Positional Disorder and Non-Stoichiometry in $Cu_{2-x}Mo_3S_4$ Compounds. II.* The Triclinic Low-Temperature Structure of $Cu_{0.9}Mo_3S_4$

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Abstract

A single-crystal analysis of $Cu_{0.9}Mo_3S_4$ has been carried out at 250 K. The compound undergoes a first-order phase transformation at 270 K from a rhombohedral high-temperature into a triclinic low-temperature modification. During the phase transition the Cu ions condense into pairs [d(Cu–Cu) = 2·58 Å]. This causes a slight rearrangement of the Mo_6S_8 building blocks and leads to a triclinic distortion of the octahedron-shaped Mo_6 cluster. The Mo–Mo intracluster distances range from 2·68 to 2·77 Å, and the Mo–Mo inter-cluster distances from 3·21 to 3·31 Å.

Introduction

The defect structure of the rhombohedral $Cu_{2-x}Mo_3S_4$ phase has been described (Yvon, Paoli, Flükiger & Chevrel, 1977). The compounds contain cube-shaped Mo_6S_8 building blocks which are separated by Cu atoms. At room temperature these atoms are distributed at random over 12 tetrahedron-shaped holes in the chalcogen network. The holes correspond to two sixfold crystallographic positions which together are not occupied by more than four Cu atoms on average. This is mainly because these positions are only about 1·3 Å apart and thus cannot all be occupied simultaneously.

An analysis of the vibrational amplitudes showed that the Cu atoms undergo a strongly anisotropic and anharmonic thermal motion. In view of their large r.m.s. amplitudes of about 0·3 Å it was concluded that they are moving between different interstices at room temperature, *i.e.* that their positional disorder in the chalcogen atom network is thermally induced (Yvon,

1978*a*). An indication in favour of this interpretation is the tendency of the MMo_3S_4 compounds (M = metal) to show lattice instabilities (for a review, see Yvon 1978*b*). In particular, all the compounds containing relatively small cations M, such as Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, undergo a structural phase transformation at or below room temperature (Lawson 1972; Chevrel, 1974; Lawson & Shelton, 1977). As to the $Cu_{2-x}Mo_3S_4$ system, several low-temperature modifications are known to exist (Flükiger, Devantay, Jorda & Müller, 1977; Johnston, Shelton & Bugaj, 1977; Flükiger, Junod, Baillif, Spitzli, Treyvaud, Paoli, Devantay & Müller, 1977). However, no structural study for any of these phases has been reported.

The purpose of the present communication is to report on the low-temperature structure of $Cu_{0.9}Mo_3S_4$ and to clarify the nature of its phase transformation. The reason for having chosen this particular Cu concentration can be found in a recently published phase diagram which shows one single low-temperature phase at this composition (Flükiger, Junod, Baillif, Spitzli, Treyvaud, Paoli, Devantay & Müller, 1977). This compound is also of interest because of its unusual properties in the superconducting state (Alterovitz & Woollam, 1978, and references therein; for a review see Fischer, 1978).

Experimental

The crystal studied in the present work was isolated from a large single crystal of composition $Cu_{0.9}Mo_3S_4$, which had been grown earlier (Flükiger, Baillif & Walker, 1978). Before cooling, the lattice parameters of the rhombohedral room-temperature modification were measured on a single-crystal diffractometer. The values obtained (a = 6·50 Å, α = 94·9°) agreed with those determined from a Guinier powder diagram taken with

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* Part I: Yvon, Paoli, Flükiger & Chevrel (1977).

the same sample. A crystal (0·08 mm) was then cooled to 250 ± 5 K in a N_2-gas stream with a Leybold–Heraeus low-temperature attachment. At this temperature it had transformed into a triclinic structure. As was later confirmed by the structural refinement, the crystal consisted of a single domain.

Integrated intensities of 1976 reflexions were recorded with continuous θ–2θ scans to a limit of $(\sin \theta)/\lambda = 0.9$ Å^{-1} and Ag $K\alpha$ radiation. After averaging of equivalent reflexions and application of an absorption correction for a spherical crystal ($\mu R = 2.0$), 1825 observed data were retained [$I > \sigma(I)$]. The structure was solved by trial and error assuming that the Mo_6S_8 building blocks are slightly tilted with respect to their orientation in the high-temperature structure. The positions of the Cu atoms were found on a difference map and the atomic coordinates were subsequently refined by the full-matrix least-squares program *CRYLSQ* of the XRAY system (1976). The weighting scheme was $w = 1/\sigma^2$ and the scattering factors and correction terms for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The final $R = \sum|\Delta F|/\sum|F_o|$ calculated with isotropic extinction and anisotropic thermal parameters for 1680 reflexions with $|F_o| > 3\sigma(F_o)$ is 0·08.*

Results and discussion

As can be seen from Fig. 1 and from the cell parameters (Table 1) and atomic coordinates (Table 2), the low-temperature structure of $Cu_{0.9}Mo_3S_4$ represents essentially a triclinic distorted version of the rhombohedral high-temperature structure. The most striking difference between the high-temperature (HT) and low-temperature (LT) modifications is the distribution of the Cu atoms. In the HT modification they

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34702 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

occupy two types of sixfold crystallographic positions. One (inner site) forms an almost planar hexagon with $\bar{3}$ symmetry around the cell origin and is occupied by 1·6 Cu atoms on average (Fig. 1a). The other (outer site) is about 1·1 Å away from the inner site. It contains only 0·2 Cu atoms and has not been represented in Fig. 1(a).

In the LT modification, however, only two of the inner sites and no outer sites are occupied (Fig. 1b). The two sites are related by an inversion centre, and their separation across the centre is 2·580 (5) Å. Thus the Cu atoms are no longer disordered but form pairs which occupy fixed lattice positions and are aligned along one direction. This transition from the disordered HT state to the ordered LT state is clearly a cooperative phenomenon which reduces the symmetry of the structure.
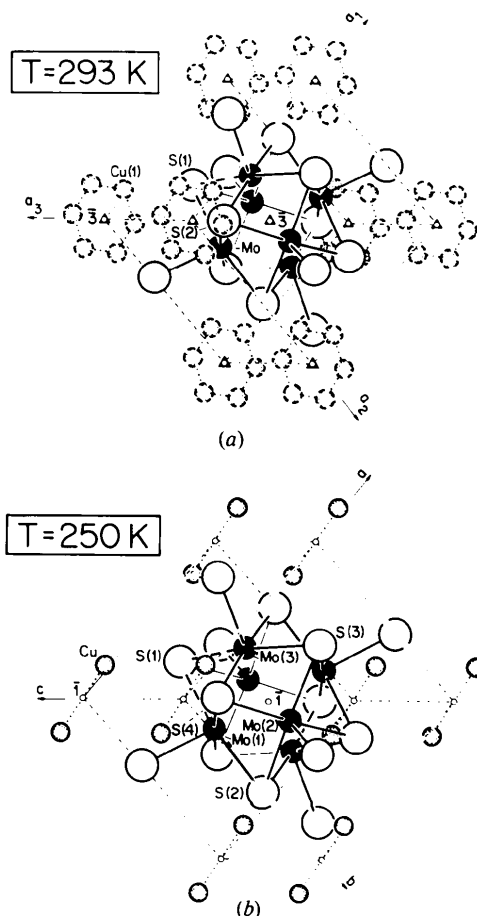

Table 1. *Crystal data for* $Cu_{0.9}Mo_3S_4$ *at 250 and 293 K*

	250 K	293 K
Space group	$P\bar{1}$	$R\bar{3}$
a (Å)	6·479 (3)	6·503 (1)
b (Å)	6·569 (3)	6·503 (1)
c (Å)	6·559 (3)	6·503 (1)
α (°)	96·89 (4)	94·93 (1)
β (°)	93·44 (4)	94·93 (1)
γ (°)	95·74 (4)	94·93 (1)
V (Å^3)	275·2 (3)	272·0 (3)
D_x (Mg m^{-3})	5·68 (1)	5·75 (1)
Z	2	2
μ(Ag $K\alpha$) (mm^{-1})	24·1	24·3

Fig. 1. (a) The rhombohedral high-temperature and (b) triclinic low-temperature structures of $Cu_{0.9}Mo_3S_4$. The atomic coordinates x, y, z of the high-temperature structure ($R\bar{3}$, rhombohedral setting) are: Mo 0·2201, 0·4049, 0·5421; S(1) 0·3790, 0·1349, 0·7216; S(2) 0·2015, 0·2015, 0·2015; Cu(1) 0·1548, −0·0558, 0·9136; Cu(2) 0·0421, 0·0016, 0·6863. The Cu(1) positions shown are partially occupied. The Cu(2) positions have been omitted for clarity.

The detailed environment of the Cu atoms has been represented in Fig. 2. The chalcogen atom network at the origin has trigonal symmetry in the HT phase but shows a triclinic deformation in the LT phase. Interestingly enough the cell volume of the triclinic modification as measured at 250 K is larger than that of the rhombohedral modification as measured at 293 K. The cell shape of the triclinic structure suggests that the lattice has expanded in this temperature interval mainly along **b** and **c**, and has contracted mainly along **a** (Table 1). Since the latter direction is roughly parallel to the interatomic vector of the Cu_2 pair, the Cu atoms within these pairs probably attract each other.

As to the occupancy factor of the Cu atom site, the refinement shows that the crystal contains about 8% of Cu defects. This agrees with the overall composition of the sample ($Cu_{0.9}Mo_3S_4$) and confirms that the crystal has transformed into a single low-temperature phase.

Structural differences between the HT and LT modifications also exist with respect to the shape and the packing of the Mo_6S_8 building blocks. As can be seen from the bond lengths and angles in Fig. 3, the symmetry of this unit is reduced from trigonal to triclinic during the phase transition. In particular, the Mo_6 cluster, which has the form of an elongated octahedron with $\bar{3}$ symmetry in the HT modification, shows a triclinic deformation in the LT modification. This deformation is clearly a consequence of the change in the packing of the chalcogen atoms during the order–disorder transition of the Cu atoms. In fact, each Mo atom interacts via strong covalent bonds with five S atoms, of which four belong to the same Mo_6S_8 unit and form an approximately square-planar configuration, and one belongs to an adjacent Mo_6S_8 unit and represents the top of a square-pyramidal configuration (Fig. 3). On the other hand, the number of valence electrons which are available for the formation of Mo–Mo bonds within the Mo_6 cluster is probably not much affected by the deformation. As shown by Yvon & Paoli (1977) this number depends mainly on

the formal oxidation state and the concentration of the Cu atoms, and it can be derived to a first approximation from the size of the Mo_6 cluster. Since the average Mo–Mo intracluster distance, $\bar{d}_{Mo-Mo}^{intra}$, changes only little during the phase transformation [$\bar{d}_{Mo-Mo}^{intra}$ = 2·73 Å (LT), and 2·72 Å (HT)], one can assume that the oxidation state of Cu is roughly the same in both the HT and LT modifications.

With respect to the electronic structure, however, the ordering of the Cu atoms should lead to more substantial changes. As shown by calculations on related $M_{0.5}Mo_3S_4$ compounds, such as $Pb_{0.5}Mo_3S_8$ (Mattheiss & Fong, 1977; Andersen, Klose & Nohl, 1978; Bullett, 1977), the Fermi level of the rhombohedral modification lies in a mixture of narrow and partially degenerate d bands which can be thought of as deriving from the molecular-orbital levels of an elongated Mo_6 octahedron. Since this cluster shows a triclinic deformation in the present compound, one expects the degeneracy of these bands to be lifted and the density-of-states curve at the Fermi level to be altered during the phase transformation.

The other structural parameters of importance with respect to the electronic structure are the Mo–Mo distances between the clusters, d_{Mo-Mo}^{inter}, and the

Table 2. *Fractional atomic coordinates* ($\times 10^4$), *thermal parameters and occupancy factors for* $Cu_{0.9}Mo_3S_4$ *at* 250 K

The e.s.d.'s are in parentheses and the isotropic temperature factor is expressed as $T = \exp[-2\pi^2 \times 10^{-1} U(2 \sin \theta/\lambda)^2]$.

The space group is $P\bar{1}$.

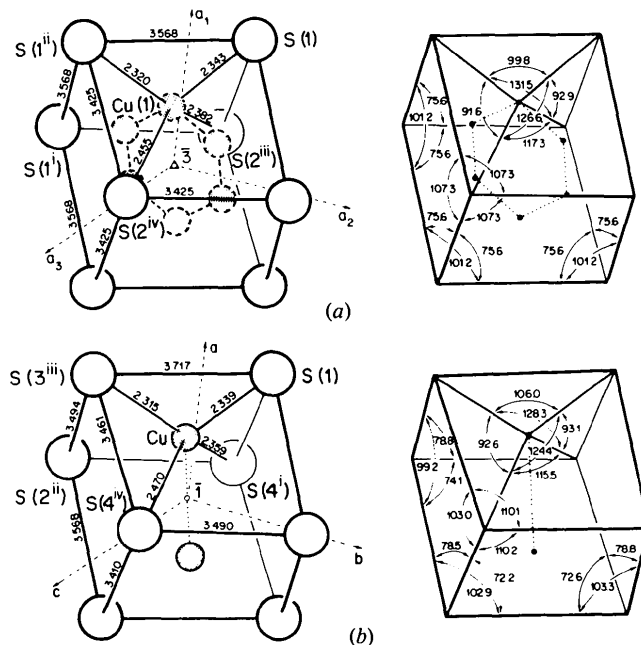|	x	y	z	Occupancy	U (Å^2)
Mo(1)	2204 (2)	4064 (2)	5433 (2)	1·00	8 (1)
Mo(2)	4057 (2)	5371 (2)	2208 (2)	1·00	8 (1)
Mo(3)	5442 (2)	2194 (2)	4013 (2)	1·00	8 (1)
S(1)	3734 (8)	1405 (7)	7155 (7)	1·00	9 (3)
S(2)	1373 (8)	7174 (7)	3814 (7)	1·00	9 (3)
S(3)	7282 (8)	3828 (7)	1261 (7)	1·00	10 (3)
S(4)	2044 (8)	1958 (7)	1995 (7)	1·00	11 (3)
Cu	1593 (5)	−576 (4)	9088 (5)	0·92(2)	17 (2)

Fig. 2. Bond distances (Å) and bond angles (°) around the Cu atoms in (a) the rhombohedral high-temperature (293 K) and (b) the triclinic low-temperature (250 K) structures of $Cu_{0.9}Mo_3S_4$. Errors of angles are 0·2°, and of distances 0·003 Å. Symmetry code: rhombohedral structure: (i) $y,z-1,x+1$; (ii) $1-z,-x,1-y$; (iii) $x,x,1+x$; (iv) $-x,-x,1-x$; triclinic structure: (i) $x,y,z+1$; (ii) $x,y-1,z+1$; (iii) $1-x,-y,1-z$; (iv) $-x,-y,2-z$. The partially occupied Cu positions in the rhombohedral structure are indicated by broken circles.
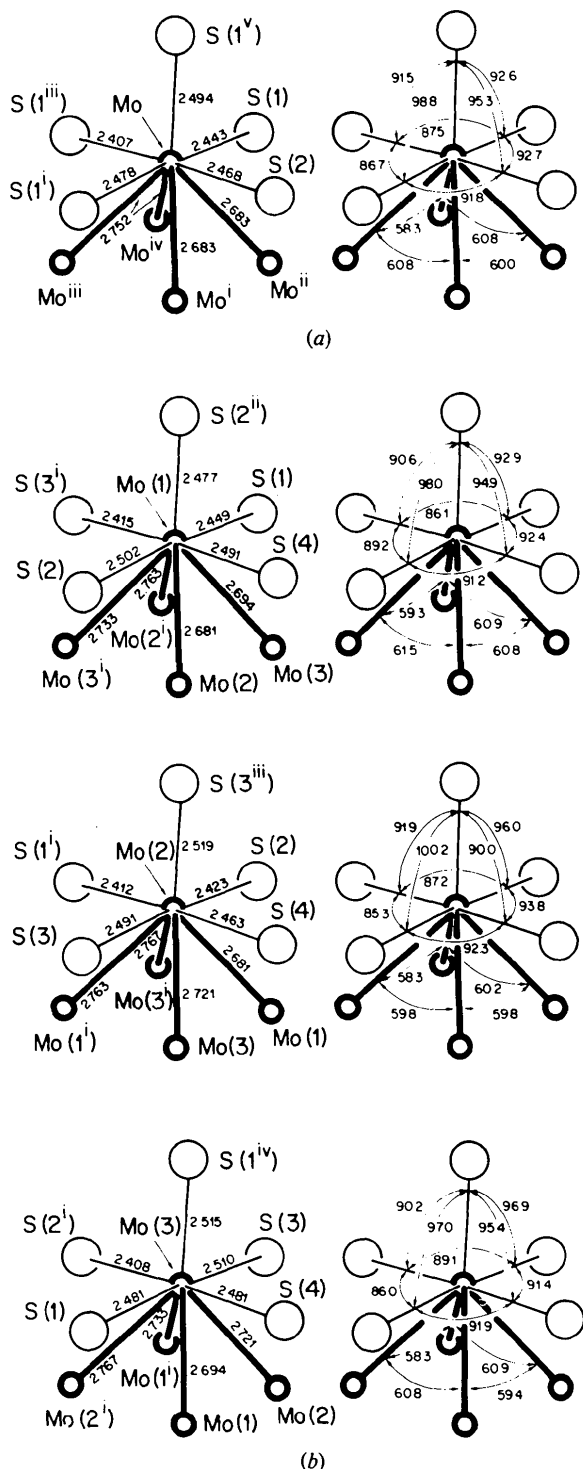
Mo—Cu distances, d_{Mo-Cu}. The former are slightly longer on average in the LT phase than in the HT phase $[d_{Mo-Mo}^{inter} = 2 \times 3.21, 2 \times 3.27, 2 \times 3.31$ Å, average 3.26 Å (LT) and 6×3.24 Å (HT)]. By contrast, the latter are slightly shorter in the LT phase than in the HT phase $[d_{Mo-Cu} = 3.05$ Å (LT) and 3.16 Å (HT)].

In conclusion, the present study confirms that the low-temperature phase transformation of $Cu_{0.9}Mo_3S_4$ is due to an order–disorder transition of the Cu atoms. Since the distribution of other cations M, such as Fe^{2+}, Co^{2+} and Ni^{2+} (Guillevic, Bars & Grandjean, 1973, 1976), in the rhombohedral room-temperature modification of the $M_xMo_3S_4$ compounds corresponds closely to that of the Cu atoms in $Cu_{0.9}Mo_3S_4$, it is likely that the same mechanism is responsible for the low-temperature phase transformations as observed for these compounds. On the other hand, one would expect those compounds which are triclinic at room temperature, such as $Ni_{0.33}Mo_3Se_4$ (Bars, Guillevic & Grandjean, 1973) or $FeMo_3S_4$ (Sergent, Chevrel & Yvon, 1979), to transform into a rhombohedral modification at higher temperatures.

With respect to the structural stability of $Cu_{0.9}Mo_3S_4$ at very low temperatures, recent X-ray powder diffraction measurements have shown that the triclinic structure remains essentially unchanged down to temperatures of 5 K (Baillif, Yvon, Flükiger & Müller, 1979). Thus the LT phase in the $Cu_{2-x}Mo_3S_4$ system which shows a superconducting critical temperature of about 11 K (Flükiger, Devantay, Jorda & Müller, 1977; Johnston, Shelton & Bugaj, 1977; Flükiger et al. 1977) is definitely that having the present triclinic structure.

Fig. 3. Bond distances (Å) and bond angles (°) around the Mo atoms in (a) the rhombohedral high-temperature (293 K) and (b) the triclinic low-temperature (250 K) structures of $Cu_{0.9}Mo_3S_4$. Errors of angles are 0·1°, and of distances 0·002 Å. Symmetry code: rhombohedral structure: (i) y,z,x; (ii) z,x,y; (iii) $1-z,1-x,1-y$; (iv) $1-y,1-z,1-x$; (v) $-y,1-z,1-x$; triclinic structure: (i) $1-x,1-y,1-z$; (ii) $-x,1-y,1-z$; (iii) $1-x,1-y,-z$; (iv) $1-x,-y,1-z$.

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Etude Structurale d'un Nouvel Halogénure Mixte de l'Etain(II): $Sn_2Br_{0,65}Cl_{3,35} \cdot 3H_2O$

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Abstract

Tin(II) bromide chloride trihydrate is monoclinic, space group $P2_1/c$, with $a = 15 \cdot 639$ (3), $b = 8 \cdot 099$ (2), $c = 7 \cdot 602$ (4) Å, $\beta = 97 \cdot 51$ (3)°, $Z = 4$, $V = 954 \cdot 6$ (9) Å^3, $d_m = 3 \cdot 20$ (1), $d_x = 3 \cdot 216$ Mg m^{-3}. The structure has been determined from a Patterson synthesis to give a final weighted R index of $0 \cdot 060$. Each Sn atom has a pyramidal three-coordinated environment and the structure consists of alternating cationic and anionic layers of $[SnBr_{0.15}Cl_{0.85}(H_2O)_3]$ and $[SnBr_{0.5}Cl_{2.5}]$ groups parallel to the (100) plane.

Introduction

L'étude des fluorohalogénures de l'étain(II) a permis de mettre en évidence plusieurs phases dans les systèmes $Sn^{II}XF$. Pour $X = Cl$ ou I, deux composés sont obtenus: $SnXF$ et Sn_2XF_3. Pour $X = Br$, les phases isolées sont $Sn_5Br_4F_6$ et Sn_3BrF_5. Des études structurales ont été réalisées sur tous ces composés à l'exception de SnIF. Ces résultats montrent que l'atome d'étain n'est lié qu'à des atomes de fluor pour les phases riches en fluor, c'est-à-dire pour Sn_2ClF_3 (Donaldson, Laughlin & Puxley, 1977), Sn_3BrF_5 (Donaldson, Laughlin & Puxley, 1977; Vilminot, Granier & Cot, 1978) et Sn_2IF_3 (Vilminot, Granier, Al Oraibi & Cot, 1978a). Lorsque la proportion d'atomes de fluor diminue, l'halogène X prend part à l'environnement de l'atome d'étain dans SnClF (Geneys, Vilminot & Cot, 1976) et $Sn_5Br_4F_6$ (Geneys & Vilminot, 1977).

La substitution de l'halogène X par un ion pseudo-halogène comme l'isothiocyanate $(NCS)^-$ permet d'aboutir à une conclusion analogue puisque dans SnF(NCS) (Vilminot, Granier, Al Oraibi & Cot, 1978b) l'ion $(NCS)^-$ participe à l'environnement de l'étain.

Il apparaissait alors intéressant de voir si les mêmes résultats sont obtenus pour des halogénures mixtes de l'étain ne contenant pas de fluor. Nous présentons ici la résolution structurale de la solution solide $Sn_2Br_xCl_{4-x} \cdot 3H_2O$ pour $x = 0,65$.

Partie expérimentale

L'action de l'acide bromhydrique sur une solution aqueuse de chlorure stanneux conduit à l'obtention d'une solution solide de formule $Sn_2Br_xCl_{4-x} \cdot 3H_2O$ dans un large domaine de composition. Afin de préciser les limites de cette solution solide, nous avons fait varier les proportions respectives de chlorure et d'acide bromhydrique. L'analyse des produits obtenus montre que la solution solide existe pour $0,5 \le x \le 2,4$. Lorsque $x \le 0,5$, le diagramme de poudre révèle la présence du mélange $SnCl_2 \cdot 2H_2O$ et de la solution solide limite $Sn_2Br_{0,5}Cl_{3,5} \cdot 3H_2O$. Lorsque $x > 2,4$, la première phase qui précipite est l'hydrate du bromure stanneux, $3SnBr_2 \cdot H_2O$. La considération des