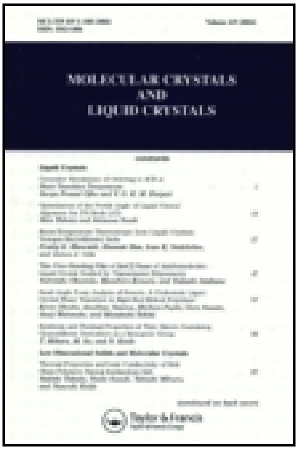

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Electrical Transport in Metal (M = Cu, Cd, Pd) Chloro-Aluminate Intercalated Graphite

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ELECTRICAL TRANSPORT IN METAL (M = Cu, Cd, Pd) CHLOROALUMINATE INTERCALATED GRAPHITE

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Abstract This paper examines the in-plane and c axis electrical resistivities, ρ_a and ρ_c, from 4.2 to 295K for first stage $M_xAl_2Cl_8$ GICs where M = Cu, Cd or Pd. It is found that $d\rho/dT > 0$ for all cases in both directions. Particularly high values of ρ_c and anisotropy (ρ_c/ρ_a) are found for the Pd containing materials, exceeding 5 Ω.cm and 10^6 at 4.2K respectively. The magnetic ordering observed elsewhere in the Cu-containing materials does not appear to influence the transport in either direction.

INTRODUCTION

Over the past several years, we have extensively studied the electrical resistivity both in the plane (ρ_a) and in the c direction (ρ_c) for a number of aluminum chloride containing graphite intercalation compounds (GICs) including stage 1 to 4 binary compounds[1,2] as well as bi-intercalation compounds (GBCs) with alternating layers of $AlCl_3$ and one other di- or trichloride[2-4]. In the present work, we have studied both ρ_a and ρ_c from 4.2 to 295K for a new family of first stage metal chloroaluminate ($M_xAl_2Cl_8$, $x \approx 1$ for M = Cu and Pd) GICs based on single crystal (SC) and pyrolytic (HOPG) graphite. Details concerning the synthesis conditions and structural characterization for the M = Cu case have been presented elsewhere[5,6] and will not be discussed in detail in the present paper. It is, however, of interest to this work to note that magnetic studies on the copper chloroaluminate GICs have revealed the existence of a rather unique (to GICs) finite chain distribution of spin 1/2 Cu^{2+} ions below about 30K[7].

EXPERIMENTAL

The reaction of MAl_2Cl_8 vapours (M = Cu, Cd, Pd) with graphite samples was carried out at 300°C for a reaction time of 3 days leading to the formation of 1st stage compounds as confirmed by the subsequent (00l) X-ray analysis. The graphite used was generally Union Carbide ZYA HOPG and in a few cases, Madagascar single crystals (SCs). All samples were in the form of 4 mm diameter discs, a few tenths of a mm thick. Transport studies were made using a noncontact technique for $\rho_a(T)$; the c axis measurements necessitated a transfer to an airtight holder as described elsewhere[8].

RESULTS AND DISCUSSION

For M = Cu and Pd, the average compositions are $C_{22}CuAl_2Cl_{8.5}$ and $C_{21.8}PdAl_2Cl_{8.5}$, respectively[9]. The Cd-containing GIC presents a stoichiometry $C_{10}(AlCl_3)(CdCl_2)_{0.2}$, probably related to an $AlCl_3$-$CdCl_2$ co-intercalation compound. (00l) X-ray analysis shows that the interplanar distances are 0.948, 0.952 and 0.965 nanometers for the M = Cu, Cd and Pd GICs respectively. The intercalate layer structures vary, manifesting different 2D organization for M = Cu and Cd but no 2D order for the Pd case[5,9].

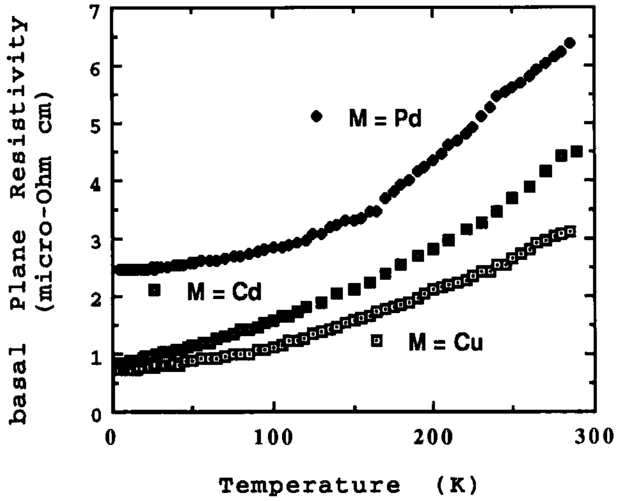

Figure 1. Basal plane resistivity versus temperature.

A dozen samples in all were examined and we show in figures 1 to 3 results for one HOPG-based sample for each of the three metals. From an overall viewpoint, the Cu-Al and Cd-Al materials are closely similar to the binary $AlCl_3$ GICs as concerns electronic transport but the Pd-containing materials clearly distinguish themselves in several respects. First, $\rho_a(T)$ is from 50 to 100% greater and the residual resistivity exceeds 2 μΩ.cm, a rather high value for a first stage acceptor type GIC. Secondly, in the c direction, the resistivity in the Pd-Al compounds can attain almost 6 Ω.cm. at 295K, two to four times that observed in the other GICs. Furthermore, although possessing the positive $d\rho_c/dT$ of the other GICs, ρ_c in this case is much less temperature sensitive. Finally, at 4.2K, the anisotropy values are the highest observed, to our knowledge, for any first stage GIC.

The inexistence of any particularities on both the $\rho_a(T)$ and the $\rho_c(T)$ curves suggests that no further ordering occurs within the intercalate layers of these compounds. It is striking to note the similarities between the behaviour of the Cu- and Cd-containing materials. This seems to suggest that factors such as the ordered structure and similar charge transfers are at least partially responsible for the features distinguishing them from the Pd-containing compounds. In deed, from the chemical viewpoint, one might have expected the Cu and Pd compounds to be more similar. It should be noted, however, that our studies on 1st stage $AlCl_3$ GICs[1], in which the intercalate layer can be in one of several different states[10,11] including liquid-like yield closely similar results.

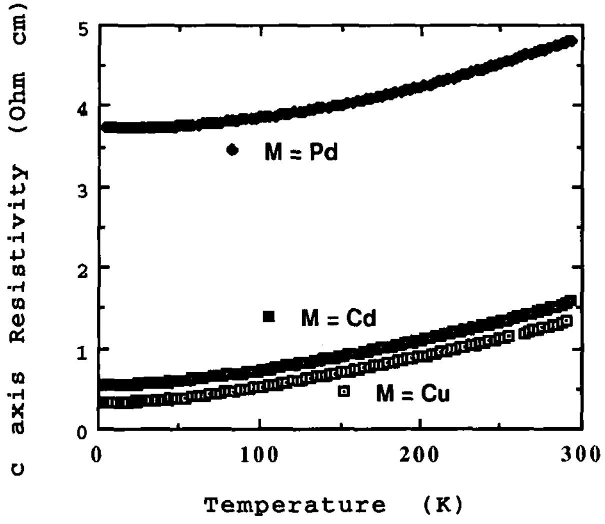

Figure 2. c axis resistivity for same samples as those of figure 1.

All the data in both directions can be well fit by 2nd order polynomials $\rho(T) = \rho_o + AT + BT^2$: results for the three compounds of figures 1 - 3 are given in Table 1. As indicated above, the Pd-containing GICs distinguish themselves markedly. In both directions, the linear term is negative. It is of the same order of magnitude in the basal plane as those of the Cu and Cd materials but two orders of magnitude less in the c direction, i.e., in the latter case, the variation is essentially quadratic with no linear contribution, as further brought out by the magnitude of the T^2 term which is twice as great for the Pd GIC as for the others. Fitting $\rho_a(T)$ to $\rho_{oa} + BT^2$ gives $\rho_{oa}= 2.387$, $10^6B = 49.73$. Even at 295K, the "residual" term still accounts for about 75% of the total c axis resistivity; for M = Cu and Cd, at room temperature, the T^2 terms contributes to a slightly greater extent than the other two.

Table 1. Parameters for second order fits for basal plane and c axis resitivity of samples in figures 1 and 2. $\rho(T) = \rho_o + AT + BT^2$

M	Basal plane $\rho_a(T)$			c axis $\rho_c(T)$		
	ρ_{oa}	10^3A	10^6B	ρ_{oc}	10^3A	10^5B
Cu	0.707	2.291	2.233	0.30	1.69	6.83
Cd	0.853	4.147	2.909	0.53	1.26	7.92
Pd	2.522	-2.998	60.04	3.73	-0.03	12.8

The negative T term in both directions in the Pd compound as well as the preponderance of the T^2 term suggest the possibility that transport is correlated between the two orthogonal directions. Although this is not the first time that such a proposal has been put forward[12] if this is so then the orders of magnitude separating ρ_a and ρ_c have not yet been fully explained. Anisotropic band conduction has been proposed and shown to be capable of explaining anisotropy ratios of the order of 10^5 in $SbCl_5$ GICs[13] . Other theories which call upon conducting paths and/or DH walls[14,15] appear less favourable candidates for two reasons. First, these are stage 1 materials so presumably with equal quantities of intercalate in each gallery spread equally among all galleries and thus without DH walls. Secondly, as noted above, the SC Cu-containing sample is a true SC, so the intergrain and interdomain boundaries found in HOPG should not be present in this case.

In addition to the HOPG-based materials of figures 1 to 3, we also examined a limited number of samples based on single crystal graphite for M = Cu and Pd. As we have observed in other GIC families[16,17], intercalated SC samples possess c axis and basal plane conductivities which are respectively greater and smaller than those of their HOPG counterparts.

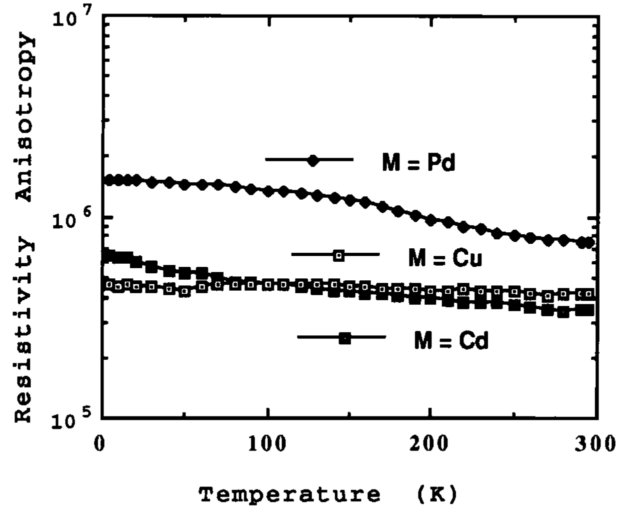

Figure 3. Resistivity anisotropy, $\rho_c(T)/\rho_a(T)$, for samples of figures 1 and 2.

Over the past years, it has been shown that the c axis resistivity often appears to be a more sensitive probe of phase transitions of many sorts than is the basal plane resistivity. Very careful measurements were thus made on the Cu containing compounds following the claim of unusual magnetic ordering in this compound below about 30K[7]. While magnetic ordering in other di- and trichloride GICs has been shown to strongly influence transport properties[4,18], no signs of such a coupling between the establishment of magnetic order and in plane or c axis transport could be observed, as is clearly illustrated in figure 4..

CONCLUSIONS

While chemical similarities exist between the $CuAl_2Cl_8$ and $PdAl_2Cl_8$ GICs, the results of this study confirm the important role played by the structural organization of the intercalate within the galleries.

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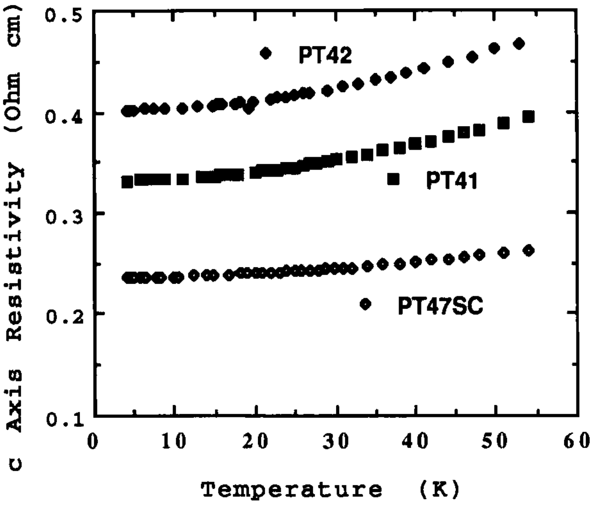

Fig. 4. Low T portion of ρ_c for $CuAl_2Cl_8$ GICs (HOPG: PT42, PT41; SC: PT47)

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