all the possible twin laws, I shall proceed as follows: Consider each element of cubic pseudo-symmetry of the cell ***ABC***, designating it by its symbol referred to Krenner's axial elements. Find out what effect the monoclinic symmetry may have on its becoming a twin element. Finally, for each predicted twin law, I shall refer by number to a list of the observations on record (see below).

Theoretical Predictions

The vertical 4-fold axis of the pseudo-cubic cell is [001]. It is not an element of the monoclinic symmetry, and it may therefore become a twin axis. It can give rise to two distinct twin laws according as the angle of rotation is 90° (see observation No. 11) or 180° (see observation No. 6). Note that the 270° rotation does not yield a distinct twin law, for a twin in which individual I is brought to coincidence with individual II by a clockwise rotation through 270° would be indistinguishable from a twin in which individual II can be made to coincide with individual I by a clockwise rotation through 90°.

The two horizontal 4-fold axes of the pseudo-cube, [110] and [$1\bar{1}0$], are symmetrical to each other in the monoclinic mirror plane. In such a case it is customary to consider only one of the two, say [110], as a twin axis (that the other can also be a twin axis is a logical necessity, due to the symmetry of the crystal). Two twin laws arise, according as the angle of rotation is 90° (see observation No. 1) or 180° (see observation No. 2). Note, as above, that the 270° rotation does not yield a distinct twin law.

Two of the four 3-fold axes of the pseudo-cube, [021] and [$02\bar{1}$], are likewise symmetrical to each other in the monoclinic mirror. Only one, therefore, is considered, say [021]. Note that it is immaterial to use a 120° or a 240° rotation, as they lead to indistinguishable twins (see observation No. 3).

The other two 3-fold axes, [201] and [$\bar{2}01$], lie in the mirror plane of cryolite and are not equivalent. They give rise to two possible twin laws (see observations No. 12 and No. 13).

Of the two horizontal 2-fold axes of the pseudo-cube, [100] and [010], only [100] can be a twin axis (see observation No. 5); [010] coincides with the monoclinic 2-fold axis.

Of the remaining four 2-fold axes, only two should be considered, say [111] (see observation No. 10) and $[\bar{1}11]$ (see observation No. 4); the other two, $[1\bar{1}1]$ and $[\bar{1}\bar{1}1]$, are their mirror-images.

Of the mirrors perpendicular to the 4-fold axes of the pseudo-cube, only two need to be considered as possible twin planes, namely (001) (see observation No. 5) and (110) (see observation No. 9). The third one, $(1\bar{1}0)$, is the mirror-image of (110).

Of the mirrors perpendicular to the 2-fold axes of the pseudo-cube, one, namely (010), coincides with the monoclinic mirror and hence cannot be a twin plane. The following must be considered: (100), quasi-normal to [100] (see observation No. 6); (112), quasi-normal to [111] (see observation No. 7); and $(\bar{1}12)$, quasi-normal to $[\bar{1}11]$ (see observation No. 8).

The center of symmetry of the pseudo-cube coincides with the monoclinic center of symmetry, and hence cannot be a twin center.

The *index* and the *obliquity* have been calculated for the predicted twins (Table 1).

Observations on Record

The observations are found in Böggild (1912), to whose figures references are made in the following list.

(1) Twin axis [110], 90° rotation. Penetration twin; common. This is "Baumhauer's Law" (Figs. 4–5, Fig. 8). Note that common, penetration twins with twin axis $[1\bar{1}0]$, 90° rotation, have also been described (Fig. 6, Fig. 7). Such twins are properly included in Baumhauer's Law.

(2) Twin axis [110], 180° rotation. The rhombic section is here $(1\bar{1}0)$. The twin is of the repeated type; it is less common than the first two (Figs. 9–10, *et ss.*).

(3) Twin axis [021], 120° rotation. Irregular composition surface. This is Böggild's "new law";[1] it is common, especially in granular cryolite; it also occurs in fine lamellae; it is probably always secondary (Figs. 21–22, Fig. 23).

(4) Twin axis $[\bar{1}11]$, 180° rotation. The rhombic section is not a possible face, but it is close to (110). This twin is of the repeated type. It is rare; never obtained by gliding; never found in granular cryolite.

(5) Twin plane (001). The same law can also be defined by means of

[1] In describing his new twin law, Böggild uses another definition, geometrically adequate, but which does not bring out the facts, (1) that a lattice row is the twin axis, (2) that the angle of rotation, in the twin operation, is of the form $360°/n$, with $n=2, 3, 4,$ or 6. Böggild agrees that definition (3) is equivalent to his own.

the twin axis [100] with 180° rotation and composition plane (001). Found on granular cryolite only, in lamellae, common.

TABLE 1. CRYOLITE TWINNING

Twin Law	Index	Obliquity
[001] 90°, 180°; (001)	1	0°11′
[110] 90°, 180°; (110)	2, 1, 1	1°58′
[201] 120°	2	0°47′
[$\bar{2}$01] 120°	2	0°55′
[100] 180°; (100)	1	0°11′
[111] 180°; (112)	2	1°29′
[$\bar{1}$11] 180°; ($\bar{1}$12)	2	1°18′

(6) Twin plane (100). The same law can also be defined by means of the twin axis [001], with 180° rotation and composition plane (100). Found on granular cryolite only, in lamellae, common.

(7) Twin and composition plane (112). Found on granular cryolite only, in lamellae, common.

(8) Twin and composition plane ($\bar{1}$12). Found on granular cryolite only, in lamellae, common.

(9) Twin and composition plane (110). This twin occurs in lamellae and is found only on granular cryolite from the Urals.

(10) Twin axis [111], 180° rotation. The rhombic section is not a possible face, but it is near (1$\bar{1}$0). This twin has not been found by Böggild, but it may possibly be Cross and Hildebrand's "law *d*" (1885).

(11) Twin axis [001], 90° rotation. This twin law is very close to (9). It is one of Paduroff's "new laws" (1925).

(12) Twin axis [201], 120° rotation. This twin law is very close to (8).

(13) Twin axis [$\bar{2}$01], 120° rotation. This twin law is very close to (7).

Böggild did not attempt to differentiate (11) from (9), nor (12) from (8), nor (13) from (7).

It is interesting to note that, when Friedel wrote his memoir (1905), he listed only four known twin laws. They were: (5), (9), (6), and (8).

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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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