

## Intercalant vibrations in stage-1 $\text{AlCl}_3$ graphite

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We report the observation of intramolecular vibrations in stage-1  $\text{AlCl}_3$ -intercalated graphite compounds. The results show that two species are simultaneously present:  $\text{Al}_2\text{Cl}_6$  molecules and a layer of solid  $\text{AlCl}_3$ .

### I. INTRODUCTION

Attempts to observe intercalant vibrations in graphite intercalation compounds (GIC's) are often met with extreme difficulties. Measurements using ordinary scattering configurations from the  $c$  face of the sample invariably failed except in cases where the intercalant species were at resonance with the exciting laser light. Ohana *et al.*<sup>1</sup> have shown that the reason for this was an inherently small penetration depth of the exciting and scattered light. They also showed that the graphite lines can be observed as a result of resonance enhancement. Ohana and Yacoby further showed that light impinging on the  $a$  face and polarized in the  $c$  direction penetrates deeper into the sample to about 10 microns and gives rise to observable Raman scattering from intercalant species. This method has been used to far in two cases, namely, stage-1  $\text{AlF}_5$ -intercalated GIC (Ref. 2) and stage-2  $\text{SbF}_5$ -intercalated GIC.<sup>3</sup> One of the difficulties in identifying intercalant vibrations is the danger of observing vibrations of the intercalating material outside the graphite in solid, liquid, or gas forms. Fortunately it is possible to identify the intercalant vibrations using the anisotropy of the GIC samples. As shown by Ohana and Yacoby, only light polarized in the  $c$  direction can penetrate and escape from the sample. Thus, only the  $zz$  components ( $z$  is parallel to the  $c$  axis) of the Raman tensor should be observed. Lines that do not satisfy this requirement should be suspected as arising from species outside the graphite sample.

### II. EXPERIMENTAL DETAILS

In order to observe the Raman scattering from the  $a$  face, the graphite layers must be smooth and parallel to each other all the way to the surface.<sup>2</sup> To achieve this, a thin highly oriented pyrolytic graphite (HOPG) sample was first clamped at its two ends and then torn apart by applying a force parallel to the graphite layers. Stage-1  $\text{AlCl}_3$ -intercalated samples were prepared by a two zone intercalation method.<sup>4</sup> The torn sample was placed in the bottleneck of a quartz cell with the  $a$  face of the sample parallel to an optically flat window. Dry  $\text{Cl}_2$  gas was passed over heated aluminum fine powder of very high purity, thus forming  $\text{AlCl}_3$  powder that got deposited in

the cooler regions of the tube. During the intercalation process the graphite temperature was maintained at about 286°C, the  $\text{AlCl}_3$  at about 235°C and the  $\text{Cl}_2$  gas was at a pressure of about 300 torr. The existence of stage-1  $\text{AlCl}_3$ -intercalated compound prepared in this way was confirmed by the appearance of a single  $E_{2g2}$  phonon at a frequency of 1633  $\text{cm}^{-1}$  in its Raman spectrum shown in the inset of Fig. 1. This frequency is characteristic of intralayer  $C-C$  stretching vibration of stage-1 GIC's.<sup>4</sup> The Raman spectrum was excited using an argon-ion laser with 50 mW power and a wavelength of 514.5 nm. Using a cylindrical lens, the light was focused on the sample's  $a$  face, with the incoming and scattered beam parallel to the graphite layers. The spectra were recorded using a Spex double monochromator equipped with a thermoelectrically cooled ITT-FW130 photomultiplier tube and a photon counting system, interfaced to a microcomputer, was used for the data collection. Since the Raman scattering from the intercalants is extremely weak a multiscan program was used to accumulate the spectra. In general, the spectra were averaged over 200 s of time constant. Noise spikes were eliminated using software.

### III. RESULTS AND DISCUSSIONS

Raman spectra from the intercalant species are shown in Fig. 1. Phonon peaks are observed at about 420, 385, 335, and 305  $\text{cm}^{-1}$  and a shoulder at about 171  $\text{cm}^{-1}$ . A peak observed at 485  $\text{cm}^{-1}$  is due to a phonon in the quartz window. Thus this peak will be disregarded in the rest of the discussion. For comparison the spectra were recorded with the incident radiation polarized both parallel and perpendicular to the graphite  $c$  axis. It may be noted that the Raman peaks are observed only when the incident and scattered radiations are polarized perpendicular to the graphite layers ( $\mathbf{E} \parallel c$ ). This result shows that the lines observed are due to phonons inside the graphite. It is worth mentioning that because of the higher penetration depth and the finite collection angle for the scattered light the graphite  $E_{2g}$  mode at 1633  $\text{cm}^{-1}$  is observed even with  $\mathbf{E} \parallel c$  axis in spite of the fact that it is nominally forbidden (see inset of Fig. 1).

Single crystals of  $\text{AlCl}_3$  are monoclinic with space group  $C2/m$  and with 2 molecules in the primitive cell.<sup>5</sup> Accordingly there are 21 optical modes of vibration dis-

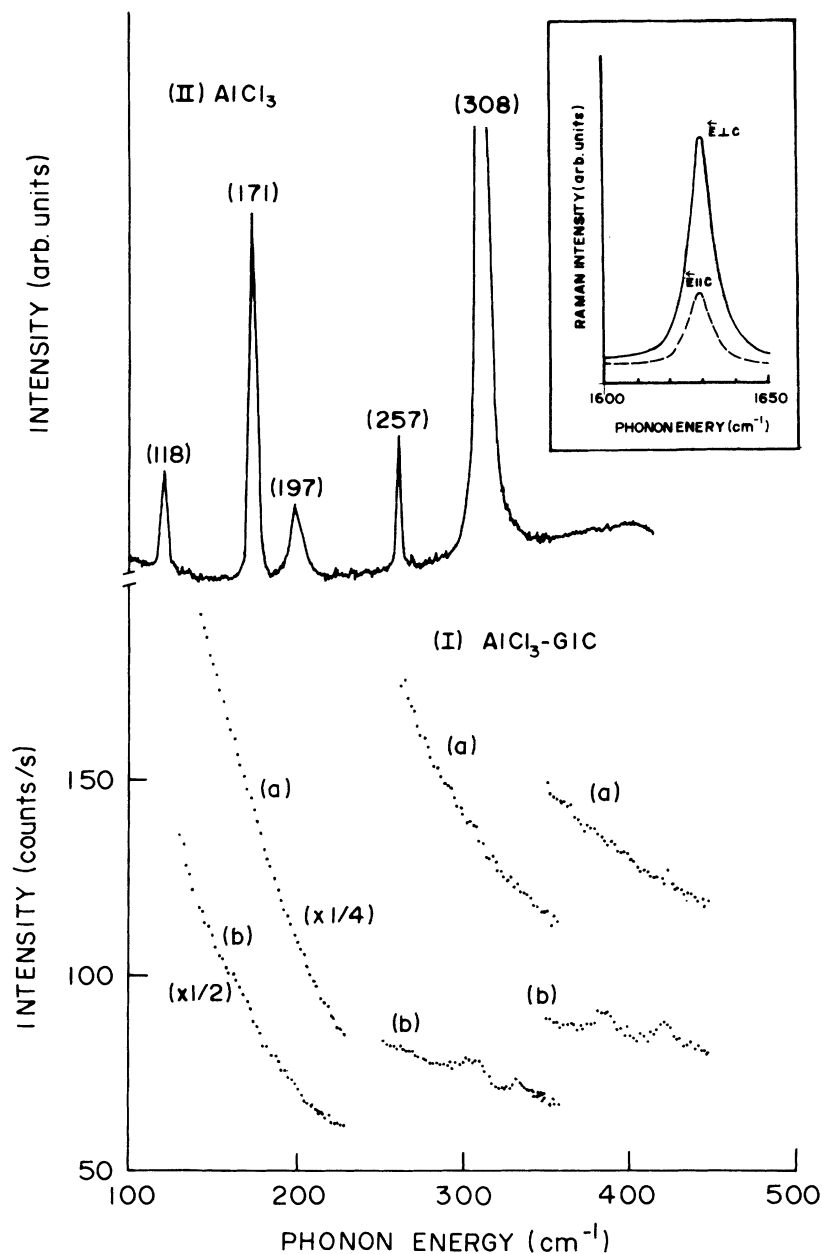


FIG. 1. I: Raman scattering from the  $a$  face of intercalant vibrations of stage-1  $\text{AlCl}_3$ -intercalated GIC for (a)  $E_{\perp c}$  and (b)  $E_{\parallel c}$ . II: Unpolarized Stokes Raman spectrum of an  $\text{AlCl}_3$  single crystal. The inset shows the polarized Raman spectrum from the  $a$  face of the graphite  $E_{2g2}$  mode in stage-1  $\text{AlCl}_3$ -intercalated GIC.

tributed as  $6A_g(Ry) + 6B_g(Rx, Rz) + 4A_u(y) + 5B_u(z, x)$ . As mentioned above only the  $zz$  component of the Raman tensor can contribute to the spectra as measured in the special experimental layout needed for the observation of the intercalant modes. Thus we can observe only  $A_g$  modes unless the crystalline symmetry of  $\text{AlCl}_3$  further reduces inside the graphite lattice. Figure 1 also shows the unpolarized Stokes Raman spectra of an  $\text{AlCl}_3$  single crystal. Only  $A_g$  modes at 118, 171, 197, 257, 308, and  $391 \text{ cm}^{-1}$  are observed, in agreement with Kanesaka *et al.*<sup>6</sup> In a recent paper Behrens *et al.*<sup>7</sup> have suggested that the  $\text{AlCl}_3$  intercalate prepared at low  $\text{Cl}_2$  pressure ( $< 17 \text{ mbar}$ ) and low temperature ( $< 200^\circ\text{C}$ ) consists of a double layer of close-packed chlorine atoms, in which aluminum atoms occupy two-thirds of the octahedral sites. On the other hand, according to these authors,

samples prepared at higher  $\text{Cl}_2$  pressure and/or higher temperatures consist in an arrangement of  $\text{Al}_2\text{Cl}_6$  molecules and  $\text{AlCl}_4^-$  ions. The molecular symmetry of  $\text{Al}_2\text{Cl}_6$  is  $D_{2h}$  and using notation compatible with the crystalline symmetry, its normal modes of vibrations are classified as  $4A_g + 2B_{1g}(Ry) + 3B_{2g}(Rx) + 3B_{3g}(Rz) + 1A_u + 4B_{1u}(y) + 4B_{2u}(x) + B_{3u}(z)$ . These notations differ from those used by Maroni *et al.*<sup>8</sup> for an isolated molecule and their  $B_{1g}, B_{2g}, B_{3g}, B_{1u}, B_{2u}, B_{3u}$  correspond to our  $B_{2g}, B_{3g}, B_{1g}, B_{2u}, B_{3u}, B_{1u}$ , respectively. The observed  $A_g$  modes for this molecule are at 115, 217, 336, and  $501 \text{ cm}^{-1}$ . The  $\text{AlCl}_4^-$  ion has tetrahedral symmetry and the nine normal modes of vibrations are distributed as  $1A_1 + 1E + 2F_2$ , with  $A_1$  mode having a frequency at  $351 \text{ cm}^{-1}$ .<sup>9</sup>

A comparison of the observed Raman peaks in stage-1  $\text{AlCl}_3$ -intercalated GIC with the various forms of  $\text{AlCl}_3$  described above clearly indicates that the peaks at 171, 305, and  $385\text{ cm}^{-1}$  are due to the crystalline form of  $\text{AlCl}_3$  present inside the graphite galleries. We, however, failed to observe the line around  $197\text{ cm}^{-1}$ . The peak at  $118\text{ cm}^{-1}$  could not be observed (even if it were present) due to strong elastic scattering appearing as a laser line tail in that region. The peak at  $335\text{ cm}^{-1}$  appears to be due to molecular structure of  $\text{Al}_2\text{Cl}_6$  type inside the graphite lattice. The peaks at  $420\text{ cm}^{-1}$  could not, however, be explained by the mere presence of any of the above structures. However, this line can be understood if we allow some sort of distortion of the intercalant structures inside the graphite lattice, so that the intercalants lose their inversion symmetry. One possible mechanism that could produce such a distortion is to assume that charge transferred from a graphite layer resides on the intercalant molecules in an asymmetric way. In this case the local crystalline symmetry would reduce to  $C_s$  from  $C_{2h}$  and that of the  $\text{Al}_2\text{Cl}_6$  molecule should reduce to  $C_{2v}$  from  $D_{2h}$ . The result is that in the crystalline form  $B_u$  modes should have a  $zz$  component in addition to  $A_g$  modes, and in the  $\text{Al}_2\text{Cl}_6$  molecular form  $B_{3u}$  modes

should show up in the  $zz$  polarization in addition to the  $A_{1g}$  modes. There is indeed a  $B_{3u}$  mode ( $B_{2u}$  in the notation of Maroni *et al.*<sup>8</sup>) observed at  $420\text{ cm}^{-1}$  for  $\text{Al}_2\text{Cl}_6$  molecule and it could explain the observation of a Raman peak at this frequency in our Raman spectra.

In conclusion, we have observed the Raman spectra of  $\text{AlCl}_3$ -intercalated graphite. The fact that the spectra show up only when the incident and scattered light are both polarized in the  $c$  direction shows that the observed lines are due to intercalant vibrations inside the graphite sample. The results reveal that, under the preparation conditions of our samples, two phases coexist, one with crystalline layers of  $\text{AlCl}_3$  and the other of  $\text{Al}_2\text{Cl}_6$  molecules. It may be mentioned that in recent ESR experiments on stage-1  $(\text{Al}_{1-x}\text{Cu}_x)\text{Cl}_3$ -intercalated GIC prepared under similar conditions, two sites for  $\text{Cu}^{2+}$  with different hyperfine splittings have been observed.<sup>10</sup>

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