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# RAMAN SCATTERING IN GRAPHITE INTERCALATION COMPOUNDS*†

J.J. Song,#‡& D.D.L. Chung,#** P.C. Eklund#† and M.S. Dresselhaus#‡

Center for Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139, U.S.A.

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Raman scattering results are reported on graphite intercalated with $Br_2$, ICℓ and IBr. In all of these acceptor compounds, the single $E_{2g_2}$ Raman peak for pure graphite is replaced by a doublet structure identified with in-plane carbon atom vibrations. In addition, Raman peaks specific to the intercalate species are found at frequencies down-shifted from the stretching modes of the free intercalate molecules.

The electronic properties of graphite intercalation compounds have been studied by numerous techniques including transport[1-5], de Haas-van Alphen[6,7], optical reflectivity[8], nuclear magnetic resonance[9] and magnetoreflection[10,11]. The general properties of lamellar and residue graphite intercalation compounds are reviewed elsewhere.[12-16] Reported here are results on the Raman spectra of graphite intercalated with the halogens $Br_2$, IBr and ICℓ for both lamellar and residue compounds. This work is significant because specific Raman lines can be identified with carbon atom vibrations in graphitic layers, and other Raman lines with intercalate modes in the intercalate monolayers, thereby allowing the graphite and the intercalate species to be studied separately. Evidence for coupling between the graphitic and intercalate modes is provided by the down-shift in frequency of the intercalate mode relative to the stretching frequency of the free molecule, and the up-shift of the graphitic mode relative to that in pure graphite.

Graphite-$Br_2$[17], graphite-IBr[18], graphite-ICℓ[19] and graphite-$HNO_3$[20] can be prepared by spontaneous intercalation of graphite, through exposure to the intercalate vapor, which is in equilibrium with the condensed intercalate held at constant temperature. The concentration of intercalate in the resulting compound is controlled by the temperature of the condensed intercalate. For graphite-$Br_2$, an alternate procedure is possible.[17] This involves immersion of graphite in a $Br_2$-$CCℓ_4$ solution; the concentration of the intercalate in the resulting compound is controlled by the $Br_2$ concentration in solution. All the residue compounds used in our study have been prepared by desorption of the parent lamellar compounds.[10] Highly oriented pyrolytic graphite[21] has been used in the preparation of all compounds.

To check the sample homogeneity, we have used both quantitative electron microprobe analysis[22] and the Raman effect by focussing the electron beam (spot size ∿ 2μm) or the incident laser light (spot size ∿ 50-100μm) at various spots on the sample. We find that residue compounds require about a month or more of annealing time to acquire a concentration homogeneity on a 1μm scale.[10] Homogeneous lamellar compounds can be produced by allowing sufficient time (several days) for the intercalation process to reach equilibrium.

The lattice modes of pure graphite have been studied by Raman scattering,[23 24 25] infrared spectroscopy[23,24,26,27] and neutron scattering.[28] The two Raman-active modes, $E_{2g_1}$ and $E_{2g_2}$, have been observed in single crystal graphite at 140±10 cm$^{-1}$ and 1582.5±1 cm$^{-1}$, respectively[24]. The Raman intensity of the $E_{2g_1}$ mode is ∿$10^2$ weaker than that of the $E_{2g_2}$ mode, and is broad.[24] The $E_{2g_2}$ mode has also been reported at 1575 cm$^{-1}$ in stress-annealed pyrolytic graphite.[25] We have observed this mode in our pyrolytic graphite material at 1582±2 cm$^{-1}$ with a halfwidth of 14 cm$^{-1}$. Of the two infrared-active modes, only the $E_{1u}$ mode has been observed at 1588±5 cm$^{-1}$ in single crystal graphite,[24] and at 1590±3 cm$^{-1}$ in highly oriented pyrolytic

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# Visiting Scientist, Francis Bitter National Magnet Laboratory, operated under support by the National Science Foundation.
‡ Also Department of Electrical Engineering and Computer Science, M.I.T.
** Also Department of Materials Science and Engineering, M.I.T.
& Present address: Department of Physics, University of Southern California, Los Angeles, CA.

graphite.[27] Because of the interlayer phase difference between the $E_{1u}$ and $E_{2g_2}$ modes (see Fig. 4 of Ref. 23), the frequency difference between these two modes ($\sim$ 10 cm$^{-1}$) is a measure of the interlayer force constants of the graphite lattice.[24]

The Raman scattering experiments were performed on the c-face of the samples using a Brewster angle back-scattering geometry. Incident radiation of 4880A and 5145Å was provided by a cw argon-ion laser. The scattered radiation was collected at 90° to the sample surface and was analyzed by a double grating monochromator. The sample composition was monitored by measurement of weight uptake. The Raman technique is particularly useful for studying graphite intercalation compounds insofar as Raman spectra can be observed over the entire range of intercalate concentrations.

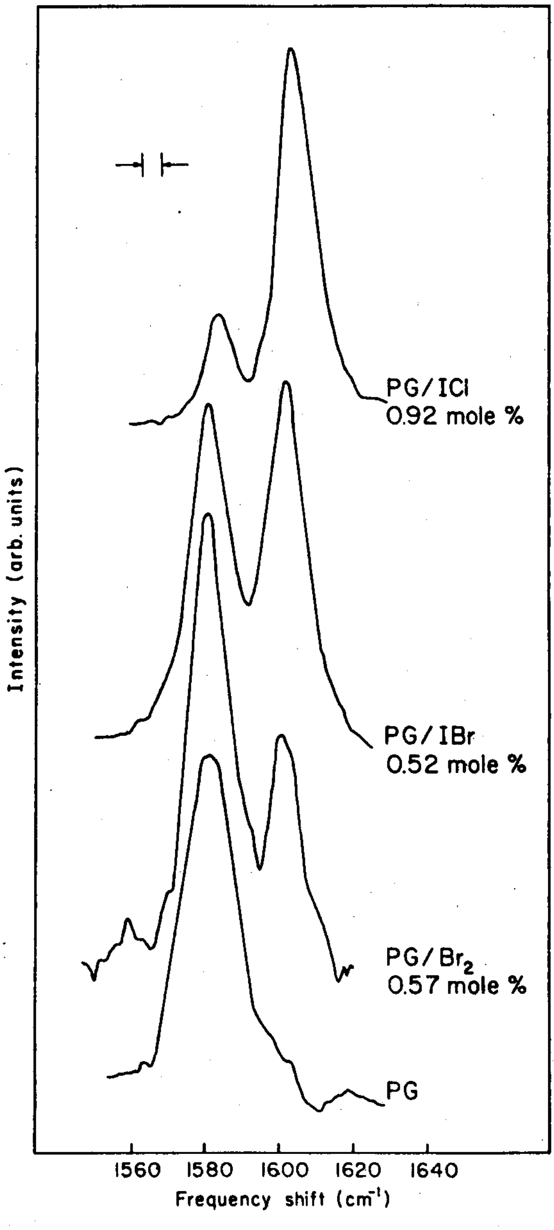


Fig. 1 Room temperature Raman spectra of graphite and the lamellar compounds of graphite-$Br_2$ (0.57 mole % $Br_2$), graphite-IBr (0.52 mole % IBr) and graphite-ICℓ (0.92 mole % ICℓ) in the high frequency region. The intensity is in arbitrary units. PG refers to highly oriented pyrolytic graphite.

Fig. 1 shows the Raman spectra for pure graphite and lamellar compounds of graphite intercalated with $Br_2$, IBr and ICℓ. The single $E_{2g_2}$ peak of pure graphite is replaced by a doublet, having a separation of $\sim$ 20 cm$^{-1}$, with the lower frequency peak near the pure $E_{2g_2}$ graphite line. The frequencies of both peaks increase slightly with increasing intercalate concentration, though the frequency difference between the two peaks remains constant (e.g. in graphite-$Br_2$ lamellar compounds, the frequency of each of the doublet components increases by $\sim$ 7 cm$^{-1}$ from a 0.9 mole % $Br_2$ compound to a 5.6 mole % $Br_2$ compound.) We have observed this doublet structure in both lamellar and residue compounds of all three graphite-halogen intercalation compounds and of graphite-$HNO_3$. Small frequency decreases of the doublet components are observed during the desorption of a lamellar compound to its residue state (e.g. in graphite-$HNO_3$, the frequency decrease for each peak is $\sim$ 7 cm$^{-1}$ when a lamellar compound of 5.6 mole % $HNO_3$ desorbs into a residue compound of 3.7 mole % $HNO_3$). Similar doublet structures have also been reported in graphite-AℓCℓ$_3$, graphite-$SbF_5$ amd graphite-Cs (stage 3)[29]. There is a slight dependence of the frequencies of the doublet components on the intercalate species. Details of this dependence will be described in a later publication. Because this dependence is relatively small, we identify both lines with carbon atom vibrations.

On the other hand, there is a strong dependence of the relative intensities of the doublet components on intercalate concentration. In Fig. 2 we show the intensity ratio ($A_2/A_1$) of the higher frequency ($A_2$) to the lower frequency ($A_1$) lines in the doublet structures of lamellar graphite-$Br_2$ and graphite-ICℓ vs. intercalate concentration. Intercalation causes $A_1$ to decrease and $A_2$ to increase such that the intensities of these two lines are equal for approximately a stage 7 graphite-$Br_2$ lamellar compound. A different concentration dependence of $A_2/A_1$ is found for the various intercalate species. For example, $A_2/A_1$ increases with intercalate concentration much more rapidly in graphite-ICℓ than in graphite-$Br_2$. Because of the small value of $A_1$ and the instability of the samples at high intercalate concentrations, the ratio $A_2/A_1$ is more precise at low and intermediate intercalation concentrations. A smaller increase in the $A_2/A_1$ ratio is found for a residue compound than for a lamellar compound of equal nominal intercalate concentration, supporting the idea that in residue compounds the intercalate tends to migrate preferentially to defect sites.[17]

We have checked the effect of the two sample preparation techniques given above on the Raman structures in graphite-$Br_2$. We find that in both lamellar and residue compounds the peak frequencies do not depend on the sample preparation technique; however such a dependence is found in the intensity ratio $A_2/A_1$ for residue compounds, but not for lamellar compounds.

Whereas the high-frequency doublet structure shown in Fig. 1 is relatively insensitive to the intercalate species, other Raman lines specific to the intercalate species are observed at low frequencies for graphite-$Br_2$, graphite-IBr and

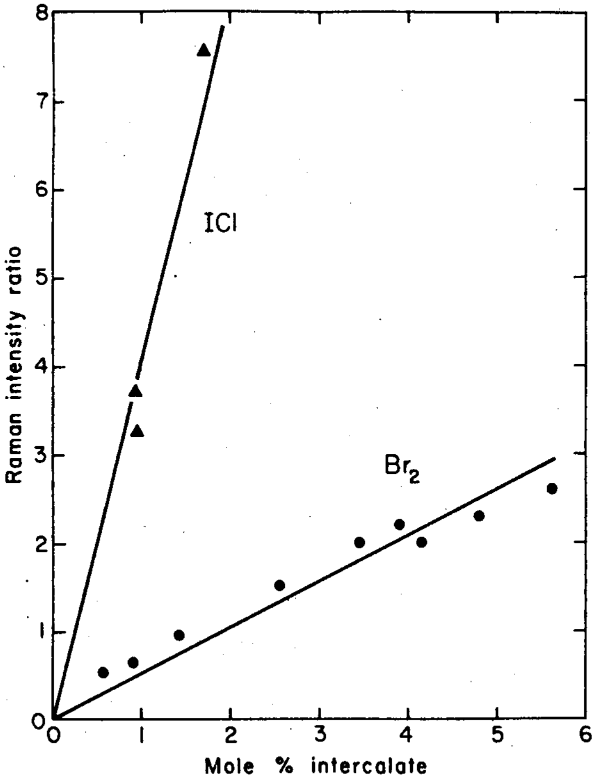


Fig. 2 Variation of the Raman peak intensity ratio ($A_2/A_1$) of the higher frequency peak ($A_2$) to that of the lower frequency peak ($A_1$) for the doublet Raman strcture in lamellar compounds of graphite-bromine (●) and graphite ICℓ (▲).

graphite-ICℓ and a partial listing of representative lines is given in Table 1. The low-frequency room-temperature Raman spectrum of a graphite-$Br_2$ lamellar compound is shown in Fig. 3. A strong peak at $\omega_0$=240 $cm^{-1}$ and a peak at $\sim 2\omega_0$(482 $cm^{-1}$) are shown along with two other low frequency modes. The frequency of the strong line is down-shifted from the vibrational frequency of the free $Br_2$ molecule (323 $cm^{-1}$)[30] and of solid $Br_2$(300 $cm^{-1}$, T $\sim$ 198°K)[31], an insulating molecular solid. Other evidence for the molecular identity of $Br_2$ in the intercalation compounds comes from study of the cutoff phenomenon for Landau level transitions observed in the far-infrared magnetoreflection spectrum.[32]

The details of the low frequency spectra in the graphite-halogen intercalation compounds are dependent on both intercalate concentration and sample temperature, in contrast with the doublet structure which shows much less sensitivity to these parameters. The room temperature spectra of graphite-ICℓ in particular show a strong frequency up-shift of the low frequency line with increasing intercalate concentration. These

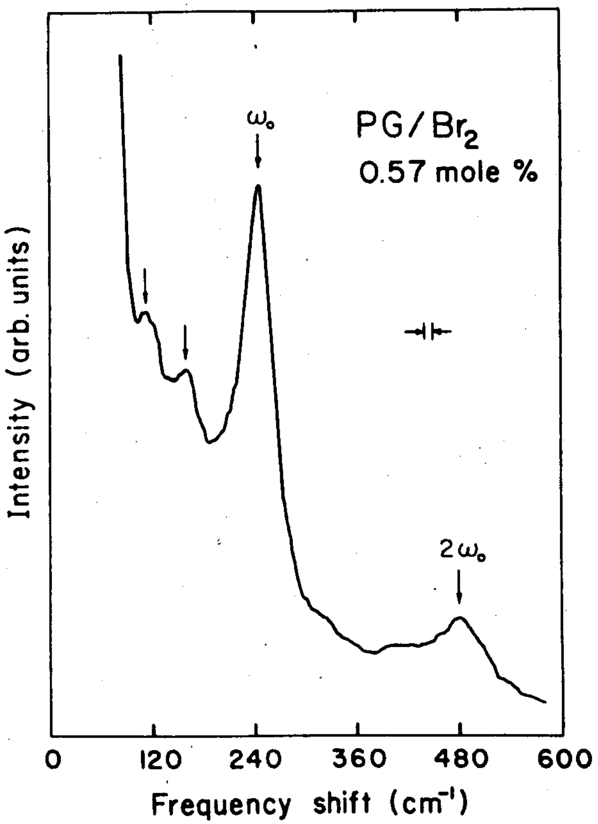


Fig. 3 Room temperature Raman spectra of a graphite-$Br_2$ lamellar compound (0.57 mole % $Br_2$) in the low frequency region. The intensity is in arbitrary units. The arrows indicate the peak positions of the low frequency 104 $cm^{-1}$ line ($\omega_0$) and its harmonic at 482 $cm^{-1}$ ($\sim 2\omega_0$). The strong increase in intensity in the low frequency end of the spectrum is due to the Rayleigh scattering of the laser light.

observations indicate that the molecular ordering and interactions vary with temperature and intercalate species. Low frequency lines have been observed in both lamellar and residue compounds. No low frequency lines were found in graphite-$HNO_3$.

Our interpretation of the origin of the high frequency doublet relates to the close proximity of the Raman-active $E_{2g_2}$ mode and the infrared-active $E_{1u}$ mode, indicating that these vibrational frequencies depend almost entirely on in-plane force constants. The interplanar force constants are weak, corresponding to frequency shifts $\sim$ 10 $cm^{-1}$. In this context we associate the $A_1$ line (near the $E_{2g_2}$ graphite line) with carbon atom in-plane vibrations in graphite layers far from the intercalate monolayer, and the higher frequency $A_2$ line with carbon atom in-plane vibrations in graphite layers close to an intercalate monolayer, which causes a stiffening of the interplanar force constant. From our results we conclude that the intensity ratio ($A_2/A_1$) is sensitive both to the relative number of graphitic and intercalate layers and to the molecular alignment of the intercalate species.

Thus, the observation that the intensity ratio $A_2/A_1$ is higher in graphite-ICℓ than in graphite-$Br_2$ for the same intercalate concentration suggests that the amount of interaction between the graphite and intercalate monolayers is larger in graphite-ICℓ than in graphite-$Br_2$, presumably due to differences in molecular orientation of the molecular species. Moreover, the observation that the frequencies of both peaks of the doublet structure increase slightly with increasing intercalate concentration indicates that the in-plane force constants stiffen slightly with increasing intercalate concentration.

Our Raman scattering results are consistent with magnetoreflection results obtained from dilute intercalation compounds of graphite with the halogens $Br_2$, IBr and ICℓ[10,11,32], from which we conclude that the crystal potential $V(\vec{r})$ and the lattice mode frequencies in the graphite layer planes several layer planes away from the intercalate layer are not sensitive to intercalation.

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Table 1. Low frequency Raman lines in lamellar graphite-halogen intercalation compounds at room temperature

| Intercalate Species | Intercalate Concentration (mole % intercalate) | Raman Frequency Shifts ($cm^{-1}$) | Comments |
|---|---|---|---|
| $Br_2$ | 0.57 to 5.60 | 240 | Strong intensity; also observed up to the harmonic $4\omega_0$; Frequency shift independent of intercalate concentration. |
| | 0.57 and 0.88 | 152,104 | Weak intensity |
| IBr | 0.52 | 230,200,110,96 | Weak intensity |
| ICℓ | 0.92<br>1.80<br>10.70 | 98<br>103<br>186 | Medium intensity; frequency shift increases with intercalate concentration. |

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