

ON THE SUPERSTRUCTURE AND TWINNING OF PYRRHOTITE

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ABSTRACT

Pyrrhotite of composition $\text{Fe}_{.889}\text{S}$ from Morro Velho, Brazil, is pseudohexagonal. Precession photographs suggest a superstructure with cell dimensions which appear to be two and four times the A and C dimensions of a NiAs-type substructure. Small displacements of superstructure reflections in the patterns indicate the presence of twinning. A previously proposed twin law does not explain the observed reflections or the symmetry of the twin.

It is shown that the true lattice is at least dimensionally monoclinic and is twinned by a 2-fold rotation about [110]. The a and b translations of the cell are twice the orthohexagonal B and A dimensions of the substructure respectively, and β is 91.79° . The c dimension and lattice type are uncertain because of certain non-space-group extinctions which are still unexplained. Patterson projections suggest that the superstructure intensities are primarily due to distortion of a NiAs-type arrangement about iron vacancies.

INTRODUCTION

The iron sulfide minerals found in nature include troilite, FeS ; pyrrhotite, having a variable composition Fe_{1-x}S with x between 0 and approximately .2; smythite, Fe_3S_4 ; and pyrite and marcasite, FeS_2 . Near composition FeS the system is extremely complex. These compositions have been studied extensively because of their unusual magnetic properties. Despite numerous investigations, the phase relations and magnetic properties are still not understood in detail.

The voluminous literature on pyrrhotite permits but a brief survey of pertinent work. The general nature of the pyrrhotite structure was determined some while ago by Alsen (1925) who assigned to it the arrangement now known as the NiAs-type (B8) structure. Hägg and Sucksdorff (1933) demonstrated that the compositional variations occurred through omission of Fe from sites normally occupied in the NiAs-type structure. Furthermore, they found that troilite and compounds with Fe deficiencies up to $\text{Fe}_{.953}\text{S}$ displayed a hexagonal superstructure with $a_1 = a_2 = \sqrt{3}A_1$, $c = 2C$ †. Following a series of studies of the magnetic properties of artificial Fe-S preparations, Haraldsen (1941) proposed a phase diagram for the system. No phases of symmetry lower than hexagonal were reported and a superstructure was again observed only for "paramagnetic" compositions near troilite. The superstructure was found to invert to a

NiAs-type structure at 138°C . Bertaut (1956) subsequently determined the crystal structure of both troilite phases and found that the superstructure was caused by small displacements of Fe atoms normal to c and small displacements of S atoms parallel to c . This structure was confirmed by Andresen (1960) who determined improved parameters using neutron diffraction. Also, it is now known that troilite is antiferromagnetic, not paramagnetic as previously proposed. At the 138°C phase transition the Fe spins shift from an alignment parallel to c to a new antiferromagnetic alignment perpendicular to c . A further transition to a paramagnetic structure occurs at a Néel temperature of 325°C . The "ferromagnetic" iron-deficient structures probably possess unbalanced antiferromagnetism, *i.e.*, ferrimagnetism.

The structures with higher iron deficiencies are less well understood. As mentioned above, Haraldsen observed no phases with symmetry lower than hexagonal, and no superstructures other than that of the "paramagnetic" troilite. Byström (1945), however, in investigating powder patterns of natural magnetic pyrrhotite from a number of Swedish localities, surprisingly discovered that the majority of these pyrrhotites were monoclinic with $a \approx B$, $b \approx A$, $c \approx C$; $\beta = 90.4^\circ$. No superstructures were observed. In a single-crystal x -ray study Buerger (1947) discovered that naturally occurring magnetic pyrrhotites from Morro Velho, Brazil, and Schneeberg, Saxony, exhibited hexagonal superstructures with $a_1 = a_2 = 2A$, $c = 4C$. The presence of non-space-group extinctions in the pattern, however, indicated that the specimens were probably twinned, and that the true symmetry of pyrrhotite was perhaps monoclinic or orthorhombic. This superstructure was confirmed by Bertaut (1953) on material of an unspecified nature. Twin-

† Throughout this paper normal lower-case symbols are used to denote the crystallographic axes of the superstructures based on the NiAs-type arrangement, since these are true unit-cell translations. The NiAs-type substructure will be denoted by the hexagonal axes A_1, A_2, C or, where convenient, by the orthohexagonal axes A, B, C with $|A| = A_1$, $|B| = \sqrt{3}A_1$. In the past, most authors have used upper-case symbols for the pyrrhotite superstructures.

ning of a monoclinic cell was used to explain the non-space-group extinctions. An additional hexagonal superstructure, $a_1 = a_2 = 3A_1$, $c = 2C$, was reported by Graham (1949) for a synthetic pyrrhotite. The composition was unknown but was presumably close to troilite since it was "non-magnetic." Erd *et al.* (1957) discovered naturally occurring Fe_3S_4 , smythite, which had a rhombohedral superstructure $a_1 = a_2 = A_1$, $c = 6C$.

Further work on the Fe-S phase relations has been done by Eliseev and Denisov (1957), and Grønvdal and Haraldsen (1952). The latter authors resolved some of these existing contradictions and, in particular, showed that Byström's monoclinic distortion of the NiAs structure did indeed exist for a very narrow range of compositions around Fe_7S_8 . This composition was taken as the limit of Fe deficiency, however, and did not extend to Fe_3S_4 . Also, superstructures (other than that for troilite compositions) were observed only in the range $\text{Fe}_{.971}\text{S-Fe}_{.924}\text{S}$ where an unidentifiable superstructure was observed at 185°C .

The superstructures exhibited by the iron-deficient structures are primarily due to ordered arrangement of the iron vacancies. These arrangements have been determined for Fe_7S_8 (Bertaut, 1953), Fe_3S_4 (Erd *et al.*, 1957) and for several defect superstructures in the iron selenide system where an analogous and equally complex situation exists (Okazaki and Hirakawa, 1956; Okazaki, 1959, 1961). With the exception of Fe_3S_4 , where unfortunately the crystals were of very poor quality, these structures have been determined only through observation of qualitative relations among the superstructure intensities, and have not been refined. The proposed pyrrhotite superstructure (Bertaut, 1953), with which most of the latter structures have been compared, was determined by finding the ordered array of vacancies which was most favorable energetically. The present study was intended as an attempt to confirm this arrangement by a direct structure determination and refinement. In view of the curious physical properties of the structure, information about atomic displacements around the vacancies and accurate interatomic distances would be of great interest.

SELECTION AND COMPOSITION OF CRYSTALS

Natural pyrrhotite from Morro Velho, Brazil, was used in the present study. This material (Harvard Cat. No. 81821) was the same as that previously used by Buerger (1947). Fragments for a single-crystal study were broken from small, well formed hexagonal platelets and ground into spheres using an apparatus

similar to that described by Bond (1951). Although care was taken to obtain specimens as free as possible from lineage structure, its effect was still present to some degree even in the best crystals. Polished sections examined in reflected light revealed no evidence for the presence of a second phase even when treated with a variety of etchants.

The pyrrhotite's composition was determined with the aid of an empirical curve relating $d_{10\cdot2}$ to metal content (Arnold and Reichen, 1962). Powder-diffractometer patterns, obtained using $\text{CuK}\alpha$ radiation, showed the $10\cdot2$ reflection to be split into two peaks of about equal intensity. This indicated symmetry lower than hexagonal. The superstructure reflections were undetectable. Following Arnold and Reichen's procedure, the powder was then annealed for 26 hours at 575°C . in a sealed, evacuated Vycor tube. This treatment removed the splitting of the $10\cdot2$ reflection. The tungsten powder used in the International Union of Crystallography precision lattice-parameter project (Parrish, 1960) was used as an internal standard. The resulting hexagonal $d_{10\cdot2}$ was found to be $2.0632 \pm .0002 \text{ \AA}$, corresponding to $\text{Fe}_{.889}\text{S}$ (supposedly accurate to $\pm .23$ atomic per cent). This composition is exactly Fe_8S_9 , although the deviation from ideal composition Fe_7S_8 is slight.

X-RAY INVESTIGATION

A single-crystal study of an unannealed spherical crystal was made using the precession method. A zero-level precession photograph taken about one of the supposedly hexagonal a axes is given in Fig. 1. The very strong reflections of the NiAs-type substructure are immediately apparent. A large number of weak superstructure reflections may also be observed which, upon first inspection, appear to require doubling of A_1 , and quadrupling of C . This would require

$$\begin{aligned} a_1 = a_2 &= 2A_1 = 6.88 \text{ \AA} \\ c &= 4C = 22.81. \end{aligned}$$

Closer inspection of the reciprocal lattice rows parallel to C , however, indicates that those rows which do not contain substructure reflections exhibit only superstructure reflections with l not equal to $4n$. In other words, these reflections occur only in triplets between l values corresponding to substructure reflections. This is the non-space-group extinction rule previously observed by Buerger (1947) and Bertaut (1953), and was found to hold true for such superstructure reflections on *all* levels.

A curious feature of these triplets is illustrated in Fig. 2, in which four sets of these spots from the same

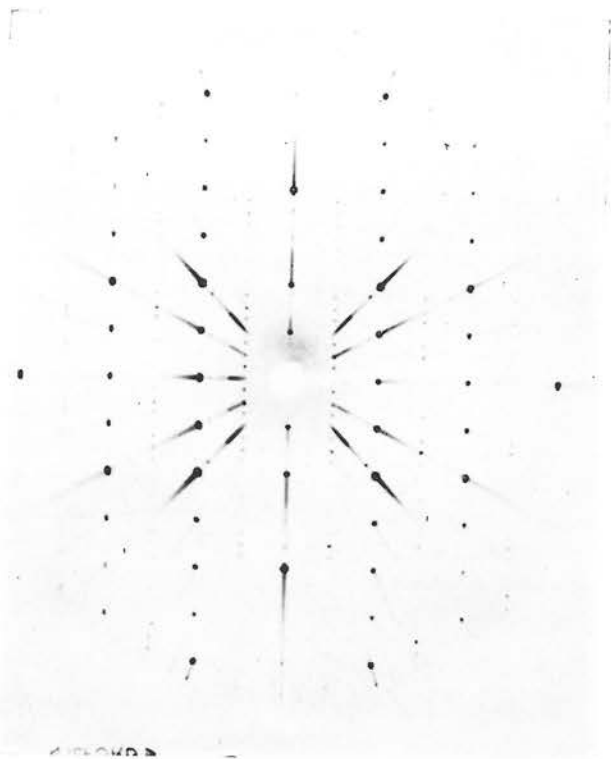


FIG. 1. Precession photograph of pyrrhotite taken about one of the pseudo-hexagonal a axes. Zero-level $\text{MoK}\alpha$, 39 Kv, 15 ma., 39 hour exposure; c^* is vertical, a^* is horizontal. The strong reflections correspond to the NiAs-type substructure.

first-level a axis precession film have been enlarged and assembled together. If pyrrhotite were hexagonal, this level should display symmetry $2mm$ and corresponding spots in the triplet should be equivalent. It may be seen, however, that the intensities do not display this symmetry. In addition, they are not equally spaced, but have small and unequal displacements parallel to C^* . The displacements of corresponding spots in the four triplets also bear no symmetric relation to one another. A general reciprocal-lattice level for an axis normal to C is therefore without symmetry of any kind. Furthermore, the irregular displacement of spots parallel to C^* indicates that the superstructure reflections cannot lie on a single reciprocal lattice. This demonstrates conclusively that pyrrhotite is twinned.

THE TWIN LAW OF PYRRHOTITE

Bertaut (1953) postulated that the pyrrhotite twin was composed of two monoclinic crystals related by a 60° rotation about the pseudo-hexagonal c axis. A unit cell was proposed with $a=2B$, $B=2a$, $c\approx 4C$, $\beta=90.45^\circ$, and space group $F 2/d$. Fig. 3 gives views

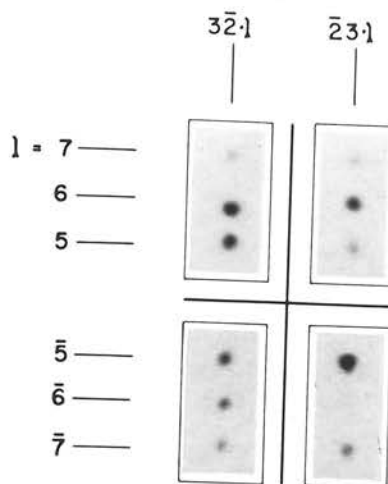


FIG. 2. Enlargement of four sets of superstructure "triplets" taken from a single first-level pseudo-hexagonal a axis precession photograph. Pseudo-hexagonal indices have been assigned to the reflections. Hexagonal symmetry would require that the triplets be equivalent. The intensities of corresponding reflections bear no symmetric relation. The spots also have small, unequal displacements parallel to c^* .

along the pseudo-hexagonal axis for two such reciprocal lattices in this orientation. The slight monoclinic distortions have been neglected. The extinction rules for reciprocal-lattice rows parallel to c^* are given by the special symbols indicated. Rows containing substructure reflections are represented by solid symbols; rows containing only superstructure reflections are represented by open symbols. Figure 3 also gives the resulting composite reciprocal lattice. It may be seen that the $l=4n$ extinction rule appears only on two zero levels. Most of the superstructure

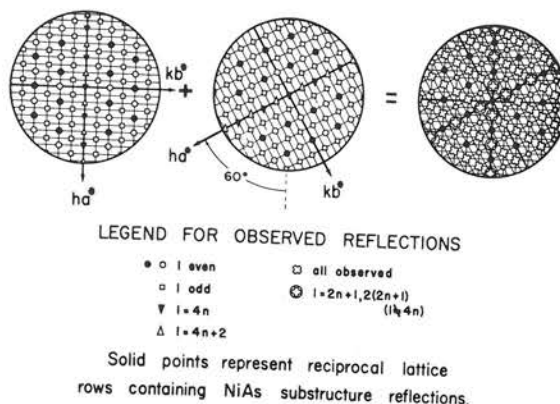


FIG. 3. The twin law previously proposed for pyrrhotite. A face-centered monoclinic cell was postulated. Views along c^* are given for two reciprocal lattices related by the twin operation, and the result of superposing the reciprocal lattices is shown. The various extinction rules are denoted by special symbols.

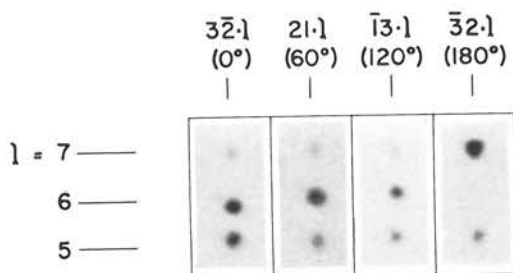


FIG. 4. Comparison of one of the superstructure reflection triplets of Fig. 2 with corresponding sets from precession photographs taken about the neighboring pseudo-hexagonal a axes. (Pseudo-hexagonal indices have been assigned to the reflections.)

rows not containing substructure reflections exhibit no extinctions, whereas this "strange" extinction rule is, in fact, observed for most of these rows. Bertaut's cell and twin law therefore do not explain the unobserved reflections.

Only a single set of NiAs-type substructure reflections are observed in the diffraction patterns. Therefore the twin operation must be one which transforms the substructure into itself (or nearly so, if slightly distorted). This situation is common in crystals having substructures, and, indeed, is the physical basis for the twinning. Clearly, no operation isogonal with a hexagonal lattice can give rise to small displacements of the superstructure spots such as those observed if the superstructure lattice is orthogonal. Therefore the true symmetry of pyrrhotite must be monoclinic or triclinic.

Buerger (1960) has shown that the symmetry of a twinned reciprocal lattice is given by the common symmetry of the individuals (when in twinned orientation) augmented by the symmetry of the twin law. If pyrrhotite is monoclinic, a 2-fold axis cannot be oriented parallel to the pseudo-hexagonal c axis since all candidate operations isogonal with a pseudo-hexagonal lattice transform this axis into itself. This would require the twin to exhibit at least 2-fold symmetry about this axis. Diffraction symmetry would then introduce a symmetry plane normal to this axis. This is not observed. Therefore if a 2-fold axis is present in pyrrhotite it must be normal to the pseudo-hexagonal axis.

To determine the symmetry of the twin, zero- and first-level precession patterns were obtained for all of the pseudo-orthohexagonal a and b axes. No rotation about the pseudo-hexagonal c axis was found which related any two patterns. Figure 4, for example, compares one of the triplets of Fig. 2 with corresponding sets from films taken at 60, 120 and 180 degree intervals. No equivalence is observed. The previously

proposed twin law, however, would require two sets to be equivalent.

Only two directions in the twin proved to give identical diffraction patterns upon suitable transformation. Two sets of pseudo-orthohexagonal b -axis photographs, for example, were found to be equivalent provided one was rotated 180°. Figure 5 compares pairs of reciprocal lattice rows in this orientation which were taken from first-level films about these two directions. The twinning operation therefore consists of a 60° rotation about the pseudo-hexagonal c axis followed by a 2-fold rotation about the pseudo-hexagonal b axis. The combination of these two operations is equivalent to a single 2-fold rotation about the pseudo-hexagonal a axis midway between the two related b axes.¹ The twin therefore contains crystals corresponding to each operation of the twin axis, unlike the twin resulting from the previously proposed mechanism.

ORIENTATION OF THE TWIN AXIS AND UNIT CELL

The preceding discussion has described a twinning operation relative to a pseudo-hexagonal lattice. The nature of the true unit cell and the orientation of the twin axis relative to it have yet to be specified. It may readily be shown that the displacement of spots observed in the precession patterns can arise only if the untwinned lattice is monoclinic.

Let a sublattice of the NiAs-type with true orthohexagonal symmetry be used as a reference system. The diffraction patterns of the twinned crystal indicate apparent doubling of A and B . With the twin operation proposed, this may occur only if the actual a and b of the individuals are doubled. Assuming that the superstructure is based on a monoclinic distortion of this substructure, two cases not precluded by the previous discussion are possible. The distortion may be such that the projection of c lies along either the orthohexagonal A or the orthohexagonal B axis of the substructure. The corresponding superstructures for the two possibilities may be expressed by the following general relations:

<i>proj. c parallel to A:</i>	<i>proj. c parallel to B:</i>
$a = 2A$	$a = 2B$
$b = 2B$	$b = -2A$
$c = -\Delta A + nC$	$c = -\Delta B + nC$

matrix for the transformation:

2	0	0	0	2	0
0	2	0	-2	0	0
- Δ	0	n	0	- Δ	n

¹ See discussion by Professor J. D. H. Donnay following this paper.

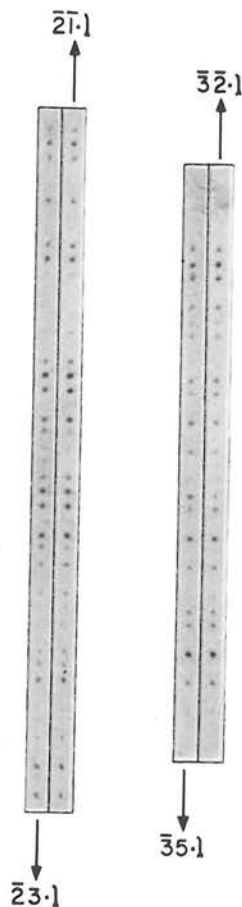


FIG. 5. Comparison of reciprocal-lattice rows related by the twin operation. Rows are compared from precession photographs taken about two first-level pseudo-orthohexagonal b axes which are separated by 60° . One of the films has been rotated 180° . These operations are equivalent to a 2-fold rotation about the pseudo-hexagonal a axis between the two axes. (Pseudo-hexagonal indices have been assigned to the reflections.)

where Δ is a fraction, and n is an integer. Corresponding matrices for the transformation in reciprocal space are given by the transpose of the inverses of the above matrices. Using this relation one obtains:

<i>proj. c parallel to A:</i>	<i>proj. c parallel to B:</i>
$a^* = \frac{1}{2}A^* + \frac{\Delta}{n}C^*$	$a^* = \frac{1}{2}B^* + \frac{\Delta}{n}C^*$
$b^* = \frac{1}{2}B^*$	$b^* = -\frac{1}{2}A^*$
$c^* = \frac{1}{n}C^*$	$c^* = \frac{1}{n}C^*$

From these relations it may be seen that a^* and b^* are halved in the directions of A^* and B^* . In both possibilities, however, a^* has an additional component along the pseudo-hexagonal axis C^* . This is the nature of the displacement of spots observed. A triclinic lattice would involve additional components normal to

C^* . Therefore the pyrrhotite lattice is at least dimensionally monoclinic.

The two monoclinic possibilities may be distinguished from the nature of the splitting of the pseudo-hexagonal peaks in the powder pattern.¹ It was noted above that the $10 \cdot 2$ reflection was split into two components. This behavior will be observed if *proj. c* is parallel to B . If *proj. c* were parallel to A , the peak would be split into three components. Therefore the distortion of the NiAs arrangement is the second of the two cases considered. As mentioned above, a and b appear to be integral multiples of B and A respectively. Since the substructure dimensions are known, it is necessary to assume only that c is also an integral multiple of C in order to permit computation of β from the splitting of a substructure reflection. From the magnitude of the $10 \cdot 2$ splitting, β was found to be 91.79° .

All possible settings of c relative to the twin axis were found to be equivalent upon suitable relabeling of the twins or redefinition of the cell. (*Proj. c* cannot, however, be normal to the twin axis, for in this case the twin operation is a symmetry element of the lattice.) The twin operation may therefore be described as a 2-fold rotation about $[110]$.

The $l=4n$ extinction rule observed for certain reciprocal lattice rows must be explained by superposition of lattice rows from each of the crystals composing the twin. Since this rule is observed on all levels, it must involve space-group extinctions due to the lattice type. The apparent doubling of A_1 can be explained only by assuming that $a=2B$ and $b=2A$. The non-space-group extinctions require superposition of rows with modulo 4 and modulo 2 extinction rules for l . It is impossible to find a lattice type which predicts absences with both of these periodicities. The lattice type and the magnitude of the c translation of pyrrhotite are therefore not certain at this time.

This difficulty might arise because of several possible reasons. The superstructure reflections are extremely weak. The superstructure may be such that reflections with a certain periodicity are too weak to be detectable. Another possibility is that further twinning exists, and that the twin actually consists of two or more crystals in twinned orientation which are then further repeated by a rotation about $[110]$. Also, the composition determined for the specimens was exactly Fe_8S_9 . While this represents but a slight excess of iron over ideal Fe_7S_8 , this result may be sig-

¹ Splitting of the peaks in the single-crystal diffraction patterns was suspect because of the presence of lineage structure. In a powder pattern, however, any splitting must be entirely due to the symmetry of the lattice.

nificant. The smallest cell containing a multiple of Fe_8S_9 requires $c=9C$. This is incompatible with the apparent quadrupling of C . It is therefore possible that the specimens investigated were actually intergrowths of two phases despite the fact that no physical evidence for this could be found.

THE NATURE OF THE SUPERSTRUCTURE

If the superstructure were primarily due to ordering of Fe vacancies, a determination of the structure would be comparatively simple. The superstructure reflections would have zero intensity if all Fe sites in the NiAs-type structure were occupied. Therefore, if only superstructure reflections are considered, the diffraction effect of an ordered arrangement of vacancies is completely equivalent to a structure in which Fe atoms alone occupy the vacancy sites. A Patterson function based on superstructure reflections should then exhibit maxima only in locations corresponding to certain of the Fe-Fe peaks of a NiAs arrangement. Consideration of the NiAs structure shows that in projection these peaks may occur only on a sublattice given by $a' = \frac{1}{2}A$, $c' = \frac{1}{2}C$; or $b' = \frac{1}{2}B$, $c' = \frac{1}{2}C$.

A complete set of three-dimensional intensities was collected from a twinned crystal of pyrrhotite. Some reflections were slightly split due to lineage structure or imperfect superposition of reflections arising from different crystals in the twin. Therefore the intensities were recorded with an integrating precession camera.

The effect of splitting of spots is minimized in this technique since all portions of the spot eventually contribute to the "plateau" of the integrated spot as the film is moved through a cycle. No symmetry was assumed for the twin. An amount of data equivalent to a complete $\text{CuK}\alpha$ sphere was recorded.

Patterson projections along the a and b axes of one of the twins were synthesized using only superstructure reflections. Surprisingly, virtually none of the peaks fell on locations corresponding to Fe-Fe interactions for a NiAs arrangement. The calculated weight of such interactions was only slightly above the background of the maps. The observed maxima were not circular, but rather suggested interactions between portions of atoms. It therefore appears that the superstructure intensities are primarily due to distortions of the NiAs-type structure about the vacancies. Analysis of 3-dimensional Patterson maps is currently in progress.

ACKNOWLEDGMENTS

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DISCUSSION

J. D. H. DONNAY (Baltimore): 1. Does the twin contain only two crystals?

2. If the twin operation consists of the product of two rotations $[c \text{ axis}]_{60^\circ} \times [\text{horizontal axis}]_{180^\circ}$, it should be possible to define it as a single rotation about another axis. If crystal I and crystal II in the twin are related by a 180° -rotation, it is easier to understand why the twinning is not repeated by further 60° -rotations. H. Curien (Paris, France) remarks that the new axis is horizontal and lies at 30° to the horizontal axis used in the two-rotation definition.

AUTHOR'S REPLY: 1. Only one operation was found which related the diffraction effects observed. Therefore it was assumed that only two crystals were present in the twin.

2. The two-rotation definition was useful since it consists of operations which may actually be performed with precession photographs, taken about different directions of the twin. It is correct that the operations may be described in terms of a single rotation and that this is obviously the best crystallographic description of the twinning operation. Accordingly, this is the final description of the twin law which has been given in the text.