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# Twenty Years of Charge Transport Studies in Intercalated Graphite

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Upon the occasion of the 10th ISIC conference, it seems appropriate to give a brief overview of some of the major advances made in our understanding of charge transport in intercalated graphite since the 1st Franco-American Conference on Graphite Intercalation Compounds held in 1977.

*Keywords:* Resistivity; Weak Localisation; Superconductivity

One of the highlights of the Franco-American Conference on Intercalated Graphite in La Napoule in 1977 was the presentation of results on $AsF_5$ and $SbF_5$ GICs showing basal plane conductivity ($\sigma_a = 1/\rho_a$) values exceeding that of copper at room temperature[1]. Enormous interest over the following years was stimulated by this discovery in spite of little success in repeating these results. Over the succeeding two decades, many new phenomena were found in both graphite and its intercalation compounds; more recently, the fullerene family and carbon nanotubes have provided new low-dimensional structures of interest both in their own right and as new hosts for intercalation. The transport behaviour of these new materials, like that of GICs and the cuprate superconductors in their normal state shows that understanding charge propagation in lamellar and tubular structures is a challenging undertaking.

Let us start with the question: in the mid-1970's, what did we know?

The single sheet of graphite, "graphene" as it is termed today, had been determined to be a zero gap semiconductor and graphite was known to have a very low carrier density of about 1 carrier per $10^4$ carbon atoms but with very high in-plane mobility ($>10^4$ $cm^2/V.s$ at 298 K and below[2]) making graphite quite a good in-plane conductor, $\rho_a \approx 40\text{-}50$ $\mu\Omega$.cm. The c axis resistivity $\rho_c$ was 1 or 2 orders of magnitude greater for natural single crystal graphite and a factor of about $10^3$ for highly oriented pyrolytic graphite (HOPG). The greatest body of results then existing on the electrical properties of GICs was that of Hennig's and Ubbelohde's groups[3]. Saturated, 1st stage materials were known to possess a free carrier density comparable to that of metals, a metallic in-plane resistivity variation for $77 \leq T \leq 300$ K and the few $\rho_c$ measurements showed that certain compounds could attain 295K $\rho_c/\rho_a$ values as great as $10^5$. The few TEP and Hall effect studies gave data on the nature and density of the charge carriers. Ubbelohde had termed the GICs "synthetic metals" and it was commonly agreed upon that this was an applicable term. The 1st stage alkali metal GICs were further known to be superconducting at temperatures below 1 K[4].

The late 1970's and early 1980's issued in a whole series of new materials and techniques. Ternary donor GICs containing a heavy alkali metal M and either Hg or Tl were developed by Lagrange *et al.*[5] with large interplanar distances, ordered in-plane structures and "high" transition $T_c$ values which attained 2.7 K in the case of $C_4KTl_{1.5}$. This excited much interest since none of the component elements was a superconductor itself. The stage variation of $T_c$ led to speculations on the possibility of a 2D superconducting state when the c axis repeat distance $I_c$ exceeded the c axis superconducting coherence length, but this could never be observed.

Studies of $\rho_a$ and $\rho_c$ over a considerably wider range of temperatures were undertaken during this period. It was experimentally observed that 1st stage $MC_8$ GICs could be "high quality" metals with $\rho_a(295K)/\rho_a(4.2K)$ ratios of several hundred[6]. Even to date, this has been observed for no other GIC.

The sensitivity of the in-plane resistivity to structural (re)-organisation which had been known for several years as concerns the lambda transition in $HNO_3$ GICs was observed in the late 1970's in the 2nd stage alkali metal compounds. The experimental $\rho_a(T)$ work of Onn *et al.*[7] below room temperature gave clear evidence of transitions, later investigated via diffraction and confirming intercalate layer ordering. Studies of $\rho_c$ under pressure shortly afterwards on stage 2 to 6 compounds were the first indicators of stage changes in these materials[8]. In this post - la Napoule era, transport studies firmly established themselves as excellent tools for detecting the onset of new states of order.

While alkali metal based intercalation compounds continued to stimulate interest during the 1980's, many different $\rho_a(T)$ and $\rho_c(T)$ studies were made on other GIC families for which it was possible to synthesise a wide range of stages. These included the acceptors $SbCl_5$ ($1 \leq s \leq 10$), $FeCl_3$ ($1 \leq s \leq 10$), $AlCl_3$ ($1 \leq s \leq 4$), $GaCl_3$ ($1 \leq s \leq 11$), and the donors M-Bi ($1 \leq s \leq 7$) and NaH ($1 \leq s \leq 6$). These investigations led to a number of significant conclusions. Whatever the stage, $\rho_a(T)$ was found to vary almost universally with a metallic dependence ($d\rho_a/dT > 0$), often a quadratic T component and residual resistivity ratios < 20. The c axis variation revealed itself to be more "interesting" in that it was a far more sensitive parameter than $\rho_a$ to T, p or s. The experimental aspects of $\rho_c(T,s)$ were reviewed in 1988[9]: there is a slow crossover from metallic ($d\rho_c/dT > 0$) to non-metallic ($d\rho_c/dT < 0$) behaviour as s rises leading to a strongly stage-dependent "residual" resistivity $\rho_c(4.2\ K)$. Such a variation was found to hold for all GICs in spite of the fact that $\rho_c(295\ K)$ varied over 5 orders of magnitude. Transport studies during this period also saw the birth of strongly anisotropic ternary donor GICs with $\rho_c/\rho_a \geq 10^6$ at liquid helium temperatures: attributing the term "low anisotropy" to all donor GICs is thus very erroneous, but the myth still lingers on in the literature!

The fact that the low stage acceptor GICs possessed $\rho_c(295\ K)$ values several orders of magnitude less than those of the richest alkali metal GICs led

to the idea that it might be possible to analyse many data, notably optical reflectivity, by considering acceptor GICs to be stacks of independent sandwiches comprising the intercalate and its surrounding graphene-sheets. This very successful Blinowski-Rigaux model[10] is still widely used today because it allows extracting carrier density and Fermi level. A second important theory of the same period related charge transfer to C-C bond length[11].

During this decade, important advances were made in the development of carbon fibres and many efforts were made to intercalate them so as to both improve their electrical properties and make them environmentally stable. The fibre diameters being of the order of tens of microns, such materials had ideal aspect ratios for galvanomagnetic studies and one of the major discoveries was that of 2D weak localisation (WL) made by the Louvain-la-Neuve group in Belgium, reviewed in Ref. 12. They examined a wide range of virgin and intercalated carbon fibres and gave many examples of the logarithmic upturn in fibre resistivity with decreasing temperature in conjunction with negative magnetoresistance, the characteristic features of the above mentioned localisation process. While anisotropy values exceeding 1 million had been observed previously in certain GICs, these works were the first to explicitly interpret the observed phenomenon as a truly 2D effect. At the end of this decade, evidence of 2D WL had further been found in pyrocarbons in which the graphene layers are turbostratically stacked with an interplanar distance exceeding that in graphite[12]. This series of works was important in establishing the low dimensional character of graphite and its intercalation compounds as electronically 2D.

The 1980's were a busy period in establishing several types of phase diagram. While the transport theories that were put forward (see below) aimed at explaining the stage and temperature dependencies of $\rho_c$ in particular, studies of the pressure dependence of the electrical resistivity were also being carried out both as a complementary technique to help determine the charge transport process(es) as well as to establish the (T,p) phase diagrams[13].

The different correlations obtained during this period furnished data that allowed theorists to advance the first $\rho_c(s,T)$ theories: significant contributions were made by Sugihara[14] who suggested a range of intervening mechanisms including impurity- and phonon-assisted hopping, interlayer conducting paths and somewhat later, small polarons. Markiewicz[15] showed the importance of the AA or AB stacking to c axis transport. The first attempt to explain $\rho_a(s,T)$ - and still the only that exist even today - was that of Pietronero and Strässler[16]. While their calculations applied specifically to the stage 1 $AsF_5$ GIC, the results were important in that they gave a firm basis for understanding the non-linear $\rho_a(T)$ relationship noted for most GICs.

The appearance of the high temperature superconductors in 1986, the $C_{60}$ molecule in 1985 and the carbon nanotubes in 1991 meant that enormous efforts have been devoted over the past decade to these other low dimensional solids, and from a transport viewpoints, less devoted to GICs; however, those studies which have been carried out clearly illustrate that while the works of the previous decade have given some understanding to overall possible charge transport mechanisms, much remains yet to be quantitatively and microscopically explained. Recent studies showing the complex interactions between the charge carriers and their environment include those of Suzuki *et al.* on magnetic intercalates[17] and ours on $PdAl_2Cl_8$ GICs[18] and the still widely studied $SbCl_5$ GICs[19]. New ternary donor GICs have been synthesised containing an alkali metal stabilised by the presence of a chalcogen and the transport properties of most are still unknown[20].

In the above, we have sketched some of those studies in GIC transport which seem relevant even today. Transport studies as functions of T, p, s, intercalate, etc. are sensitive probes of many types of organisation. Galvanomagnetic studies under both low and high magnetic fields have proved to be useful in determining the dimensionality of GICs through the weak localisation phenomenon and the SdH effect respectively. Nevertheless, many

open questions remain concerning the conduction mechanisms in these synthetic metals. Furthermore, many parallels can be drawn between the conductive properties of cuprate superconductors in their normal state and GICs. One of the biggest challenges which remains in these families of lamellar compounds as for other superstructured materials is the determination of the mechanism by which charge propagates in the direction perpendicular to the planes.



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