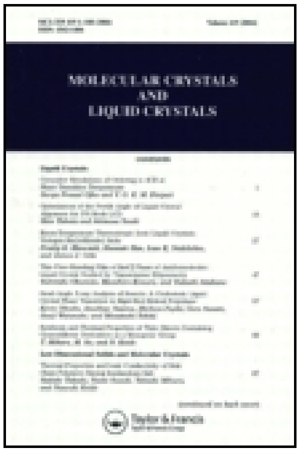

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The c-Axis Magnetoresistance and Thermoelectric Power of $CuCl_2$ Graphite Intercalation Compounds

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The c-axis magnetoresistance and thermoelectric power of $CuCl_2$ graphite intercalation compounds

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$CuCl_2$ graphite intercalation compounds (GICs) having $CuCl_2$ magnetic intercalate layers are expected to give novel magnetic layer effect on their transport phenomena, through the π-d interaction. We investigate the transport properties of stage 1-4 $CuCl_2$ GICs by means of c-axis magnetoresistance (MR) and thermoelectric powers. In stage-1 compound, anomalously large MR is observed for the field perpendicular to the c-axis, indicating a remarkable difference in the magnetic field direction dependence from that of in-plane MR governed by the cyclotron motion of the carriers. This implies the important role of the magnetic layers in the c-axis hopping process. The c-axis thermoelectric power shows an anomalous change around 70-100 K where a short range order hump appears in the magnetic susceptibility.

Keywords: magnetic graphite intercalation compound; transition metal-chloride; magnetoresistance; thermoelectric power

INTRODUCTION

Magnetic $CuCl_2$ GICs are expected to show interesting transport properties due the alternating layers of conducting π-electrons and localized magnetic d-electrons Cu^{2+}-ions. Pristine $CuCl_2$ forms two dimensional distorted triangular Heisenberg antiferromagnetic system consisting of Cu^{2+} ions with spin $S = 1/2$ and an antiferromagnetic nearest-neighbor interaction. Specific heat[1,2] and magnetization and susceptibility[3] suggest long-range antiferromagnetic order below $T_N = 23.9$ K, accompanied by a short range order effect appearing around 70 K. Similar to the pristine $CuCl_2$, $CuCl_2$ GICs[4] show a broad peak in magnetic susceptibility at 70-75 K indicating an in-plane short-range antiferromagnetic order, but the absence of long-range (3D) magnetic order indicates enhanced two-dimensionality in $CuCl_2$ GICs[5]. From the aspect of the π-d interaction, Sugihara suggests the presence of strong interaction between magnetic layers and conducting graphite layers in magnetic GICs, which is expected to give novel effects of magnetic layers on the c-axis transport properties, although only a few experimental works have been reported so far [6]. In the present paper, we focus on the transport properties of graphitic π-electrons from the viewpoint of interaction with magnetic $CuCl_2$ layers, with the employment of c-axis magnetoresistance and the c-axis thermoelectric power, which are sensitive to the effects of magnetic layers.

EXPERIMENTAL

The samples were prepared in a single zone furnace, with graphite (Kish-graphite (Kish) and type ZYA highly oriented pyrolytic graphite (HOPG)) and $CuCl_2$ in a vacuum sealed Pyrex tube[6]. Synthesizing temperatures were between 500-550 °C depending on stage number and host graphite. After synthesis the sample weight uptakes were measured and (00*l*) X-ray diffraction was used to determine stage fidelity. The magnetoresistance measurements were carried out in a superconducting magnet system with a maximum applied field of 6.5 T using standard DC four-terminal measurement. In-plane and c-axis thermoelectric power were measured using conventional sample holders and calibrated Chromel-Constantan thermocouples for measuring the temperature difference.

RESULTS AND DISCUSSION

In Figure 1 we show the data of c-axis MR as a function of magnetic field at 10 K for field (A) parallel and (B) perpendicular to the c-axis. For both the HOPG and the Kish graphite based stage-2 samples the MR is much larger for magnetic field parallel, MR ~ 300 % at 6.5 T, than perpendicular to the c-axis, MR ~ 150 % at 6.5 T. The trend on the magnetic field dependence is explained by the major contribution of the Lorentz motion of the carriers in the basal plane. The similar magnetic field dependence of the resistivity of the stage-2 compounds are reflected in their similar magnitudes of resistivity at room temperature,

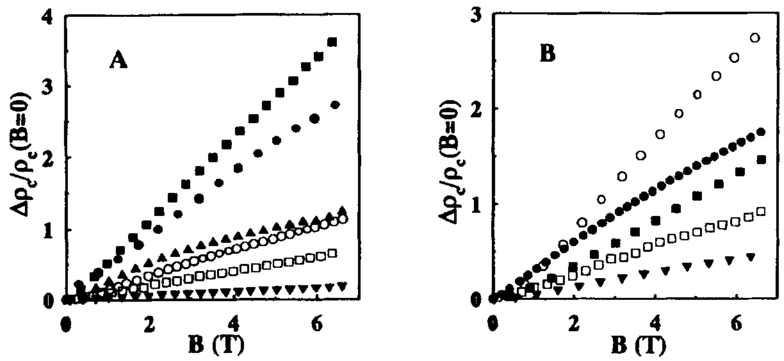

FIGURE 1 Magnetoresistance as a function of applied field at 10 K. (A) B // c-axis, (B) B ⊥ c-axis. O stage-1 (HOPG), □ stage-1 (Kish), ● stage-2 (HOPG), ■ stage-2 (Kish), ▲ stage-3 (Kish), and ▼ stage-4 (Kish).

ρ_c(295 K) = 0.39 Ωcm and 0.34 Ωcm for the HOPG and the Kish-graphite based sample respectively. For all the other stage compounds we have the opposite trend, that is, the magnetoresistance is larger for magnetic field perpendicular to the c-axis than parallel. This is most pronounced for the stage-1 HOPG-based sample where MR is ~ 300 % at 6.5 T for field perpendicular to the c-axis and only about 100 % for field parallel to the c-axis. The very large magnetoresistance with field perpendicular to the c-axis suggests that the magnetic intercalate plays an significant role in modifying the c-axis conduction in these compounds, since for field perpendicular we have no contribution from the Lorentz motion of the electrons, taking into account the large anisotropy in resistivity between the in-plane and the c-axis direction[7], $\rho_c/\rho_a > 10^5$. From stage-2 and above the magnetoresistance is decreasing with increasing stage number, which can be understood by a weaker coupling between the π-electrons and the spins of the localized magnetic Cu^{2+} -ions when the stage indices increases. From stage-2 and above we will also have a contribution to magnetoresistance due to multi carriers with different masses and mobilities. As shown by Figure 2A, for the stage-2 HOPG based sample at low magnetic fields and field parallel to the c-axis we observe an anomaly in the magnetoresistance for temperatures below 75 K, which is seen as a sudden change of curvature at about 0.1 T. This anomaly, however, is only seen in this particular sample and only for field parallel to the c-axis. The temperature dependence of the resistivity of this sample goes from metallic at low magnetic fields to non-metallic at high fields, see Figure 2B, although for all the other samples we always have metallic temperature dependence of the resistivity independent of the strength of the applied field. There have been reports on weak-localization in low stage $CuCl_2$ carbon fiber intercalation compounds[8] which is accompanied by a resistivity increase at low temperatures, however, for all our samples there is no increase in the c-axis resistivity at low temperatures instead it tends to saturate, see Figure 2B. This can be related to the in-plane magnetic short-range order occurring at around 75 K. Around 75 K the Cu^{2+} ion spins are fluctuating much, but as the temperature is decreased the fluctuation becomes smaller leading to less magnetic scattering and hence satu-

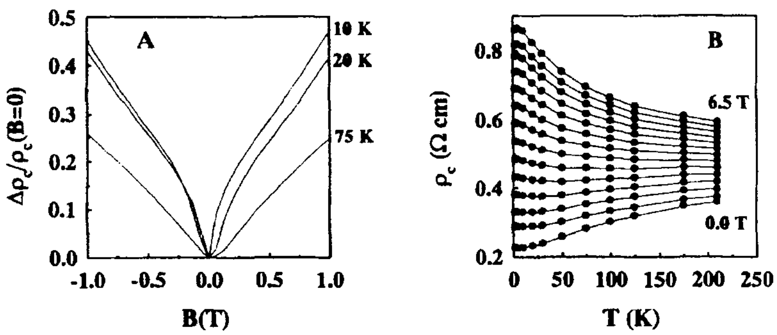

FIGURE 2 (A) The magnetoresistance and (B) The temperature dependence of the c-axis resistivity at different fields (**B** = 0.0, 0.5, 1.0,..., 6.5 T) for the stage-2 HOPG-based compound, in the field parallel to the c-axis.

rated magnetoresistance. The c-axis magnetoresistance in the $CuCl_2$ GICs is large compared with the c-axis magnetoresistance of other magnetic and non-magnetic GICs[6,9]. And if we compare with the in-plane magnetoresistance[10] we find an opposite angular dependence for c-axis magnetoresistance, except for the stage-2 compounds. For the in-plane magnetoresistance we have the largest magnetoresistance for field parallel to the c-axis[10]. The in-plane magnetoresistance of $CuCl_2$ GICs is explained in terms of spin-disorder scattering and a Lorenz motion effect[10]. In Sugihara's theory[11] for c-axis conductivity the c-axis conductivity is governed by the in-plane carrier scattering and the c-axis hopping processes. The angular dependence of the magnetoresistance observed for the stage-1 (HOPG and Kish) and stage-4 (Kish) cannot be explained solely by a modified in-plane conductivity, for which we would have the largest magnetoresistance with magnetic field applied parallel to the c-axis direction. We also have to consider that the hopping process and conduction through paths across the layers are affected by the magnetic intercalate layers through the π-d interaction. In this connection, the mechanism that we have to consider is the possibility of magnon-assisted tunneling[12]. Magnon-assisted tunneling would give a positive magnetoresistance and a magnetoresistance that would be strongly dependent on the magnetic field.

In Figure 3A and 3B we show the temperature dependence of the in-plane and c-axis thermoelectric power. The overall temperature dependence is similar but the absolute magnitude of the c-axis thermoelectric power is less than half of the in-plane thermoelectric power. In the Kish-graphite based samples the trend seems to be that the magnitude of the thermoelectric power is increasing with increasing stage number which reflects the decreasing trend of the c-axis magnetoresistance with increasing stage indices. The c-axis thermoelectric power deviates from the normal linear electron diffusion dependence[13] as expected for ordinary behavior of the c-axis thermoelectric power. The deviation demonstrates the participation of different in-plane electron scattering processes whose relaxation times have different energy dependence and has been explained by Sugihara et al.[14] as electron diffusion which is modified by in-plane scattering processes; electron-phonon, electron-impurity scattering. In addition to these scattering mechanism we also think the π-d interaction in the magnetic $CuCl_2$ GIC plays an important role, especially around 75 K where in-plane short-range order occurs. A more detailed analysis of the c-axis magnetoresistance and the in-plane and c-axis thermoelectric power will be given in a later paper[15].

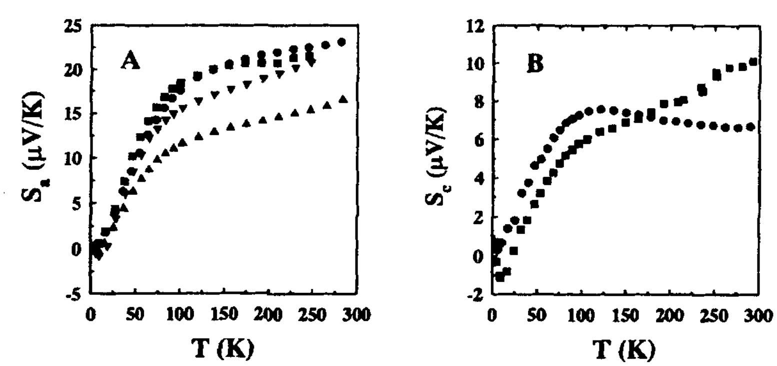

FIGURE 3 The temperature dependence of (A) in-plane and (B) c-axis thermoelectric power. ● Stage-1 (HOPG), ■ Stage-2 (HOPG), ▲ Stage-2 (Kish), and ▼ Stage-3 (Kish).

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