JOURNAL OF SOLID STATE CHEMISTRY **47**, 307–313 (1983)

Electron Transport and Magnetic Properties of Some Mixed-Valent Alkalithiocuprates

BIJOY PROSAD GHOSH, MUKTIMOY CHAUDHURY, AND K. NAG*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received August 16, 1982; in revised form December 2, 1982

Electrical transport properties of some two-dimensional isostructural compounds KCu_4S_3, $RbCu_4S_3$, and $CsCu_4S_3$ and a one dimensional conductor $Na_3Cu_4S_4$ have been investigated. Conductivities have been measured on pelletized materials in the temperature range 300 to 150 K. All of them behave as metallic conductors. The room temperature conductivities of these compounds are KCu_4S_3, 1600 Ω^{-1} cm^{-1}; $RbCu_4S_3$, 1400 Ω^{-1} cm^{-1}; $CsCu_4S_3$, 1250 Ω^{-1} cm^{-1}; $Na_3Cu_4S_4$, 700 Ω^{-1} cm^{-1}. The observed trend in conductivities among the isostructural compounds may be rationalized either on the basis of shortest Cu–Cu distances or on the carrier charge concentrations per unit volume. All of these compounds behave as Pauli paramagnetic materials.

Introduction

The relationship of structural properties in transition metal chalcogenides is a subject of interest to physicists and chemists. Considerable attention has been paid in determining electrical and magnetic properties of these materials (*1–5*). So far as copper chalcogenides are concerned, their electrical transport properties vary from semiconducting to metallic and magnetic properties vary from diamagnetism to temperature independent paramagnetism. Low T_c superconducting transitions have been reported for a number of copper pyrite dichalcogenides CuX_2 (X = S, Se, Te) (*6–8*).

About 30 years ago Rüdorff *et al.* (*9*) discovered a series of ternary sulfides of copper and alkali metals whose composition indicated formal mixed valence state of coppers. X-ray structural studies of the isotypic series KCu_4S_3 (*9, 10*), $RbCu_4S_3$ (*9*), and $CsCu_4S_3$ (*11*) have revealed that a crystallographic differentiation between copper(I) and copper(II) sites is not possible. These compounds are characterized by a layered structure in which the copper atoms occupy double layers of tetrahedral sites built up by sulfur atoms and these two layers are separated by another layer of alkalimetal atoms. Another ternary sulfide, $Na_3Cu_4S_4$ (*12*), contains copper–sulfur arrays that form one dimensional strands in which the copper atoms have coordination number three. The equivalence of copper atoms coupled with short Cu–Cu distances place these compounds in the class 3B of the Robin and Day classification of mixed-valence compounds (*13*), as a result they are expected to show metallic conductivity. However, recent X-ray photoelectron spectroscopic studies (XPS) on a number of copper sulfides, including KCu_4S_3 (*14*) and $Na_3Cu_4S_4$ (*15*), have demonstrated that in

---

* To whom correspondence should be addressed.

0022-4596/83 $3.00

all these compounds copper is present exclusively in monovalent state. It has been suggested (*14, 16*) that the deficit of electrons is present as holes in the sulfur $3p$ valence band giving rise to p-type metallic conduction and weak, essentially temperature independent paramagnetism.

In fact Rüdorff *et al.* (*9*) reported considerably high room temperature conductivities for KCu_4S_3 (40 $\Omega^{-1}cm^{-1}$) and $RbCu_4S_3$ (60 $\Omega^{-1}cm^{-1}$). During the course of this study Brown *et al.* (*10*) have investigated structure, electrical, and magnetic properties of KCu_4S_3. Their reported values for pressed pellets is 4100 $\Omega^{-1}cm^{-1}$, and for single crystals is 3000 $\Omega^{-1}cm^{-1}$ at 300 K. After the completion of this work we noted a recent publication by Peplinski *et al.* (*17*) in which they reported electrical transport properties of $Na_3Cu_4S_4$. The bulk conductivity reported for the pelletized specimen is 300 $\Omega^{-1}cm^{-1}$ at room temperature, whereas for single crystals $\sigma_{\parallel}$ is 15,000 $\Omega^{-1}cm^{-1}$. We report here the electrical and magnetic properties of KCu_4S_3, $RbCu_4S_3$, $CsCu_4S_3$, and $Na_3Cu_4S_4$.

Experimental

Preparation of Compounds

The methods for preparation of KCu_4S_3 (*9*), $RbCu_4S_3$ (*9*), $CsCu_4S_3$ (*11*), and $Na_3Cu_4S_4$ (*12*) are described in the literature. In obtaining these compounds some modification has been made of these procedures. $RbCu_4S_3$ was prepared essentially in the same way as described in the literature. A mixture of copper powder, sulfur powder, and alkali metal carbonates taken in a ratio of 1 : 6 : 6 was placed in a porcelain crucible and covered with a lid. This in turn was contained in two basins of increasing diameters equipped with snuggly fitted covers. The assembly was heated in an electric furnace in an atmosphere of nitrogen. The temperature and time periods for heating were KCu_4S_3: 800°C, 1 hr; $CsCu_4S_3$: 700°C, 1.5 hr; $Na_3Cu_4S_4$: 600°C, 1 hr. The melt was furnace cooled and then digested in a mixture of 1 : 1 ethanol–water bath. Crystals were collected by filtration, washed repeatedly with ethanol–water mixture, and finally with acetone.

The compounds were analyzed by decomposing with HNO_3–HCl mixture. Copper was estimated gravimetrically as CuSCN (*18*). Alkali metals were estimated gravimetrically as their sulfates (*18*) after electrolytic deposition of copper from a solution containing sulfuric acid (*18*). For estimation of sulfur the compounds were dissolved in a mixture of HNO_3, HCl and bromine, and the oxidized sulfur was gravimetrically estimated as $BaSO_4$ (*18*). Analytical data are provided in Table I.

Electrical Conductivity Measurement

Bulk conductivities of the specimens were measured in the form of pellets which were of 13.5 mm diameter and of about 2

TABLE I
ANALYTICAL DATA

Compound	% Alkali metal		% Copper		% Sulfur	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
KCu_4S_3	9.6	10.02	66.0	65.29	25.1	24.67
$RbCu_4S_3$	20.2	19.62	57.8	58.39	21.6	22.04
$CsCu_4S_3$	26.8	27.52	52.1	52.59	20.1	19.87
$Na_3Cu_4S_4$	15.7	15.28	55.8	56.31	28.9	28.41

mm thickness. Compaction of the materials were achieved by applying a pressure of 10 metric tons/cm^2. A linear four probe dc conductivity measurement technique due to Valdes (*19*) was adopted. A spring loaded cell holder made of teflon with stainless steel pressure contact probe was used for measurements. Conductivity measurements at subambient temperatures (up to 150 K) were made by inserting the sample holder in a locally fabricated cryostat. Temperature measurements were made with a calibrated copper-constantan thermocouple. Current was applied on the two terminal probes by a MP-1026A regulated current source unit (Mckee Pedersen Instruments, Calif.). The voltage drop at the two central probes was measured by a Leeds–Northup Type K-4 potentiometer in conjunction with a Keithley-155 microvoltmeter/null detector.

Magnetic Measurement

A PAR Model 155 vibrating sample magnetometer in combination with Walker/Magnion L-75 electromagnet and a PAR (Walker/Magnion) Power Supply Control unit was used for magnetic susceptibility measurements. The magnetic field was varied in the range 7.5–9.5 kOe. Calibration of the magnetometer was made with HgCo(SCN)$_4$. About 350 mg of powdered specimen contained in a screw-capped polyacrylate sample holder was used. Diamagnetic corrections were made with data available in literature (*20*).

Results and Discussion

From initial experiments it turned out that maintenance of an inert atmosphere and an overpressure of sulfur yields compounds of desired stoichiometry. The three crucible arrangement assembly has been useful in this respect. The purity of the compounds were checked by chemical analysis and also from powder diffraction data. In all cases compounds were obtained in crystalline form but they were not large enough for reliable single crystal transport property measurements. Ohm's law was veritifed for each specimen during conductivity measurement.

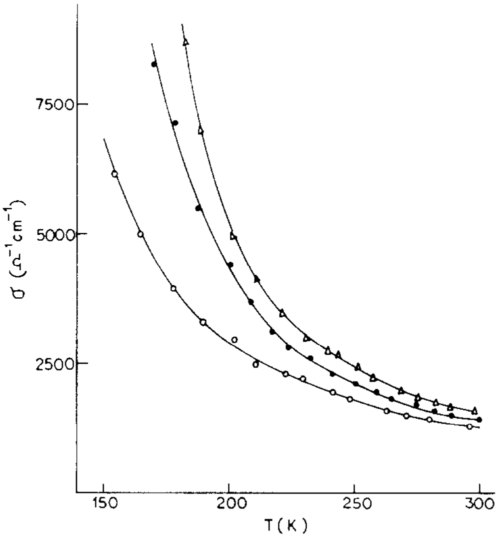

FIG. 1. Conductivities of M^ICu$_4$S$_3$ compounds as a function of temperature. △, KCu$_4$S$_3$; ●, RbCu$_4$S$_3$; ○, CsCu$_4$S$_3$.

Conductivities of KCu$_4$S$_3$,RbCu$_4$S$_3$, and CsCu$_4$S$_3$ as a function of temperture are shown in Fig. 1. The room temperature conductivity values for these compounds are KCu$_4$S$_3$: 1600 Ω^{-1} cm^{-1}; RbCu$_4$S$_3$: 1400 Ω^{-1} cm^{-1}; CsCu$_4$S$_3$: 1250 Ω^{-1} cm^{-1}. It may be noted that the conductivities of these materials increase rapidly with decrease in temperature. In Fig. 2 resistivities are plotted against temperature. In the case of simple metals resistivity is a linear function of temperature, whereas for molecular metals resistivity varies with square of temperature (*21*). Good straight line fits of ρ vs T in all three compounds clearly indicate their metallic behavior. The slopes of these lines being approximately parallel indicate a similar conduction mechanism in these compounds.

Rüdorff *et al.* (*9*) reported room tempera-

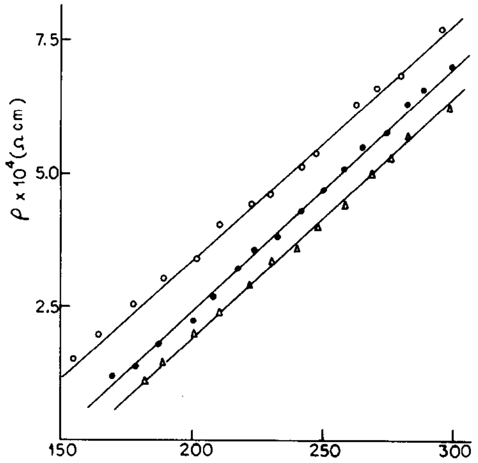

FIG. 2. Resistivities of $M^{I}Cu_4S_3$ compounds as a function of temperature. △, KCu_4S_3; ●, $RbCu_4S_3$; ○, $CsCu_4S_3$.

ture conductivities of 40 Ω^{-1} cm^{-1} for KCu_4S_3, and 60 Ω^{-1} cm^{-1} for $RbCu_4S_3$ in the form of pellets. Brown *et al.* (*10*) obtained an average value of $4.1 \pm 1.1 \times 10^3$ Ω^{-1} cm^{-1} for pressed pellets of KCu_4S_3, but the average value for the same material measured on single crystals was 3×10^3 Ω^{-1} cm^{-1}. The general relation between the average conductivity, $\langle\sigma\rangle$ and the conductivity, σ_i measured in a particular crystallographic axis is

$$\langle\sigma\rangle = \tfrac{1}{3}\sum_{i=1}^{3}\sigma_i. \qquad (1)$$

Therefore $\sigma_{\parallel}$ values of these two dimensional conductors would be considerably greater than bulk conductivities obtained with pelletized specimens. If our $\langle\sigma\rangle$ for KCu_4S_3, 1.6×10^3 Ω^{-1} cm^{-1} is compared with $\sigma_{\parallel}$, 3×10^3 Ω^{-1} cm^{-1} as reported by Brown *et al.* (*10*), a consistent relationship is obtained.

The metallic conductivity of these compounds may be thought to originate from the mixed-valence states of copper atoms. If the sulfur atoms are considered to be present as S^{2-} ion, $M^{I}Cu_4S_3$ may be formulated as $M^+Cu_3^+Cu^{2+}(S^{2-})_3$. However, the occurrence of mixed-valence states is not an essential criterion for metallic conductivity. For example, CuS_2, a copper(II) compound which constains S_2^{2-} anion (*7*), has a room temperature conductivity of 6.67×10^3 Ω^{-1}cm^{-1} (*6, 7*). Similar high room temperature conductivities are observed with apparently copper(I) sulfides, viz. Cu_2S (*22*), 10^2 Ω^{-1}cm^{-1}, and $BaCu_4S_3$ (*23*), 5 Ω^{-1}cm^{-1}. Another way to account for metallic conductivity is to invoke the criterion of critical internuclear distance of metal ions due to Goodenough (*24*). According to this model when metal–metal distance falls below a critical value, the interaction between metal atoms would cause collective electrons behavior to set in, as against localization. For a copper(II) sulfide this critical distance is estimated to be 3.1 Å (*10*), which is well above the copper–copper distances observed in these compounds (Table II). This model becomes inadequate in the case of CuS_2 where the metal atoms are too far apart ~4 Å (*7*), yet the material shows metallic conductivity.

The observed trend in conductivities of the three isostructural compounds at any particular temperature is $KCu_4S_3 > RbCu_4S_3 > CsCu_4S_3$. It may be noted from Table II that in these compounds there are four equivalent copper–copper distances of a given type which are short, and there is one of the longer type. The trend in the shorter copper–copper distances is $CsCu_4S_3 > RbCu_4S_3 > KCu_4S_3$. Thus, on the basis of extent of metal ion interactions (*13*) the observed trend in conductivities is in conformity with expectation.

In the light of recent XPS studies (*14, 15*) on binary and ternary copper sulfides the notion of mixed-valence copper, however, is no longer valid. Inasmuch as there is no evidence for the presence of copper(II) sites or intermediate oxidation states, the compounds MCu_4S_3 should be reformulated as $M^+Cu_4^+(S^{2-})_2S^-$, and $Na_3Cu_4S_4$, as

TABLE II

STRUCTURAL PARAMETERS, CONDUCTIVITIES AND MAGNETIC SUSCEPTIBILITIES OF $M^{I}Cu_4S_3$ COMPOUNDS

Compound	Lattice constant[a]	Cu–Cu distance (Å)	Carrier concentration (cm^{-3})	300 K	
				($\Omega^{-1}cm^{-1}$)	(emu/mole)
KCu_4S_3	$a = 3.899$ Å, $c = 9.262$ Å	2.757,[b] 2.970[c]	7.1×10^{-21}	1600	110×10^{-6}
$RbCu_4S_3$	$a = 3.920$ Å, $c = 9.41$ Å	2.78,[b] 2.98[c]	6.9×10^{-21}	1400	100×10^{-6}
$CsCu_4S_3$	$a = 3.975$ Å, $c = 9.689$ Å	2.81,[b] 2.922[c]	6.5×10^{-21}	1250	60×10^{-6}

[a] Tetragonal unit cell.
[b] Four equivalent bonds of a given type.
[c] Single bond.

$Na_3^+Cu_4^+(S^{2-})_3S^-$, according to the scheme of Folmer and Jellinek (*14*). In these compounds the Fermi level falls within the sulfur $3p$ band which is placed higher than copper $3d$ level. It should be noted, however, that they may still be regarded as class 3B mixed-valence sulfur compounds (*13*) since S^{2-} and S^- sites are not distinguishible in XPS spectra and there is likelihood of a valence fluctuation (with a frequency below 10^{16} sec^{-1}) involving all the sulfur atoms (*14*).

The conductivity is related to the mobility by

$$\langle\sigma\rangle = ne\,\langle\mu\rangle \qquad \ldots \quad (2)$$

where n is carrier concentration, and e the charge of carrier. For isostructural compounds it is reasonable to believe that the average mobility of the carrier will be same. This means that conductivity will depend primarily on carrier concentration. $M^{I}Cu_4S_3$ compounds contain a single hole per molecule, and there is one formula unit per unit cell. The carrier concentrations (Table II) of these compounds follow the trend observed in conductivities.

The room temperature susceptibilities of these compounds (Table II) indicate their Pauli paramagnetic behavior. For a free electron gas, the susceptibility (*25*) is

$$\chi = \frac{N\mu_B^2}{\epsilon_F} \qquad \ldots \quad (3)$$

where N is the number of atoms per unit volume, μ_B is Bohr magneton, an ϵ_F is the Fermi energy. The relation between the Fermi energy and the carrier concentration (N/V) is

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \qquad \ldots \quad (4)$$

where m is the mass of electron. From Eqs. (3) and (4) the susceptibility should be inversely proportional to carrier concentration. Contrary to the expected trend we find that the susceptibility values have decreased in the order of $KCu_4S_3 \sim RbCu_4S_3 > CsCu_4S_3$. It is not clear at this stage how this anamolous trend arises, due to uncertainty in the magnetization measurements.

From structural point of view $Na_3Cu_4S_4$ (*11*) should act as an one-dimensional conductor. Figure 3 shows the increase in con-

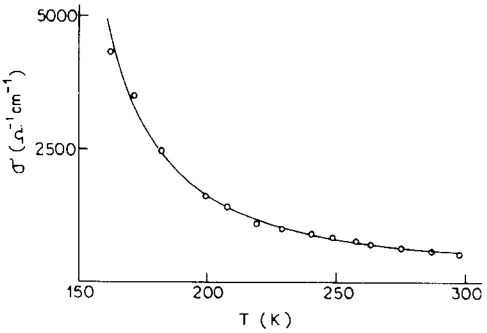

FIG. 3. Variation in conductivities of $Na_3Cu_4S_4$ with temperature.

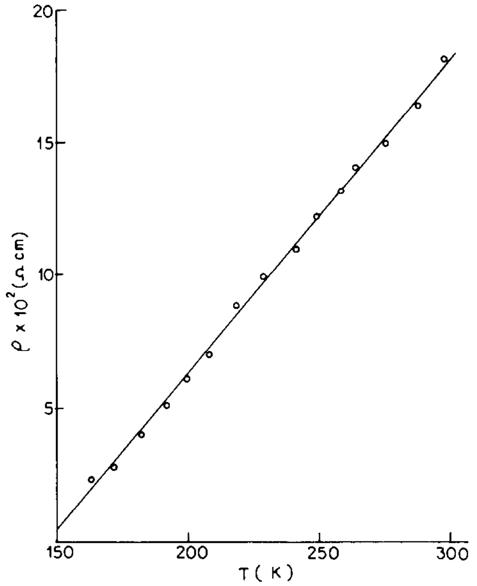

FIG. 4. Variation in resistivities of $Na_3Cu_4S_4$ with temperature.

ductivity of the pressed material with decrease in temperature. In Fig. 4 the straight line relationship between resistivity and temperature again shows its metallic behavior. The room temperature conductivity of $Na_3Cu_4S_4$, $7 \times 10^2\ \Omega^{-1}cm^{-1}$, is considerably lower as compared to the other two-dimensional conductors. It may be pointed out that Peplinski et al. (*17*) obtained somewhat lower conductivities 290–350 $\Omega^{-1}cm^{-1}$ at room temperature for pelletized specimens. Their conductivity values parallel to the needle axis, which corresponds to the direction of the one-dimensional $[Cu_4S_4^{3-}]_\infty$ column, vary in the range 12,500–18,700 $\Omega^{-1}cm^{-1}$ at 300 K. The room temperature susceptibility of this compound, 170×10^{-6} emu/mole, as measured by us is slightly greater than the reported value, 150×10^{-6} emu/mole (*17*).

Acknowledgments

Thanks are due to Council of Scientific and Industrial Research, India, for funding and for awarding a research fellowship to one of us (B.P.G.). Our thanks are also due to Dr. Ajoy K. Ray for his help in constructing the equipment.

References

1. C. N. R. RAO AND K. P. R. PISHARODY, *Progr. Solid State Chem.* **10,** 207 (1976).

2. W. BRONGER, *Angew. Chem. Int. Ed. Engl.* **20,** 52 (1981).

3. F. HULLIGER, *Struct. Bonding* **4,** 83 (1968).

4. J. A. WILSON AND A. D. YOFFE, *Adv. Phys.* **18,** 193 (1969).

5. F. HULLIGER, *in* "Physics and Chemistry of Materials with Layered Structure" (F. Levy, Ed.), Vol. 5, Reidel, Dordrecht (1976).

6. T. A. BITHER, C. J. PREWITT, J. L. GILSON, P. E. BIERSTEDT, R. B. FILLIPEN, AND H. S. YOUNG, *Solid State Commun.* **5,** 331 (1971).

7. T. A. BITHER, R. J. BOUCHARD, W. H. CLOUD, P. C. DONOTRUE, AND W. J. SIEMENS, *Inorg. Chem.* **7,** 2208 (1968).

8. R. A. MUNSON, W. DESORBO, AND J. S. KOUVEL, *J. Chem. Phys.* **47,** 1769 (1967).

9. W. RÜDORFF, H. G. SCHWARZ, AND M. WALTER, *Z. Anorg. Allg. Chem.* **269,** 141 (1952).

10. D. B. BROWN, J. A. ZUBIETA, P. A. VELLA, J. T. WROBELSKI, T. WATT, W. E. HATFIELD, AND P. DAY, *Inorg. Chem.* **19,** 1945 (1980).

11. C. BURSCHKA, *Z. Anorg. Allgem. Chem.* **463,** 65 (1980).

12. C. BURSCHKA, *Z. Naturforsch. Teil B* **34,** 396 (1979).

13. M. B. ROBIN AND P. DAY, *Adv. Inorg. Chem. Radiochem.* **10,** 248 (1967).

14. J. C. W. FOLMER AND F. JELLINEK, *J. Less-Common Met.* **76,** 153 (1980).

15. H. RUPP AND U. WESER, *Bioinorg. Chem.* **6,** 45 (1976).

16. F. JELLINEK, "MTP Int. Rev. Sc. Inorg. Chem. Ser. One," Vol. 5, p. 339, Butterworths, London (1972).

17. Z. PEPLINSKI, D. B. BROWN, T. WATT, W. E. HATFIELD, AND P. DAY, *Inorg. Chem.* **21,** 1752 (1982).

18. A. I. VOGAL, "Quantitative Inorganic Analysis," 3rd ed., ELBS–Longman, London (1962).

19. L. B. VALDES, *Proc. IRE* **42,** 420 (1954).

20. B. N. FIGGIS, *in* "Techniques of Inorganic Chemistry," Vol. 4, p. 137, Interscience, New York (1965).

21. C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, *J. Amer. Chem. Soc.* **102,** 6702 (1980).
22. G. B. Abullaer, Z. A. Aliyarova, E. H. Zamanova, and G. A. Asaclov, *Phys. Status Solidi* **26,** 65 (1968).
23. Z. Elizer and H. Steinfink, *Mater. Res. Bull.* **11,** 385 (1976).
24. J. B. Goodenough, "Magnetism and Chemical Bond," Interscience, New York (1963).
25. C. Kittel, "Introduction to Solid State Physics," 5th ed. Wiley–Eastern Ltd, New Delhi (1976).