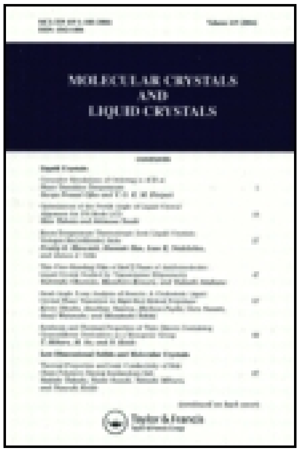

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c-Axis Conduction in Lamellar Solids: High Stage Graphite Intercalation Compounds

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We have examined the c axis electrical resistivity ρ_C of high stage ($5 \leq s \leq 12$) $GaCl_3$ intercalated graphite from $4.2 \leq T \leq 295$ K. All materials are highly anisotropic. There is a progressive change from "metallic" behaviour with $d\rho_c/dT > 0$ over the full T range to semiconductor-like ($d\rho_c/dT < 0$) as s rises. It is shown that interstratification and intercalate layer crystallization strongly influence $\rho_C(T)$.

Keywords: graphite; intercalation; $GaCl_3$; electrical conductivity

INTRODUCTION

Determining and understanding the mechanisms by which electric charge is transported across the planes in lamellar solids remains a challenge in many families, including the cuprate superconductors above T_c[1] and graphite intercalation compounds[2]. Various theories have been proposed but none is universally applicable, although each has its merits and acceptable fits can be made over certain ranges of temperature, concentration, pressure, etc. In both families, efforts have been made both theoretically and experimentally to determine the roles played by e.g., impurities, stacking faults, tortuosity and interlayer bridges. In the present work, we have particularly looked at the possible role of interstratification in GICs. It is by now well established that while truly single stage materials can be synthesized for richer compounds, higher stage materials almost invariably comprise a small amount of at least one of the two neighbouring stages[3].

RESULTS

We have examined $\rho_c(T)$ for stage 1 to >12 $GaCl_3$ GICs; we concentrate here on the high stage materials where by "high", we imply $s \geq 5$. There is thus at least one inner "true" graphene layer between two other higher electron or hole density graphene layers before contact is made with the intercalate-bounding layer of even much greater free carrier density. Synthesis conditions, structural properties and basal plane resistivity studies on $GaCl_3$ GICs can be found elsewhere[4-6]. All $\rho_c(T)$ measurements were made upon slowly cooling the samples.

We will first make some general comments on our observations. The overall stage-dependence of $\rho_c(T)$ resembles that observed for $SbCl_5$ GICs[7]. All samples examined from s = 1 to 10 possess $\rho_C(295\ K)$ values > 1 Ω.cm and at room temperature (RT), $d\rho_c/dT$ is always positive. Logarithmic derivatives are similar, $d\ln\rho_\chi/dT$ lying between 2-4 x $10^{-3}\ K^{-1}$ as for ordinary metals. There is a progressively developing negative $d\rho_c/dT$ component as s rises, i.e., for s=4, $d\rho_c/dT > 0$ over the full T range; for stage 5, $T_{min} \approx 115$ K and for stage 10, T_{min} is about 215 K, where T_{min} is the temperature below which ρ_c starts to rise. We have previously discussed the in-plane resistivity, $\rho_a(T)$[6] and based on this earlier work, RT values of anisotropy, ρ_c/ρ_a are of the order of 10^6. These are thus among the most highly anisotropic GICs known[2].

We show in figures 1 and 2 the detailed behaviour for the highest stage materials examined. We observe on figure 1 that the qualitative features are similar for all three stage nine compounds; however, the two samples for which *(OOl)* analysis showed a small admixture of upper and lower stages are somewhat more conductive and the difference is particularly noteworthy at low temperature. The behaviour of the more stage-pure sample (PT79) is even more remarkable when compared with the results of figure 2, for the stage 8 and 10 samples: the low-T values of ρ_c are all just below 4 Ω.cm. The sample indicated as being stage >12, certainly strongly interstratified, possesses a c axis resistivity well below the others.

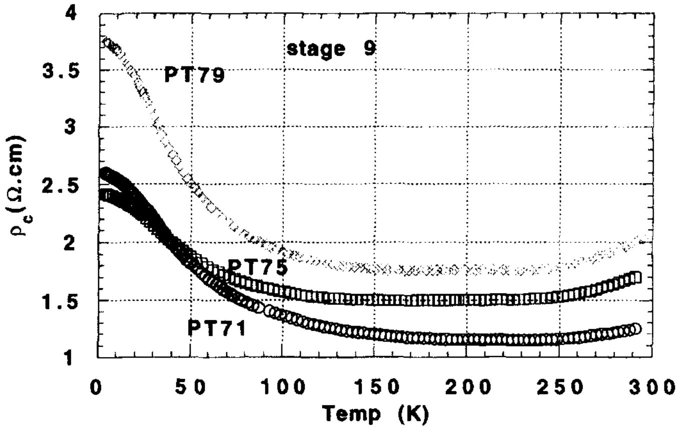

FIGURE 1 ρ_c(T) for three nominally stage 9 samples: "pure" stage 9 (PT79), stage 9 + ε stage 8 (PT75), stage 9 + ε stage 10 (PT71).

DISCUSSION

We note first that all samples appear to manifest the disorder to order transition which has been studied in detail in stage 1 materials, around 240 K[5]. In these intercalate-rich GICs, the intercalate layer is liquid-like above the transition temperature, while below, several superlattices appear to be formed, similar to what occurs in the more extensively studied $SbCl_5$ GICs[8], and there is simultaneously a graphene stacking change from A/A/A to A/B/A. All compounds we examined from stage 5 to 10 showed a clearly reduced slope as T decreased below this temperature. Similar effects of intercalate layer crystallization and graphene stacking changes have been observed in both $SbCl_5$[7] and AsF_5[9] GICs. While it has been predicted[10] that graphene stacking plays a role in determining ρ_c, it is experimentally difficult, if not impossible, to isolate such an A/A → A/B change from the intercalate layer modifications with which it is associated.

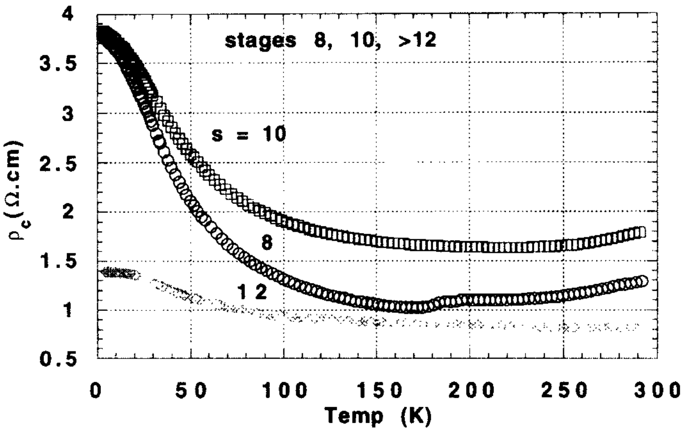

FIGURE 2 c axis resistivity for stage 8, 10 and >12 $GaCl_3$ GICs.

Some interesting effects of interstratification are clearly observed on both figures 1 and 2, notably the strong reduction in ρ_c at low T. We have clearly shown that ρ_c(4.2 K) *versus* stage attains a maximum around stage 10 for all GICs studied to date[2]. Furthermore, an *in situ* study of the intercalation of potassium confirmed a similar trend at room temperature[11], a result which we interpret in the following manner: intercalation into the host causes an increase in free carrier density, but this is more than compensated for by the increasing disorder, e.g., introduction of stacking faults and local stage mixtures. By the time 10th stage is attained, the c axis order becomes sufficient that it can be detected via X-ray diffraction, and increasing intercalation causes a conductivity increase in the c direction. Tenth stage is thus a sort of threshold before which disorder dominates, raising ρ_c, and beyond which carrier density increases and c axis order is established causing ρ_c to decrease. As regards figures 1 and 2, the more pure

8th, 9th and 10th stage compounds manifest their good stage purity by high values of $\rho_c(4.2\ K)$, whereas the GIC of stage >12, is a mixture of higher stages, this interstratification lowering ρ_c over the full T range. We conclude that intralayer transport allowing carriers to travel along the c axis via pleats or screw dislocations may play a role; however, in view of the anisotropy, this role must be minor. The dominating factor appears to be assumed by the well-stacked regions.

Finally, we note that a "residual" T- independent term is present in all materials, as is observed for the in-plane resistivity. Furthermore, recent galvanomagnetic studies on $MoCl_5$ have also shown this[12]. In this study, the authors assumed that c axis conduction was dominated by the in-plane conduction such that the combined negative magnetoresistance and logarithmic $\rho_c(T)$ behaviour they observed in some cases could be attributed to a weak localization phenomenon within the plane. In our case, while resistivity versus log T gave linear fits over limited T ranges between 30 and 80K, the existence of the residual term below 30K leads us to question such an interpretation in our materials.

In conclusion, the experimental results show that in high stage materials, complementary or competing mechanisms must be called upon. Various structural factors have been put forward as determining elements: bounding layer stacking around the intercalate layer[10], impurities[13] and interlayer conducting paths[14]. Here, we have experimentally demonstrated that interstratification is also important. For high stage GICs, it tends to enhance c axis conductivity over the value expected for a stage-pure GIC, whereas at the initial stage of intercalation, where we have graphite "interstratified" with widely separated filled galleries, c axis resistivity is enhanced. Throughout the composition range $1 \leq s \leq \infty$, there is a constant interplay of carrier density and structural order/disorder. Going further into the meaning and consequences of interstratification will require re-examining our concepts of stage mixtures and stage disorder.

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