RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

X-ray scattering study of charge-density waves in $K_3Cu_8S_6$

R. M. Fleming, L. W. ter Haar, and F. J. DiSalvo
AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070
(Received 22 December 1986)

Two phase transitions have previously been identified in $K_3Cu_8S_6$, a second-order transition at 153 K and a first-order transition at 55 K. In this x-ray scattering study we show that the 153-K transition, which is associated with a decrease in the conductivity, corresponds to the onset of an incommensurate charge-density wave (CDW) with a wave vector of $\mathbf{q}=(0,(1-\delta)/2,0)$. The 55-K transition, which is accompanied by an increase in the conductivity, results in a significant modification of the host structure and the creation of a superlattice with a commensurate periodicity given by $\mathbf{q}=(\frac{1}{2},\frac{1}{2},0)$. The temperature dependence of the CDW order parameter is unusual. First, at temperatures just above the first-order transition, oscillations in the order parameter as a function of temperature are observed. Similar oscillations have previously been observed in the conductivity and the magnetic susceptibility. Second, like the transport properties, the order parameter shows a large hysteresis ($\sim$60 K) as the temperature is scanned through the first-order transition.

Recently we reported the physical properties associated with two phase transitions seen in $K_3Cu_8S_6$.[1] $K_3Cu_8S_6$ has a second-order phase transition at 153 K and a first-order transition with large hysteresis at 55 K. Although the behavior of the electron-transport properties, particularly those near the 153-K transition, suggested that the phase transitions were due to a charge-density wave (CDW), some features of $K_3Cu_8S_6$ are different from the usual CDW material. For example, the 55-K transition is associated with a dramatic increase in the conductivity. In other CDW materials, phase transitions at temperatures below the CDW onset typically result from a commensurate-incommensurate (CI) transition. CI transitions can be either first or second order.[2,3] In layered compounds, first-order CI transitions usually cause a *decrease* in the conductivity, second-order CI transitions have only a weak effect on the conductivity.

An additional feature of $K_3Cu_8S_6$ that is different from other CDW materials is the nature of the conduction band. Normally, in mixed-valent materials, one assigns the odd valence to the metal sites. For example, one could balance the valence electrons by the formulation $K_3^{1+}Cu_7^{1+}Cu^{2+}(S^{2-})_6$. However, an oxidation state of Cu^{2+} is not consistent with x-ray photoelectron spectra[4] which indicate that copper only exists as Cu^{1+} in other copper sulfides. A description of the valence states consistent with the photoemission experiments is $K_3^{1+}Cu_8^{1+}(S^{2-})_5S^{1-}$. Since all copper atoms are singly ionized in this formulation, the copper d bands will be completely filled (e.g., the copper filling is d^{10}) and the Cu d bands will lie lower in the energy than the top of the sulfur p bands. The S^{1-} indicates that the compound is one electron short of filling the sulfur-based p bands. Therefore, one expects that the conduction states are holes in the valence (sulfur p type) band. There may be some contribution from copper d electrons from the hybridization discussed above; however, the mixing cannot be too large at the Fermi energy or else the Cu photoemission spectra[4] would be asymmetric. The occurrence of anion-based carriers at the Fermi surface, as well as the lack of an early transition metal (group IV, V, or VI), makes $K_3Cu_6S_8$ an unusual material to have a CDW.

In this Rapid Communication, we report the results of x-ray scattering experiments on $K_3Cu_8S_6$ and we show that the two phase transitions are associated with a charge-density wave. The second-order transition at 153 K marks the onset of an incommensurate CDW with a wave vector of $\mathbf{q}=(0,(1-\delta)/2,0)$. The parameter δ, which measures the incommensurability of the CDW, moves toward zero as the temperature is lowered, indicating the usual competition between the CDW periodicity and the lattice periodicity. At 55 K another structural phase transition occurs, producing a new periodicity with a wave vector of $\mathbf{q}=(\frac{1}{2},\frac{1}{2},0)$. The 55-K transition also results in large changes in the intensity of the Bragg peaks of the host lattice. Other CDW materials exhibit CI transitions to states that are commensurate in one or more directions;[5-7] however, in these materials δ moves continuously to zero, and large changes in the structure of the host lattice are not present. This suggests that the change in the wave vector from $(0,(1-\delta)/2,0)$ to $(\frac{1}{2},\frac{1}{2},0)$ is not a CI transition in the usual sense.

$Ku_3Cu_8S_6$ is a metastable phase that can be "trapped" as $K_2Cu_8S_6$ is made to transform to $K_3Cu_9S_6$ by heating. The room-temperature structure[8] of $K_3Cu_8S_6$ is shown in Fig. 1. The basic structural unit is an infinite $[Cu_4S_4]$ chain with slightly distorted trigonal Cu-S coordination. The $[Cu_4S_4]$ chains are bonded into planes with edge-sharing tetrahedra. The material is monoclinic and grows in the shape of the needles with the monoclinic b axis and the $[Cu_4S_4]$ chains parallel to the needle axis. There are two types of Cu-S coordination within the structure, threefold coordination within the $[Cu_4S_4]$ chains and fourfold coordination within the intervening tetrahedral network. The elliptical shapes at the fourfold Cu sites in Fig. 1 indicate that these sites are either disordered or they have large thermal parameters. The potassium atoms are ionically bonded between the planes. The result is a monoclin-

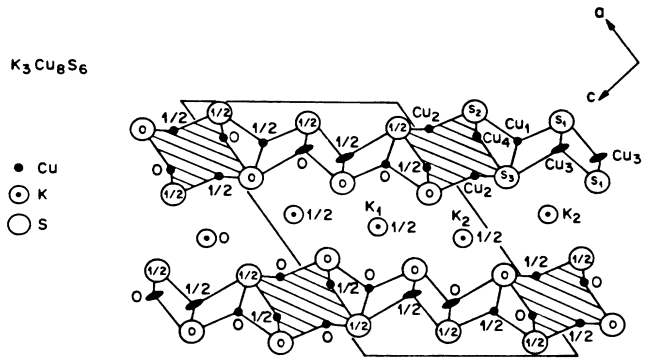

FIG. 1. The structure of $K_3Cu_8S_6$ as viewed down the chain axis (after Ref. 7).

ic planar structure with substantial in-plane structural anisotropy, in contrast to the basal plane isotropy of the transition metal dichalcogenides. In terms of a general description of chains bonded into layers with intervening alkali ions, $K_3Cu_8S_6$ is more reminiscent of the "blue bronze," $K_{0.30}MoO_3$.[9,10]

A single-crystal needle of $K_3Cu_8S_6$ was mounted on a quartz post and sealed in a cell with a He atmosphere. Temperature control was achieved with a closed-cycle helium refrigerator. X-ray scattering was performed with focused Cu $K\alpha$ x rays from a rotating anode source using a singly bent pyrolytic graphite monochromator and a flat pyrolytic graphite analyzer to minimize scatter from the cryostat windows. This arrangement, which is designed to maximize the intensity from weak CDW peaks, has a direct-space instrumental resolution of about 50 Å, i.e., structures with a coherence length in excess of 50 Å will result in resolution-limited diffraction peaks. The cryostat was mounted on a four-circle goniometer capable of full access to the reciprocal lattice.

At 153 K, $K_3Cu_8S_6$ undergoes a transition to an incommensurate CDW with a wave vector given by $\mathbf{q} = (0(1-\delta)/2,0)$. As expected from the opening of a CDW gap at the Fermi surface, the phase transition is accompanied by a decrease in both the conductivity and the magnetic susceptibility and an anomaly in the specific heat.[1] The charge-density wave is parallel to b^* (the $[Cu_4S_4]$ chain axis) with a wave vector that is initially about 10% smaller than $b^*/2$. Figure 2 shows three scans along $(0k0)$ through a CDW superlattice position. At 156 K, three degrees above the CDW ordering temperature, a peak about twice the instrumental resolution is observed. At 3 K above T_c the short-range order has a coherence length of approximately 30 Å, as determined from the x-ray linewidth. As the temperature is lowered, resolution-limited peaks are seen by 150 K, and the peaks remain resolution limited at all temperatures above the first-order transition at 55 K. At 60 K the maximum superlattice intensity is on the order of 10^{-3} times the intensity of an "average" peak of the host lattice indicating that the lattice distortions associated with the charge-density wave are small.

The temperature dependence of the charge-density wave incommensurability δ is shown in Fig. 3. The parameter δ

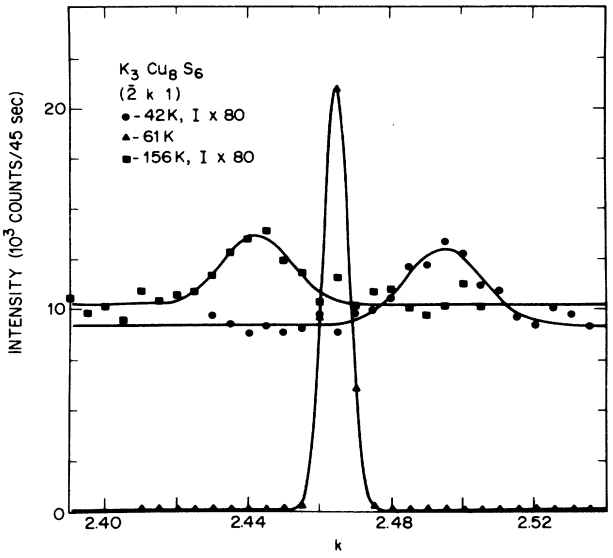

FIG. 2. Scans along $(0k0)$ through a $(0,(1-\delta)/2,0)$ superlattice peak at three temperatures. The scans at 156 K, three degrees above the CDW onset temperature, and at 42 K, below the first-order transition, are broader than resolution.

measures the difference between the measured wave vector and $b^*/2$ ($q = (1-\delta)b^*/2$). At onset $\delta \approx 0.11b^*/2 \approx 0.088$ Å^{-1}. In the temperature range 100–152 K, the temperature dependence of δ is reminiscent of the behavior of 2H-$TaSe_2$,[5] where the temperature dependence of δ shows upward curvature. (Simple models of a CI transition predict downward curvature of δ vs T with an infinite slope at the CI transition.[11]) Below 100 K, δ begins to de-

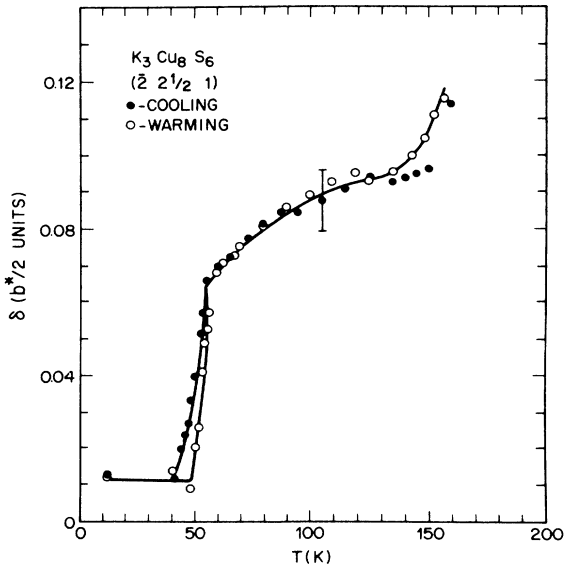

FIG. 3. The incommensurability of the $(0,(1-\delta)/2,0)$ superlattice as a function of temperature. The solid lines are guides to the eye. The error bar indicates the instrumental resolution (full width half maximum).

velop downward curvature, however, at 55 K, where $\delta \approx 0.07b^*/2$, a first-order structural phase transition occurs and the intensity of the $(0,(1-\delta)/2,0)$ superlattice decreases essentially to zero. Some scattering remains at temperatures below 55 K, as shown by the scan at 42 K in Fig. 2. The intensity and the linewidth of the scattering at $T < 55$ K are comparable to the diffuse scattering shown in Fig. 2 for $T = 156$ K, just above the onset temperature. Within the resolution of the instrument, the wave vector of the diffuse peak for $T < 55$ K is commensurate. The appearance of diffuse scattering below 55 K at $\mathbf{q} = (0, \frac{1}{2}, 0)$ suggests that a soft phonon may exist in the low-temperature phase at the same wave vector as the high-temperature CDW. It is also possible that there are microscopic inclusions of a second, nontransforming phase in this metastable material.

The temperature dependence of the charge-density wave amplitude, shown in Fig. 4, is highly unusual. The intensity of a CDW superlattice peak, which is proportional to the square of the CDW order parameter, begins to increase at 153 K, although weak diffuse scattering can be observed at slightly higher temperatures. For temperatures above about 100 K, the data are typical of other CDW materials. Between 55 and 90 K, however, both the warming and the cooling data show unusual oscillations of the CDW amplitude. The statistical errors in the data shown in Fig. 4 are smaller than the points, but systematic errors in the intensity can occur because of movement of the sample in the x-ray beam as the temperature is changed. However, since the oscillations only appear in the superlattice peak intensities, we believe that the data are valid. In addition, the behavior of the resistance and the magnetic susceptibility[1] mimic the temperature dependence of the CDW order parameter. Unusual oscillations of the resistance and the susceptibility are seen at temperatures above the 55-K transition, but only in data taken on cooling. At 55 K, the first-order transition occurs and the x-ray intensity near $\mathbf{q} = (0, \frac{1}{2}, 0)$ abruptly vanishes. On warming, there is large hysteresis in the intensity of the $(0,(1-\delta)/2,0)$ peaks. Although the onset of the 55-K transition has a hysteresis of only a few degrees, the intensity of the $(0,(1-\delta)/2,0)$ peaks does not equal the value seen on cooling until about 125 K, 70 K above the first-order transition. Large hysteresis in the same temperature interval is also seen in resistance and susceptibility measurements.[1]

In addition to the disappearance of the $(0,(1-\delta)/2,0)$ superlattice, the 55-K transition is also associated with the appearance of a new periodicity with a wave vector of $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$. Figure 5 shows the integrated intensity of the intensity of a $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$ superlattice peak as well as the (0,2,0) peak of the host lattice as a function of temperature. At the same temperature, where the intensity of the $(0,(1-\delta)/2,0)$ superlattice vanishes, new peaks appear at $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$. Unlike the high-temperature superlattice, the intensities of the $(\frac{1}{2}, \frac{1}{2}, 0)$ peaks are comparable to Bragg peaks of the host lattice. This indicates that the distortions associated with the 55-K transition are much larger than the high-temperature transition. Also note that the 55-K transition is accompanied by about a 40% change in the intensity of the (0,2,0) peak. Since this is one of the strong peaks of the host lattice, this also implies a significant change in the structure factor of the host lattice. At the CDW onset transition, little or no change in the intensity of the Bragg peaks of the host lattice can be seen.

The charge-density wave transition in $K_3Cu_8S_6$ is unusual both from a structural/chemical point of view and in the types of phase transitions that occur. $K_3Cu_8S_6$ is the first inorganic material where the charge carriers and the

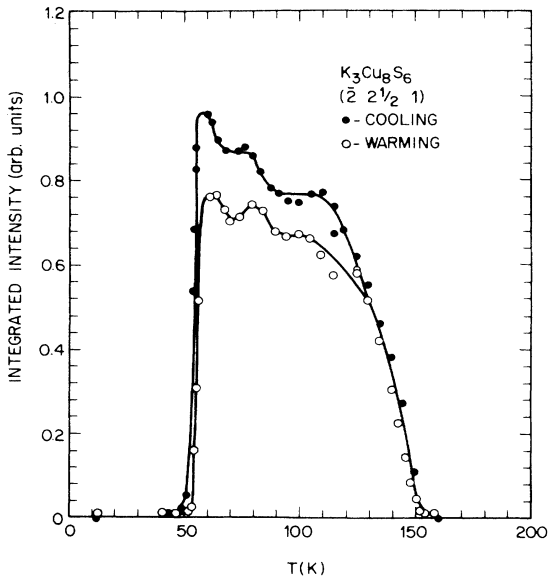

FIG. 4. The integrated intensity of a $(0,(1-\delta)/2,0)$ peak as a function of temperature. The unusual oscillations and the large hysteresis are also seen in resistance and magnetic susceptibility measurements (Ref. 1).

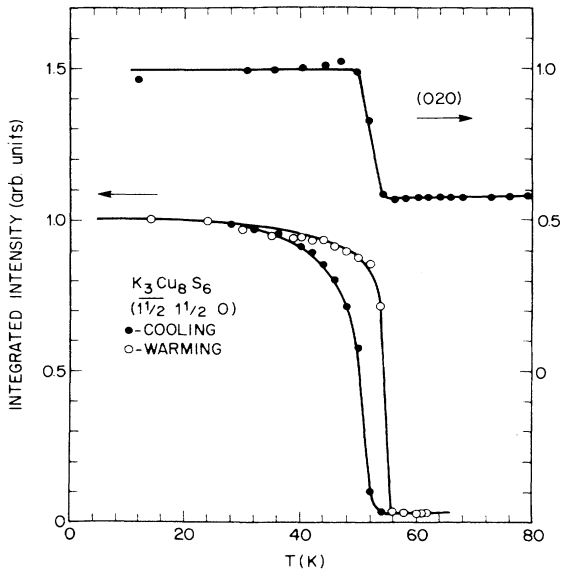

FIG. 5. The temperature dependence of the (0,2,0) peak and a $(\frac{1}{2}, \frac{1}{2}, 0)$ peak as a function of temperature.

subsequent charge-density wave have significant p character (i.e., the metallic conductivity is via holes in the sulfur valence band). $K_3Cu_8S_6$ is also unusual in the sense that the onset of a commensurate structure is associated with a dramatic increase in the conductivity. Although some layered compounds are better metals at temperatures below the CDW onset, there is no example of a similar increase in the conductivity at a CI transition in other CDW materials.[2,3] The atomic displacements associated with the two structural phase transitions in $K_3Cu_8S_6$ are not known, so one cannot assign particular distortions or displacements to the phase transitions. Given that the 55-K transition results in large changes to the structure, the 55-K transition may be driven by an independent mechanism rather than a CI transition, driven by a competition between the lattice periodicity and the CDW periodicity.

Several possible scenarios exist for the two phase transitions. First, the CDW onset transition appears to be conventional in the sense that one can describe the transition as the opening of a Peierls gap and the associated loss of conductivity due to the condensation of carriers into a CDW. The 55-K transition can be viewed in several ways. The first way is to think of the transition as a commensurate-incommensurate transition, but at 55 K the charge-density wave modulation on neighboring $[Cu_4S_4]$ chains slips by $\pi/2$, thereby doubling the unit cell in the a_0 direction. In this picture, the distortions of the low-temperature phase would be generally in the same directions as the high-temperature phase, but the amplitudes of the distortions would be much larger. A second interpretation is to think of the 55 K as a destruction of the CDW and the Peierls gap by an independent structural phase transition. In this case the distortions that produce the low-temperature phase have no relation to the high-temperature distortions. Consequently one does not think of the low-temperature structure in terms of a commensurate CDW with a Peierls gap. A possible driving force for an independent phase transition is an order-disorder transition of the copper atoms. Previous structural studies showed that some of the Cu sites in the tetrahedral network connecting the $[Cu_4S_4]$ chains are either disordered or have large thermal parameters (see Fig. 1). It is therefore possible that the 55-K transition is driven by an ordering of the Cu sublattice. Another possibility is that the transition is associated with the onset of fast ionic conductivity of the copper atoms which make up the tetrahedral network between the $[Cu_4S_4]$ chains. Such a transition, seen in superionic materials (e.g., AgI, $RbAg_5I$),[12] is associated with a "melting" of the cation sublattice. This would be consistent with the fact that Cu is mobile at room temperature in many copper-sulfide compounds. However we consider long-range diffusion of Cu to be a less likely mechanism for the low-temperature phase transition as one would expect any Cu mobility to be thermally activated and very small at 55 K.

The temperature dependence of the CDW order parameter $K_3Cu_8S_6$ is different from other CDW materials. Other materials such as 2H-$TaSe_2$, show considerable structural hysteresis; however, in 2H-$TaSe_2$ the hysteresis is associated with the CDW wave vector rather than the amplitude.[5] Hysteresis in the CDW wave vector is expected for several reasons. For materials with a temperature-dependent wave vector, a change in the temperature implies a change in the CDW phase relative to the host lattice. Locally, this is similar to electric field-induced motion of the CDW in $NbSe_3$ and related materials.[10,13] (We observe no electric-field-induced motion of the CDW in $K_3Cu_8S_6$.) Since the CDW phase moves relative to the lattice as the temperature is changed, impurities or defects can locally pin the CDW and produce hysteresis in the wave vector. Similarly, if the number of conduction electrons is somehow different between cooling and warming through 55 K (e.g., a different phase on warming), one would expect the change to be reflected in the Fermi surface dimensions and consequently in the CDW wave vector. Instead, in $K_3Cu_8S_6$, large hysteresis and unusual oscillations are only seen in the CDW order parameter (and the electron-transport properties). No measurable hysteresis is seen in the magnitude of the wave vector.

There is a superficial similarity between the behavior of $K_3Cu_8S_6$ and CuV_2S_4, a CDW compound with a spinel structure.[14] In CuV_2S_4 an incommensurate CDW forms along $\langle 110 \rangle$ in a second-order transition at 90 K and a continuous CI transition to $\mathbf{q} = \frac{1}{4}\langle 110 \rangle$ occurs at 75 K. At 50 K a first-order transition shifts the wave vector to $\frac{1}{3}\langle 110 \rangle$. A decrease in the magnetic susceptibility χ is seen at the second-order transition and a subsequent increase in χ is seen at the first-order transition, just as in $K_3Cu_8S_6$. However, in CuV_2S_4, χ is greatly enhanced because of electron-electron interactions. In addition, the conduction band in CuV_2S_4 is based primarily on V d electrons.

We would like to thank R. J. Cava, S. L. Issler, and P. B. Littlewood for helpful conversations.

[1]L. W. ter Haar, F. J. DiSalvo, H. E. Bair, R. M. Fleming, J. V. Waszczak, and W. E. Hatfield, Phys. Rev. B (to be published).
[2]F. J. DiSalvo, J. A. Wilson, B. G. Bagley, and J. V. Waszczak, Phys. Rev. B **12**, 2220 (1975).
[3]F. J. DiSalvo, D. E. Moncton, J. A. Wilson, and S. Mahajan, Phys. Rev. Lett. **14**, 1543 (1976).
[4]J. C. W. Folmer, F. Jellinek, J. Less-Common Met. **76**, 153 (1980); C. F. van Bruggen, Ann. Chim. (Paris) **7**, 171 (1982).
[5]R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Phys. Rev. Lett. **45**, 576 (1980).
[6]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. B **26**, 184 (1982).
[7]K. K. Fung, S. McKernan, J. W. Steeds, and J. A. Wilson, J. Phys. C **14**, 5417 (1981).
[8]C. Burschka, Z. Naturforsch. **34b**, 675 (1979).
[9]J. Graham and A. D. Wadsley, Acta Crystallogr. **20**, 93 (1966).
[10]R. M. Fleming, Synth. Met. **13**, 241 (1986).
[11]W. L. McMillan, Phys. Rev. B **12**, 1187 (1975); **14**, 1496 (1976); **16**, 643 (1977).
[12]See, for example, A. R. West, *Solid State Chemistry and its Applications* (Wiley, New York, 1984), Chap. 13.
[13]See, for example, *Charge Density Waves in Solids,* edited by Gy. Hutiray and J. Solyom, Lecture Notes in Physics, Vol. 217 (Springer-Verlag, Berlin, 1985).
[14]R. M. Fleming, F. J. DiSalvo, R. J. Cava, and J. V. Waszczak, Phys. Rev. B **24**, 2850 (1981).