Title: Transport and Magnetic Studies of New Mixed-Valence Compounds: K3Cu8Se6, KCu3Se2, K3Cu8Te6 and BaCuS3-x

Author: I. Jacyna-Onyszkiewicz, M. Sidowski, W. Starodub, Alicja Ratuszna, S. Robaszkiewicz

Citation style: Jacyna-Onyszkiewicz I., Sidowski M., Starodub W., Ratuszna Alicja, Robaszkiewicz S. (2000). Transport and Magnetic Studies of New Mixed-Valence Compounds: K3Cu8Se6, KCu3Se2, K3Cu8Te6 and BaCuS3-x. "Acta Physica Polonica. A" (Vol. 91, nr 2 (1997), s. 405-408).

Vol. 91 (1997) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the European Conference "Physics of Magnetism 96", Poznań 1996

TRANSPORT AND MAGNETIC STUDIES OF NEW MIXED-VALENCE COMPOUNDS: $K_3Cu_8Se_6$, KCu_3Se_2, $K_3Cu_8Te_6$ AND $BaCuS_{3-x}$

I. Jacyna-Onyszkiewicz[a], M. Sidowski[a], W. Starodub[b], A. Ratuszna[c] and S. Robaszkiewicz[a]

[a]Institute of Physics, A. Mickiewicz University
Umultowska 85, 61-614 Poznań, Poland
[b]Department of Physics, Kharkov State University, Kharkov, Ukraine
[c]Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

New mixed-valent copper chalcogenides $BaCuS_{3-x}$ and $K_3Cu_8X_6$ with X = Se or Te and KCu_3Se_2, with chemical patterns corresponding to the recently investigated $K_3Cu_8S_6$ and KCu_3S_2, were synthesized. For these new samples the results of resistivity and magnetic susceptibility measurements are presented. For $BaCuS_{3-x}$, $K_3Cu_8Se_6$ and KCu_3Se_2 the metal–insulator transition is observed with the low temperature phase being metallic, which is untypical, whereas $K_3Cu_8Te_6$ is a metal in the investigated temperature range. The temperature dependence of magnetic susceptibility of the studied samples testifies to their diamagnetic or weakly paramagnetic behaviour.

PACS numbers: 71.30.+h, 75.20.–g

1. Introduction

The alkali metal-copper-chalcogenides family includes both binary and ternary members which belong to two main categories: the valence-precise and the mixed-valent ones. The mixed-valent compounds have been of particular interest and subject to numerous physical investigations because they exhibit such properties as metallic conductivity, superconductivity and charge-density waves (CDW) [1,2].

In this paper we report the synthesis, electric and magnetic properties of new mixed-valent ternary copper-chalcogenide phases: $BaCuS_{3-x}$, $K_3Cu_8Se_6$, KCu_3Se_2, and $K_3Cu_8Te_6$. The physical properties of these compounds are compared to those of the already known $K_3Cu_8S_6$ and KCu_3S_2 compounds.

2. Results and discussion

Samples. The compounds $K_3Cu_8Se_6$ and KCu_3Se_2 were synthesized from K, Cu and CuSe mixtures at the molar ratios 3:2:6 (batch I) and 1:1:2 (batch II), respectively. The mixtures were transferred to quartz tubes and evacuated (2×10^{-4} Pa). The batches (I and II) were heated in a multistep process to 1150 K and 1180 K, respectively, then sintered for 24 h period (I) and 8 h period (II).

This procedure was followed by multistep cooling to room temperature. The $K_3Cu_8Te_6$ specimen was synthesized in the reaction K, Cu and Te, at the molar ratio 3:8:6 at 1270 K for 2.5 h period. The sample of nominal composition $BaCuS_3$ was prepared from BaS, CuS and S mixture with the [Ba]:[Cu]:[S] molar ratio in the mixture equal to 1:1:3. Preparative conditions for the synthesis for this sample were following: temperature of isothermal sintering 1373 K and sintering time 14 h. All samples were obtained in the form of black chunky crystallites of metallic sheen.

Charge-transport measurements. DC electrical resistivity measurements were carried out in the usual four-probe geometry. Temperature measurements from 12 to 340 K were performed in a closed helium cryostat (CS-202 System APD). The $\rho(T)$ data were obtained from the computer-automated system.

Magnetic studies. The magnetic response of the studied compounds were measured over the 4–300 K temperature range using a cryogenically equipped Faraday balance. Magnetic susceptibility as a function of field strength (0–1.5 T) at a few temperatures was first investigated to determine if the samples had experienced saturation of their magnetic signal. We report the susceptibility data for which diamagnetic corrections for the constituent atoms were not made.

Crystallographic studies. The obtained samples were examined by X-ray diffraction (XRD) method for phase identification. Accurate d_{hkl} spacings were obtained from the powder patterns recorded on a Siemens-5000-computer-controlled powder diffractometer with Ni-filtered Cu K_α radiation. Structural details of the studied samples are given in Table.

Results of ρ vs. T measurements of the studied samples for cooling cycles are displayed in Figs. 1–4. The dependences reveal a few anomalies. Below 100 K, an insulator–metal transition was observed for $K_3Cu_8Se_6$ sample (Fig. 1). Surprisingly, the low-temperature phase was metallic while the high-temperature one was semiconducting, which is unusual for metal–insulator transitions [3]. Moreover, in the semiconducting phase of this substance we observed a multistep temperature dependence of resistivity which indicates the occurrence of two unidentified phase transitions. The multi-stepwise character of $\rho(T)$ can be partially attributed to a specific microstructure of the samples. The effect of temperature hysteresis was not observed only for the high temperature transition. A similar temperature behaviour of resistivity was detected for KCu_3Se_2 (see Fig. 4), whereas $K_3Cu_8Te_6$ was found to exhibit purely metallic behaviour (Fig. 2). Measurements of resistivity of $BaCuS_{3-x}$ compound, Fig. 3, reveal the occurrence of a metal-to-semiconductor transition at about 270 K with metallic phase stable at low temperatures.

The obtained results of $\chi(T)$ measurements proved that the studied mixed-valent materials do not show any magnetic ordering in the range 4–300 K. According to the results of the magnetic studies they behave as diamagnetics or very weak paramagnetics (for example Fig. 4). However, the metallic-to-semiconductor behaviour was not supported by magnetic measurements. The representative physical data for the studied samples are collected in Table. In this table we also give the data about the recently investigated copper-chalcogenides: $K_3Cu_8S_6$ and KCu_3S_2, for comparison.

The studies reported in this paper were stimulated by the finding that the

TABLE

The representative results of physical investigations for several chosen copper chalcogenides.

Compound (Reference)	Crystal structure	Resistivity $\rho(t)$	Magnetic susceptibility $\chi(T)$
KCu_3S_2 $K^{1+}Cu_3^{1+}(S^{2-})_2$ [4,5]	monoclinic, space group $C2$, layer-type structure	semiconductor	paramagnetic (Curie–Weiss law)
$K_3Cu_8S_6$ $K_3^{1+}Cu_8^{1+}(S^{2-})_5S^{1-}$ [1,4]	monoclinic, space group $C2$, layer-type structure	metal with CDW instability, $\rho_{290K} = 5 \times 10^{-4}\ \Omega\cdot cm$	CDW instability at 155 K, Pauli–Landau and Van-Vleck paramagnetic contributions, $\chi_{300K} = -0.12 \times 10^{-6} emu/g$
KCu_3Se_2 $K^{1+}Cu_3^{1+}(Se^{2-})_2$ this work	new structure type of low symmetry, not isotypic with structure of KCu_3S_2 type	metal–insulator transition (165 K) $\rho_{165K}/\rho_{15K} = 1.5$, unidentified transition at ≈ 240 K and 300 K $\rho_{290K} = 5.6 \times 10^{-5}\ \Omega\cdot cm$	diamagnetic $\chi_{280K} = -3.1 \times 10^{-7} cm^3/g$
$K_3Cu_8Se_6$ $K_3^{1+}Cu_8^{1+}(Se^{2-})_5Se^{1-}$ this work	new structure type of low symmetry, not isotypic with structure of $K_3Cu_8S_6$ type	metal–insulator transition (95 K) $\rho_{80K}/\rho_{20K} = 1.2$ unidentified transition at ≈ 180 K and 305 K $\rho_{290K} = 2 \times 10^{-4}\ \Omega\cdot cm$	diamagnetic $\chi_{280K} = -3.1 \times 10^{-7} cm^3/g$
$K_3Cu_8Te_6$ $K_3^{1+}Cu_8^{1+}(Te^{2-})_5Te^{1-}$ this work	new structure type	metallic (12–340 K) behaviour $\rho_{290K}/\rho_{14K} = 5.6$	diamagnetic or weakly paramagnetic
$BaCuS_{3-x}$ $Ba^{2+}Cu^{1+}S^{2-}(S^{1-})_2$ this work	monoclinic $a \doteq 9.324$ Å $b = 4.775$ Å $c = 8.990$ Å $\beta = 118.60°$	metal–insulator transition (95 K) $\rho_{270K}/\rho_{50K} = 1.5$	diamagnetic $\chi_{280K} = -2.3 \times 10^{-7} cm^3/g$

layered $K_3Cu_8S_6$ exhibited a CDW phenomenon [1,2,4] which is typical of low-dimensional metals. The $K_3Cu_8S_6$ compound is the first inorganic material where the charge carriers and the subsequent CDW phenomenon have significantly *p* character (i.e. the metallic conductivity via holes in the sulphur valence band). On the basis of these data we speculated on the existence of a CDW instability in $K_3Cu_8Se_6$ and $K_3Cu_8Te_6$ whose chemical patterns correspond to those of the previously investigated chalcogenide. We found metal–insulator transition in $BaCuS_{3-x}$, $K_3Cu_8Se_6$ and KCu_3Se_2 while $K_3Cu_8Te_6$ remains a metallic phase. The observed complex character of the temperature dependence of resistivity for $K_3Cu_8Se_6$ and KCu_3Se_2 is similar to that discovered in $K_3Cu_8S_6$ which suggests

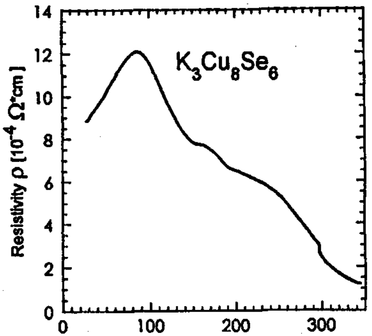

Fig. 1

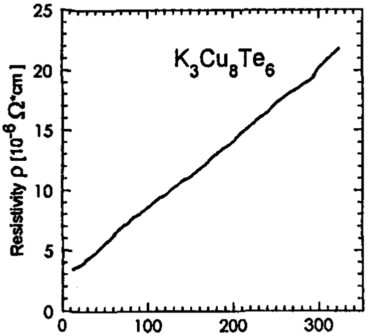

Fig. 2

Fig. 1. Electrical resistivity data as a function of temperature for a sample $K_3Cu_8Se_6$.
Fig. 2. Electrical resistivity data as a function of temperature for a sample $K_3Cu_8Te_6$.

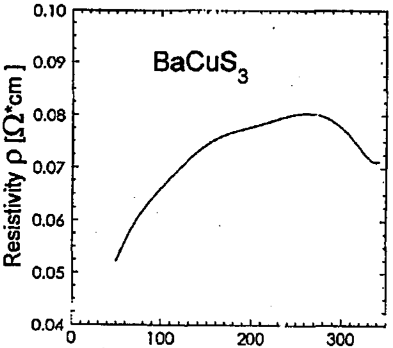

Fig. 3

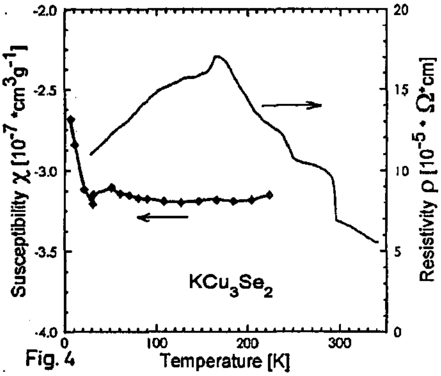

Fig. 4

Fig. 3. Electrical resistivity data as a function of temperature for a sample $BaCuS_{3-x}$.
Fig. 4 Temperature dependence of the electric resistivity and the magnetic susceptibility for KCu_3Se_2.

a possibility of CDW transitions also in these systems. However, further detailed structural and magnetic studies are necessary for definite resolution of this problem.

We are grateful to the Committee for Scientific Research (Poland, project no. 2 P302 038 07) for financial support. We would like to thank Dr. J. Dubowik for the help in susceptibility measurements.

References

[1] R.M. Fleming, L.W. ter Haar, F.J. Di Salvo, *Phys. Rev. B* **35**, 5388 (1987).

[2] M. Zimpel, S. Robaszkiewicz, *Acta Magn.* **VIII**, 35 (1991).

[3] F.J. Di Salvo, in: *Electron–Phonon Interactions and Phase Transitions*, Ed. T. Riste, Plenum Press, New York 1977, p. 107.

[4] L.W. ter Haar, F.J. Di Salvo, H.E. Bair, R.M. Fleming, J.V. Waszczak, *Phys. Rev. B* **35**, 1932 (1987).

[5] C. Burschka, W. Bronger, *Z. Nat.forsch.* **326**, 11 (1977).