The study of Magnon-drag effects in the Thermopower of
CuCr$_2$X$_4$ (X = S, Se and Te)

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Abstract. The electrical resistivity $\rho$ and thermopower $S$ of metallic ferromagnets CuCr$_2$X$_4$ (X=S,Se or Te) are measured at low temperatures and in an external magnetic field of 1.5 Tesla. These properties are dominated by strong scattering effects in their ferromagnetic phase, resulting in (a) $\rho(T) \sim A T^2$ dependence with very large value of coefficient $A \approx 1 - 3 \times 10^{-8}$ $\Omega$-cm/K$^2$ in resistivity and (b) a peak in the thermopower around $T_C/3$. Thermopower is further increased by crystalline order and by the alignment of magnetic domains in an external magnetic field as has been found for Cu$_{1+x}$Cr$_2$Te$_4$. We have interpreted these effects as due to strongly coherent momentum conserving electron-magnon scattering giving a large $T^2$ contribution in resistivity and a large drag effect in thermopower.

Key words: Spinels, thermopower, magnon drag, phonon drag.

Introduction

The Chromium chalcogenide spinels containing Copper, CuCr$_2$X$_4$ (X = S, Se or Te ) are ferromagnetic above room temperatures with $T_C$ of about 360K-460K$^{(1)}$. The remarkably high $T_C$ has been attributed to their metallic nature and to Zener-exchange mechanism through electron transfer among mixed-valent Cr$^{3+}$--Cr$^{4+}$ ions in an ionic model with valence distribution Cr$^{2+}$[Cr$^{3+}$$_{1/2}$Cr$^{4+}$$_{1/2}$]$_2^2$-X$_2^2$$^{-}$ (with holes $\delta \approx 0.1$) for these compounds$^{(1)}$. Quite similar exchange mechanism is also proposed for the self doped CrO$_2$--metallic ferromagnets in which only d-electrons are involved in conduction and correlation effects dominate the electronic properties. However, the mixed valency of Cr and so the Zener-exchange mechanism for ferromagnetism in case of CuCr$_2$X$_4$ are disputed. The Cr$^{3+}$ state is believed to be unstable in these covalent chalcogenide compounds. The neutron scattering and NMR studies gave spin density expected from nearly integral Cr$^{3+}$-ions. But, at the same time, Cu was found to be non magnetic without localized spin density$^{(2)}$.

The electronic conduction in our Cr–chalcogenide spinels is neither primarily through Cr d-bands nor is the metallic nature a precondition for the ferromagnetic order as required for the Zener-exchange mechanism. The corresponding Zn, Cd and Hg spinels of Cr are semiconductors with ferromagnetic $T_C$ around 100K. In these, 90$^{0}$-super-exchange interactions involving Cr$^{3+}$X$^{-}$--Cr$^{3+}$ leads to ferromagnetic order. Nevertheless, the cause for the substantially higher $T_C$ for our metallic compounds is not clear. The transport properties including the Curie-point anomaly in electrical conductivity and thermopower in CuCr$_2$X$_4$, as will be presented later in figure (1), have qualitative similarities with the elemental Nickel and Gadolinium etc., which indicates conduction in relatively wide band and a model of spin disorder scattering, as proposed by Mott$^{(3)}$, may also be applicable in these compounds.

The previous studies of thermoelectric power (TEP) of ferromagnetic Ni, Fe and their alloys have shown that the drag effects in TEP sensitively depend on the nature of charge carrier scattering; the drag effects are found to be larger for Fe where the scattering is from the spin
disorder caused by localized spin fluctuations of the d-electrons, compared to Ni where the s-d scattering i.e. the scattering of mobile s-electron into the empty states of the d-bands is dominant\(^{(6)}\). For the localized nature of the d-electrons of Cr\(^{4+}\)-ions in CuCr\(_2\)X\(_4\), we expect substantial drag component in TEP from the momentum conserving electron-magnons scattering.

We have undertaken a detailed study of the electronic and thermal transport properties in order to examine the nature of conduction and dominant exchange interactions in Chromium Chalcogenides. Here, we present the results of electrical resistivity \(\rho\) and the Seebeck coefficients \(S\) from 15K to 300K of few compounds CuCr\(_2\)Se\(_4\) and Cu\(_{1+x}\)Cr\(_2\)Te\(_4\) (\(x = 0\) and 0.9) with the highest and the lowest \(T_c\) of 423K and 180K respectively among the family. The external magnetic field of 1.5Tesla was applied to discern possible magnon contribution in S.

### Experimental

All the compounds were obtained by reaction of pure elements at 600-700\(^\circ\)C in sealed quartz tubes. The sintering of the pelletized powder for an extended period of 5-7 days gave polycrystalline compound; the purity of phase was verified by the X-ray diffraction analysis. The purity especially for Tellurides, and the mechanical quality of the compact is considerably improved by using about 5% of excess Te and a lower temperature for the sintering.

The electrical conductivity was measured on circular pellets by van der Pauw method using silver paste for the contacts. The thermopower \(S\) and thermal conductivity \(\kappa\) was measured simultaneously by conventional steady state method on the pellets of rectangular shape (4x9x0.5 mm) between 15K – 300K in a closed cycle helium refrigerator. At each stabilized temperature small heat current was passed alternatively from both ends of the pellet. The ratio of the difference in thermovoltage measured with respect to copper and the temperature gradient using differential Au(Fe)/Chromel thermocouple gave S thus eliminating the spurious voltages in the circuit.

### Results and Discussion

#### Curie point anomalies:

The electrical resistivity \(\rho\) and the Seebeck coefficient \(S\) of four different compounds are shown in figure 1. They show metallic dependence of \(\rho\) and \(S\) on temperature. The anomalies at their respective ferromagnetic transition are surprisingly similar to pure Nickel and Gadolinium, where it was found that the temperature derivative \(d\rho(T)/dT\) and \(dS(T)/dT\) vary like a lambda – peak around the Curie point \(T_c\) similar to the magnetic contribution \(C_m\) in their specific heat at \(T_c\)\(^{(5,6)}\). This specific feature of Curie-point anomalies has been explained by Fisher and Langer\(^{(6)}\) due to dominance of scattering from the short range localized spin-fluctuations near the ferromagnetic transition. The special interest in our case is that this scattering can cause substantial increase in the TEP of the ferromagnetic phase.

The thermopower in all the compounds, irrespective of its sign, is strongly enhanced and passes through a maximum around \(T_c/3\), as shown in the lower panel of figure (1). The scaling of the maximum in TEP with the ferromagnetic \(T_c\) strongly suggest its magnetic origin and the possibility of magnon drag effects in these compounds. We will present more results and discuss this possibility in the following.

![Figure 1](image-url)

**Figure 1.** Resistivity \(\rho(T)\) plotted as \(\rho-\rho_0\) and Thermopower S of CuCr\(_2\)Se\(_4\), CuCr\(_2\)Te\(_4\), Cu\(_{1+x}\)Cr\(_2\)Te\(_4\)(3) and Cu\(_{1+x}\)Cr\(_2\)Te\(_4\)(2) showing anomalies (\(\uparrow\)) at ferromagnetic transition temperatures \(T_c\). The temperature of \(S_{max}\) in TEP scales with respective \(T_c\).

#### \(T^2\) dependence in \(\rho(T)\): The strong effects of the scattering on the electronic transport can be seen in the low temperature resistivity of all compounds in figure 2, where it varies as \(\rho = \rho_0 + AT^2\) from 2K to 40K with the value of A from 1 -- \(3\times10^{-8}\) \(\Omega\)-cm/K\(^2\). This coefficient A is two to three orders of magnitude larger than for d-band metals, where s-d scattering dominates, but is comparable to the highly correlated Fermi liquid systems dominated by e-e scattering. Neither of them can explain \(T^2\)-dependence in our ferromagnetic
compounds. It can also be seen in figure 2 that for non-stoichiometric compound Cu$_{1+x}$Cr$_2$Te$_4$ (x=0.9) T$^2$-dependence changes to T$^{3/2}$. In case of strong electron–magnon scattering a T$^{2}$-dependence is expected from the spin periodicity and the wave-vector conserving coherent part of the electron–magnon scattering, while T$^{3/2}$ term results from the incoherent scattering where the scattering rate is proportional to the number of magnons. With the excess Cu in Cu$_{1+x}$Cr$_2$Te$_4$, the T$_c$ is strongly reduced and probably the strong s-p-d-hybridization effects of Tellurium and impurity atoms leads to wave-vector non-conserving transition of conduction electrons resulting in the incoherent scattering and T$^{3/2}$-dependence in resistivity. We will also see in figure 3 that drag effect in the TEP in this case is also reduced.

![Figure 2](image)

**Figure 2.** The T$^2$ dependence of ρ(T) between 0–40K for CuCr$_2$Se$_4$, CuCr$_2$Se$_4$, CuCr$_2$Te$_4$(1) and Cu$_{1.5}$Cr$_2$Te$_4$(2). T$^{3/2}$ dependence is shown in inset for Cu$_{1.5}$Cr$_2$Te$_4$(2).

**Effect of magnetic field in thermopower:** We report the results of Seebeck coefficient for CuCr$_2$Se$_4$ and for three different samples of CuCr$_2$Te$_4$ in fig. 3 in zero and in an external magnetic field of 1.5 Tesla. A large increase and a maximum in the TEP of ferromagnetic phase were already noted in figure 1. In figure 3, we see that the maximum in TEP is noticeably affected by the impurity phases, defects and also by external magnetic field. For non-stoichiometric Cu$_{1.5}$Cr$_2$Te$_4$ (sample 2) TEP is negative and the maximum is reduced. A long annealed and impurity free phase of CuCr$_2$Te$_4$ (sample 1) can be seen with a large peak compared to a broad and reduced maximum in TEP of CuCr$_2$Te$_4$ (sample 3), which contained about 5% of Cr$_2$Te$_3$–impurity phase.

The results of the TEP in an external field of 1.5 Tesla applied transverse to the heat current is shown for CuCr$_2$Se$_4$ and CuCr$_2$Te$_4$. TEP of both of them is increased by magnetic field. We also found that this increase is substantially larger for the better ordered phase of CuCr$_2$Te$_4$. It is significant to note that TEP increases down to lowest temperature of our measurement in a modest field of 1.5Tesla. Except for the alignment of magnetic domains the applied field is quite weak for the suppression of the magnon excitations. We therefore believe that the increase in TEP is related to the reduction of the magnon scattering on the domain walls due to their alignment in field and consequently the increase in the drag effect in thermopower.

![Figure 3](image)

**Figure 3.** The effect of transverse magnetic field (1.5Tesla) on the thermopower of CuCr$_2$Se$_4$ and CuCr$_2$Te$_4$. The increase in TEP is more for long annealed sample1.

**Conclusions:** Normally the magnons drag electrons poorly, and in contrast to phonons the drag effects in TEP due to magnons have not been definitely identified so far. It should be remarked that our compounds are rather unique ferromagnets with intrinsic metallic properties. They have remarkably high T$_c$, cubic symmetry of lattice and high degree of lattice perfection. Here the magnetic excitations are coherent-gapless magnons at low temperature. We have shown that an extraordinary large AT$^2$–term in resistivity can be explained by strong electron–magnon scattering. The same coherent scattering causes drag effects in TEP. The sensitivity of TEP to magnetic fields clearly indicates its magnetic origin. In our compounds the extraordinary TEP properties are due to combination of
low carrier density, large exchange coupling of Cr (d$^3$) ions and low stiffness of magnons in their cubic structures. There may be alternate explanations of the peak in TEP possibly based on phonon drag effects and its increase in external magnetic field especially if magneto-elastic coupling is large. This possibility can only be verified by relevant magnetostrictive measurements etc. which are not available so far.

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