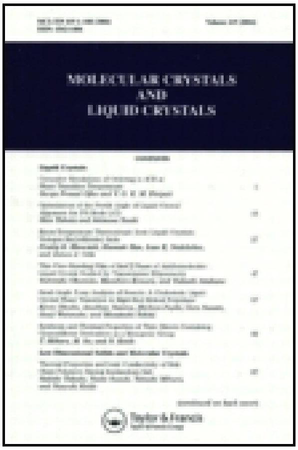

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EPR, ^{13}C and ^{11}B NMR of Boronated Carbons Intercalated with Heavy Alkali Metals (K, Rb and Cs)

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B_xC_{1-x} host materials ($0.1 < x < 0.25$) and their intercalation compounds with heavy alkali metals prepared from the vapor reaction or from the reaction of cesium in ammonia solution were characterized using ^{13}C and ^{11}B NMR and EPR. ^{13}C NMR shifts and EPR dysonian lines (typical of conductors) found in intercalation compounds are qualitatively similar to those observed in their GIC analogues. Evidence are reported in favor of a breaking of the local axial symmetry due to interstitial boron atoms for highest x values and partial recover of this symmetry in the intercalation compounds.

Keywords: intercalation; Cs; Rb; K; NMR; EPR; boron; carbon

INTRODUCTION

Boron is known to form solid solutions B_xC_{1-x} with carbons ($0 < x < 0.25$). In the solid solution domain, lamellar boron substituted carbons were obtained by CVD at 1100°C [1]. The structure of B_xC_{1-x} solid solutions is known to be lamellar and boron atoms are substituted to carbon ones on the honeycomb of the graphitic planes [1]. Host materials are defective turbostratic materials and the thermal treatment enables to increase the cristallinity but B_4C boron carbide impurities were found to be formed at T> 1700 °C [2]. As x increases from 0.1 to 0.25, more boron atoms are in interstitial sites so that the cristallinity of B_xC_{1-x} decreases [1]. The presence of electron acceptor boron in such compounds was expected to increase the intercalation rate of alkali metals. Previous studies have shown that boronated carbons are able to be intercalated in the vapor phase by heavy alkali metals [3-4] giving $M(B_{0.25}C_{0.75})_{10}$ and $M(B_{0.25}C_{0.75})_8$ first stage intercalation compounds with a composition close to MC_8 GICs. The simulations of the X-ray diffraction *00l* lines have suggested the presence of less than 10 % of $M(B_xC_{1-x})_5$ dense structure interstratified in the compounds obtained from the vapor phase reaction. Cesium intercalation compounds were also prepared in liquid ammonia solution, with $B_{0.25}C_{0.75}$ host, as deposited and heat treated respectively at 1600°C and 2000°C in order to study the influence of host heat treatment on the intercalation.

In this paper, the results of ^{13}C and ^{11}B NMR and EPR characterization of host materials and their intercalation compounds are presented.

EXPERIMENTAL

B_xC_{1-x} ($x = 0.1$ and $x = 0.25$) powders of oriented platelets were allowed to react in the vapor phase with K, Rb and Cs using the conventional two bulbs method in a Pyrex glass tube carefully evacuated at 10^{-6} mbar. The temperatures of boronated carbon (T_{host}) and alkali metal (T_M) were selected in order to obtain the first stage derivatives. They were respectively $T_M = 310°C$ and $T_{host} = 350°C$ for cesium derivatives, whereas lower temperatures (typically $T_{host} = 270°C$ and $T_M = 250°C$) were used with potassium and rubidium in order to avoid the reaction of the alkali metal with the Pyrex glass.

$B_{0.25}C_{0.75}$ as deposited and heat treated compounds (15 min at 1600°C and 2000°C under Argon flux) were intercalated by cesium in liquid NH_3 solution. The B_xC_{1-x} platelets were dipped several days into the blue solution formed by excess of cesium diluted in liquid ammonia at $T = -40°C$ in an evacuated Pyrex tube (10^{-5} mbar). They were washed with pure liquid ammonia and the excess of ammonia was removed using 10^{-5} mbar vacuum. In host heat treated at 2000°C and intercalated, two segregated $Cs(B_xC_{1-x})_8$ and $Cs\ (B_xC_{1-x})_{10}$ first stage structures were pointed out. Their respective cesium atoms 2D lattices are 2×2 and 2.23×2.23 [4]. The presence of those two structures was assigned to the heterogeneity of the host material induced by the formation of B_4C boron carbide domains and the consecutive deboronation of B_xC_{1-x} lamellar phase with the temperature treatment [4].

The samples obtained as a powder of small oriented particles were transferred in sealed pure quartz tube in order to avoid any ^{13}C and ^{11}B NMR signal from the container. ^{13}C and ^{11}B NMR was performed using a Bruker DSX 360 spectrometer ($H_0 = 8.5$ T). EPR was performed on a Bruker spectrometer at 9.47 GHz.

RESULTS

^{13}C NMR

Host materials

In graphite the large diamagnetic shift of the δ_c component (several hundreds of ppm) is induced by the macroscopic local field due to the large diamagnetic susceptibility (Fig. 1). Two components attributed to the two kinds of atomic positions A and B were found for δ_c using a graphite HOPG sphere [5]. In carbons slightly doped with boron (x<0.006), the Fermi level is shifted to lower values and the diamagnetic susceptibility is drastically reduced with increasing boron content in agreement with the measurements of Soule [6]. As a result, comparing slightly boron substituted carbon to graphite, the H_0// c component is low-field shifted but the δ_{ab} one is unchanged. The δ_{ab} and δ_c positions are then the "graphene shifts" while x=0.005 (respectively 184 and 15 ppm/TMS). This residual anisotropy (≈ 170 ppm) results mainly from the Van Vleck paramagnetic shift of the (a,b) component relatively to the (c) one which remains unaffected due to local ternary (or axial) symmetry.

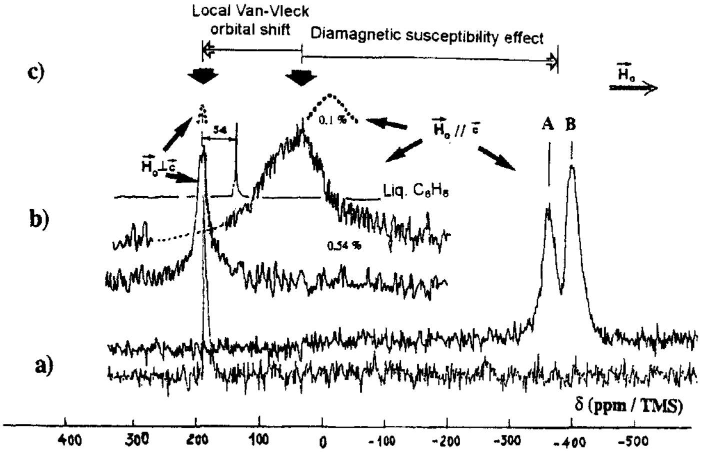

Figure 1: ^{13}C NMR ($H_0 \perp$ c and H_0 // c components) in: (a) HOPG, (b) boronated oriented graphite x=0.001 (dotted line) and 0.0054 (full line). (c): arrows corresponding to the graphene (i.e. HOPG corrected from demagnetising and Lorentz fields [5]) shifts ($H_0 \perp$ c and H_0 // c components).

B_xC_{1-x} host materials (x = 0.1 and x= 0.25) ^{13}C NMR showed a main peak at 180 ppm versus TMS, similar to the δ_{ab} shift obtained in graphite (Fig. 2). Furthermore, the axial anisotropy shape tends to disappear as boron content increases from 0.1 to 0.25. In B_xC_{1-x} (x > 0.1), as the content of boron is increased, part of the boron atoms are not substituted to graphitic carbons but are in interstitial sites breaking the local axial symmetry. This symmetry loss could induce a recover of the Van Vleck orbital paramagnetic interaction for the H_0// c component, explaining the shift of this component in the δ_{ab} direction. However, compared to the ^{13}C NMR of slightly boron doped carbon, the lines are broadened. This broadening is attributed to the dipolar interaction of ^{13}C nucleus with the magnetic momentum of boron.

Heat treatment of $B_{0.25}C_{0.75}$ under argon atmosphere at 2000°C led to a deboronation of the sample and the formation of B_4C domains pointed out by X-ray diffraction. The ^{13}C line width is reduced from 7000 to 900 Hz after heat treatment at 2000°C. This line narrowing is attributed to the deboronation of the lamellar phase B_xC_{1-x}. The position of the line is similar to the δ_{ab} shift previously observed in as deposited $B_{0.25}C_{0.75}$. A broad peak with weak intensity attributed to B_4C is superposed to the previous line.

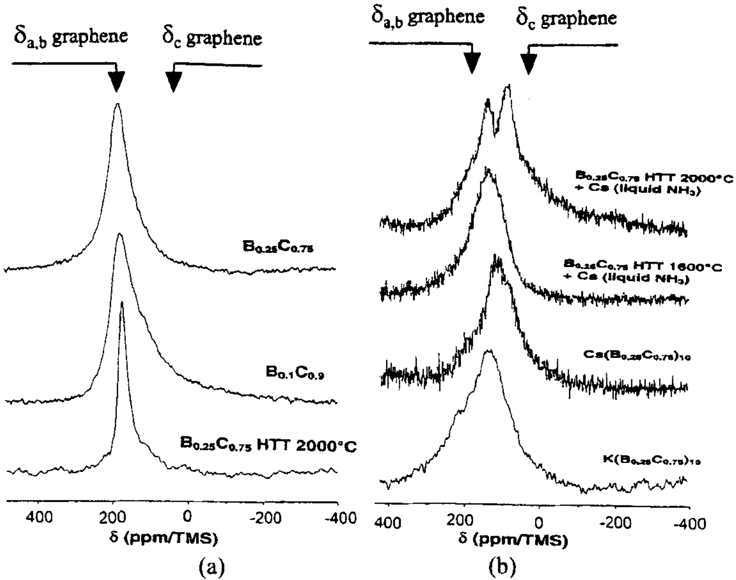

Figure 2: ^{13}C NMR of host materials (a) and first stage intercalation compounds obtained from $B_{0.1}C_{0.9}$ in the vapor phase (b).

1st stage vapor reaction intercalation compounds of B_xC_{1-x} (x = 0.1, 0.25)

The ^{13}C NMR high-field shift of the main peak of approximately 50-60 ppm relatively to the host one was observed similarly in $M(B_{0.25}C_{0.75})_{10}$, $M(B_{0.1}C_{0.9})_8$ (Fig. 2b). The maximum of the peak should correspond to the contribution $H_0 \perp c$.

In first stage GICs, the inversion of the asymmetry relatively to pristine graphite is interpreted as due to the shift of the (a,b) and (c) components in reverse directions (paramagnetic for δ_c and diamagnetic for δ_{ab}) due to the dipolar interaction of the ^{13}C nucleus with the π electrons [5].

For $B_{0.25}C_{0.75}$ pristine materials, due to the partial loss of local axial symmetry, the observation of an axial anisotropy is hindered: only δ_{ab} comparable to the graphite one is revealed (Fig. 2a). However, axial anisotropy is clearly observed again in the doped material (Fig. 2b). The increase of the interlayer distance after intercalation might have induced a partial recover of the axial symmetry, thus reducing the paramagnetic Van Vleck interaction and shifting the (c) component towards its graphene position. The interlayer alkali atoms could then induce a dipolar interaction proportional to the density of states at the Fermi level similarly to GICs.

Furthermore, the Van Vleck paramagnetic interaction for $H_0 \perp c$ should be reduced relatively to pristine materials as in 1st stage GICs. This reduction would be induced by the expansion of the π orbitals following the charge transfer. As a result a high-field shift of this component due to this effect would add to the dipolar shift of this compound.

Cesium intercalation in liquid ammonia

Cesium in liquid ammonia of as deposited $B_{0.25}C_{0.75}$ gave a very diluted $Cs(B_{0.25}C_{0.75})_{35}$ compound formed of 1st stage structure interstratified in pure $B_{0.25}C_{0.75}$. ^{13}C NMR is similar to the host materials. The same ^{13}C NMR spectra was obtained for intercalation compound of $B_{0.25}C_{0.75}$ heat treated at 1600 °C and for the 1st stage compound prepared from the vapor phase reaction (Fig. 2b). These results are in agreement with the X-ray diffraction indicating that this compound is a pure $Cs(B_{0.25}C_{0.75})_{12}$ 1st stage compound. $B_{0.25}C_{0.75}$ samples heat treated at 2000°C give after intercalation two kinds of first stage intercalated phases in which the cesium atoms 2D lattices are respectively 2×2 and 2.23×2.23 [4]. Two ^{13}C NMR peaks (at 120 ppm and 70 ppm) were found (Fig. 2b), these peaks could be interpreted as two ^{13}C positions relative to the alkali atoms in the two 2D structures. Two peaks were also found in powder 2nd stage GICs ^{13}C NMR and attributed to different positions of carbon relatively to the alkali atoms [7].

^{11}B NMR

The ^{11}B NMR spectrum present in each cases 2 (or 3) components at practically the same positions for host materials and intercalated compounds. Thus, the doping by alkali metals has negligible influence on the ^{11}B NMR. The lines could be interpreted in terms of dipolar interaction between the first neighbors or in terms of a 2nd order quadrupolar interaction associated to a high electric field gradient.

EPR

Among the host materials (x = 0.1, 0.17 and 0.25) only $B_{0.25}C_{0.75}$ gives a signal. The line is "dysonian", typical of a conductive material, at $g \approx 2$ and ΔH_{pp} (peak to peak width) equal to 2 Gauss.

The 1st stage intercalation compounds of potassium (x = 0.1 and 0.25) give dysonian lines with respectively 70 and 35 Gauss ΔH_{pp} (Fig. 3).

On the contrary, no line was observed in the 1st stage intercalation compounds of cesium (x=0.1 and 0.25), probably because of the very strong broadening due to spin orbite interaction on this heavy alkali metal [5].

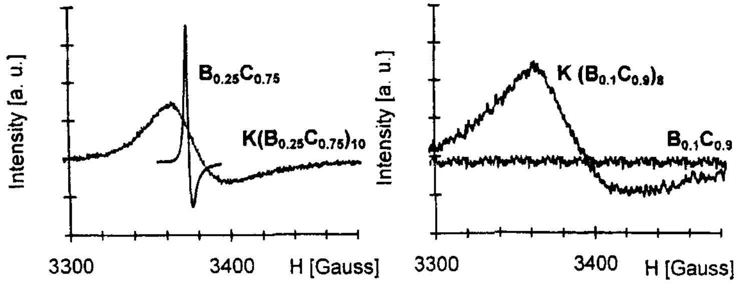

Figure 3: EPR lines of B_xC_{1-x}, (x = 0.1 and 0.25) and their first stage intercalation compound with K

CONCLUSION

Results of the ^{13}C NMR of highly boronated carbon (B_xC_{1-x}, x = 0.1 and 0.25) suggest that the presence of interstitial boron has partially broken the axial symmetry. ^{13}C NMR on 1st stage intercalation compounds yields broad peaks, with reversed anisotropy as compared to B_xC_{1-x} host materials. Line shape and shifts are qualitatively similar to those obtained in 1st stage alkali GICs. The partial recover of axial symmetry after intercalation and the dipolar interaction of the π bands electrons with the ^{13}C nucleus can explain these results. The ^{13}C NMR on $B_{0.25}C_{0.75}$ intercalated in cesium ammonia solution has confirmed the X-ray diffraction characterization showing that 1st stage can be prepared from $B_{0.25}C_{0.75}$ heat treated at 1600°C and confirming the presence of two 1st stage 2D lattices obtained from $B_{0.25}C_{0.75}$ heat treated at 2000°C [4]. ^{11}B NMR is quite similar in host materials and in their intercalation compounds and not fully interpreted.

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