

## Triclinic Iron Trimolybdenum Tetrasulphide, Containing Fe Pairs

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**Abstract.**  $\text{FeMo}_3\text{S}_4$  is a triclinic distorted variant of the rhombohedral  $M\text{Mo}_3\text{S}_4$  compounds ( $M = \text{metal}$ ); space group  $P\bar{1}$ ,  $a = 6.502$  (2),  $b = 6.466$  (2),  $c = 6.481$  (2) Å,  $\alpha = 95.94$  (3),  $\beta = 97.37$  (3),  $\gamma = 91.33$  (3)°,  $Z = 2$ ,  $D_x = 5.83$  Mg m<sup>-3</sup>;  $R = 0.06$  for 1619 reflexions with  $|F_o| > 3\sigma(F_o)$ . The configuration of the Fe pairs [Fe–Fe = 2.513 (4) Å] is different from that of the Cu pairs in the low-temperature modification of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$ . The compound transforms into a rhombohedral high-temperature modification above room temperature.

**Introduction.** The influence of the cations  $M$  on the structure and the physical properties of the  $M\text{Mo}_6X_8$  ( $X = \text{S, Se, Te}$ ) cluster compounds has been examined extensively during the past few years (for reviews see Fischer, 1978; Yvon, 1979). The majority of these compounds have trigonal symmetry (space group  $R\bar{3}$ ), the rhombohedral angle depending essentially on the size and the thermal-vibrational amplitudes of the  $M$  atoms (Yvon, 1978). However, there also exist triclinic  $M\text{Mo}_6X_8$  compounds such as  $\text{Ni}_{0.33}\text{Mo}_3\text{Se}_4$  (Bars, Guillevic & Grandjean, 1973),  $M\text{Mo}_3\text{S}_4$  ( $M = \text{Fe, Mg, Zn, Mn and Cd}$ ) (Chevrel, 1974) and the low-temperature modification of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$  (Baillif, Yvon, Flükiger & Müller, 1979; Yvon, Baillif & Flükiger, 1979). The distribution of the  $M$  atoms in most of these compounds is not yet known. In the  $\text{Fe}_x\text{Mo}_3\text{S}_4$  system, for instance, the distribution of the Fe atoms has only been measured for the Fe-deficient rhombohedral compound  $\text{Fe}_{0.66}\text{Mo}_3\text{S}_4$  (Guillevic, Bars & Grandjean, 1976). No structural study, however, has been reported on the triclinic compound at the Fe-rich phase limit. In view of recent Mössbauer spectroscopy measurements in this system (Rangel, Bolz & Pobell, 1979; Stafford, Barnett, Kimball & Fradin, 1979) a single-crystal analysis of this compound was therefore of interest.

A sample of composition  $\text{FeMo}_3\text{S}_4$  was prepared from the elements by reaction in a quartz tube at 1373 K. A Guinier photograph taken at room temperature

confirmed that the structure was triclinic, the lattice parameters being close to those of the trigonal phase ( $\text{Fe}_{0.66}\text{Mo}_3\text{S}_4$ :  $a = 6.497$  Å,  $\alpha = 94.78^\circ$ ; Guillevic, Bars & Grandjean, 1976). A single crystal of irregular shape (mean diameter 80  $\mu\text{m}$ ) was isolated from the crushed sample and analysed on an automatic four-circle diffractometer. X-ray intensities for 1896 reflexions were recorded with  $\theta$ – $2\theta$  scans out to a limit of  $\sin \theta/\lambda = 0.89$  Å<sup>-1</sup> ( $\lambda = 0.5608$  Å) and corrected for absorption by approximating the crystal to a sphere [ $\mu(\text{Ag K}\alpha) = 24.3$  mm<sup>-1</sup>]. The structure was refined with *CRYLSQ* (XRAY system, 1976), with as starting parameters the atomic coordinates and the anisotropic temperature factors of the triclinic low-temperature modification of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$  (Yvon, Baillif & Flükiger, 1979). The final  $R$  for 1619 reflexions with  $|F_o| > 3\sigma(F_o)$  was 0.06.\*

**Discussion.** Comparing the atomic coordinates and the interatomic distances of triclinic  $\text{FeMo}_3\text{S}_4$  with those of rhombohedral  $\text{Fe}_{0.66}\text{Mo}_3\text{S}_4$ , one sees that the former compound is a distorted variant of the latter (Tables 1 and 2). Their main structural difference concerns the distribution of the Fe atoms. In the rhombohedral Fe-deficient compound they occupy two different lattice sites, each representing six symmetry-equivalent point positions. The average occupancies of these sites are 0.166 and 0.05 respectively (Guillevic, Bars & Grandjean, 1976). In the triclinic Fe-rich compound they occupy only one lattice site, which represents two symmetry-equivalent point positions. As shown by a refinement of the occupancy factors these sites are fully occupied. They are related by an inversion centre, the distance across the centre being 2.513 Å. Thus the Fe

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35006 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms form pairs which are centred on the corners of the triclinic cell.

The centre of the cell is occupied by the octahedral Mo cluster. As can be seen from the list of bond lengths given in Table 2, the Mo—Mo distances both within and between these clusters are close to those found in the rhombohedral compound ( $\text{Fe}_{0.66}\text{Mo}_3\text{S}_4$ :  $d_{\text{Mo—Mo}}^{\text{intra}} = 2.693$  and  $2.732$  Å;  $d_{\text{Mo—Mo}}^{\text{inter}} = 3.221$  Å). However, in contrast to the latter compound in which the Mo cluster forms an elongated octahedron of symmetry  $\bar{3}$ , the Mo octahedron in the present compound is triclinic distorted. Thus the structural relationship between these two compounds is analogous to that between the high- and low-temperature modifications of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$ . In the latter compound there occurs a structural phase transformation slightly below room temperature, which is due to an order—disorder transition of the Cu atoms. In the rhombohedral high-temperature modification, the Cu atoms are disordered, whereas in the triclinic low-temperature modification they are ordered and form pairs (Yvon, Baillif & Flükiger, 1979). Interestingly, the orientation of these pairs with respect to the cell axes and their chalcogen-atom environment is different from that of

the Fe-atom pairs found in the present compound. As can be seen from Fig. 1, the Cu atoms in  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$  are coordinated by four S atoms, forming an approximately tetrahedral configuration, whereas the Fe atoms in  $\text{FeMo}_3\text{S}_4$  are coordinated by five S atoms forming an approximately square-pyramidal configuration.

The present compound represents another example of the very complex structural behaviour of the  $M$  atoms in the  $M\text{Mo}_3\text{S}_4$  compounds. Its similarity to the triclinic low-temperature modification of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$  suggests that the phase diagram of the  $\text{Fe}_x\text{Mo}_3\text{S}_4$  system ( $0 \leq x \leq 1$ ) has common features with that of the  $\text{Cu}_x\text{Mo}_3\text{S}_4$  system ( $0 \leq x \leq 2$ ) (Flükiger *et al.*, 1977; Tovar, DeLong, Johnston & Maple, 1979; Flükiger, Baillif, Müller & Yvon, 1980). In particular, the peritectoid decomposition of the rhombohedral high-temperature modification as found in  $\text{Cu}_x\text{Mo}_3\text{S}_4$  is probably shifted to higher temperatures in  $\text{Fe}_x\text{Mo}_3\text{S}_4$ . In fact, a preliminary X-ray powder diffraction study at 473 K showed that the triclinic  $\text{FeMo}_3\text{S}_4$  phase transforms into the rhombohedral modification above room temperature, thus suggesting the occurrence of an order—disorder transition of the Fe atoms similar to that of the Cu atoms in  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$ .

Table 1. Positional ( $\times 10^4$ ) and thermal ( $\text{Å}^2 \times 10^4$ ) parameters for the triclinic modification of  $\text{FeMo}_3\text{S}_4$  (space group  $P\bar{1}$ )

The e.s.d.'s of the last significant digits are given in parentheses. The equivalent values of the Debye—Waller factor,  $U_{\text{eq}}$ , have been calculated from the anisotropic thermal parameters in the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klc^*b^*)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Mo(1)	2241 (2)	4155 (1)	5373 (1)	49 (3)
Mo(2)	4019 (2)	5429 (1)	2200 (1)	48 (3)
Mo(3)	5491 (2)	2225 (1)	4087 (1)	48 (3)
S(1)	3885 (5)	1430 (4)	7227 (4)	71 (9)
S(2)	1191 (6)	7330 (5)	3634 (4)	83 (9)
S(3)	7280 (6)	3609 (4)	1381 (4)	81 (9)
S(4)	2137 (6)	2058 (5)	1877 (4)	81 (9)
Fe	951 (5)	-3 (4)	8431 (4)	265 (9)

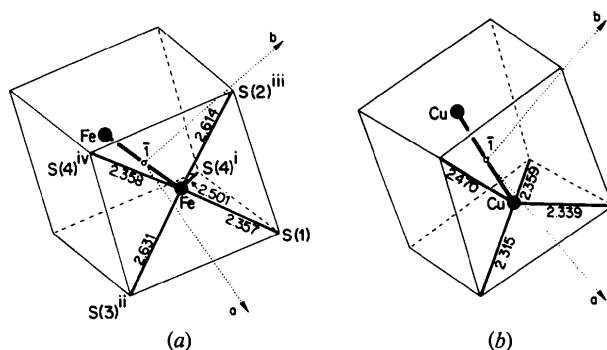


Fig. 1. The S-atom environment of (a) the Fe atoms in  $\text{FeMo}_3\text{S}_4$  and (b) the Cu atoms in the low-temperature phase of  $\text{Cu}_{0.9}\text{Mo}_3\text{S}_4$ . Errors in distances are 0.004 Å. Symmetry code: (i)  $x, y, 1 + z$ ; (ii)  $1 - x, -y, 1 - z$ ; (iii)  $-x, 1 - y, 1 - z$ ; (iv)  $-x, -y, 1 - z$ .

Table 2. Mo—Mo and Mo—S distances (Å) and their e.s.d.'s for  $\text{FeMo}_3\text{S}_4$

The Mo—Mo distances marked by an asterisk are those between the  $\text{Mo}_6$  clusters.

Mo(1)—Mo(1)	3.133 (2)*	Mo(2)—Mo(1)	2.676 (1)	Mo(3)—Mo(1)	2.660 (2)
—Mo(2)	2.676 (1)		2.713 (2)		2.705 (1)
		—Mo(2)	3.272 (2)*	—Mo(2)	2.650 (1)
—Mo(3)	2.660 (2)	—Mo(3)	2.650 (1)	—Mo(3)	2.687 (1)
			2.687 (1)		3.302 (1)*
—S(1)	2.426 (3)	—S(1)	2.389 (3)	—S(1)	2.489 (3)
—S(2)	2.509 (3)	—S(2)	2.462 (4)	—S(2)	2.497 (3)
		—S(3)	2.511 (3)	—S(2)	2.446 (4)
—S(3)	2.407 (3)		2.537 (4)	—S(3)	2.455 (3)
—S(4)	2.510 (3)	—S(4)	2.451 (4)	—S(4)	2.444 (4)

## References

- BAILLIF, R., YVON, K., FLÜKIGER, R. & MÜLLER, J. (1979). *J. Low Temp. Phys.* **37**, 231–237.
- BARS, O., GUILLEVIC, J. & GRANDJEAN, D. (1973). *J. Solid State Chem.* **6**, 335–339.
- CHEVREL, R. (1974). Thesis, Series B, No. 186/112. Univ. of Rennes, France.
- FISCHER, Ø. (1978). *Appl. Phys.* **16**, 1–28.
- FLÜKIGER, R., BAILLIF, R., MÜLLER, J. & YVON, K. (1980). *J. Less-Common Met.* To be published.
- FLÜKIGER, R., JUNOD, A., BAILLIF, R., SPITZLI, P., TREYVAUD, A., PAOLI, A., DEVANTAY, H. & MÜLLER, J. (1977). *Solid State Commun.* **23**, 699–702.
- GUILLEVIC, J., BARS, O. & GRANDJEAN, D. (1976). *Acta Cryst.* **B32**, 1338–1342.
- RANGEL, R., BOLZ, J. & POBELL, F. (1979). *Verh. Dtsch. Phys. Ges.* p. 372.
- STAFFORD, B., BARNET, C. D., KIMBALL, C. W. & FRADIN, F. Y. (1979). Conference on Superconductivity in *d*- and *f*-band Metals, La Jolla, California, June 1979.
- TOVAR, M., DELONG, L. E., JOHNSTON, D. C. & MAPLE, M. B. (1979). *Solid State Commun.* **30**, 551–557.
- XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- YVON, K. (1978). *Solid State Commun.* **25**, 327–331.
- YVON, K. (1979). *Current Topics in Materials Science*, Vol. 3, pp. 53–129. Amsterdam: North-Holland.
- YVON, K., BAILLIF, R. & FLÜKIGER, R. (1979). *Acta Cryst.* **B35**, 2859–2863.

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## Structure of Potassium *catena*-Di- $\mu$ -fluoro-difluorotetraoxo-di- $\mu$ -sulphato-diuranate(VI) Hydrate

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**Abstract.**  $K_2[UF_2O_2(SO_4)] \cdot H_2O$ , monoclinic; at 298 K:  $P2_1/c$ ,  $a = 9.2634$  (18),  $b = 8.6722$  (18),  $c = 11.0195$  (15) Å,  $\beta = 101.60$  (1)°,  $V = 867.15$  (27) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.83$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 18.805$  mm<sup>-1</sup>. The overall coordination geometry around the uranyl group is pentagonal planar. The uranyl groups [U—O 1.770 (8), 1.776 (8) Å] are coordinated by two O atoms [U—O 2.401 (8), 2.345 (8) Å] from the sulphate groups, and three F atoms, two of which are bridging [U—F 2.349 (8), 2.354 (7) Å] and one is terminal [U—F 2.204 (7) Å]. The sulphate acts as a bridging ligand.

**Introduction.** The crystal structure of this salt has been investigated since no other uranium fluoride sulphate structures are known. The crystals were prepared by mixing aqueous uranyl fluoride and potassium sulphate solutions in a 1:1 molar ratio, followed by evaporation over concentrated H<sub>2</sub>SO<sub>4</sub> (Chakravorti & Bharadwaj, 1979). The structure determination has shown that the compound is hydrated; as originally reported (Chernayev, Ellert, Shubochkin & Shchelokov, 1963), and not the anhydrous salt claimed in Chakravorti &

Bharadwaj (1979); the unit-cell parameters of the latter paper are also in error, as is the observed density of 1.37 Mg m<sup>-3</sup> ( $D_m$  in this work >3.1 Mg m<sup>-3</sup>, as the crystals sink in cadmium borotungstate solution). Data were collected with a Syntex  $P2_1$  diffractometer. Cell constants were determined from the centred positions of 15 reflections (with e.s.d.'s from the least-squares fit). Data were collected to  $2\theta = 55^\circ$  (graphite-monochromatized Mo  $K\alpha$  radiation) with  $\omega/2\theta$  scans at rates ( $2\theta$ ) between 1 and 29.3° min<sup>-1</sup>. The scan range was  $\pm 0.85^\circ$  in  $2\theta$  around the  $\alpha_1$  and  $\alpha_2$  positions. Three standard reflexions showed no significant change in intensity during collection. After correction for Lorentz, polarization, and absorption effects (Alcock, 1970), 1869 reflections were considered observed out of a total of 2261 [ $I/\sigma(I) > 3.0$ ] and used in refinement. The maximum and minimum X-ray transmission factors of the crystal examined (dimensions 0.10 × 0.19 × 0.19 mm) were 0.179 and 0.048. The systematic absences were  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ), indicating space group  $P2_1/c$ .

The structure was solved by the use of the heavy-atom method. Scattering factors were corrected for