stronger in tarbuttite than in adamite, and lends support to the contention that it is also stronger in paradamite than in adamite.

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Refinement of 3C Pyrrhotite, Fe7S8

BY ASAO NAKANO, MASAYASU TOKONAMI AND NOBUO MORIMOTO

Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

Abstract. A metastable form of Fe_7S_8, trigonal, $P3_121$, $a = 6.8652$ (6), $c = 17.046$ (2) Å, $Z = 3$, $D_x = 4.59$ Mg m^{-3}. The crystal structure was refined to $R = 0.043$ for 1026 reflections. The apparent space group $P6_222$ is explained by the twin-related domains with trigonal symmetry. The supercell contains ordered vacancies in alternating Fe layers normal to the c direction. The Fe atom is octahedrally coordinated with a mean Fe–S distance of 2.445 Å.

Introduction. Fleet (1971) determined the structure of 3C Fe_7S_8 assuming the twin-related domains with space group $P3_1$. The structural study of synthetic 3C Fe_7S_8 was made by Nishiguchi (1977), also based on $P3_1$. Their structures are essentially the same as that of 3C Fe_7Se_8 reported by Okazaki & Hirakawa (1956) which has the symmetry $P3_121$. However, Fleet and Nishiguchi did not examine the possibility of $P3_121$. This study has been carried out to obtain the true symmetry and to determine precisely the actual displacements of atoms from the ideal structure.

The 3C Fe_7S_8 was prepared by the dry method and quenched from 973 K into ice water. A spherical crystal, 140 μm in diameter, was used for data collection on an automatic four-circle diffractometer, using the ω–2θ scan technique ($2\theta_{max} = 65°$) with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), monochromatized by pyrolytic graphite. The observed Laue symmetry ($6/mmm$) and the systematic absences ($00l$ with $l \neq 3n$) indicate an apparent space group $P6_222$ or $P6_422$. Because the ordered 3C type of Okazaki & Hirakawa's (1956) model must have a trigonal symmetry of $P3_121$ ($P3_221$) or $P3_1$ (or $P3_2$), the apparent $P6_222$ (and/or $P6_422$) symmetry of the specimen has been explained by many small domains related by 180° rotation about [001] and/or by reflection across (100) in the specimen.

Observed structure factors, $F_o(hkl)$, were calculated from the observed intensities, $I_o(hkl)$, by the following relation:

$$|F_o(hkl)|^2 = (Lp)^{-1} A E_s I_o(hkl) I_c(hkl)/[I_c(hkl) + I_c(khl)].$$

$F_o(hkl)$ were corrected for the usual Lorentz and polarization factors (Lp), absorption $[A, \mu(\text{Mo } K\alpha) = 12.8$ mm^{-1}, transmission factors between 0.27 and 0.33] and isotropic secondary extinction $[E_s, c = 0.59$ (1) × 10^{-5}; Zachariasen, 1963]. $I_c(hkl)$ and $I_c(khl)$ were calculated at each cycle of the least-squares refinements, and the computing program ORFLS (Busing, Martin & Levy, 1962) was modified for this purpose. The scattering factors for neutral

Table 1. *Positional parameters for 3C Fe₇S₈*

Standard deviations of the respective parameters are in parentheses.

	x	y	z
Fe(1)	0·0234 (4)	0	$\frac{1}{3}$
Fe(2)	0·0283 (4)	0	$\frac{1}{3}$
Fe(3)	0·4641 (3)	0	$\frac{5}{6}$
Fe(4)	0·0085 (5)	0·5268 (3)	0·82504 (5)
Fe(5)	0·0079 (5)	0·5125 (4)	0·33564 (4)
S(1)	0·1641 (4)	0·3380 (6)	0·75301 (7)
S(2)	0·1671 (4)	0·8419 (4)	0·74183 (7)
S(3)	0·6608 (6)	0·3321 (6)	0·75129 (12)
S(4)	0·6624 (6)	0·8352 (4)	0·75642 (7)

atoms were taken from *International Tables for X-ray Crystallography* (1974). The number of observed structure factors was 1026 including those with $F_o = 0$.

The initial atomic parameters for the $P3_1$ model were taken from Nishiguchi's (1977) final model. Those for the $P3_121$ model were obtained by inserting diad axes into Nishiguchi's final model of $P3_1$ with minimum shifts of atoms. The isotropic temperature factors were applied for atoms of both models except for the Fe atoms lying on the diad axis of the $P3_121$. After several least-squares cycles, the weighted R factors for the $P3_1$ and $P3_121$ models were reduced to 0·040 and 0·038, respectively. At this stage, the $P3_1$ model was discarded. Applying the anisotropic temperature factors to all atoms, the $P3_121$ model was refined and the weighted and unweighted R factors converged to 0·033 and 0·043, respectively. The final atomic parameters are given in Table 1.*

Discussion. The supercell of $3C$ Fe₇S₈ is composed of 12 NiAs-type subcells and the vacant sites for Fe atoms are distributed in every second layer as in other types of pyrrhotites (Morimoto, 1978) so that they are as far as possible from each other. All the Fe atoms are octahedrally coordinated with S atoms and the octahedra are not much distorted.*

The distributions of vacancies and Fe—Fe distances are illustrated schematically in Fig. 1. The structure has both filled and vacancy-containing rows of Fe atoms along the c axis. In the basal layers, all the Fe—Fe distances are longer than 3·0 Å, with the mean value of 3·437 Å, except for the Fe(2)—Fe(3) distance of 2·992 Å. Fe(3) is displaced by 0·25 Å from the ideal site towards Fe(2). All the Fe—Fe distances along the c axis are less than 3·0 Å. Fe(4) is displaced by 0·14 Å along

* Lists of structure factors, thermal parameters and interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34077 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
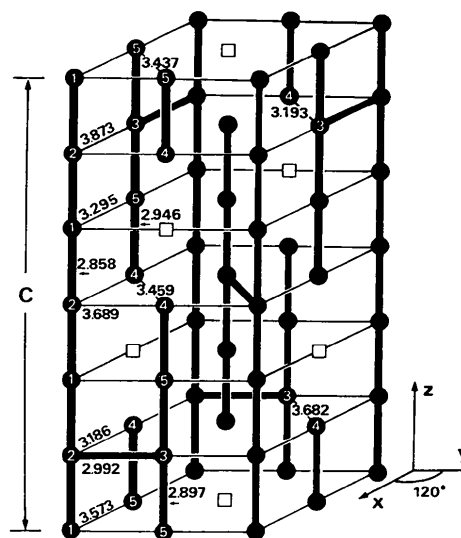

Fig. 1. Structure of $3C$ Fe₇S₈. Only Fe atoms are shown. Crystallographically different atoms are indicated by numbers in solid circles. The Fe—Fe distances are given by the numbers near the lines connecting the atoms. The thick lines represent the Fe—Fe distances less than 3·0 Å.
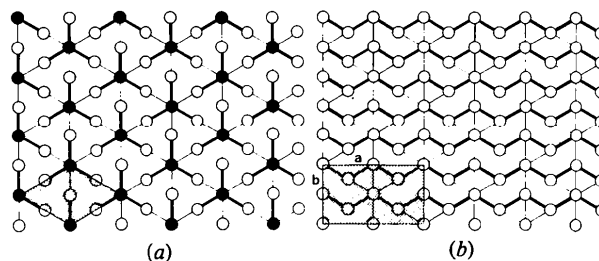

Fig. 2. Comparison of the Fe clusterings in the structures of (a) $3C$ Fe₇S₈ and (b) $4C$ Fe₇S₈ both projected on (001). Solid circles represent the filled rows and open circles the vacancy-containing ones. Thick lines represent the Fe—Fe couplings. Shaded areas represent the unit cells of $3C$ and $4C$ Fe₇S₈.

the c axis towards the nearest vacant site and by 0·18 Å in the basal layer towards Fe(2). The Fe atoms seem to move not only to reduce the vacancy space but also to form coupling between Fe atoms as in the $4C$ type (Tokonami, Nishiguchi & Morimoto, 1972). The triangular groups reported in the structure of troilite, FeS (Bertaut, 1956; Evans, 1970), are not observed in the $3C$ structure.

According to Goodenough (1962), the critical value below which the d electrons of Fe atoms must be treated as a collective system rather than as a localized model is about 3·0 Å in the structure of FeS. In this sense, both an infinite row and a five-Fe-atoms row terminated by vacancies are considered to be collective units. The infinite row is connected with the five-Fe-atoms row through the Fe(2)—Fe(3) couplings in the

basal layers resulting in an infinite columnar unit along the c axis. In the 4C type structure, the clustering is the complicated three-dimensional chain (Tokonami, Nishiguchi & Morimoto, 1972). Thus the 3C and 4C Fe$_7$S$_8$ structures differ not only in the arrangement of vacancies but also in the shape of the Fe clusterings (Fig. 2).

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Refinement of the Crystal Structure of Silicon Diphosphate, SiP$_2$O$_7$ AIV — A Phase with Six-Coordinated Silicon

BY K.-F. HESSE

Mineralogisch-Petrographisches Institut der Universität Kiel, 2300 Kiel, Federal Republic of Germany

Abstract. Synthetic SiP$_2$O$_7$ AIV, monoclinic, $P2_1/n$, $a_o = 4\cdot713$ (1), $b_o = 11\cdot987$ (2), $c_o = 7\cdot628$ (2) Å, $\beta = 91\cdot20$ (2)°, $Z = 4$; R (unweighted) $= 0\cdot050$, R (weighted) $= 0\cdot035$. [PO$_4$] tetrahedra are linked in pairs to form [P$_2$O$_7$] groups. Si is octahedrally coordinated, with a mean Si—O distance of $1\cdot766$ Å.

Introduction. SiP$_2$O$_7$ was prepared by Liebau, Bissert & Köppen (1968). A SiO$_2$.mP$_2$O$_5$.H$_2$O mixture was held for 64 h at 1223 K in a silica-glass ampoule.

The structure was solved by Liebau & Hesse (1971) by means of multiple-film methods using $hk0$ and $0kl$ reflections only; R ($hk0$) was 8·7% and R ($0kl$) was 9·9%. The aim of the present work was to refine the structure from general hkl reflections.

A crystal measuring $0\cdot1 \times 0\cdot06 \times 0\cdot03$ mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å) and a θ–2θ scan ($\theta_{max} = 30°$). The intensities of 2804 crystallographically independent reflections were measured; 608 of these had $|F_o| > 3\sigma(|F_o|)$ and were used in the subsequent refinement. The standard deviation, $\sigma(F_o)$, was estimated from the formalism presented by Stout & Jensen (1968).

Lorentz and polarization corrections were applied, but no correction was made for absorption [μ(Mo $K\alpha$) $= 1\cdot251$ mm^{-1}]. The structure as determined by Liebau & Hesse (1971) was proven using Fourier techniques and was refined by full-matrix least-squares analysis with the program *ORFLS* of Busing, Martin & Levy (1962), starting with the atomic coordinates given by Liebau & Hesse (1971). (The x coordinates of their Table 1 are incorrect and have to be replaced by $0\cdot5 - x$.) Isotropic refinement of the crystal structure

Table 1. *Positional* ($\times 10^4$) *and thermal parameters with standard deviations*

	x	y	z	B (Å^2)
Si	2195 (4)	8505 (2)	3474 (3)	0·48 (3)
P(1)	7991 (4)	5182 (2)	1962 (2)	0·35 (3)
P(2)	7203 (4)	6970 (2)	4483 (3)	0·34 (3)
O(1)	7073 (10)	5725 (4)	3743 (6)	0·44 (8)
O(2)	805 (10)	4645 (4)	2364 (6)	0·60 (9)
O(3)	5788 (10)	4350 (4)	1412 (6)	0·45 (9)
O(4)	8249 (10)	6109 (4)	651 (6)	0·57 (8)
O(5)	6224 (9)	6873 (4)	6315 (6)	0·34 (8)
O(6)	215 (10)	7364 (4)	4303 (6)	0·53 (9)
O(7)	5153 (9)	7624 (4)	3379 (6)	0·51 (9)