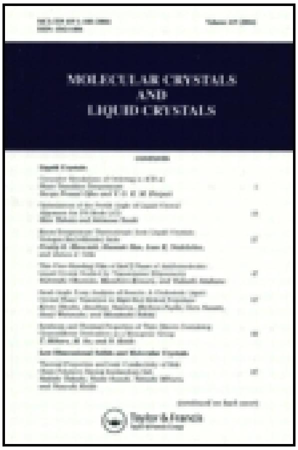

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New Directions in Intercalation Research

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NEW DIRECTIONS IN INTERCALATION RESEARCH

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Abstract

Since the start of this decade (the 1990's), intercalation has become a more important tool for modifying the structure and properties of host materials, both because of the important new systems to which intercalation has been applied and because of the new science and technology that has been made possible by these discoveries. Recently, the intercalation of fullerenes by alkali metals have demonstrated intercalation in zero-dimensional systems. The observation of relatively high T_c superconductivity in certain alkali metal intercalated fullerenes has attracted much attention. Even more recent is the introduction of guest species into one-dimensional carbon nanotubules. Intercalation has also been used to gain insights into the properties of high T_c cuprates. A review is given here of recent advances in the intercalation of GICs and of new materials systems with particular relevance to the implication of this work on more traditional areas of intercalation physics.

1 Introduction

Historically the series of International Conferences on Graphite Intercalation Compounds (GICs), starting with the first conference in La Napoule in May, 1977, have played a seminal role in stimulating new research directions for the field. For more than a decade since the La Napoule conference, leaders in the field of graphite intercalation compounds met together every 2-3 years to discuss progress in the field without much interaction with researchers working in other areas of intercalation physics and chemistry. Through these meetings the GIC field has progressed rapidly, and, after a decade, GICs became a mature field of investigation. In recent years intercalation research has reached out into new areas, and the international conferences have likewise expanded their focus to address the intercalation process more broadly. In this review, we discuss some of the recent new directions that

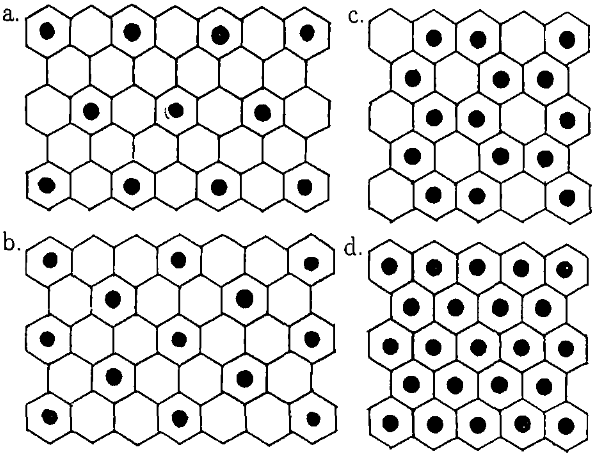

Figure 1: Structure of the intercalate layer for dense alkali metal GICs corresponding to the stoichiometries: (a) C_8M, (b) C_6M, (c) C_3M, and (d) C_2M [7].

have been taken, major advances that have been made, and suggested directions for future work.

2 Graphite Intercalation Compounds

First we review recent developments in the field of graphite intercalation compounds, insofar as this field has provided the nucleation center for this series of conferences. Several new directions have been taken recently, in part stimulated by papers presented in the last few international conferences, including the structure and properties of dense alkali metal GICs [1], the transition from ionic to covalent compounds [2, 3, 4], new graphite host materials for intercalation [5], and new tools such as scanning tunneling microscopy to study GICs [6].

Dense phases of alkali metal GICs were pioneered by Russian workers and became widely known through a stimulating presentation at the Fifth International Symposium on GICs in Berlin [1] where T_c values as high as 5 K were reported for dense alkali metal phases: C_2Na (5 K), C_3Na (3.8–2.3 K), C_2Li (1.9 K), C_3Li (<0.35 K), C_3K (3 K), C_6K (1.5 K) [7] (see Fig. 1). These high density alkali metal phases have been shown to form first stage commensurate GICs as shown in Fig. 1 where the conventional $(2 \times 2)R0°$ structure is shown for the C_8M compound, the $(\sqrt{3} \times \sqrt{3})R30°$ structure for the C_6M compound, a honeycomb structure for C_3M and a dense triangular lattice for C_2M. These pioneering works [1, 7] stimulated efforts worldwide, and a number of collaborations have developed between Russian and western researchers to study the structure and properties of these new materials in more detail and to produce more homogeneous, higher quality samples. Advances have been made both in gaining understanding of the normal state properties in terms of the electronic structure, lattice structure, crystalline compressibility for the normal state [7], and the mechanism for superconductivity at low temperatures [8]. Several papers reporting recent advances on this topic are presented at this conference.

In the Fourth International Symposium on Graphite Intercalation Compounds held in Jerusalem in 1987, a paper was presented on fluorine graphite intercalation compounds [9], introducing researchers to a new class of ionic compounds. This was of particular interest insofar as the compounds $(CF)_n$ and $(CF_2)_n$ are known to be non-conducting and covalent [10]. Stimulated by this exciting new direction, several workers moved into this field by the time of the Berlin Conference in 1989, first studying the transport properties [11, 12], and optical properties [13, 14], and later leading to extensive studies of weak localization phenomena in these compounds [2, 4].

Only fluorine and oxygen form covalent compounds with graphite. Whereas oxygen forms only covalent (but never ionic) compounds, fluorine exhibits either ionic or covalent bonding with graphite. Another special feature of fluorine intercalation into graphite is the intercalate-induced introduction of a large density of defects into the graphene layers [2], whereas for most other GICs, the intercalation process introduces only marginal disorder. The density of defects in F-GICs increases with increasing intercalate concentration and is related to the two types of possible C–F bonds, as indicated above. Since the covalent regions have sp^3 bonds, it is expected that the covalent bonds partially destroy the planarity of the graphene layers [3]. Strong structural evidence for these defects is provided by high resolution transmission electron microscopy, where the highly wavy layers are indicative of the breakdown of the planar structure. One consequence of this disorder is the ability to synthesize first stage F-GICs over a large range of stoichiometry. This disorder has recently been exploited to study 2D weak localization phenomena in the regime of large carrier-carrier interactions [2, 4]. Because of the wide range of disorder that can be achieved in a controlled way by fluorine intercalation, these materials are uniquely suited for the study of 2D localization and carrier-carrier interaction phenomena. The characteristic logarithmic temperature dependence of the resistivity at low T is shown in Fig. 2 for several fluorine concentrations for stage 1 C_xF fibers, where the magnitude of the logarithmic correction term is found to increase dramatically with increasing [F] concentration.

Much of the most significant research on GICs was made possible by the early development of a suitable host material for intercalation, namely HOPG (highly oriented pyrolytic graphite) [15, 16, 17]. Recently, interesting new graphite host materials have been prepared from polymer precursors. One example of such a precursor is polyimide films (such as kapton), which show well developed graphitic structure and great promise of a new host material for intercalation [18, 19]. The quality of these new film materials is rapidly improving, and more experience is being gained with the intercalation of these materials. Several papers at this conference are directed to these new opportunities. The availability of quality thin film materials should be especially useful for various transport studies and for the inves-

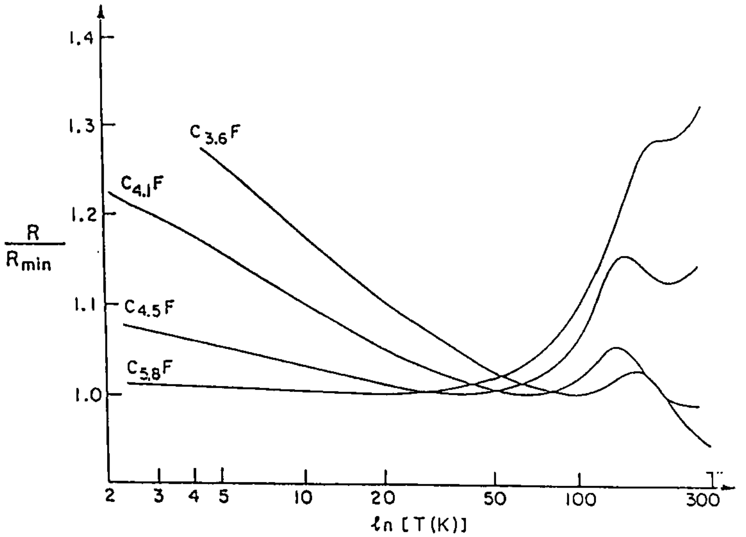

Figure 2: The temperature-dependent resistance, normalized to the minimum in resistance $R_{\min}$, for the fluorine-intercalated fibers C_xF in the weak disorder regime ($x \geq 3.6$). The logarithmic correction at low temperatures is characteristic of weak disorder in the fibers. As expected, the magnitude of the low-temperature correction increases with increasing fluorine concentration [4].

tigation of ion implantation phenomena in graphite and its intercalate compounds [20].

The GIC field was invigorated in the late 1980's by the introduction of new experimental techniques such as the scanning electron microscope to investigate the structure and properties of GICs. An influential review of early accomplishments in the field were presented by Wiesendanger at the Berlin conference [6], who clearly identified a variety of alkali metal commensurate phases. Since then STM studies on GICs have been one of the most important research directions in this field [21] for the past 4 years, and several papers using STM techniques are featured in the present conference.

3 High T_c Cuprates

The intercalation of guest species into high T_c cuprates has recently provided a new research direction which has attracted attention by researchers both in the intercalation field and in the field of high T_c superconductivity, with particular reference to interactions spanning a single unit cell and interactions between unit cells. In particular the intercalation of I_2 into the high T_c layered bismuth cuprate Bi-Sr-Ca-Cu-O superconductor series has been carried out successfully [22, 23]. The study of this intercalation compound has added significantly to our understanding of possible mechanisms for high T_c superconductivity, with particular reference to

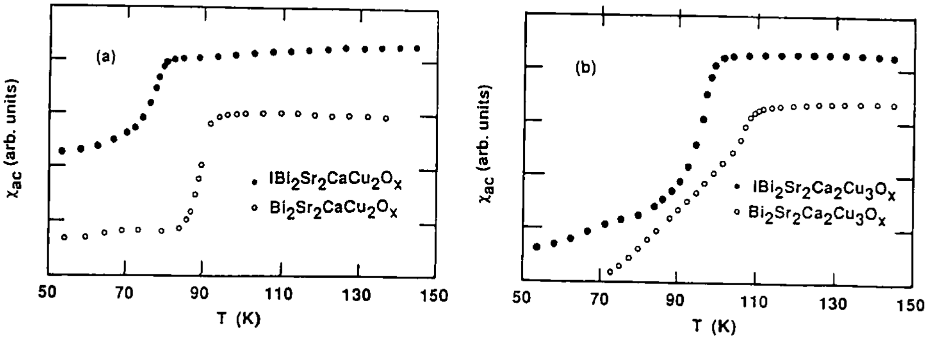

Figure 3: ac magnetic susceptibility of pristine (open circles) and intercalated (solid circles) Bi for (a) 2:2:1:2 single crystals and (b) Bi 2:2:2:3 polycrystalline samples [22].

interactions spanning a single unit cell and interactions between unit cells. Intercalation of stage 1 and stage 2 materials has been demonstrated with high resolution transmission electron microscopy performed on a face normal to the layer planes [22]. Unfortunately, the overall effect of I_2 intercalation is a lowering, rather than an increase, of the T_c for this system. Nevertheless, intercalation can be used to provide control of the transition temperature for the $Bi_2Sr_2CaCu_2O_x$ system (see Fig. 3).

One interesting research opportunity that has been identified by STM studies of high T_c cuprates is the possibility of exploring the c-axis charge distribution on an atomic scale using scanning tunneling spectroscopy measurements on a suitably prepared a-face (containing both c-axis and a-axis unit vectors). In the case of the high T_c cuprates, such studies demonstrated that the CuO_2 layers were far more conducting than the BiO layers. The exploration of these techniques for the study of the c-axis charge distribution in both donor and acceptor GICs could prove to be of significant interest.

4 Fullerenes

The intercalation of alkali metals into C_{60} to a stoichiometry M_3C_{60} (where M = K, Rb) has yielded relatively high T_c superconductors (T_c up to 33 K). This discovery has spurred a great deal of interest in the doping and intercalation of C_{60}-related materials. A brief review is given here of the unusual features of the doping and intercalation of fullerenes.

Each carbon atom in a C_{60} molecule is identical to every other carbon atom. Each carbon atom has 4 valence electrons which bonds to each of the 3 nearest-neighbor carbon atoms. Two of the bonds are single bonds on a pentagonal face, and the third is a double bond between two hexagons (see Fig. 4). Since all the bonding requirements of the carbon atoms are satisfied, it is expected that C_{60} is

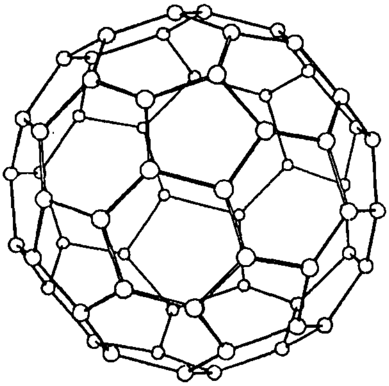

Figure 4: Structure of a C_{60} fullerene molecule each carbon atom is at an equivalent position on the corners of a regular truncated icosahedron. There are 12 pentagonal and 20 hexagonal faces.

an insulator (semiconductor) with a band gap between the occupied HOMO and unoccupied LUMO states. To make C_{60} (and also other fullerenes) conducting, doping is necessary to provide charge transfer.

Since the charge transfer associated with doping tends to produce delocalized charge on the shell of the fullerene, the distinction between double and single bonds, which have slightly different bond lengths for undoped C_{60}, becomes less important as charge transfer proceeds. This effect is supported by both experimental observations [24] and theoretical calculations, showing that the bond lengths for the single bonds a_5 decrease from 1.46Å for neutral C_{60} to form a C_{60}^{-n} anion upon charge transfer, while the bond length for the double bond increases from its value of $a_6 = 1.40$Å for neutral C_{60} [25]. The high degree of charge transfer observed for alkali metal doped C_{60} compounds indicates that these compounds are highly ionic, just as the alkali metal doped GICs.

The doping of fullerenes differs in several ways from the doping of other materials. Firstly, there are three different ways to dope fullerenes: endohedral doping, substitutional doping, and exohedral doping or intercalation. The doping possibilities for fullerenes relate closely to intercalation, except that the host material is not a layered material. Not all fullerene intercalation compounds result in charge transfer, and in almost all cases where charge transfer has been observed, it is electrons (rather than holes) that are transferred to the fullerenes.

In the case of endohedral doping, a rare earth, alkaline earth or alkali metal ion is introduced into the interior of the C_{60} ball to form an endohedrally doped molecular unit. There is no analog to endohedral doping in the layered intercalation compounds. For the smaller fullerene molecules such as C_{60}, either one or two ions are introduced into interior of the fullerene, while for larger fullerenes, up to four ions have been introduced [26, 27]. Up to now, the most popular endohedral dopants have been La^{3+}, Y^{3+} and Sc^{3+} which are all filled shell ions, corresponding to angular momentum $J = 0$, and therefore having no magnetic moments. The insertion of other endohedral dopants could lead to non-zero J values and hence to magnetic moments. Thus far, only very small quantities of endohedrally-doped fullerenes have been prepared and their study has been limited to investigations of isolated endohedrally doped fullerenes. In the case of endohedral doping of an ion such as La^{3+}, the three valence electrons are transferred to the fullerene where they are delocalized on the fullerene surface.

A second doping method is the substitution of an impurity atom with a different valence state for a carbon atom on the surface of a C_{60} ball. Substitutional doping is common for group IV solids, including diamond and graphite. Since a carbon atom is so small, and since the average nearest neighbor C–C distance denoted by a_{C-C} is only 1.42Å in graphite, the only likely substitutional dopant is boron [28]. However, for diamond, which has a C–C nearest neighbor distance of a_{C-C} = 1.544Å, both boron and nitrogen can enter the diamond lattice substitutionally [29]. Since a_{C-C} on the C_{60} surface is only 1.44Å [30], the only species that is expected to substitute for a carbon atom on the C_{60} ball surface is boron, making the charged ball *p*-type. Smalley and coworkers have demonstrated that it is possible to replace more than one carbon atom by boron on a given ball [27]. Since a_{C-C} on the C_{60} ball is somewhat larger than in graphite, and since the force constants are somewhat weakened by the curvature of the C_{60} surface, it may be possible also to dope the C_{60} with nitrogen, though this has not yet been clearly demonstrated. Since boron is in column III of the periodic table, the charge transfer associated with this substitutional doping results in a *p*-type fullerene where the hole is delocalized over the fullerene surface. Because of the high electron affinity for C_{60}, the achievement of positively charged C_{60} by doping is unusual.

The third and most common method of doping fullerene solids is exohedral doping (also called intercalation). In this case, the dopant (usually, an alkali metal or an alkaline earth, M) is introduced into an interstitial position between adjacent fullerene balls (exohedral locations) in a solid structure. This method of doping closely parallels the charge transfer that occurs when an alkali metal is intercalated into graphite [31]. Because of the large size of the fullerene molecules (~10Å) relative to the size of the typical atoms (~2Å), the cavities between the molecules can also be large enough to accommodate various metal guest species in these cavities. Charge transfer can take place between the M atoms and the balls, so that the M atoms become positively charged ions and the balls become negatively charged with predominately delocalized electrons. This method of doping forms exohedral fullerene solids and closely parallels the process of intercalating alkali metal ions into layers that are sandwiched between carbon layers in graphite [31]. It has also been reported that it is possible to place a potassium atom endohedrally inside the C_{60} ball while at the same time substituting a boron for a carbon atom on the surface of the ball [27].

In the solid state, the C_{60} molecules crystallize into a cubic structure with a lattice constant of 14.11Å [32]. At room temperature the balls are rotating, and the crystal structure is FCC with one C_{60} ball per unit cell. Below about 250 K, the molecules are reported to become oriented and the structure becomes simple cubic with four C_{60} molecules per unit cell [33]. When doped with an alkali metal to the composition M_3C_{60}, the large C_{60} molecules are arranged in a FCC structure (see

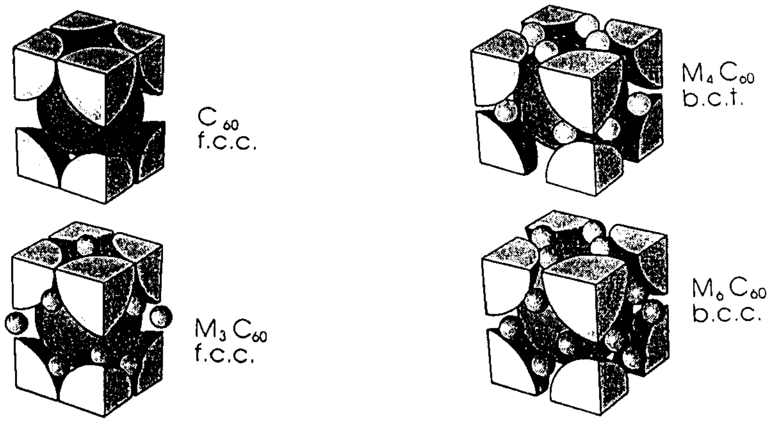

Figure 5: Structures for the solid C_{60}, M_3C_{60}, M_4C_{60}, and M_6C_{60} (M= K, Rb, Cs). The large balls denote C_{60} molecules and the small balls are alkali metal atoms. For FCC M_3C_{60} which has four C_{60} balls per unit cell, the M atoms can either be on octahedral or tetrahedral sites. For BCC M_6C_{60} all the M atoms are on distorted tetrahedral sites. For BCT M_4C_{60} the dopant is also found on distorted tetrahedral sites [34].

Fig. 5), and the alkali metal can sit on either tetrahedral (1/4,1/4,1/4) sites which are twice as numerous as the octahedral (1/2,0,0) sites (referenced to a simple cubic coordinate system). The two other stable phases for the heavy alkali metal (M = K, Rb) M_xC_{60} system are M_4C_{60}, which is more difficult to prepare and has a body centered tetragonal structure (BCT) [34], and M_6C_{60} which has a body centered cubic structure (BCC) (see Fig. 5). From the standpoint of the near neighbors, the K guest species in M_3C_{60} sit between two C_{60} balls, on any of four tetrahedral sites or two octahedral sites. Locally at each tetrahedral dopant site of K_3C_{60}, the environment looks rather similar to a first stage alkali metal graphite intercalation compound. For the tetrahedral sites, the radius of the K^+ ion is 1.12Å while for an octahedral site it is 2.07Å[32], as compared with 1.03Å in the stage 1 GIC C_8K. The shortest distance between a K^+ ion at a tetrahedral site and the freely rotating C_{60} is 2.66Å[32] which is to be compared with 2.68Å in C_8K. Another factor affecting the metal ion uptake is the size of the metal ion (see Table 1). Also a guest ion inserted at the center of a C_{60} molecule is at a distance of 3.4Å which is equal to the interlayer separation of the graphene layers in turbostratic graphite. Just as in the case of graphite intercalation compounds, the addition of alkali metal dopants expands the lattice, but in the case of the fullerenes, the lattice expansion effects are small. Since the FCC lattice is more compact, higher doping levels favor the more open BCC lattice. These similarities further justify the comparison of doped C_{60} with graphite intercalation compounds. The structures of the various phases of intercalated C_{60} are illustrated in Fig. 5, where the C_{60} molecules are denoted by

Table 1: Radii for various metal ions.

Alkali metal	r_i (Å)	Alkaline earth	r_i (Å)
Li^+	0.76	Be^{+2}	0.30
Na^+	1.02	Mg^{+2}	0.65
K^+	1.38	Ca^{+2}	1.00
Rb^+	1.52	Sr^{+2}	1.13
Cs^+	1.67	Ba^{+2}	1.34

large balls and the M atoms by small balls [34].

Among the alkali metals, Li, Na, K, Rb, and Cs [35] have all been used as exohedral dopants for C_{60}, as well as intermetallic mixtures of these alkali metals such as Na_2K [36, 37] and Rb_xCs_y [38]. The doping of C_{60} with alkali metals can be achieved in a two temperature zone oven, similar to the apparatus used to prepare alkali-metal graphite intercalation compounds [39]. The in-situ progress of the intercalation reaction can be monitored qualitatively by the color change observed in the films and more quantitatively by the doping-induced down-shift of the strongest C_{60} Raman line or by changes in the electrical conductivity. The doping reaction in C_{60} single crystals is carried out in a two-zone furnace for longer times (~1 to 2 weeks) than for thin films, because of the larger distances that the dopant must travel in the crystalline material [22, 23, 40].

Alkaline earth dopants, such as Ca, Ba, and Sr have all been successfully intercalated into C_{60} [41, 42]. The intercalation of alkaline earth dopants generally require higher temperatures than for alkali metals [43] just as for GICs. In the case of the alkaline earth dopants, two electrons per metal atom M are transferred to the C_{60} balls for low concentrations of metal atoms, while for high concentrations, the charge transfer is less than two electrons per alkaline earth ion. In general, the alkaline earth ions are smaller than the corresponding alkali metals in the same row of the periodic table. For this reason the crystal structures formed with alkaline earth doping are often different from those for the alkali metal dopants and more than one alkali metal ion is introduced into the octahedral sites. Unlike alkali-metal-doped C_{60}, where each M atom transfers one electron to C_{60}, the alkaline-earth metal dopants have been reported to transfer two electrons per metal dopant for low metal concentrations, but lower charge transfer values for higher calcium concentrations [41]. The charge transfer is however believed to be sufficient to completely fill the states corresponding to the T_{1u} level and to partially occupy states in the T_{1g} level.

Doping fullerenes with acceptors has been more difficult than with donors because of the high electron affinity of C_{60}. A stable crystal structure has nevertheless been identified upon doping C_{60} with iodine, where the iodine is reported to form a sheet between layers of C_{60} balls; no measurable conductivity has, however, been observed in the case of iodine doping of fullerenes [44, 45], so presumably no charge transfer takes place in this case.

The above discussion shows many parallels between doped fullerenes and GICs with regard to structure. On the other hand, C_{60} is an insulator with very narrow bandwidths near the Fermi level while graphite is a semimetal with bandwidths of several electròn volts. Thus C_{60} forms a highly molecular and strongly electron correlated solid while graphite is a highly anisotropic band-like solid. Thus many differences are found in the lattice, electronic, transport and superconducting properties of GICs relative to the doped fullerenes. Thus far, knowledge of the structure and properties of GICs has significantly influenced progress with the investigation of doped fullerenes, though less impact has been felt in the GIC field from the rapid progress that has recently been made in increasing our understanding of doped fullerenes. The recent introduction of foreign species into the centers of carbon nanotubes may provide a new research frontier, relating doped carbon nanotubes to intercalated carbon fibers.

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