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STRUCTURAL INVESTIGATION AND ^{119}Sn MÖSSBAUER STUDY OF GRAPHITE/SnF_4 INTERCALATION COMPOUND

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ABSTRACT : The intercalation of tin tetrafluoride into graphite has been carried out in fluorinated anhydrous HF. For long reaction times, a stage-2 compound has been obtained with an identity period of 11.53 Å. The structural characteristics of the intercalated species have been determined on Weissenberg patterns of a single crystal of $C_{24}SnF_5$ composition.

A ^{119}Sn Mössbauer resonance investigation has been performed over the temperature range $4.2 \leqslant T \leqslant 293$ K on HOPG-based GIC. The value of the isomer shift clearly indicates that tin is present in the (IV) oxidation state. An important broadening of the spectrum is observed with decreasing temperature, which has been related to the size of the intercalated particles.

MATERIALS INDEX : Graphite intercalation compounds, Tin tetrafluoride

INTRODUCTION

Most graphite intercalation compounds (GIC) containing fluoride species have been obtained by exposing graphite to fluoride vapors, the presence of a fluorinating agent being often required to favor the reaction. However, as a result of its low vapor pressure, tin tetrafluoride cannot be intercalated by this method : SnF_4-based GIC's could be prepared using a reaction medium involving anhydrous HF saturated with fluorine [1, 2].

Among the physical characteristics previously determined on these materials, preliminary results obtained by Mössbauer spectroscopy had shown a behavior evolving between room temperature and 77 K [3].

It seemed worthwhile thus to investigate further such behavior and to try to understand it : Mössbauer spectroscopy has indeed shown to be a suitable technique to get information on intermolecular or intramolecular bonding in solids since the lattice dynamical interactions are sensitive to oxidation state and bonding details of the atoms used as probes. This technique is particularly fruitful for tin compounds [4, 5].

This paper is focused on a structural investigation using Weissenberg patterns analysis as well as Mössbauer characterization vs temperature.

PREPARATION AND EXPERIMENTAL TECHNIQUES

1) Preparation

Various types of graphite have been used : highly oriented pyrolitic graphite (HOPG) (5×5 mm^2 ; 0.5-1 mm thick) and flaky natural graphite (NG) from Madagascar ($\leqslant$ 1 mm large), vacuum-heated at 500°C. Tin tetrafluoride was prepared by fluorination of tin difluoride at 400°C. The intercalation, carried out in Kel-F tubes, was performed during several days at 15°C in anhydrous HF (AHF) saturated with fluorine : it led to a stage-2 compound.

Elemental analyses of C, Sn and F on several samples gave in every case a F/Sn ratio equal to 5. The chemical composition of the various materials synthesized was found to be C_xSnF_5 with $x \simeq 24-30$ depending on the experiment.

2) Physical characterizations

Structural information was obtained using data derived from :

- powder diffraction patterns (using Cu K_α radiation), which permitted to detect the presence of pure or mixed stages, the identity period I_c and the thickness of the intercalated species.
- Weissenberg photographs on single crystals using Mo K_α radiation, in order to determine the arrangement of the tin sublattice.

Mössbauer resonance measurements were performed using a constant acceleration Halder-type spectrometer with a room temperature $Ca^{119}SnO_3$ source in a transmission geometry.

The samples used were thin sheets extracted from a piece of HOPG, set out side by side in order to cover disks of 20 mm diameter. In the temperature range 4.2 K $\leqslant$ T $\leqslant$ 293 K the spectra were recorded in a variable temperature cryostat. All isomer shifts have been reported with respect to a spectrum of $CaSnO_3$ at 293 K.

STRUCTURAL PROPERTIES OF C_xSnF_y

The structural investigation has been carried out on NG-based samples of nominal composition $C_{24}SnF_5$. A schematization of the precession photograph of a (hk0) plane is represented in Fig. 1. The most intense spots correspond to the hexagonal graphite lattice ; the additional ones belong to the inserted layer. All these weaker spots -except those which have been circled- may be taken into account by using a rectangular lattice, as shown in Fig. 2, which exhibits three possible orientations related to each other by 60° rotation. Assuming that the C-C bond distance in the GIC does not significantly differ from that observed in pure graphite, the reciprocal unit cell of Fig. 2 can be transformed in the direct space into a rectangular unit cell with a_o = 14.76 Å and b_o = 11.93 Å. The correlation of size and orientation between graphite and intercalate unit lattices is shown in Fig. 3. Lattice constant a_o is exactly 6 times that of the graphite lattice constant, but along b_o noparticular relationship could be detected and the two lattices are therefore incommensurate along this axis.

The area of the intercalate unit cell is about 67.2 times that occupied by one C atom. Hence the composition of the GIC can be written : $C_{67.2n}Sn_uF_y$, formula in which n

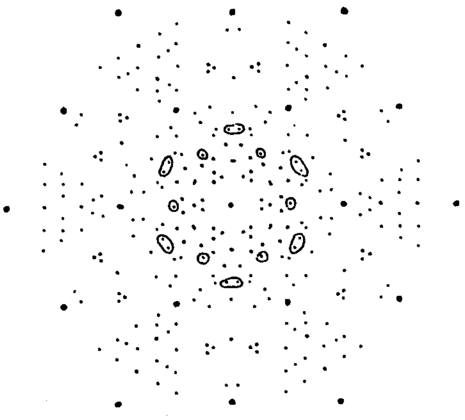

Fig. 1 Schematization of the (hk0) plane photograph at room temperature [circled spots are not considered using the proposed rectangular sublattice cell].

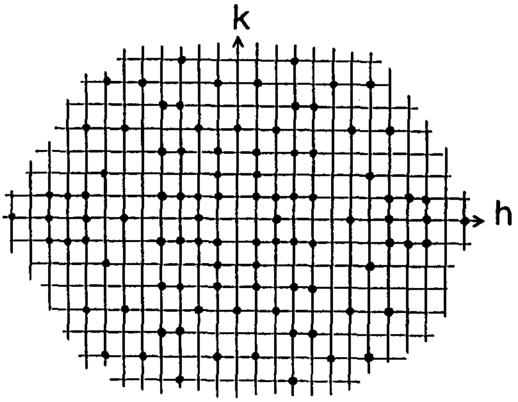

Fig. 2 (hk0) spots obtained from one orientation of the intercalate lattice (reciprocal space).

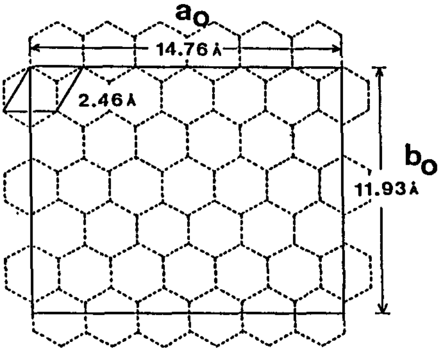

Fig. 3 Relative orientation of the intercalated tin fluoride cell to the graphite sublattice (direct space).

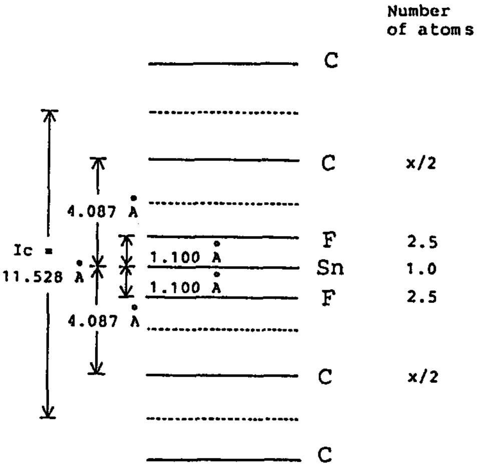

Fig. 4 Schematized structural model for intensity calculation of (00ℓ) diffraction lines of C_xSnF_5.

represents the stage number [i.e. n = 2 in the present case], u and y being integers. u and y have to respect the following requirements :

-i) As far as tin fluoride-GIC is an acceptor-type compound, the inserted species has to be negatively charged. ^{119}Sn Mössbauer results have shown that the oxidation state of tin is IV. Hence we may conclude that $4u-y<0$.

- ii) An EXAFS study has suggested tin to be in an octahedral coordination [6]. If the inserted species are exclusively formed of isolated SnF_6 octahedra, it would yield $y=6u$. If additional condensation of octahedra by corner- or edge-sharing is supposed, $y \leqslant 6u$.

With these two requirements in mind, possible compositions of $C_{67.2n}Sn_uF_y$ with $n = 2$ can be written as follows for $4 \leqslant u \leqslant 7$:

$u = 4$ $C_{134.4}Sn_4F_y$ i.e. $C_{33.6}SnF_{y'}$,
$u = 5$ $C_{134.4}Sn_5F_y$ i.e. $C_{26.9}SnF_{y'}$,
$u = 6$ $C_{134.4}Sn_6F_y$ i.e. $C_{22.4}SnF_{y'}$,
$u = 7$ $C_{134.4}Sn_7F_y$ i.e. $C_{19.2}SnF_{y'}$,
with $y' = y/u$.

By setting the average ratio $y' = F/Sn = 5$, as determined from elemental analyses, one may calculate the relative intensity of the (00ℓ) diffraction lines of the powder pattern from the interplane distances schematized in Fig. 4. Following equation has been used :

$$I_{00\ell} = |F_{00\ell}|^2 \times LP,$$

where $F_{00\ell}$ is the structure factor and LP stands for Lorentz-polarization factor $\left[LP = \frac{1+\cos^2 2\theta}{\sin 2\theta}\right.$ for samples with 2D geometry, such as HOPG and GIC].

The best agreement between simulated pattern and observed one is obtained for u = 6, i.e. for a theoretical formulation $C_{22.4}SnF_5$ as shown in Fig. 5. This composition is in quite good agreement with that provided by elemental analysis. Since the X-ray diffraction intensities largely depend on the amount of the atom having a large atomic number -Sn in our case- it should be ,however, pointed out that an accurate value of the fluorine concentration (y' variable) cannot be obtained from this method.

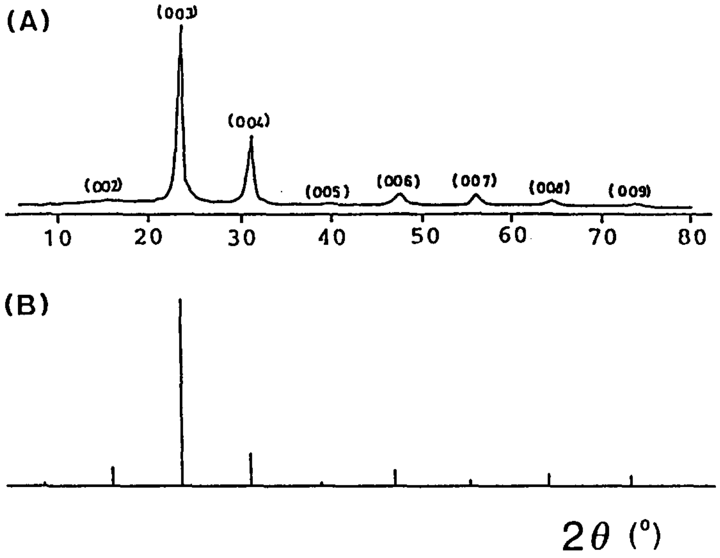

Fig. 5 Comparison of the experimental X-ray pattern (A) with a simulated pattern of a stage-2 compoundwith calculated $C_{22.4}SnF_5$ composition (B).

^{119}Sn MÖSSBAUER STUDY

Mössbauer resonance measurements have been performed on thin sheets extracted from an HOPG sample of nominal composition $C_{30}SnF_5$.

The values of the isomer shift δ and of the quadrupole splitting Δ at 293 K of this second-stage GIC are given in Table I. They are compared with those of either (II) or (IV) tin fluorides and tin fluorocompounds. The isomer shift of $C_{30}SnF_5$ clearly indicates that in the GIC tin is present in oxidation state IV. When compared with the values found for several fluorostannates, e.g. $CdSnF_6$, Na_2SnF_6 and $CaSnF_6$, the value found for δ for $C_{30}SnF_5$ may be attributed to an increase of the covalent character of the Sn^{IV}-F bonding, which brings it close to those of pure tin fluorides.

It can be pointed out also from Table I that no quadrupole splitting is detectable for $C_{30}SnF_5$ on contrary to that observed for SnF_4 [7]. The quadrupole splitting is a function of the departure from spherical symmetry of the electrical charge distribution around the nucleus. Δ is obviously strongly dependent on the distortion of the coordination shell of the first nearest neighbors ; but it is clear also that Δ is related to the three-dimensional ordering of the compound : SnF_4 exhibits, for instance, a large quadrupole splitting, whereas Δ is equal to zero for other Sn(+IV) compounds with isolated SnF_6 octahedra (e.g. $CdSnF_6$, Na_2SnF_6 and $CaSnF_6$).

TABLE I

Isomer shift δ and quadrupole splitting Δ of $C_{30}SnF_5$ compared to the values found for some tin(II) and tin(IV) compounds (at 293 K).

Compound	Sn oxidation state	δ (mm s^{-1})	Δ (mm s^{-1})
$C_{30}SnF_5$	IV	- 0.33	0
Sn^{IV} in α-Sn_3F_8		- 0.315	0.51
SnF_4		- 0.359	1.82
$CdSnF_6$		- 0.421	0
Na_2SnF_6		- 0.471	0
$CaSnF_6$		- 0.477	0
$PbSnF_4$	II	3.24	1.56
$NaSn_2F_5$		3.27	1.86
α-SnF_2		3.43	1.53

As observed from both EXAFS experiments and δ-value, it can be assumed, therefore, that the distortion of the shell of the first nearest neighbors of Sn(IV) in $C_{30}SnF_5$ is similar to that of pure SnF_4, whereas the long-range ordering totally differs, giving rise to different Δ values. Corner sharing SnF_6

octahedra with faces parallel to graphite planes is indeed a reasonable hypothesis consistent with these features.

The temperature dependence of the Mössbauer spectra down to 4.2 K is shown in Fig. 6. An important broadening is observed with decreasing temperature and around 160-140 K an additional doublet appears, which characterizes a strong quadrupole splitting. Below this temperature range, the spectra can be described as the superposition of the single line as observed at 293 K and of a doublet, both showing nearly identical isomer shifts. Such a phenomenon can also be reported from the thermal variation of the full width at half-maximum of the absorption peak, in which a discontinuity takes place in the same temperature range (Fig. 7). This alteration in behavior may suggest that the size of the intercalated species ranges around a critical value.

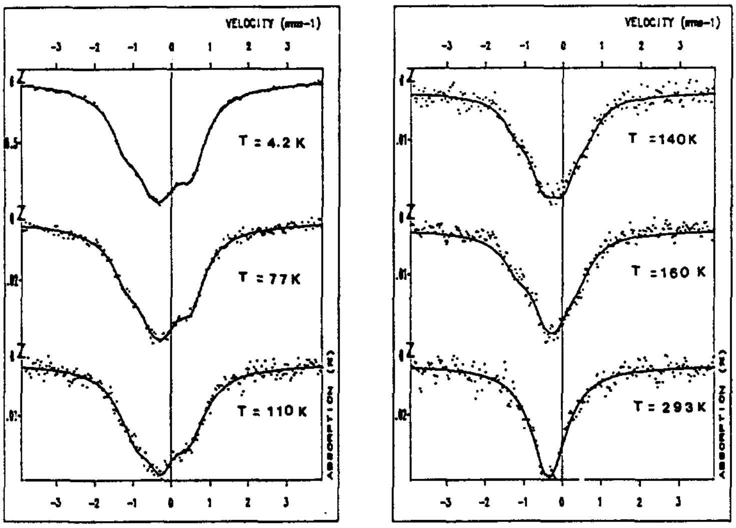

Fig. 6 Mössbauer resonance spectra of $C_{30}SnF_5$ at various temperatures.

A hypothesis can be formulated to explain these results, if we point out that the amount of tin is low in this stage-2 GIC of nominal average composition $C_{30}SnF_5$. The clusters having a smaller size than the critical value may be considered as strongly bonded to the graphite lattice : the tin nuclei, which could not recoil, could therefore be detected by Mössbauer spectroscopy at 293 K (singlet line). On the other hand, tin nuclei belonging to the largest clusters which are loosely bonded to the graphitic lattice would not induce a signal at room temperature, as they are able to move more easily.

Since the recoilless fraction f increases with decreasing temperature, those latter tin nuclei would become discernable at low temperature only, giving rise to an additional component. Below 160-140 K the clusters having a larger size than the critical value would, therefore, lead a quadrupole splitting (doublet peak) which could be related to a freezing effect of fluorine atoms in these particles.

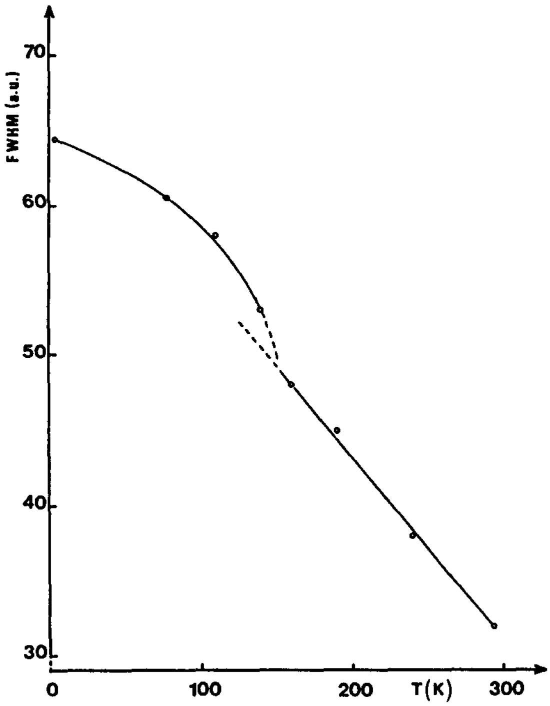

Fig. 7 Temperature dependence of the full width at half-maximum of the absorption line observed in $C_{30}SnF_5$.

Nevertheless, according to previous results obtained on tin dioxide aerosols [8], an alternative proposal, though quite different, cannot be excluded a priori. In such materials the Lamb-Mössbauer factor f has been found to depend on the particles size. A value of $f = 0$ has been attributed to the small particles (which can move easily in the aerosol) and $f \neq 0$ to the bigger ones. Consequently the particles having a smaller size than the critical value cannot be detected in that case by Mössbauer spectroscopy at room temperature and the signal observed at 293 K would result from the largest species.

For both types of clusters the f factor has a similar temperature dependence and a second component appears below a certain temperature. The quadrupole splitting of tin(IV) has been found here to increase when the temperature decreases, as in α-Sn_2F_6 [9], so that we may suppose that the singlet line appearing at 293 K would convert for the larger clusters into a doublet peak below 160-140 K, the smallest clusters giving rise to a singlet at low temperature.

Nevertheless, if we consider the layer structure of the GIC compounds, the behavior of which differs largely from that of aerosols, the first assumption is probably more adapted to the structural characterization.

CONCLUSIONS

In conclusion clusters of average composition SnF_5 have been detected in stage-2 GIC with variable extension. The constituting SnF_6 octahedral units seem to have faces parallel to the graphite layers.

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