IN-PLANE ELECTRICAL PROPERTIES OF FERRIC CHLORIDE INTERCALATED GRAPHITE

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ABSTRACT

The in-plane resistivity of HOPG and stages 2,3,4,5,6 and 8 $FeCl_3$-GIC's was measured in a temperature range from 300 K down to about 10 K. The resistivity of all stages and the HOPG sample exhibited a metallic-like behavior characterized by a strong temperature dependence in the high temperature region. The experimental data were fitted to empirical models and it was found that the HOPG data and the intercalated samples data did not fit to the same model. Two different fits were used and the deduced fitting parameters indicate that the intercalation processes introduce structural defects to the samples. The overall behavior of the resistivity of the high and low stages looks similar but the residual resistivity depends strongly on the stage of the intercalated samples. Stage 5 which was classified as an intermediate stage exhibited different behavior from that of other stages as expected.

INTRODUCTION

The extremely high anisotropy in most of the physical properties of highly oriented pyrolytic graphite (HOPG) makes this system an interesting candidate for low dimensional studies. Moreover this anisotropy can be increased by the intercalation of acceptor or donor compounds into the graphite [1]. The electrical resistivity of graphite intercalation compounds (GIC's) is one of the properties most drastically changed by intercalation of both acceptor and donor materials [2,3], it is also one which holds the greatest promise for technological applications [4].

Systematic measurements of physical properties as a function of the GIC stage (the stage number denotes the number of graphite layers separating two successive intercalant layers) have revealed a number of interesting features. Thermal conductivity measurements [5] have shown that the electronic thermal conductivity of the graphite bounding layers increases upon intercalation, whereas the lattice thermal conductivity decreases. Magnetic susceptibility measurements [6] on $FeCl_3$-GIC's indicate the existence of a low-temperature magnetic phase transition. Hall effect and magnetoresistance have been measured [7,8] for various stages of $FeCl_3$-GIC's. The results of these measurements indicate that both quantities have a complicated field and temperature dependence. Ibrahim et al. [7] showed that the magnetoresistance has exhibited strong Shubinkov-de Hass oscillations at helium temperature.

Due to the high anisotropy in the GIC's, more careful requirements are needed if one wants to investigate the transport properties of these compounds. The C-axis resistivity measurements are a straightforward procedure, on the other hand, measuring the in-plane resistivity is not an easy task. The non-uniformity of the current distribution along the sample complicates the resistivity measurements in these compounds. The C-axis data of several GIC's have been reported [9,10] and it seems that most of the compounds exhibit a universal behavior in which low stage compounds have a metallic-like conduction and higher stages exhibit activated behavior.

One of the widely-used approaches in the measurements of the electric resistivity in GIC's is the low-frequency eddy-current technique [11]. The disadvantage of this technique is the limit of obtaining reliable values of the magnitude of the resistivity. The eddy-current technique also requires a complicated procedure for the

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experimental set-up. Therefore the four-probe technique is another alternative for measuring the in-plane resistivity in the GIC's. A special technique to overcome the non-uniform current distribution throughout the sample was reported in ref.11. In this technique a critical thickness of the sample is required to guarantee the even spread of the current on both sides of the sample.

Preliminary in-plane resistivity data for a few stages of $FeCl_3$-GIC's were measured using the four-probe technique and the results of these measurements were reported in ref. 12, however no detailed analysis of the data were reported. The purpose of the present work is to report the results of the experimental measurements of different stages of $FeCl_3$-GIC's, and also to include a comprehensive analysis of the data. We have used two different empirical formulae, one to fit the HOPG data, and the second to fit the $FeCl_3$-GIC's data.

EXPERIMENTAL

The $FeCl_3$-GIC samples were prepared at Boston University, Boston, MA, using a standard two-zone furnace technique [4] where stage index was controlled by the temperature difference between the graphite host and the $FeCl_3$ powder. The graphite samples were in the form of thin rectangular plates of dimensions 1.5 x 0.5 x 0.1 cm^3.

As mentioned above, the thickness of the sample is a crucial factor in the determination of the current distribution throughout the sample. It has been found that a minimum thickness of 10μm is required to achieve a uniformity in the current distribution. Therefore, samples of thicknesses about 10μm were cleaved from the intercalated samples by using a scotch tape.

The electrical resistivity was measured by a conventional four-probe method. The dc current was kept low, a typical value was 10 mA, to prevent joule heating of the sample. The samples were cooled down via a closed cryogenic refrigeration system model Displex employing helium as a working medium. The sample temperature was monitored by Kp-Au 0.07 at.% Fe thermocouple and stabilized with the aid of a temperature controller within about ± 0.1 K. The electrical contacts between the sample and the leads were made by using silver paint. The current source provides both positive and negative current. This technique enabled us to subtract out any ambient or spurious voltage from that created by the measuring current. The accuracy of the electrical resistivity measurements was better than 5%.

RESULTS AND ANALYSIS

HOPG Data

The HOPG experimental in-plane resistivity data normalized to the room temperature value were fitted to a model given by:

$$\rho(T) = A + Be^{-C/T}, \tag{1}$$

where A, B and C are the fitting parameters, and T is the temperature. The fit of this model and the experimental data are plotted versus temperature in Figure (1), the dashed line is the fit of the above equation and the symbols are the experimental data. As shown in the figure the data are well fitted to the above model in a temperature range from 300 K down to 10 K. The values of the fitting parameters are: A = 0.12, B = 0.98 and C = 46.3 K. A and B are normalized to the room temperature resistivity value. The value of the constant A is related to the residual resistivity of the HOPG sample, this value will be compared with the values of the intercalated samples in order to study the effect of the intercalation processes on the samples. The values of the constants B and C determine the scattering mechanisms which contribute to the conduction in the system. As the constants B and C have finite values, the phonon scattering would be significant ($d\rho(T) / dT \neq 0$).

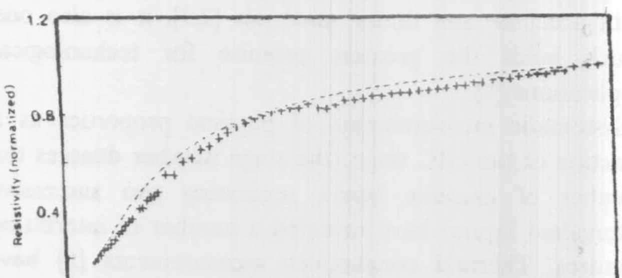

Figure 1. The in-plane normalized resistivity of HOPG versus temperature, (+) experimental data. The dashed line fits the data to equation (1), see text.

$FeCl_3$-GIC's *Data*

Figure (2) shows the in-plane electrical resistivity, normalized to room temperature value, for stages 2, 3, 4, 5, 6 and 8 $FeCl_3$-GIC's measured in a temperature range from room temperature down to about 10 K. The data plotted in Figure (2) enable us to compare low stage samples (1 < n < 5) with high stage samples (5 < n < 9); n is the stage index. Stage 5 has been classified as intermediate stage between low and high stages [10]. It has been reported [6,9,12] that almost all physical properties exhibited different behavior for the low and high stage samples. Stage 9 and higher stages have exhibited the HOPG behavior for most of the properties.

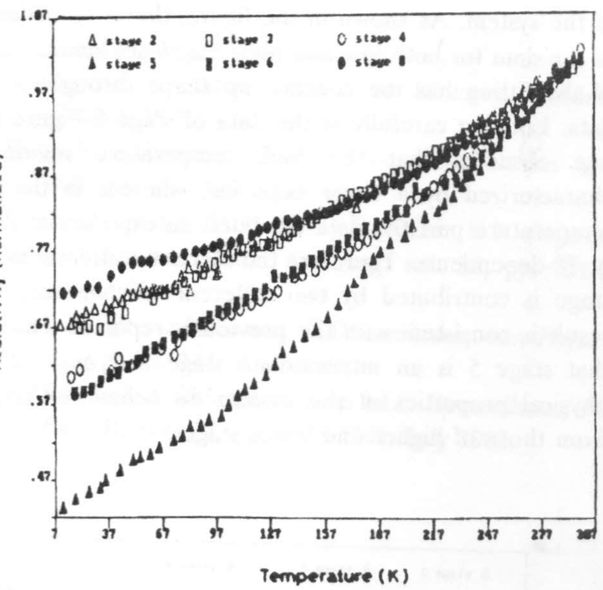

Figure 2. The in-plane normalized resistivity for various stages of $FeCl_3$-GIC's versus temperature.

On the contrary to the c-axis resistivity measurements [10], the data in Figure (2) show that the resistivity first decreases with stage index up to stage 5, and then starts to increase again for the higher stages. This result for low stages emphasized the argument that the conduction takes place in the graphite layers adjacent to the intercalant layers [4]. But one expects that the increase in the number of graphite layers between the intercalant layers screens the out-of-plane scattering and thus force the charge carriers to move in the (001) plane. Therefore, high stage compounds are expected to possess in-plane conduction higher than that of low stages, which is not consistent with the present results. However, since the in-plane conduction is associated with band conduction, one assumes that for high stages new conduction band channels open across the graphite layers and an out-of plane scattering arises. Thus the spacing between the intercalant layers is not one of the major factors which control the in-plane conduction in this system. However, in other physical properties such as the magnetic susceptibility the spacing between the intercalant layers is a crucial factor which makes the magnetic properties of the system depend strongly on the stage index of the sample.

The experimental in-plane resistivity data of all intercalated samples were fitted to an empirical model given by :

$$\rho(T) = A + BT + CT^2.$$

The temperature-independent term is related to the residual resistivity, while the temperature-dependent terms are attributed to electron-phonon and carrier-carrier scattering, respectively. A similar model was used for other GIC's [4,13,14]. The values of the coefficients A,B and C, normalized to room temperature resistivity value, for the different stages are given in Table (1). As listed in Table (1), the fitting parameters of different stages were not similar. One can see that the parameter A which is related to the residual resistivity decreases as the stage index increases from 2 to 5, while it increases with the stage index up to stage 8. Moreover, as mentioned above, the parameter A for HOPG is much smaller than that of any stage in Table (1). The important conclusion which one can extract from this result is that the intercalation process introduces structural defects to the system. Therefore, as the number of intercalated layers increases in the system the contribution of the defects in the scattering mechanism becomes more significant. It is clear from the values of the parameters B and C Table (1) that at low temperatures the quadratic term becomes more dominant and thus the contribution of the phonons to the scattering is insignificant.

Table 1. The in-plane normalized resistivity coefficients A,B and C of equation (2) for various stages of $FeCl_3$-GIC's (see text)

Stage	A	B(10^{-4} K^{-1})	C(10^{-6} K^{-2})
2	0.667	7.01	1.47
3	0.642	11.00	0.47
4	0.584	7.03	2.50
5	0.410	14.00	2.14
6	0.567	11.00	1.18
8	0.724	2.98	2.04

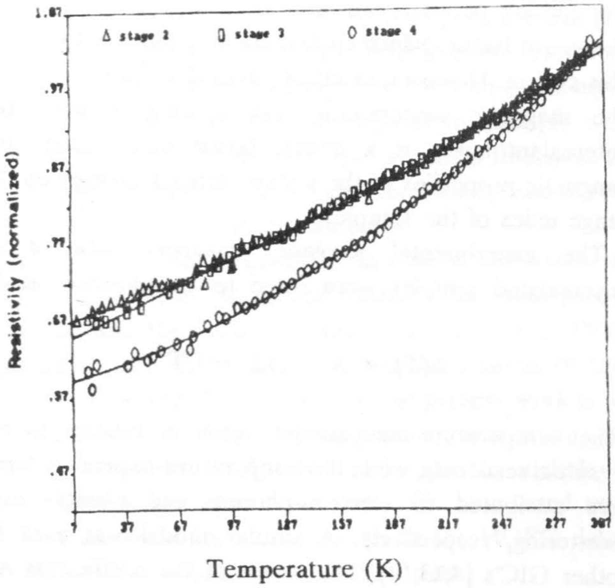

Figure 3. The in-plane normalized resistivity for low stages of $FeC1_3$-GIC's versus temperature, (symbols) experimental data. The solid lines fit the data to equation (2), see text.

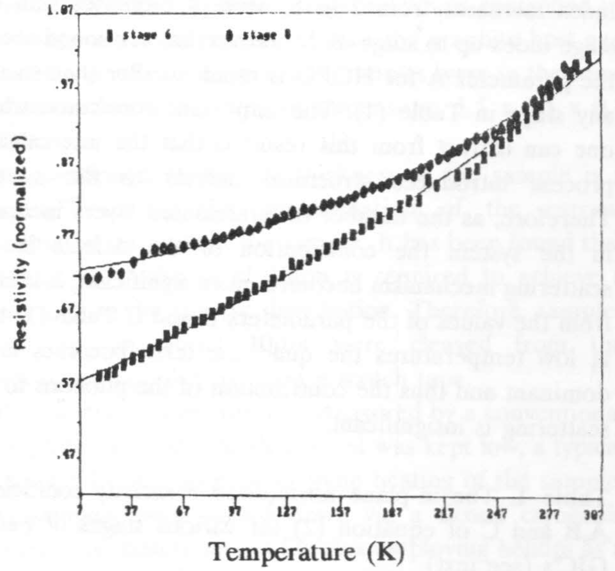

Figure 4. The in-plane normalized resistivity for high stages of $FeC1_3$-GIC's versus temperature, (symbols) experimental data. The solid lines fit the data to equation (2), see text.

For the sake of comparison the data are plotted on three different graphs; one is for low stage samples, the second is for high stage samples, and the last one is for one sample of each category besides the intermediate stage (stage 5). The data plotted in Figure (3) are the experimental in-plane normalized resistivity (symbols) and their fits (solid lines) versus temperature for stages 2, 3 and 4. As shown in the figure all samples exhibited metallic - like behavior and no major difference existed between different stages. The in-plane resistivity data of high stages (6 and 8) are plotted versus temperature in Figure (4) (symbols). The solid lines are the fits to the empirical model given by equation (2).

In Figure (5), we have chosen one stage from each category : low (2), high (8), and intermediate (5) stages, and this enables us to compare between the various stages of the system. As shown in the figure, the main behavior of the data for both low and high stages are similar, each of the fitting has the concave up shape throughout the data. Looking carefully at the data of stage 5 Figure (5), one observes that the high temperature region is characterized by a linear behavior, whereas in the low temperature part the data exhibited an exponential - like or T^2-dependence. Therefore the carriers scattering in this stage is contributed by two different mechanisms. This result is consistent with the previously reported data [10] that stage 5 is an intermediate stage and most of the physical properties of this system do behave differently from those of higher and lower stages.

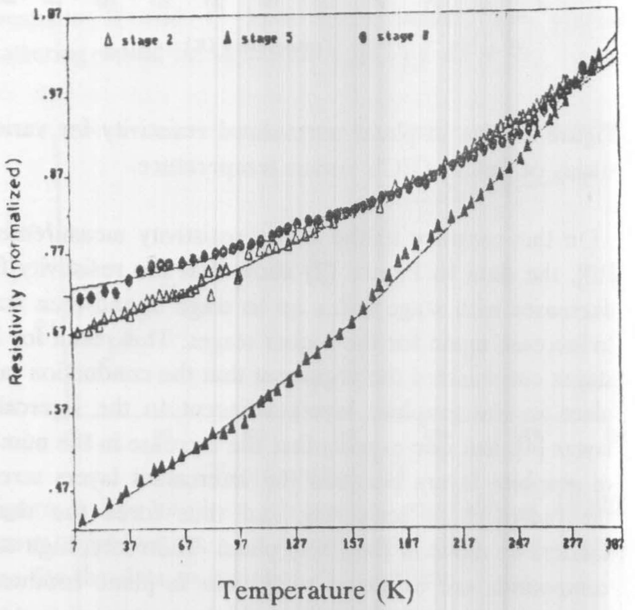

Figure 5. The in-plane normalized resistivity for low (2), high (8) and intermediate (5) stages of $FeC1_3$-GIC's (symbols) experimental data. The solid lines fit the data to equation (2), see text.

In conclusion, the in-plane resistivity of all stages of $FeCl_3$-GIC's as well as the HOPG have exhibited a metallic - like behavior. The data of the intercalated samples were fitted to an empirical model which is different from that for the HOPG sample. The results of the fits indicate that the intercalation processes introduce structural defects in the system. Stage 5, as expected, has exhibited a behavior which is different from all other stages.

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