MAGNETO-OPTICAL STUDIES OF GRAPHITE INTERCALATION COMPOUNDS*

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Invited paper

High field magnetoreflection measurements are reported on the first observation of interband Landau level transitions in residue and lamellar compounds of graphite intercalated with the halogens Br_2, IBr and ICl. These magnetoreflection spectra are interpreted to yield a model for the magnetic energy level structure of these intercalation compounds in the dilute limit corresponding to stage ≥ 5. In this dilute limit, the insensitivity of the magnetoreflection resonances to intercalate concentration shows that near the Fermi level for pure graphite the electronic structure of the intercalation compounds is essentially independent of intercalate concentration. This conclusion results from analysis of both infrared and far-infrared magnetoreflection spectra for Landau level transitions within ±0.1 eV of the graphite Fermi level. The model for the electronic structure deduced from the magnetoreflection spectra is supported by Raman scattering results presented for the in-plane lattice modes of carbon atoms in the graphitic layer planes.

Graphite intercalation compounds have recently received considerable attention because of observations of room temperature in-plane electrical conductivity exceeding that of copper in an acceptor compound [1] and superconductivity in alkali donor compounds where neither species alone undergoes a superconducting transition [2]. We have carried out magnetoreflection, Raman scattering and electron microscopy studies of graphite intercalated with Br_2, IBr and ICl in order to correlate the electronic, lattice and structural properties of similarly prepared lamellar and residue compounds. Our report here is mainly on the use of the high field magnetoreflection technique in the first observation of interband Landau level transitions in lamellar and residue graphite intercalation compounds and on the implication of the magnetoreflection results on the electronic structure and lattice modes of dilute graphite intercalation compounds.

Graphite intercalation compounds are a class of layer compounds in which the foreign species reside in interstitial layer planes. These compounds can be classified into two groups: lamellar and residue compounds [3]. The lamellar compounds contain the intercalate in the form of ordered layers stacked between the carbon layers. The number of carbon layers between the two nearest intercalate layers defines the "stage" of the compound. Most lamellar compounds are only stable when in equilibrium with the external intercalate. The residue compounds are formed after the intercalate in the parent lamellar compound has been partially desorbed and has come to equilibrium with a zero partial pressure of the external intercalate. The residual intercalate tends to concentrate at structural defects.

Graphite reacts with the halogens to form intercalation compounds. However, only two members of the group, fluorine and bromine, react readily in elemental form. Iodine does not react with graphite at all and chlorine reacts slowly under favorable conditions. Graphite fluoride has covalent bonding. On the other hand, IBr and ICl react readily with graphite to form intercalation compounds. Therefore we have chosen Br_2, ICl and IBr as intercalates for our study. Since Br_2 intercalation compounds have been studied most extensively, our work is mainly addressed to graphite-bromine.

The lamellar compounds of graphite–Br_2, graphite–IBr and graphite–ICl all exist in stages, with the saturated compounds having compositions $C_{16}Br_2$ (stage 2), $C_{18}IBr$ (stage 2) and $C_{8.5}ICl$ (stage 1), respectively [5, 6]. In graphite–bromine, stages 2–5 with Br_2 concentrations of 6.25 mole% ($C_{16}Br_2$), 4.17 mole% ($C_{24}Br_2$), 3.13 mole% ($C_{32}Br_2$), and 2.50 mole% ($C_{40}Br_2$), respectively, have been identified by X-ray diffraction [4].

In most intercalation compounds, the structure within an intercalate layer has not been fully elucidated, but in graphite–potassium, this ordering has been determined. In the saturated

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lamellar compound C_8K, which is first stage, the potassium atoms are ordered according to the pattern shown in fig. 1 [7]. On a given K layer, K atoms sit above the center of one out of four carbon hexagons. Labelling this location as site 1, the next three K layers will have K atoms on sites 2, 3, and 4 respectively, while in the fifth layer the K atoms again lie above the positions indicated by the open circles. This stacking sequence repeats periodically, forming a face-centered unit cell. Denoting the intercalate layer by I, the stacking arrangement for higher stage compounds would follow a sequence AB ... ABI_1BA ... BAI_2AB ... ABI_3BA ... BAI_nAB ... ABI_1 ... in which the subscript m on I_m refers to one of the n possible sites for K atoms and AB refers to the stacking of graphitic layers in the pure graphite crystal. It should be mentioned that for higher stage potassium intercalation compounds, the arrangement of the K atoms in the K layers is no longer face-centered. One could argue that the intercalate arrangement shown in fig. 1 is a possible model for graphite intercalated with Br_2, IBr and ICl when appropriately modified for the intercalates in molecular form.

Graphite–Br_2 lamellar compounds can be prepared by exposing graphite to bromine vapor of various pressures or by immersing graphite in Br_2–CCl_4 solutions of various concentrations [8]. Graphite–IBr and graphite–ICl lamellar compounds covering a range of intercalate concentrations can be prepared by exposing graphite to IBr or ICl vapor at various pressures. Residue compounds of Br_2, ICl and IBr can all be prepared by desorption of the parent lamellar compounds.

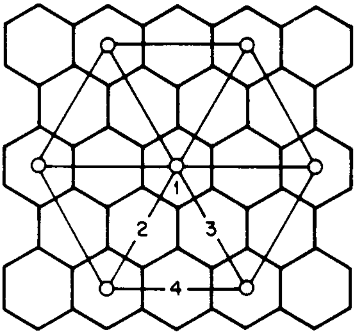

Fig. 1. Arrangement of potassium atoms (open circles) on a potassium monolayer relative to the carbon atom arrangement on a graphite layer plane for the compound C_8K. The positions of the K atoms on different K layers are indicated by the layer numbers 1, 2, 3, and 4.

Magnetoreflection has provided the most powerful experimental technique for studying the electronic energy band structure of pure graphite because the various intraplanar and interplanar interactions can each be examined individually. For this reason magnetoreflection is also attractive for the study of graphite intercalation compounds.

For both experimental and theoretical reasons, it is desirable to carry out magnetoreflection studies on intercalation compounds starting from the dilute limit. We define the dilute limit to correspond to compounds of stage $n \gtrsim 5$, since the band overlap responsible for the semimetallic properties of graphite arises from interactions between carbon atoms two layer planes distant. This definition of the dilute limit is also consistent with dc electrical conductivity measurements [9]. The observation of Landau level transitions by the magnetoreflection technique requires an electron or hole to complete a cyclotron orbit before scattering, and this condition is expressed by the relation $\omega_c\tau \gg 1$. Since this scattering time τ decreases upon intercalation [10, 11], resonant phenomena, such as (1) the de Haas–van Alphen effect and (2) Landau level transitions in the magnetoreflection spectra, are observed predominantly for low intercalate concentrations. From a theoretical point of view, the electronic dispersion relations near the Fermi level of pure graphite should be only slightly modified by the intercalation process in the limit of low intercalate concentrations. Thus the theoretical interpretation of resonant Landau level transitions in the magnetoreflection spectra should be relatively simple in the dilute limit.

The electronic structure of the four Π-bands of graphite near the Fermi level is well-described by the Slonczewski–Weiss–McClure (S–W–McC) band model [12] which treats the electronic dispersion relations along the c-axis by tight binding and in the layer planes by $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory. This electronic structure is specified by 7 band parameters which are identified with the pertinent overlap and transfer integrals of the tight binding model. The significance of these parameters together with their numerical values is given in ref. 13 for pure graphite. Of significance is the fact that the study of resonant Landau level transitions in the magnetoreflection spectra provide an excellent means for the determination of the 5 parameters γ_0, γ_1, γ_3, γ_4 and Δ. If the magnetic energy level structure in the dilute limit could be represented by a similar model, then the effect of intercalation on the nearest neighbor in-plane interactions (γ_0) and on each of the more distant interlayer interactions (γ_1, γ_3, γ_4 and Δ) could be determined independently.

Resonant Landau level transitions have recently been observed in the magnetoreflection spectra of graphite intercalation compounds [11]. The first observations were made on graphite–bromine residue compounds because of the high stability of these intercalation compounds on the time scale of a magnetoreflection run. These graphite–bromine residue compounds were prepared by first exposing highly oriented pyrolytic graphite to saturated bromine vapor for variable lengths of time, then partly desorbing the bromine by heat treatment at 100°C in a stream of nitrogen gas, and finally annealing the samples at room temperature in air for about 1 month to achieve bromine concentration homogeneity on a 1μ scale. We have applied a similar method of preparation from the vapor to the fabrication of residue samples suitable for magnetoreflection experiments with the halogen intercalates IBr and ICl. In the case of graphite–bromine, a second method of preparation was also used. With this method, intercalation proceeds by immersion of the graphite host specimen in a solution of bromine in carbon tetrachloride; desorption takes place in air at room temperature for several months.

To make magnetoreflection measurements on the more fundamental lamellar compounds, which desorb their intercalates in the absence of equilibrium with the external intercalate, we have devised a technique in which the sample is quickly cooled to liquid helium temperature and held at this temperature throughout the measurement. In this way, the lamellar compounds are stable in composition for the duration of a magnetoreflection run, as confirmed by weighing the samples before and after each run. To check that the operation of the magnetoreflection experiment under low temperature-vacuum conditions does not cause desorption of the intercalate in the lamellar compounds, magnetoreflection measurements were also carried out at liquid helium temperature on samples placed in an environment of helium exchange gas. Identical results with regard to the locations of the resonant magnetic fields and to the relative intensities of the resonant structures were obtained under these different experimental conditions. Because of the large changes in the Raman spectra as a function of intercalate concentration, Raman scattering experiments were made on the same samples that were used in the magnetoreflection measurements in order to provide a further check on the quality of our magnetoreflection samples.

Magnetoreflection measurements have been carried out on both lamellar and residue compounds of graphite–Br_2 and graphite–ICl, as well as lamellar graphite–IBr compounds. In particular, for graphite–Br_2, measurements have been made on series of lamellar and residue samples of different Br_2 concentrations to study the dependence of the magnetoreflection spectra on intercalate concentration. All measurements were made at constant photon energy using a globar source and a monochromator for photon energy selection. Magnetic fields up to 152 kG were provided by a Bitter solenoid. The measurements were made with the sample in a cold-finger Dewar containing liquid helium. Figures 2 and 3 show experimental recorder traces of typical magnetoreflection spectra for pure graphite and lamellar compounds of Br_2 (0.21 mole%), IBr (0.22 mole%) and ICl (1.66 mole%) taken at photon energies of $\hbar\omega =$ 0.149 eV, 0.149 eV, 0.140 eV and 0.145 eV, respectively. For each sample the corresponding spectra are shown for ⊕ and ⊖ senses of circular polarization in fig. 2 and fig. 3, respectively. Each structure is identified with a Landau level transition at the K-point of the graphite Brillouin zone, and is specified by the quantum numbers for the initial and final states in accordance with the notation in refs. 14 and 15. Of significance are the great similarities in the observed spectra between pure graphite and the various intercalation compounds in terms of the relative intensities of the various resonant structures and the values of their resonant magnetic fields and photon energies. The dependence of the resonant magnetic fields and photon energies on intercalate species and concentration can be obtained by plotting these

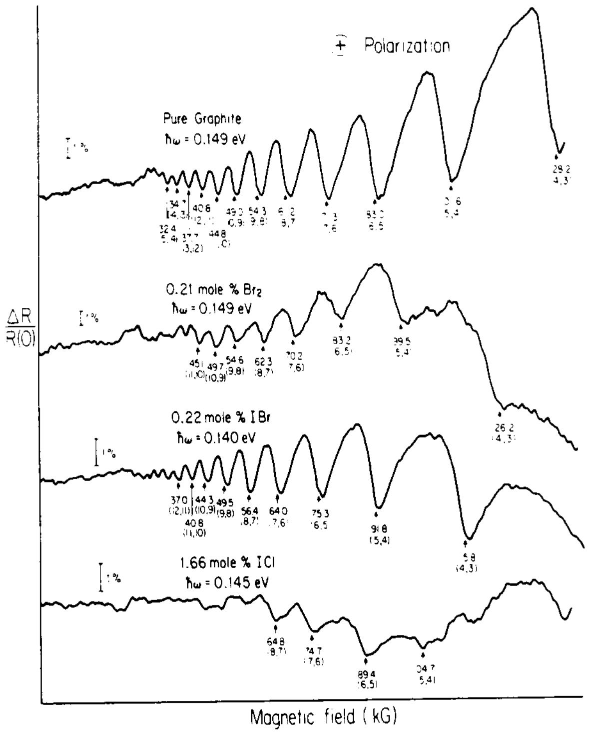

Fig. 2. Change in reflectivity with magnetic field normalized to the zero field reflectivity for pure graphite and for lamellar compounds of graphite with Br_2, IBr and ICl intercalates using ⊕ circularly polarized radiation. Each structure is labeled by the (initial, final) state quantum numbers for the Landau level transitions and by the resonant magnetic field.

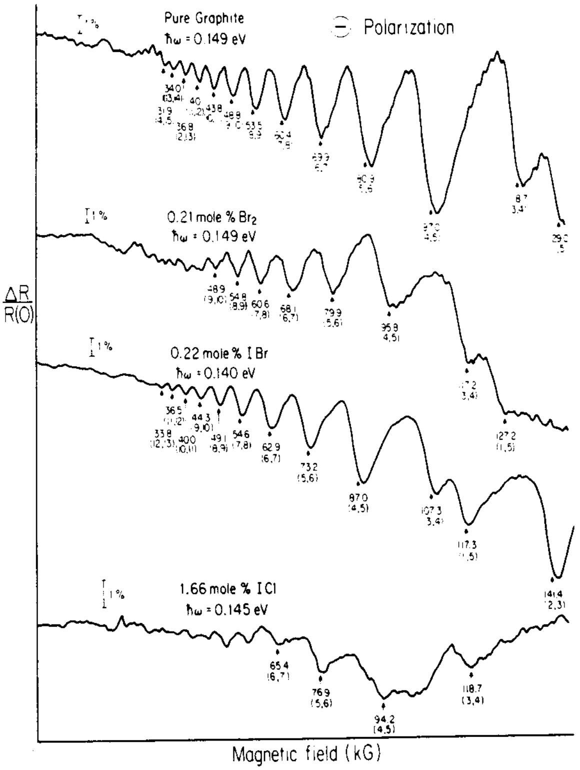

Fig. 3. Change in reflectivity with magnetic field normalized to the zero field reflectivity for pure graphite and for lamellar compounds of graphite with Br_2, IBr and ICl intercalates using ⊖ circularly polarized radiation. Each structure is labeled by the (initial, final) state quantum numbers for the Landau level transitions and by the resonant magnetic field.

quantities in fan charts as shown in fig. 4 for the ⊖ sense of circular polarization for a lamellar graphite–bromine sample containing 0.21 mole% Br_2. Such plots show that the resonant magnetic fields and photon energies for both senses of circular polarization are almost the same for pure graphite and for all the lamellar and residue compounds which have been measured. We interpret these results to show that in the dilute limit the magnetic energy level structure within ±0.1 eV of the graphite Fermi level is well described by the S–W–McC band model with only slightly modified values of the band parameters. Because of the selection rules of $\Delta n = \pm 1$ for allowed Landau level transitions for circularly polarized light with the magnetic field along the c direction [13, 16], analysis of these magnetoreflection data for both senses of circular polarization can be interpreted to yield Landau level separations or cyclotron effective masses for the K-point valence and conduction bands [12]. This analysis shows that the cyclotron effective masses do not change significantly with intercalation for all the lamellar and residue compounds that were studied by the magnetoreflection technique. Because these masses are sensitive to the ratio γ_0^2/γ_1, and because the difference between the valence and conduction band masses is sensitive to γ_4, these results show that the band parameters associated in the tight binding sense with both intraplanar and interplanar interactions are not significantly affected by intercalation in the dilute limit [11]. It should also be mentioned that in addition to the allowed Landau level transitions which follow the selection rules $\Delta n = \pm 1$, certain forbidden transitions following the selection rules $\Delta n = \pm(1 \pm 3m)$ where $m = \text{integer} \geq 1$ are also observed in pure graphite and in the halogen intercalation compounds shown in figs. 2 and 3 [14, 16]. Since these forbidden transitions are very sensitive to the S–W–McC parameter γ_3, a comparison of the forbidden transitions [such as the (1, 5), (0, 4), (l, 3) transitions in fig. 4] in pure graphite and in the graphite intercalation com-

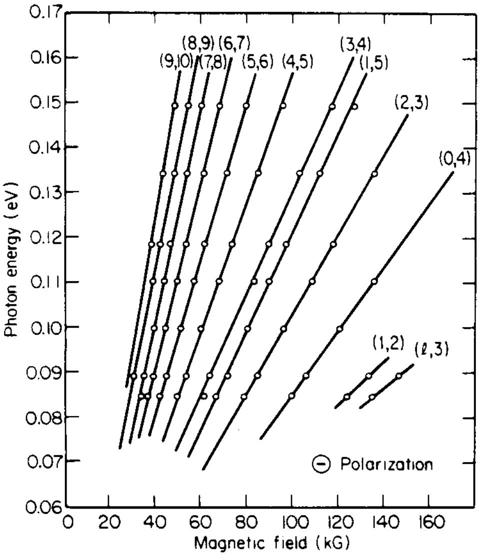

Fig. 4. Fan chart of the principal K-point transitions observed in the magnetoreflection experiment using ⊖ circularly polarized radiation for a graphite–bromine lamellar compound of 0.21 mole% Br_2. Each Landau level transition is labeled by the (initial, final) Landau level indices in accordance with the notation in ref. 14. The $n = 0$ leg level is labeled as "l" in accordance with the notation in ref. 15.

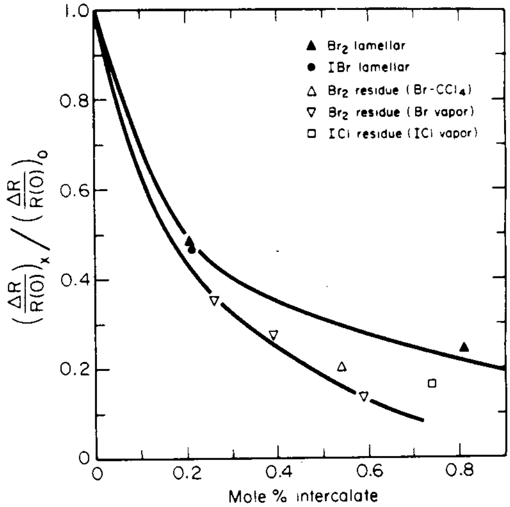

Fig. 5. Variation of the peak intensity of the (5, 4) resonant magnetoreflection structure with intercalate concentration. The peak intensity is measured as the difference between the reflectivity maximum and minimum about the resonance point, normalized to the zero field reflectivity, and the data for different intercalation compounds (×) are normalized to the peak intensity for pure graphite (O). The upper curve is for lamellar graphite–bromine and the lower for residue graphite–bromine.

pounds shows that γ_3 also is not affected by intercalation in the dilute limit. From these data we conclude that the S–W–McC band model describes the magnetic energy level structure of the intercalation compounds in the dilute limit with little change in the values of the S–W–McC band parameters for pure graphite.

On the other hand, as shown in fig. 5, intercalation significantly reduces the intensity of each magnetoreflection resonance so that for samples with intercalate concentrations in excess of ≈ 1 mole% intercalate, the intensity is found to be too weak for quantitative study with present techniques. Currently, the magnetoreflection technique can be applied to study the electronic energy bands of graphite intercalation compounds up to ≈ 10% of the saturation intercalate concentration, and perhaps with improved experimental techniques higher intercalate concentrations can also be studied. The observed decrease in resonant intensity is interpreted as a decrease in the relaxation time τ, so that the condition for the observation of these resonances $\omega_c\tau \gg 1$ is no longer satisfied. Of particular significance is the fact that, for the same nominal intercalate concentration, the intensity of a given resonant structure is higher for lamellar graphite–bromine than residue graphite–bromine. This result indicates that the scattering time is longer in the ordered lamellar compounds as compared with the less ordered residue compounds of equal nominal intercalate concentration. Moreover, the concentration dependence of the intensity is different for different intercalates. For example, for a graphite–ICl lamellar compound containing 1.66 mole% ICl (not indicated in fig. 5), the intensity of the (5, 4) transition, normalized to that of pure graphite, is 0.06 which is almost too low to be observed. It is also of interest to note that the two aforementioned methods of preparing graphite–bromine, namely using bromine vapor or a bromine–carbon tetrachloride solution, lead to similar magnetoreflection results.

In addition to the infrared magnetoreflection experiments described above, far-infrared magnetoreflection measurements were carried out for photon energies less than or comparable with the band overlap for pure graphite ($\Delta E \approx 0.04$ eV), using the Fourier interferometric technique [17]. In this photon energy range, the magnetoreflection technique is expected to be sensitive to the Fermi level location because of the following argument. According to the Pauli principle, Landau level transitions occur from an occupied initial state to an unoccupied final state. When an acceptor intercalate such as bromine is added, holes are introduced and the Fermi level drops [10]. As the intercalation concentration increases, interband Landau level transitions from a specified initial state will continue to occur until the Fermi level falls below the energy of this initial state, thereby defining the cutoff energy for the Landau level transition. Thus, by identifying the cutoff energy for a resonant interband Landau level transition in the magnetoreflection spectra, the location of the Fermi level can be estimated.

Far-infrared magnetoreflection results obtained on residue graphite–Br_2 compounds up to 0.5 mole% Br_2 show the magnetoreflection resonant locations to be insensitive to intercalate concentration in agreement with the results discussed above for the infrared frequency range. A study of the cutoff phenomenon for the intensity of the (1, 2) Landau level transition was made in accordance with the discussion given above. The results that were obtained indicate that the Fermi level falls slowly with Br_2 intercalation. These results also yield an estimate that one hole is created by the addition of ≈ 50 Br_2 molecules, suggesting that in graphite–bromine the bromine retains much of its molecular identity.

From the magnetoreflection spectra of dilute intercalation compounds of graphite with the halogens Br_2, IBr and ICl, we conclude that the electronic band structure near the Fermi level is well-described by the graphite S–W–McC band model, in which the same order of perturbation theory and approximately the same values of the S–W–McC band parameters are used. This result implies that the potential $V(\boldsymbol{r})$ in the graphite layer planes (several layer planes away from the intercalate monolayer) is not sensitive to intercalation in the dilute limit, and suggests that the graphite lattice modes should also be insensitive to intercalation in this limit.

The lattice modes of pure graphite have been studied by Raman scattering [18], infrared spectroscopy [18, 19] and neutron scattering [20]. Two zone-center in-plane optical phonon modes of approximately the same frequency are found, with the Raman-active E_{2g_2} mode lying at $\approx 1580\,cm^{-1}$ and the infrared-active E_{1u} mode lying at $\approx 1590\,cm^{-1}$. The close proximity of these two frequencies indicates that these vibrational frequencies depend almost entirely on in-plane force constants with only weak coupling to atoms on adjacent layers. On the other hand, the small measurable frequency difference between the Raman and infrared lines indicates that the interplanar force constants give rise to frequency shifts of the order of $10\,cm^{-1}$.

When a halogen intercalate such as Br_2, ICl or IBr is intercalated into graphite, the Raman line at $1580\,cm^{-1}$ persists without change of frequency, though its intensity is attenuated with increasing intercalate concentration. The absence of a frequency shift is consistent with the interpretation of the magnetoreflection spectra given above. On the other hand, the difference in frequency between the Raman-active and infrared-active in-plane modes indicates that the frequency of the in-plane carbon atom vibrations in graphite layers adjacent to intercalate monolayers could be shifted from the corresponding pure graphite vibrational frequencies by several cm^{-1} because of the changes in the interplanar force constants caused by the adjacent intercalate monolayers.

Inspection of the Raman spectra of all the halogen intercalation compounds (graphite–Br_2, graphite–ICl and graphite–IBr) and of graphite–HNO_3 reveals a second Raman line shifted upward in frequency from the line at $1580\,cm^{-1}$ by $\approx 20\,cm^{-1}$, indicating a stiffening of the interplanar force constants associated with the coupling to the intercalate monolayers. An argument against a stiffening of the in-plane force constants is the observation that the frequency separation between these two Raman lines is independent of the intercalate species and of the concentration of a given intercalate species. The Raman doublet shown at high frequencies in fig. 6 for a 0.93 mole% Br_2 lamellar compound is typical of the Raman spectra observed in the above-mentioned acceptor compounds as well as in graphite intercalated with $AlCl_3$ and SbF_5 [21].

Although the frequency shift of this doublet is insensitive to the intercalate concentration, a strong dependence of the relative intensities of the doublet components on intercalate concentration is found. This is illustrated in fig. 7 where we have plotted the relative intensity at room temperature of the Raman lines at 1599 and $1580\,cm^{-1}$ as a function of bromine concen-

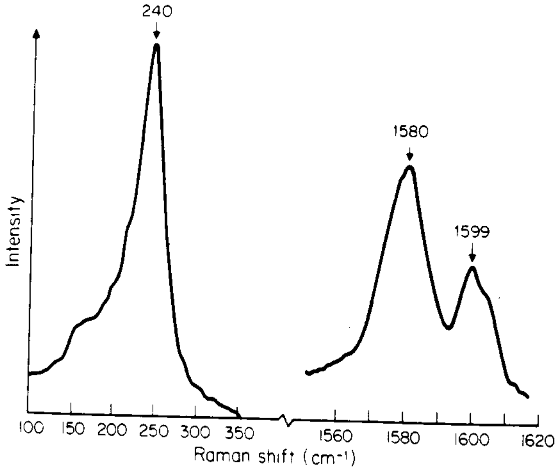

Fig. 6. Room temperature Raman spectra of a graphite–bromine lamellar compound of 0.93 mole% Br_2. The intensity is indicated in arbitrary units and the intensity scale is different for the spectra shown at low and high frequencies. The spectrum observed at high frequencies is identified with in-plane vibrations of carbon atoms while the low frequency spectrum is specific to each intercalate species.

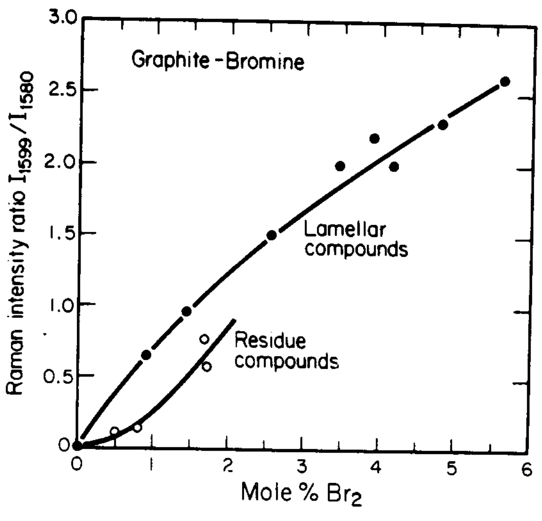

Fig. 7. Variation of the ratio of the intensities of the Raman peaks at 1599 cm⁻¹ and 1580 cm⁻¹ with bromine concentration for lamellar and residue compounds of graphite–bromine at room temperature. Note that the saturation Br_2 concentration for lamellar graphite–Br_2 (6.25 mole%) corresponds to a stage 2 compound.

tration. Intercalation causes the intensity of the line at 1580 cm⁻¹ (associated with carbon atom in-plane vibrations in graphite layers far from the intercalate monolayer) to decrease, and the line at 1599 cm⁻¹ (associated with carbon atom in-plane vibrations in graphite layers close to an intercalate monolayer) to increase, such that the intensities of these two lines are equal for a stage 6 or 7 lamellar compound. A smaller increase in the intensity of the 1599 cm⁻¹ line is found for a residue compound with nominal intercalate concentration equal to that of a lamellar compound, supporting the idea that in residue compounds the intercalate tends to migrate preferentially to defect sites [8]. Also of significance is the observation that Raman scattering experiments can be carried out over the entire range of intercalate concentrations.

Whereas the high-frequency doublet structure shown in fig. 6 is insensitive to the intercalate species, other Raman lines specific to the intercalate species are observed at low frequencies. Thus the low frequency Raman spectra observed for graphite–Br_2, graphite–IBr and graphite–ICl are each very different. Shown in fig. 6 at low frequencies is a structure characteristic of graphite–Br_2 lamellar and residue compounds. Of interest is the proximity of this structure to the vibration frequency of the free bromine molecule at 323 cm⁻¹ [22]. A detailed study, directed toward the elucidation of the orientation of the Br_2 molecules in the intercalate monolayers is now in progress [23, 24].

The picture that emerges from this interpretation of the infrared and far-infrared magnetoreflection data for the graphite-halogen intercalation compounds is that the electronic structure within ± 0.1 eV of the graphite Fermi level is essentially unchanged by intercalation in the dilute limit. Thus, the Slonczewski–Weiss–McClure band model adequately represents the electronic dispersion relations for approximately the same values of the 7 Slonczewski–Weiss–McClure band parameters as for pure graphite. This interpretation is consistent with the identification of the two high frequency Raman lines with in-plane carbon atom vibrations, the line at ≈ 1580 cm⁻¹ associated with carbon atoms in layer planes far from an intercalate monolayer, and the line at ≈ 1599 cm⁻¹ associated with carbon atoms in layer planes close to such intercalate monolayers. Support for the hypothesis that the bromine intercalate maintains its molecular identity is provided both by the weak dependence of the Fermi level on intercalate concentration and by the observation of Raman structure associated with the intercalate species and close to the vibrational frequency of the free molecule.

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