

LETTER TO THE EDITOR

Pressure enhancement of the electrical conductivity of graphite intercalation compounds†

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Abstract. A novel approach to achieve high electrical conductivity in graphite intercalation compounds is suggested. It is based on a recently observed pressure-induced staging transition in GICs which leads to a higher areal density of the intercalant while the quasi-2D character of the structure, believed to exhibit lower carrier scattering, is still preserved.

Research into the structure and properties of graphite intercalation compounds (GICs) is currently one of the most spectacular growth areas of materials science. A fundamental feature of the GICs is the formation of ordered sequences ('stages') of graphite and intercalant layers (Rüdorff and Schulze 1954). Thus a stage n compound is one where n layers of carbon atoms are interposed between every pair of intercalant layers. Within each layer the carbon atoms form a hexagonal network with a strong covalent-type C–C bond. The stack of layers, however, is held together through a weak van der Waals type of bond and even large molecular species can be intercalated (Fischer 1980). Although the details concerning the staging mechanisms are still a contentious issue (Salzano and Aronson 1965, Safran and Hamann 1979), the prime reason why the intercalation process works so well in graphite is its high degree of structural anisotropy.

Graphite intercalation compounds offer several unusual and exciting physical situations, such as various ordered and disordered forms (Clarke *et al* 1979) with quasi-two dimensional (2D) characteristics, realisation of several lattice gas models (Bak and Domany 1979), and structural arrangements conducive to the study of effects of dimensionality on the melting transition (Bak 1980, Halperin and Nelson 1978).

From a practical point of view one of the most fascinating discoveries so far is an observation by Vogel *et al* (1977) of extremely high electrical conductivity (exceeding that of pure copper) of certain acceptor-type graphite intercalation compounds, notably that of C_8AsF_5 . This immediately caused great excitement and led Vogel (1977) to speculate on the use of the GICs in applications such as high-current/low mass-density conductors. Unfortunately, the expectation of further rapid improvement of the conductivity as the state of the art of GICs became more refined over the past four years has not materialised. In fact, subsequent efforts by, among others, Bartlett *et al* (1980), Interrante *et al* (1980) and Moran *et al* (1981) to reproduce Vogel's results have been unsuccessful. On the basis of these measurements it appears that a more realistic value

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for the highest conductivity acceptor compounds is only about a half of that of copper. While there still is an avenue for improvement by e.g. reducing the number of intrinsic defects of HOPG graphite, it is unclear whether this can be easily achieved.

In this note I should like to draw attention to a novel approach which might lead to achieving high conductivity in GICs. It is based on the use of the pressure-induced staging transition discovered recently by Clarke *et al* (1980). The idea is as follows. It is a well known fact (e.g. Vogel *et al* 1977) that the highest basal plane conductivities are observed not in the most concentrated (stage 1) compounds but around the stage number 3. It is believed (Batallan *et al* 1978) that a partly 2D character of the Fermi surface of higher stage compounds exhibits a lower carrier scattering which compensates for the smaller intercalant intake. Obviously, if one could induce and sustain a local layer stoichiometry which corresponds to higher local density of the intercalant and, at the same time, make use of the less resistive, partly 2D character of the higher stage compounds, the overall effect should lead to an enhancement of the conductivity.

The pressure-induced staging transition provides exactly the mechanism we require—a modest hydrostatic pressure (6 kbar) sets up a reversible, first-order phase transition from a lower stage to a higher stage. In this process no intercalant is lost by being squeezed out of the sample but is merely redistributed between the graphite layers. This leads to the formation of what we can call *supercharged intercalant layers* which have enhanced areal density of the intercalant. Thus, in the Stage 2 to Stage 3 transition of KC_{24} observed by Clarke *et al*, the areal density of K atoms increases by a factor of $\frac{3}{2}$. At the same time the effective mobility of donor-type graphites measured by Onn *et al* (1979) as a function of stage at 300 K approximately doubles on going from stage 2 to stage 3 (table 1). Hence in such a pressure-induced transition one might expect an overall 3 times increase in the *a*-axis electrical conductivity of donor compounds.

Table 1. Stage dependence of the effective mobility of potassium-graphite measured by Onn *et al* (1979) at 300 K. Similar behaviour is observed for other donor compounds.

Compounds	Effective mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
KC_8 (Stage 1)	130
KC_{24} (Stage 2)	251
KC_{36} (Stage 3)	466
KC_{48} (Stage 4)	2300

There are two additional features which make this process attractive. First, due to a very high anisotropy of GICs a uniaxial pressure along the *c* axis ('soft direction') would have had exactly the same effect as the hydrostatic pressure. Secondly, the stage 3 appears already at much lower pressure (2 kbar) and, if the pressure is held constant, the stage 3 phase slowly grows at the expense of stage 2. Theoretical justification of this phenomenon was given recently by Safran and Hamann (1979). The above two features are particularly appealing from the practical point of view; one requires only a relatively low pressure and this need not even be hydrostatic.

While an expected enhancement by a factor of 3 of the conductivity for donor compounds appears spectacular, from the practical point of view one is more interested in the behaviour of acceptor compounds which show much higher intrinsic conductivity. Unfortunately, there are as yet no pressure measurements available which would con-

vincingly demonstrate the existence of the pressure-induced transition in the acceptor compounds, neither are there data on the stage dependence of the mobility. Furthermore, and this applies to the donor compounds as well, one should inquire whether the applied pressure does not drastically disturb the in-plane graphite structure with the consequence of much reduced carrier mobility.

Most recently Iye *et al* (1980) have observed pronounced steps on the resistivity of HNO_3 -graphite at pressures of about 6 kbar. It is possible that this anomaly is associated with the change in staging order but confirmation of this must come from x-ray measurements.

The study of the effect of pressure on the properties of GICs is still in its infancy and the effect of pressure on the electronic transport is only one of the many exciting phenomena which await further study. The practical potential of the pressure enhanced conductivity should be explored in detail.

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