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MAGNETOREFLECTION STUDY OF GRAPHITE INTERCALATED WITH BROMINE*†

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We report here the first observation of interband Landau level transitions in graphite intercalation compounds. Magnetoreflection measurements are reported for residue compounds of graphite intercalated with up to 1.2 at.% Br. The observed magnetoreflection resonances show evidence for domains in which the electronic band structure and Fermi energy are only slightly dependent on bromine concentration. These conclusions are in general agreement with recently reported de Haas-van Alphen results for these compounds.

THE ELECTRONIC PROPERTIES of the intercalation compounds of graphite have attracted considerable attention[1–4] because the intercalate has been shown to go into the lattice in ordered arrays located in specific layer planes and not in others.[5] As graphite is intercalated with various acceptors, a large enhancement in the electrical conductivity[6–9] is observed, and it has been suggested that this class of materials has the potential for providing electrical conductors with room temperature conductivity higher than that of copper.[10] We report here the first observation of interband Landau level transitions in this class of materials. The analysis of these Landau level transitions provides detailed information on the effect of bromine intercalation on the electronic energy band structure for bromine concentrations up to 1.2 at.%.

Graphite intercalation compounds can be classified into two groups: lamellar and residue compounds.[1–4] The lamellar compounds contain the intercalate in the form of ordered layers stacked between the carbon layers, and are stable only in equilibrium with the external intercalate. Residue compounds are formed after the intercalate in the parent lamellar compound has been desorbed by removal from equilibrium with the external intercalate, and the residual intercalate is concentrated at structural defects.

For the magnetoreflection measurements reported here a series of residue graphite-bromine samples was prepared with bromine concentrations ranging up to 1.4 at.%,[11] though quantitative results were obtained only for samples with concentrations $\leqslant$ 1.2 at.%. This range of concentrations was achieved by first exposing highly oriented pyrolytic graphite[12] to saturated bromine vapor for varying lengths of time[3] and then partly desorbing the samples by heating them at 100°C in a stream of nitrogen gas. Room temperature annealing of the resulting residue compounds for about one month produced samples which were homogeneous on a 1 μm scale as determined by quantitative electron microprobe analysis,[13] using KBr as a standard. Transport measurements made on a 1.4 at.% residue sample indicated that this bromination process increased the electrical conductivity and reversed the Hall constant from negative to positive, consistent with the results of other workers.[9]

We have also prepared residue compounds by another method,[6,14] in which the desorption occurs at room temperature. With this method, the residue compound with the lowest bromine concentration was prepared by immersing a sample of pristine pyrolytic graphite in a solution of bromine in carbon tetrachloride (mole fraction of bromine in solution = 0.08) for 39 days, followed by desorption in air at room temperature

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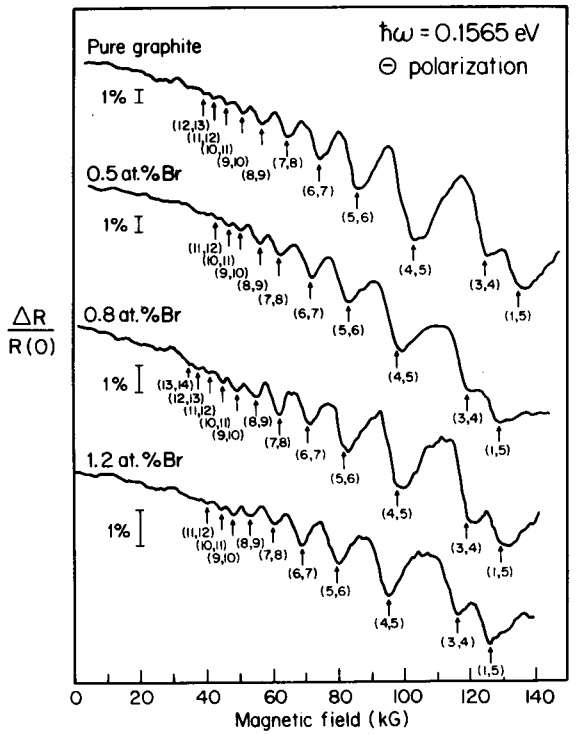

Fig. 1. Change in reflectivity with magnetic field normalized to the zero field reflectivity for various concentrations of intercalated bromine using (−) circularly polarized radiation at a photon energy of $\hbar\omega = 0.1565$ eV. Each structure is labeled by the (initial, final) state quantum numbers for the Landau level transitions.

for 115 days. This resulted in a residue compound of 1.4 at.% Br. Though the condition $\omega_c\tau \gg 1$ was not well satisfied for this sample due to the high bromine concentration, magnetoreflection data indicated that the spectra of this sample were similar to those of the samples prepared by the method described earlier. Since we have found that an intercalation threshold[14] occurs at a bromine mole fraction of about 0.06, a range of dilute residue compounds which are suitable for the magnetoreflection experiment could only be prepared by desorption at higher temperature (e.g. 100°C).

The magnetoreflection measurements were made at constant photon energy using a globar source and a monochromator for photon energy selection.[15] 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. Although the carrier density for pure graphite is 4×10^{-5} carrier/atom,[16] the lowest concentration of bromine relative to carbon which had a measurable effect on the magnetoreflection spectrum was two orders of magnitude greater or 5×10^{-3} atom Br/C.

Figure 1 shows results for the magnetoreflection spectrum of pyrolytic graphite intercalated with

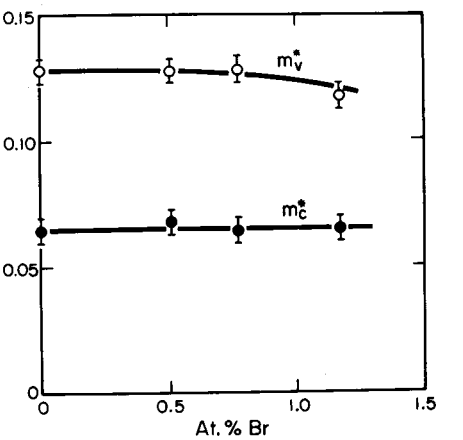

Fig. 2. Variation with intercalated Br concentration of m_v^* and m_c^*, the cyclotron effective masses for the valence and conduction bands respectively.

varying amounts of Br. For the (−) sense of circular polarization[17] shown in Fig. 1, well-resolved structure is observed for bromine concentrations up through 1.2 at.% and extending up to Landau level index 14. Each structure is identified with the Landau level transition specified by the quantum numbers for the initial and final states. Of special interest are the great similarities in the observed spectra between the pure graphite sample and the various intercalated samples in terms of the resonant magnetic field values[18] and the relative intensities of the various resonant structures. Similar results are also found at this photon energy for the magnetoreflection spectra taken with the (+) sense of circular polarization and for spectra taken with either sense of circular polarization over a wide range of photon energies. These similarities imply that the band parameters describing the electronic band structure[16–19] do not change significantly with bromination for Br concentrations $\leqslant 1.2$ at.%. Because of the selection rules of $\Delta n = \pm 1$ for allowed Landau level transitions for circularly polarized light with the magnetic field **H** along the **c** direction, analysis of these magnetoreflection spectra for both senses of circularly polarized radiation can be interpreted to yield Landau level separations or cyclotron effective masses for the K-point valence and conduction bands.[20] The results for the dependence on bromine concentration of the cyclotron effective masses m_c^* and m_v^* corresponding respectively to the conduction and valence bands are given in Fig. 2. Because these masses are sensitive to the ratio γ_0^2/γ_1, and the difference between the masses is sensitive to γ_4, these results show that the band parameters associated in the tight binding sense with interactions in the layer planes and between neighboring layer planes[20] are not significantly affected by bromination for concentration $\leqslant 1.2$ at.% according to the intercalation procedures described above.

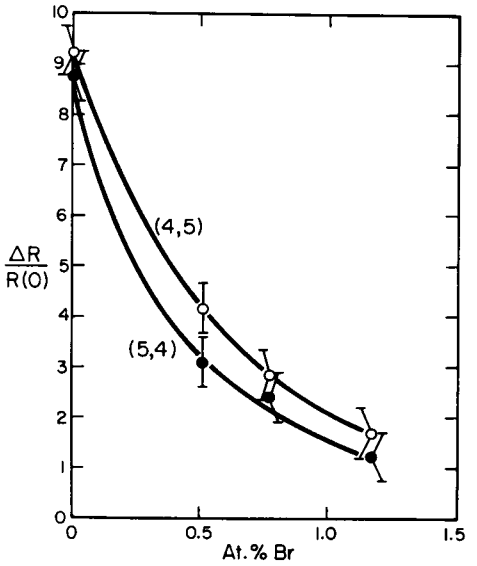

Fig. 3. Variation of the peak intensity of the (4, 5) and (5, 4) resonant magnetoreflection structures with bromine concentration. The peak intensity of a particular resonance is measured as the difference between the reflectivity maximum and minimum about the resonance point, normalized to the zero field reflectivity and the data are presented as percent changes.

However, as shown in Fig. 3, the addition of bromine significantly reduces the intensity of the magnetoreflection resonances so that for samples with Br concentrations in excess of 1.2 at.% the intensity was found to be too weak for quantitative study. This decrease in 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.

Magnetoreflection experiments are not only sensitive to the band parameters describing the electronic band structure, but also to the Fermi energy, because Landau level transitions must occur from an occupied to an unoccupied state. Since the Fermi energy in graphite is $E_F = -0.025$ eV,[21] far infrared magnetoreflectance measurements were carried out in the photon energy range comparable to the band overlap $0.006 < \hbar\omega < 0.043$ eV using Fourier interferometric techniques.[22] Here again the general features of the spectra were found to be independent of bromine intercalation and the Fermi energy was found to be insensitive to bromine concentration for concentrations up to 1.0 at.% Br. These magnetoreflection results are consistent with recent de Haas–van Alphen measurements[23] showing majority electron and hole periods which are independent of bromine intercalation for concentrations up to 3 at.% Br, though major changes in the Fermi surface were found for concentrations > 3 at.% Br.[23]

Since the electrical conductivity and Hall effect in graphite intercalated with bromine undergo major changes for this range of bromine concentrations, we must conclude that the carrier densities increase significantly with intercalation. On the other hand. the magnetoreflection and de Haas–van Alphen results suggest that domains of essentially pure graphite larger than the size of electronic cyclotron orbits are present in these samples and that these domains shrink as the bromine concentration increases.

Preliminary Raman scattering results have also been obtained from the same samples as were used in the present magnetoreflection study as well as from samples with higher bromine concentrations.[11,24] These results show that light scattering techniques are more sensitive to small amounts of bromination than either the magnetoreflection or de Haas–van Alphen techniques. New Raman lines are found and identified with the bromine intercalation process, though the frequency shifts for these new lines are relatively insensitive to the bromine concentration. There is however a strong bromine dependence on the intensity of these lines. The relative insensitivity of the Raman shifts to bromination[24] is consistent with a domain or segregation model for the residue compounds described here. Structural studies using electron microscope techniques are now in progress to provide more definitive information on the location of the bromine in these residue compounds. If such segregation does occur, the resulting domain structure should significantly affect the transport properties of graphite residue intercalation compounds.

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