Observation of charge-density waves in the cubic spinel structure CuV_2S_4

R. M. Fleming, F. J. DiSalvo, R. J. Cava, and J. V. Waszczak
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 16 March 1981)

We have observed charge-density-wave (CDW) phase transitions in the cubic spinel structure CuV_2S_4. At 90 K a CDW forms with a reduced wave vector $\vec{q}=(1/4-\delta)[110]$. The incommensurability δ decreases with decreasing temperature, and lock-in ($\delta=0$) occurs at 75 K. At about 50 K a first-order transition to a new incommensurate CDW structure with $\vec{q}\approx(1/3)[110]$ occurs. Anomalies in the magnetic susceptibility and the resistance occur at 90 and 50 K.

Charge-density waves (CDW's) are now a frequently observed feature of anisotropic metals such as the one-dimensional conductors[1] and the two-dimensional layered compounds.[2] Although our understanding of the microscopic mechanism of CDW formation is incomplete, the simplest models suggest that the low dimensionality produces anisotropic Fermi surfaces with regions of low curvature which are generally favorable to CDW formation due to "nesting" of the low-curvature regions. Since the Fermi surface of a three-dimensional metal is likely to have more curvature (i.e., less anisotropy), the likelihood of a CDW state in a three-dimensional material via a nesting mechanism is significantly diminished. The experimental signature of a CDW is an incommensurate structure that occurs below an onset temperature with a wave vector determined by the Fermi-surface geometry. Only a few three-dimensional metals have thus far been found to have an incommensurate structure: ZrV_2,[3] $\alpha-U$,[4] and $Ti_{50}Ni_{47}Fe_3$.[5] For completeness, we point out that incommensurate phases can occur without the presence of a CDW (i.e., due to some microscopic mechanism other than a Fermi-surface instability).[6] For example, incommensurate structures are observed in insulators such as $BaMnF_4$ (Ref. 7) and K_2SeO_4.[8] Finally, Overhauser proposed[9] that a CDW may also occur in metals with a spherical Fermi surface (i.e., no nesting) to reduce the correlation energy, but diffraction studies show no evidence of a CDW.[10]

We have found evidence of CDW formation in CuV_2S_4, a compound with the cubic spinel structure. Previous workers observed a phase transition near 70 K and suggested that it was probably electronic in origin.[11] An anomaly in the magnetic susceptibility was observed and NMR experiments[11,12] showed a broadening of the Cu line and an abrupt shift of the V resonance. Our experiments show the existence of three phase transitions at 90, 75, and about 50 K. We observe these phase transitions in the resistance, magnetic susceptibility, and by x-ray diffraction. The 90-K phase transition appears to be second order and results in an incommensurate superlattice with a reduced wave vector of $\vec{q}=(\frac{1}{4}-\delta)[110]$. The incommensurability δ smoothly decreases with decreasing temperature and a commensurate structure ($\delta=0$) is obtained at 75 K. At about 50 K a first-order phase transition occurs and the $\frac{1}{4}[110]$ commensurate superlattice abruptly shifts to a weakly incommensurate superlattice with a wave vector $\vec{q}\approx\frac{1}{3}[110]$. At temperatures below 50 K Bragg peaks at (200), (600), and (420), which are forbidden by symmetry in the spinel space group also appear in addition to the $\frac{1}{3}[110]$ superlattice.

CuV_2S_4 has a face-centered-cubic (fcc) structure[11] in which the sulfur ions form cubic close-packed (111) planes. Two types of metal (111) planes alternate between the close packed sulfur planes. In the first type of metal plane, vanadium atoms occupy $\frac{3}{4}$ of the octahedral interstices in lines along $\langle 110\rangle$ directions. In the second type of plane, vanadium atoms occupy $\frac{1}{4}$ of the octahedral interstices and copper atoms occupy $\frac{1}{4}$ of the tetrahedral interstices. As a result, all vanadium atoms are located in VS_6 edge-shared octahedra which form interlocking chains in the six $\langle 110\rangle$ directions. All copper atoms occur in CuS_4 tetrahedra between planes of VS_6 octahedra.

CuV_2S_4 single crystals were obtained by iodine-vapor transport in sealed quartz tubes in a temperature gradient of 850 to 750 °C. The resulting crystals were small octahedra with a maximum size of about $1\times1\times1$ mm^3. Powder samples were also prepared by first reacting stoichiometric amounts of the elements in sealed quartz tubes at 650 °C. The powders were then pressed into pellets, reacted a second time at 600 °C, and slow cooled to room temperature. Susceptibility data were taken in a Faraday balance and resistivity measurements were made by attaching four small gold leads to a single-crystal sample with conducting silver epoxy. X-ray scattering as a function of temperature was performed on both powders and single-crystal specimens. Powder samples were

prepared by evaporation of methanol from a slurry of methanol and crushed crystals on a Pt substrate. Copper $K\alpha$ x rays from a rotating anode source with a fine focus (0.2×2 mm^2) projected spot were employed. A singly bent graphite monochromator and a flat graphite analyzer gave a $\vec{Q}$ resolution with a full width of about 0.02 Å^{-1}. A two-circle goniometer permitted scans within a selected plane in reciprocal space [usually the (*hhl*) zone].

The magnetic susceptibility and the resistance as a function of temperature are shown in Fig. 1. The resistance shows a weak cusp at 90 K and a knee at about 50 K. The susceptibility data in Fig. 1 were taken on a sample consisting of many single crystals. The susceptibility is very high for a metal with no local moments. (At room temperature on a per mole of V basis, it is higher than that of Pd metal.) A reversible decrease in the susceptibility occurs at 90 K and an abrupt transition to a more paramagnetic value is seen at about 50 K. Both the susceptibility and the resistance show hysteresis of about 10 K associated with the 50-K transition indicating that this transition is first order. The rising susceptibility at low temperatures is likely a Curie contribution due to paramagnetic impurities.

The observation of two phase transitions in the electronic properties of CuV_2S_4 prompted us to investigate their structural nature by x-ray diffraction. Weak lines, in addition to those at room temperature, were initially observed in low-temperature powder patterns. These lines were then identified in single-crystal specimens as coming from two different superlattices associated with the two phase transitions. At 90 K a superlattice which is initially incommensurate forms with a reduced wave vector of $\vec{q} = (\frac{1}{4} - \delta)[110]$ with incommensurability $\delta \approx 0.06a^*/4 \approx 0.01$ Å^{-1}. Satellites at $\pm\vec{q}$ were observed for about 20 reflections in the (*hhl*) zone. Figure 2

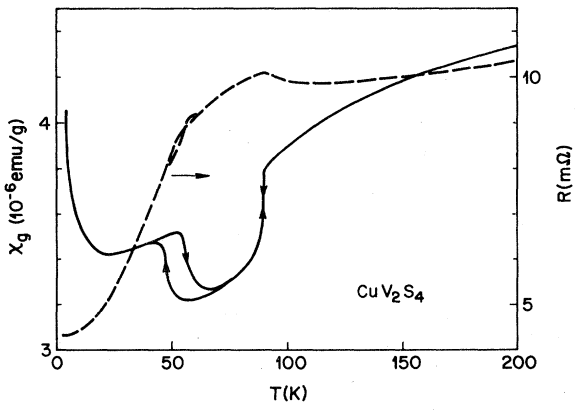

FIG. 1. Magnetic susceptibility and resistance as a function of temperature. Anomalies at 90 and about 50 K are apparent.

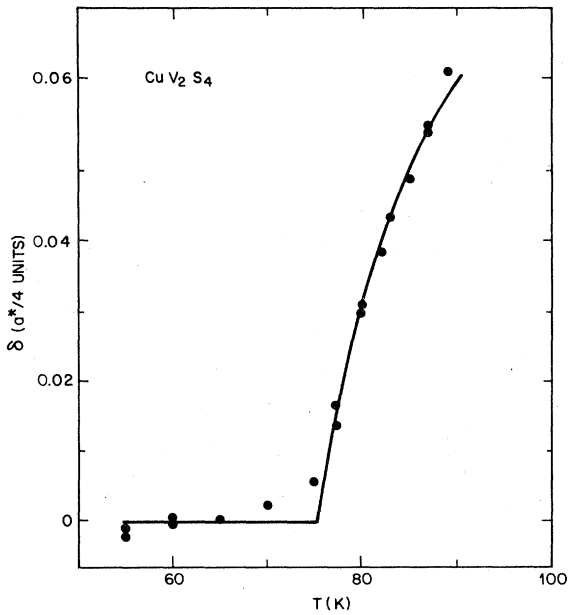

FIG. 2. Incommensurability as a function of temperature for the $\vec{q} = (1/4 - \delta)[110]$ superlattice which occurs between 90 and 50 K.

shows a plot of δ as a functon of temperature. The shape of δ vs T has downward curvature as expected of a conventional commensurate-incommensurate transition of the Frank–Van der Merwe type[13,14] and a lock-in transition ($\delta = 0$) occurs at 75 K. Strong second-order scattering was also seen at $2\vec{q} = (\frac{1}{2} - \delta)[110]$. In some regions of reciprocal space the second-order peaks were more itense than first-order peaks. The normalized intensities of superlattice peaks near $(2\frac{3}{4}\,2\frac{3}{4}\,2)$ and $(3\frac{1}{2}\,3\frac{1}{2}\,2)$ are shown in Fig. 3. The solid lines are guides to the eye. Qualitatively the second-order scattering scales as a higher power of the order parameter as expected for a displacive phase transition.

At about 50 K the wave vector of the commensurate $\frac{1}{4}[110]$ superlattice abruptly shifts to $\vec{q} = (\frac{1}{3} - \delta)[110]$. Scans along [*hh*2] showing the first- and second-order peaks of the $\frac{1}{4}[110]$ superlattice at 60 K and the first-order peak of the $\frac{1}{3}[110]$ superlattice at 11 K are shown in Fig. 4. The low-temperature superlattice peaks are broader than resolution and slightly incommensurate. We find $\delta \approx 0.03a^*/3 \approx 0.006$ Å^{-1} at 11 K. Because we had only moderate $\vec{Q}$ resolution, we were not able to investigate any temperature dependence of δ in this lower-temperature phase. We observed little variation of the intensities of the $\frac{1}{3}[110]$ peaks as a function of temperature. The excess width of the $\frac{1}{3}[110]$ peaks over resolution indicates a coherence length of about 100 Å. In addition, for temperatures below 50

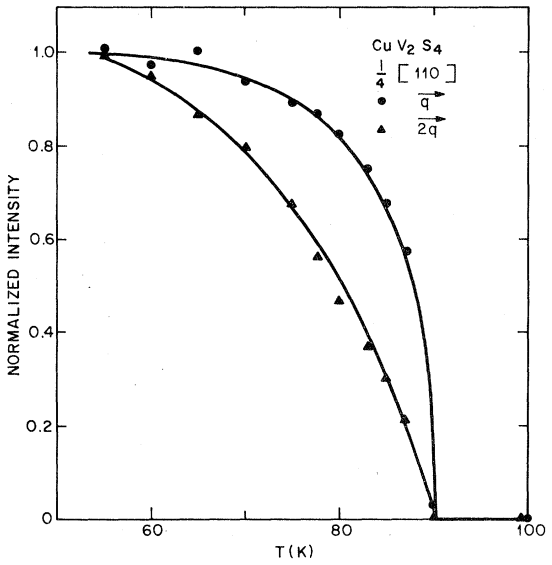

FIG. 3. Normalized, integrated intensity of first- and second-order scattering from $\vec{q}=(1/4-\delta)[110]$ as a function of temperature.

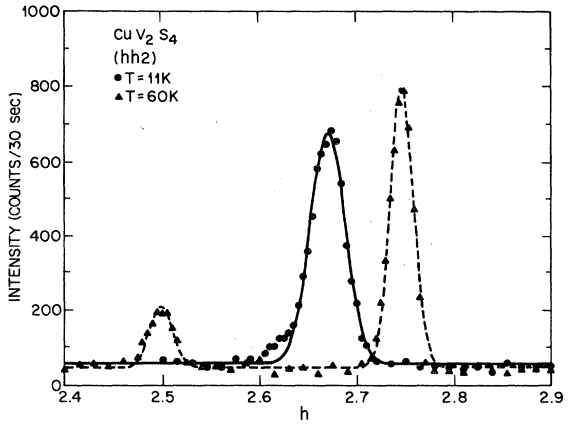

FIG. 4. Scans along [$hh2$] showing first- and second-order peaks from the $\vec{q}=(1/4-\delta)[110]$ superlattice at 60 K and first-order scattering from $\vec{q}\approx(1/3)[110]$ at 11 K.

K weak intensity is seen at the (200), (600), and (420) Bragg peaks. These peaks are not allowed in the spinel space group $Fd3m$ and their presence at low temperatures indicates that the symmetry of the host lattice has been lowered. The structure, however, appears to remain fcc and no splittings or major changes in the intensities of other Bragg peaks are seen. This indicates that the space group of the low-temperature average structure is changed to $F\bar{4}3m$. The lower symmetry of $F\bar{4}3m$ allows the following relaxations of the spinel structure: (1) The 32 equivalent sulfur atoms in $Fd3m$ are split into two nonequivalent sets of 16; (2) the eight equivalent copper atoms in $Fd3m$ are split into two nonequivalent sets of four; and (3) the vanadium atoms remain equivalent but in $F\bar{4}3m$ they occur in positions which allow them to be displaced (on average) from their ideal spinel positions.

The data suggest that CDW's exist in CuV_2S_4; however, in the strictest sense we have not proven that the incommensurate phase is directly connected to the Fermi surface. At present no other mechanism is known which will produce a nonmagnetic, incommensurate phase in a metal. "Proof" of the existence of CDW's has actually been shown for only a limited number of materials. In the layered compound $1T-Ta_{1-x}Ti_xS_2$ a direct connection to the Fermi surface was made by decreasing the Fermi surface (in a rigid-band way) through alloying and thereby changing the CDW wave vector.[15] In principal one might also connect the phase transition to the Fermi surface by accurate band-structure calculations. Less direct but compelling evidence may be obtained from microscopic measurements such as NMR or x-ray photoemission spectroscopy (XPS). NMR measurements of the Knight-shift profiles directly measure the charge modulation of the electrons inherent to a CDW and can give detailed information about the CDW as has been shown in the layered compounds $2H$-$NbSe_2$ (Ref. 16) and $2H$-$TaSe_2$.[17] Further suggestive evidence of CDW's is the observation of anomalies in the electrical and magnetic properties (such as those shown in Fig. 1) due to CDW-induced gaps over portions of the Fermi surface.

The observation of a CDW in a cubic material is quite unusual. In the few other cases mentioned previously,[3–5] a strong coupling to a uniaxial strain is apparent and it is likely that the distortions are a single-$\vec{q}$ state (i.e., only one wave vector is necessary to characterize the local distortions). In the layered compounds, however, the CDW is triple $\vec{q}$.[18] In CuV_2S_4, since there are six $\langle 110\rangle$ directions, the order parameter could potentially have 12 components. At present no evidence exists to suggest that the overall cubic symmetry of CuV_2S_4 is broken. Future diffraction and NMR experiments will address the possibility of a multiple-$\vec{q}$ CDW in CuV_2S_4 as well as determine lattice displacements as a function of temperature.

We would like to acknowledge helpful conversations with D. E. Moncton, D. B. McWhan, and T. M. Rice. We thank D. B. McWhan for the use of his x-ray scattering apparatus.

[1]For reviews of recent work see the following conference proceedings: *Molecular Metals,* edited by William E. Hatfield (Plenum, New York, 1979); *The Physics and Chemistry of Low Dimensional Solids,* edited by Luis Alcãcer (D. Reidel, Boston, 1980).

[2]For a review see F. J. DiSalvo, in *Electron-Phonon Interactions and Phase Transitions,* edited by Tormod Riste (Plenum, New York, 1977), p. 107

[3]D. E. Moncton, J. D. Axe, J. Bostock, and M. Levinson, Bull. Am. Phys. Soc. 25, 199 (1980).

[4]H. G. Smith, N. Wakabayashi, W. P. Crummett, R. M. Nicklow, G. H. Lander, and E. S. Fisher, Phys. Rev. Lett. 44, 1612 (1980).

[5]M. E. Meichle, M. B. Salamon, S. M. Shapiro, C. M. Wayman, and C. M. Hwang, Bull. Am. Phys. Soc. 24, 429 (1979).

[6]For a general review of structural phase transitions see R. A. Cowley and A. D. Bruce, Adv. Phys. 29 (1980).

[7]D. E. Cox, S. M. Shapiro, R. M. Cowley, M. Eibschütz, and H. J. Guggenheim, Phys. Rev. B 19, 5754 (1979).

[8]M. Iizumi, J. D. Axe, G. Shirane,and K. Shimaoka, Phys. Rev. B 15, 4392 (1977).

[9]A. W. Overhauser, Phys. Rev. 167, 691 (1968).

[10]S. A. Werner, J. Eckert, and G. Shirane, Phys. Rev. B 21, 581 (1980).

[11]N. Le Nagard, A. Katty, G. Collin, O. Gorochov, and A. Willig, J. Solid State Chem. 27, 267 (1979).

[12]P. Locher, Z. Angew. Phys. 24, 277 (1968).

[13]F. C. Frank and J. H. Van der Merwe, Proc. R. Soc. London 198, 205 (1949).

[14]W. L. McMillan, Phys. Rev. B 14, 146 (1976).

[15]F. J. DiSalvo, J. A. Wilson, B. G. Bagley, and J. V. Waszczak, Phys. Rev. B 12, 2220 (1975).

[16]C. Berthier, D. Jerome, and P. Molinie, J. Phys. C 11, 797 (1968), and F. Borsa, D. R. Torgeson, and H. R. Shanks, Phys. Rev. B 15, 4576 (1967).

[17]B. H. Suits, S. Courturie, and C. P. Slichter, Phys. Rev. Lett. 45, 194 (1980).

[18]D. E. Moncton, J. D. Axe, and F. J. DiSalvo, Phys. Rev. B 16, 801 (1977).