THE CELL AND SYMMETRY OF PYRRHOTITE

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Abstract

According to the literature, ferromagnetic pyrrhotite exists in the composition range $Fe_{.48}S_{.52}$ to $Fe_{.466}S_{.534}$ and has the nickel arsenide type structure with cell dimensions $a = 3.43$ Å, $c = 5.68$ Å; paramagnetic "troilite" is confined to the composition range $Fe_{.50}S_{.50}$ to $Fe_{.48}S_{.52}$, and has two kinds of structures: nickel arsenide type in the high sulfur half of the field, and a superstructure type in the region near the ideal composition FeS.

New results are reported here which are at variance with this information. Single crystals of ferromagnetic pyrrhotite from Schneeberg, Saxony, and from Morro Velho, Brazil, were investigated by the precession method. The photographs show a hexagonal cell much larger than any hitherto proposed for either troilite or pyrrhotite. Its dimensions are $a = 6.87$ Å, $c = 22.7$ Å. This cell has sixteen times the volume of a nickel arsenide type cell. The diffraction symbol of pyrrhotite is $6/mmm\ C\ 6_3/---$. If this effect arises from a single crystal the space group is $C6_32$, but there is a possibility that the diffraction effect may arise from a twin. This supercell is not the same as the one hitherto reported in the literature for troilite, and it belongs to a type of pyrrhotite outside of the troilite range where no superstructure is supposed to occur.

Status of "Pyrrhotite"

The arrangement of atoms in pyrrhotite was deduced by Alsén[1] from data derived from rotating-crystal, Laue and powder photographs of crystals from Kongsberg, Sweden, as well as from powder photographs of other material. Alsén assigned to pyrrhotite the structure now known as the nickel arsenide arrangement, with the following cell dimensions:

$$a = 3.43 \text{ Å}$$
$$c = 5.68 \text{ Å}$$

Subsequently Hägg and Sucksdorf[2] investigated artificial preparations of varied iron:sulfur ratio, using the powder method. They demonstrated that the variation of composition was due to omission of iron atoms from the structure. They also discovered that, while the powder photographs showed the nickel arsenide pattern found by Alsén, provided that the sulfur content was above about $51\frac{1}{2}$ atomic per cent, preparations with less sulfur gave powder photographs with superstructure lines. They were able to index these photographs on the basis of hexagonal or trigonal symmetry for a hexagonal cell having the following dimensions:

[1] Alsén, Nils, Röntgenographische Untersuchung der Kristallstruckturen von Magnetkies, Breithauptite, Pentlandite, Millerite und verwandten Verbindungen: *Geol. Fören. Förhandl. Stockholm,* **47,** 19–72 (1925).

[2] Hägg, Gunnar, and Sucksdorff, Ingrid, Die Kristallstruktur von Troilit und Magnetkies: *Zeit. physik. Chem.,* **B22,** 444–452 (1933).

$$a = 6.946 \text{ Å } (\approx \sqrt{3} \times 3.43\text{Å})$$
$$c = 11.720 \text{ Å } (\approx \quad 2 \times 5.68\text{Å}).$$

The a axis of this supercell is the long diagonal of Alsén's cell, the c axis is twice that of the Alsén's cell, and its volume is six times that of Alsén's cell. This supercell occurs only in the neighborhood of the ideal formula FeS.

Sidhu and Hicks[3] studied ferromagnetic crystals from Minas Geraes, Brazil, and paramagnetic crystals from Maggiadone, Italy, by the rotating-crystal and Laue methods. In these materials they found no evidences of a superstructure. On the other hand, powder photographs of natural material from Kisbanya, Roumania, and Rossland, B. C., as well as synthetic material supplied by Roberts[4] showed the superstructure lines of Hägg and Sucksdorf. (In a later abstract, Sidhu and Hicks[5] report a superlattice in magnetic pyrrhotite, having the same characteristics as Hägg and Sucksdorf's superlattice.)

More recently, a very thorough magnetic investigation has been made of artificial Fe-S preparations by Haraldsen,[6,7,8,9,10] whose study was accompanied by powder photograph identification of phases. As a result of his investigation, Haraldsen presented a rather complicated phase diagram.[10] For the purposes of the present paper, Haraldsen's findings can be summarized as follows: There are two different kinds of ferrous sulfide, α and β. The α form occurs from $Fe_{.50}S_{.50}$ to approximately $Fe_{.48}S_{.52}$ while β occurs beyond $Fe_{.48}S_{.52}$. These ranges correspond to paramagnetic and ferromagnetic ferrous sulfide. The boundary between these two does not, however, correspond with the boundary between superstructure and simple structure. This occurs at $Fe_{.49}S_{.51}$. In other

[3] Sidhu, Surian S., and Hicks, Victor, The space lattice and "superlattice" of pyrrhotite: *Phys. Rev.*, **52,** 667 (1937).

[4] Roberts, Howard S., Polymorphism of FeS-S solid solutions: *Jour. Am. Chem. Soc.*, **57,** 1034–1038 (1935).

[5] Sidhu, S. S., and Hicks, Victor, On the superstructure and magnetism of pyrrhotite (Abstract): *Phys. Rev.*, **53,** 207 (1938).

[6] Haraldsen, Haakon, Eine thermomagnetische Untersuchung der Umwandlungen im Troilit-Pyrrhotin-Gebiet des Eisen-Schwefel-Systems: *Zeit. anorg. allgem. Chem.*, **231,** 78–96 (1937).

[7] Haraldsen, Haakon, Die Umwandlungen des Eisen (II)-Sulfids: *Zeit. Elektrochem.*, **45,** 370–372 (1939).

[8] Haraldsen, Haakon, Omvandlingene i Troilit-Blandkrystallområdet: *Tidsskrift for Kjemi og Bergvesen*, Nr. **9** (1939).

[9] Haraldsen, Haakon, Über die Eisen (II)-Sulfidmischkristalle: *Zeit. anorg. allgem. Chem.*, **246,** 169–194 (1941).

[10] Haraldsen, Haakon, Über die Hochtemperaturumwandlungen der Eisen (II)-Sulfidmischkristalle: *Zeit. anorg. allgem. Chem.*, **246,** 195–226 (1941).

[11] Buerger, M. J., The photography of the reciprocal lattice: *ASXRED Monograph*, No. **1** (1942).

words, the α magnetic type has a superstructure near ideal composition FeS, but is without it from $Fe_{.49}S_{.51}$ to approximately $Fe_{.48}S_{.52}$. At this point the α magnetic type gives way to the β magnetic type, but without sharp structural change. Furthermore, the superstructure which oc'urs near ideal composition FeS vanishes on heating above a critical temperature of 138° C. This inversion is a first order one, characterized by a sudden change of about one per cent in the length of the c axis. Thus the superstructure is confined to a small, nearly rectangular, field on the
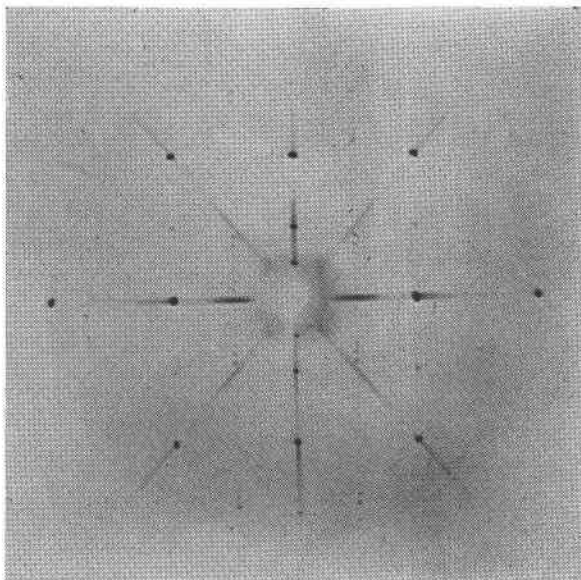

Fig. 1. Zero level, "*b*" axis precession photograph of pyrrhotite from Morro Velho, Brazil; MoKα radiation. (c^* vertical, a^* horizontal).

phase diagram whose upper temperature limit is about 138° C. and whose composition limit is $Fe_{.49}S_{.51}$.

NEW X-RAY STUDY OF PYRRHOTITE

The writer examined single crystals of pyrrhotite by the precession[11] method. This method offers a very rapid and convenient way of determining the cell dimensions and diffraction symmetries of single crystals, for the photographs are undistorted enlargements of the reciprocal lattice.

Pyrrhotite crystals are notoriously imperfect; they are usually curved and display exaggerated lineage[12] structure. Fragments for the precession study were detached from comparatively good crystals from Schnee-

[12] Buerger, M. J., The lineage structure of crystals: *Zeits. Krist.* (A), **89**, 195–220 (1934).

berg, Saxony, and Morro Velho, Brazil. Crystals from both of these localities are ferromagnetic. Their precession photographs are essentially identical. Both displayed the diffraction symmetry $6/mmm$ and both immediately revealed superstructure characteristics. The following cell dimensions were computed for the Schneeberg material:

$$a = 6.87\text{Å} \quad (= 2 \times 3.43\text{Å})$$
$$c = 22.7\text{Å} \quad (= 4 \times 5.68\text{Å}).$$

It will be noted that this cell has twice the a axis, four times the c axis, and sixteen times the volume of the nickel arsenide-like cell assigned to pyrrhotite by Alsén. However, this cell does not have the dimensions of the superstructure cell first found by Hägg and Sucksdorf[2] and confirmed by Haraldsen for the small region near ideal FeS. Furthermore, it occurs, not in the paramagnetic troilite region, but in the ferromagnetic pyrrhotite region.

The diffraction record contains no systematic extinctions of space group type, except $00l$ absent when l is odd. (There are other systematic absences but they are not of space group type.) The diffraction symbol is therefore apparently $6/mmm\ C6_3/---$. If this is an accurate representation of the space group symmetry, the space group is $C6_32$. It is possible that the missing $00l$ spectra are due to a fortuitous circumstance and that the diffraction symbol is actually $6/mmm\ C-/---$. If this is the case, the space group might be one of the following: $C\bar{6}2m$, $C\bar{6}m2$, $C6mm$, $C62$, $C6/mmm$.

Diffraction effects lacking extinctions due to glide planes, as those of pyrrhotite do, are open to the suspicion that they may arise from twinned aggregates.[13] It is, therefore, not unlikely that pyrrhotite belongs either to a lower hexagonal symmetry or to an orthorhombic or monoclinic symmetry.

Conclusions

As a consequence of the new cell data for pyrrhotite, it is evident that this crystal cannot have the nickel arsenide arrangement, at least in ideal form. It is possible, however, that it may have a structure related to the nickel-arsenide structure by some distortion of it to a superstructure. On the other hand, the metal atoms in the nickel arsenide structure do not have an environment similar to the environment of iron atoms in the only other ferromagnetic sulfide, cubanite.[14] For this reason it is desirable to withhold judgment on the nature of the structure of pyrrhotite until it is critically investigated.

[13] Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group: *Zeits. Krist.* **95(A)**, 99–102 (1936).

[14] Buerger, M. J., The structure of cubanite, $CuFe_2S_3$, and the coordination of ferromagnetic iron: *Jour. Am. Chem. Soc.*, **67**, 2056 (1945).