ON THE SUPERSTRUCTURE AND TWINNING OF PYRRHOTITE

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Abstract

Pyrrhotite of composition FeS_{1.5}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 \( \beta = 91.79^\circ \). 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 0.2; smithyite, FeS_{1.5}; 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 Fe_{0.5}S displayed a hexagonal superstructure with \( a_1 = a_2 = \sqrt{3}A, c = 2C \). 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 \( a=B, b=A, c=C; \beta = 90.4^\circ \). 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-
ning of a monoclinic cell was used to explain the non-

space-group extinctions. An additional hexagonal

superstructure, \(a_1 = a_3 = 3A_1, c = 2C\), was reported by

Graham (1949) for a synthetic pyrrhotite. The composi-
tion was unknown but was presumably close to
troilite since it was "non-magnetic." Erd et al. (1957)
discovered naturally occurring Fe\(_3\)S\(_4\) smithite,
which had a rhombohedral superstructure
\(a_1 = a_3 = A_1, c = 6C\).

Further work on the Fe-S phase relations has been
done by Eliseev and Denisov (1957), and Grønvold
and Haraldsen (1952). The latter authors resolved
some of these existing contradictions and, in particu-
lar, showed that Byström's monoclinic distortion of
the NiAs structure did indeed exist for a very narrow
range of compositions around Fe\(_{2.97}\)S\(_{3.99}\). This composition
was taken as the limit of Fe deficiency, however, and
did not extend to Fe\(_3\)S\(_4\). Also, superstructures (other
than that for troilite compositions) were observed
only in the range Fe\(_{0.77}\)S-Fe\(_{0.98}\)S where an unidentifi-
able superstructure was observed at 185° C.

The superstructures exhibited by the iron-deficient
structures are primarily due to ordered arrange-
ment of the iron vacancies. These arrangements have
been determined for Fe\(_3\)S\(_4\) (Bertaut, 1953), Fe\(_2\)S\(_4\) (Erd
et al., 1957) and for several defect superstructures in
the iron selenide system where an analogous and
equally complex situation exists (Okazaki and Hira-
kawa, 1956; Okazaki, 1959, 1961). With the excep-
tion of Fe\(_3\)S\(_4\), where unfortunately the crystals were
of very poor quality, these structures have been
determined only through observation of qualitative re-
lations 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 de-
termined by finding the ordered array of vacancies
which was most favorable energetically. The present
study was intended as an attempt to confirm this ar-
rangement by a direct structure determination and
refinement. In view of the curious physical properties
of the structure, information about atomic displace-
ments around the vacancies and accurate inter-
atomic 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 apparat

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 sec-
tions examined in reflected light revealed no evi-
dence 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 \(d_{00.2}\) to
metal content (Arnold and Reichen, 1962). Powder-
diffractometer patterns, obtained using CuK\(_{\alpha}\) radi-
ation, showed the 10·2 reflection to be split into two
peaks of about equal intensity. This indicated sym-
metry lower than hexagonal. The superstructure re-
fections 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 10·2 reflection. The tungsten powder used in the In-
ternational Union of Crystallography precision lattice-parameter project (Parrish, 1960) was used as an
internal standard. The resulting hexagonal \(d_{00.2}\) was
was found to be 2.0632±.0002 Å, corresponding to
Fe\(_{88.5}\)S (supposedly accurate to ±.23 atomic per-
cent). This composition is exactly Fe\(_3\)S\(_4\), although the-deviation from ideal composition Fe\(_3\)S\(_4\) 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 sub-
structure are immediately apparent. A large number
of weak superstructure reflections may also be ob-
erved which, upon first inspection, appear to require
doubling of \(A_1\), and quadrupling of \(C\). This would re-

quire

\[
\begin{align*}
a_1 &= a_2 = 2A_1 = 6.88 \text{ Å} \\
c &= 4C = 22.81.
\end{align*}
\]

Closer inspection of the reciprocal lattice rows par-
allel 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 re-
fections. This is the non-space-group extinction rule
previously observed by Buerger (1947) and Bertaut
(1953), and was found to hold true for such super-
structure 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
first-level \(a\) axis precession film have been enlarged and assembled together. If pyrrhotite were hexagonal, this level should display symmetry \(2\text{mm}\) 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. The spots also have small, unequal displacements parallel to \(c^*\). 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 \(60^\circ\) rotation about the pseudohexagonal \(c\) axis. A unit cell was proposed with \(a=2B\), \(B=2a\), \(c=4C\), \(\beta=90.45^\circ\), and space group \(P 2/d\). Fig. 3 gives views along the pseudohexagonal 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 superstructure 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
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 pseudohexagonal 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 pseudohexagonal 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. 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 ortho-hexagonal 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:

\[
\begin{align*}
\text{proj. } c \text{ parallel to } A: & & \text{proj. } c \text{ parallel to } B: \\
\mathbf{a} = & 2A & \mathbf{a} = & 2B \\
\mathbf{b} = & 2B & \mathbf{b} = & -2A \\
\mathbf{c} = & -\Delta \mathbf{A} + n\mathbf{C} & \mathbf{c} = & -\Delta \mathbf{B} + n\mathbf{C} \\
\end{align*}
\]

**Matrix for the transformation:**

\[
\begin{bmatrix}
2 & 0 & 0 \\
0 & 2 & 0 \\
-\Delta & 0 & n \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
0 & 2 & 0 \\
-2 & 0 & 0 \\
0 & -\Delta & n \\
\end{bmatrix}
\]

See discussion by Professor J. D. H. Donnay following this paper.
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21.1

32.1

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 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 pseudohexagonal a axis between the two axes. (Pseudohexagonal indices have been assigned to the reflections.)

where \( \Delta \) 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:

\[
\begin{align*}
\text{proj. } c \text{ parallel to } A: & & \text{proj. } c \text{ parallel to } B: \\
\alpha^* &= \frac{1}{2} A^* + \frac{\Delta}{n} C^* & \alpha^* &= \frac{1}{2} B^* + \frac{\Delta}{n} C^* \\
\beta^* &= \frac{1}{2} B^* & \beta^* &= -\frac{1}{2} A^* \\
\gamma^* &= \frac{1}{n} C^* & C^* &= \frac{1}{n} C^*
\end{align*}
\]

From these relations it may be seen that \( \alpha^* \) and \( \beta^* \) are halved in the directions of \( A^* \) and \( B^* \). In both possibilities, however, \( \alpha^* \) has an additional component along the pseudohexagonal 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. It was noted above that the 10.2 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, \( \alpha \) and \( \beta \) 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 \( \beta \) from the splitting of a substructure reflection. From the magnitude of the 10.2 splitting, \( \beta \) 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\(_8\)S\(_9\). While this represents but a slight excess of iron over ideal Fe\(_7\)S\(_8\), 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.
significant. The smallest cell containing a multiple of Fe₉S₉ 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' = 1/4A, c' = 1/4C; or b' = 1/2B, c' = 1/4C.

A complete set of three-dimensional intensities was collected from a twinned crystal of pyrrhotite. Some reflections were slightly split due to lineal 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 CuKα 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 three-dimensional Patterson maps is currently in progress.

Acknowledgments

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References


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 [\( c \text{ axis} \times \text{horizontal axis} \)], 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.