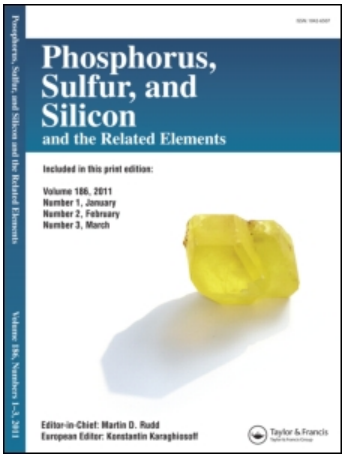

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ELECTRONIC PROPERTIES OF LOW-DIMENSIONAL TERNARY COPPER CHALCOGENIDES A-Cu-X (A=Na,K,Rb,Cs; X=S,Se)

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Abstract Electronic properties of $Na_3Cu_4S_4$, $K_3Cu_8S_6$, $Rb_3Cu_8S_6$, $Rb_3Cu_8Se_6$, KCu_3S_2, and $CsCu_3S_2$ are discussed on the basis of the measurements of resistivity and thermopower.

INTRODUCTION

Recently, many phases of ternary A-Cu-X (A=Na,K,Rb,Cs; X=S,Se) system have been discovered. Most of them have low-dimensional structures (sheets or chains) composed of copper and chalcogen separated by alkali metal. However, physical properties of this A-Cu-X system have not yet been studied systematically. In order to elucidate the relation between physical properties and the characteristic low-dimensional structure, we have investigated the electronic properties of the title compounds.

EXPERIMENTAL

All samples were prepared from the mixture of alkali carbonate, copper, and sulfur or selenium by keeping at 800-900°C in N_2 atmosphere. Resistivity measurements were performed for single crystals by four probe method. Thermopower measurements were carried out for single crystals by a conventional method.

RESULTS AND DISCUSSION

$Na_3Cu_4S_4$

The crystals of $Na_3Cu_4S_4$ are blue metallic lustrous needles. As shown in Fig.1a, $Na_3Cu_4S_4$ is composed of $[Cu_4S_4]$ chains separated by sodium atoms.[1] So, its structure has been regarded as one-dimensional. Z. Peplinski et al.[2] have already reported that its resistivity is metallic between 15K and 300K. We are interested in the fact that it has

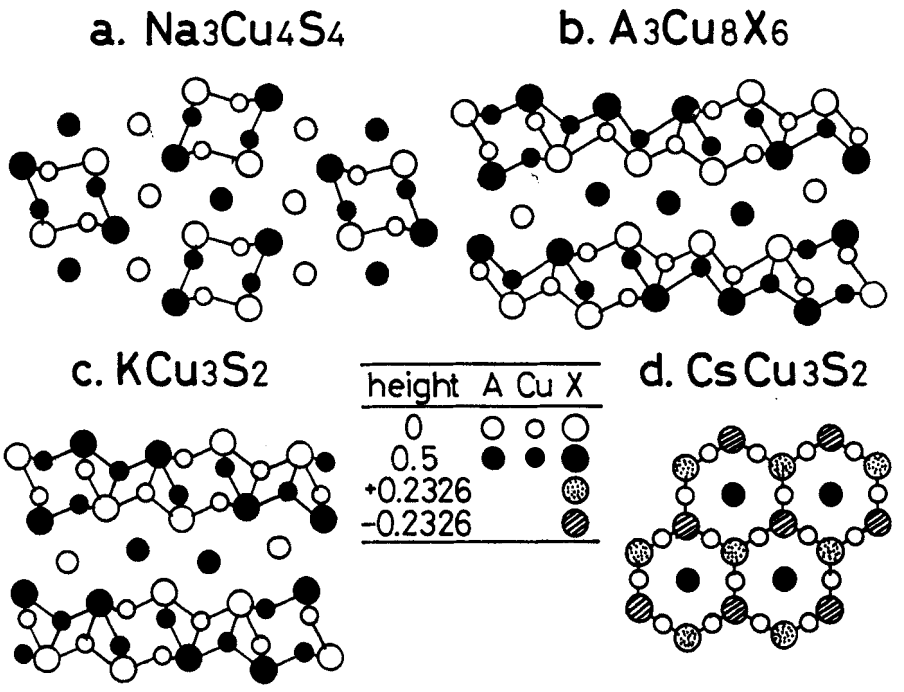

FIGURE 1 The crystal structures of A-Cu-X compounds.

no charge-density wave (CDW) transitions in spite of the one-dimensional structure. Therefore, we measured the resistivity of $Na_3Cu_4S_4$ down to 1.4K. As shown in Fig.2, the resistivity is metallic down to 1.4K. The residual resistivity ratio (R.R.R) is about 300. Recently, M.-H. Whangbo et al.[3] has discussed the reason why $Na_3Cu_4S_4$ has no CDW transition, by performing a tight-binding band calculation based on the extended Hückel method. They have attributed the reason to the stability of $[Cu_4S_4]$ chain against the distortion.

$K_3Cu_8S_6$

$K_3Cu_8S_6$, $Rb_3Cu_8S_6$, $Rb_3Cu_8Se_6$, and $Cs_3Cu_8Se_6$ are isostructural, and they have a structure intermediate between one and two-dimensional, which is shown in Fig.1b.[4] It is composed of layers separated by potassium atoms. The layers include $[Cu_4S_4]$ chain structures. In addition, there are columns composed of edge-shared CuS_4 tetrahedrons between the $[Cu_4S_4]$

chains. The crystals are blue-black metallic lustrous needles. Recently, CDW transitions have been found in this compound.[5] As shown in Fig.3, the resistivity shows two phase transitions at T_1 (153K) and at T_2 (55K). Between T_1 and T_2, an incommensurate superstructure appears and below T_2 a commensurate one appears. Therefore, the transition at T_1 is an incommensurate CDW transition. However, the origin of the transition at T_2 is not clear. It may by either a lock-in transition of the incommensurate CDW or some structural phase transition independent of the CDW.

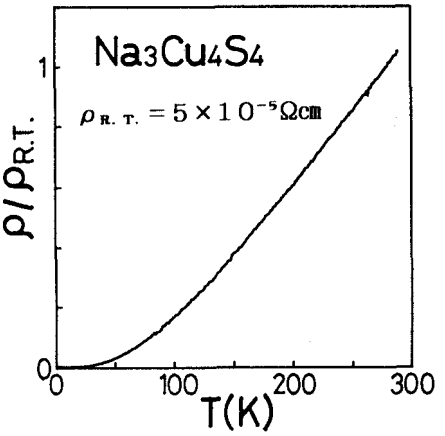

FIGURE 2 The resistivity of $Na_3Cu_4S_4$.

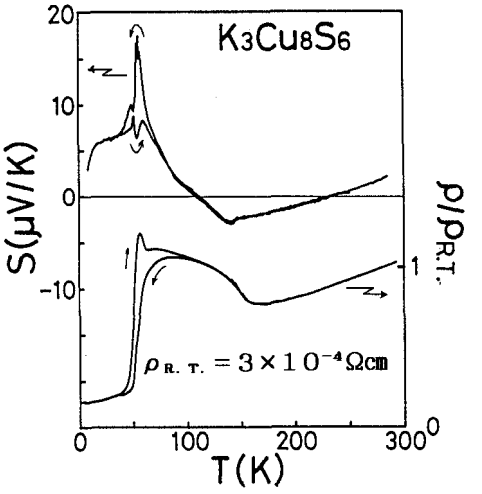

FIGURE 3 The resistivity and the thermopower of $K_3Cu_8S_6$.

We carried out the measurements of thermopower in order to investigate the carriers. Generally, the thermopower of a simple p-type metal is positive and proportional to temperature. However, as shown in Fig.3, our result is too complicated for a p-type metal. Thermopower is barely positive at room temperature. On cooling, it decreases linearly down to 140K, crossing the zero line at 230K. This suggests the coexistence of both p-type and n-type carriers. At 140K, the thermopower begins to increase suddenly, and continue to increase down to 55K, crossing the zero line at 110K. Around 55K, the thermopower is accompanied by a hysteresis and its behavior is more complicated than that of the resistivity. This anomalous behavior corresponds to that of the resistivity around T_2. The behavior of the resistivity shows that a part of carriers disappears owing to the formation of the CDW. Therefore, the increase in the ther-

mopower below 140K means that the carriers extinguished by the CDW are n-type. This indicates that the n-type carriers have more low-dimensional Fermi surface than that of the p-type carriers.

$Rb_3Cu_8S_6$

As shown in Fig.4, the resistivity decreases down to 120K, increases between 120K and 50K, and decreases again below 50K with decreasing temperature. The thermopower is also shown in Fig.4. Its behavior suggests that n-type carriers disappear below 120K, as well as in $K_3Cu_8S_6$. An incommensurate superstructure was observed by our preliminary x-ray scattering measurement between 95K and 15K. Therefore, the transition at about 120K is a CDW transition corresponding to the T_1 transition of $K_3Cu_8S_6$. However, there is no T_2 transition because the superstructure does not change and there is no thermal hysteresis. The resumption of metallic behavior below 50K is probably attributed to the incomplete destruction of carriers, as seen in $NbSe_3$.[6]

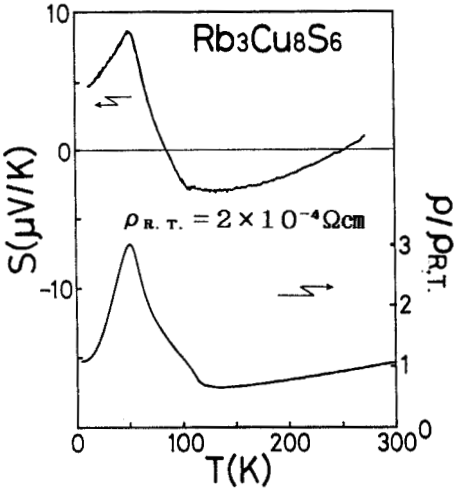

FIGURE 4 The resistivity and the thermopower of $Rb_3Cu_8S_6$.

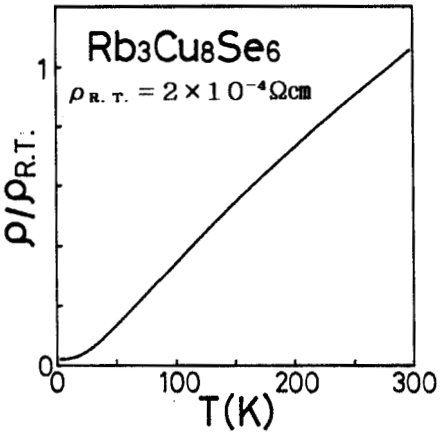

FIGURE 5 The resistivity of $Rb_3Cu_8Se_6$.

$Rb_3Cu_8Se_6$

As shown in Fig.5, the resistivity is of normal metal and shows no CDW transition. This suggests that the chalcogen substitution has larger effect on conduction electrons than the alkali substitution.

KCu_3S_2

As shown in Fig.1c, the crystal structure of KCu_3S_2 resembles that of $K_3Cu_8S_6$.[7] The crystals of KCu_3S_2 are blue-black metallic lustrous needles. As shown in Fig.6, the resistivity shows a metallic behavior in spite of its compositional ratio which suggests insulating electronic

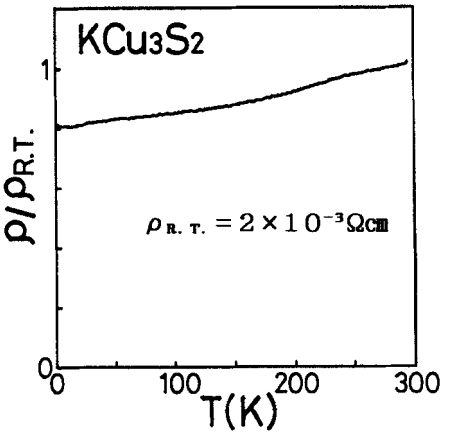

FIGURE 6 The resistivity of KCu_3S_2

state. This indicates that there is no energy gap between the 3p band of S and the 4s band of Cu and that the 4s band spreads enough to overlap with the 3p band. It is worth noting that there are zigzag chain structures of copper in the columns of edge-shared CuS_4 tetrahedrons. The bond length between the copper atoms in these columns is 2.63Å, comparable to that of copper metal (2.55Å). Therefore, these chains can form a wide 4s band. Very small R.R.R. suggests that the carrier density is dependent on temperature due to poor overlap of the 3p band and the 4s band. So, we regard KCu_3S_2 as a semimetal denoted as $K^+Cu^{(1-2x)+}{}_3S^{(2-3x)-}{}_2$. The reason why KCu_3S_2 has no CDW transition in spite of its low-dimensional structure may be attributed to the low carrier density.

$CsCu_3S_2$

As shown in Fig.1d, the crystal structure[8] of $CsCu_3S_2$ is quite different from that of KCu_3S_2 in spite of their same compositional ratios. The crystal is a colorless transparent plate. As expected from its composition and color, $CsCu_3S_2$ is a poor electric conductor ($\rho > 10^3 \Omega$cm).

However, we found that its color easily changes into black by some chemical treatments. For example, by soaking in ammonium solution, it becomes blue black metallic lustrous without any change in shape. By soaking, the resistivity decreases drastically ($\rho < 10^{-2}\Omega$cm). Our preliminary EPMA result shows the compositional ratio of ammonium-soaked crystal is $Cs_{0.04}Cu_2S_{0.9}$. This chemical treatment can be a new method of getting new phase of conductive copper sulfide and the detailed study is in progress.

CONCLUSION

In order to investigate the electronic properties of A-Cu-X compounds systematically, we carried out the measurements of the resistivity and the thermopower for $Na_3Cu_4S_4$, $K_3Cu_8S_6$, $Rb_3Cu_8S_6$, $Rb_3Cu_8Se_6$, KCu_3S_2, and $CsCu_3S_2$. The results show that the variety of their electronic properties reflects their characteristic low-dimensional structures and their compositional ratios.

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