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Metallic Hole Conduction in CuS

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The electrical resistivity, Hall coefficient, magnetoresistance, and magnetic susceptibility of CuS are reported. The compound exhibits excellent metallic conduction among 3*d* transition metal sulfides. A peculiar temperature dependence of the Hall coefficient is interpreted in terms of two bands of majority holes and minority electrons. The source of the hole carriers is discussed based on Hall effect data and structural considerations. It is concluded that conduction is due to holes in a valence band which is mainly constituted from the 3*p* orbitals of sulfur. A phase transition close to 55 K is confirmed from the temperature dependence of resistivity and the Hall coefficient.

Introduction

It has been shown by recent X-ray photoelectron spectroscopy studies (*1–3*) that in several copper sulfides and selenides, such as CuS, Cu_3Se_2, Cu_2Se, CuSe, $CuSe_2$, and CuS_2, Cu is in the monovalent state, even though in almost all of these compounds the presence of Cu^{2+} is suggested by the composition (*1*). The metallic conduction of CuS (*4, 5*) and the observed superconductivity with $T_c = 1.6$ K (*6*) are attributed to holes in the valence band which is associated with the 3*p* orbitals of sulfur (*1*). The Hall effect data of CuS have not been reported so far; metallic hole conduction should be confirmed by a Hall effect study. Furthermore, it is interesting to study the conduction mechanism of CuS, because recent high T_c superconductivity is commonly associated with metallic conduction in the valence band of anion *p* orbitals.

A recent X-ray crystal structure analysis has shown that CuS distorts from hexagonal symmetry ($P6_3/mmc$) to orthorhombic symmetry (*Cmcm*) below 55 K (*4*). No indication of this structure change has been reported in the data of resistivity and magnetic susceptibility (*4*); however, a small anomaly has been observed in a heat capacity study (*7*). A more detailed study of physical properties of CuS is therefore indicated.

The present report aims to confirm the *p*-type conduction of CuS and investigate the conduction mechanism through resistivity, Hall effect, magnetoresistance, and magnetic susceptibility experiments. A second aim is to search any change of physical properties associated with changes in crystal structure near 55 K.

Experimental

The compound CuS was synthesized both by sulfurization of Cu metal and by deoxylation of $CuSO_4$. In the former case, thin

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plates were cut off from a Cu rod (99.99% in purity) and heated with appropriate amounts of S (99.999%) at 300°C for 2 weeks in an evacuated sealed quartz tube. In the latter case, the deoxylation process was performed at 300°C for 32 hr under 1 atm H_2S; the sulfide powder was pressed at 10^3 kg/cm^2, followed by anealing under 1 atm H_2S atmosphere at 300°C for 10 hr. The compositions were determined by the gravimetric method, showing that $CuS_{1.00}$ was produced. X-ray powder diffraction experiments revealed no other phases. No deviations in stoichiometry of CuS were encountered in our synthesis under various conditions. Specimens used for electrical measurements were thin plates of rectangular form (1.5 × 8.0 × 0.19 and 1.9 × 8.0 × 0.22 in mm^3) obtained by polishing sulfurized materials. Resistivity, Hall effect, and magnetoresistance measurements were performed by standard dc four-probe methods, respectively. Electrical contacts were made using Au paste. Magnetic susceptibility measurements were performed on a Faraday-type magnetometer.

Results

The temperature dependence of resistivity of both specimens prepared by sulfurizing Cu metal and $CuSO_4$, respectively (called sample A and sample B), is metallic. That for the former decreases slightly more steeply below about 55 K, indicated as T_t in Fig. 1, than does the latter. The difference between the resistivity changes of samples A and B around 55 K are more clearly seen in the derivatives of the temperature dependence of resistivity (Fig. 2). The derivative of sample A increases below about 57 K, while that of B does not. The magnitude of the resistivity at 5 K for the sample A is 0.6 $\mu\Omega$ cm and that for B is 3 $\mu\Omega$ cm. The ratios between resistivity at 300 K and that at 5 K are 177 for A and 33 for B, respectively. These magnitudes, particularly for sample A, indicate that CuS is an excellent metal among transition metal sulfides. The transverse magnetoresistance measured at 4.6 K (Fig. 3) increases almost linearly with field strength and reaches 16% at 0.96 T for A, while that for B is quite small (0.5%).

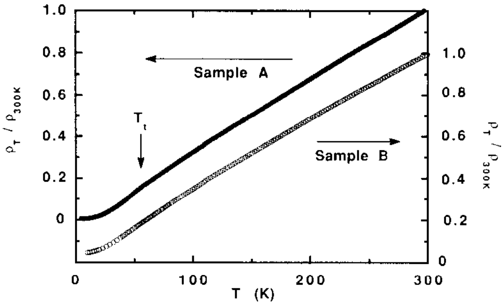

FIG. 1. Electrical resistivity of CuS. Solid and open circles represent the resistivities of samples A and B, respectively, normalized to those at 300 K. T_t corresponds to a temperature reported at which crystal structure changes.

Both Hall coefficients of CuS are positive but vary with temperature in a rather complicated manner (Fig. 4). The Hall coefficient for sample A exhibits a minimum value close to 58 K and clearly rises below 55 K. The transition temperature may be specified by the beginning of the steep increase of the Hall coefficient. The ratio of the maximum value near 10 K to the minimum one is about 6.5. These features are much less pronounced for sample B, where the Hall coef-

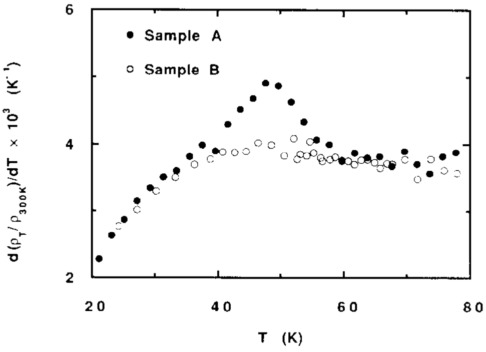

FIG. 2. Derivatives of temperature dependence of resistivity for samples A and B.

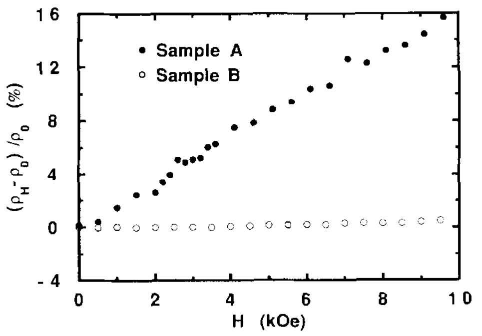

FIG. 3. Magnetoresistances of samples A and B measured at 4.6 K.

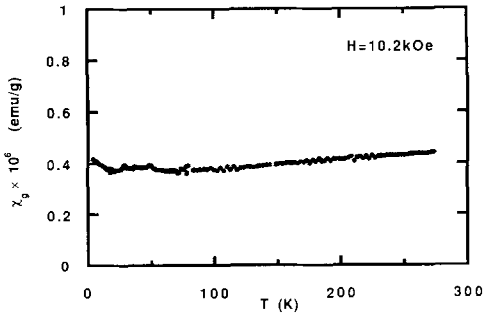

FIG. 5. Temperature dependence of magnetic susceptibility for sample A.

ficient gradually increases below about 80 K and more steeply below about 55 K. The transition temperature can not therefore be clearly specified.

The magnetic susceptibility of CuS for sample A is almost temperature independent (Fig. 5), consistent with the metallic character of CuS, although previous studies have reported some temperature dependence (*4*, *5*). The structural transition is not reflected in the temperature dependence of magnetic susceptibility within the experimental accuracy.

Discussion

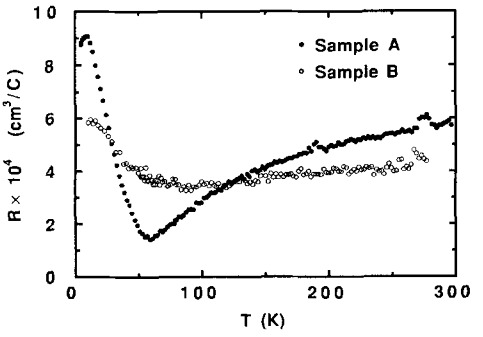

FIG. 4. Temperature dependences of Hall coefficients for samples A and B.

The electrical properties of CuS specimens for samples A and B are very different. Therefore, the differences in the specimens are discussed first. It has often been observed for sulfurized Cu metal plates (sample A) that tabular crystallites are connected to each other by tight bridges. This indicates that atomic diffusion (probably of Cu) is prominent in this process. On the other hand, annealing plates prepared by pressing CuS powder (sample B) did not show such a phenomenon. It is therefore presumed that the grain boundaries of CuS differ between samples A and B. The residual resistivity of the B specimen is one order larger than that of the A specimen, probably due to relatively large grain boundary scattering in case B.

The magnetoresistance of sample A is very large (16%). By contrast that of sample B is quite small (0.5%). The magnetoresistance is of the order of magnitude of $(\omega_c\tau)^2$ (*8*), where ω_c and τ are the cyclotron frequency and relaxation time, respectively. One can evaluate the ratio between the relaxation time of sample A and that of B at 5 K using the ratio of the residual resistivities. The magnetoresistance of B at 0.96 T is thus expected to be about 0.6% (16 × $(\tau_B/\tau_A)^2$ %), which agrees with the experimental value. A more electrically pure state at low temperatures is therefore realized in sample A rather than sample B. The temperature dependence of the resistivity and the Hall coefficient of sample A appear to exhibit the intrinsic features of CuS more clearly. The properties of sample A are therefore discussed at first.

The resistivity of sample A shows a slight decrease and the Hall coefficient steeply increases below about 55 K. These phenomena clearly correspond to the crystal structure change as observed in the previous structure analysis (*4*). In spite of the small change of resistivity, a clear transition is observed close to 55 K in the Hall coefficient data, the reason for which is discussed below.

No evidence for a structure change was detected in the temperature dependence of susceptibility. This indicates that the structural transition involves little change in the density of state near the Fermi level and little change in carrier density. Furthermore, the large magnetoresistance of 4.6 K strongly suggests two overlapping bands. The complicated temperature dependence of the Hall coefficient can therefore be interpreted in terms of a two-band system involving holes and electrons. The conductivity σ and Hall coefficient R are therefore given by

$$\sigma = \sigma_e + \sigma_h \quad \text{and} \quad R = (1/n_h q) \times \{\alpha^2 - (n_h/n_e)(1 - \alpha)^2\} \quad (\alpha = \sigma_h/\sigma),$$

where σ_e and σ_h are electron and hole conductivities, n_e and n_h are carrier densities, and q is the absolute value of the electric charge of electron. It is reasonable to assume that n_e and n_h are constant because of the metallic conductivity and because of the temperature independence of susceptibility. Therefore, the peculiar temperature dependence of the Hall coefficient is due to the difference of temperature variations of the electron and hole mobilities. Since the Hall coefficient is always positive, α is in the range of $1/\{1 + (n_e/n_h)^{1/2}\} < \alpha \leq 1$, in which R varies from 0 to $1/n_h q$. The small change of resistivity around 55 K suggests that neither mobility changes significantly when the structure transition occurs. It is thus presumed that the variation of α is also small. In spite of the small variation of α, the Hall coefficient steeply increases below about 55 K. If $n_e \ll n_h$, α can only vary in a small range from slightly less than 1 to 1 below about 55 K. This small variation of α can however drastically alter R from a small positive value to the maximum of $1/n_h q$, which agrees with the present behavior of the Hall coefficient of sample A below about 55 K. Above about 60 K, the Hall coefficient gradually decreases with decreasing temperature. This is also realized by a very small decrease of α, which implies that the electron mobility increases a little faster with decreasing temperature than the hole mobility. Thus, the temperature dependence of the Hall coefficient can be explained by the assumption of $n_e \ll n_h$, that is, $\alpha \approx 1$. The present conclusion that CuS is an intrinsically *p*-type conductor is consistent with the XPS result (*1*).

It, therefore, appears that the structure change below 55 K mainly influences the scattering mechanism of hole conduction by phonons. Furthermore, it appears to have little effect on the electronic structure, as observed in the susceptibility data. These features suggest that the structure change does not originate with an electronic instability but is due to the lattice dynamics of CuS.

If one can neglect the contribution of electron conduction to the Hall coefficient at about 10 K where the maximum occurs, the number of hole carriers is obtained as 0.23 per formula unit. The Hall mobility of holes at 4.7 K is given by 1440 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$.

In contrast with the Hall coefficient of sample A, that of sample B less pronouncedly reflects the transition so its temperature can less evidently be specified. The maximum magnitude of the Hall coefficient for case B, which also occurs at about 10 K, is about $\frac{2}{3}$ that for case A, while the minimum of the Hall coefficient for B, which occurs at about 85 K, is 2.4 times larger than that for A (at about 58 K). Thus, the temperature variation of the Hall coefficient for B is smaller than that of A, which implies that α for B may change in a small range within the variation range of α for A. The temperature dependence of the Hall coefficient for B can therefore be phenomenologically interpreted in terms of the smaller variation of α. On the other hand, the fact that the resistivity of B is much less affected by the transition is probably attributed to the transition for sample B sluggishly proceeding over some temperature range. This statement is consistent with the broad change of the Hall coefficient for B near the transition. If the transition would occur sharply enough, as observed for A, the transition should be reflected in the resistivity of B even with the large residual resistivity. Since the phonon scattering contribution near the transition temperature is several times larger than that of temperature-independent scatterings which cause the large residual resistivity, the change of phonon scattering due to the transition should affect the resistivity as observed for sample A. The broad transition for sample B implies that there may exist a certain kind of imperfection in the specimen such as the deviation of stoichiometry or other defects.

No sign of the structure change was observed in the previous resistivity data (*4*). It should be noted that the present value of resistivity at 55 K, 17 $\mu\Omega$ cm for sample A, is considerably smaller than that previously reported (450 $\mu\Omega$ cm) (*4*). Thus, such a small resistivity change as observed in the present resistivity at about 55 K would naturally be masked in the previous resistivity data. The resistivity ratio at 300 K and 5 K for sample A is 177, as mentioned above, and is probably larger than that inferred from Ref. (*4*), but of the same order as that reported for CuS specimens used in a superconductivity study (*6*). Furthermore, our results, that is, the slight decrease of resistivity associated with the transition is evidently observed for case A but less clearly for case B, are reproduced by other specimens for their respective cases. In any case, the Hall coefficients for both cases clearly reflect the phase transition.

The excellent metallicity and *p*-type conduction indicate that the conduction of CuS is not due to the narrow 3*d*· band of Cu but occurs mainly due to holes in a valence band derived principally from the 3*p* orbitals of sulfur, as already mentioned in the previous XPS study (*1*). The sulfur bonding in CuS must thus be considered.

In CuS, there exist two crystallographic sites of sulfur: one third of S are triangularly coordinated to Cu(1) in the *c* plane and linked to two Cu(2) atoms along the *c* axis, while two thirds of S form S–S bonding with a shorter bond length (2.07 Å) than that observed in pyrite (*9*). Each sulfur of the pair links to one Cu(2) atom. The valency of S–S pair in CuS_2 has been reported to be monovalent (*10*), while that in FeS_2 is commonly accepted to be divalent. Therefore, the formal charge of the S–S pair in CuS is considered to be either -1 or -2. In terms of the ionic model and the result of X-ray photoelectron spectroscopy (i.e., copper is monovalent), the bonding of CuS can be described as either $(Cu^{1+})_3S_2^{2-}S^{1-}$ or $(Cu^{1+})_3S_2^{1-}S^{2-}$. In either case, there exist one third of holes per formula unit in CuS. This is in good agreement with the carrier number obtained by the Hall effect experiment.

Acknowledgments

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