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Low-temperature structural distortion in CuS

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Abstract. The crystal structure of CuS has been studied by powder X-ray and neutron diffraction methods between 6 and 730 K. At room temperature the hexagonal structure was confirmed. At low temperature (~ 55 K) a second order phase transition takes place with a space group change from $P6_3/mmc$ to the "translationengleiche" subgroup *Cmcm*. This orthorhombic distortion causes only small, but significant changes in the Cu–S and S–S bonding distances. The most pronounced changes occur for the Cu–Cu distances, indicating metal–metal bond formation to be the main cause of the transition.

Introduction

The crystal structure of covellite, CuS, is remarkably complex. This has in the years following Oftedal's report on the structure in 1932, triggered several single crystal X-ray diffraction studies. The originally described structure was thereby confirmed and reliable values for the interatomic distances reported (Berry, 1954; Kalbskopf et al., 1975; Evans and Konnert, 1976; Ohmasa et al., 1977).

CuS is of hexagonal symmetry (space group $P6_3/mmc$) at room temperature and the unit cell contains six formula units. Two copper atoms (Cu1) are triangularly co-ordinated to sulfur and four (Cu2) are tetrahedrally coordinated. The CuS_4-tetrahedra are partly linked together along the *c* axis by S–S bonds (between the S2 atoms). The S–S bond length is short, ~207 pm (Evans and Konnert, 1976), about as found in pyrites and marcasites (Brostigen and Kjekshus, 1970). Furthermore the Cu–S bonding distances in the triangular groups are remarkably short, 219 pm (Evans and Konnert, 1976). The electronic state of CuS has been probed by XPS measurements (Nakai et al., 1978; Folmer and Jellinek, 1980). No distinction is observed for the two types of Cu atoms in CuS, whereas a doublet is found for sulfur, revealing two types of S atoms in covellite (Folmer and Jellinek, 1980). In terms of the ionic model the bonding can thus be described as $(Cu^+)_3S_2^{2-}S^-$.

The crystal structure of CuS has been studied under applied hydrostatic pressure up to 33 kbar (Takeuchi et al., 1985). The main effect on the crystal structure is a considerable increase of the S–S distances, whereas the Cu–S separations are correspondingly shortened. However, for the description of the temperature dependence of the crystal structure of CuS, no detailed data are yet at hand.

In a recent heat capacity study, Westrum et al. (1987) reported a small anomaly around 55 K. Furthermore, the heat capacity was found to be proportional to T^2 in the temperature range 5–20 K, which, based on the Debye theory, may be indicative of a quasi two-dimensional crystal structure at low temperatures. Such properties may seem reasonable considering that the CuS type crystal structure has a somewhat layer-like character. This work will report on the temperature dependence of the crystal structure of CuS between 6 and 780 K, as studied by means of powder X-ray and neutron diffraction.

Experimental

CuS was synthesized by direct reaction of the elements. The mixture of the elements (Cu, continuous rod, 99.999+ mass% pure, American Smelting and Refining Co., New Jersey; and S, crystals, 99.9999 mass% pure, Koch-Light Laboratories Ltd.) was heated in an evacuated and sealed vitreous silica tube, constricted in the central part. The copper was placed in one end of the tube while sulfur in the other. The tube was placed in a slightly inclined tube furnace with the sulfur-containing compartment protruding. The copper was heated to 620 K and the sulfur was allowed to melt and flow into the hotter part of the tube. After most of the sulfur had combined with the copper, a heating pad was wound around the outer end of the silica tube in order to bring the remaining sulfur into reaction during one night. The emptied half of the tube was sealed off before annealing the sample at 670 K for 24 h.

Powder X-ray diffraction data were obtained in a Guinier camera [using Cr$K\alpha_1$ or Cu$K\alpha_1$ radiation and Si (Deslatters and Henins, 1973) as internal standard] at room temperature. Low- and high-temperature powder diffraction data were collected in a Guinier-Simon camera between 90 and 780 K at the University of Oslo, and for temperatures between 6 and 300 K on a similar modified instrument equipped with a specially developed helium flow cryostat (Simon and Müller-Käfer, to be published) at the Max-Planck-Institut für Festkörperforschung, Stuttgart, both using Cu$K\alpha_1$ radiation.

Powder neutron diffraction data were recorded between 8 and 295 K with the OPUS III diffractometer accommodated at a radial channel of the JEEP II reactor, Kjeller. Neutrons of wavelength 187.7 pm were obtained by reflection from the (111) plane of a Ge crystal. A Displex cooling system was used to obtain temperatures between 8 and 300 K. Intensity data were recorded between $2\theta = 5°$ and $100°$ in steps of $\Delta 2\theta = 0.05°$. The Hewat version (Hewat, 1973) of the Rietveld profile refinement program (Rietveld, 1969) was applied in the fitting of the crystal structure parameters. The scattering lengths $b_{\mathrm{Cu}} = 7.718$ and $b_{\mathrm{S}} = 2.847$ fm were taken from Koester and Rauch (1981).

The magnetic susceptibility was measured between 10 and 300 K by the Faraday method with a flow cryostat using quartz sample holders. Electrical conductivity was measured between 1.7 and 295 K using the van-der-Pauw method with the sample compressed by means of a quartz piston (van der Pauw, 1958).

Results and discussion

The powder X-ray and neutron diffraction patterns of CuS at room-temperature were found to agree completely with the reported crystal structure, and the unit cell dimensions are $a = 379.17(8)$ and $c = 1634.2(3)$ pm. Some spread occurs in the earlier reported values for the c axis and the presently reported value agrees well with that of the single crystal study by Evans and Konnert (1976).

The temperature dependence of the unit cell dimensions of CuS between 6 and 700 K is shown in Fig. 1. The variation of a and c with temperature is approximately linear between 300 and 700 K, with $\alpha_a = 1/a_{293\,\mathrm{K}}\,\Delta a/\Delta T = 1.2 \cdot 10^{-5}\,\mathrm{K}^{-1}$ and similarly $\alpha_c = 1.5 \cdot 10^{-5}\,\mathrm{K}^{-1}$. For temperatures between ~90 and 300 K, a and c remain roughly constant, whereas a significant contraction takes place below ~90 K. In addition, below approximately 55 K a gradual line splitting of some reflections is seen in the Guinier-Simon photographs. The $hk0$ and hkl reflections are generally split, whereas the $00l$ reflections remain sharp even at the lowest temperatures. It does not seem probable that the line splitting is connected with a tempera-

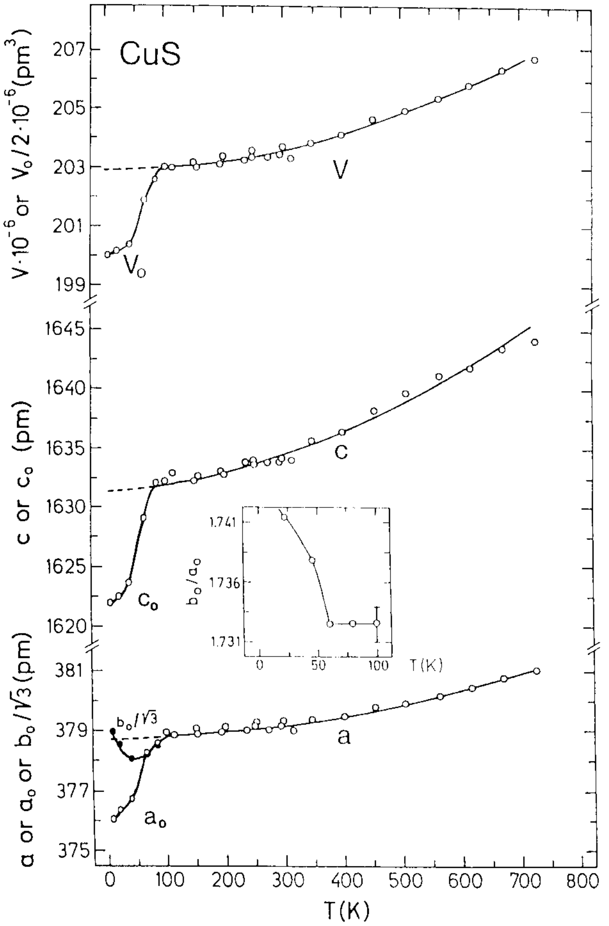

Fig. 1. Variation of unit cell dimensions of CuS between 6 and 700 K. Inset shows variation of the axial ratio b_0/a_0 for the orthorhombically distorted low-temperature phase.

ture dependent homogeneity range of CuS, since such a range has been shown to be very small [<0.0005 in the Cu/S ratio (Potter, 1977)].

The phase transition is clearly manifested in the thermal expansion properties (Fig. 1). Related intensity changes of reflections and line-broadening were observed in the powder neutron diffraction measurements. The temperature dependence of the integrated intensity of the 110 reflection is shown in Figure 2. The marked intensity change at ~50 K corresponds to the line-splittings in the X-ray photographs and to a small heat capacity anomaly (Westrum et al., 1987) in the same temperature range.

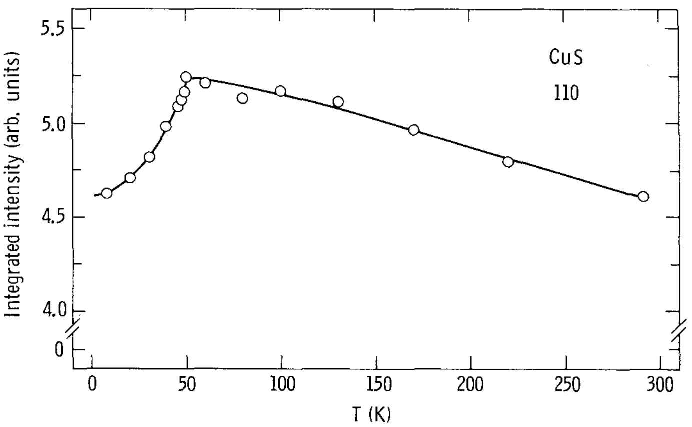

Fig. 2. Variation of integrated intensity of 110 (hexagonal setting; powder neutron diffraction) between 8 and 295 K.

Table 1. Comparison of atomic parameters for CuS in the hexagonal high temperature phase ($P6_3/mmc$) at 295 K.

Authors	z(Cu2)	z(S2)
Ohmasa et al.	0.10724(9)	0.0637(2)
Kalbskopf et al.	0.1073(3)	0.0622(4)
Evans and Konnert	0.10733(9)	0.06337(15)
Present 295 K	0.1072(2)	0.0611(8)
Present 55 K	0.1068(3)	0.0624(11)

The neutron diffraction data collected at 8, 55 and 295 K were used for deriving positional parameters of CuS via Rietveld type refinements (Rietveld, 1969). It turned out that the introduction of a preferred orientation parameter, gave significantly improved fits, which suggests a tendency for CuS to form platelets perpendicular to the hexagonal c axis.

The obtained values for the unconstrained positional parameters (space group $P6_3/mmc$ with Cu1 in 1/3, 2/3, 3/4, Cu2 in 1/3, 2/3, z, S1 in 1/3, 2/3, 1/4 and S2 in 0,0,z) at 295 K ($R_n = 0.042$), $z_{Cu2} = 0.1072(2)$ and $z_{S2} = 0.0611(8)$, comply with values derived from single crystal X-ray diffraction studies, which are summarized in Table 1. For the refinements at 55 K carried out according to orthorhombic symmetry (see below), the obtained values for the additional, unconstrained positional parameters comply with the hexagonal description within two calculated standard deviations ($R_n = 0.056$).

The pattern of line splitting observed for $T < 55$ K suggests that the low temperature phase is orthorhombic. Indeed, the X-ray diagram can easily

Table 2. Positional parameters for the low-temperature modification of CuS (space group *Cmcm*, No. 63) in comparison with the parameters for the hexagonal high-temperature modification ($P6_3/mmc$, No. 194, orthorhombic setting), isotropic temperature factors $B_{Cu} = 0.20$ and $B_S = 0.35 \cdot 10^4$ pm^2.

Atom	8 K			295 K[a]		
	x	y	z	x	y	z
Cu1	0	0.3623(11)	3/4	0	1/3	3/4
Cu2	0	0.3372 (9)	0.1070(2)	0	1/3	0.10733
S1	0	0.3068(29)	1/4	0	1/3	1/4
S2	0	0.0008(17)	0.0627(7)	0	0	0.06337

[a] Evans and Konnert (1976).

be indexed assuming a slightly distorted orthohexagonal cell with $a_0 = a$, $b_0 = a\sqrt{3}$ and $c_0 = c$. The temperature dependencies of a_0, $b_0/\sqrt{3}$ and c_0 are shown in Figure 1. It should be noted that, e.g. the hexagonal 102 reflection splits into two at low temperatures, with the weaker one at the lower scattering angle. The observation of the nuclear 202 reflection in front of 112 in the orthorhombic regime implies that $b_0/a_0 > \sqrt{3}$. This type of distortion was confirmed by refinements of the neutron diffraction data collected at 8 K. From Figure 1 it is evident that the anomalous contraction in unit cell volume starts already at ~90 K, whereas the orthorhombic distortion, with $b_0/a_0 > \sqrt{3}$, initiates at 55 K (see inset to Fig. 1). Considering also the heat capacity and neutron diffraction data, one is led to conclude that the major distortion and atomic displacements take place at about 55 K. Yet, the same reflections which become split below 55 K, are already broadened at some 150–200 K. This suggests that the lowering of symmetry gradually starts at a significantly higher temperature than 55 K.

A convincing refinement of the low-temperature structure of CuS is possible in space group *Cmcm*. The positional parameters at 8 K are given in Table 2, together with the corresponding parameters at 295 K (orthohexagonal setting). The residual at 8 K is $R_n = 0.048$. The structural phase transition takes place from the hexagonal space group $P6_3/mmc$ to a maximal non-isomorphic subgroup, thus fulfilling the Landau criterion for a second order transition. The symmetry reduction represents a step which is "translationengleich" (Bärnighausen, 1980), and can be expressed according to

$$\begin{array}{c} P\,6_3/m\,2/m\,2/c \\ | \\ \mathrm{t}3 \\ \mathbf{a}_1,\ \mathbf{a}_1 + 2\mathbf{a}_2,\ \mathbf{c} \\ \downarrow \\ C\,2/m\,2/c\,2_1/m \end{array}$$

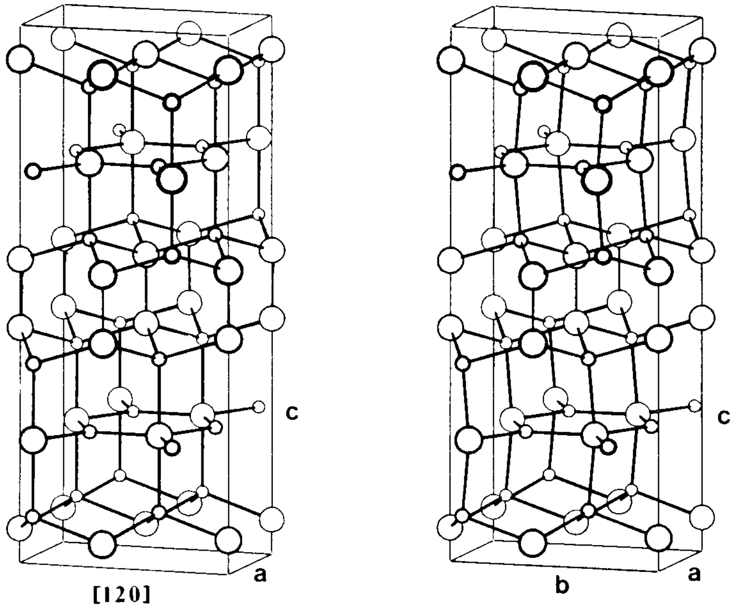

Fig. 3. Comparison of the crystal structure of CuS at 295 K (left, orthohexagonal setting) and 8 K (right). Cu1 (small circles) lie in plane with S1 (large circles). Cu2 is tetrahedrally coordinated and S2 form S_2 units.

The effect of the distortion at low temperature on the CuS-type structure is illustrated in Figure 3. In Table 3, selected interatomic distances for CuS at 295 and 8 K are given. The corresponding distances for a hypothetical hexagonal structure at 8 K (on the basis of the extrapolated unit cell dimensions $a = 378.7$, $c = 1631.3$ pm and positional parameters at 55 K) are included for comparison.

The interatomic distances of hexagonal CuS at 295 K, agree well with those reported from single crystal X-ray diffraction studies by Evans and Konnert (1976). The lowering of the temperature from 295 to 8 K, as well as the progressing orthorhombic distortion at low temperatures, imply only small, yet significant, changes in the interatomic distances. The essential effect of the distortion below 55 K is a shift of the BN-like layers formed by Cu1 and S1 relative to the slabs formed by Cu2 and S2. The distortion results in a slight deformation of the trigonal coordination of S1 around Cu1 as well as in the nearly tetrahedral coordination of S1 and S2 around Cu2. Moreover, the shift implies a significant change of the angle Cu2—S1—Cu2 from 180° in the hexagonal modification to 170° in the orthorhombic one. The distortion leads to a rather close approach of Cu1 and Cu2 (304 pm). Figure 4 summarizes the characteristic changes for the

Table 3. Interatomic distances (in pm) less than 330 pm in orthorhombic CuS at 8 K. Also given are data for a hypothetical hexagonal structure at the same temperature. Calculated standard deviations in parentheses. Single crystal X-ray diffraction data at 295 K are included for comparison.

	Orthorhombic 8 K	Hypothetical hexagonal 8 K	Hexagonal 295 K[a]
Cu1 – S1	2 × 218(2)	3 × 218.6	3 × 219.05(2)
– S1	1 × 217(2)		
Cu2 – S1	1 × 232.8(4)	1 × 233.3	1 × 233.1(2)
– S2	1 × 232(2)	3 × 230.3	3 × 230.5(1)
– S2	1 × 228.1(8)		
S2 – S2	1 × 203(2)	1 × 204.6	1 × 207.1(4)
Cu1 – Cu2	1 × 326.0(5) 2 × 304.4(7)	6 × 319.7	6 × 319.9(4)

[a] Evans and Konnert (1976).

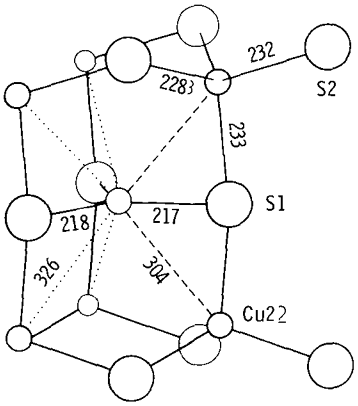

Fig. 4. Cu – Cu and Cu – S distances in CuS at 8 K (Cu1 in the center).

coordination around Cu1 and Cu2 with the orientation of the structural unit as shown in the projection in Figure 3 (right). The formation of metal – metal (M – M) bonds between Cu1 and Cu2 (dashed lines) seems to be the driving force for the hexagonal-to-orthorhombic transition. One has to admit though, that the distance $d(\mathrm{Cu-Cu}) = 304$ pm is rather long for a M – M bond. On the other hand, the characteristic distortions of the coordination polyhedra of both Cu1 and Cu2 add further weight to the idea that increased M – M bonding interactions are essential for the occurrence of the phase transition. The entire trigonal unit of S1 around Cu1 is shifted towards Cu2, and, vice versa, Cu2 is shifted towards Cu1 with

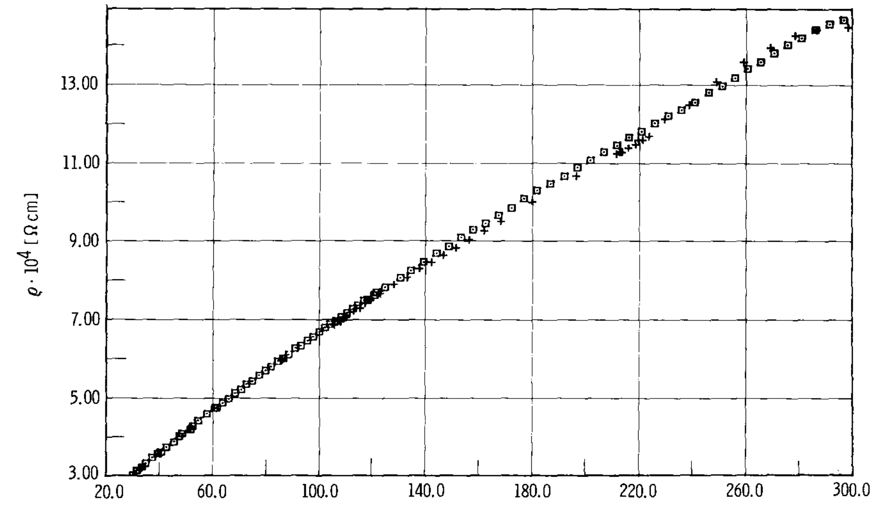

Fig. 5. Specific resistivity ϱ (Ω cm) of CuS (pressed pellet) versus temperature; crosses with decreasing temperature, squares with increasing temperature.

respect to its environment of S2 atoms, see Figure 4. The existence of bonding interaction between the closed-shell ions Cu^+ (and even more enhanced between Ag^+ ions) is well known from complexes (Beck and Strähle, 1985) and solids (Jansen, 1980). The quadrupolar deformability of the ions due to $d-s$ excitations is responsible for the easy clustering of these ions (Bilz, 1985).

It should be noted that a similar orthorhombic distortion as for CuS, most probably also exists for CuSe (klockmannite, isostructural to covellite at least at high temperatures). Stevels and Jellinek (1971) reported CuSe to be orthorhombic (with $b_0/a_0 > \sqrt{3}$) in an intermediate temperature range between 320 and 390 K, but no structural details are known.

The electric and magnetic properties of CuS show hardly any changes to be associated with the phase transition. Metallic behaviour (Fig. 5) is found (300 K: $\varrho = 1.45 \cdot 10^{-3}$ Ω cm, 30 K: $\varrho = 3.00 \cdot 10^{-4}$ Ω cm) in fairly good agreement with earlier measurements (Okamoto et al., 1969). The continuous behaviour of ϱ is somewhat surprising. The proposed Cu – Cu bond formation in CuS at low temperatures should result in a change of the free carrier concentration and/or the carrier mobility. The magnetic properties as measured are shown (χ given in c.g.s. units) in Figure 6. The $1/\chi$ vs. T plot reveals a Curie-Weiss behaviour with $\theta \sim 10$ K. Below ~30 K small deviations towards lower χ are found. The resulting, small magnetic moment μ_{eff} ranging between 0.24 and 0.30 μ_B, is in agreement with earlier

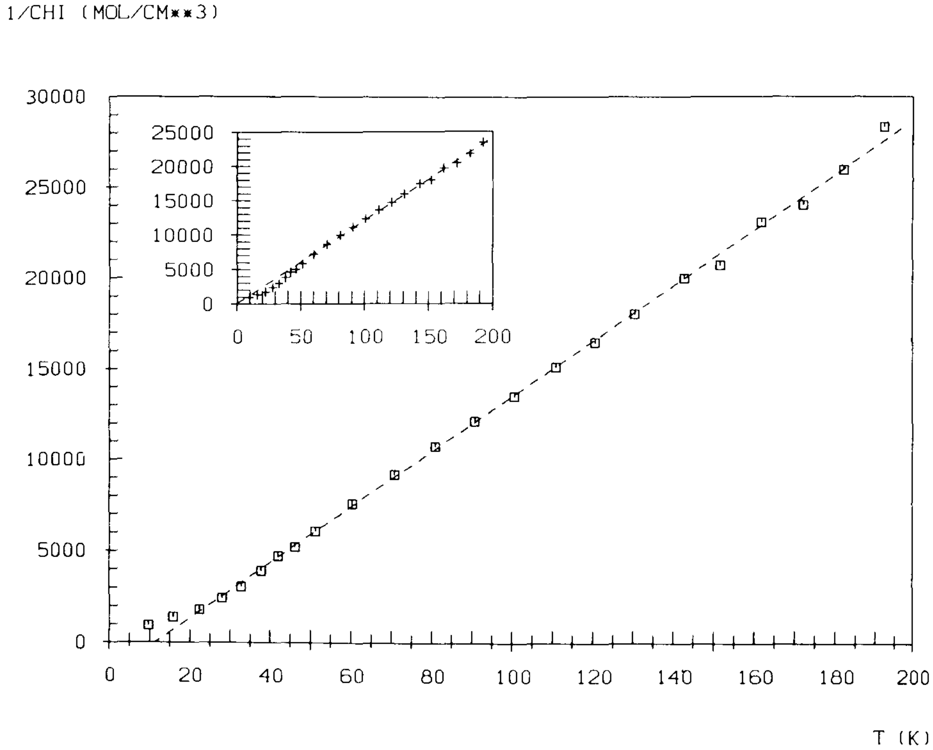

Fig. 6. Reciprocal molar susceptibility of CuS plotted versus T. Inset shows data corrected for $\chi_{TI} = -7.4 \cdot 10^{-6}$ cm^3 mol^{-1}.

results (Okamoto et al., 1969). The existence of a magnetic moment may indicate a partial d^9 character of the Cu atoms or residual spin density of the covalently bonded S1 atoms. To account for temperature independent contributions (diamagnetism and Pauli paramagnetism) χ vs. $1/T$ was plotted, and the temperature independent part χ_{TI} found to be $-7.4 \cdot 10^{-6}$ cm^3 mol^{-1}. The $1/\chi$ vs. T plot in the inset to Figure 5 refer to magnetic susceptibility data corrected for χ_{TI}. The deviation from a simple Curie-Weiss behaviour starting at approximately 60 K, may be related to the structural phase transition.

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