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Effects of competing magnetic interactions on the electronic transport properties of $CuCrSe_2$

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ABSTRACT

We have synthesized single-phase samples of the $CuCrSe_2$ phase that exhibits hexagonal-rhombohedral layered crystal structure with space group $R3m$. Here we present a detailed study of electronic transport and magnetic properties of $CuCrSe_2$. We moreover investigate the heat capacity of $CuCrSe_2$ in comparison to that of $CuCrS_2$. The electrical resistivity of $CuCrSe_2$ shows metallic-like behavior down to 2 K, while the thermoelectric power is large around 100 $\mu V\,K^{-1}$ at 300 K. A weak anomaly in resistivity and a rounded maximum in magnetic susceptibility are observed around 55 K. No sharp transition at 55 K is observed in the heat capacity of $CuCrSe_2$, rather a visible maximum is seen. At low temperatures from 2 to 14 K, the magnetic heat capacity follows T^2-dependence. We tentatively believe this behavior of $CuCrSe_2$ to be due to competing magnetic interactions between intralayer Cr atoms. The ferromagnetic Cr–Se–Cr indirect exchange among intralayer Cr atoms is enhanced in the selenide compound (that is more metallic than the sulfide compound), and competes with the antiferromagnetic Cr–Cr direct interactions. The interlayer antiferromagnetic exchange through Cu atoms leads to magnetic ordering at low temperature at $T_N=55$ K.

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1. Introduction

In the layered Cr chalcogenides $ACrX_2$ with $X=$S or Se, triangular layers of Cr in a sandwich of X–Cr–X alternate with a layer of non-magnetic A atoms ($A=$Na, K, Cu or Ag) to give hexagonal-rhombohedral structures. The weak interlayer coupling results in the relatively low magnetic ordering temperature of $T_N=20$–55 K, while interactions among the Cr atoms within the layer are strong [1–5]. Neutron diffraction studies have revealed non-collinear magnetic ordering as a function of the Cr–Cr separation, originating from the competition of interactions from the distant neighbors in these compounds [4–6]. The direct exchange interaction between the Cr atoms is antiferromagnetic because of the half-filled t_{2g} orbitals of trivalent chromium while the indirect $\sim 90^\circ$ Cr–X–Cr superexchange interaction is ferromagnetic; in the $X=$Se compounds with the increase in Cr–Cr separation the direct interaction gets weaker [4,5]. The asymptotic value of the paramagnetic Curie temperature θ_{CW} related to the dominating intralayer interactions has been found to vary with the Cr–Cr separation from a large negative value of -250 K to a positive value of $+250$ K, in $LiCrS_2$ and $KCrSe_2$ respectively [1–6].

Recently some studies were directed towards understanding the non-collinear magnetic ordering and associated magneto-elastic properties of (Cu/Ag)CrS_2 in the model of "geometric frustration" of a Heisenberg antiferromagnet on a triangular lattice (HAFT), shown to be applicable in case of the corresponding oxides AMO_2 ($M=$Al, Cr, Fe), most notably in $CuCrO_2$ [6–10]. However, in case of the more covalent sulfide and selenide compounds a similar model of HAFT may not be applicable, since in these compounds the non-Heisenberg interactions such as the indirect exchange interactions—superexchange or kinetic exchange interactions via different routes dominate, and it is the competition among them that gives rise to the observed non-collinear or helical order. In case of $ACrX_2$ with $X=$S or Se, the modulation period of the magnetic moments of the Cr atoms within the layer increases with the Cr–Cr separation and in $KCrSe_2$ the moments are ferromagnetically ordered while remaining anti-parallel in the alternate layers [3–5].

Electronic transport properties of the $ACrX_2$ compounds, especially those containing Cu or Ag, have not been studied properly. Different studies have reported quite contrasting conductivity behaviors, from $\rho(300\text{ K})=0.025\ \Omega$ cm in crystals [11] to immeasurably high resistivity of pure $CuCrS_2$ and finally the appearance of an insulator-to-metal transition by V-substitution of Cr atoms, etc. [12]. In our recent work we found that, contrary to previously believed insulating nature, our $CuCrS_2$ samples were clearly non-insulating but exhibited a complex $\rho(T)$ dependence with a minimum in the resistivity around 100 K. The thermopower was remarkably large and nearly saturated at high temperatures [13–15]. We believe this behavior to be the intrinsic property of

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$CuCrS_2$, explained by a model similar to the self-doped Kondo-insulator. Here the “Kondo-insulator” like excitation gap can be realized due to the hybridization of narrow 3*d* band (instead of 4*f* bands of rare-earth elements) with the valence band of S or Se atoms in their paramagnetic phase [16,17].

In this paper we discuss the $CuCrSe_2$ phase, and present the results of structural analysis and physical-property measurements (electrical resistivity, Hall mobility, thermoelectric power, magnetic properties and specific heat) for it. Our results clearly show non-insulating nature of $CuCrSe_2$ similar to that of $CuCrS_2$.

2. Experiments

Single-phase samples of $CuCrSe_2$ were prepared by a direct reaction of pure elements in a required molar ratio in a sealed quartz tube. Our initial synthesis efforts carried out using a slow heating to 950 °C, resulted in samples with a significant contamination of cubic spinel compound $CuCr_2Se_4$ which is ferromagnetic at room temperature. To avoid the formation of this ferromagnetic impurity phase the starting mixture (Cu+Cr+2 Se) was placed in a vacuum-sealed quartz tube and rapidly heated in 10–20 h up to 950 °C. Explosion of the tube could be avoided by using a sufficiently long tube to generate a large temperature gradient. Thorough grinding of the reacted mass, pelletizing at 5-ton pressure, sintering at 950 °C in a sealed tube over 5–7 days followed by air quenching completely eliminated the ferromagnetic impurity phase, as could be confirmed by magnetization measurements at room temperature.

The samples were characterized by X-ray powder diffraction (XRD) using a Philips diffractometer (PANalytical X’pert PRO) with Cu$K\alpha$ radiation source for the crystal structure and by energy dispersive X-ray spectroscopy (EDAX) attached to a scanning electron microscope (SEM) for the chemical composition. Structural parameters (lattice parameters, atomic positions and site occupancies) were refined in space group $R3m$ using a Rietveld refinement software GSAS (EXPGUI) [18]. Electrical resistivity (ρ) and Hall mobility (μ_H) measurements were carried out on thin circular polycrystalline pellets in the van der Pauw geometry using Ag paint for the electrical contacts. Seebeck coefficient, $S(\equiv \Delta V/\Delta T)$, was measured with respect to copper in the temperature interval of 15–300 K in an apparatus built in a closed-cycle helium refrigerator system. At each temperature a small temperature difference was created across the sample length of 5–7 mm. A differential thermocouple (Au (0.05%Fe)/Chromel) gave the temperature difference. The spurious and the offset voltages of the measuring circuit were eliminated by reversing the directions of temperature gradient and averaging the measured thermal voltages. Magnetic measurements were carried out in a MPMS (Quantum Design) with 14 T magnetic field. A Quantum Design PPMS was used to measure the heat capacities of $CuCrSe_2$ and $CuCrS_2$ (for comparison).

3. Results and discussion

3.1. Phase purity and crystal structure

X-ray diffraction patterns indicated that our synthesis yielded phase-pure $CuCrSe_2$ samples. The XRD pattern for $CuCrSe_2$ was readily refined in space group $R3m$; in this crystal structure (shown in Fig. 1) all the atoms occupy 0 0 *z* positions with the rhombohedral lattice translations (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3). The refined structural parameters with standard deviations are presented in Table 1. By taking the occupancies for each atom equal to unity, minimum values were gotten for χ^2 and $R(F^2)$. This is in good agreement with the EDAX data, which gave the atomic ratio Cu:Cr:Se around 1.03:1.06:2. In Fig. 2, we present the calculated, observed and error XRD patterns for $CuCrSe_2$.

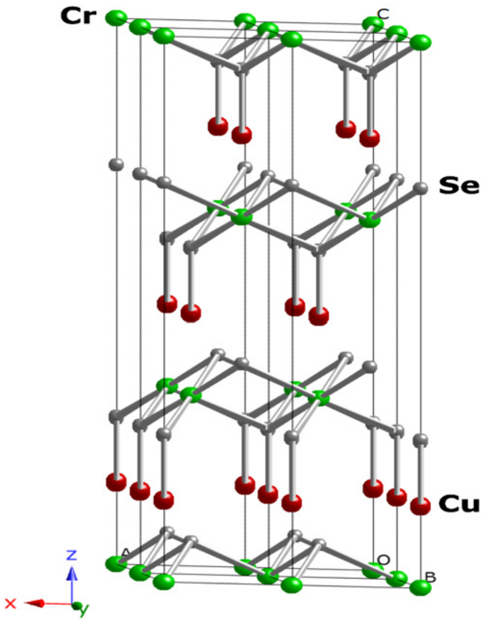

Fig. 1. Layered crystal structure of $CuCrSe_2$.

Table 1
Refined atomic parameters for the three $CuCrSe_2$ (950 °C).

Atom	*x*	y	*z*	Occupancy
$CuCrSe_2$ (950 °C)				
Cr	0	0	0	1
Cu	0	0	0.145(4)	1
Se(I)	0	0	0.264(5)	1
Se(II)	0	0	0.743(1)	1
$a=b=3.679(1)$ Å, $c=19.385(5)$ Å				
$\chi^2=1.13$, $R(F^2)=0.0631$, $R_{wp}=0.0500$				
Preferred orientation coefficient=0.81				

3.2. Electronic transport properties

3.2.1. Electrical resistivity

In Fig. 3 we show electrical resistivity ρ vs. temperature data for $CuCrSe_2$ measured on thin circular pellet from 2 to 340 K. On cooling from room temperature ρ decreases down to 2 K without significant effects due to ordering at $T_N=55$ K. In the inset shown is the derivative of resistivity $d\rho/dT$ in the vicinity of the magnetic transition temperature. Sharp change in $d\rho/dT$ is visible at T_N. It is similar to that found at the magnetic transition in metallic ferromagnets like Ni, Gd, etc. Similar effects are also seen in the chemically related Cr chalcogenide spinels of $CuCr_2X_4$ (X=S, Se or Te) at their ferromagnetic transitions ($T_C=320$–460 K) [19]. Moreover another anomaly is seen at 110 K. We believe that the 110 K anomaly may be related to the short-range ordering effect, which builds up in the system much above the magnetic transition. The magnetic susceptibility also shows deviation from the Curie-Weiss law around this temperature.

3.2.2. Hall mobility

The Hall coefficient (R_H) was measured on thin circular pellets of $CuCrSe_2$ from 2 to 300 K. The positive sign of R_H indicates hole-type conduction and is in agreement with the positive sign of Seebeck coefficient. The Hall mobility of the carriers (μ_H) was calculated

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