

# Raman microprobe observation of intercalate contraction in graphite intercalation compounds

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(Received 10 September 1984)

Raman microprobe spectra of  $\text{SbCl}_5$ ,  $\text{Br}_2$ , and  $\text{FeCl}_3$  graphite intercalation compounds have been obtained with a spatial resolution of  $2\ \mu\text{m}$ . Depletion of the intercalate was observed within  $10\ \mu\text{m}$  of the sample edge in the  $\text{SbCl}_5$ -graphite samples, and this observation is found to be consistent with a model in which the intercalate contracts thermally as the sample is cooled after the intercalation reaction is completed. No depletion was observed in the  $\text{Br}_2$  and  $\text{FeCl}_3$  graphite intercalation compounds, consistent with the low intercalation temperature of the former and the small thermal expansion coefficient of the latter.

## I. INTRODUCTION

Raman spectroscopy has proved to be a very useful probe for the characterization of graphite intercalation compounds (GIC's).<sup>1</sup> The spectra associated with compounds of various stages are quite distinct, particularly at low stages, and the characterization process is simple and nondestructive. The optical skin depth of these compounds ( $\sim 1000\ \text{\AA}$ ) restricts the probe to the near-surface region, and useful comparisons may often be made with results obtained from deeper probes such as x-ray diffraction.

In this work we have used a specialized Raman instrument to study the spatial variation of staging in graphite intercalated with  $\text{SbCl}_5$ , with  $\text{Br}_2$ , and with  $\text{FeCl}_3$ . The Raman microprobe allows acquisition of spectra at a spatial resolution of  $2\ \mu\text{m}$  and thus the observation of inhomogeneities on a much smaller scale than is possible with conventional Raman optics or standard x-ray techniques.

The variation of the Raman frequency shift with stage in graphite intercalation compounds is well established.<sup>1</sup> For compounds of stage 1 or stage 2, the first-order spectrum in the vicinity of  $1600\ \text{cm}^{-1}$  consists of a single peak arising from the  $E_{2g,2}$  vibration mode of the graphite layers. In both stage-1 and stage-2 compounds all the graphite layers are adjacent to intercalate layers, and the spectrum therefore consists of a single peak. This peak is shifted to higher frequencies relative to that of pure graphite ( $1582\ \text{cm}^{-1}$ ) because the force constants within the bounding carbon layer and between an intercalate plane and a carbon plane differ from those in pristine graphite. The in-plane vibration of the  $E_{2g,2}$  mode is dominated by the in-plane force constants, so the effect of the change in interplanar force constants can be considered as a perturbation which gives rise to a small fre-

quency shift. The shifts for stage-1 compounds differ from those for stage-2 due to the different geometrical environments of the graphite layers which give rise to different force constants. For stages 3 and higher, an additional Raman peak is present, arising from the vibration of the graphite interior layers which are adjacent only to carbon layers. The nearly complete screening of the carbon-intercalate interaction by the carbon layer adjacent to the intercalate<sup>2</sup> causes the interior layer modes to be only slightly affected by the presence of the intercalate. The frequency of the interior layer peak is therefore closer to that observed in pure graphite than is that of the bounding layer peak. The frequency of the bounding layer peak and to a lesser extent that of the interior layer peak are also observed to change linearly with inverse stage.<sup>1</sup> In acceptor compounds this shift is toward higher frequencies with increasing inverse stage, and in donor compounds the shift is toward lower frequencies. This stage-dependent shift is attributed to an in-plane contraction of the carbon layers in acceptor compounds and an expansion in donor compounds, as has been observed directly in high-resolution x-ray diffraction studies and is consistent with simple charge-transfer considerations.<sup>3</sup> The stage of the illuminated region can thus be determined from the position of the peaks in the Raman spectrum. For stages 3 and higher, the stage identification can be confirmed by examining the ratio of the intensities of the interior and the bounding layer peaks, which should correspond to the ratio of the Raman scattering cross sections of the two layers multiplied by  $(n-2)/2$ , where  $n$  is the stage index. This confirmation is especially useful for high-stage compounds where the frequency shifts are small. We have used this technique to determine the spatial homogeneity of staging in graphite intercalated with  $\text{SbCl}_5$ , with  $\text{Br}_2$ , and with  $\text{FeCl}_3$ .

## II. EXPERIMENTAL METHOD

### A. Sample preparation

Stage-2  $\text{SbCl}_5$  GIC samples were prepared by the two-zone vapor-phase method previously reported.<sup>4</sup> Highly oriented pyrolytic graphite (HOPG) samples of planar dimensions  $\sim 10 \text{ mm} \times 4 \text{ mm}$  and thicknesses of either  $\sim 0.5 \text{ mm}$  or  $3 \text{ mm}$  were placed in one end of a glass ampoule and doubly-distilled  $\text{SbCl}_5$  liquid was placed in the other. The ampoules were inserted into a furnace such that the graphite was held at a temperature of  $170^\circ\text{C}$  and the  $\text{SbCl}_5$  liquid was held at  $120^\circ\text{C}$ . The reaction was allowed to proceed for 4 d, whereupon the intercalated samples were removed from the ampoules and x-ray diffraction scans were taken to identify their stage indices. The (00 $l$ ) reflection peaks observed corresponded to single-staged ( $n=2$ )  $\text{SbCl}_5$  GIC's with no detectable admixture of secondary phases.

Stage-2  $\text{Br}_2$  GIC samples were prepared in glass tubes of rectangular cross sections which had been bent into a saw-tooth shape. HOPG samples of dimensions  $\sim 2 \text{ mm} \times 1 \text{ mm} \times 0.2 \text{ mm}$  were placed in one "valley" of the tube and a small quantity of cotton batting was used to press the graphite against the wall of the tube. The end of the tube was sealed, a small quantity of  $\text{Br}_2$  liquid was introduced into the adjacent valley, and the other end of the tube was then sealed. The reaction was allowed to proceed at room temperature for 4 d, whereupon the portion of the tube containing the intercalated samples was sealed off. It is worth noting that for the specified conditions this intercalation technique usually produces  $n=4$  samples, but the presence of the cotton batting appears to enhance the intercalation process. The cotton becomes saturated with  $\text{Br}_2$  and its contact with the samples presumably promotes the intercalation reaction so that it proceeds to  $n=2$ .

$\text{FeCl}_3$  GIC samples were prepared by the well-known two-zone vapor-phase method.<sup>5</sup> HOPG samples of dimensions  $\sim 2 \text{ mm} \times 2 \text{ mm} \times 0.2 \text{ mm}$  were placed in an ampoule together with a small quantity of Fe wire. The  $\text{FeCl}_3$  was prepared *in situ* by heating the wire in the presence of  $\text{Cl}_2$  gas. The ampoule was sealed under a pressure of 300 Torr of  $\text{Cl}_2$  gas and placed in a furnace. The graphite was held at a temperature of  $350^\circ\text{C}$  and the  $\text{FeCl}_3$  at  $300^\circ\text{C}$  for 7 d. X-ray diffraction studies were performed, as for the  $\text{SbCl}_5$  GIC's, and all the (00 $l$ ) reflection peaks corresponded to a stage-2 compound with no detectable admixture of other phases.

### B. Micro Raman spectroscopy

The Raman spectra were taken with a Raman microprobe equipped for multichannel detection. This instrument consists of a Czerny-Turner double-axis spectrometer (Spex Industries model No. 1400-11) with a microscope attachment (Spex Industries model No. 1482) which focuses the incident laser beam to a  $2\text{-}\mu\text{m}$ -diameter spot on the surface of the sample. The backscattered light is collected by the microscope optics and directed into the spectrometer, where it is spectrally dispersed by the gratings. A Tracor Northern model No. 6121 intensified diode array is used to collect the spectrum. With 1200-

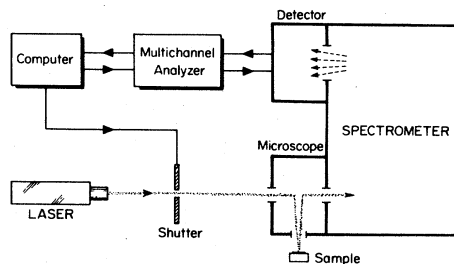


FIG. 1. Schematic representation of the experimental apparatus.

grooves/mm gratings the spectral resolution of the diode array is  $0.322 \text{ \AA}/\text{diode}$  or  $1.15 \text{ cm}^{-1}/\text{diode}$  in the spectral region of interest. The samples were illuminated with a 14-W cw Ar-ion laser operator at  $4880 \text{ \AA}$ .

To reduce sample heating and allow background subtraction in real time the laser beam is interrupted by a shutter before it reaches the microscope. Computer-generated signals control the opening of the shutter, the scanning of the detector array, and the addition or subtraction of the spectrum from memory. By opening and closing the shutter and adding and subtracting the signal and background scans from memory, a spectrum in the absence of dark noise can be obtained while holding sample heating to an acceptable level. A rough calculation gives an estimate of the temperature elevation of  $\sim 40 \text{ K}$  relative to room temperature for low laser power levels ( $\sim 50\text{-mW}$  incident on the sample). For encapsulated samples such as  $\text{Br}_2$  GIC's the power incident on the sample, and therefore the sample heating, would be lower. The acquisition frequencies used were typically 2–10 Hz with a 50% duty cycle, and total illumination times were of the order of 2–10 min. A schematic picture of the experimental apparatus may be seen in Fig. 1.

## III. RESULTS AND ANALYSIS

Several  $\text{SbCl}_5$  GIC samples of similar planar dimensions but thicknesses differing by a factor of approximately 6 (0.5 and 3 mm) were studied, and both the upper surfaces and the interior cleaved surfaces were examined. The characteristics displayed by all the samples may be summarized as follows. Raman spectra taken in regions far from the edges of the sample contained a single peak at a frequency shift of  $1618 \text{ cm}^{-1}$ , as has been previously observed in  $n=2$  acceptor compounds.<sup>1</sup> This peak is associated with the vibration of the carbon bounding layers. Spectra taken within 5 to  $15 \mu\text{m}$  of the sample edge contained two peaks with frequency shifts of  $1586$  and  $1615 \text{ cm}^{-1}$ , characteristic of a stage-3 acceptor compound. Typical spectra may be seen in Fig. 2 for various distances  $x$  from the edge of the sample. The inset in Fig. 2 shows the positions on the sample at which the various spectra were taken. This depletion of intercalate in the edge region of the sample was found in all the samples examined, and spectra taken on the interior surface of a thick (3-mm) sample which had been cleaved with a razor blade (Fig. 3) indicate that this depletion is not a surface phenomenon but occurs throughout the sample.

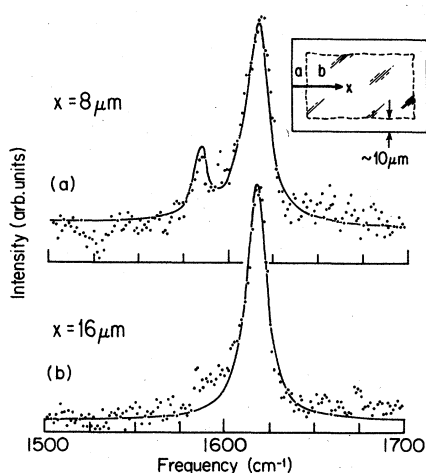


FIG. 2. Raman spectra from the upper surface of as-grown 0.5-mm-thick  $\text{SbCl}_5$  GIC for two distances  $x$  from the sample edge. (a)  $x = 8 \mu\text{m}$ . Spectrum shows depletion of intercalate at sample edge. (b)  $x = 16 \mu\text{m}$ . Spectrum is characteristic of stage  $n = 2$ . Insert shows a scanning pattern.

The Raman shift of the peaks observed in the spectra are plotted in Fig. 4 as a function of distance from the edge of the sample. A clearly defined boundary can be seen between the  $n = 3$  region near the edge and the  $n = 2$  region in the center of the samples. One spectrum taken at this boundary showed three peaks, indicating that the illuminated volume included regions of both  $n = 2$  and  $n = 3$  ordering.

This depletion of intercalate at the edges of the sample can be understood by considering the thermal contraction of the intercalated  $\text{SbCl}_5$  during the cooling of the samples as they are removed from the furnace after the intercalation reaction has taken place. The thermal expansion

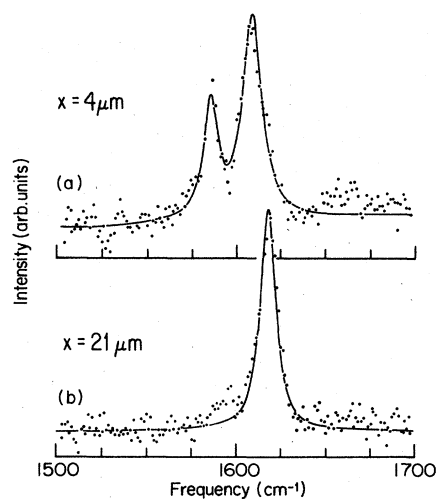


FIG. 3. Raman spectra from interior (cleaved) surface of 3-mm-thick  $\text{SbCl}_5$  GIC for two distances  $x$  from the sample edge. (a)  $x = 4 \mu\text{m}$ . Spectrum is characteristic of stage  $n = 3$ . (b)  $x = 21 \mu\text{m}$ . Spectrum is characteristic of stage  $n = 2$ . (Compare with Fig. 2.)

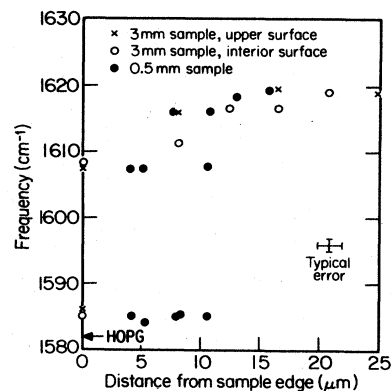


FIG. 4. Raman peak frequency vs distance  $x$  from sample edge for  $\text{SbCl}_5$  GIC's.

coefficient of  $\text{SbCl}_5$  in graphite has been determined to be  $7.6 \times 10^{-5} \text{ K}^{-1}$  (Ref. 6) and the thermal expansion of graphite is negligible in this temperature range,<sup>7</sup> so for a sample of planar dimensions  $4 \text{ mm} \times 10 \text{ mm}$  and a temperature drop of 150 K, the intercalate can be expected to contract relative to the graphite host, leaving a depleted region  $23 \mu\text{m}$  wide along the short edges and  $57 \mu\text{m}$  wide along the long edges. This compares qualitatively with the observed depleted region of  $\sim 10 \mu\text{m}$  width.  $\text{SbCl}_5$  intercalated into graphite forms a structure which is commensurate with the host lattice, and this "locking in" may prevent the intercalate from contracting fully.

$\text{FeCl}_3$  does not form a commensurate structure when intercalated into graphite,<sup>8</sup> and one might therefore expect to see a larger shrinkage of the intercalate than was observed in  $\text{SbCl}_5$  GIC, but despite the larger temperature range of the post-intercalation cool down the small thermal expansion coefficient of  $\text{FeCl}_3$  [ $1.7 \times 10^{-5} \text{ K}^{-1}$  (Ref. 9)] makes the expected effect smaller than the spa-

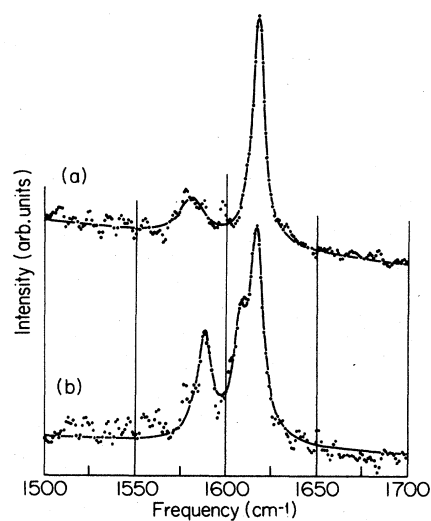


FIG. 5. Raman spectra from  $\text{FeCl}_3$  GIC sample for two locations in the central area of the sample. The spectra labeled (a) and (b) were taken at positions  $5 \mu\text{m}$  apart.

tial resolution of the instrument. In addition,  $\text{FeCl}_3$  GIC's tend to show variations in stage over distances on the order of microns. Figure 5 shows spectra taken from two locations  $5 \mu\text{m}$  apart in the central area of the sample. The spectrum in (a) of 5 shows a mixture of stage-2 and unintercalated regions, whereas the spectrum in (b) of Fig. 5 shows a mixture of  $n=2$  and  $n=3$  regions within the scattering volume. Such variations would mask the small effect to be expected from shrinkage of the intercalate. When spectra were taken close to the edge of the sample as had been done for the  $\text{SbCl}_5$  GIC samples, no tendency toward intercalate depletion was seen. The phenomenon of intercalate contraction can be described in terms of the Daumas-Hérolé pleated-layer model<sup>10</sup> by noting that as the temperature of the sample is lowered, less energy is available for the formation of Daumas-Hérolé domain boundaries. Conditions are therefore favorable for the expansion and consolidation of domains, and when this occurs at the expense of the edge regions, a depleted region is formed. This allows both a reduction in the number of domain walls and an increase in the average density of the intercalate regions as vacancies are filled.

It might be argued that the depletion observed in the  $\text{SbCl}_5$  GIC samples is attributable not to intercalate contraction but to gradual desorption of the intercalate from the sample edges (although these compounds have been reported to be relatively air stable<sup>4</sup>). To discriminate between these two possibilities a piece of  $\text{SbCl}_5$  intercalated graphite was cut from one of the samples with a razor blade. If desorption were responsible for the depletion it would be expected to occur at the freshly cut edge as well, but as Fig. 6 shows, spectra taken before and after cutting show no shift from the characteristic  $n=2$  spectrum seen throughout the center of the sample. In addition, spectra taken on a stage-3 sample prepared  $\sim 6$  months earlier also showed a depleted region  $\sim 10 \mu\text{m}$  wide. These observations are consistent with the argument that the depletion is due to intercalate shrinkage during cooling.

In order to confirm the model of intercalate shrinkage

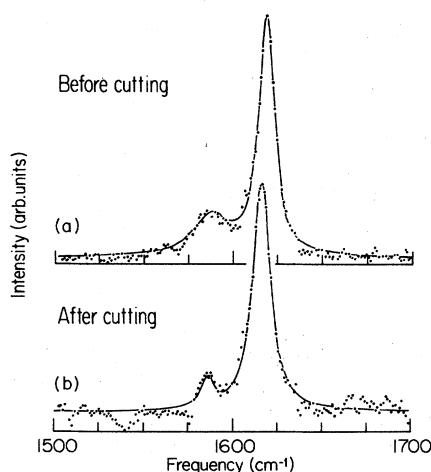


FIG. 6. Raman spectra from freshly cut edge of 0.5-mm-thick  $\text{SbCl}_5$  GIC sample: (a) before cutting; (b) same location after cutting.

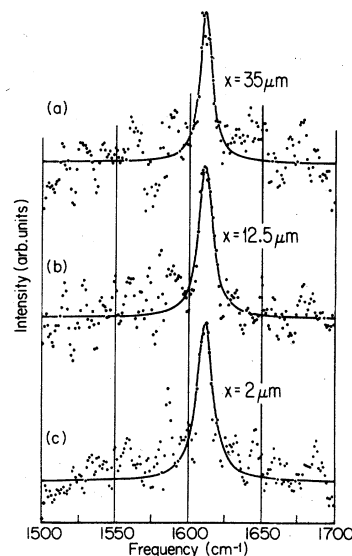


FIG. 7. Raman spectra from  $\text{Br}_2$  GIC sample for three distances  $x$  from the sample edge. Diffuse background due to scattering from glass ampoule has been subtracted. (a)  $x = 35 \mu\text{m}$ . (b)  $x = 12.5 \mu\text{m}$ . (c)  $x = 2 \mu\text{m}$ .

the experiment was repeated with samples intercalated at room temperature with  $\text{Br}_2$ . Since the intercalation and the observation both occur at room temperature, the model predicts that no shrinkage of the intercalate should be observed. The spectra shown in Fig. 7 display a single peak at a frequency shift of  $1611 \text{ cm}^{-1}$ , characteristic of stage-2 donor compounds.<sup>1</sup> The spectra for various regions of the sample are virtually identical, and no depletion of intercalate from the edges of the sample was observed. Within  $2 \mu\text{m}$  of the sample edge some broadening of the  $E_{2g,2}$  peak occurs (the full width at half maximum increases from  $\sim 5.5 \text{ cm}^{-1}$  to  $6.6 \text{ cm}^{-1}$ ) and there is some indication of the presence of unintercalated material within the scattering volume [(c) of 7], but no shift of the  $E_{2g,2}$  peak is observed. Due to the instability of the  $\text{Br}_2$  GIC samples in the absence of  $\text{Br}_2$  vapor it was not possible to cleave them and examine the interior surfaces or to prepare a freshly cut edge.

On the basis of the observed dependence of the Raman spectra on the distance from the sample edge in  $\text{SbCl}_5$ ,  $\text{Br}_2$ , and  $\text{FeCl}_3$  GIC's it appears reasonable to conclude that the intercalate contracts thermally within the graphite as the sample is cooled after the intercalation reaction has been completed. This work represents the first direct, quantitative observation of this phenomenon in graphite intercalation compounds.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. M. S. Dresselhaus for helpful discussions. One of the authors (L.E.M.) would like to thank the IBM Corporation for support. This work was performed with the support of U. S. Air Force Office of Scientific Research (AFOSR) Contract No. F-49620-83-C-0011.

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