Raman Scattering from Nonresonant Intercalant Modes in Stage-1 C-AsF$_5$

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Nonresonant Raman scattering from intercalant vibrational modes in graphite intercalation compounds, measured on the a face, is reported here for the first time. The penetration depth of light with polarization $E \parallel c$ is enhanced by 2 orders of magnitude compared with the penetration depth of light with $E \perp c$. We have observed in stage-1 C-AsF$_5$ three lines at 683, 698, and 753 cm^{-1}. They are identified as the breathing modes of the intercalant molecules AsF$_6^-$, AsF$_3$, and AsF$_5$, respectively.

Considerable efforts have been made in the last decade to observe intercalant vibrations in graphite intercalation compounds (GIC). Both Raman and infrared techniques were tried with relatively little success. The only case where Raman scattering of an intercalant has been observed with certainty is C-Br$_2$.[1-3] The success in this case can be attributed to the fact that the measurements were performed under resonance conditions. Other reports on the observation of intercalant vibrations, for example C-FeCl$_3$,[4] -IBr, and -ICl,[1] are still in doubt.[5] A careful study by Eklund, Falardeau, and Fischer[6] attributes the low-frequency peaks in the observed spectra of C-AsF$_5$, C-HNO$_3$, and C-SbCl$_5$ to scattering from the surrounding gas in the first two cases and to the formation of a crystalline layer in the latter.

Raman scattering in GIC is usually performed on the c face. In this case **E** is parallel to the carbon layers and thus the penetration depth of the electromagnetic beam is only a few hundred angstroms. In spite of this the C-C vibrations with the $\hat{E}_{2g2}$ symmetry are observable. In stage-1 acceptor-type GIC the intensity of this Raman line is relatively high and it has been shown to be a result of a resonance enhancement.[7,8] The fact that the intercalant vibrations are not observable is not surprising for several reasons: The intercalant does not participate in the electronic resonance in the graphite layers, the scattering volume is very small, and the relative density of the intercalant molecules even in stage 1 is only about 16 mole% or less.

The obvious way to increase the Raman-scattering efficiency of nonresonant vibrations is to find conditions under which the penetration depth is larger. We tried two different approaches: (a) conducting the scattering on the c face of the compounds with the exciting laser-beam energy between the plasma edge and the absorption edge, (b) performing the measurements on the a face of the compounds with $E \parallel c$. In the following we will explain the two ways.

In stage 1 the direct allowed absorption edge of the GIC is in the region 1.8 eV $< \hbar\omega_T <$ 2.45 eV (in stage 1 C-AsF$_5$ $\hbar\omega_T =$ 2.45 eV[8]). Above this energy one would expect an increase of the absorption. The large amount of free carriers defines a plasma edge (Drude edge). In stage-1 acceptor-type GIC it is in the range of 1.4 eV $< \hbar\omega_D <$ 1.7 eV (in stage-1 C-AsF$_5$, $\hbar\omega_D =$ 1.7 eV[8]). Below this energy the reflectivity is almost 100%. Between the two edges there is an "optical window"; namely, a region where the penetration depth of the electromagnetic wave has a maximum. We performed the Raman-scattering measurement on the c face of stage-1 C-AsF$_5$ with a 2-eV laser beam. However, we failed and we believe that the reason is as follows: Below the absorption edge there are not direct electronic transitions, but the phonon-assisted transitions are allowed. The expression for these transitions contains terms with an energy denominator equal to $E_1(k) - E_2(k) - \hbar\omega$, where $E_1(k)$ and $E_2(k)$ refer to the conduction and valence π electronic bands, respectively. Thus, not far from the direct gap this denominator would be very small. Furthermore, the sum over final states for each initial state spans an entire surface in k space. This is in contrast to the direct transitions which have only one final state. The conclusion is that the contribution of the phonon-assisted transitions to the absorption coefficient may be quite large. Indeed, the absorption coefficient calculated on the basis of reflectivity measurements[9] is in agreement with the above discussion. The ratio between the absorption coefficients of stage-1 acceptor-type GIC above and 0.3 eV below the absorption edge is only 6. This improvement in the penetration depth is not sufficient.

The second approach proved successful. In stage-1 acceptor-type GIC the graphite layers are quite isolated from each other and possess a reflection symmetry plane perpendicular to the c axis. Consequently, direct optical transitions between π bands are forbidden for light polarized parallel to the c axis. Moreover, those terms in the phonon-assisted transitions which have a small denominator involve the π electronic conduction band as an intermediate state and these are also forbidden. Since these are the dominant terms, the phonon-assisted absorption is also very much reduced. Strictly speaking, the transitions are not completely forbidden if one takes into account the nonzero interaction between the graph-

ite and the intercalant layers. Principally, the penetration depth is limited only by the strength of this interaction. Practically, it is limited by the poor quality of the a face.

There are two requirements for the a face: The graphite layers must be parallel to each other all the way to the surface and the surface has to be smooth over a typical scale of 1000 Å. The first requirement is needed to prevent scattering from bent layers which are effectively c face. The latter one is important for not decreasing the penetration depth and the efficiency of the Raman-scattering process. All our efforts to obtain these requirements with a knife-cut surface as well as with a polished surface failed. No intercalant lines were observed in the Raman measurements. It seems that the only simple and successful way to achieve a good a-face sample is by tearing. A highly-oriented pyrolitic graphite sample ($20 \times 5 \times 0.2$ mm^3), kindly supplied by Union Carbide, was clamped at its two ends. It was torn into two parts by applying a force parallel to the graphite layers. The quality of the surface of the torn sample can be seen in
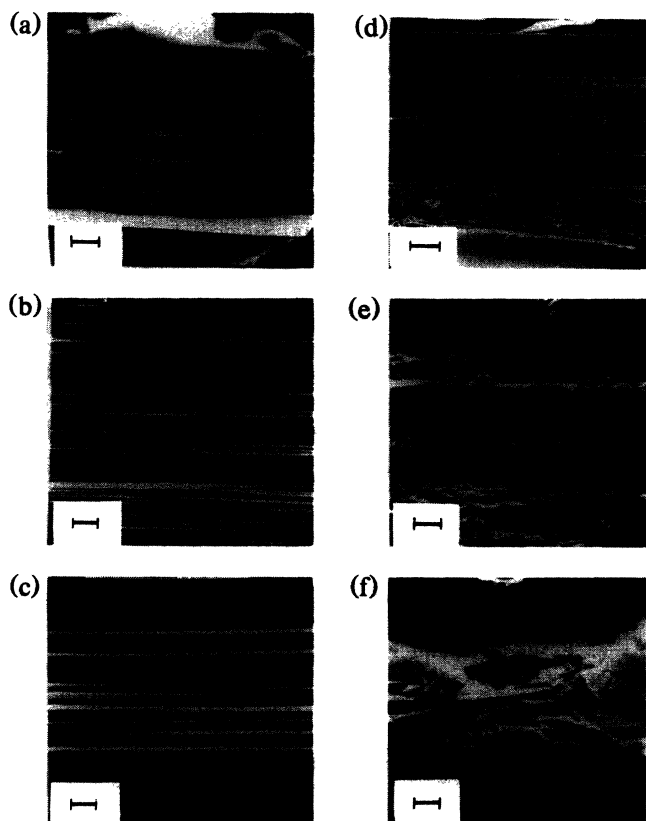

FIG. 1. Scanning–electron-microscope pictures of the a faces of two different samples. (a)–(c) The surface of a torn sample. (d)–(f) Pictures with different scales of a knife-cut sample. The lines in the pictures indicate the scale: 100, 10, and 1 μm in (a) and (d), (b) and (e), and (c) and (f), respectively.

the pictures from a scanning electron microscope shown in Fig. 1. For comparison we also show the pictures of a knife-cut sample. It is clear that the layers in our torn sample are undamaged all the way to the surface. Its surface is smooth in the direction parallel to the layers, but in the c axis the smoothness is poor with a typical scale of about 1000 Å. It will be shown that it is sufficient for Raman scattering.

The torn samples were mounted in a long Pyrex tube with the good a face near an optical window (quartz or sapphire). Compounds of stage-1 C-AsF$_5$ were prepared by the usual technique[10,11] of exposing them to a 1 atm of AsF$_5$ gas at room temperature. After four days the color of the samples changed into deep blue, indicating the formation of stage 1. The ampoules were then disconnected from the intercalation system such that the sample was still exposed to 1 atm of AsF$_5$ gas. The Raman measurements were performed in a backscattering configuration with $\mathbf{E}$ parallel to the c axis of the compounds and $\mathbf{k}$ parallel to the carbon layers. The incident laser beam was cylindrically focused on the torn surface. The scattering light was collected into our versatile spectrometer[12] used as a triple monochromator, which was equipped with an S-20 photomultiplier. The spectra were taken with different energies of the exciting laser beam but no changes were observed.

In Fig. 2 we present the Raman spectra taken on the a face of stage-1 C-AsF$_5$ [Fig. 2(a)]. We also present for comparison the Raman spectra of the surrounding gas taken by just moving the incident laser beam away from the sample. The line at 735 cm^{-1} appears in both spectra. It is assigned to the most intense γ_1 (A_{1g}) breathing mode of the gaseous AsF$_5$ molecules surrounding the sample. The frequency of this mode has been reported to be at 733 or 734.3 cm^{-1}.[13,14] The other three lines in
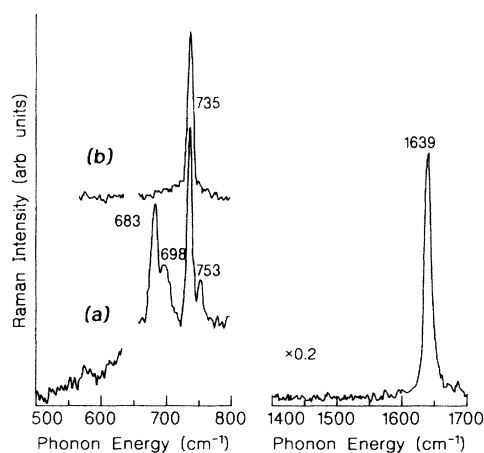

FIG. 2. (a) Raman scattering on the a face of stage-1 C-AsF$_5$. The interpretation of the lines is discussed in the text. (b) Raman scattering from the surrounding AsF$_5$ gas. The spectra were taken by moving the laser beam away from the sample.

the energy region of 600–800 cm^{-1} are attributed to intercalant vibrations. The line at 683 cm^{-1} is identified with the γ_1 mode of AsF$_6^-$. This mode has also been observed in other salts containing AsF$_6^-$ molecules, e.g., in K$^+$AsF$_6^-$ and in AsCl$_4^+$AsF$_6^-$. The γ_1 modes of these molecules are located at 679 and 682 cm^{-1}, respectively.[15] The line at 698 cm^{-1} is attributed to the neutral molecule AsF$_3$. The frequency of the γ_1 mode of the free AsF$_5$ molecule has been reported to be at 707 cm^{-1}.[16] The third line at 753 cm^{-1} is attributed to the γ_1 mode of the AsF$_5$ molecules intercalated into graphite, although its frequency is shifted upward by 18 cm^{-1} with respect to the γ_1 mode of the free molecules. The last line at 1639 cm^{-1} is the well-known Raman line of the C-C vibration with the $\hat{E}_{2gs}$ symmetry.

Our results are essentially in agreement with the reaction proposed by Barttlet et al.[17]; namely, that the intercalation reaction is $3AsF_5 + 2e \rightarrow 2AsF_6^- + AsF_3$. However, some AsF$_5$ molecules also intercalate into stage-1 compounds as has been proposed by others.[18]

The lowest limit of the scattering length can be estimated by comparison of the intensities of the intercalant modes with the intensity of the γ_1 modes of the surrounding AsF$_5$ gas. We assume that the polarizabilities of the three molecules are similar. The gas pressure and the scattering length of the AsF$_5$ gas are known. We find that the lowest limit of the scattering length is about 10 μm. Thus the scattering length in this case is more than two orders of magnitude larger than that in the ordinary scattering configuration. Yet this value is still small compared to the actual value for the following reasons: (a) The surface is not optically smooth (the smoothness scale is about 1000 Å) and therefore the intensity of the collected scattered light is considerably reduced. (b) Light which propagates at an angle to the surface is attenuated because of the losses produced by an electric field component parallel to the graphite planes.

The scattering efficiency for the $\hat{E}_{2g2}$ line should be much smaller for $\mathbf{E}_L \| \mathbf{c}$ than for $\mathbf{E}_L \perp \mathbf{c}$. This is because the scattering process of this mode in the former configuration is no longer allowed. The experiments, however, show that the line intensity for $\mathbf{E}_L \|$ is only a factor of 5 smaller than for $\mathbf{E}_L \perp \mathbf{c}$. This result is not surprising if one considers the fact that light propagating almost parallel to the graphite planes and polarized perpendicular to it penetrates 2 orders of magnitude deeper than light polarized parallel to the planes. This increases the reduction factor to about 500. The line does not completely disappear because of imperfect alignment of the torn layers.

The method discussed here for observing Raman scattering from intercalants in GIC is based on symmetry considerations and on the assumption that the graphite layers in stage-1 compounds can be approximated by a 2D layer. Therefore, this method should be applicable to a wide range of GIC. It opens the way to identification of the types of molecules present in these compounds and to the study of their dynamical properties. It also offers a new possibility to observe phase transitions in these compounds.

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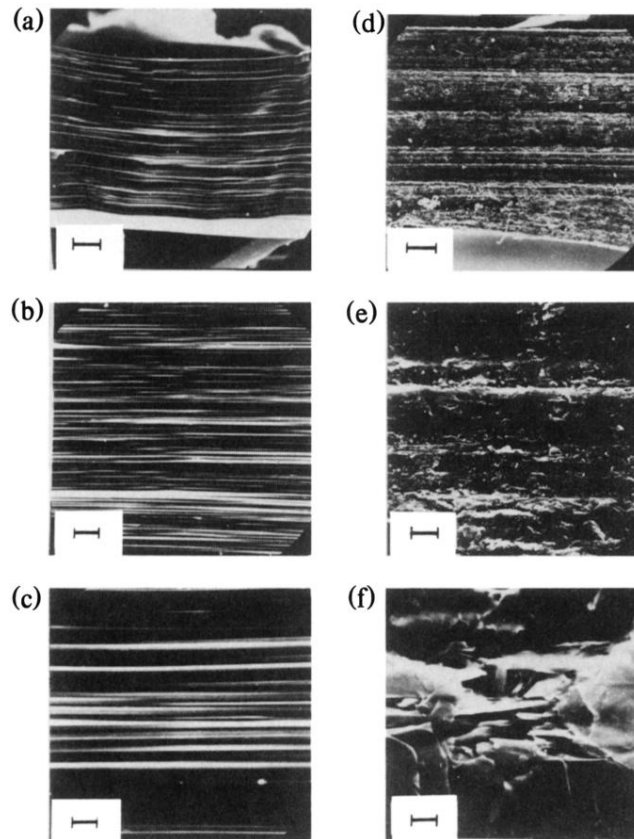[18]H. Selig, Inorganic Solid Fluorides (Academic, New York, 1985), p. 356, and references therein.

FIG. 1. Scanning–electron-microscope pictures of the *a* faces of two different samples. (a)–(c) The surface of a torn sample. (d)–(f) Pictures with different scales of a knife-cut sample. The lines in the pictures indicate the scale: 100, 10, and 1 μm in (a) and (d), (b) and (e), and (c) and (f), respectively.