Electrical and Magnetic Properties of $K_3Cu_8S_6$

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Four-probe electrical conductivity measurements from 15 to 300 K demonstrate that the mixed-valence compound $K_3Cu_8S_6$ is metallic at higher temperatures and below 160 K it forms less-conducting structural phases. The changes in conductivity in the range 160—100 K are connected with changes in magnetic susceptibility. A rough estimate of the density of states at the Fermi level has been made.

Several years ago Rudorff *et al.*[1] prepared a number of crystalline mixed-valence thiocuprates of formula $M_xCu_yS_z$ where M represents an alkali metal. The compound KCu_4S_3, which adopts a layered structure, exhibits the electrical conductivity and magnetic properties of a metal;[2] $Na_3Cu_4S_4$ consists of one-dimensional columns with $Cu_4S_4^{3-}$ chains and shows a high anisotropy in the electrical conductivity, being classified as a one-dimensional metal.[3] Goodenough[4] has defined a critical internuclear separation of metal ions below which high conductivity electrons should be present. For a d^9 copper complex with sulphide ligands, this distance is predicted to be *ca.* 3.10 Å. The compounds KCu_4S_3 and $Na_3Cu_4S_4$ satisfy the Goodenough criterion, and their metallic properties are consistent with the theory. Recently Burschka[5] reported the structures of two other mixed-valence thiocuprates: $K_3Cu_8S_6$ and $Rb_3Cu_8S_6$.Both the compounds crystallize with an unusual type of structure. Crystalline $K_3Cu_8S_6$ contains two different arrangements of atoms, one corresponding to that in KCu_4S_3 and the other to that in KCu_3S_2. The potassium ions occur in layers in which they are seven- and eight-co-ordinated. Distances between neighbouring copper ions satisfy the Goodenough criterion.

On account of its unusual structure and in a search for new conducting materials, we have studied the electric and magnetic properties of $K_3Cu_8S_6$.

Results and Discussion

The electrical conductivity of a pressed pellet of $K_3Cu_8S_6$ measured as a function of temperature is given in Figure 1. Using the four-probe technique, the room-temperature conductivity was found to be 480 Ω^{-1} cm^{-1}, in contrast to the value of 70 Ω^{-1} cm^{-1} previously reported for the same compound.[1] The room-temperature conductivity of a single crystal (Figure 2) measured along the needle axis is higher by a factor of *ca.* 8 than the bulk conductivity and is comparable to that of other known metallic materials with layer structures.[6] The difference between the single-crystal and bulk conductivity may arise from both the inherent anisotropy of the solid and the interparticle resistance. The conductivities of both the single crystal and a pressed pellet do not change regularly with temperature as observed for simple and molecular metals or for the previously investigated thiocuprates KCu_4S_3 or $Na_3Cu_4S_4$.[2,3] Upon cooling the sample, the conductivity begins to increase, reaches a maximum, decreases between 160 and 100 K, then increases again, and, after passing a second maximum, decreases to a relatively low value.

To gain additional information on the nature of the observed anomalies, we studied the temperature dependence of the magnetic susceptibility of a polycrystalline sample. The obtained data are shown in Figure 3. An inspection of the $\chi(T)$ curve shows that there is a small hump near 150 K. In order to examine this more closely we subtracted out the Curie contribution by the following procedure. Using a least-squares treatment, we fit the data between 10 and 100 K with an expression of the form $\chi = [C/(T + \theta)] + \chi_0$, where $C = 21.8 \times 10^{-6}$ e.m. units K g^{-1} ($= 1.73 \times 10^{-3}$ m^3 K kg^{-1}), $\theta = 2.4$ K, and $\chi_0 = -0.074 \times 10^{-6}$ e.m. units g^{-1} ($= 5.9 \times 10^{-6}$ m^3 kg^{-1}). Assuming that C and θ are the same at all temperatures but that χ_0 could be temperature-dependent for $T > 100$ K, we plotted $\Delta\chi = \chi_{meas.} - [C/(T + \theta)]$ to produce Figure 4.

Figure 4 shows a very clear anomaly beginning near 160 K and ending at *ca.* 100 K. This is obviously connected with the resistive anomaly seen in Figures 1 and 2. We consider that the simultaneous change in conductivity and in magnetic susceptibility in the range 160—100 K is very likely due to a second-order structural phase transition. Much less visible in Figure 4 is the second anomaly in the low-temperature region, due to a large scattering of the susceptibility data arising from instrumental errors.

The obtained results give a rough estimate of the density of states at the Fermi level. Using the expression for Pauli

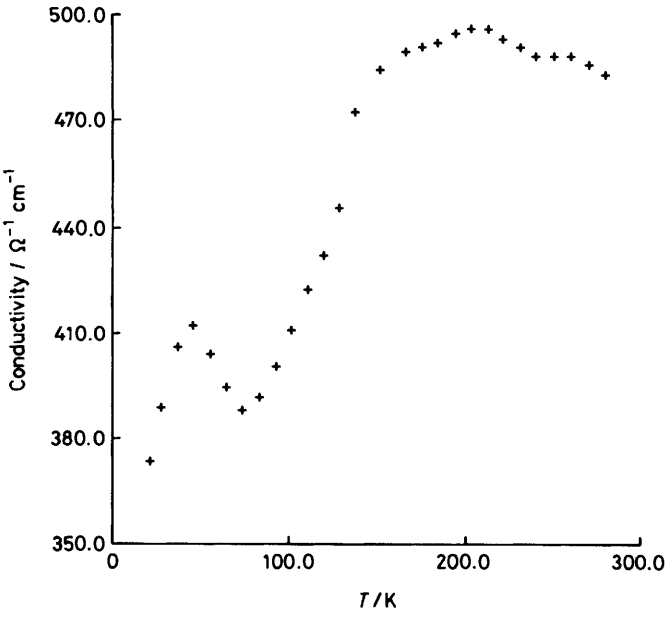

Figure 1. Electrical conductivity as a function of temperature for a pressed pellet of $K_3Cu_8S_6$

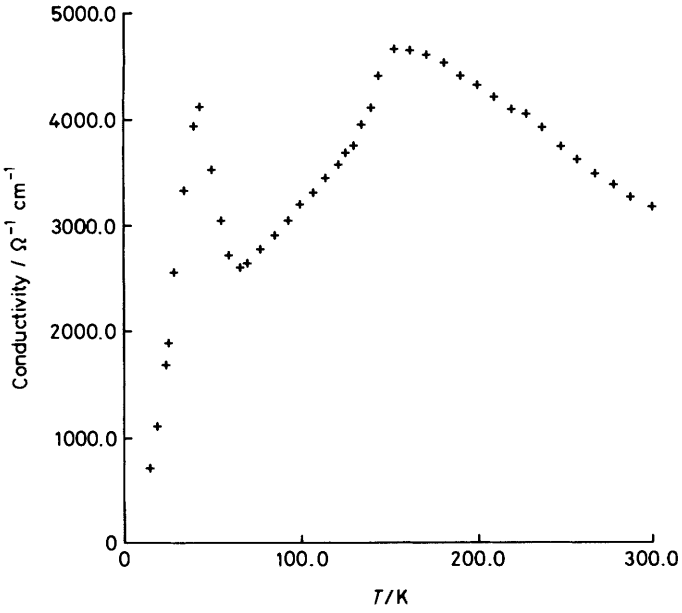

Figure 2. Electrical conductivity as a function of temperature for a single crystal of $K_3Cu_8S_6$. Four-probe conductivities were measured parallel to the needle axis

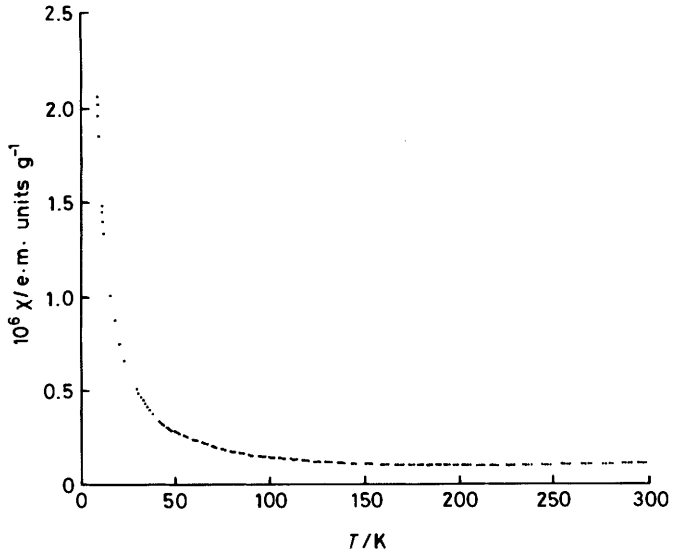

Figure 3. Magnetic susceptibility of polycrystalline $K_3Cu_8S_6$ as a function of temperature

paramagnetism, $\chi_{Pauli} = \chi_0 + \chi_{diam.}$ (cores), and the values of χ_0 and $\chi_{diam.}$, the latter calculated from the diamagnetic contribution of all the atoms or ions in the molecule per gram, we obtained $\chi_{Pauli} = 0.2 \times 10^{-6}$ e.m. units g^{-1} ($= 16 \times 10^{-6}$ m^3 kg^{-1}) and the density of states at the Fermi level, $N(E_F) = 0.32$ states per Cu atom per eV. So both the high conductivity and the value of the density of states at the Fermi level indicate the metallic character of $K_3Cu_8S_6$. The compound differs, however, from the related thiocuprates KCu_4S_3 and $Na_3Cu_4S_4$ in that below 160 K it forms less-conducting structural phases.

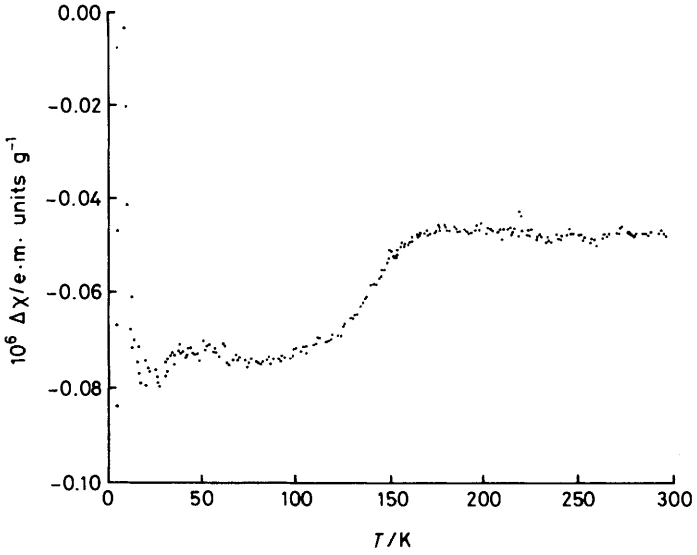

Figure 4. The difference between the measured magnetic susceptibility, $\chi_{meas.}$, and the calculated Curie contribution $C/(T + \theta)$ for $K_3Cu_8S_6$, with $C = 21.8 \times 10^{-6}$ e.m. units K g^{-1} and $\theta = 2.4$ K

Experimental

The compound $K_3Cu_8S_6$ was prepared by heating a mixture of potassium carbonate, copper, and sulphur in the ratio 6:1:6 to 900—1 000 °C in an argon atmosphere for 1—2 h. After cooling, the crystalline material was washed with water, ethanol, and diethyl ether and dried *in vacuo* (Found: Cu, 62.4; K, 14.3; S, 23.7. Calc. for $K_3Cu_8S_6$: Cu, 62.1; K, 14.3; S, 23.5%). Copper was analysed by titration with ethylenediaminetetra-acetate using murexide as indicator following decomposition in *aqua regia*. Potassium was determined by atomic absorption spectrometry. The sulphur determination was performed by Schwarzkopf Analytical Laboratories.

Magnetic Susceptibilities.—Magnetic susceptibilities of randomly oriented crystals were measured with a conventional Faraday balance calibrated with $HgCo(SCN)_4$. Diamagnetic corrections were made as follows: K^+, -13×10^{-6}; Cu^+, -12×10^{-6}; S, -15×10^{-6} e.m. units mol^{-1}.

Electrical Conductivity.—Measurements of the conductivities of polycrystalline compactions and of the single crystal were made with the four-probe van der Pauw technique as described earlier.[3] Since crystals of $K_3Cu_8S_6$ were thin and fragile, the electrical conductivity of a single crystal could be measured only along the needle axis.

References

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