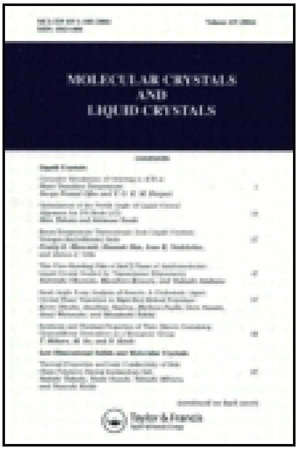

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Anomalous Angular Dependence of Magnetoresistance in MCl_2-GIC's (M=Cu and Co)

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Angular dependence of the c-axis magnetoresistance of stage-1 and stage-2 MCl_2 GIC (M=Cu and Co) was measured. Stage-1 $CuCl_2$ GIC shows an angular dependent magnetoresistance oscillation (ADMRO) characteristic in the systems having a periodically-warped cylindrical Fermi surface (FS). This means that the conduction along the c-axis is band-like in spite of extremely large anisotropy in conductivity. On the other hand, the angular dependence of the magnetoresistance of stage-2 $CuCl_2$ GIC and stage-1 $CoCl_2$ GIC can be interpreted as the mixture of ADMRO based on a band conduction and incoherent interlayer hopping. Stage-2 $CoCl_2$ GIC shows only incoherent hopping. In low magnetic field region, the c-axis resistances of stage-1 and stage-2 $CoCl_2$ GIC are affected by the magnetic phase transitions. Spin-dependent tunneling effect can explain this phenomenon.

Keywords: graphite intercalation compounds; transition metal chlorides; magnetoresistance; antiferromagnetic transition; dimensional crossover; quantum oscillation

INTRODUCTION

Transport properties of GIC with magnetic guest materials have aroused much attention because of their π-d interaction, that is, the interaction between the conducting π-electrons in graphene sheets and the localized magnetic moments of the transition metal ions.[1, 2, 3, 4, 5, 6] In this paper, we report the c-axis (out-of-plane) magnetoresistance of magnetic GIC's, stage-1 and stage-2 MCl_2 GIC's (M=Cu and Co). The reason why we are interested in the c-axis transport properties is that they should reflect the π-d interaction more directly than in-plane cases. As schematically shown in Fig. I, the magnetic guests have the effect no more than second order perturbation for in-plane conduction. However, they have dominant effect for c-axis conduction if there are no direct conduction paths between

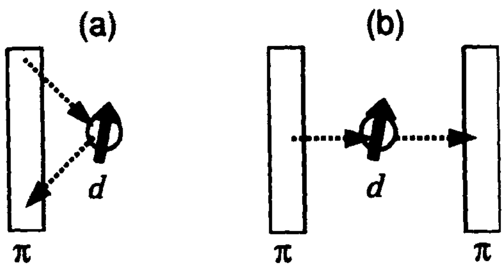

FIGURE I The effect of the π-d interaction (a) on the in-plane conduction and (b) on the c-axis conduction. The solid arrows show the spins in d orbitals and the broken arrows indicate the conduction paths of electrons.

adjacent graphitic layers.

Since acceptor-type GIC's have large anisotropy in conductivity, the mechanism of c-axis conduction is controversial. There is an interpretation based on a three-dimensional (3D) band model with large anisotropy,[7] whereas there is a model based on two-dimensional (2D) electronic states where the c-axis conduction is governed by incoherent hoppings.[8] We will show that the investigation of angular-dependent magnetoresistance aids us to understand the c-axis conduction mechanism and the dimensionality of electronic states.

EXPERIMENTAL

The samples for the present measurements were synthesized from HOPG (Union Carbide Co.) for $CuCl_2$ GIC and from kish graphite (for $CoCl_2$ GIC).[9, 10] The magnetoresistances down to 1.6 K were measured by using a 15-Tesla superconducting magnet (Oxford Instruments) with a sample rotator. A conventional DC four-wire technique was used for the magnetoresistance measurements.

RESULTS AND DISCUSSION

Figure II(a) shows the angular dependence of the c-axis magnetoresistance for stage-1 $CuCl_2$ GIC under 15 T and at 1.6 K. An oscillating behavior appears with peaks located at 63° and at 76°. Because the oscillation survives even at high temperatures up to 100 K[11] and the peak positions are not dependent on the magnitude of the magnetic field, it is not due to a Shubnikov de Haas (SdH) effect.

The oscillation is attributed to an angular dependent magnetoresistance oscillation (ADMRO) effect[12] characteristic of quasi 2D systems. The standard model of ADMRO[13, 14] predicts that the resistance exhibits peaks when the cross section of FS cut by a plane perpendicular to the magnetic field is constant regardless of the position of the plane. This corresponds to the condition,

$$\tan\theta = \frac{\pi}{I_c k_F}\left(n - \frac{1}{4}\right), \tag{1}$$

where I_c, k_F and n are the c-axis identity period, the Fermi wave number and arbitrary integer numbers, respectively. When we put $I_c = 9.40$Å and $k_{F\|}$=0.145 Å^{-1}, obtained from the Shubnikov de Haas oscillation result,[11] the first and the second peaks should be located at 60.0° and 76.1°, respectively, showing a good agreement with the observation. The $\rho_c(\mathbf{B} \perp \mathbf{c}) > \rho_c(\mathbf{B} \parallel \mathbf{c})$ behavior is also consistent with the standard theory of ADMRO. The existence of an ADMRO means that the electric conduction along the c axis is governed by a band mechanism, as well as the in-plane conduction. ADMRO's have been also reported in $SbCl_5$ GIC's (stage-2 and stage-3) by Iye *et al.*[15, 16]

The above result is in contrast with the Sugihara's model[8] in which the c-axis conduction is governed by non-intrinsic hopping process and consequently it behaves similarly to the in-plane conduction because the carriers spend most of the time for in-plane conduction. According to his model, the c-axis magnetoresistance should simply reflect the 2D electronic states of each graphene sheet and depends on $B\cos\theta$, where B and θ are the magnetic flux density and the angle between the c axis and the magnetic field, respectively. Then $\rho_c(\mathbf{B} \perp \mathbf{c}) < \rho_c(\mathbf{B} \parallel \mathbf{c})$ behavior is expected because ρ_c has positive magnetoresistance.[6]. This apparently contradicts our result.

Next, we show the angular dependence of the magnetoresistance of the stage-2 $CuCl_2$ GIC in Fig. II(b). Unlike the stage-1 compound, the resistance is larger for $\mathbf{B} \parallel \mathbf{c}$ than for $\mathbf{B} \perp \mathbf{c}$. The asymmetry with respect to $\theta = 0°$ is probably due to some extrinsic reasons such as mosaicity of the sample. The oscillation observed around $\theta = 0°$ is due to a SdH oscillation.[11, 17] There are peaks around $\theta = \pm 70°$. The calculation based on the SdH result gives the position of the first ADMRO peak at 69.5°, in good agreement with the observed peak around 70°. However, the $\rho_c(\mathbf{B} \perp \mathbf{c}) < \rho_c(\mathbf{B} \parallel \mathbf{c})$ behavior conflicts with the standard model of ADMRO. Therefore, we can interpret the experimental result as a mixture of ADMRO and positive in-plane magnetoresistance mentioned above. In other words, the c-axis conduction includes two processes; a coherent band conduction and an incoherent hopping conduction. This suggests that electronic states of stage-2 $CuCl_2$ GIC is just on the boundary of 3D case (the wave function is coherent for all the directions) and 2D case (the wave function is coherent within each plane but incoherent along the c-axis).

Figure II(c) shows the angular dependence of the magnetoresistance of stage-1 $CoCl_2$ GIC under 15 T. Contrary to the case of stage-1 $CuCl_2$ GIC, $\rho_c(\mathbf{B} \perp \mathbf{c}) < \rho_c(\mathbf{B} \parallel \mathbf{c})$. There are small humps around $\pm 65°$. Since

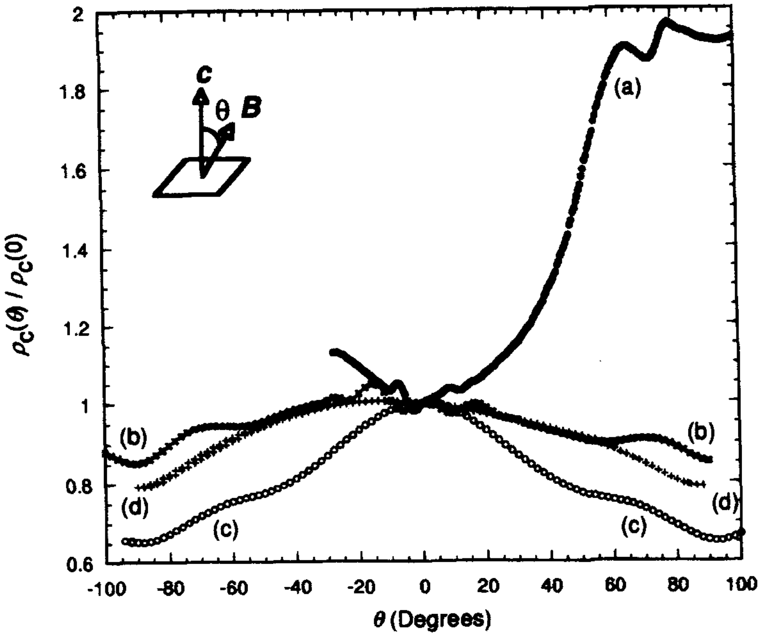

FIGURE II The angular dependence of the magnetoresistances, (a) for stage-1 $CuCl_2$ GIC (1.6 K, 15 T), (b) for stage-2 $CuCl_2$ GIC (1.5 K, 15 T), (c) for stage-1 $CoCl_2$ GIC (100 K, 15 T), and (d) for stage-2 $CoCl_2$ GIC (50 K, 15 T).

we observed them at high temperature (not shown in the figure), they are considered to be the first peaks of ADMRO. As well as in stage-2 $CuCl_2$ GIC, the $\rho_c(\mathbf{B} \perp \mathbf{c}) < \rho_c(\mathbf{B} \parallel \mathbf{c})$ dependence shows the deviation from the standard model. This can be also attributed to mixture of coherent band conduction and incoherent hopping conduction along the c axis.

In the case of stage-2 $CoCl_2$ GIC, as shown in Fig. II(d), the angular-dependent measurements under high magnetic fields show $\rho_c(\mathbf{B} \perp \mathbf{c}) < \rho_c(\mathbf{B} \parallel \mathbf{c})$ behavior but no oscillations due to an ADMRO effect. This means that the interlayer coupling of stage-2 $CoCl_2$ GIC is so weak that the c-axis conduction is mainly governed by incoherent hoppings.

In the case of $CoCl_2$-GIC's, the magnetoresistance is also sensitive to the magnetically ordered state of Co ions. Therefore, we investigated the angular dependence of the magnetoresistance with the magnetic field low enough not to affect the orbital motion of carriers but high enough to change the magnetism of cobalt layers. Stage-1 $CoCl_2$ GIC undergoes a magnetic phase transition at T_N (=9.8 K) into a layer-type antiferromagnetic phase, where each $CoCl_2$ layer has a ferromagnetic order but the interlayer ordering is antiferromagnetic. As shown in the inset of Fig. III, the c-axis resistance sharply increases just below 9.8K. This is related to the folding of Brillouin zone due to the formation of a magnetic superlattice along the c axis.[11]

The angular dependence of the magnetoresistance of stage 1 $CoCl_2$ GIC in the low field region is shown in Fig. III(a). The magnetoresistance is almost zero for $|\theta| < \theta_c$, where θ_c is a critical angle. This is because the antiferromagnetism is converted into forced ferromagnetism when the in-plane component of the applied field exceeds B_c.

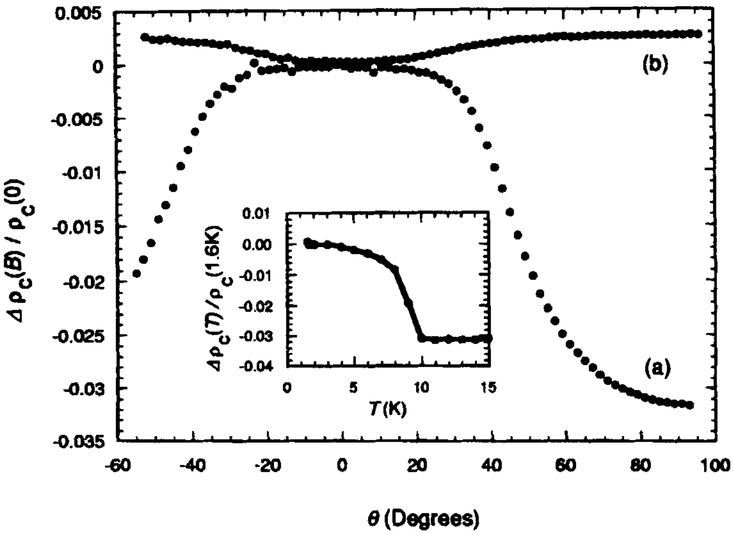

FIGURE III The angular dependence of the magnetoresistances in , (a) for stage-1 $CoCl_2$ GIC (1.7 K, 80 mT), and (b) for stage-2 $CoCl_2$ GIC (1.7 K, 80 mT). The inset shows the temperature dependence of the resistivity of stage-1 $CoCl_2$ GIC without magnetice field.

Figure III(b) shows the angular dependence of the magnetoresistance of stage-2 $CoCl_2$ GIC in low-field region where the magnetic ordering of the guest layer is the most effective. Contrary to the stage-1 case, $\rho_c(\mathbf{B} \parallel \mathbf{c}) < \rho_c(\mathbf{B} \perp \mathbf{c})$. This observation is opposite to what is expected from the BZ folding effect which successfully explains the behavior of stage-1 $CoCl_2$ GIC. As we already mentioned, a band picture is no longer correct for the c-axis conduction of stage-2 $CoCl_2$ GIC. A quantitative model based on incoherent hopping picture is desired for further analysis.

Acknowledgments

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