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^{19}F NMR Study of Niobium Pentafluoride-Graphite Intercalation Compounds Prepared under Fluorine Atmosphere

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^{19}F NMR of several graphite intercalation compounds with NbF_5 is studied, from 200 to 300 K. Entities such as NbF_5, NbF_6^- and NbF_7^{2-} are identified and the observation of the relaxation time T_1 suggests a reorientation motion of these species as well as a strong fluorine exchange occurring between them. The fluorine concentration (i.e., F/Nb ratio) is shown to have an effect on the NMR lines. The mechanism of the compounds formation previously reported is confirmed.

Introduction

^{19}F nuclear magnetic resonance spectroscopy has been previously used as an investigational technique in the study of graphite intercalation compounds (GICs) with fluorides, in order to identify the intercalated species and to study their dynamic properties. Ebert *et al.* (*1*) have studied the temperature dependence of the linewidth in SbF_5–GIC and suggested a translational motion of the SbF_5 species. On AsF_5–GIC, Weinberger *et al.* (*2*) observed a decrease in the number of contributing nuclei below 220 K and suggested a gradual condensation of intercalated AsF_5 to more ordered state. Resing *et al.* (*3*) and Facchini *et al.* (*4*) showed that the SbF_5–GIC spectrum exhibits both broad and narrow lines assigned respectively to SbF_5 and SbF_6^-. The following reaction has been suggested to explain the presence of SbF_6^- in the compound:

$$3SbF_5 + 2e^- \rightarrow SbF_3 + 2SbF_6^-. \quad (1)$$

Ebert *et al.* (*5*) and more recently Stang *et al.* (*6*) suggested the formation of $Sb_nF_{5n+1}^-$ polyanions in order to explain the temperature dependence of the linewidth in SbF_5–GICs. as well as in PF_5–GIC($P_2F_{11}^-$) and in BF_3–GIC($B_2F_7^-$) (*5*).

In this paper, we present the ^{19}F NMR measurements in NbF_5–GICs prepared under fluorine atmosphere. Facchini *et al.* (*4*) have briefly reported that, at room temperature, two fluorine populations are present in the compound prepared under chlorine atmosphere. A series of first stage compounds with different compositions prepared under fluorine atmosphere has been

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studied by the NMR spectroscopy technique. From this study, different intercalated species have been separated, allowing us to suggest some interaction mechanisms occurring between them. The temperature dependence of the relaxation time T_1 is also discussed here.

Experimental Section

Synthesis

The synthesis of the compounds has already been described (*7*). NMR experiments have been carried out on three different composition NbF_5–GICs powder samples of first stage. Their compositions are given in Table I, where d_1 is the identity period along the *c* axis. These d_1 values are given with a standard error of 0.01 Å. Both $KNbF_6$ and K_2NbF_7 fluorides were prepared as mentioned in Ref. (*8*) and identified from X-ray diffraction powder patterns. NbF_5 was obtained by direct action of fluorine on niobium powder samples at 120°C.

NMR Technique

The high field (7 T) ^{19}F NMR lineshapes versus temperature were recorded on a BRUKER MSL 300 spectrometer. For this study, a fluorine specific probe perfected in our laboratory was used. This probe shows no fluorine signal whatever under the experimental conditions, in particular at low temperature, when using wide sweep widths for signal acquisitions. This result could be obtained by using coaxial wiring with polyethylenic dielectrics, and by making the different insulating components of Pyrex. We used a single pulse program which consists in the application of a $\pi/2$ pulse (4 μsec) at the resonance frequency of the fluorine nucleus (282.49 MHz). The signal was then recorded after a dead time of 2 μsec. The recycle delay was about 5 sec. The relaxation time T_1 measurements at different temperatures were carried out with a BRUKER SXP 4-100 spectrometer, using the π–τ–$\pi/2$ sequence with an 8 μsec pulse delay. A specific sequence for $T_{1\rho}$ measurements consists in the application of a $\pi/2$ pulse (4 μsec), followed up by a "spin-lock" pulse during a variable delay. Another fluorine specific probe was also used in this experiment.

TABLE I

COMPOSITION AND IDENTITY PERIOD ALONG THE *c* AXIS FOR USED SAMPLES (CHEMICAL FORMULA: $C_{8-10}NbF_x$)

Sample	d_1 (Å)	F/Nb(x)
1	8.25	5.96
2	8.28	5.79
3	8.30	5.67

Results

At room temperature, the fluorine spectra of the three compounds are identical: they exhibit a single narrow line centered at −220 ppm with respect to the external reference CF_3COOH. All the chemical shifts are given with a precision of ±5 ppm. When the temperature is decreased, the existence of several distinct lines, corresponding to fluorine populations, clearly appears in the spectra for each compound. Figure 1 shows the evolution of the bands with temperature for sample 3. In all cases, the narrow line observed at room temperature broadens with decreasing temperature, and then splits into at least three components between −50 and −400 ppm. Their positions are presented in Table II.

Simultaneously, a broad line appears, centered at +55 ppm and splits into two lines: a broad line at +50 ppm and a narrow one at +100 ppm. We also note that the relative intensities of all these lines depend on the composition of the compounds. Figure 2 presents the spectrum of each com-

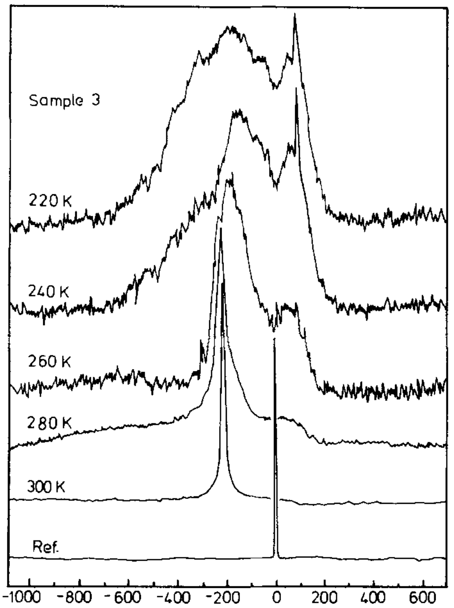

FIG. 1. ^{19}F NMR spectra of sample 3 at different temperatures.

pound recorded at 220 K. When the F/Nb ratio is increased, the intensity of these low field lines (+50 and +100 ppm) decreases while that of the high field lines increases. The temperature dependence of the relaxation times T_1 and $T_{1\rho}$ is shown in Fig. 3. At low temperature, the longitudinal magnetization recovery is clearly nonexponential and concentration dependent.

TABLE II

CHEMICAL SHIFTS IN THE DIFFERENT SAMPLES BETWEEN 260 AND 220 K (ppm/CF_3COOH)

Assignment	Sample 1	Sample 2	Sample 3
NbF_5 monomeric	−310	−320	−310
NbF_6^-	−190	−190	−190
NbF_7^{2-}	−160		
F^-	+50	+50	+50
NbF_5 polymeric	+100	+90	+90
Average value due to F^- motion	−220	−220	−220
F_2	−500		

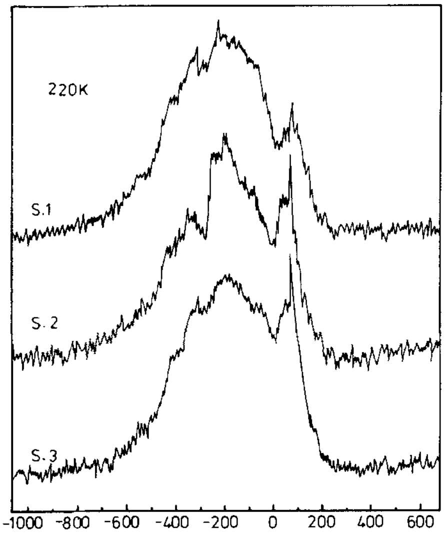

FIG. 2. Low temperature (220 K) ^{19}F NMR spectra of three compounds. (1) F/Nb = 5.96; (2) F/Nb = 5.79; (3) F/Nb = 5.67.

Discussion

At room temperature, the narrow line observed at −220 ppm in the three compounds is rather consistent with NbF_6^- species. The NMR signal of $KNbF_6$ fluoride has been recorded and shows a narrow line centered at −193 ppm. This value is in good agreement with the result reported by Gaduba *et al.* (*9*), who found a line at −189 ppm.

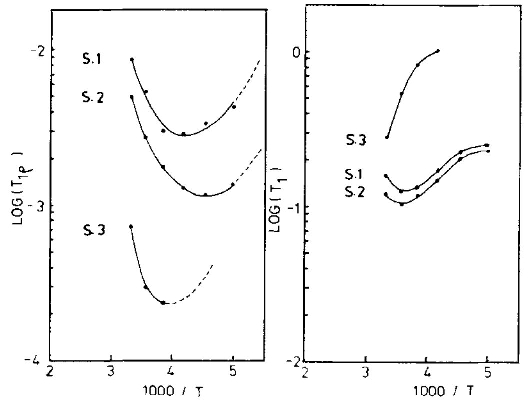

FIG. 3. Relaxation times T_1 and $T_{1\rho}$ vs temperature.

TABLE III

CHEMICAL SHIFTS IN THE FLUORINATED SPECIES (ppm/CF_3COOH)

Reference	NbF_5	$NbF_6^-(K^+)$	NbF_7^{2-}	F^-
Our results	Solid: +92	−193	−152 in solid K_2NbF_7	+45 in solid KF
(10)	—	—	−175 in HF solution	—
(9)	Solid: +91 Liq.: −270 Gas: −340	−189	—	—
(11)	—	—	—	+44

Table III gives the chemical shifts of some Nb–F salts reported in the literature as well as those of our own measurements. Facchini *et al.* *(4)* have observed two lines in the room temperature ^{19}F NMR spectrum of NbF_5–GIC prepared under chlorine atmosphere. The difference with our result may be due to the synthesis method: under chlorine atmosphere, species such as NbF_5Cl^- should also be formed.

When the temperature is decreased, different fluorinated species are distinguished. The high field broad lines at −190 and −160 ppm can be assigned to NbF_6^- and NbF_7^{2-}, respectively (NbF_7^{2-} is more easily distinguished in the fluorine richer compounds such as sample 1). Indeed, the NMR signals we recorded for $KNbF_6$ and K_2NbF_7 were respectively at −193 and −152 ppm. NbF_7^{2-} is reported to give a signal at −175 ppm in an anhydrous HF solution. Our result was obtained from solid K_2NbF_7, which could explain the difference between the chemical shifts. Gabuda *et al.* *(9)* reported that gaseous NbF_5 (which is in monomeric form) gives a signal at −340 ppm. This signal appears at −320 ppm in our spectra. We can thus verify the presence of monomeric NbF_5 in our compounds.

It can be noted that, in sample 3, the different lines seem to be symmetric and to belong to the same fivefold line representing only one species. However, when the spectrum is recorded with a higher accumulation rate, this phenomenon disappears. We can thus assign the lines to several different species and not to a single one, fluorine of which would be coupled. The solid NbF_5 spectrum exhibits a line at +91 ppm *(9)*: the same value was obtained with our own measurements; the spectra are shown in Fig. 4a. F^- ions give a line at +45 ppm in solid KF (Fig. 4b). These two species are detected in our compounds by the low field lines +100 and +50 ppm, respectively. It

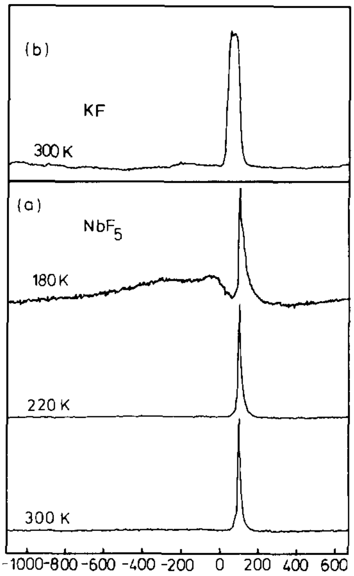

FIG. 4. (a) ^{19}F NMR lines of pure solid NbF_5 at different temperatures. (b) ^{19}F NMR line of pure solid KF at room temperature.

can be noted that NbF_5 gives a narrow line even at low temperature, while F^- in KF has a rather broad line. This has also been observed in our compounds.

The existence of several fluorinated species is consistent with the nonexponential longitudinal magnetization recovery observed in T_1 measurements. The nonexponential behavior shows that there are at least two kinds of motions. These motions could probably be identified as a diffusion motion of F^- ions on one hand, and as a molecular orientation of NbF_5, NbF_6^-, and NbF_7^{2-} species on the other hand. But other motions can be considered too.

Our compounds are synthesized under fluorine atmosphere and we have pointed out by chemical analyses that they contained an excess of fluorine relative to the stoichiometry of NbF_5. Infrared spectroscopy has shown that this excess of fluorine takes the form of complexed ions NbF_6^- and NbF_7^{2-}, as shown by the mechanism we previously suggested (*7*). At room temperature, a rapid exchange between the different fluorinated species occurs. It leads to a single average NMR line, close to NbF_6^- which is the main species.

Decreasing the temperature should induce three important changes among the species. First, the fluorine exchange should be slowed down and then may be stopped, so that the entities NbF_5, NbF_6^-, and NbF_7^{2-} are distinguished. This can explain the decrease of the average line at -220 ppm and the appearance of the lines ascribed to monomeric NbF_5, NbF_6^-, and NbF_7^{2-}. Another change concerns the equilibria of formation of the anions:

$$NbF_5 + F^- \rightleftharpoons NbF_6^- \qquad (2)$$

$$NbF_5 + 2F^- \rightleftharpoons NbF_7^{2-}. \qquad (3)$$

Indeed, at low temperature, the dissociation of the anions (i.e., the formation of NbF_5 and F^-) should take place. Thus, the line from F^- appears. Finally, monomeric NbF_5 condenses into polymeric NbF_5 at low temperature.

A rather weak line can be observed around -500 ppm. This line can be attributed to the F_2 molecule (-504 ppm). The existence of F_2 may be explained by the reaction

$$F^- \rightleftharpoons \tfrac{1}{2}F_2 + e^-. \qquad (4)$$

In a previous paper (*7*), we have pointed out that the mechanism of intercalation would start by oxidation reaction of graphene layers, which can be expressed by

$$nC \rightarrow C_n^+ + e^- \qquad (5)$$

$$\tfrac{1}{2}F_2 + e^- \rightarrow F^- \qquad (6)$$

These reactions involve a charge transfer between graphite and intercalant. If we take into account Facchini *et al.*'s results (*4*), which have shown that charge transfer decreases with decreasing temperature, then, in our compounds this decrease of charge transfer would correspond to the reverse of reaction (*6*). At 220 K, the F_2 line can particularly be seen in the fluorine richest compounds (sample 1) where the charge transfer is more important.

As we have already noted, the lines intensities are species concentration dependent: the higher the fluorine rate, the higher the line intensities on the high field side (NbF_6^-, NbF_7^{2-}) relative to those of the low field side (NbF_5, F^-). Such a phenomenon was already pointed out in the IR spectra (*7*). It can be explained by the fact that for the highest F/Nb ratio, the amount of NbF_6^- (and NbF_7^{2-}) is important and remains so even when NbF_5 and F^- are formed. On the contrary, the lowest F/Nb rate indicates a low amount of NbF_6^- species, and probably no NbF_7^{2-}, whereas NbF_5 species are preponderant even at room temperature. Its line is thus important, while the F^- line is rather weak.

The influence of the concentration can also be seen in the T_1 measurements. For the higher F/Nb ratio, the minimum of T_1 is detected at the external field frequency, while for the lower F/Nb ratio, the minimum can only be reached for $T_{1\rho}$, i.e., at lower frequency. Indeed, for high fluorine rate, when NbF_6^- are predominant, an important diffusion motion of F^- occurs, which has a high frequency; for low fluorine rate, this motion is weaker and has a lower frequency.

In conclusion, the ^{19}F NMR allows us to determine that the different species intercalated into graphite, which had also been identified by other analyses (IR), are exchanging fluorine in a rapid motion. Moreover, it allows us to report experimentally the oxidation of graphite by F_2, which is responsible for the charge transfer in the intercalation compounds. This is another step in confirming the mechanism we had suggested.

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