Magnetic properties of copper chalcogenide spinels

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Following the discovery of a charge-density wave in the cubic chalcogenide spinel CuV_2S_4,[1] the other known copper chalcogenide spinels were synthesized and their magnetic susceptibility measured to look for similar phase transitions. No phase transitions were observed in these other compounds. The present data also show that the electrons in metallic CuV_2S_4 are highly correlated (the magnetic susceptibility is greatly enhanced). Data concerning the effects of alloying and nonstoichiometry on the magnetic properties of CuV_2S_4 are also presented.

INTRODUCTION

The recent observation of incommensurate lattice distortions in the metallic compound CuV_2S_4,[1] which has the cubic spinel structure, prompted us to search for phase transitions in related copper chalcogenide spinels.[2] Present evidence suggests that the phase transitions in CuV_2S_4 are due to a charge-density wave (CDW) at low temperatures. Such CDW instabilities are common in lower-dimensional metals, such as in quasi-one-dimensional $NbSe_3$ (Ref. 3) and in quasi-two-dimensional $TaSe_2$,[4] but are rare in metals with strong three-dimensional bonding, as occurs in these cubic spinels. With the exception of the ferromagnetic chromium spinels,[5] the magnetic properties of many of these spinels have not been examined in any detail. Since the phase transitions in CuV_2S_4 produce distinct changes in the magnetic susceptibility but weaker anomalies in the electrical resistivity,[1] we chose to measure the temperature-dependent magnetic susceptibility of other copper spinels (CuM_2S_4 with $M =$ Ti, Zr, Hf, V, Co, Rh, and $CuRh_2Se_4$). Although these spinels are metallic,[6] we have not observed evidence for phase transitions similar to those of CuV_2S_4. However, the magnetic properties of these spinels reflect the evolution of the band structure and many-body interactions as the d-band occupation increases. Further, the effects of nonstoichiometry and substitutional doping on the phase transitions of CuV_2S_4 are examined.

SAMPLE PREPARATION

The compounds were usually prepared in polycrystalline form by heating the appropriate quantities of the elements in sealed evacuated quartz tubes at $600-800\,^\circ$C for several days. The samples were then ground and pressed into pellets at 40 000 psi and refired in sealed tubes for several more days at $600\,^\circ$C to produce homogeneous products. The resulting product was identified by powder x-ray diffraction. Finally, single crystals of CuV_2S_4 were grown by iodine vapor transport at growth temperatures from 720 to $800\,^\circ$C. The lower growth temperature was empirically determined to be the lowest temperature at which reasonable growth rates could be obtained. All that growth temperature crystals of ~ 0.2 mm in diameter were obtained after a one month growth time.

MAGNETIC MEASUREMENTS

We first present the results of the measurements on the undoped, stoichiometric spinels. Since we are searching for phase transitions similar to those observed in CuV_2S_4, the magnetic susceptibility of CuV_2S_4 is presented first in Fig. 1. The magnetic susceptibility of CuV_2S_4 is large and paramagnetic exhibiting only a weak temperature dependence above 100 K. Previous NMR studies[7] as well as electrical and magnetic studies[8] indicated some anomalous behavior below 100 K. Both the magnetic susceptibility and the electrical resistivity (inset Fig. 1) show a reversible transition at 90 K (probably second order) and a first-order transition with considerable hysteresis near 55 K.[1] X-ray diffraction studies[1] show that an incommensurate lattice distortion appears below 90 K with a wave vector $\vec{q}$ parallel to [110], $\vec{q} = (|a^*|/4)(1+\delta)[110]$. The incommensurability δ is temperature dependent, decreasing from 0.06 to 0 (commensurate) at approximately 75 K. No anomalies were observed
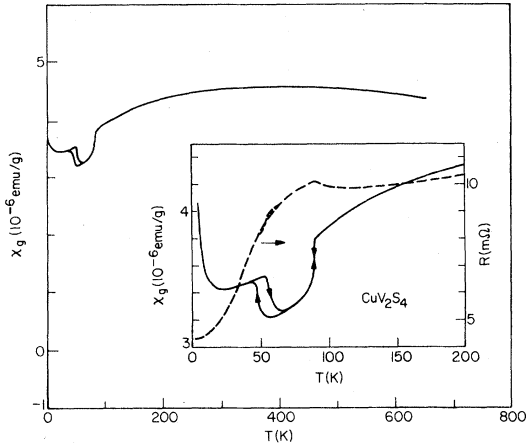
FIG. 1. Magnetic susceptibility of CuV_2S_4 is only weakly temperature dependent below 700 K and shows two sharp changes at low temperatures. The inset shows both the electrical resistance and the magnetic susceptibility of single crystals in the region of the phase transitions near 90 and 55 K.

in the physical properties near this 75-K lock-in transition.

The magnetic susceptibility of CuM_2S_4 powders with M =Ti,Zr,Hf is shown in Fig. 2. Single-phase powders of $CuTi_2S_4$ could be prepared at 650 °C, but reaction temperatures of 800 °C were required for Zr and Hf. A small Curie contribution due to paramagnetic impurities has been subtracted from the actual data to obtain Fig. 2. The data were least-squares fit at low temperatures ($\lesssim 25$ K) to the form $X_0 + C/(T + \Theta)$, and $C/(T + \Theta)$ was subtracted from the data at all temperatures, as previously described.[9] The susceptibility of the Zr and Hf
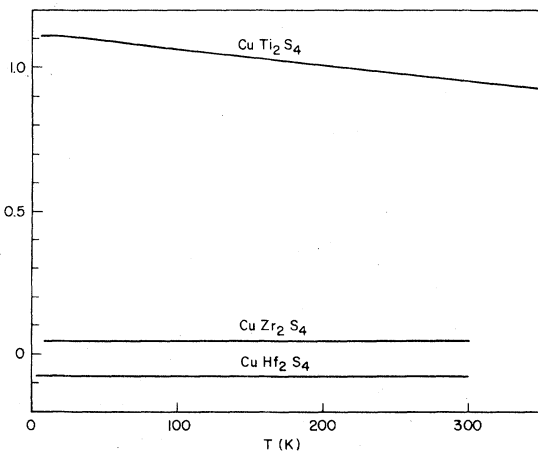
compounds is temperature independent and quite small. The susceptibility of $CuTi_2S_4$, however, shows some temperature dependence and is much larger than that of its $4d$ and $5d$ analogs.

The magnetic susceptibility of $CuRh_2S_4$ and $CuRh_2Se_4$ is shown in Fig. 3. Again, small Curie contributions have been subtracted from the actual data. The susceptibilities of the Rh compounds are somewhat more temperature dependent than those of the compounds of the earlier transition metals, although the magnitude of the susceptibility is not as large as that of typical transition-metal compounds with a high density of states.

Although powder x-ray diffraction measurements showed the $CuCo_2S_4$ samples to be single phase, a ferromagnetic transition was observed near 120 K. The magnitude of the ferromagnetic component varied from sample to sample, and is tentatively ascribed to a very low level of CoS_2 impurity phase. CoS_2 is ferromagnetic with a Curie temperature near 120 K.[10] One sample had a very small ferromagnetic component and the measured susceptibility showed no other anomalies (just the ferromagnetism of CoS_2). The susceptibility obtained by subtracting this ferromagnetic component is temperature independent at $X_g = 1.6 \times 10^{-6}$ emu/g, somewhat larger than that of $CuTi_2S_4$ but still much smaller than that of CuV_2S_4.

Other materials investigated included $CuTiVS_4$ and $CuTiSnS_4$. In the former compound, V appears to develop a local moment producing a large paramagnetic susceptibility.[11] The data for $CuTiVS_4$ could be fitted with the following Curie-Weiss formula from 50 to 300 K:

$$X_g = 7.0 \times 10^{-4}/(T + 40) + 2.9 \times 10^{-6},$$

FIG. 2. Although the transition metals Ti, Zr, and Hf are in the same group, the susceptibility of $CuTi_2S_4$ is much larger than that of its $4d$ and $5d$ analogs.
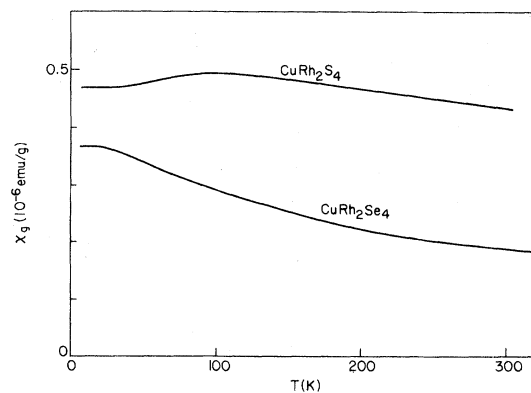

FIG. 3. Superconductors $CuRh_2S_4$ ($T_C = 4.3$ K) and $CuRh_2Se_4$ ($T_C = 3.5$ K) have magnetic susceptibilities that are somewhat more temperature dependent than those of the other chalcogenide spinels.
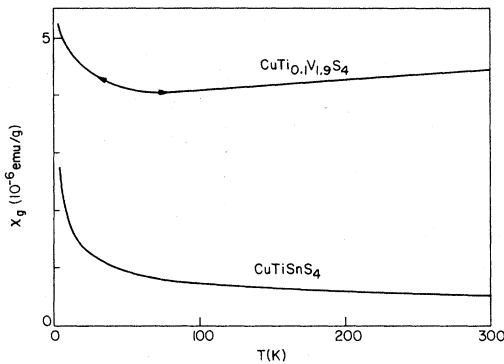
FIG. 4. No evidence for phase transitions is seen in the magnetic susceptibility of the spinels $CuTi_{0.1}V_{1.9}S_4$ or $CuTiSnS_4$.

in units of emu/g. The magnetic moment calculated from the Curie constant is $1.3\mu_B$ per formula unit. The susceptibility of $CuTiSnS_4$ is shown in Fig. 4. If the data are fitted with a Curie-Weiss formula below 50 K, a low magnetic moment of $0.2\mu_B$ per Ti is obtained. At higher temperatures, if the temperature dependence is interpreted as due to magnetic moments, a value of $0.4\mu_B$ is calculated. In neither compound was any anomalous behavior similar to that seen in CuV_2S_4 observed. It is possible, however, that the expected random occupation of the octahedral site in the spinel structure by the V-Ti or Sn-Ti would suppress any phase transition. Such a suppression occurs upon alloying in the layered compounds that show CDW's.[4] Indeed, $CuV_{1.9}Ti_{0.1}S_4$ showed no evidence of a phase transition in our magnetic measurements (Fig. 4).

Now we return to CuV_2S_4. The effects of nonstoichiometry were investigated by preparing powder samples with the composition $Cu_{1+x}V_{2+y}S_4$ for $-0.1 < x < 1.0$ and $-0.1 < y < 0.1$. For sufficiently large values of x and y, second phases could be detected in x-ray diffraction patterns. Previous studies on copper chalcogenide spinels suggest that both a copper deficiency[12] or excess[13] is possible. However, the range of nonstoichiometry for the transition metal appears to be small. If $y = 0$, the observed phase transitions rapidly broadened and moved to lower temperatures as the copper content is changed from $x = 0$, indicating that the copper stoichiometry can be changed but that the disorder produced perturbs the phase transition. If $x = 0$, the phase transitions moved to slightly higher temperatures when y was greater than zero ($y < 0.10$). For example, at $y = 0.08$ the midpoint of the upper transition was at 92.0 K and the hysteresis of the lower transition had narrowed

to 4 K centered at 55 K. At these values of y, a second phase appears in the diffraction patterns. This second phase probably has atoms with a local paramagnetic moment, since the low-temperature Curie contribution increased over the nominally stoichiometric material. It seems likely that the "CuV_2S_4" prepared with excess V in the reaction is the most stoichiometric, since the upper transition is at the highest temperature and the hysteresis of the lower transition is minimal. This stoichiometric CuV_2S_4 appears to be in equilibrium with a second phase (presently unidentified). However, when single crystals were prepared from the powder samples containing excess V, results similar to Fig. 1 were obtained. It appears then that crystals grown at 720 °C or above are slightly nonstoichiometric (the powder samples were prepared at 600 °C).

The last series of samples that we examined were $CuV_{2-x}Cr_xS_4$. It is known from previous work that $CuCr_2S_4$ is ferromagnetic at $T_c = 398$ K (Ref. 14), and that for x as low as 0.25 the compound is still ferromagnetic at low temperatures.[15] Figure 5 shows the susceptibility of Cr-doped CuV_2S_4 at $x = 0.05$ and 0.12. Both show sizable Curie contributions at low temperatures. We assume that the susceptibility is given by $X_g = C_g/(T + \Theta) + X_0$. Since the susceptibility of CuV_2S_4 is temperature dependent, we expect that in these alloys X_0 will also show some temperature dependence, except at some sufficiently low temperature, where it will be constant. To analyze the present data, we assume X_0 is constant below 50 K, and the least-squares method fits the data below 50 K to the above
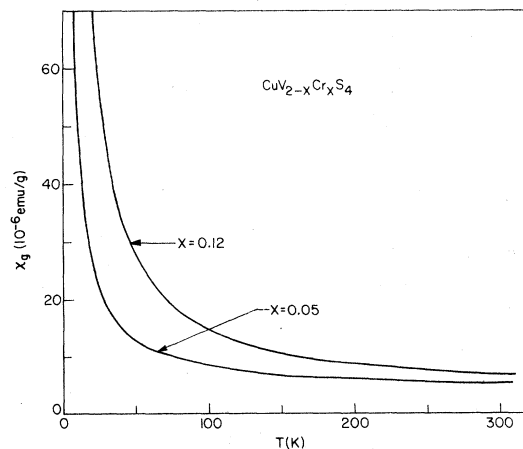

FIG. 5. Magnetic susceptibility of $CuV_{2-x}Cr_xS_4$ shows a large Curie contribution at low temperature even at low values of $x = 0.05$ and 0.12.

Curie-Weiss form. We obtain $C_g = 4.60 \times 10^{-4}$ emu/g K, $\Theta = -0.8$ K, and $X_0 = 3.30 \times 10^{-6}$ emu/g at $x = 0.05$, and $C_g = 1.28 \times 10^{-3}$ emu/g K, $\Theta = -2.0$ K, and $X_0 = 1.02 \times 10^{-6}$ emu/g at $x = 0.12$. At $x = 0.05$ the compound is not ferromagnetic down to 1.5 K, but at $x = 0.12$ the ferromagnetic ordering temperature is 1.7 K as determined by an Arrott plot.[16] The effective magnetic moment per Cr can be directly calculated from the Curie constant C_g to obtain $\mu_{\text{eff}} = 4.65\mu_B$ at $x = 0.05$ and $\mu_{\text{eff}} = 5.0\mu_B$ at $x = 0.12$. These moments are considerably above that expected for a localized Cr^{3+} ion $(3.87\mu_B)$. In a localized electron approximation, near-neighbor V atoms must develop a local moment to account for the large moment per Cr. Alternatively, in the delocalized or band limit, the enhancement could be explained as a result of spin polarization of the conduction band. Assuming that the magnetic moment and the exchange energy (or equivalently Θ) are independent of temperature to at least 300 K, the Curie contribution to the susceptibility can be subtracted from the measured susceptibility to obtain the temperature dependent X_0 from 4.2 to 300 K as shown in Fig. 6. The small anomalies in the susceptibility near 120 K suggest some remnant of the phase transitions in CuV_2S_4 remain.

DISCUSSION

The main purpose of this study was to look for phase transitions in copper chalcogenide spinels and to further examine the properties of CuV_2S_4. Some crystal-chemical questions were not addressed. For example, the accepted structure of CuV_2S_4 at room
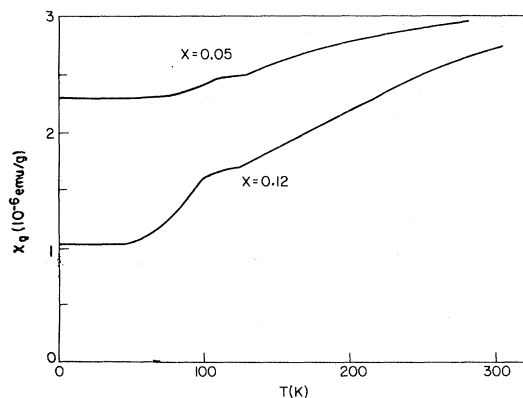

FIG. 6. Magnetic susceptibility of $CuV_{2-x}Cr_xS_4$ with the Curie contribution subtracted out (see text for procedure).

temperature is the "normal" spinel structure[17,18]— e.g., Cu is found in an ordered arrangement in tetrahedral sites, and V is ordered on octahedral sites. The possibility of inversion[18] (the presence of V in tetrahedral sites and vice versa) is not examined here. The x-ray powder diffraction intensities for all the compounds studied agreed with that calculated assuming the normal spinel structure, but a small degree of exchange between Cu and the other transition metal cannot be ruled out by this method. However, copper is always found in (highly distorted) tetrahedral sites in binary sulfide compounds, while vanadium is found in octahedral sites in binary sulfide compounds. The strong site preferences of Cu and V suggest that only a very small exchange of Cu and V occurs. Similar observations can be made about the other compounds studied here.

The magnetic susceptibility studies of copper chalcogenide spinels detect anomalies due to structural phase transitions only in CuV_2S_4. The two transitions detected in magnetic susceptibility in the samples containing the most stoichiometric spinel are a second-order transition at 92 K and a first-order transition centered at 55 K with a 4-K total hysteresis (although a small amount of second phase is also present in those samples).

Since the phase just below 92 K has an incommensurate structure, the mechanism of transformation is thought to be a CDW.[1] That is, the electrons at the Fermi surface, coupled to the phonons, become unstable at low temperatures. The wave vector of the distortion is related to Fermi-surface geometry and the transition produces gaps over portions of the Fermi surface. At present the band structure of these spinels is unknown. There has been some controversy concerning the valence state of the copper (i.e. monovalent or divalent) and whether the states at the Fermi level have significant Cu d character. However, recent photoemission experiments suggest that the copper is monovalent,[19] so that the conduction-band states would be based primarily on d orbitals of the transition metal (V). In that case, the mechanism of transformation could well be similar to that producing the CDW observed in VS_2 (Ref. 20) or VSe_2 (Ref. 21).

A second factor that may bear on the mechanism of transformation in CuV_2S_4 is apparent from the observed trends in the magnitude of the magnetic susceptibility as the transition metal is changed. The magnetic susceptibility of CuV_2S_4 at 300 K is 6.65×10^{-4} emu per mole of vanadium. This value is quite large, larger even than that of Pd metal at the same temperature $(5.5 \times 10^{-4}$ emu/mole). The

susceptibility of Pd metal is known to be greatly enhanced by electron-electron interactions,[22] so that it is almost ferromagnetic. It is suggested then that the susceptibility of CuV_2S_4 is also highly enhanced. On the other hand, if we assume that the large susceptibility of CuV_2S_4 is due only to Pauli and Van Vleck paramagnetism (with no electron-electron enhancement), a comparison with the known high density of states and high superconducting transition temperature compounds of the $A15$ structure (such as Nb_3Sn and V_3Si) suggests that CuV_2S_4 would have a very high density of states indeed. For V_3Si at 300 K the susceptibility is 2.6×10^{-4} emu/mole of vanadium.[23] Further, recent studies indicate that the susceptibility of the $A15$'s is already considerably enhanced.[24] Consequently, it is quite reasonable to conclude that the large susceptibility of CuV_2S_4 can only be due to a considerable electron-electron enhancement. That the susceptibility of CuV_2S_4 is enhanced is further supported by another analogy to metallic Pd. Alloys of $Pd_{1-x}Fe_x$ show large moments per Fe (about $10\mu_B$/Fe atom) due to spin polarization of the Pd d band by the magnetic Fe atoms, and the alloys are ferromagnetic at low temperatures for x as small as 0.002.[25] The data of Fig. 5, the large moments per Cr derived from these data, and ferromagnetism at low Cr concentrations in $CuV_{2-x}Cr_xS_4$ all suggest that the conduction electrons in CuV_2S_4 are highly correlated. Lastly, a recent tight-binding band-structure calculation[26] for CuV_2S_4 gives a density of states at the Fermi level of 1.5 states/(vanadium atom eV spin). The Pauli susceptibility calculated from this density of states is 1.0×10^{-4} Curie per mole of vanadium. While this value is indeed quite large, it is clear that the total susceptibility is considerably enhanced, even if a rather large Van Vleck contribution to the susceptibility is assumed.

The susceptibility of $CuTi_2S_4$ is smaller than that of CuV_2S_4, but is still substantial, and $CuCr_2S_4$ is ferromagnetic with $T_C = 398$ K.[14] Also the susceptibilities of $CuZr_2S_4$ and $CuHf_2S_4$ are much lower than that of $CuTi_2S_4$. The following model of the properties of the early transition-metal copper sulfide spinels is thus suggested. The d bands narrow on going from $5d$-$4d$ to $3d$ elements and the electron-electron correlation increases rapidly on proceeding from Ti to V to Cr so that ferromagnetism is apparent in the latter spinel. Evidently, in CuV_2S_4 the electron-phonon interactions are also large and dominate the net electron-electron interactions to produce a CDW.[27]

SUMMARY

CuV_2S_4 is unique among the copper chalcogenide spinels in showing anomalies in its magnetic properties. These anomalies have previously been shown to be due to structural phase transitions that are characterized by an incommensurate lattice distortion[1] (a CDW). If such a phase transition were to occur in the other spinels, they would be expected to be visible as "anomalies" in the magnetic susceptibility—as in the transition-metal dichalcogenides.[4]

The magnitude of the magnetic susceptibility of CuV_2S_4 strongly suggests that the conduction electrons in this metal are highly correlated. The enhancement of the magnetic susceptibility is much larger than that of the other chalcogenide spinels, with the exception of the $CuCr_2X_4$ spinels—which are ferromagnetic with Curie temperatures above room temperature.

ACKNOWLEDGMENTS

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