Unusual physical properties of $KCu_{7-x}S_4$ at diffusive one-dimensional ordering transitions

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Single crystals of quasi-one-dimensional sulfides $KCu_{7-x}S_4$ with $x = 0.00$, 0.12, and 0.34 were prepared by electrochemical methods. Temperature-dependent properties of resistance, thermal conductivity, thermoelectric power, and heat capacity C_P were studied on single-crystal samples. These measurements show several anomalies which we associate with phase transitions, with the transition temperatures and physical properties depending strongly on x. Most interestingly, measurements of C_P with an ac technique show very unusual hysteresis and frequency dependence. The present work indicates that these phase transitions are due to vacancy ordering involving Cu^+-ion diffusion along the Cu(2)-Cu(2) zigzag chains. [S0163-1829(98)02006-2]

I. INTRODUCTION

Quasi-one-dimensional (Q1D) metals exhibit a number of interesting phenomena such as charge-density waves (CDW), spin-density waves (SDW), and superconductivity.[1] The Q1D sulfides $ACu_7S_4 (A = Tl, K, Rb)$ recently prepared by Ohtani *et al.* are metallic or semiconducting around room temperature and show phase transitions in both transport and thermodynamic measurements below room temperature.[2] Electron diffraction measurements of KCu_7S_4 showed two superstructures, one below 250 K with wave vector $\mathbf{q}_1 = \frac{1}{2}\mathbf{c}^*$ and the other below 180 K with $\mathbf{q}_2 = \frac{1}{3}(\mathbf{a}^* + \mathbf{b}^*) + \frac{2}{3}\mathbf{c}^*$.[3] These phase transitions were postulated to be CDW's.[2] However, this was questioned[4] because the stoichiometric ACu_7S_4 phase cannot be a metal according to the oxidation state $(A^+)(Cu^+)_7(S^{2-})_4$, which suggests that ACu_7S_4 has no partially filled bands. For the as-grown material to be metallic, its true formula was suggested to be nonstoichiometric (e.g., $ACu_{7-x}S_4$),[4] since the top portion of the valence band becomes partially empty in such a case. This is indeed the case: $TlCu_{7-x}S_4$ (Ref. 5) and $KCu_{7-x}S_4$ (Ref. 6) are found to be semiconducting when $x = 0$, and metallic when $x > 0$. A recent electronic band structure study shows that the Fermi surface of $ACu_{7-x}S_4$ is spherical and therefore lacks Q1D character.[6] Thus it was concluded that the resistivity anomalies and the superlattice modulations of $ACu_{7-x}S_4$ are not caused by a CDW instability.[6] Structurally, there are two kinds of Cu sites in $KCu_{7-x}S_4$, i.e., Cu(1) and Cu(2).[4] As shown in Fig. 1, the Cu(1) atoms are located at the trigonal planar sites of the Cu_4S_4 columns running

along the **c** axis. The Cu(2) atoms, located at the tetrahedral sites between adjacent Cu_4S_4 columns, form Cu(2)-Cu(2) zigzag chains along the **c** axis. Each Cu(1) site is fully occupied, while the occupancy of each Cu(2) site is $(3-x)/4$ in $ACu_{7-x}S_4$.[3,6,7] It was proposed that the resistivity anomalies and superlattice modulations of $ACu_{7-x}S_4$ are caused by an ordering of the vacancies in the Cu(2)-Cu(2) zigzag chains.[4,7]

An electrochemical synthetic procedure was employed to prepare single crystals of $KCu_{7-x}S_4$ with $x = 0.00$, 0.12, and 0.34 at low temperature.[7] This is to our knowledge the first electrochemistry synthesis of a conducting inorganic solid in a nonaqueous solvent. In the present work, resistance R, thermal conductivity κ, thermoelectric power S, and heat capacity C_P (measured with both differential scanning calo-
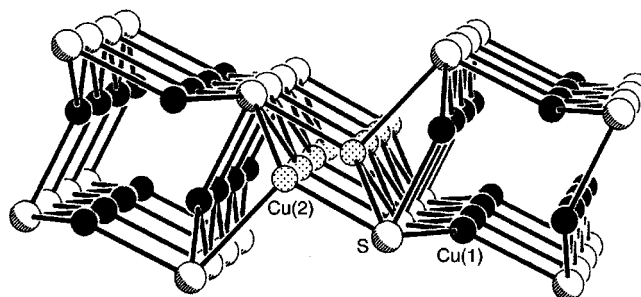

FIG. 1. Partial structure of the $KCu_{7-x}S_4$ phase viewed down along the needle axis. The Cu_4S_4 column is made of three-coordinated copper Cu(1) and bridging sulfur. Two adjacent columns are interconnected by tetrahedrally coordinated cations Cu(2).

rimetry and ac calorimetry) of single crystals of $KCu_{7-x}S_4$ ($x = 0.00, 0.12, 0.34$) were measured as a function of temperature. These measurements show several sharp anomalies associated with phase transitions, at temperatures which depend on x. In particular, the ac heat capacities show hysteresis and frequency dependence, in apparent violation of thermodynamic principles. To explain these anomalous behaviors, we considered a model in which the phase transitions are caused by an ordering of the vacancies in the Cu(2)-Cu(2) zigzag chains.

II. EXPERIMENTS

A. Sample preparation, structure, and x-ray study

The synthesis was carried out in a two-electrode cell with an equimolar mixture of K_2S_n and CuCl in ethylenediamine solution. Whisker-shaped single crystals as long as two centimeters were grown on the Cu anode by an electrocrystallization process in as little as four hours at 110°C. Nonstoichiometric $KCu_{7-x}S_4(0 < x < 0.34)$ can be prepared by adjusting the concentration of electrolyte and the electropotential. The cell constants vary linearly as a function of x based on single-crystal x-ray refinements. The value x was estimated by interpolation of the cell volume vs x plot.[8] The preferential crystal growth direction is along the crystallographic **c** axis. Electrochemical synthesis has advantages over the conventional solid state method in that it produces single crystals at a lower reaction temperature in a shorter time. The synthetic details are reported elsewhere.[8]

The crystal structure of the $KCu_{7-x}S_4$ series adopts the $(NH_4)Cu_7S_4$ structure.[9] The unit cell is body-centered tetragonal at room temperature and contains two formula units with $I4/m$ symmetry. Single-crystal x-ray studies of $KCu_{7-x}S_4$ show that the nonstoichiometry originates from extended Cu vacancies occurring in the Cu(2)-Cu(2) zigzag chains, which gives rise to the general formula $K[Cu_4S_4]Cu_{3-x}$.[7] In the Cu(2)-Cu(2) zigzag chains there is, on average, one vacancy for every four Cu(2) atom positions for the $x = 0$ phase ($KCu_{7.0}S_4$), and two vacancies for every six Cu(2) atom positions for the $x = 0.34$ phase ($KCu_{6.66}S_4$). Possible vacancy arrangements in the Cu(2)-Cu(2) zigzag chains of $KCu_{7-x}S_4$ are illustrated in Fig. 2: the average disordered structure in Fig. 2(a), a **c**-axis doubling structure for $x = 0$ in Fig. 2(b), and a **c**-axis tripling structure for $x = 0.34$ in Fig. 2(c). Structural studies at various temperatures were done on our samples with a Scintag XDS 2000 $\theta - \theta$ powder diffractometer with a hi-low temperature chamber. A tetragonal to monoclinic ($T \rightarrow M$) phase transition was found for $KCu_{7-x}S_4(x = 0.12, 0.34)$ between 185 and 195 K. No other superstructures were observed down to 150 K. No $T \rightarrow M$ phase transition was found for $KCu_{7.0}S_4$, which exhibits a **c**-axis doubling at room temperature. The crystallographic and structure information is summarized in Table I.

B. Electrical resistance

Electrical resistivity measurements were carried out for 4 K $< T <$ 350 K using a conventional four-probe method on single crystals. Electrical contacts were made by first evaporating four indium pads on the sample, spaced along the longest dimension (**c** axis) of the sample, and then applying
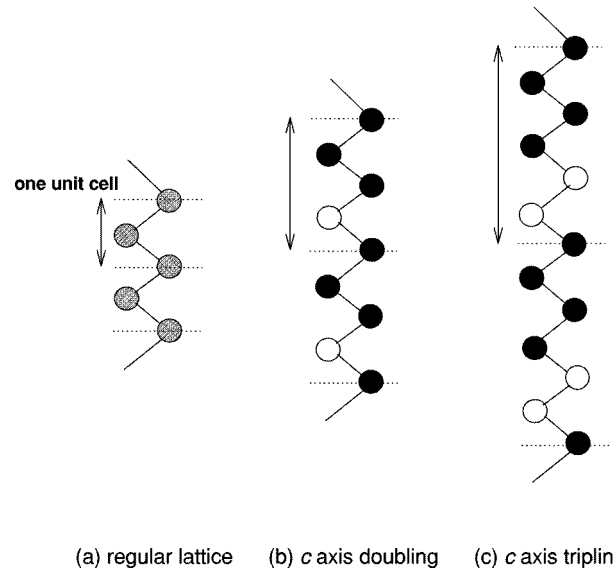

(a) regular lattice   (b) *c* axis doubling   (c) *c* axis tripling

FIG. 2. Zigzag Cu(2)-Cu(2) chains of $KCu_{7-x}S_4$ showing vacancy orderings. (a) The average structure in which all sites have the site occupancy of 0.75. (b) An ordered structure for the case of one vacancy in every four Cu(2) sites. (c) An ordered structure for the case of one vacancy in every three Cu(2) sites.

silver paint. A stable contact resistance of ~ 5 Ω was obtained. The contact resistance of a direct silver paint contact often became quite large after several hours. This has also been observed for single crystals of another ternary copper chalcogenide, $K_3Cu_8S_6$, and was attributed to $Ag^+ \rightarrow Cu^+$ ion exchange.[10] The room temperature resistance was about 5 Ω for nonstoichiometric samples ($x = 0.12, 0.34$), and about 500 Ω for stoichiometric samples ($x = 0.0$). From the typical sample cross section of 50 μm$\times$5 μm and the distance between voltage contacts of 1 mm, it is estimated that the room temperature resistivity along the **c** axis is about 100 $\mu\Omega$ cm for the nonstoichiometric phases, and 10 mΩ cm for the stoichiometric phase. This estimation can be off by at least a factor of 2, due to the uncertainty in the sample thickness.

C. Thermal conductivity

The thermal conductivity κ along the **c** axis was measured from 100 to 290 K by the classic longitudinal method with Nb as a standard in series with the sample, as described elsewhere.[11] Nb was chosen in place of an alloy for reproducibility, low κ, and small temperature dependence compared with other pure metals. At all temperatures, κ has at least the same quantitative uncertainty as ρ, again due to the uncertainty in the sample size. Above 200 K it is likely that κ has a considerable error due to radiation losses, which can quantitatively alter the slope of the κ-versus-T curve but is unlikely to add slope changes such as those seen at our transitions. We believe the data are qualitatively correct across the measurement range, but are most reliable at lower temperatures.

D. Thermoelectric power

The temperature dependence of the Seebeck coefficient S along the **c** direction was measured on single crystals in the

TABLE I. Crystallographic and physical information for $KCu_{7-x}S_4(x=0.00, 0.12, 0.34)$.

Chemical formula	$KCu_{7.0}S_4$	$KCu_{6.88}S_4$	$KCu_{6.66}S_4$
Formula weight (g/mol)	612.5	604.5	590.7
Space group	P4/n	I4/m	I4/m
c-axis doubling	Yes	No	No
Tetragonal to monoclinic transition around 190 K	No	Yes	Yes
a (Å)	10.177	10.176	10.179
c (Å)	7.722	3.834	3.790
T_{C1} (K)	280	200	210
T_{C2} (K)	180	182	?

range 80 K$<T<300$ K. Because $KCu_{7-x}S_4$ is quite brittle, most samples broke by thermal contraction during the first cooling if the ends of the sample were fixed to different thermal baths. For this reason, we fixed only one end of sample to a controlled thermal bath. The other end was suspended freely in vacuum, except for an electrical (and not-very-good thermal) contact made by connecting a fine silver wire from the free end of the sample to the other thermal bath. For the same reason, some measurements of resistance were also performed with all four leads on the sample suspended. ΔT between the two thermal baths was $1–2$ K during the measurements. Since ΔT between the thermal baths does not correspond to ΔT between the two ends of sample, our measurements of S are only qualitative. Nevertheless, the sign of S and the qualitative T dependence of S are expected to be valid. The contribution of the copper leads to the measured S was not subtracted, so that the reported S is relative to that of copper.

E. Heat capacity

1. Differential scanning calorimetry (DSC)

DSC measurements with samples in both loose needle and pressed pellet forms were performed with a Perkin-Elmer DSC7 system, with a precision of 3%.[12] DSC measurements are very sensitive to latent heat, but require a mass (on the order of 10 mg) that is much larger than the mass of a single one of our samples ($\sim 20 \mu$g). The only value of x that had enough material for DSC measurements was $x=0.34$. Figure 3 shows the differential heat flow measured for the pressed pellet with a sweep rate 15 K/min (converted to an effective specific heat[12]). The transition width for the pellet sample is considerably broader than that for a bunch of needles, presumably due to strains frozen into the pellet.

2. ac calorimetry

Much more precise (but less accurate) data were obtained on single crystals of all three phases with ac calorimetry, using chopped light as a source of heat.[13] The average (T_{dc}) and oscillating (T_{ac}) temperatures of the sample were measured with a very fine (25 or 12.5 μm diameter) chromel/constantan thermocouple. The sample was supported in a helium exchange gas cryostat by the thermocouple leads. The crystals investigated have typical dimensions of 30μm$\times 5 \mu$m$\times 2$ mm with masses m ranging from ~ 10 to $\sim 20 \mu$g. At least two samples for each composition were examined to check reproducibility.

In the absence of latent heat, and for one-dimensional (1D) heat flow (heat transport only across the sample thickness), the temperature oscillation T_{ac} at a chopping frequency ω is related to the total heat capacity C (i.e., the heat capacity of the sample plus the addendum[13]) by

$$T_{ac}(\omega)=2P/[\pi\omega CD(\omega)], \qquad (1)$$

with $D(\omega)=[1+(\omega\tau_2)^2+(1/\omega\tau_1)^2+6.32\tau_2/\tau_1]^{1/2}$. Here P is the absorbed optical power, and τ_1 and τ_2 are the external and internal time constants, respectively. Since the absorbed optical power P is not known, we only determine relative values of C. The addendum, which is made up of the part of the thermocouple that participates in the temperature oscillation plus a small amount of silver paint used as glue to attach the thermocouple to the sample, is not small compared with the sample in these experiments. Appropriate chopping frequencies were found by measuring the frequency dependence of T_{ac} to determine τ_1 and τ_2 at a few temperatures. Under the condition $\tau_2\ll 1/\omega\ll\tau_1$, C is inversely proportional to ΔT_{ac} because $D(\omega)\approx 1$. Generally, chopping frequencies of $1–6$ Hz satisfied these inequalities for those $KCu_{7-x}S_4$ samples at room temperature and lower temperatures. However, no frequency would satisfy the inequality

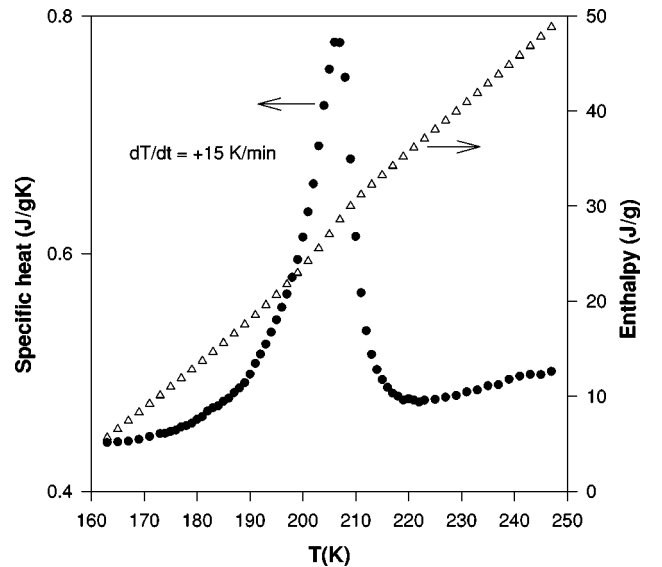FIG. 3. Differential heat flow into a pressed pellet of $KCu_{6.66}S_4$, measured with a differential scanning calorimeter and converted into an effective specific heat (closed circles). The corresponding enthalpy is also shown (open triangles).

near the phase transitions as a result of the observed frequency dependent heat capacity (anomalies).

Equation (1) must be modified near a first-order phase transition, for which there is a latent heat L. In this case, the effective heat capacity can be written as[13]

$$\acute{C} = CD(\omega) + dL/dT, \qquad (2)$$

if L is spread out slightly by sample inhomogeneities. If the latent heat has an intrinsic time dependence t_L as a result of a diffusion process or energy barrier associated with the transition, the equation must be further modified as[13]

$$\hat{C} = CD(\omega) + [1 + (\omega t_L)^2]^{-1/2} dL/dT. \qquad (3)$$

In this case, $\hat{C}$ depends on the frequency and the time constant t_L. The second term in Eq. (3) decreases with increasing ω. For a detailed description and simulation of the frequency dependence of the ac thermocouple voltage in the presence of time-dependent latent heat, see Ref. 13.

All the derivations mentioned above are based on the assumption of 1D heat flow. In particular, we neglect heat loss from the sides of the crystal, which is not a good assumption for our whisker-shaped crystals. Further, the samples are small compared with the addendum, which makes the addendum correction very difficult. For these reasons, we did not attempt to extract absolute values from our ac heat capacity results. Since the addendum has no anomalies, the qualitative features of our heat capacity measurements should still be correct.

III. RESULTS

A. KCu$_{7.0}$S$_4$

1. Resistance

At room temperature the resistivity of KCu$_{7.0}$S$_4$ is about 10 mΩ cm, approximately 100 times larger than that for KCu$_{7-x}$S$_4$ with $x = 0.12$ and 0.34. For 280 K $< T$ < 370 K, dR/dT is almost zero, although slightly negative (Fig. 4). Near room temperature there is an upward jump in $|dR/dT|$, indicating the presence of a transition at T_{C1} ≈ 280 K. Most samples show a bump in the R-versus-T plot at $T_{C2} \approx 180$ K (Fig. 6). As shown in Fig. 4, R is hysteretic for $T_{C2} < T < T_{C1}$. R is lower on warming than on cooling, which suggests that the sample is more ordered after having been at low temperature. As T decreases below 180 K, R increases more slowly than exponentially. See inset in Fig. 4. Thus the sample is not semiconducting in the usual sense, because there is no discernible gap, nor does it fit a variable range hopping model.

2. Thermal conductivity

There are anomalies in the thermal conductivity κ around T_{C1} and T_{C2} as well as around 210 K (Fig. 5). The peak of κ at T_{C1} is unusual. This may be real although its observation is difficult in our apparatus. It is clear that the electronic thermal conductivity cannot be more than a few percent of κ over the measured temperature range.
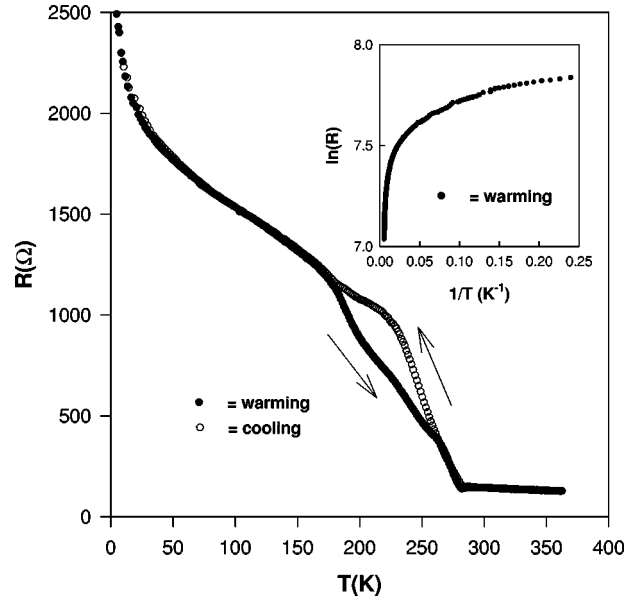

FIG. 4. Temperature dependence of the resistance R of a single crystal of KCu$_{7.0}$S$_4$. Closed circles indicate data taken while warming and open circles data taken while cooling. R is hysteretic between $T_{C2} \approx 180$ K and $T_{C1} \approx 280$ K. Above T_{C1}, R is nearly independent of the temperature. The inset shows an Arrhenius plot of R for $T < 180$ K.

3. Thermoelectric power

As one would expect from the semiconductinglike behavior, the thermoelectric power S for the $x = 0$ samples is much larger than that of the samples with $x > 0$, and has a temperature dependence similar to that found for R around T_{C1} (Fig. 6). At about 240 K, however, thermoelectric power has a maximum and decreases monotonically as T decreases.
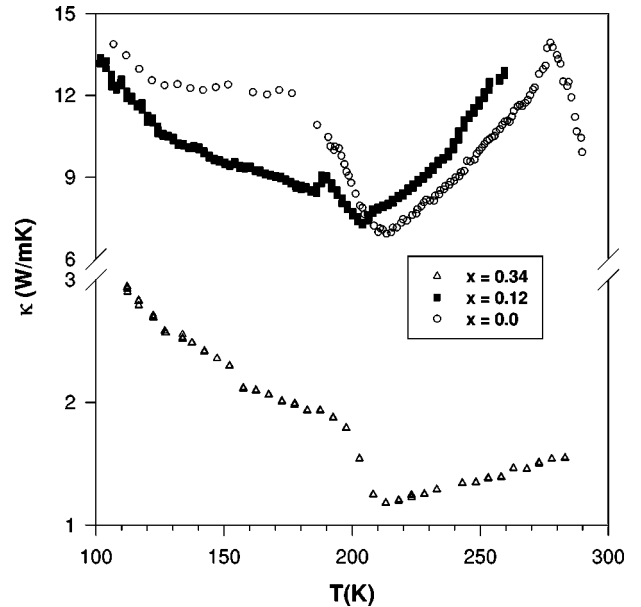

FIG. 5. Temperature dependence of the thermal conductivity κ of single crystals of KCu$_{7.0}$S$_4$ (circles), KCu$_{6.88}$S$_4$ (filled squares), and KCu$_{6.66}$S$_4$ (triangles). Due to uncertainties in the cross section of the samples, there is at least a factor of 2 scaling uncertainty in κ.
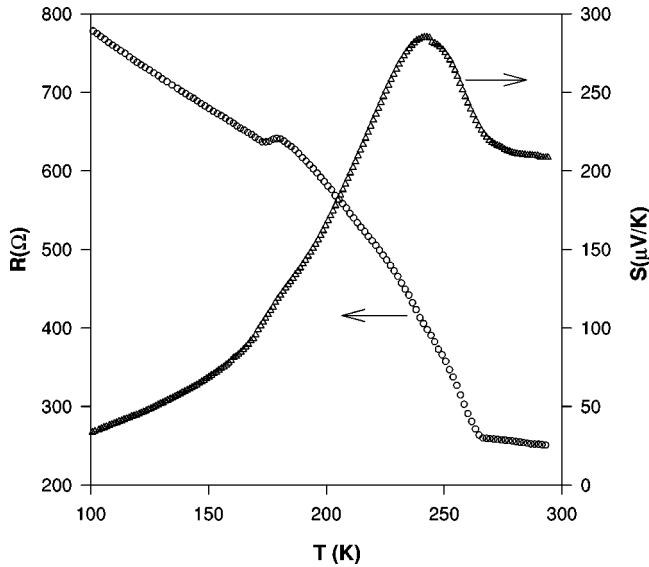
FIG. 6. Temperature dependence of the thermoelectric power S (right scale, triangles) and resistance R (left scale, circles) of a single crystal of $KCu_{7.0}S_4$. All data were taken while warming.

There is a small anomaly near T_{C2}. Thermoelectric power is positive, which implies that the carriers are holes.

4. Heat capacity

Figure 7 shows that there are two anomalies in the ac measured C_P. The addendum has a mass larger than the sample, and the addendum has no phase transitions in the temperature region of our study. Therefore, the heat capacity peaks of Fig. 7 are a much larger fraction of the background
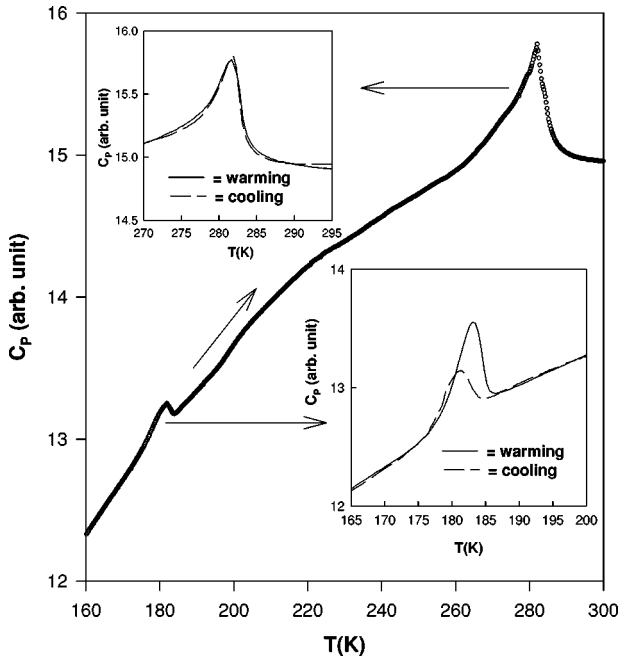

FIG. 7. Temperature dependence of the heat capacity C_P of a single crystal of $KCu_{7.0}S_4$ as measured by an ac calorimeter at 3 Hz while warming. There are transitions $T_{C1} \approx 280$ and $T_{C2} \approx 180$ K. The upper transition shows negligible hysteresis (upper left inset) but the lower transition shows history dependence (lower right inset).
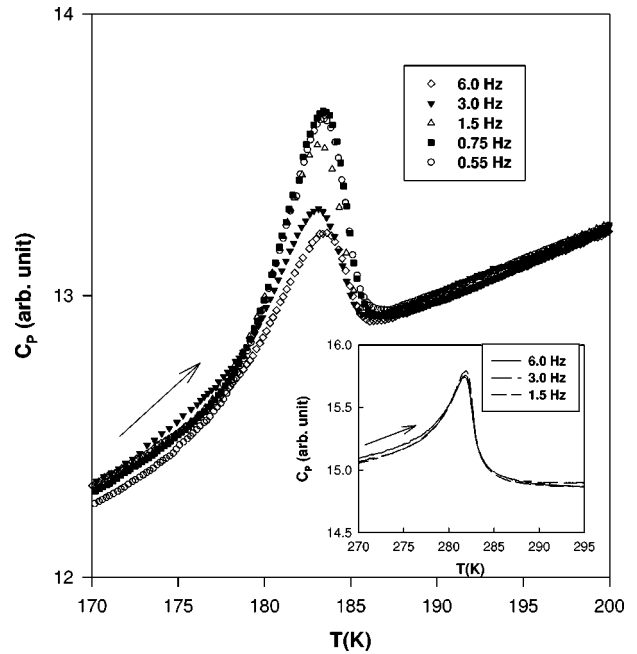

FIG. 8. Temperature dependence of the heat capacity C_P of a single crystal of $KCu_{7.0}S_4$ measured by an ac calorimeter on warming at several frequencies. At higher frequencies the anomaly is less prominent. This frequency dependence is probably due to a diffusionlike process (see text), and saturates below 0.75 Hz. The inset shows that the upper transition is nearly frequency independent.

C_P of the sample than is apparent in the figure. The area under the peak (i.e., the enthalpy change) is much larger for the upper transition. Unlike the upper peak, the lower peak shows strong hysteresis and frequency dependence. This hysteresis of the measured heat capacity, if rigorously true, would imply that C_P is not a state function. (One might suggest that if the measurements were sufficiently precise and slow, C_P would not be hysteretic.) The typical sweep rate $|dT/dt|$ of these measurements was about 1 K/min. Apparently, the warming peak at T_{C2} involves a larger entropy change than does the cooling peak, unless there are considerable entropy changes not observable in these experiments.

The amplitude of the anomaly at T_{C2} also has a frequency dependence (Fig. 8). The anomalous heat capacity at T_{C2} could result from the phase transition at T_{C2} being first order with a latent heat that has an intrinsic time dependence, as in the case of $(TMTSF)_2BF_4$, which has an anion ordering transition at 37 K.[13] Further details of the frequency dependence and hysteresis will be discussed with the $x=0.12$ compound.

B. $KCu_{6.88}S_4$

1. Resistance

The resistivity of the $x=0.12$ compound at room temperature is about 100 $\mu\Omega$ cm. At temperatures between 320 and 200 K, dR/dT is almost zero with a very shallow minimum around 250 K (Fig. 9). On cooling, the resistance suddenly drops at $T_{C1} \approx 200$ K, reaches a minimum at about 190 K, and has a cusp at $T' \approx 187$ K. On cooling below T' by 5 K, the resistivity jumps up by a factor of about 10 reaching a maximum at $T_{C1} \approx 182$ K. Unlike the $x=0$ compound, the resistance is not hysteretic between T_{C1} and T_{C2} but exhibits
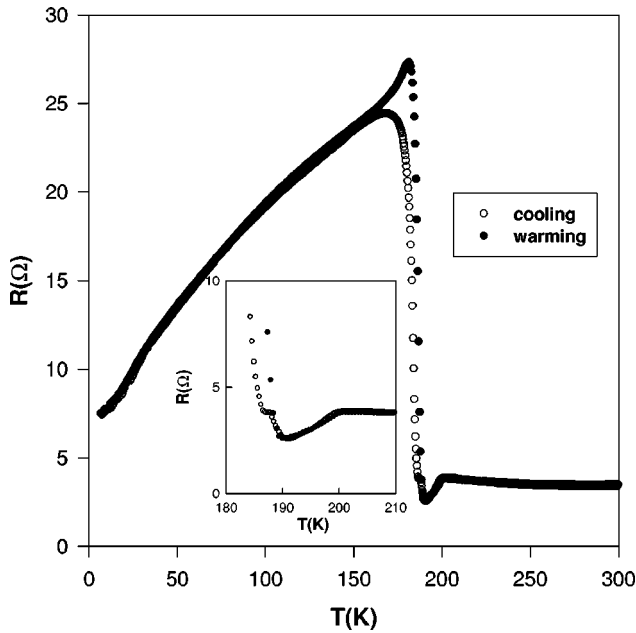
FIG. 9. Temperature dependence of the resistance R of a single crystal of $KCu_{6.88}S_4$. R is hysteretic between 150 K and T_{C2} ≈ 190 K and varies by a factor of nearly 5 depending on the history of the sample. Above T_{C1}, R is nearly independent of the temperature, as in the case of $KCu_{7.0}S_4$. The inset shows a close-up plot near the transitions.

hysteresis between T' and 150 K. In contrast to the case of the $x=0$ compound, the resistance is larger on warming than on cooling, and there is a spike in the resistance on warming. Below 150 K, the $x=0.12$ compound is metallic.

Because of the possibility of ionic conduction, we checked the frequency dependence of the resistance. Our measurements show that there is less than a 1% difference in the room-temperature resistance values measured between 1 Hz and 100 KHz.

2. Thermal conductivity

There are anomalies in the thermal conductivity κ around T_{C1} and T_{C2} (Fig. 5). κ increases as the temperature is lowered below T_{C2}, which is consistent with the sample becoming more ordered.

3. Thermoeletric power

The thermoelectric power S shows a slope change at T_{C1} and a sharp drop at T_{C2}, staying positive down to 70 K, as shown in Fig. 10. The change in S and R around T_{C1} have opposite signs, an unusual behavior.

4. Heat Capacity

Figure 11 shows that there are two anomalies associated with phase transitions observable in the ac heat capacity. As in the case of the $x=0$ compound, the entropy change is larger at the upper transition. Both anomalies, like the lower one in the $x=0$ compound, show hysteresis and frequency dependence. For all values of $x(=0.0, 0.12, 0.34)$, C_P does not show frequency dependence when the chopping frequency is below 0.75 Hz. As the frequency increases, the sizes of the C_P peaks asymptotically approach zero (Fig. 12).
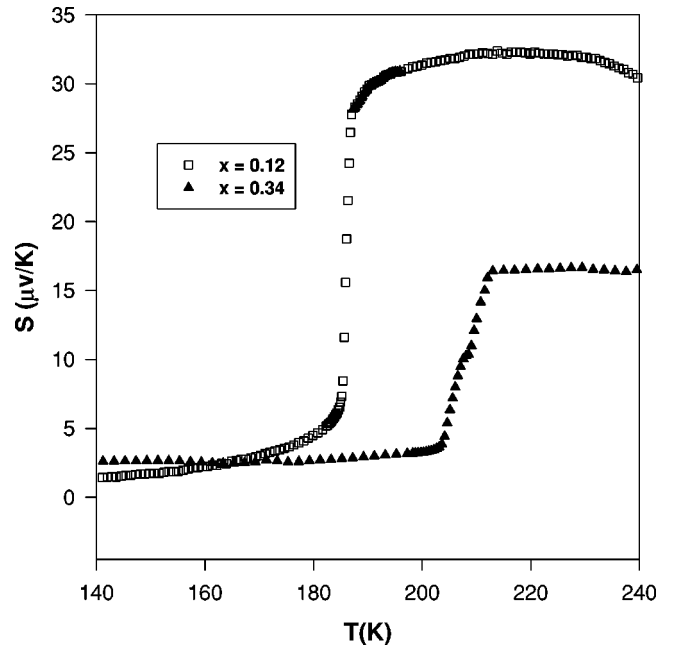

FIG. 10. Temperature dependence of the thermoelectric power S of single crystals of $KCu_{6.88}S_4$ (open squares) and $KCu_{6.66}S_4$ (filled triangles) near their transitions. Both curves were taken on warming. Because of measurement problems, the values of S are only qualitative (see text).

In ac calorimetry, the amplitude of the temperature oscillation is larger at lower frequencies if the light intensity is constant. Thus the frequency dependence might be related to the amplitude of the temperature oscillation. If there were an energy barrier for the transition, then the measured C_P might depend on the amplitude of the temperature variation. To check this point, we decreased the intensity of the light
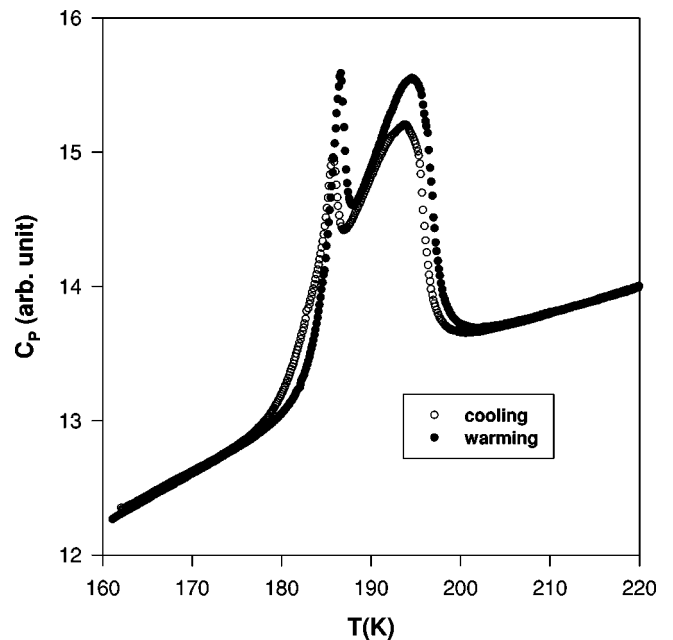

FIG. 11. Temperature dependence of the heat capacity C_P of a single crystal of $KCu_{6.88}S_4$ measured by an ac calorimeter at 0.75 Hz near the transitions. Thermal hysteresis is seen in both transitions, but is larger for the lower temperature transition.
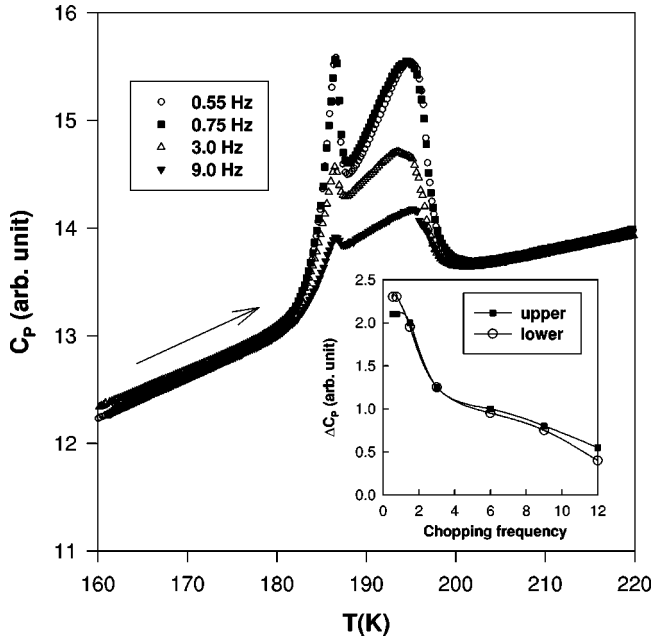
FIG. 12. Frequency dependence of the heat capacity anomalies of a single crystal of $KCu_{6.88}S_4$ measured by an ac calorimeter on warming around the two transitions. The lower temperature transition shows a stronger frequency dependence, which saturates around 0.75 Hz, as detailed in the inset.

source at 0.55 Hz by a factor of 25, which gives approximately the same amplitude as the ac temperature would have at 12 Hz. We found no variation in the measured C_P. Thus the frequency dependence of the ac C_P anomalies is due solely to the time scale of the temperature variation and must be associated with a diffusionlike process.

As in the case of the lower transition of the $x=0$ compound, C_P on warming is larger than on cooling for both transitions. We have studied four minor hysteresis loops in various temperature ranges (Fig. 13). For the temperature range below T_{C2}, there is no hysteresis (loop No. 4). For the temperature range above T_{C1}, there is hysteresis with a positive area for the hysteresis loop in a plot of C_P/T vs T (loop No. 3). If we warm past T_{C2} but stay below T_{C1}, then hysteresis appears with a nearly vanishing area for the hysteresis loop (loop No. 2). If we cool past T_{C1} and stay above T_{C2}, then hysteresis appears with a positive area for the loop (loop No. 1). We went around these loops many times reproducibly. The time to go around one loop was about 30 min, so that $|dT/dt|$ was less than 1 K/min. All of these effects cannot be explained by a single time constant, since the hysteresis was seen in loops taken at 0.55 Hz. The time constant of 1 s deduced from the frequency dependence of the anomalies is probably associated with local vacancy movement in the zigzag chains. In addition, there must be a longer time constant ($1\,s \ll \tau \ll 30$ min) or metastability associated with the hysteresis. This may be due to longer range ordering along or between the zigzag chains.

C. $KCu_{6.66}S_4$

1. Resistance

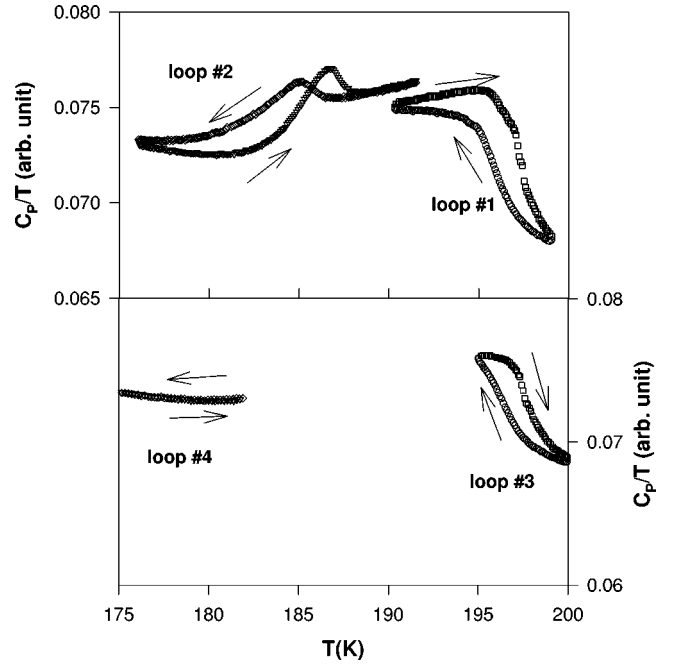The resistivity of the $x=0.34$ compound at room temperature is about 100 $\mu\Omega$ cm. For 210 K$<T<$320 K, dR/dT is

FIG. 13. A C_P/T vs T plot of minor hysteresis loops for a single crystal of $KCu_{6.88}S_4$ measured by ac technique at 0.55 Hz around the two transitions. Loop No. 1 is offset from loop No. 2 for clarity. Notice that the area enclosed by each loop is positive or zero, with loop No. 4 closing up.

slightly positive (Fig. 14). On cooling, R suddenly drops by a factor of approximately 4 at $T_{C1} \approx 208$ K. One sample (out of ten) showed an increase in R at $T_{C2} \approx 185$ K. Perhaps this sample had x not exactly equal to 0.34. Below 200 K, the $x=0.34$ compound is metallic: both dR/dT and d^2R/dT^2 are positive.
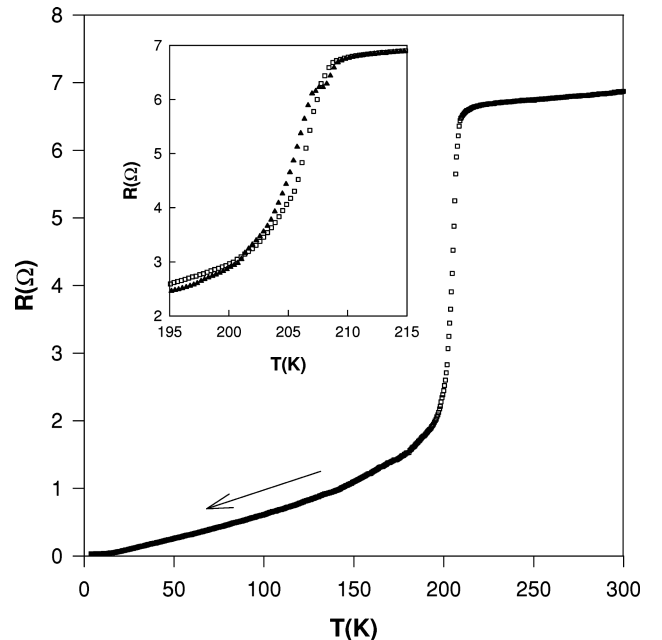

FIG. 14. Temperature dependence of the resistance R of a single crystal of $KCu_{6.66}S_4$ on cooling. Unlike the $x=0.0$ and 0.12 samples, there is only a very weak hysteresis in R, as shown in the inset.
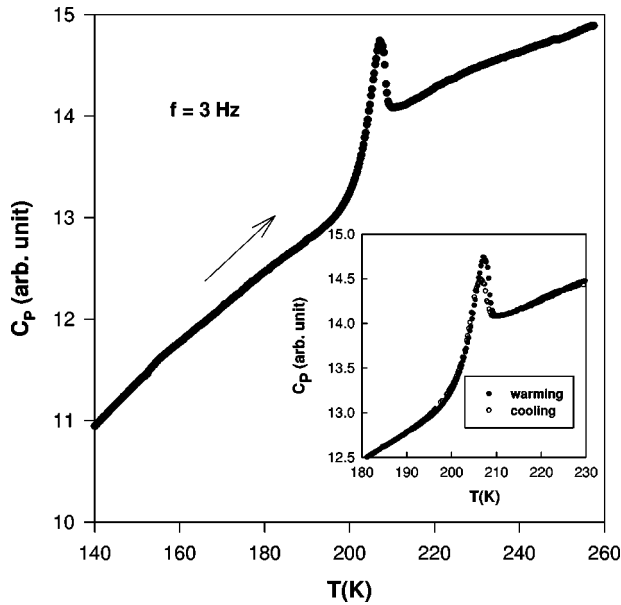
FIG. 15. Temperature dependence of the heat capacity C_P of a single crystal of $KCu_{6.66}S_4$ measured by an ac calorimeter on warming at 3.0 Hz. At this frequency, the background heat capacities above and below the transition do not match up. There is hysteresis in the data taken on warming and cooling, as in $KCu_{7.0}S_4$ and $KCu_{6.88}S_4$.

FIG. 16. Frequency dependence of the heat capacity C_P of a single crystal of $KCu_{6.66}S_4$ measured by an ac calorimeter on warming. This effect saturates at low frequencies and higher temperature (see inset), which is consistent with the proposed diffusion model (see text).

2. Thermal conductivity

Within the precision of our data, there is only one anomaly in the thermal conductivity κ, at 210 K (Fig. 5), below which κ increases by a factor of about 2. Below 210 K, the thermal conductivity increases, in agreement with the idea that the system is more ordered below T_{C1}.

3. Thermoelectric power

The thermoelectric power S shows a sharp drop at T_{C1} and then stays slightly positive down to 100 K (Fig. 10). Unlike the $x=0.12$ samples at T_{C2}, the change in S and R around T_{C1} have the same sign. Both R and S have a small glitch in the middle of the transition on warming.

4. Heat capacity: DSC

Figure 3 shows that the heat capacity of a pressed pellet has a peak centered at 205 K. The phase transition is considerably broader than seen in the resistance. The enthalpy change involved ($\Delta H = 5.0 \pm 0.5$ J/g) is too large for an electronic or minor crystal structure change, but is consistent with an ordering transition. Further, the enthalpy change on warming is larger than that on cooling: $\Delta H = 5.0 \pm 0.5$ J/g on warming and $\Delta H = 3.5 \pm 0.4$ J/g on cooling. Since the enthalpy must be a state function, this implies that the phase transition involves some kind of diffusion process (see below for further discussion).

5. Heat capacity: ac calorimetry

Figure 15 shows the one transition usually observable in the ac heat capacity C_P. (One sample showed a second anomaly around 188 K.) The transition shows hysteresis
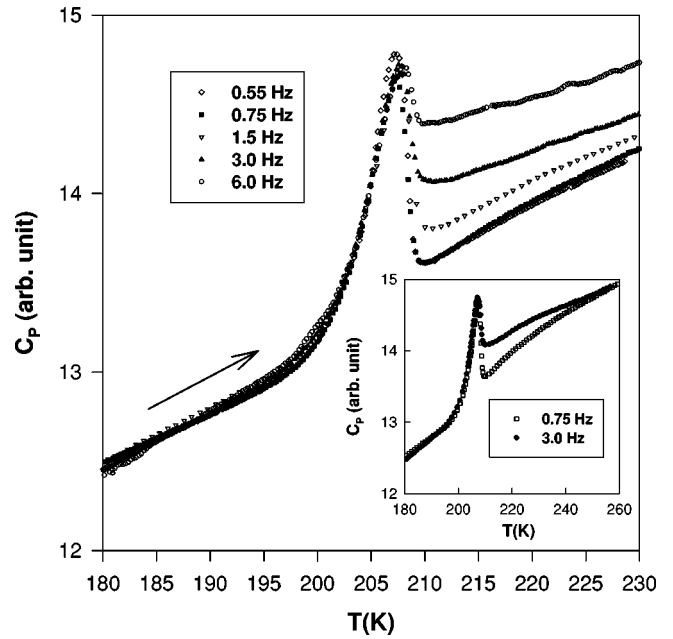
similar to that found for the lower transition of $x=0.0$ and both transitions of $x=0.12$, but it exhibits an unusual dependence on the chopping frequency f. As shown in Fig. 15 (for 3 Hz), the background C_P's above and below the transition do not match up. This is not expected unless there is a severe structural change at the transition. Figure 16 shows that if we normalize the C_P-versus-T plots at low T, the peak height is the same for all frequencies. The low frequency results seem to have a normal background and do not depend on frequency when $f \lesssim 0.75$ Hz. The background C_P above the transition for all frequencies converges to the low frequency background at high enough temperature (see the inset of Fig. 16). This highly unusual behavior occurs on both warming and cooling. However, R is independent of frequency within 0.1% between 0.5 and 40 Hz.

IV. DISCUSSION

The anomalies of $KCu_{7-x}S_4$ involve large entropy changes, are hysteretic, and the ac C_P depends on the frequency of the temperature oscillations. A summary of the transition temperatures is in Table I. The electronic band structure of $KCu_{7-x}S_4$ study shows that $KCu_{7-x}S_4$ does not have a CDW instability.[6] The changes in ρ around the transition temperatures can be understood by considering the potentials associated with vacancy ordering in the Cu(2)-Cu(2) zigzag chains, although the difference in the sign of ΔR in the $x=0.12$ and 0.34 materials is not understood.[6] Thus it is appropriate to discuss the present experimental results in terms of a model in which the phase transitions of $KCu_{7-x}S_4$ are caused by an ordering of the vacancies in the Cu(2)-Cu(2) zigzag chains. Specifically, we propose that the

anomalous physical properties of $KCu_{7-x}S_4$ are associated with a **c**-axis doubling transition for $x=0$ at 280 K and with a **c**-axis tripling transition for $x=0.34$ at about 210 K. For $x=0.12$, we propose that there are both **c**-axis doubling and tripling transitions. These occur at about 185 and 195 K, but structural studies are needed to sort out which temperature is which transition.

At present we have no structural evidence for this proposal. In the temperature region of our investigations, only one structural change is observed in x-ray diffraction of powder samples of our material. This transition, found for the $x=0.12$ and 0.34 samples, is a $T \to M$ transition at 180–190 K ($\Delta\theta=0.27°$, $\Delta c/a=1.37\%$). It is probably associated with the smaller C_P peak seen in some samples. From our x-ray diffraction study of powder samples at various temperatures, it was not possible to detect a **c**-axis doubling for $x=0.0$ and 0.12 as well as a **c**-axis tripling for $x=0.12$ and 0.34. However, Ohtani *et al.*'s electron diffraction study[3] of $KCu_{7-x}S_4$ grown by conventional high-temperature ceramic methods shows the occurrence of an ordering that doubles and triples the **c**-axis length. Electron diffraction studies of our $KCu_{7-x}S_4(x=0.0, 0.12, 0.34)$ samples are necessary to provide structural evidence for our proposal.[14]

A. $KCu_{7.0}S_4$

We observe two transitions, one at about 280 K and the other at 180 K. If the 280 K transition is due to the ordering of one vacancy in every four Cu(2) sites in the Cu(2)-Cu(2) zigzag chains (1-in-4 ordering), then the discontinuous change in dR/dT around 280 K is explained as a change in the electronic structure from a disordered semiconductor above the transition to an ordered semiconductor below the transition. It is possible that the 180 K transition seen in some samples is due to the ordering of two vacancies in every six Cu(2) sites (2-in-6 ordering), which is possible if the x value of $KCu_{7-x}S_4$ is not exactly 0.0. Then the increase in $|dR/dT|$ at the transition is related to the increased semiconducting nature of the more ordered material below T_{C2}. Moreover, the hysteretic behavior observed between the transitions would be caused by the many metastable orderings possible until the 2-in-6 ordering occurs at T_{C2}.

In our model of vacancy ordering, the increase in κ that occurs when the temperature is lowered toward T_{C1} would be caused by an increase in κ due to ordering.

The jump in S at T_{C1} may be associated with a disordered semiconductor above the transition to an ordered semiconductor below the transition. It is not clear why S decreases below 240 K.

The entropy change at T_{C1} as deduced from the heat capacity peak is consistent with 1-in-4 ordering (see below) in the Cu(2)-Cu(2) zigzag chains, if we assume the $x=0.0$ sample has the same addendum as the $x=0.34$ sample for which we have DSC data. The smaller area under the heat capacity peak at T_{C2} is explainable if x is nearly equal to zero, because there would not be many extra vacancies to be ordered at T_{C2}.

The anomaly in C_P at the T_{C2} transition is frequency dependent while the T_{C1} transition is not. This might be due to (a) a first-order sluggish latent heat at T_{C2}, (b) an energy barrier between metastable states that exist at T_{C2} but not at T_{C1}, or (c) a diffusion process that is faster at the higher temperature T_{C1}. If the reason were (a), then Eq. (3) holds (e.g., if it has a latent heat and a small spread in transition temperature), which would explain the frequency dependence. However, it is difficult to see why the 2-in-6 transition would be first order while the 1-in-4 transition is not. Further both transitions for the $x=0.12$ material are frequency dependent. To check the validity of (b), as we mentioned above, we changed the power of the light source by a factor of 25, while keeping the frequency constant. The anomaly was unchanged, ruling out an energy barrier as the cause. If the transition involves a diffusion process, then the diffusion rate at T_{C1} should be much higher than at T_{C2}. In the range of chopping frequencies available to us, no frequency dependence would be expected at T_{C1}, 100 K higher than T_{C2}, in agreement with experiment. Thus it is likely that (c) is correct: the frequency dependence is due to a diffusion process. A diffusion process would act similar to a sluggish latent heat to reduce the apparent C_P as seen in our samples. From a structural viewpoint, this is reasonable because the vacancy ordering in each Cu(2)-Cu(2) zigzag chain requires a diffusion of Cu^+ ions along the chain.

The entropy of our samples appears to be history dependent, in contradiction to the entropy being a state function of the sample. Thus there must be some entropy changes that are concealed in the heat capacity away from the transition, or there must be metastable states available to the samples. If the sample were in a metastable state, then we would not be measuring the equilibrium thermodynamic C_P.

B. $KCu_{6.88}S_4$

This material has two transitions, at about 195 and 185 K, which we assume to be due to 1-in-4 ordering and 2-in-6 ordering. Between the two transitions the ac measured C_P is hysteretic. Both anomalies in C_P are frequency dependent and hysteretic. This is consistent with the diffusion model described above, because both transitions are at low temperature. Further, the frequency dependence of the C_P anomaly at the lower transition is greater, consistent with a slower diffusion rate at lower temperature. Both seem to saturate at about 0.75 Hz; but our precision in the saturation frequency is poor (Fig. 12). The difference in the peak values of C_P on warming and cooling is similar to that for the lower transition in the $x=0$ material, and is bigger at the lower transition, as expected for a diffusion process. The differences between the T_C's on heating and cooling are difficult to define because the two transitions overlap, and it is difficult to deconvolute them without models for their shapes. The resistivity is nearly independent of T above T_{C1}, and is almost two orders of magnitude lower than the $x=0$ material. The lower resistivity is in accord with the electronic band structure study of $ACu_{7-x}S_4$,[6] which was carried out for an ordered arrangement of the vacancies in the Cu(2)-Cu(2) zigzag chains. The disordered material should have a very short mean free path, so the temperature independence of resistance above T_{C1} would be due to the disorder limited mean free path. The jumps in R and S at the transition would be caused by a change in the electronic structure on ordering, and the metallic dR/dT below the transition by a phonon

limited electronic mean free path. The apparent rise in κ above 220 K may be instrumental.

C. KCu$_{6.66}$S$_4$

This material usually has only one transition from 4 to 300 K. We assume it to be due to the 2-in-6 ordering. The hysteresis in C_P on warming and cooling is similar to that of the lower transition in the $x=0$ material and both transitions in the $x=0.12$ material. Unlike the other materials there is only a very weak hysteresis in R, similar to the T_{C1} transition in the $x=0.12$ material, as shown in Fig. 14.

The DSC measurements seem to show that the enthalpy change ΔH at the transition depends on whether one is cooling or heating. This would suggest that H was not a state function. However, if there were a slow diffusion process at the transition, then ΔH on cooling would be spread out to lower temperatures and the transition width used to calculate ΔH might miss a portion of it. On warming, a diffusion process would be faster above the transition and easier for ΔH to occur within these bounds. This would mean about 40% of ΔH occurs at temperatures lower than we have picked to be part of the transition, or too close to the background to be observable. To calculate what ΔH should be for a 1-in-4 order-disorder transition; $\Delta H/T = (kln\Omega) = (klnC_N^{4N}) \approx 2.2R$. Note that a 2-in-6 ordering has about the same value: $(2.6R)$. From the DSC measurement, $\Delta H/T \approx (5 \text{ J/g})/(200 \text{ K}) \approx (3000 \text{ J/mol})/(200 \text{ K}) \approx 1.8R$, in close enough agreement with the proposal that this is an order-disorder transition mediated by a diffusion process.

The most striking feature of this compound is that the frequency dependence and the thermal hysteresis of C_P happens at different temperature intervals, as shown in Figs. 15 and 16. The frequency dependence of C_P above the transition temperature in the $x=0.34$ material is highly unusual, in that (unlike the other compositions), the apparent heat capacity decreases with decreasing frequency, saturating below 1 Hz. (The effect disappears for $T > 250$ K.) Since latent heat should not extend over 50 K in a good single crystal, we discuss the frequency dependence in terms of Eq. (1), which applies for 1D heat flow through the thickness of the sample. The sign of the frequency dependence suggests that the internal time constant τ_2, proportional to the thermal diffusivity perpendicular to the copper chains, is about 1s. However, for a 5 μm thick crystal with a specific heat of ~ 0.5 J g^{-1} K^{-1}, this would imply that the transverse thermal conductivity has an unphysically small value $(< 10 \mu$W m^{-1} K^{-1}). Therefore, while we assume that this anomalous dependence is again due to a diffusion process, we cannot explain the observed frequency dependence, or why the diffusion process takes place over such a wide temperature interval.

As already mentioned, powder x-ray diffraction measurements on our material show a $T \rightarrow M$ phase change at 180–190 K for $x=0.12$ and 0.34. However, the temperature dependencies of the resistance for $x=0.12$ and 0.34 are quite different. This implies that the $T \rightarrow M$ transition is not the cause of these resistance changes. The entropy change expected from such a transition is much smaller than we observe. The $x=0$ samples appear to be already ordered at room temperature in x-ray crystallography. Thus x-ray crystallography does not shed much light on the nature of the phase transitions reported in the present work. Ohtoni *et al.*[3] have seen two ordering transitions in their electron diffraction studies on polycrystalline samples grown by another process. It is most likely that these two transitions are associated with the phase transitions we observe. Electron diffraction studies of our samples are needed to confirm this point.[14]

V. CONCLUDING REMARKS

The present work indicates that the phase transitions of KCu$_{7-x}$S$_4$($x=0.0, 0.12, 0.34$) are order-disorder transitions mediated by diffusion. First, κ always increases below these phase-transition temperatures, indicating that the sample is more ordered below each of these transitions. Second, the size of the entropy change at the transition is much too large to have an electronic origin or to be associated with the weak structural change (i.e., the $T \rightarrow M$ phase change) seen in x-ray crystallography, but is consistent with an order-disorder transition. Third, the frequency dependence and hysteresis of the ac heat capacity anomalies imply that there is a diffusion process involved around these transitions. Fourth, the resistance is a very weak function of temperature above the upper transition in each material, indicating that the material is disordered above the transition. Finally, the crystal structure of KCu$_{7-x}$S$_4$ provides a medium for a diffusion process, i.e., the vacancy ordering in each Cu(2)-Cu(2) zigzag chain can take place by a diffusion of Cu$^+$ ions along the chain.

The transitions seen in the KCu$_{7-x}$S$_4$($x=0.0, 0.12, 0.34$) materials are very unusual. The characteristic time associated with diffusion at the transitions, indicated by the chopping frequency dependence of the measured heat capacities, is about one second, implying that the Cu$^+$ ions do not move far. This is understandable because the Cu$^+$ ion movement is confined within a 1D channel of each Cu(2)-Cu(2) zigzag chain and because a Cu$^+$ ion can move only by hopping into an adjacent vacancy site (if available). However, slower diffusion processes are indicated by the observed thermal hysteresis.

The phase transitions of KCu$_{7-x}$S$_4$($x=0.0, 0.12, 0.34$) are associated with 1D diffusion and occur well below room temperature. This is in sharp contrast with other well-known order-disorder transitions. For example, beta brass has an ordering transition that involves three-dimensional (3D) diffusion.[15] This compound is 3D in structure, and its phase transition is much less sharp than those found for KCu$_{7-x}$S$_4$. There are vacancy ordering transitions in two- and three-dimensional materials, for example, Ni$_{2-x}$Te$_2$ and TiO, respectively.[16] However, their transition temperatures are much higher, and the physical property changes at the transition temperatures are not known. There are orientation ordering transitions in materials such as C60,[17] which are 3D in structure and do not involve diffusion. Such quasi-one-dimensional orientation and/or CDW transitions as found for (TMTSF)$_2$X[18] and NbSe$_3$[1] are not diffusionlike and do not show hysteresis. Certainly, the KCu$_{7-x}$S$_4$ materials have unique and interesting transitions worthy of further study.

ACKNOWLEDGMENTS

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[14] Currently, electron diffraction studies of our samples are being carried out by Professors T. Ohtani and Y. Yokota and their co-workers. Their preliminary results support our proposal.

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