Far-infrared magnetoreflection studies of graphite intercalated with bromine*†

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An estimate of the hole generation rate in graphite-bromine residue compounds has been made from the interpretation of far-infrared magnetoreflection data. From the cutoff of the (1,2) Landau level transition due to the lowering of the Fermi energy upon bromine intercalation, we estimate that one hole is generated by 55 ± 10 Br_2 intercalate molecules. This result is shown to be consistent with estimates based on transport measurements. Furthermore, the observed magnetoreflection resonances confirm that for these compounds ($\lesssim 1$ mole% Br_2) the electronic structure in the band overlap region is well described by the Slonczewski-Weiss-McClure band model for approximately the same values of the band parameters as for pure graphite.

The free-carrier generation rate in graphite intercalation compounds has been a subject of controversy.[1-5] The main focus of this paper is to estimate the hole generation rate in the acceptor intercalation compound graphite-bromine. This rate is expressed here in terms of the quantity f defined as is the fractional number of holes generated by each Br_2 molecule.

The first estimate for f in graphite-bromine was given by Hennig[1] who compared the electrical properties of graphite bisulfate and graphite-bromine, and found that at any given value of the relative resistance, the Hall coefficients for these two intercalation compounds were in close agreement. Therefore, using the known chemical formula for graphite bisulfate, he estimated that $f = 0.44$ and $f = 0.29$ for the graphite-bromine residue and lamellar compounds, respectively.[1] A second and different estimate for f was made by Blackman *et al.*[2] based on the electrical resistivity measurements on graphite-bromine lamellar compounds. These measurements were interpreted to suggest that the degree of ionization is nearly unity at low intercalate concentrations (i.e., $f = 2$ or each intercalate bromine molecule generates one hole per Br atom). Blackman *et al.*[2] further suggested that as the concentration increases, the degree of ionization quickly drops below unity, reaching a value of ~0.15 ($f = 0.30$) for a 0.25-mole% Br_2 compound, which is very dilute in comparison with the saturated compound C_8Br (6.25-mole% Br_2). Closely related is the work of Yajima *et al.*,[3] who measured the electrical resistivity in residue graphite-bromine compounds (in contrast with the *lamellar* compounds studied by Blackman *et al.*[2]) and interpreted their results to suggest that the degree of ionization of bromine is nearly unity in graphite-bromine residue compounds. Also related to the work of Blackman *et al.*[2] and Yajima *et al.*[3] are the studies of Sasa *et al.*[4] on the electrical conductivity of lamellar graphite-bromine.

They found that the electrical conductivity of rapidly brominated graphite is higher than that of stepwise brominated graphite with the same nominal bromine concentration. They interpreted their results to indicate that if bromination does not occur under near-equilibrium conditions, the resulting more dilute local bromine distribution (which occurs under transient conditions during the rapid bromination process) increases the degree of ionization of the bromine intercalate. Tashiro *et al.*[5] measured the resistivity, magnetoresistance and Hall effect of graphite-bromine residue compounds and concluded qualitatively that the ionization efficiency of the halogen intercalate is low. Of significance are the large quantitative differences between the various sets of in-plane conductivity data[2-6] and the consequent uncertainties implied for the hole generation f. The first to suggest a low value of f was McClure,[7] who compared his calculated magnetic susceptibility of graphite for different Fermi energies with the experimental data of Hennig and McClelland[8] on the magnetic susceptibility of graphite-bromine residue compounds. McClure's estimate for graphite-bromine residue compounds was $f = 0.04$.

To address the unsolved problem of the carrier generation rate due to the intercalation process, we have employed the magnetoreflection technique to obtain information on the location of the Fermi level, thereby providing a more direct and accurate determination of the degree of ionization of the intercalate. In this work we have investigated interband Landau-level transitions as observed in the far-infrared magnetoreflection spectra and have obtained an estimate for the number of holes generated per Br_2 intercalate molecule in graphite-bromine residue compounds. Similar data from the infrared magnetoreflection spectra[9-11] of both residue and lamellar graphite-Br_2 are interpreted to provide an upper bound for f in these compounds.

Magnetoreflection studies of lamellar and residue compounds of graphite intercalated with the halogens Br_2, IBr, and ICl up to concentrations of ~1 mole % intercalate provide strong evidence that for this range of intercalate concentrations, the electronic energy band structure within ±0.1 eV of the Fermi level in pure graphite E_F^0 is well described by the Slonczewski-Weiss-McClure (SWMcC) band model with the same values of the band parameters as for the graphite host crystal.[9-11] Since these measurements were carried out for photon energies large compared with the graphite band overlap energy,[12] these infrared magnetoreflection studies were not interpreted to provide information on the dependence of the Fermi level on the intercalate concentration. However, by using photon energies less than the band overlap (~0.04 eV), the magnetoreflection technique becomes more sensitive to the location of the Fermi level in accordance with the arguments presented below.
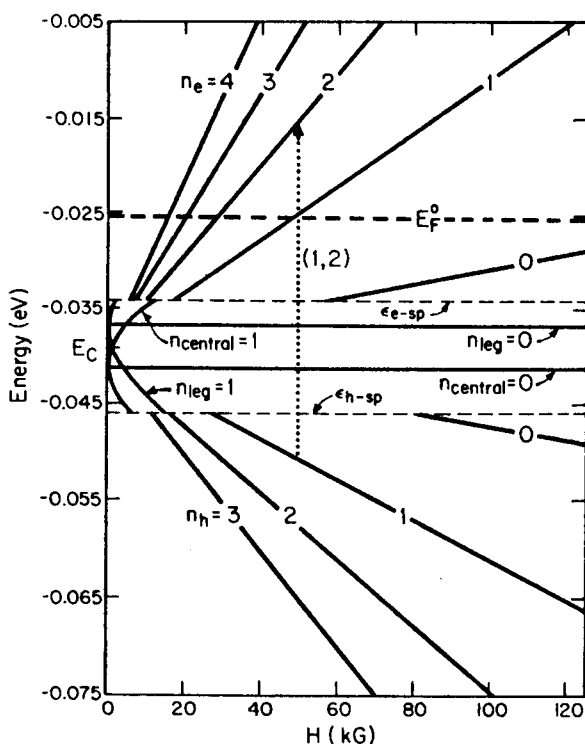
In Fig. 1, the magnetic energy levels according to the SWMcC band model are plotted as a function of magnetic field (H) for the valence and conduction E_3 bands at point K in the Brillouin zone.[13] According to the Pauli principle, interband Landau-level transitions occur from an occupied initial state to an unoccupied final state. For example, consider the transition at $H = 50$ kG from valence level 1 to conduction level 2, which is indicated as (1, 2) in the figure and is prominent in the far-infrared magnetoreflection spectrum of pure graphite,[14] as shown in Fig. 2. When an acceptor intercalate such as bromine is added, holes are introduced[1] and the Fermi level E_F drops. As the intercalation process proceeds, interband Landau-level transitions will continue to occur until E_F falls below the initial state for the transition

FIG. 1. Magnetic field dependence of the Landau levels at the K point. The majority Landau levels labeled by the index n_e for the conduction band and the index n_h for the valence band are cut off, respectively, at energies labeled by ϵ_{e-sp} and ϵ_{h-sp}, between which are the "leg" Landau levels and the "central" Landau levels labeled by the indices n_{leg} and $n_{central}$, respectively. The interband Landau-level transition from n_h = 1 to $n_e = 2$ labeled by (1, 2) is indicated on the figure at a magnetic field $H = 50$ kG. The Fermi energy for pure graphite is indicated by E_F^0.
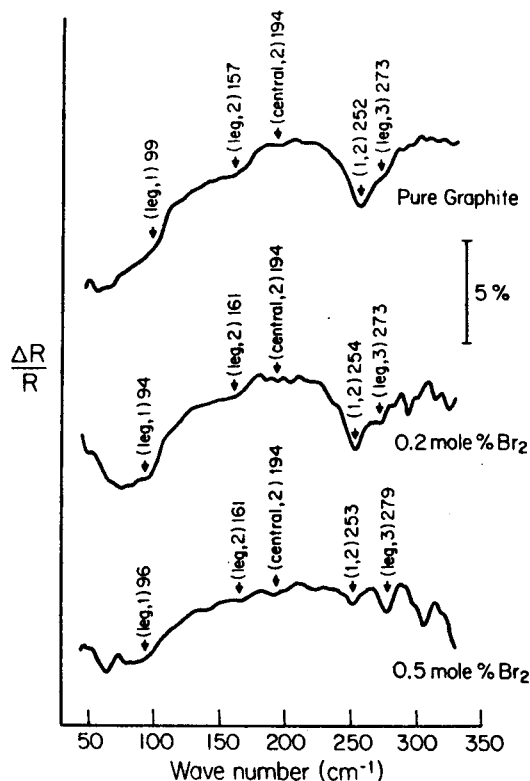

FIG. 2. Far-infrared magnetoreflection spectra taken at a magnetic field of 50 kG for pure graphite and graphite-bromine residue compounds of composition 0.2- and 0.5-mole% Br_2 (corresponding to bromine wt. % of 3.2 and 6.7). Resonant transitions are marked by arrows and identified with Landau-level transitions at the K point, as labeled by the (initial, final) state quantum numbers. Here "leg" refers to the $n_{leg} = 0$ leg level and "central" refers to the $n_{central} = 0$ central level. The resonant frequency of each transition is indicated in units of cm^{-1}. The intensity is indicated in percent as the change in reflectivity normalized to the reflectivity at $H = 0$ kG.

[which in this case corresponds to —0.051 eV for the (1, 2) transitions at 50 kG]. Thus if a particular Landau-level transition is observed, the Fermi level must lie between the extrema of the pertinent valence and conduction Landau-level subbands. This property can then be used to set limits for the location of the Fermi level. However, if we can identify the photon energy at which a particular interband Landau-level transition is cut off, then this cutoff phenomenon can be used to determine the Fermi level more precisely. In the present investigation the magnetoreflection spectra for various concentrations of the intercalate are interpreted both to identify the cutoff energy for the (1, 2) transition and to set lower bounds for the Fermi level using other Landau-level transitions. From the relation between the Fermi-level cutoff (or bounding value) and the intercalate concentration as determined from magnetoreflection measurements, and the relation between the Fermi level and the hole concentration as determined from the SWMcC model,[15] a value for f can be found. The major advantages of the application of the magnetoreflection technique for the determination of f are: (i) it is relatively direct compared with transport measurements; (ii) the model for the electronic structure determined by analysis of the Landau-level transitions in the magnetoreflection spectra is the model that is used in relating the Fermi level to the carrier generation; (iii) interpretation of the magnetoreflection spectra is relatively insensitive to the value or to the model assumed for the relaxation time τ, provided that $\omega_c \tau \gg 1$ and the resonant Landau-level transitions can be observed.

The interpretation of the far-infrared magnetoreflection spectra depends on the magnetic energy-level structure within the band overlap, and in this energy range the magnetic energy-level structure is complicated by the trigonal warping of the constant-energy surfaces.[13,16] This trigonal warping introduces additional energy-band extrema away from the Brillouin-zone edge HKH where all the band extrema are located when there is no trigonal warping. These extrema give rise to new sets of Landau-level ladders, called "special" Landau levels (sp), of which the ones due to the off-axis extrema are called "leg" Landau levels and the ones due to the axial extremum are called "central" Landau levels.[13] Leg and central Landau levels are present only between the two extremal energies denoted in Fig. 1 by ϵ_{h-sp} and ϵ_{e-sp}. For the magnetic field range of interest in the present magnetoreflection experiment ($H \gtrsim 20$ kG), only the lowest quantum number $n_c = 0$ central level and $n_{leg} = 0$ leg level can be supported between these extremal energies.[13] Much of the

structure observed in the far-infrared magnetoreflection spectrum of pure graphite has been identified with Landau-level transitions originating from these leg and central levels.[14]

Figure 2 shows far-infrared magnetoreflection spectra for pure graphite and for two residue compounds containing 0.2- and 0.5-mole % Br_2 (corresponding to 3.2- and 6.7-wt. % bromine, respectively). The two compounds used in the present investigation were previously used in a magnetoreflection study at higher photon energies and their preparation and characterization have been described elsewhere.[9,10] The far-infrared measurements were made at a variety of constant magnetic fields using Fourier interferometric techniques[14] and the spectra shown in Fig. 2 were all obtained for $H = 50$ kG. The structures appearing in these spectra are identified with specific Landau-level transitions and are labeled by their appropriate initial and final states according to the notation in Refs. 13 and 17. The $n_c = 0$ central level is denoted by "central" and the $n_{leg} = 0$ level by "leg" and the majority Landau-level transition (1, 2) connects the $n_h = 1$ valence level with the $n_e = 2$ conduction level as indicated in Fig. 1. Since the resonant structures appear at almost the same photon energy independent of the intercalate concentration, we conclude that the magnetic energy-level structure for the dilute residue intercalation compounds can be described by the SWMcC band model using the same order in perturbation theory and approximately the same values of the band parameters as for pure graphite, in agreement with the results in graphite-Br_2, graphite-IBr, and graphite-ICl previously reported at higher photon energies.[9-11] To estimate f from magnetoreflection measurements it is advantageous to consider Landau-level transitions between two majority levels because these transitions are most clearly resolved, having the largest singularity in the joint density of states. Thus the majority Landau-level transitions occur predominantly for wave vectors close to the K point in the Brillouin zone, while the leg transitions receive significant contributions from other regions of the Brillouin zone.[13,16] Since Landau-level transitions must occur from an occupied initial state to an unoccupied final state, the Fermi-level cutoff phenomenon described above should be observable if the hole concentration due to the acceptor intercalate lowers E_F sufficiently so that the initial state is no longer occupied.

The only well-resolved majority Landau-level transition in the far-infrared magnetoreflection spectra (see Fig. 2) is the (1, 2) majority transition. On the basis of the above arguments for the cutoff of Landau-level transitions, the observation

of the (1, 2) transition at 50 kG in graphite-bromine residue compounds with bromine concentrations up to 0.5-mole% Br_2 implies that the Fermi level lies above −0.0051 eV (see Fig. 1). On the basis of the SWMcC model, $E_F = -0.0051$ eV corresponds to an increase in hole concentration $p - p_0 = 1.3 \times 10^{19}$ cm⁻³, and a decrease in electron concentration $n_0 - n = 2.7 \times 10^{18}$ cm⁻³, where p_0 and n_0 are the hole and electron concentrations, respectively, in pure graphite.[15] Since the bromine concentration for a compound containing 6.7-wt.% Br is 1.4×10^{21} Br/cm³, more than 45 Br_2 intercalate molecules are required to generate a single hole, giving an upper bound for f of 0.022 holes/Br_2. (The acceptor generation rate, which is calculated from $p - n = 1.5 \times 10^{19}$ cm⁻³, is 1 acceptor for more than 37 Br_2 molecules.)

Additional support for the small value of f for graphite-bromine is provided by the infrared magnetoreflection data taken for photon energies large compared with the band overlap for pure graphite. For example, analysis of the magnetoreflection spectrum taken on a 0.6-mole% Br_2 sample at $\hbar\omega = 0.104$ eV reveals well-resolved Landau-level transitions. Application of the magnetic energy-level structure shown in Fig. 1 to this spectrum indicates that E_F lies above −0.074 eV. These infrared data thus provide a lower limit for E_F which in turn implies an upper limit for f, $f < 0.043$ holes/Br_2. Though less restrictive than the far-infrared limit imposed on f, the consistency between the infrared and far-infrared results is significant because of the very much better signal-to-noise ratio in the infrared spectra.

However, if the cutoff of a given Landau-level transition can be identified, a more precise value for f can be obtained. The identification of such a cutoff is difficult in practice because the signal-to-noise ratio on the experimental traces becomes increasingly poor as the cutoff is approached, thereby making its exact determination difficult. On the other hand, as the cutoff is approached, the difference between the upper bound of f and the actual value of f at cutoff progressively decreases. In the present work, the intensity of the (1, 2) majority Landau-level transition was studied as a function of bromine intercalate concentration and the results based on a number of experimental traces are shown in Fig. 3. Since the relaxation time decreases with increasing bromine concentration,[9] a decrease in the intensity of all Landau-level resonant transitions is found as the intercalate concentration increases. However, the decrease in intensity for the (1, 2) transition appears to be more sudden than that observed for the higher quantum-number majority Landau-level transitions which occur further from the Fermi
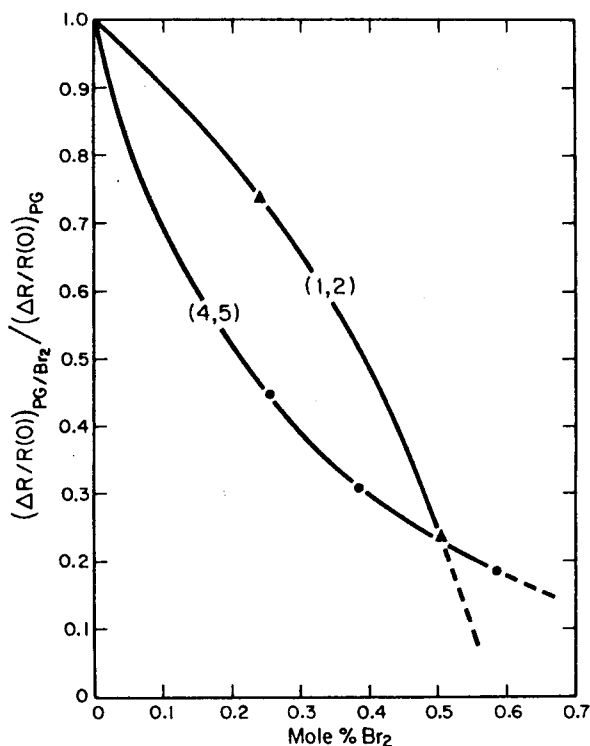

FIG. 3. Variation with Br_2 concentration of the peak intensities of the (4, 5) and (1, 2) resonant magnetoreflection structures in graphite-bromine residue compounds (PG/Br_2), normalized to those of pure graphite (PG). The peak intensity is measured as the difference between the reflectivity maximum and minimum about the resonance point, normalized to the zero-field reflectivity. The data for the (4, 5) transition (●) are observed at ~98 kG and 0.157 eV (Ref. 6) and the data for the (1, 2) transition (▲) are observed at 50 kG and ~253 cm⁻¹ (0.031 eV). Similar results are obtained when these transitions are observed at different resonant magnetic fields and photon energies.

level.[9,11] This difference in behavior is presented in Fig. 3 by comparing the dependence of the intensities for the (1, 2) and (4, 5) transitions as a function of intercalate concentration. If the quenching of the (1, 2) transition in Fig. 3 is identified with the Fermi-level cutoff phenomenon, then E_F is equal to −0.051 eV for a 0.6-mole% Br_2 residue compound, yielding a value of $f = 0.019$ hole/Br_2. Because the Br_2 concentration at which the (1, 2) transitions is cut off can only be identified very approximately, a large uncertainty is given for the estimate of f from analysis of magnetoreflection data, $f = 0.019 \pm 0.003$ hole/Br_2. Despite the large uncertainty of this estimate, the *order of magnitude* of f is well established from analysis of magnetoreflection data. The small hole-carrier generation rate implied by the magnetoreflection results suggest that when bromine intercalates into graphite, the bromine largely retains its mo-

lecular identity.

Another estimate for the acceptor generation rate can be obtained from interpretation of Hall-effect data. Let us consider the transition from a two-carrier regime where the Fermi level E_F is above the K-point extremum of the E_3 band (and the Hall constant increases with hole generation) to a one-carrier hole regime where E_F is below the K-point extremum[15] (and the Hall constant decreases with further hole generation); this transition from the two-carrier to one-carrier regimes is identified with the extremal point in the plot of Hall constant R_{Hall} versus intercalate concentration. Now the SWMcC model gives a hole concentration of 8.8×10^{18} cm^{-3} when E_F crosses the K-point E_3 band extremum[15] ($E_F = -0.041$ eV). From Hennig's R_{Hall} data for residue compounds, this extremal point corresponds to a Br$_2$ concentration $\approx 2.5 \times 10^{20}$ Br$_2$/cm^3 so that $f = 0.020 \pm 0.006$ holes/Br$_2$. Because of the difficulty in identifying the extremal points accurately in Hennig's data, this estimate for f is very approximate.

An estimate for f in lamellar graphite-Br$_2$ can also be made from analysis of Hennig's R_{Hall} data for these compounds.[1] Such an analysis was carried out using the R_{Hall} data for lamellar compounds with intercalate concentrations in the dilute limit[15] (more dilute than a stage 5 compound) and in the one-carrier regime, where E_F is below the E_3-band K-point extremum and R_{Hall} decreases with increasing intercalate concentration. The result thus obtained is $f = 0.022 \pm 0.005$ hole/Br$_2$.

The agreement between the estimates for the hole carrier production by Br$_2$ intercalation as obtained from Hall data and magnetoreflection cut-off data is subject to question. The magnetoreflection data are taken on highly ordered pyrolytic graphite samples[18] and at liquid-helium temperature where thermal excitation plays little role in the carrier generation process. Although Hennig's Hall effect data on graphite-bromine residue compounds are for room temperature and for a pitch-bonded artificial graphite host material,[1] his result is in general agreement with more recent Hall data[5] at 77 °K for a reactor-grade polycrystalline graphite host material. Additional evidence in support of the quality of the Hall-effect host material comes from the close similarity of the room-temperature in-plane electrical conductivity taken on the Hall samples[1] with conductivity measurements taken recently by Yajima et al.[3] on graphite-bromine residue compounds prepared from a pyrolytic graphite host material. To compare the Hall-effect and magnetoreflection estimates for the hole generation rate, it would be useful to carry out low-temperature (77 °K) Hall-effect measurements on graphite-halogen inter-

calation compounds based on a highly oriented pyrolytic graphite host material.

It is difficult to estimate f from analysis of in-plane electrical conductivity (σ_a) data because (i) the interpretation of such data are very sensitive to the model assumed for the relaxation time, (ii) the available data are for room temperature and the model available for the analysis is a low-temperature model,[15] and (iii) the data for σ_a reported by different authors are in diagreement.[1-6] A small value of f can be shown to be consistent with some in-plane electrical conductivity data. For example, a good fit to Sasa et al.'s conductivity data for lamellar graphite-bromine[4] can be obtained[15] with regard to both the magnitude of the saturated conductivity and its dependence on intercalate concentration in the dilute limit using a suitably modified SWMcC model and assuming scattering to be due to both defects ($1/\tau_d$ independent of energy) and phonons ($1/\tau_p$ proportional to the density of states). In this calculation a good fit is obtained for $f = 0.025 \pm 0.009$ hole/Br$_2$, which is consistent with the magnetoreflection results presented above. On the other hand, a similar analysis of Ubbelohde's room-temperature σ_a data[6] suggests a value of $f \gtrsim 0.1$ holes/Br$_2$.

Additional support for the molecular intercalation of Br$_2$ with a low value of f is found in the Shubnikov–de Haas measurements on graphite-bromine lamellar compounds, as studied by Bender and Young.[19] In all their compounds (0.01–0.36 mole% Br$_2$) they observed a hole period which is very close to that of pure graphite, and additional shorter hole periods which can possibly be identified with large breakthrough orbits introduced by the change of periodicity resulting from intercalation.[15]

It should be emphasized that large values for f are inconsistent with magnetoreflection results. For example, using Hennig's estimate of $f = 0.44$ hole/Br$_2$, the SWMcC model yields a Fermi level of -0.291 eV for a 0.6-mole% Br$_2$ residue compound.[15] For such a low value for the Fermi level, all the infrared magnetoreflection spectra observed for photon energies less than 0.2 eV should be cut off. In fact, the observation of Landau-level resonances in the magnetoreflection spectra for $\hbar\omega \lesssim 0.2$ eV requires a smaller value of f than all previous estimates given for the degree of ionization of the intercalate Br$_2$.[1-3,7] It should however be kept in mind that the present estimate for f has been obtained for dilute residue compounds of graphite-bromine ($\lesssim 0.5$-mole% Br$_2$), and it is possible that f depends on the intercalate concentration, particularly for low stage intercalation compounds.[2,20] In this connection it would be useful to extend the magnetoreflection measurements

to the highest possible intercalate concentrations and to the lowest photon energies where resonant Landau-level transitions can be observed.

In conclusion, analysis of far-infrared magnetoreflection spectra yields an estimate for the hole generation rate of $f = 0.019 \pm 0.003$ hole/Br_2 for residue graphite-bromine. No far-infrared magnetoreflection data are presently available for lamellar graphite-bromine. Analysis of near-infrared magnetoreflection data yields a less restrictive lower bound of $f < 0.05$ hole/Br_2 for both lamellar and residue graphite-bromine compounds. These magnetoreflection results are shown to be compatible with Hall data.[1] The small hole-carrier generation rate is interpreted to imply that the bromine intercalate retains its molecular identity upon intercalation. This conclusion is also supported by the observation of low-frequency Raman lines in graphite-bromine which are specific to the intercalate species and are close to the vibrational frequency of the free Br_2 molecule.[21]

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