

## Short Communications

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**Two-dimensional superstructure in hydrothermally synthesized pyrrhotite.** By SHIGEO HORIUCHI\* and HIROAKI WADA, *National Institute for Researches in Inorganic Materials, Honkomagome 2-29-3, Bunkyo, Tokyo, Japan*

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Hydrothermally synthesized pyrrhotite, being a thin plate-like crystal, has a two-dimensional superstructure:  $a=2A$  and  $c=C$ , where  $A$  and  $C$  are the lattice parameters of the hexagonal subcell of the NiAs type structure.

4.5 ml of 0.6 mol.litre<sup>-1</sup> Mohr's salt solution was mixed with 4.5 ml of 1.2 mol.litre<sup>-1</sup> Na<sub>2</sub>S solution in a Pyrex tube (10 mm in diameter and 150 mm in length) at room temperature. Black particles, which gave no X-ray diffraction peaks (Bernier, 1964) but diffuse lines of mackinawite on an electron diffraction pattern, were formed in the solution. The tube was sealed and autoclaved in a silicon oil bath at 200°C. Dark-brown particles were formed in the solution. On heating for 5 hr, the black particles disappeared almost completely.

The dark-brown particles were examined with an electron microscope (Hitachi 11D, 100 kV). They consist of hexagonal plate-like crystals (Fig. 1). One dimension of the hexagonal plates is of the order of one  $\mu\text{m}$ . The plates are rigid, although they are very thin (apparently about 200 Å in thickness). Fig. 2 is an electron diffraction pattern from the crystal, the plate normal of which is almost parallel to the electron beam. It is identified as a reciprocal lattice plane perpendicular to the  $c^*$  axis of pyrrhotite. Extra reflexions occur at the midpoints between the usual spots for a NiAs-type subcell, showing the existence of a supercell with  $a=2A$ , where  $a$  and  $A$  are the lattice parameters of the supercell and of the subcell respectively.

In Fig. 1 a number of lines parallel to the edges of a hexagonal plate, *i.e.* to the  $a$  axes, can be observed. Their optical density varies from crystal to crystal and is closely related to the flexibility of the crystals; the lower the density, the more flexible the crystal and the more frequently diffraction contours due to bending are observed.

Detailed observations were carried out using a tilting apparatus. Diffraction patterns could be obtained from crystals whose plate normal was tilted by less than 70° to the incident beam, and the following results were obtained: (1)

an intensity distribution about each reciprocal lattice point is spread out along the  $c^*$  direction. The intensity decreases smoothly from the centre; (2) the half-peak width of each reflexion is in the range  $\frac{1}{2}$  to  $\frac{1}{10}$  of  $|g_{001}|$ , where  $g$  is a reciprocal lattice vector; (3) extra reflexions, suggesting the existence of a supercell in the  $c^*$  direction, are not observed. Fig. 3 is an example of a diffraction pattern from a tilted specimen. Short streaks are observed here.

All types of the superstructure so far reported for natural (Carpenter & Desborough, 1964) and synthetic (Morimoto & Nakazawa, 1968) pyrrhotites are three-dimensional. It is impossible, however, to attribute the elongation of each reflexion, described above, to a superstructure, because the intensity decreases smoothly from the centre. Observation (1) above owes its origin only to the fact that the crystal is very thin. From observation (2), the real thickness of the crystals is estimated to be of the order of 30 to 60 Å.

Based on these results, a hexagonal plate of a pyrrhotite is considered to have a cross-section as shown in Fig. 4; there are steps and kinks ( $d$  in Fig. 4), both of which are observed as lines parallel to edges of the hexagonal plate. The thicknesses  $a$ ,  $b$  and  $c$  are 30 to 60 Å. Because of the existence of kinks, however, the total thickness of a plate,  $e$ , apparently becomes about 200 Å. Steps and kinks make it rigid in spite of its small thickness. When the optical density is low, the crystal is flexible and bending is detected as a diffraction contour.

The existence of kinks can be confirmed as follows: the intensity distribution about each reciprocal lattice point would be spread out along the directions normal to edges of the hexagonal plate, *i.e.*, along the  $a^*$ -axis directions, if the thickness at kinks is small. This assumption is proved to be valid by a diffraction pattern reproduced in Fig. 5, showing streaks in these three directions. A half-peak width of the longest streak suggests a thickness of about 30 Å. These streaks disappear when the specimen is tilted slightly.

An attempt was made by the use of an electron micro-

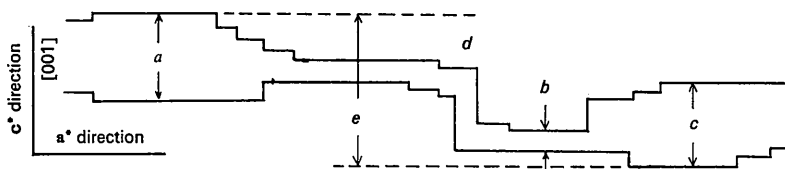


Fig. 4. Part of a cross-section of a pyrrhotite plate.

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Fig. 1. Pyrrhotite hydrothermally synthesized from  $\text{Na}_2\text{S}$  and Mohr's salt solution at  $200^\circ\text{C}$ . The small particles are mackinawite.

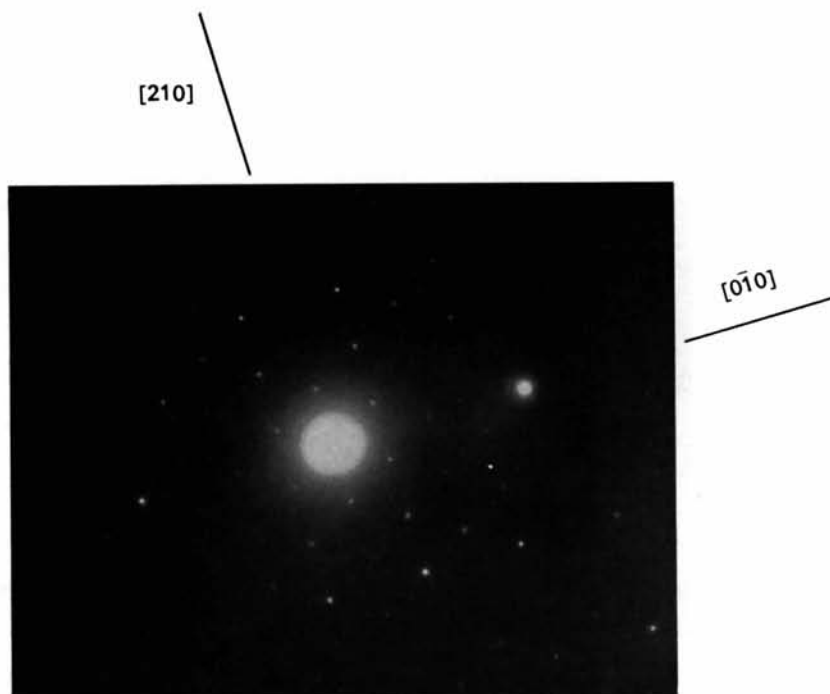


Fig. 2. Electron diffraction pattern, showing a reciprocal lattice plane perpendicular to the  $c^*$  axis.

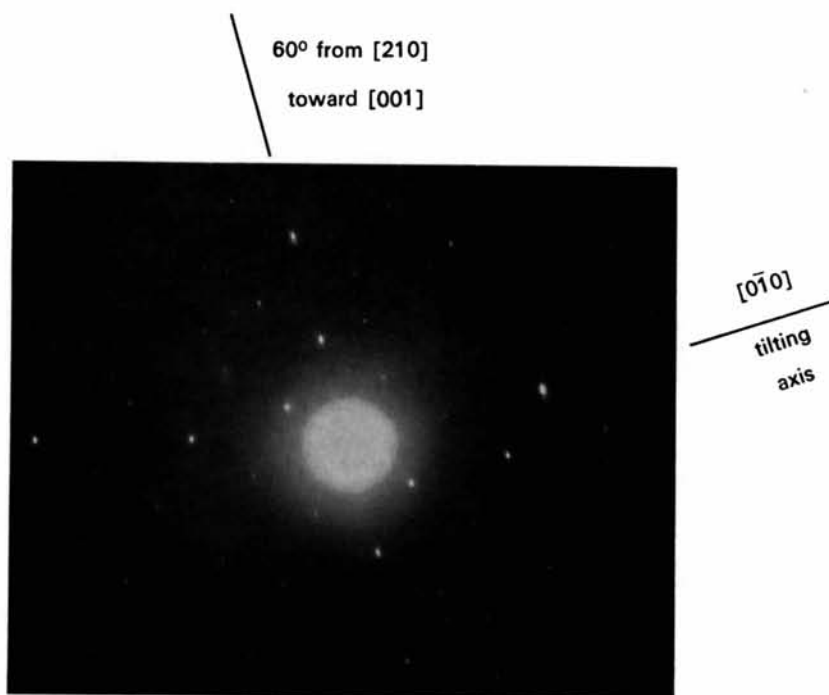


Fig. 3. Diffraction pattern from a crystal whose plate normal is tilted about  $[0\bar{1}0]$  axis by  $60^\circ$  to the incident beam. Short streaks appear as a result of the intersection of the reflexion sphere with a reciprocal lattice rod elongated along the  $c^*$  direction.

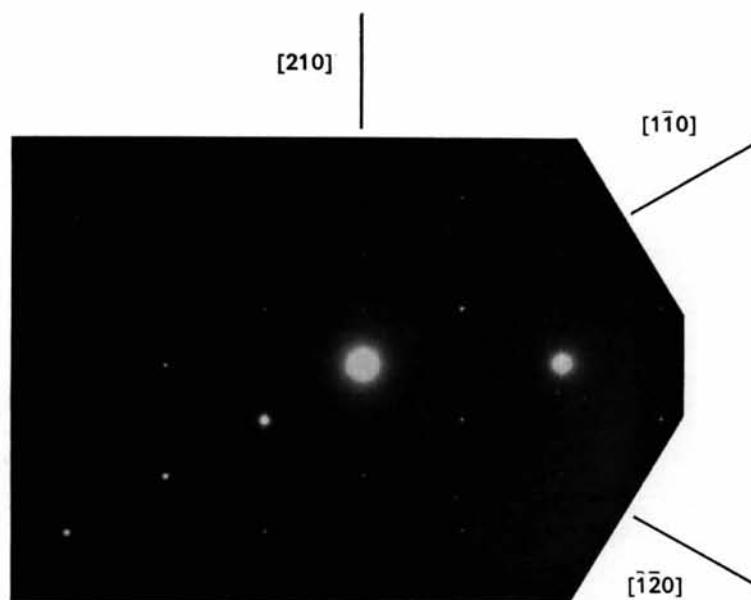


Fig. 5. Diffraction streaks along the directions normal to edges of the hexagonal plate, suggesting the existence of kinks as in Fig. 4.

scope with an accelerating voltage of 650 kV (Hitachi 650) to take a diffraction pattern with the incident beam parallel to a hexagonal plate. A pattern with streaks along the  $c^*$  direction about the 002 reciprocal lattice point could be obtained. The results obtained with the 100 kV electron microscope were confirmed.

It was also shown by the X-ray powder method that the pyrrhotite is dimensionally hexagonal with  $a = 2A = 6.90 \text{ \AA}$  and  $c = C = 5.76 \text{ \AA}$ .  $d(102)$  is  $2.072 \text{ \AA}$ , showing an iron composition of 47.75% (Arnold & Reichen, 1962).

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**A monoclinic modification of germanium disulfide,  $\text{GeS}_2$ .** By M. RUBENSTEIN and G. ROLAND, *Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235, U.S.A.*

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Crystals of the high-temperature modification of  $\text{GeS}_2$  were grown by solidification of  $\text{GeS}_2$  melts and by vapor transport. The crystals are monoclinic ( $P2_1/a$ ) with  $a = 11.46 \pm 0.05$ ,  $b = 16.1 \pm 0.5$ ,  $c = 6.69 \pm 0.08 \text{ \AA}$ ,  $\beta = 90^\circ 48' \pm 9'$ ,  $Z = 16$ . A possible structural relation between  $\text{GeS}_2$  and  $\text{CdI}_2$  is discussed.

### Introduction

In a recent paper dealing with phase relations in the Ge-S system, Viaene & Moh (1970) reported that germanium disulfide,  $\text{GeS}_2$  has both high-temperature and low-temperature structural modifications. We have grown crystals of the high-temperature modification ( $\alpha\text{-GeS}_2$ ) and find that it is monoclinic. Orthorhombic modifications of  $\text{GeS}_2$  have previously been reported by Zachariasen (1936) and Ch'ün-hua, Pashinkin & Novoselova (1963) and a tetragonal form with a three-dimensional network structure has been synthesized at high pressure (Prewitt & Young, 1965). The crystal growth and symmetry determination of monoclinic  $\text{GeS}_2$  are described in this note.

### Crystal synthesis

Crystals were prepared using both melt and sealed tube vapor transport methods. The sulfur used was purity 99.999+ wt.% (ASARCO) and the germanium was undoped material having a resistivity  $> 40 \Omega \cdot \text{cm}$  (Allegheny Electronics Chemical Co.). In preparation from the melt, powdered Ge and S ( $\text{GeS}_{1.1}$  composition) were reacted in a sealed, evacuated quartz tube by raising temperature slowly and stepwise to  $875^\circ \text{C}$  (above the congruent melting point). The Ge:S ratio was increased stepwise to the final composition,  $\text{GeS}_2$ , by repeatedly quenching the charge, adding more sulfur, and remelting. Several days heating of the final composition were necessary to obtain homogeneous  $\text{GeS}_2$  liquid. Plate-like crystals covered the surface of the slowly cooled melt. Crystals were also prepared by thermally transporting  $\text{GeS}_2$  through a temperature gradient of  $800^\circ \text{C}$  (source) to  $600^\circ \text{C}$  (deposit) in initially-evacuated, quartz tubes. The close comparison of the X-ray powder patterns of ground crystals with the data for  $\alpha\text{-GeS}_2$  reported by Viaene & Moh (1970), and the identity of the patterns with those we obtain from microscopically pure synthetic  $\text{GeS}_2$  powder, serves to demonstrate that the crystals are in fact crystals of  $\alpha\text{-GeS}_2$  and not of some other phase in the Ge-S system.

Both methods of synthesis yielded plate-like  $\text{GeS}_2$  crystals commonly two to three mm on an edge and occasionally as thick as 0.3 mm. Individual plates are colorless, but aggregates and powders have a distinctly yellowish tint. The plates are highly birefringent under polarized light. Twins were not observed. Crystals deformed readily by translation gliding in the plane of the plates and bending about any axis lying in that plane - features characteristic of a layer structure.

### Crystal symmetry

With the help of a petrographic microscope, we were able to isolate a few platelets of  $\alpha\text{-GeS}_2$  that could be studied using a Buerger precession camera. The area of the plates was larger than the X-ray beam and edge effects could be minimized by carefully positioning them such that the beam did not encounter obvious distortion. Zero, first, and second level precession photographs were taken using Mo  $K\alpha$  radiation with the beam normal and parallel the large face of the plates. The crystals are monoclinic (class  $2/m$ ) with the unique twofold axis lying in the plane of the prominent face, which is (100) in second setting. Because of the plate-like morphology,  $0kl$  reflections were broadened and  $h0l$  reflections were streaked so that the precession photographs were not well suited for measurements of the cell dimensions. Averaged measurements from several zero level photographs yielded the values  $a = 11.46 \pm 0.05$ ,  $b = 16.1 \pm 0.5$ ,  $c = 6.69 \pm 0.08 \text{ \AA}$ ,  $\beta = 90^\circ 48' \pm 9'$ . There are numerous structural absences in the reciprocal lattice but  $0k0$  absent when  $k$  is odd and  $h0l$  absent when  $h$  is odd were the only systematic absences. These uniquely define the space group as  $P2_1/a$ . The density measured using pycnometer is  $2.88 \text{ g.cm}^{-3}$  which gives  $Z = 16$  ( $D_{\text{calc}} = 2.94 \text{ g.cm}^{-3}$ ).

Ch'ün-hua *et al.* (1963) deduced from powder X-ray data that the structure of  $\text{GeS}_2$  is a highly deformed modification of the cadmium iodide ( $\text{CdI}_2$ ) eight-layer structure and related their orthorhombic cell to hexagonal  $\text{CdI}_2$  by  $a = \sqrt{3}a_{\text{CdI}_2}$ ,  $b = 3a_{\text{CdI}_2}$ , and  $c = 3c_{\text{CdI}_2}$ . In this context, an interesting feature of the monoclinic  $\text{GeS}_2$  lattice found in this