

# Vacancy Ordering as the Cause for the Electrical Resistivity Anomalies and Superlattice Modulations in $ACu_{7-x}S_4$ ( $A = Tl, K, Rb$ )

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Received March 10, 1997; in revised form May 30, 1997; accepted June 2, 1997

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**The electronic structure of  $KCu_7S_4$  was calculated using the extended Hückel tight binding method, and the origin of the resistivity anomalies and the superlattice reflections of  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) was probed. The present work shows that  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) can be metallic only for  $x > 0$  and that the superlattice modulations of  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) are caused by the vacancy ordering in the Cu(2) atom sites. The resistivity anomalies of  $ACu_{7-x}S_4$  are explained in terms of the vacancy ordering in the Cu(2)-Cu(2) chains.** © 1997 Academic Press

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## 1. INTRODUCTION

Several ternary copper chalcogenides are metallic and exhibit resistivity anomalies and superlattice modulations.  $Na_3Cu_4S_4$  consists of isolated  $Cu_4S_4$  columns (1) which are made up of 3-coordinate copper atoms (Fig. 1a). Such  $Cu_4S_4$  columns are fused with quadruple copper-sulfur tetrahedral chains in  $K_3Cu_8S_6$  (Fig. 1b) (2) and with double copper-sulfur tetrahedral chains in  $ACu_7S_4$  (Fig. 1c) (3-5). The Cu sites of the double tetrahedral chains in  $ACu_7S_4$  are one-fourth empty. (Hereafter the Cu atoms of  $Cu_4S_4$  columns are referred to as the Cu(1) atoms, and those of the tetrahedral chains as the Cu(2) atoms.) Both  $K_3Cu_8S_6$  (6, 7) and  $ACu_7S_4$  (4, 5) exhibit resistivity anomalies and superlattice modulations, whereas  $Na_3Cu_4S_4$  does not (8) despite its one-dimensional (1D) metallic character (9).

Metallic copper sulfides are expected to have a mixed-valence representation for the oxidation states of their sulfur atoms (10) because the copper atoms of these compounds are in the oxidation state  $Cu^+$  ( $d^{10}$ ) (11). Stoichiometric ternary sulfides  $ACu_7S_4$  ( $A = Tl, K, Rb$ ) are described by  $A^+(Cu^+)_7(S^{2-})_4$ , which implies the absence of any partially filled bands. Thus stoichiometric  $ACu_7S_4$  phases cannot be metallic, as pointed out earlier (10). The resistivity versus temperature plots for  $ACu_7S_4$  ( $A = Tl, K, Rb$ ) reported by Ohtani *et al.* (4, 5) exhibit a maximum as a function of temperature. This can be explained if there occurs an additional vacancy in the Cu(2) sites so that the true formula is  $ACu_{7-x}S_4$ . That this is indeed the case was recently shown by Hwu *et al.* (12), who prepared both stoichiometric and nonstoichiometric  $KCu_{7-x}S_4$  ( $x = 0.0, 0.18, 0.34$ ) using electrochemical synthesis and characterized their crystal structures and electrical properties. In the present work, we calculate the electronic structures of  $KCu_{7-x}S_4$  using the extended Hückel tight binding (EHTB) method (13) and analyze the origin of the electrical resistivity anomalies and superlattice reflections of  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) reported by Ohtani *et al.* (5).

## 2. EXPERIMENTAL

Samples of  $ACu_{7-x}S_4$  were synthesized by employing an electrochemical reaction in a nonaqueous solvent. A typical reaction was carried out from an equimolar mixture of  $K_2S$  and  $CuCl$  in ethylenediamine solution. The phase nucleation was initiated by an electrocrystallization process on the copper anode at 110°C. This reaction temperature is much

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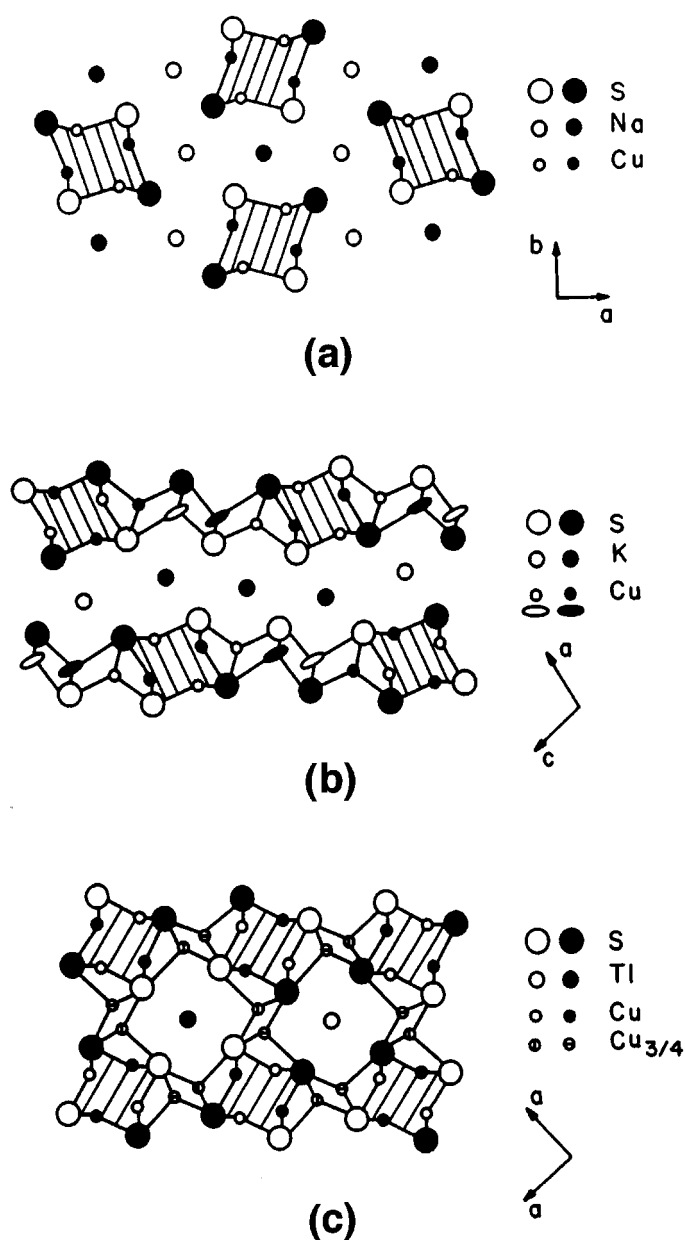


FIG. 1. Projection views along the  $\text{Cu}_4\text{S}_4$  column (indicated by shading) direction of (a)  $\text{Na}_3\text{Cu}_4\text{S}_4$ , (b)  $\text{K}_3\text{Cu}_8\text{S}_6$ , and (c)  $\text{TiCu}_7\text{S}_4$ .

lower than  $800^\circ\text{C}$  employed for the solid state synthesis by Ohtani *et al.* (4, 5). By controlling the electrochemical potential and the concentration of electrolytes, the  $\text{KCu}_{7-x}\text{S}_4$  phase can be synthesized for the first time with a specific copper stoichiometry. The details of the synthesis and structure characterization are reported elsewhere (12).

### 3. ELECTRONIC BAND STRUCTURE OF $\text{KCu}_7\text{S}_4$

To calculate the electronic structure of  $\text{KCu}_7\text{S}_4$ , it is necessary to adopt an ideal structure in which the vacancies

of the  $\text{Cu}(2)$  sites are ordered. A formula unit  $\text{KCu}_7\text{S}_4$  contains one  $\text{Cu}_4\text{S}_4$  column and two double copper-sulfur tetrahedral chains, so it is convenient to represent  $\text{KCu}_7\text{S}_4$  as  $\text{K}(\text{Cu}_4\text{S}_4)(\text{Cu}_{1.5})_2$ . A unit cell of  $\text{KCu}_7\text{S}_4$  has two formula units,  $\text{K}_2(\text{Cu}_4\text{S}_4)_2(\text{Cu}_{1.5})_4$  and therefore has four zigzag  $\text{Cu}(2)$ - $\text{Cu}(2)$  chains. In a single  $\text{Cu}(2)$ - $\text{Cu}(2)$  chain, the occupancy of each  $\text{Cu}(2)$  site is  $\frac{3}{4}$  at room temperature (Fig. 2a). Figure 2b shows the simplest possible ordered structure of this chain, where a vacancy occurs in every fourth  $\text{Cu}(2)$  site. The repeat distance of this chain along the  $c$ -direction is twice that of the average chain structure of Fig. 2a. Thus from the viewpoint of electronic band structure calculations based on the ordered vacancy model of Fig. 2b, the unit cell is given by  $\text{K}_4(\text{Cu}_4\text{S}_4)_4(\text{Cu}_3\blacklozenge)_4$ , where  $\blacklozenge$  represents a vacancy site. In order to make the vacancy ordering as isotropic as possible, we assign all different heights (along the  $c$ -axis direction) for the vacant sites in the four  $\text{Cu}(2)$ - $\text{Cu}(2)$  chains of a unit cell.

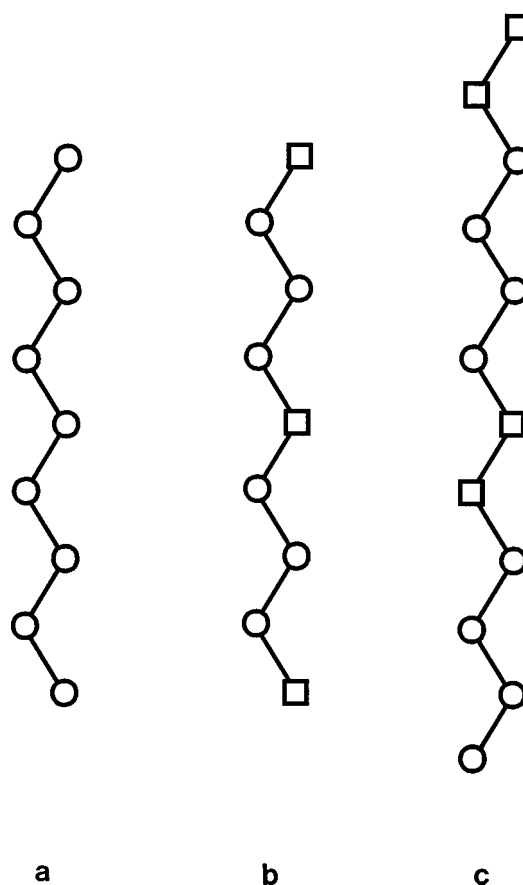


FIG. 2. Zigzag  $\text{Cu}(2)$ - $\text{Cu}(2)$  chains of  $\text{ACu}_{7-x}\text{S}_4$  and their vacancy ordering: (a) the average structure in which the occupation number of each  $\text{Cu}(2)$  site is  $\frac{3}{4}$ ; (b) an ordered structure in which one vacancy occurs in every fourth  $\text{Cu}(2)$  site; (c) an ordered structure in which two consecutive vacant sites alternate with four consecutive occupied sites.

Results of our EHTB calculations for the ordered structure of  $KCu_7S_4$  described above are summarized in terms of the projected density of states for the Cu(1), Cu(2), and S atoms (Fig. 3a). It is clear from Fig. 3a that stoichiometric  $KCu_7S_4$  does not possess a partially filled band and cannot be metallic. A zoomed-in view of the top portion of the highest occupied bands is presented in Fig. 3b, which shows that the orbitals of the Cu(2) atoms do not contribute much to the top portion of the bands. Consequently, the transport properties of  $KCu_{7-x}S_4$  ( $x = 0.18, 0.34$ ) can be discussed using the electronic band structure calculated for  $KCu_7S_4$  by simply lowering the Fermi level accordingly (i.e., 0.18 and 0.34 electrons per formula unit for  $x = 0.18$  and 0.34, respectively), because the Fermi levels for  $x = 0.18$  and 0.34 lie in the energy region of the small peak (above  $-11.4$  eV in Fig. 3b) where Cu(2) contributions are small. The Fermi surfaces of  $KCu_{7-x}S_4$  calculated for  $x = 0.18$  and 0.34 using the above rigid band approximation are shown in Figs. 4a and 4b, respectively. These Fermi surfaces are essentially given by spheres overlapping along the  $\Gamma$ - $X$  and  $\Gamma$ - $Y$  directions. The size of the Fermi sphere, and hence the carrier density of  $KCu_{7-x}S_4$ , increases with increasing  $x$ .

#### 4. RESISTIVITY ANOMALY AND SUPERLATTICE REFLECTIONS OF $ACu_{7-x}S_4$

Figure 5 shows the electrical resistance of  $KCu_{7-x}S_4$  ( $x = 0.0, 0.18, 0.34$ ) measured as a function of temperature (12). The  $KCu_7S_4$  sample is not metallic, as expected. The  $KCu_{6.82}S_4$  sample shows a resistivity hump around 190 K and is metallic below  $\sim 190$  K. The  $KCu_{6.66}S_4$  sample is metallic at all temperatures and exhibits a sharp drop in resistivity between  $\sim 225$  and  $\sim 180$  K. At any given temperature, the resistance of  $KCu_{7-x}S_4$  decreases with increasing  $x$ . The resistivity plots for the “ $ACu_7S_4$ ” ( $A = Tl, K, Rb$ ) samples reported by Ohtani *et al.* (5) show resistivity humps (Fig. 6). Thus the true composition of these samples must have been  $ACu_{7-x}S_4$  ( $x > 0$ ). At any temperature below 250 K the resistivity of the  $ACu_{7-x}S_4$  samples increases in the order  $KCu_{7-x}S_4 < TlCu_{7-x}S_4 < RbCu_{7-x}S_4$ . This can be explained if the  $x$  values increase in the order  $KCu_{7-x}S_4 > TlCu_{7-x}S_4 > RbCu_{7-x}S_4$ .

The electron diffraction study of  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) by Ohtani *et al.* (5) show that all  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) samples exhibit satellite spots described by the vector  $q_1 = c^*/2$  below  $\sim 250$  K. Both  $KCu_{7-x}S_4$  and  $TlCu_{7-x}S_4$  show additional superlattice spots described by the vectors  $q_2(KCu_{7-x}S_4) = \pm (a^* + b^*)/3 + 2c^*/3$  and  $q_2(TlCu_{7-x}S_4) = (a^* + b^*)/2 + c^*/3$ , which are believed to occur below the temperature where the resistivity maximum occurs (i.e.,  $\sim 180$  and  $\sim 160$  K for  $KCu_{7-x}S_4$  and  $TlCu_{7-x}S_4$ , respectively). For  $RbCu_{7-x}S_4$  additional superlattice spots were not observed down to  $\sim 30$  K. These superlattice modula-

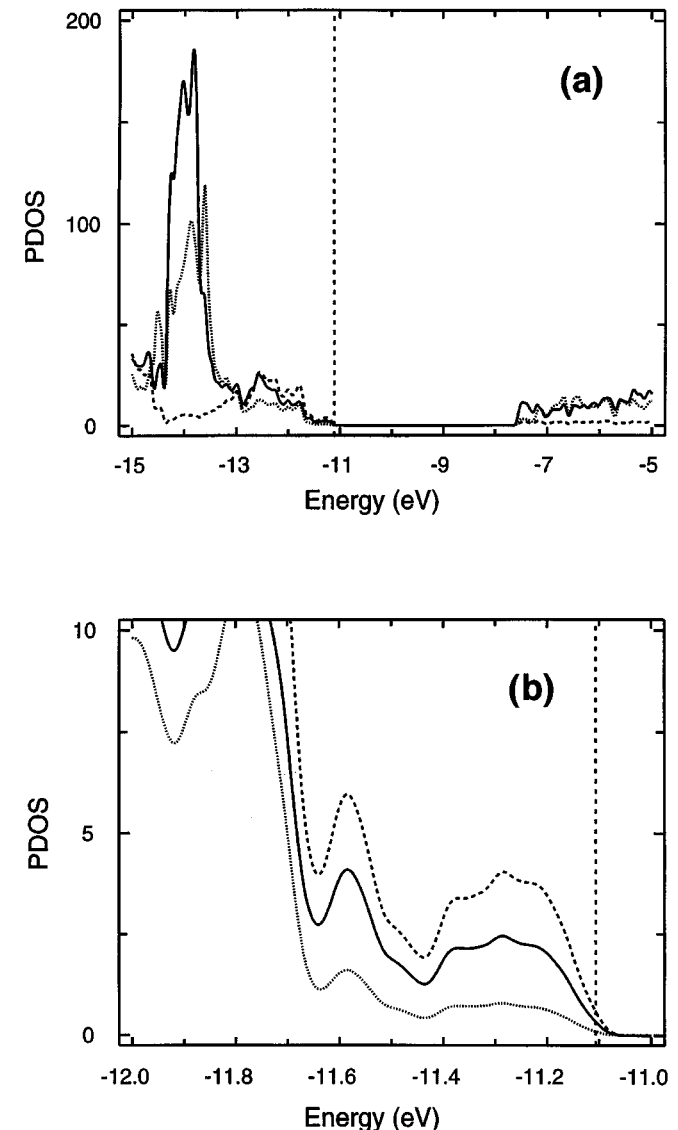
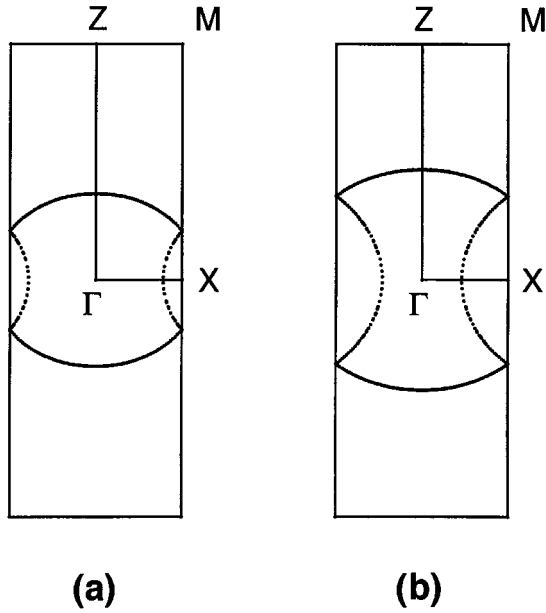


FIG. 3. (a) Plots of projected density of states (PDOS) calculated for the Cu(1) (solid line), Cu(2) (dotted line), and S (dashed line) of  $KCu_7S_4$ , where the dashed vertical line refers to the Fermi level. (b) Zoomed-in view of Fig. 3a in the region of the top portion of the highest occupied bands.

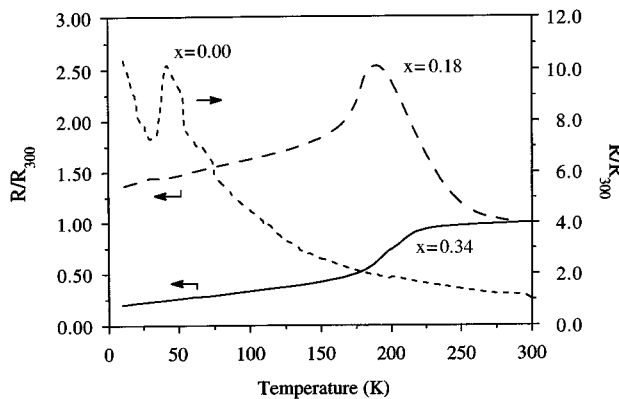
tions are not charge density waves (CDWs) expected for 1D metallic systems because  $ACu_{7-x}S_4$  becomes metallic at the end of the two superlattice modulations and because the Fermi surface of  $ACu_{7-x}S_4$  is spherical and hence cannot cause a CDW instability.

These superlattice spots can be explained in terms of vacancy ordering in the Cu(2) sites. The  $c$ -axis doubling given by the vector  $q_1$  means that the vacancies of the Cu(2)-Cu(2) zigzag chains order as depicted in Fig. 2b. Statistically, it is probable that the  $q_1$ -ordering starts at various different locations of each chain. The superlattice



**FIG. 4.** Fermi surface of  $\text{KCu}_7\text{S}_4$  associated with the three partially filled bands of Fig. 3: (a) for  $x = 0.18$  and (b)  $x = 0.34$ . Here  $\Gamma = (0, 0, 0)$ ,  $X = (a^*/2, 0, 0)$ ,  $Z = (0, 0, c^*/2)$ , and  $M = (a^*/2, 0, c^*/2)$ .

spots of  $q_1$  imply an ordering not only along the  $c$ -axis but also along the  $a$ - and  $b$ -directions. Thus there should occur slabs which have the  $q_1$ -ordering (Fig. 7). In the regions between these  $q_1$ -ordered slabs, the extent of the  $\text{Cu}(2)$  atom vacancy is larger than  $1/4$  and can be close to  $1/3$ . If so, these regions can undergo a vacancy ordering that triples the  $c$ -axis length. An ordered example of such a chain is presented in Fig. 2c. Such an ordering should be responsible for the  $q_2$  ordering found for  $\text{KCu}_{7-x}\text{S}_4$  and  $\text{TiCu}_{7-x}\text{S}_4$ , which triples the  $c$ -axis length. With decreasing  $x$ , the amount of the  $q_1$ -ordered regions increases while decreasing that of  $q_2$ -ordered regions. This would make it difficult to detect the

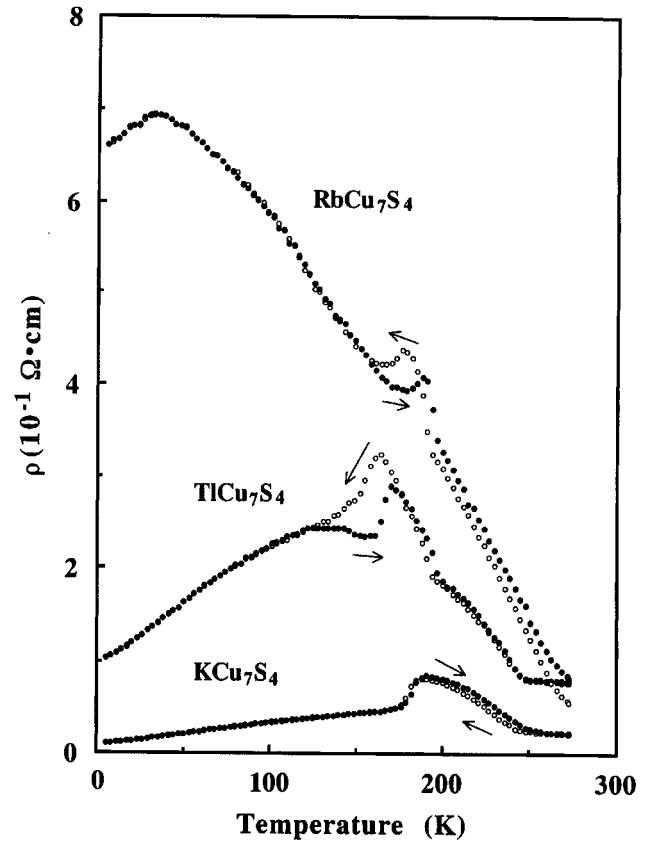


**FIG. 5.** Relative electrical resistance of  $\text{KCu}_7\text{S}_4$  (dotted line),  $\text{KCu}_{7.68}\text{S}_4$  (dashed line), and  $\text{KCu}_{6.66}\text{S}_4$  (solid line) as a function of temperature.

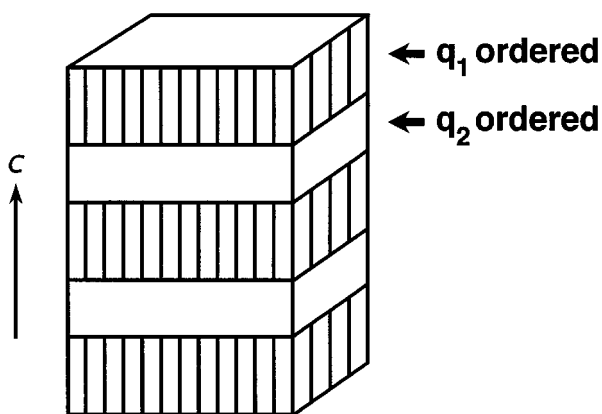
$q_2$ -ordering as  $x$  approaches zero. It may have been the case in the Ohtani *et al.*'s experiment for  $\text{RbCu}_{7-x}\text{S}_4$ .

It is of interest to examine how the resistivity humps in Figs. 5 and 6 can be understood in terms of the vacancy ordering model discussed above. As noted earlier, the Fermi sphere of  $\text{ACu}_{7-x}\text{S}_4$  increases its size with increasing  $x$  (see Figs. 4a and 4b). A decrease in carrier density increases the resistivity of a system and makes the system more susceptible to random potentials. The latter promote trapping of current carriers, thereby suppressing metallic character. Both  $\text{KCu}_{7-x}\text{S}_4$  and  $\text{TiCu}_{7-x}\text{S}_4$  would not become metallic above their  $q_2$ -ordering temperatures because, unless the vacant sites of the regions between the  $q_1$ -ordered slabs are ordered, the associated random potentials will trap current carriers (14). The occurrence of metallic behavior in  $\text{RbCu}_{7-x}\text{S}_4$  below  $\sim 30$  K can be explained if the regions between the  $q_1$ -ordered slabs become ordered below that temperature.

The above reasoning leads to an interesting prediction for  $\text{KCu}_{6.66}\text{S}_4$ . It is metallic at all temperatures and undergoes a sharp resistance drop around 200 K. The latter can be explained if the vacant sites of the  $\text{Cu}(2)$ - $\text{Cu}(2)$  chains order completely below at  $\sim 200$  K.  $\text{KCu}_{6.66}\text{S}_4$  can be written as



**FIG. 6.** Electrical resistivity of  $\text{ACu}_{7-x}\text{S}_4$  ( $A = \text{Ti, K, Rb}$ ) as a function of temperature (adapted from the work of Ohtani *et al.* (5)).



**FIG. 7.** Schematic diagram showing the occurrence of  $q_1$ -ordered slabs in  $ACu_{7-x}S_4$ , which are indicated by shading. The unshaded regions undergo a  $q_2$ -ordering.

$A(Cu_4S_4)(Cu_{1.33})_2$ , which shows that each  $Cu(2)$ - $Cu(2)$  chain has one vacancy for every three  $Cu(2)$  sites. Therefore,  $KCu_{6.66}S_4$  is expected to exhibit superlattice modulations characterized by the vector  $c^*/3$  below  $\sim 200$  K. The poor metallic behavior of  $KCu_{6.66}S_4$  above  $\sim 200$  K may be caused by the high mobility of the  $Cu^+$  ions in the  $Cu(2)$ - $Cu(2)$  chains.

## 5. CONCLUDING REMARKS

The present work shows that  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) can be metallic only for  $x > 0$  and that the superlattice modulations of  $ACu_{7-x}S_4$  ( $A = Tl, K, Rb$ ) are not caused by a CDW instability but by the vacancy ordering in the  $Cu(2)$  atom sites. The resistivity anomalies of  $ACu_{7-x}S_4$  are

explained in terms of the vacancy ordering in the  $Cu(2)$ - $Cu(2)$  chains.

## ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences, under Grant DE-FG05-86ER45259. Work at The Catholic University of Korea was supported by Grant C044677-I and by Grant BSRI-96-3421 from Ministry of Education. Acknowledgment is also made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research (S.J.H.).

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