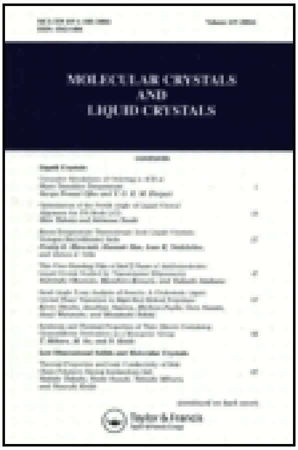

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Physical Properties and C-F Bonding in Fluorine-Graphite Intercalation Compounds as Seen by NMR

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Physical properties of fluorine-graphite intercalation compounds (GICs), namely semimetal-metal and metal-insulator transitions and localization effects, are discussed based on ^{13}C and ^{19}F NMR data. NMR view on the nature of C-F bonding in fluorine-GICs and graphite fluorides is presented.

Keywords: graphite intercalation compounds; NMR

INTRODUCTION

Graphite reacts with fluorine gas in a wide range of temperatures, yielding two kinds of compounds with different electrical properties [1]. Graphite fluorides $(CF)_n$ and $(C_2F)_n$ are electrical insulators. Their carbon skeletons consist of trans-linked cyclohexane chairs with sp^3 bonding [1,2]. C-F bonds are considered to be completely covalent [1]. Fluorine-GIC, C_xF, is a conductor. It exhibits a behavior that is different from all other GICs [3-5]. For most GICs the in-plane electrical conductivity initially increases upon intercalation due to the increase in carrier density resulting from injection of carriers from the intercalate species to the graphite layers. This results in a transformation of the semimetallic graphite into a metal. In fluorine-GIC the in-plane conductivity also increases with the increase of fluorine content for dilute compounds, $x>8$, has a plateau for $8>x>6$, but then, in contrast to the other GICs, drops sharply with further intercalation [3-5]. Based on XPS data, it was suggested that the nature of C-F bonding changes from ionic to semicovalent (or semi-ionic) with increased fluorine content [1,4,5]. Such a change in the character of the C-F bond was expected to reduce the carrier density and cause a rapid decrease in conductivity. In the present paper, we discuss the semimetal-metal and metal-insulator transformations and the nature of C-F bonding in fluorine-GICs as seen from NMR spectra.

PHYSICAL PROPERTIES OF FLUORINE-GIC: NMR OUTLOOK

NMR study of fluorine-GIC [6] shows that for dilute compounds ($x>8$), in which semimetal-metal transformation with increasing fluorine content takes place, the room temperature ^{19}F spectra are represented by only a narrow line attributed to mobile fluorine species. It was suggested that this species is an electron acceptor which, like for the other GICs, injects holes into conduction band of the host graphite and thus is responsible for the increase of conductivity in the dilute compounds. This increase comes to an end at $x\sim8$ where, as seen from our spectra, a broad line attributed to covalent C-F bonds starts to occur.

In the region from $x=8$ to 3.8, in which the conductivity has a plateau and starts to decrease, the position and shape of the broad line are practically independent on fluorine content. This indicates the almost unchanged character of the C-F bond. The amplitude ratio of broad to narrow line decreases with decrease of fluorine content (Figure 1), until the broad line practically disappears at $x\sim8.5$. The correlation between the growth in the number of the covalent C-F bonds and the drop in conductivity for the fluorine concentrations above the value corresponding to σ_{max} allow to suggest that this drop is caused by a percolation mechanism rather than by a change in bond length. When such a covalent C-F bond is formed, each fluorine atom blocks one node in the conductive graphite network, and this node does not take part in the conductivity any longer. For x~3, where conductivity drops distinctly, the number of unbound carbons determined by NMR is around 70%, close to the threshold of percolation for a two-dimensional honeycomb lattice. Thus the covalent C-F bonds are responsible for the percolation decrease in conductivity.

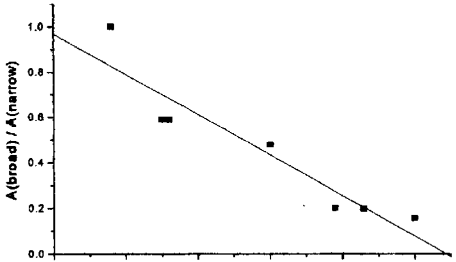

FIGURE 1 Intensity ratio of broad to narrow ^{19}F line in F-GIC at room temperature

Distribution in ^{19}F NMR chemical shifts has also been obtained and associated with a disorder in F sites. Such disorder was considered to result in the weak localization effects in fluorine-GICs [5].

CHEMICAL BOND IN FLUORINE-GIC AS SEEN BY NMR

^{13}C and ^{19}F NMR chemical shifts (CS) are sensitive to the local bonding. Paramagnetic contribution to the CS, $(\delta_p)_{zz} \sim \Sigma\{<\psi_0|L_z/r^3|\psi_n><\psi_n|L_z|\psi_0>/\Delta_n\}$, results from the mixing between the occupied ground state and the unoccupied excited states. (Δ_n is the difference in energy of the ground and excited state). This term strongly depends on the structure of external molecular orbitals taking part in chemical bonding and thus is sensitive to the nature of the chemical bond.

^{13}C CS measurements [6,7] in fluorine-GIC (Figure 2) show that ^{13}C resonances fall into two regions, assigned to graphitic carbons and C-F carbons, respectively. The former ones show the position close to that determined in graphite. The chemical shift of C-F carbons is intermediate between sp^2 graphitic carbons and sp^3 aliphatic carbon atoms in diamond. Thus we suggest that, during intercalation, fluorine attaches to the carbon plane and partially destroys the delocalized electronic state of graphite in its immediate vicinity creating covalent C-F bonds which corrugate the carbon plane. ^{13}C CS's of C-F carbons in insulator graphite fluorides [8,9] and in fluorine-GICs are close to each other. No continuous transformation of the CS and no intermediate regime characteristic for a smooth transition from ionic to semi-ionic/semicovalent and then to covalent C-F bonding have been observed. Thus one can conclude that at least known ^{13}C spectra (as well as physical properties) can be explained in the frames of a model which does not involve uncommon semi-ionic/semicovalent bond.

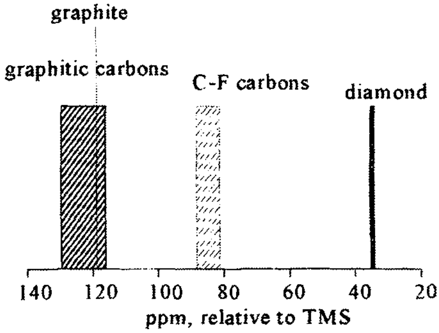

FIGURE 2 ^{13}C chemical shift in F-GICs [6, 7]

Some difference in ^{19}F CS for fluorine-GIC (-150 ppm [6]) and graphite fluoride (-175 to -197 ppm [6,8]) is seen from ^{19}F spectra indicating a difference in chemical bond. However, the resonance of $(CF)_n$ which is considered to be completely covalent, shows a shift to high field in comparison to C_xF. This is in contradiction with the common fluorine CS scale, where a more covalent compound exhibits a downfield shift [10,11]. Thus this difference in CS does not accord with the aforementioned idea of ionic to covalent transformation of C-F bonding with increasing fluorine content based on XPS data. From our data, we can conclude that CF-groups adjacent to aromatic sp^2 carbons in nonsaturated C_xF compound exhibit a downfield chemical shift, while those adjacent to sp^3-hybridized CF species in the fully fluorinated and saturated compound $(CF)_n$ exhibit highfield chemical shift. To understand the nature of C-F bonding in these compounds, we note that Pauling [12] related partial ionic character of the single bond between atoms A and B to the difference in their electronegativities x_A and x_B :

$$I = 1 - \exp[-(x_A - x_B)^2/4] \qquad (1)$$

Pauling calculated that C-F bond is expected to have 44% ionic character because the electronegativity of fluorine (x_F=3.95) is larger than that of carbon (x_C=2.5). Thus we conclude that C-F bond in fluorine compounds $(CF)_n$ and C_xF is partially ionic, with electrons preferably located at F atom rather than at C atom (Figure 3). According to the ^{19}F CS scale and our data, and suggesting that the energy gap Δ between the ground and excited states is practically

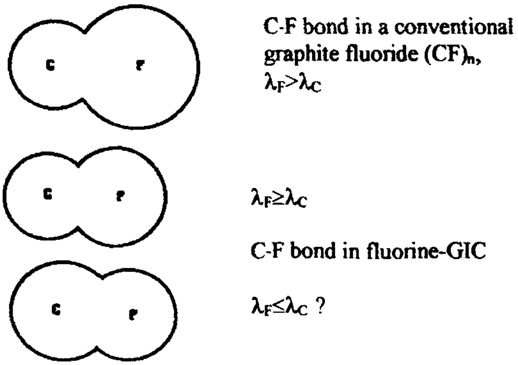

FIGURE 3. Suggested electron distribution on a hybrid bonding molecular orbital of the C and F atoms, $\Psi=\lambda_C\psi_C+\lambda_F\psi_F$, in graphite fluoride and fluorine-GIC. For simplicity, diagrams show an isolated pair of atoms, but the same changes are expected to occur in an extended structure.

constant, one can even speculate that fluorine-GICs show an electron distribution on the C-F bond with the electrons slightly moved from fluorine to carbon atom in comparison with graphite fluorides.

CONCLUSION

NMR study allows us to suggest that the physical properties of fluorine-graphite intercalation compound are mostly caused by a competition of two mechanisms. Mobile fluorine acceptor species is responsible for the increase of conductivity in the dilute compound, while the growth in the number of the covalent C-F bonds with fluorine content yields a decrease in conductivity owing to percolation.

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