Low field Hall coefficient measurements of graphite ferric chloride intercalation compounds

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Extensive investigations have been carried out on various graphite intercalation compounds (GICs), but the nature of the microscopic mechanisms have not been fully understood. The transport properties of these compounds show drastic changes from the parent graphite [1] and require more theoretical investigations.

As an extension of our studies on graphite ferric chloride intercalation compounds (GFeCl3) of both pure and mixed stages, we report our measurements of the Hall coefficient at low magnetic fields.

The graphite ferric chloride intercalation compounds of pure and mixed stages were prepared by the conventional two-zone vapour transport technique with the graphite zone at higher temperature than the intercalant zone. The temperature conditions used for the synthesis are given in Table I. This particular system was found to be environmentally stable. The samples were characterized initially by the increase in weight percentage over that of initial graphite.

X-ray characterization was carried out using CoK_α radiation of wavelength 0.17902 nm. The stages were identified from the (0 0 1) reflections of the X-ray diffractogram. According to the classical model of staging [2], the c axis repeat distance I_c is related to the stage number n by the simple relation:

$$I_c = (n - 1)c_0 + d_s$$

where c_0 is the interlayer distance in pure graphite, d_s is the intercalant sandwich thickness given as $d_i + c_0$, where d_i refers to the intercalant layer thickness. For a stage n compound, the $(00n + m)$ peak is found to be maximum where $m = d_s/c_0 \approx 2$ for GFeCl3 compound [3]. The X-ray diffractogram for a stage 4 compound is given in Fig. 1.

The four-probe d.c. method of measuring resistivity has limitations due to electrical contact and complicated sample geometry. Hence, a contactless method developed by McRae and coworkers [4, 5] was

TABLE I Reaction temperatures and times

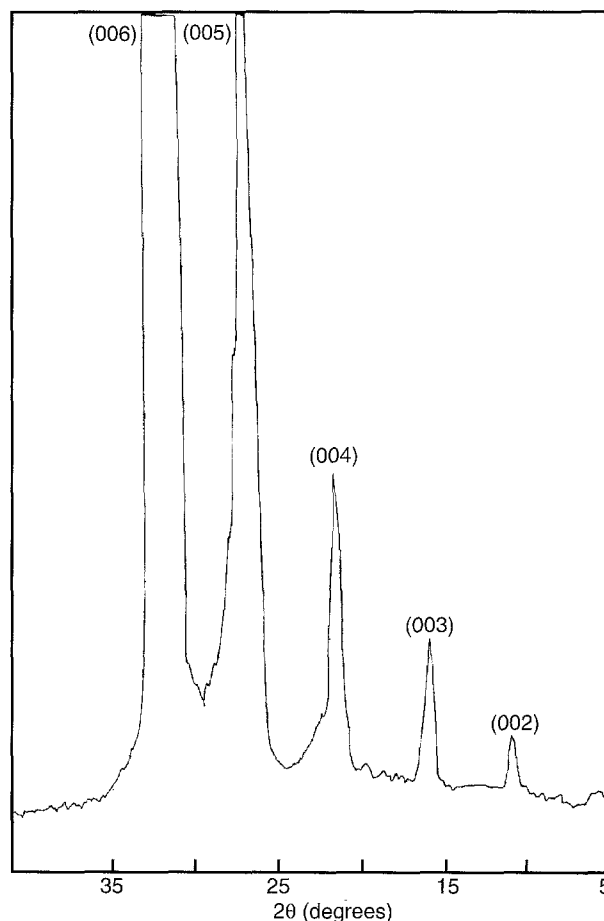| Stage	Temperature		Reaction time (hs)
	$T_g(°C)$	$T_i(°C)$	
2	370	330	21
2/3	360	315	22
3	350	300	21
3/4	350	250	21
4	350	230	21
6	350	212	24

Figure 1 X-ray diffractogram of stage 4 GFeCl3 compound.

utilized to study the conductivity of GICs. The principle involved in this method is that when a sample is introduced into an air-core inductance coil, which forms a part of the tank circuit of a inductance and capacitance (LC) resonant circuit, the resonance frequency of the circuit changes due to the eddy currents introduced into the sample. The frequency of operation was fixed at 160 kHz measured using an HP5352 microwave frequency counter. The LC circuit was the tank circuit of the Colpitt's oscillator [6]. This set-up was calibrated initially at room temperature for resonance frequency difference with thickness for metals like silver, copper, aluminium and brass, with conductivity ranging from 6.2×10^7 Ωm to 1.3×10^7 Ωm. Highly oriented pyrolytic graphite (HOPG) was also used as one of the calibration materials, with its conductivity about 1/22 that of Cu. The variation of resistivity with $1/n$ is given in Fig. 2. From the figure it can be seen that conductivity is maximum for the stage 2 compound.
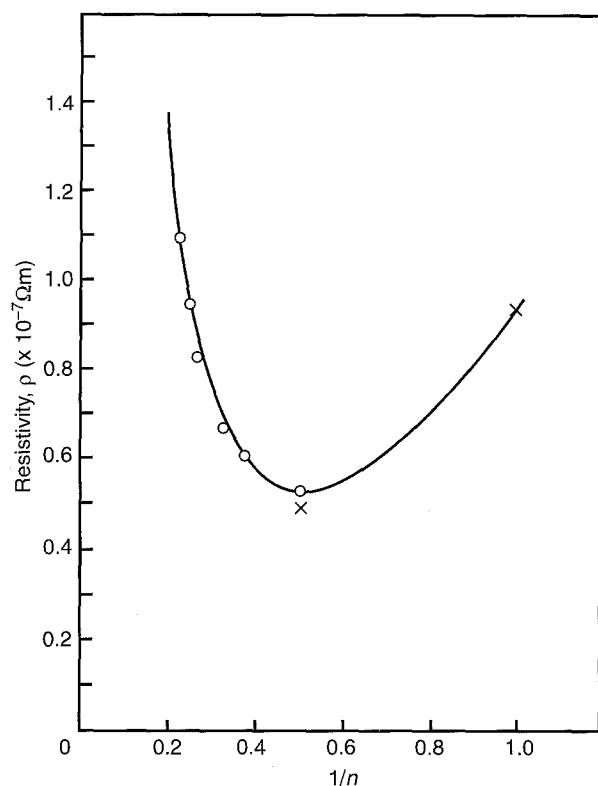
Figure 2 Variation of resistivity with $1/n$, where n is the stage number. (○), This work; (×), literature value.

Figure 3 Variation of Hall coefficient with $1/n$, where n is the stage number. (×), Mixed stages; (⊙), pure stages.

Hall coefficient measurements for $GFeCl_3$ compounds of pure and mixed stages were performed using very low magnetic fields in the range 0.03–0.15 T. The standard four-point configuration was used with two current contacts and two voltage contacts perpendicular to each other and to the magnetic field, which was applied along the c axis of the compound. The samples used for the study were square pieces of area about $1\,cm \times 1\,cm$ and thickness ranging from 0.2 mm to 0.4 mm. The voltage developed was a fraction of microvolts, hence a nanovoltmeter (Keithley Instruments) was used.

The first result observed was a dramatic change in the sign of the Hall coefficient from negative for graphite, indicating electrons as the majority carriers in graphite, to positive for the intercalated compound, indicating holes as the majority carriers.

The Hall coefficient can be related to the carrier concentration by treating the GICs as single carrier or semi-metals, with majority carrier concentration swamping out the minority carriers, as in doped semiconductors. Thus, the stage variation of Hall coefficient simply gives the change in carrier concentration. The carrier concentration n_c is related to the Hall coefficient R_H by the relation:

$$R_H = 1/n_c e$$

where e is the electronic charge. We expect an increase in carrier concentration as the stage number decreases. But this is not the case observed. As shown in Fig. 3, the Hall coefficient is maximum for stage 3, hence a two-carrier model has to be used to calculate the concentration of the carriers in the $GFeCl_3$ system. Based on the single carrier model,
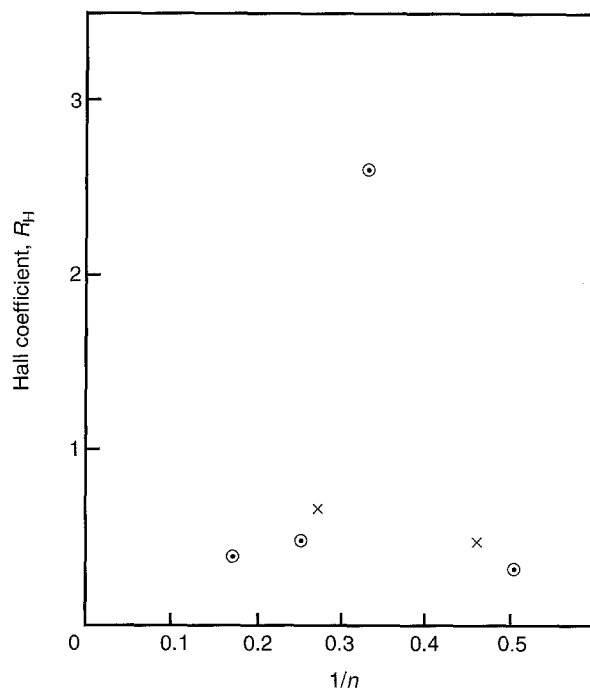
the carrier concentration for stage 2 compound is calculated as $1.67 \times 10^{26}\,m^{-3}$ which agrees fairly with that reported by Abou Ali et al. [7].

Comparing the conductivity data, the maximum conductivity occurs for a stage 2 compound. There is a maximum charge transfer since all of the graphite layers are bounding layers. Considering the stage 3 and other higher stages, there is a significant contribution from the graphite interior layers. Even though graphite is a semi-metal with a carrier density of about 10^{-4} carriers per atom, the mobility of the carriers is maximum. Therefore mobility must be playing a major role in determining the conductivity. In fact, the presence of holes as charge carriers, with a much higher number than in graphite, shows these charge carriers to have come about because of the charge transfer from intercalant to graphite layers. This shows the ionic nature of the bonding in the graphite ferric chloride system.

In conclusion, the Hall coefficient of $GFeCl_3$ was found to be positive, showing holes to be the majority carriers. From the variation of the Hall coefficient with the stages, it is seen that a single carrier model cannot be applied to find the carrier concentration, hence a two-carrier model has to be used. The nature of bonding between the intercalant and the graphite was found to be ionic.

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