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LOCAL ENVIRONMENT OF Sn IN TIN FLUORIDE-GIC

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ABSTRACT

When carried out in anhydrous HF, the intercalation of tin tetrafluoride into graphite yields a stage-2 compound with a repeat distance $I_c \approx 11.53 \text{ \AA}$

The +IV oxidation state of the intercalated Sn species has been unambiguously confirmed by ^{119}Sn Mössbauer spectroscopy. The study of X-ray precession patterns of a crystal of composition $\text{C}_{30}\text{SnF}_5$ has shown that the lattice of the intercalate is incommensurate with the a -parameter of graphite. The local environment of tin in both SnF_4 and $\text{C}_{30}\text{SnF}_5$ has been determined at room temperature from X-ray absorption (EXAFS) spectra. The first coordination shell is formed of axially flattened octahedra of fluoride ions.

INTRODUCTION

A large number of fluoride-based graphite intercalation compounds (GIC) are currently obtained by heating graphite in the presence of volatile fluorides. A convenient method permitting the intercalation of involatile fluorides has been recently developed by using a dissolution process of fluorides in anhydrous HF (AHF) saturated with F_2 [1-3]. Using this method, SnF_4 -based GICs have been previously prepared and characterized by powder X-ray diffraction, NMR and in-plane electrical conductivity measurements [4].

This work deals with the characterization of C_xSnF_y using single crystal precession analysis, EXAFS and Mössbauer spectroscopy.

EXPERIMENTAL

SnF_4 -based GICs have been prepared in Kyoto from AHF saturated with fluorine gas using a procedure which has been already described [2-4]. Various pristine graphites have been used : HOPG chips ($5 \times 5 \text{ mm}^2$, 0.5-1mm thick) and flaky natural graphite (NG) from Madagascar ($< 1 \mu\text{m}$ large).

The characterization of the materials has been carried out using X-ray diffraction, electron microprobe and elemental analysis of C, Sn and F. The crystallographic arrangement of the intercalated species has been determined from precession photographs using Mo-K α radiation.

The local environment of tin has been obtained from EXAFS experiments performed at LURE-Orsay. The absorption spectra were recorded using the synchrotron radiation emitted by the DCI ring which permits the study of the Sn K-edge at 29200 eV. Various problems arose from this high energy value, which is close to the limit of the emission spectrum of DCI : intensity of the flux which was detected by the ionization chambers, stabilization of the incident beams. In order to increase the diffraction angle and to insure a better energy resolution, the X-ray beam was monochromatized using a (511) Si single crystal. The other experimental requirements have been previously described [3, 5].

The Mössbauer parameters were obtained from a transmission spectrometer with constant acceleration using a ^{119}Sn radioactive source. The temperature dependence of the spectra has been studied down to 4.2 K in Bordeaux using a cryostat. All isomer shifts given below refer to CaSnO_3 at 293 K.

STRUCTURAL CHARACTERIZATION OF C_xSnF_y

For long duration reactions, a stage-2 compound is currently obtained, either from HOPG or from NG pristine materials. The X-ray powder pattern has been previously characterized with a repeat distance $I_c \approx 11.53 \text{ \AA}$, which may indicate that the intercalant thickness $d_i = I_c - 3.35 \text{ n} \approx 4.83 \text{ \AA}$ is mainly governed by octahedral SnF_6 units.

Room-temperature precession photographs of a stage-2 single crystal show weak spots corresponding to the intercalated fluoride sublattice in addition to the graphite network. All these spots can be indexed with a rectangular cell of parameters $a = 11.93 \text{ \AA}$ and $b = 14.76 \text{ \AA}$. Three different orientations of this cell are observed which are related to each other by a 60° rotation. Since the ratio of the parameter of this sublattice to the a-parameter of graphite, $a_{\text{orthorh.}}/a_{\text{graph.}}$ (with $a_{\text{graph.}} = 2.46 \text{ \AA}$), is not an integer, the two cells are incommensurate in this direction. The surface ratio is :

$S_{\text{interc.}}/S_{\text{perCatom}} = 67.2$. This value can be taken into account by assuming that 6 Sn atoms are present in the large cell. This hypothesis is consistent with a stage-2 compound having a composition $\text{C}_{22}\text{SnF}_y$, with $4 \leq y \leq 6$. This value is in good agreement with that found from elemental analyses, i.e. C_xSnF_5 with $x \approx 25-30$.

The excess of fluorine relative to the SnF_4 stoichiometry may be accounted for by at least three assumptions:

- presence of metal vacancies,
- partial filling of the intercalated layers, with the presence of islands, chains, and of variable size,
- presence of HF and/or HF_2^- arising from the intercalation method.

EXAFS STUDY

Choice of the standard

For a Sn(IV) standard, we have chosen Na_2SnF_6 because of its stability in air. This compound which is isostructural with Na_2NbF_6 crystallizes in the trirutile-type structure ($\text{P4}_2/\text{mm}$ space group) [6]. The network of Na_2SnF_6 consists of a three-dimensional arrangement of distorted NaF_6 and SnF_6 octahedra which are linked together by edges and corners. Within the SnF_6 polyhedra, the Sn-F distances are the following : $4 \times 1.97 \text{ \AA}$; $2 \times 2.04 \text{ \AA}$ [6].

Determination of the environment of tin in SnF_4 and in stage-2 C_xSnF_y

The structure of SnF_4 has been determined from powder data by Hoppe and Dahne [7]. The tetrafluoride crystallizes in the tetragonal system ($\text{I4}/\text{mmm}$ space group ; $a = 4.048 \text{ \AA}$ and $c = 7.930 \text{ \AA}$). The structure consists of layers of SnF_6 octahedra which are interconnected by four of their corners. The four equatorial distances are longer than the two axial distances: $4d_{\text{eq.}} = 2.02 \text{ \AA}$; $2d_{\text{ax.}} = 1.94 \text{ \AA}$.

The absorption spectrum of HOPG-based $\text{C}_{30}\text{SnF}_5$ (second stage compound) at Sn K-edge is shown in Fig. 1 for the 29000-30000 eV energy range. The normalized EXAFS modulations have been treated using standard procedures [3,5,8].

Fig. 1. Absorption spectrum of HOPG-based $\text{C}_{30}\text{SnF}_5$ at Sn K-edge (29000-30000 eV energy range).

These modulations are known to be dependent upon the scattering factors and upon the structural parameters N_j , R_j and σ_{ij} , i.e. number of neighbors,

distance and average distribution (Debye-Waller factor) of the j^{th} shell of neighbors, respectively. Backscattering amplitudes and phase shifts have been provided by using the absorption spectra of the standard Na_2SnF_6 . The experimental EXAFS oscillations relative to the first coordination shell of tin in $\text{C}_{30}\text{SnF}_5$ are shown in Fig. 2. By adjustment of R and N parameters, a simulated curve has been obtained (dotted line). The results of the data fitting are given in Table 1.

Fig. 2. EXAFS oscillations relative to the first coordination shell of tin in $\text{C}_{30}\text{SnF}_5$ (— experimental curve ; ... theoretical curve).

TABLE 1

EXAFS results for pristine and intercalated SnF_4 , compared with crystallographic data of Na_2SnF_6 (first coordination shell)

	$\text{C}_{30}\text{SnF}_5$		SnF_4		Na_2SnF_6 [from 6]	
N_1	2.2	3.1	1.9	3.5	4.	2.
R_1 (Å)	1.95	2.07	1.92	2.06	1.97	2.04
$\Delta\sigma$	0.01	0.02	0.02	0.02	0	0
ΔE	0.10		0.7		-	
Reliab. factor	0.36×10^{-4}		0.6×10^{-5}		-	

Using the same calculation procedure the fitting of the experimental absorption spectrum of SnF_4 leads to R and N parameters given also in Table 1. From the comparison of the above results, it can be seen that the coordination shells of the first nearest neighbors in both SnF_4 and $\text{C}_{30}\text{SnF}_5$ are very similar and can be described as having axially flattened octahedra. The assumption of an octahedral environment of tin in the GIC is therefore confirmed as well as the axial flattening of SnF_6 octahedra in SnF_4 .

Only the calculation of the first coordination shell has been fully treated. However, the complete radial distribution functions around Sn atoms for the two samples and for the standard are grouped in Fig.3. A preliminary examination shows that the peaks corresponding to the second coordination shell of tin in the GIC differ considerably from those observed in SnF_4 . It is therefore possible to rule out the hypothesis of intercalated layers of SnF_6 octahedra linked by corners as in pristine SnF_4 . A damping occurs for the further peaks of the GIC, which prevents an accurate study of the next nearest neighbors.

Fig. 3. Radial distribution functions (Fourier transform) around tin for several compounds (a : SnF_4 ; b : SnF_4 -based GIC ; c : Na_2SnF_6).

^{119}Sn MÖSSBAUER STUDY

The ^{119}Sn Mössbauer spectrum measured at 293 K shows a relatively narrow line and leads to an isomer shift $\delta = -0.33 \text{ mms}^{-1}$ (Fig. 4). The isomer shift of $\text{C}_{30}\text{SnF}_5$ lies in between those of SnF_4 ($\delta = -0.36 \text{ mms}^{-1}$) and tetravalent tin in $\alpha\text{-Sn}_3\text{F}_8$ ($\delta_{\text{Sn IV}} = -0.31_5 \text{ mms}^{-1}$), which unambiguously indicates that in the GIC the oxidation number of tin is (+IV).

The Mössbauer spectrum obtained at 4.2 K is also reported in Fig. 4. An important broadening is observed with decreasing temperature. In particular, from 160-140 K an additional doublet arises, which is characterized by an important quadrupole splitting. Below this range of temperatures the spectra can be described as superpositions of a single line and a doublet, both showing identical isomer shifts. This change in behavior can be explained by considering the difference in size of the intercalated particles which varies around a critical value.

Fig. 4. ^{119}Sn Mössbauer spectra of $\text{C}_{30}\text{SnF}_5$ at 4.2 and 293 K.

At room temperature, because of the thermal energy, Mössbauer spectroscopy is unable to distinguish among the different clusters; therefore an average site is observed in the spectrum. Below 160-140 K, those clusters having a larger size than the critical value are associated with a quadrupole splitting (doublet peak). This splitting may arise from a freezing effect of fluorine atoms in these particles. In other words, the interactions between SnF_6 octahedra may have a more pronounced "long range" character. On the other hand, those particles which have a smaller size than the critical value exhibit the same type of behavior all along the temperature range (singlet line).

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