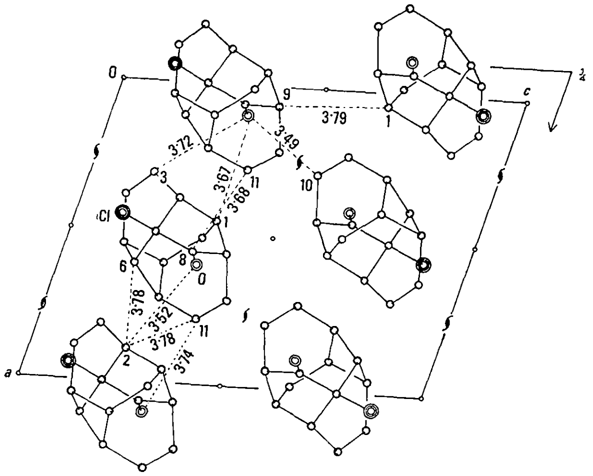

Fig. 7. Projection of the crystal structure along the *b* axis. Intermolecular short distances less than 3·8 Å are shown by broken lines.

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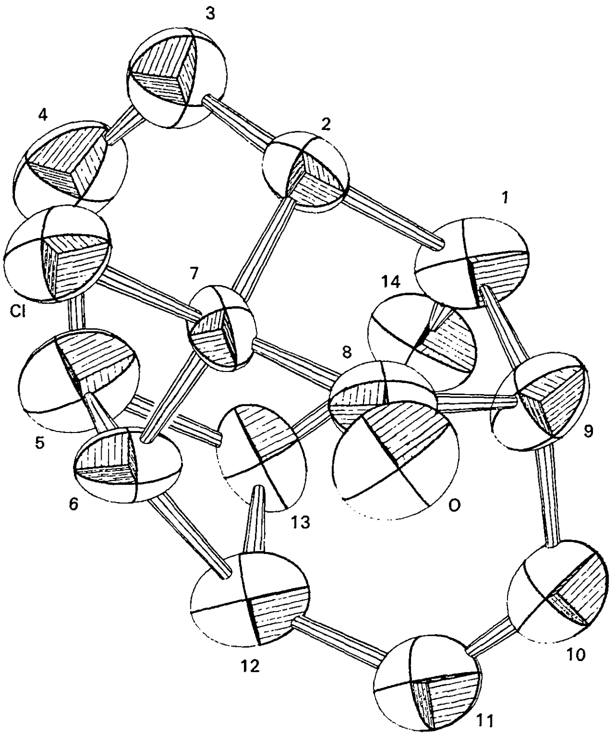

Fig. 8. Projection of the molecular structure along the *b* axis showing the ellipsoids of thermal vibration. The centres of atoms are included in the ellipsoids with 50% probability.

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Crystallography of Pyrrhotite

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(*Received* 8 *May* 1968)

Pyrrhotite crystals (Fe_7S_8) from the sulphide ore of the Mosaboni mine, India, are found to have a monoclinic supercell, $a_0=11·90$, $b_0=6·87$, $c_0=22·88$ Å, $\beta=90°30'$, $Z=8$ with density 4·60 g.cm^{-3}, and the space group $C2/c$ (or Cc). The hexagonal supercell, $a_0=6·88$, $c_0=22·90$ Å, $Z=4$ with density 4·58 g.cm^{-3}, is also observed in pyrrhotite crystals, and the space group $P6/mcc$ (or $P6cc$) has been assigned to the hexagonal phase.

Buerger (1947) proposed a hexagonal superstructure for pyrrhotite with $a=6·87$, $c=22·7$ Å; this supercell has 16 times the volume of the Ni–As-type cell. Moreover, he suggested that the observed diffraction effect in precession photographs is probably due to twinned aggregates and that the true symmetry is perhaps monoclinic or orthorhombic. Bertaut (1953) postulated that the pyrrhotite twin is composed of two monoclinic crystals, related by a 60° rotation about the pseudohexagonal c axis and he proposed a unit cell with the parameters 11·9, 6·865, 22·72 Å, $\beta=90·45°$ (Byström, 1945) and the space group $F2/d$. Wuensch (1963) observed that the pyrrhotite lattice is at least dimensionally monoclinic (with $\beta=91·79°$) and is twinned by a

2-fold rotation about [110], and that the c dimension and lattice type are uncertain because of the presence of certain non-space group extinctions in the precession photographs.

Pyrrhotite crystals were available from the sulphide ores of Mosaboni mines, Singhbum, India (Mukherjee, 1968), and a crystal fragment almost plate-like with striated faces (off an ore sample from level-19) was detached from the subparallel hexagonal platelets for single-crystal study. Rotation and Weissenberg photographs and the 15° oscillation photographs (Fe $K\alpha$) about [010] and [001] revealed pseudohexagonal symmetry, and the parameters of the monoclinic supercell were deduced as: $a=11{\cdot}90$, $b=6{\cdot}87$, $c=22{\cdot}88\pm0{\cdot}02$ Å, and $\beta=90°30'$ which was computed from the high-angle reflexions. The conditions limiting possible reflexions are: hkl with $h+k=2n$, $k+l=2n$, $l+h=2n$; $h0l$ with $l=2n$, $h=2n$, $h00$ with $h=2n$; $0k0$ with $k=2n$; $00l$ with $l=2n$; and this indicates the space group as one of $C2/c$ (C_{2h}^6), $Cc(C_s^4)$. The presence of a number of weak reflexions in the pattern at the position of the non-space-group extinctions could be explained as

Table 1. *Powder data of monoclinic and hexagonal pyrrhotites*

Monoclinic pyrrhotite indexed with $a=11{\cdot}90$, $b=6{\cdot}87$, $c=22{\cdot}88$ Å, $\beta=90°30'$					Hexagonal pyrrhotite indexed with $a=6{\cdot}88$, $c=22{\cdot}90$ Å				
I/I_1	d (Å)	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$	I/I_1	d (Å)	$\sin^2\theta_{obs}$	$hkil$	$\sin^2\theta_{calc}$
15	5·93	0·0266	200	0·0265	10	5·94	0·0265	1 0 $\bar{1}$ 0	0·0264
30	5·73	0·0286	004	0·0287	20	5·74	0·0285	0 0 $\bar{0}$ 4	0·0286
15	5·26	0·0338	202	0·0339	7	5·27	0·0337	1 0 $\bar{1}$ 2	0·0336
7	4·11	0·0555	204	0·0556					
15	3·43	0·0796	020	0·0794	7	3·44	0·0793	1 1 $\bar{2}$ 0	0·0792
7	3·20	0·0915	206	0·0916					
40	2·975	0·1059	400 220	0·1059 0·1059	40	2·98	0·1058	2 0 $\bar{2}$ 0	0·1056
15	2·865	0·1141	222 402 008	0·1133 0·1136 0·1146	10	2·87	0·1136	2 0 $\bar{2}$ 2 0 0 $\bar{0}$ 8	0·1127 0·1143
60	2·634	0·1350	224 404	0·1350 0·1355	50	2·64	0·1343	2 0 $\bar{2}$ 4	0·1342
7	2·562	0·1428	208 026	0·1420 0·1437					
7	2·340	0·1712	226 406	0·1710 0·1717					
10	2·250	0·1851	420	0·1852	10	2·255	0·1843	2 1 $\bar{3}$ 0	0·1847
10	2·202	0·1932	422 028	0·1930 0·1939	7	2·207	0·1925	2 1 $\bar{3}$ 2 1 1 $\bar{2}$ 8	0·1919 0·1934
100	2·057	0·2216	228 408	0·2214 0·2223	100	2·064	0·2200	2 0 $\bar{2}$ 8	0·2199
7	1·982	0·2385	600	0·2382	7	1·987	0·2373	3 0 $\bar{3}$ 0	0·2375
10	1·905	0·2582	0.0.12 0.2.10	0·2578 0·2584	7	1·909	0·2572	0 0 $\bar{0}$ 12 1 1 $\bar{2}$ 10	0·2572 0·2577
10	1·763	0·3016	428	0·3017	7	1·769	0·2993	2 1 $\bar{3}$ 8	0·2991
50	1·717	0·3178	620 040	0·3176 0·3176	40	1·720	0·3167	2 2 $\bar{4}$ 0	0·3167
15	1·633	0·3513	0.0.14 242	0·3510 0·3514	10	1·636	0·3500	0 0 $\bar{0}$ 14 3 1 $\bar{4}$ 2	0·3500 0·3502
7	1·600	0·3658	2.2.12 4.0.12 4.2.10	0·3652 0·3665 0·3666	7	1·606	0·3632	2 0 $\bar{2}$ 12 2 1 $\bar{3}$ 10	0·3627 0·3633
15	1·487	0·4235	800 440	0·4235 0·4235	10	1·490	0·4220	4 0 $\bar{4}$ 0	0·4222
10	1·474	0·4312	0.2.14 442 802 048	0·4303 0·4310 0·4317 0·4321	7	1·476	0·4301	1 1 $\bar{2}$ 14 4 0 $\bar{4}$ 2 2 2 $\bar{4}$ 8	0·4292 0·4294 0·4309
20	1·437	0·4536	444 4.0.$\overline{14}$ 804	0·4530 0·4534 0·4539	10	1·442	0·4507	4 0 $\bar{4}$ 4	0·4508
15	1·430	0·4582	0.0.16 2.2.14	0·4583 0·4584	20	1·433	0·4564	2 0 $\bar{2}$ 14 0 0 $\bar{0}$ 16 3 1 $\bar{4}$ 8	0·4556 0·4572 0·4573
20	1·427	0·4601	248 4.0.14	0·4597 0·4603					
20	1·325	0·5336	4.2.$\overline{14}$ 824 80$\bar{8}$	0·5328 0·5334 0·5343					
15	1·321	0·5369	44$\bar{8}$ 0.2.16	0·5362 0·5376	20	1·321	0·5366	1 1 $\bar{2}$ 16 4 0 $\bar{4}$ 8	0·5364 0·5365

Table 1 (*cont.*)

Monoclinic pyrrhotite indexed with $a=11{\cdot}90$, $b=6{\cdot}87$, $c=22{\cdot}88$ Å, $\beta=90°30'$					Hexagonal pyrrhotite indexed with $a=6{\cdot}88$, $c=22{\cdot}90$ Å				
I/I_1	d (Å)	$\sin^2\theta_{\text{obs}}$	*hkl*	$\sin^2\theta_{\text{calc}}$	I/I_1	d (Å)	$\sin^2\theta_{\text{obs}}$	*hkil*	$\sin^2\theta_{\text{calc}}$
25	1·316	0·5408	4.2.14 448 808	0·5397 0·5400 0·5418					
7	1·292	0·5614	$4.0.\overline{16}$ $2.2.\overline{16}$ $64\bar{2}$	0·5606 0·5622 0·5622					
15	1·288	0·5648	642 $82\bar{6}$ 2.2.16	0·5637 0·5645 0·5659	10	1·291	0·5621	$4\,1\,\bar{5}\,2$ $2\,0\,\bar{2}\,16$	0·5614 0·5628
10	1·283	0·5691	4.0.16 826	0·5682 0·5702					
10	1·177	0·6764	$8.0.\overline{12}$ $8.2.\overline{10}$ $4.4.\overline{12}$	0·6756 0·6770 0·6776					
20	1·171	0·6829	$4.0.\overline{18}$ $2.2.\overline{18}$ 4.4.12	0·6818 0·6836 0·6839	10	1·174	0·6795	$4\,0\,\bar{4}\,12$	0·6794
20	1·168	0·6873	8.2.10 8.0.12 $10.0.\bar{4}$ 2.2.18	0·6868 0·6872 0·6879 0·6880					
15	1·164	0·6915	4.0.18 10.0.4	0·6905 0·6925	7	1·167	0·6881	$5\,0\,\bar{5}\,4$	0·6883
15	1·124	0·7418	260 840 10.2.0 064	0·7410 0·7411 0·7411 0·7429	7	1·125	0·7400	$4\,2\,\bar{6}\,0$ $3\,3\,\bar{6}\,4$	0·7390 0·7411
15	1·105	0·7674	$10.2.\bar{4}$ $8.0.\overline{14}$ $84\bar{4}$	0·7674 0·7678 0·7678					
25	1·102	0·7716	$4.4.\overline{14}$ 844 $10.0.\bar{8}$ 10.2.4	0·7711 0·7715 0·7716 0·7720	15	1·105	0·7674	$4\,2\,\bar{6}\,4$	0·7675
20	1·098	0·7769	0.4.16 4.4.14	0·7759 0·7776	10	1·101	0·7731	$4\,0\,\bar{4}\,14$ $2\,2\,\bar{4}\,16$ $5\,0\,\bar{5}\,8$	0·7723 0·7739 0·7740
20	1·095	0·7813	10.0.8 8.0.14	0·7811 0·7812					
7	1·069	0·8201	460	0·8202					
10	1·063	0·8287	462 068	0·8281 0·8289	7	1·065	0·8260	$5\,1\,\bar{6}\,2$ $3\,3\,\bar{6}\,8$	0·8253 0·8268
10	1·049	0·8511	464 $10.2.\bar{8}$ $84\bar{8}$	0·8500 0·8509 0·8517					
20	1·044	0·8597	848 10.2.8	0·8594 0·8604	10	1·048	0·8531	$4\,2\,\bar{6}\,8$	0·8532
20	0·9917	0·9528	660 12.0.0 $8.2.\overline{16}$	0·9525 0·9528 0·9532	7	0·9930	0·9502	$6\,0\,\bar{6}\,0$	0·9501
7	0·9838	0·9680	$4.0.\overline{22}$ 8.2.16	0·9673 0·9687					
15	0·9783	0·9790	4.0.22 $12.0.\bar{4}$ 10.4.0 $66\bar{4}$	0·9782 0·9788 0·9792 0·9798	7	0·9785	0·9787	$6\,0\,\bar{6}\,4$	0·9786
15	0·9760	0·9836	664 12.0.4	0·9830 0·9842					

being due to the presence of a hexagonal phase (see below) being associated as a minor intergrowth with the monoclinic phase in the crystal fragment. The value of $d(408, 228)$, corresponding to 2·057 Å in the powder patterns of the same crystals (Table 1), indicates that the composition of the crystal should be Fe_7S_8 (stoichiometric, having about 46·67 atomic per cent iron; Desborough & Carpenter, 1965). The powder patterns, taken with Fe $K\alpha$ radiation in a Debye–Scherrer camera of 114·6 mm diameter, were indexed using the crystal elements obtained from single-crystal photographs. The density for the same crystals was determined by the

Berman density balance, using bromoform, as 4·60 ± 0·01 g.cm^{-3}. With the above values of axial lengths and the angle β ($V=1871$ Å^3), the molecular weight ($M=648$ for Fe_7S_8) and the observed density, the number of formula units per unit cell is calculated to be 8 ($Z=7{\cdot}998$), and the calculated density is 4·602 g.cm^{-3}.

The rotation and Weissenberg photographs and the 15° oscillation photographs about [010] and [001] of a crystal fragment, detached from hexagonal platelets (off an ore sample from level-16), showed superstructure characteristics having a hexagonal supercell $a=6{\cdot}88$, $c=22{\cdot}90\pm0{\cdot}02$ Å; the high angle reflexions did not show any separation characteristic of the monoclinic system. The conditions limiting possible reflexions are: $hh\overline{2h}l$ only with $l=2n$; $h\bar{h}0l$ only with $l=2n$; and $hkil$ with no conditions except $l=2n$; indicating the space group as one of $P6/mcc$ (D_{6h}^2), $P6cc$ (C_{6v}^2). The presence of a number of weak reflexions in the patterns could be explained as being due to the monoclinic phase (see above) which was a minor intergrowth with the hexagonal phase in the crystal fragment. The density for the same crystals was determined as 4·58 ± 0·01 g.cm^{-3} and the number of formula units per unit cell was calculated to be 4 ($Z=3{\cdot}998$) from the above values of axial lengths ($V=939$ Å^3), the observed density and the molecular weight [$M=648$ for Fe_7S_8 although the composition might have a slight excess of iron (Desborough & Carpenter, 1965)]; the calculated density is 4·582 g.cm^{-3}.

The monoclinic and hexagonal pyrrhotites (superstructure types) were found to be associated mainly with chalcopyrite and pyrite in the ores of different levels (Mukherjee, 1968); the monoclinic phase was predominant in the pyrrhotite-rich ores containing pyrite as a minor constituent, and the hexagonal phase was predominant in the pyrrhotite-poor ores containing chalcopyrite and pyrite as major constituents.

The author sincerely thanks Mr G. C. Chaterji, Director General of the Geological Survey of India for his keen interest in the work, and Professor B.S.Basak of the Presidency College, Calcutta, for valuable discussions.

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Acta Cryst. (1969). B**25**, 676

The Structure of Copper Ammonium Sulfate Hexahydrate from Neutron-Diffraction Data*

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(*Received* 8 *April* 1968)

The structure parameters of the Tutton salt $Cu(NH_4)_2(SO_4)_2.6H_2O$ have been refined by the method of least squares from three-dimensional neutron-diffraction data. The e.s.d.'s of the atomic coordinates are from 0·0010 to 0·0023 Å for the N, S, O atoms and 0·0025 to 0·0053 Å for the H atoms. The value derived for f_S, the coherent scattering amplitude of sulfur, is 0·283(4), significantly different from the value 0·31 in Bacon's table; values derived for f_O and f_N are also slightly different from the tabulated values. Although the heavy-atom coordinates differ significantly in a purely statistical sense from those of the three-dimensional X-ray analysis of Montgomery & Lingafelter, the two descriptions of the heavy-atom structure agree quite well from the point of view of molecular geometry. The hydrogen-bonding pattern from the X-ray study is confirmed.

Introduction

In the last half decade there has been much interest shown, in a number of laboratories, in the crystal structures of Tutton's salts, a well-known series of isomorphous double sulfates with the general formula $XY_2(SO_4)_2.6H_2O$. In an accurate redetermination by X-ray analysis of the structure of $Mg(NH_4)_2(SO_4)_2.6H_2O$, Margulis & Templeton (1962) were able to locate the hydrogen atoms approximately and to deduce the pattern of hydrogen bonding, after first revising the coordinates of the oxygen atoms from incorrect values reported from the original X-ray determination (Hofmann, 1931). At about the same time and independently, Chidambaram & Rao (1963) con-

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* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

† Guest scientist 1964–65, sponsored by the United States Agency for International Development, from the Bhabha Atomic Research Centre, Trombay, Bombay-74, India.