

Two-Dimensional Structure of Bromine Intercalated Graphite*

D. Ghosh and D.D.L. Chung
Department of Metallurgical Engineering and Materials Science
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

(Received May 26, 1983; Communicated by S. Amelinckx)

ABSTRACT

Synchrotron and sealed tube x-ray diffraction studies on the quasi two-dimensional stage-2 graphite-bromine commensurate phase, prepared with single crystals of graphite, are presented. The two-dimensional structure of the intercalate bromine and the carbon plane has been derived from intensity data measured with a four-circle diffractometer. The bromine structure, having nearest neighbor distances of 2.25, 2.38, 2.55 and 2.86 Å in the (001) plane, exhibits a novel long-chain polymeric form. The distances are comparable to the interatomic bond lengths in the existing polymeric bromides.

Introduction

Eeles and Turnbull (E-T) (1) were among the first investigators who attempted to derive the bromine atom positions in intercalated graphite from x-ray and electron diffraction studies. However, the complicated nature of the in-plane diffraction pattern of the system and the lack of high quality intensity data prevented any unambiguous determination of the structure. Other structural studies, using Raman scattering and EXAFS, have often produced contradictory results (2-4). A major factor which contributed significantly to the confusion is that little is known about the bromine chemistry. Historically, in graphite intercalation compounds, results of weight-gain experiments had been used to predict the in-plane structure, and bromine was no exception (2). Weight-gain measurement indicated a stoichiometry of C_8Br for the saturated stage-2 compound (5,6). However, the stoichiometry in the ordered phase in the atomic level does not necessarily correspond to the overall weight gain of the graphite crystal (7). The mysterious nature of this anionic intercalate system is again reflected in the results of charge trans-

*Research sponsored by the Ceramics Program of the National Science Foundation, Grant No. DMR-7926242.

fer measurements. A wide range of numbers has been reported, ranging from 0.02 to 0.5 (4,8,9).

The early paper of Eeles and Turnbull (1) stands out alone as the most significant work for having characterized several aspects of the material correctly. The quasi two-dimensional nature of the bromine layers was revealed. The twinned in-plane diffraction pattern was indexed using a large orthorhombic unit cell ($a = 8.5 \text{ \AA}$, $b = 34.5 \text{ \AA}$). The structure they derived exhibited a stoichiometry of C_7Br . The nearest Br-Br distance was 2.13 \AA , about 0.14 \AA shorter than the intramolecular distance in solid bromine (10). EXAFS data, on the contrary, reported the distance of 2.34 \AA in intercalated graphite-bromine (4) and about 2.31 \AA for bromine adsorbed on grafoil (3). A somewhat larger intramolecular distance, 2.53 \AA , was found for a residue compound (4). More recent calculations on the charge transfer (9) suggested that there is a transfer of $0.34e$ per bromine atom from the C-plane. This large value of charge transfer seems to indicate that the intercalate bromine does not exist in molecular form. An increase in interatomic distance would be consistent with this hypothesis.

All these studies, when put together, fail to depict a single coherent picture of the structural chemistry of the system. We had undertaken a systematic study of the structural architecture of the graphite-bromine system using x-ray and electron diffraction techniques. The in-plane diffraction pattern was re-indexed, using a three-fold twinned monoclinic unit-cell model (11). This small unit cell ($a = 8.87 \text{ \AA}$, $b = 4.26 \text{ \AA}$, $\gamma = 103.9^\circ$) represents the real asymmetric unit in the lattice, and consequently contains a smaller number of bromine atoms than the E-T unit cell. That bromine layers are uncorrelated along the graphite c-axis was established from diffraction photographs showing Bragg rods along the c^* -direction (12). In this paper, intensity data collected using a four-circle x-ray diffractometer were used to locate the in-plane bromine positions. The derived structure was refined using the least-square technique. Furthermore, the location of the carbon planes relative to bromine atoms was established.

Experimental

The results from two experiments are presented here. The first experiment was performed with a standard fine-focus sealed x-ray tube; the second experiment was performed with a synchrotron source. The results from both experiments are very similar and complement each other. However, the results from the synchrotron study only will be explained in detail. Henceforth, these two sets of data will be referred to as E1 and E2, respectively. The in-plane arrangement of bromine atoms derived from E1 is virtually the same as that from E2. Interestingly, this structure has close resemblance to the one proposed by E-T. However, because of the smaller number of bromine atoms in the asymmetric unit and the larger and higher quality data set, we could least-square refine the atomic parameters and obtain a more accurate description of the structure.

Single crystals of graphite (0.5 - 1.0 mm in diameter, $\sim 0.05 \text{ mm}$ thick) were examined before and after intercalation, using x-ray precession photographs (with filtered $M\alpha$ radiation) for nets ($hki\bar{l}$), $l=0,1,2$, etc. Intercalation and diffraction experiments were performed at room temperature ($\sim 24^\circ\text{C}$). Stage 2 samples at room temperature exhibit two forms, Type A (intercalated with Br_2 vapor) and Type B (intercalated with liquid Br_2). Type A is the commensurate phase while Type B is strongly incommensurate along the a^* -direction (13). In this paper, we describe the results from the commensurate stage-2 material, i.e. Type A. A full account of the in-plane diffraction

pattern has been given elsewhere (11). Of importance to note is that the in-plane unit cell from all higher stage commensurate phases is the same, although differences in the in-plane arrangement of intercalate atoms is possible. Such differences were found in Type C graphite-bromine, which was obtained by room temperature desorption of Type A. In Type C, the in-plane unit cell contains two Br atoms rather than four, resulting in a one-carbon-layer-to-one-bromine-layer stoichiometry of C₂Br. The detailed structure of Type C will be published elsewhere. In general, the in-plane diffraction patterns also show some streaks and weak reflections in incommensurate positions which cannot be indexed with the commensurate unit cell. This indicates in-plane disorder and/or presence of other incommensurate phases.

Sealed tube intensity data (E1) was collected at room temperature (~24°C) on an Enraf-Nonius CAD-4 four-circle diffractometer in the Chemistry Department of Purdue University, using Zr filtered Mo-radiation. Integrated intensities were measured at nine unique superlattice reciprocal points. In addition, six graphitic reflections were measured away from the (*hki*0) graphite plane, at hypothetical *hkl* ($\lambda=1$) positions, to avoid contamination from any free graphite contribution. Finally, six 00*l* reflections were also measured. These were the only reflections with $I > \sigma(I)$ (and hence $F > 2.0\sigma(F)$) between θ limits of 1° and 20°. All other reflections were weak and unobserved. Integrated intensities were corrected for Lorentz and polarization factors. No absorption correction was attempted because of the inhomogeneity of the sample. Since a very thin cylindrical capillary was used, no correction was made for glass scattering either.

The synchrotron experiment was performed at the Cornell High Energy Synchrotron Source (CHESS) on a modified Picker four-circle x-ray diffractometer. The crystal, ~1.0 mm in diameter, was sealed in a cylindrical pyrex glass capillary and was mounted on the diffractometer with the *c*-axis along the beam direction. The beam was tuned to 9.731 ± 0.002 KeV. The photon flux was $\sim 10^{10}$ photons/sec on the crystal, at ~5 GeV and 15 mA. A $\omega/2\theta$ step scan was used; the step size was 0.01667 degree. Taking the HWHM of the graphite *h, k* peaks as the resolution, the *Q* resolution was 0.01 \AA^{-1} . However, the actual resolution was better than this value because of the inherent broadening in the graphite peaks. The FWHM of the 3,0₀ superlattice peak was 0.03 \AA^{-1} with synchrotron x-rays, as compared to 0.18 \AA^{-1} with fine-focus MoK α radiation. The improvement in the signal-to-noise ratio for the strong superlattice reflections was about an order of magnitude over the standard 1 KW fine-focus tube set-up. Eighteen superlattice reflections between θ limits of 3° and 40° had measured structure amplitudes $F > 5\sigma(F)$. The intensities were corrected for the Lorentz factor. Polarization correction was applied assuming that 80 % of the beam was polarized in the horizontal plane, parallel to the ω -axis. Again, no absorption correction was applied.

Analysis

The atomic positions were determined from the Patterson synthesis using 18 superlattice reflections from E2. This synthesis showed two peaks in the asymmetric part, Br1 and Br2, which established the structure (Fig. 1). The *x* and *y* coordinates, the Debye-Waller factors of the atoms and a scale factor relating the observed and calculated structure amplitudes were least-square refined using standard programs (14). The monoclinic cell in two dimensions was assumed to be centrosymmetric; thus, half of the unit cell was actually asymmetric. Therefore, we had a maximum of 7 variables at a time. The disagreement factor *R* (15) between the observed and calculated structure amplitudes converged to about 28% with the bromine atoms. Refinement was also attempted

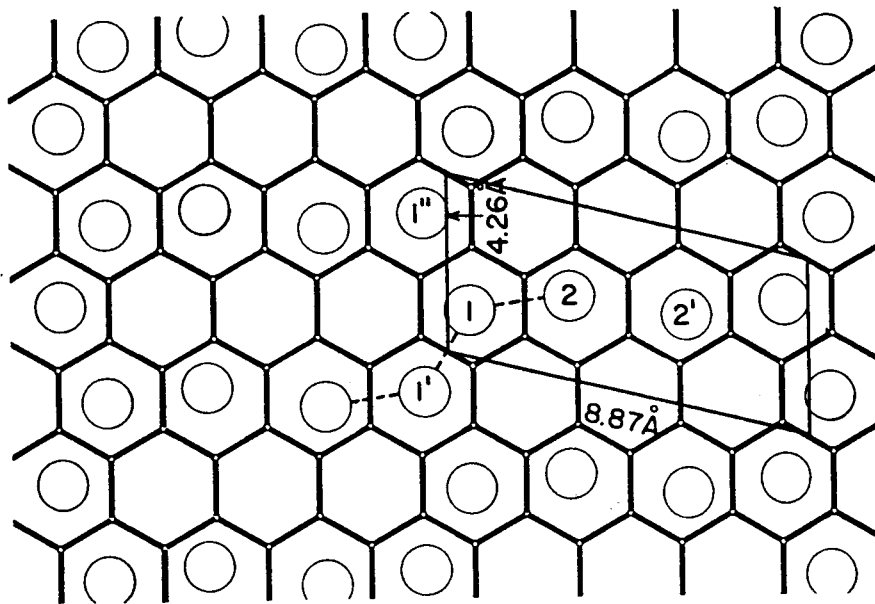


FIG. 1

Two-dimensional structure of Type A graphite-bromine at room temperature. The unit cell is indicated by the parallelogram. The interatomic distances are Br1-Br1': 2.25 Å, Br1-Br2: 2.38 Å, Br1-Br1'': 2.55 Å, and Br2-Br2': 2.86 Å.

assuming the unit cell to be non-centric, i.e. using all four bromine atoms in the unit cell. This, however, did not change the R factor and the refined coordinates remained center-related. All the subsequent calculations were carried out using the centric cell.

A difference Fourier synthesis was made with the bromine atoms and the 18 superlattice reflections to reveal the electron densities which were not accounted for. This map was interpreted as being mainly due to the carbon atoms plus some noise. Five carbon positions out of seven could be identified. Importantly, with the sample being of stage-2, one would expect 14 carbon atoms in the asymmetric part in two-dimensional projection, if the two layers adjacent to the bromine plane were in A-B stacking. On the contrary, these five positions plus the missing two constituted a single carbon plane, suggesting A-A (or B-B) type stacking of the two carbon planes adjacent to the bromine plane. To verify this conclusion further, structure factor calculations were performed with the carbon atoms either in A-B or in A-A stacking. That the R factor was lower for A-A stacking, with carbon positions doubly occupied, strongly supported the argument for the carbon planes in the intercalated part of the graphite crystal being in A-A stacking. Another independent support in favor of A-A stacking came from the E1 data, where all fifteen reflections, including the six off-plane ($l=1$) graphite reflections (described before), were used in the difference synthesis to reveal the graphite structure in two-dimensional projection. This map, shown in Fig. 2(a), exhibits a single unique position of the carbon plane. A similar map, in contrast, calculated with 18 superlattice reflections and 6 in-plane ($l=0$) graphite reflections from the E2 data, displayed A-B stacking in projection (Fig. 2(b)). This result probably indicates that there is considerable signal at the graphite points on the zero-layer from the three-dimensionally oriented "free" graphite lattice. Alternately,

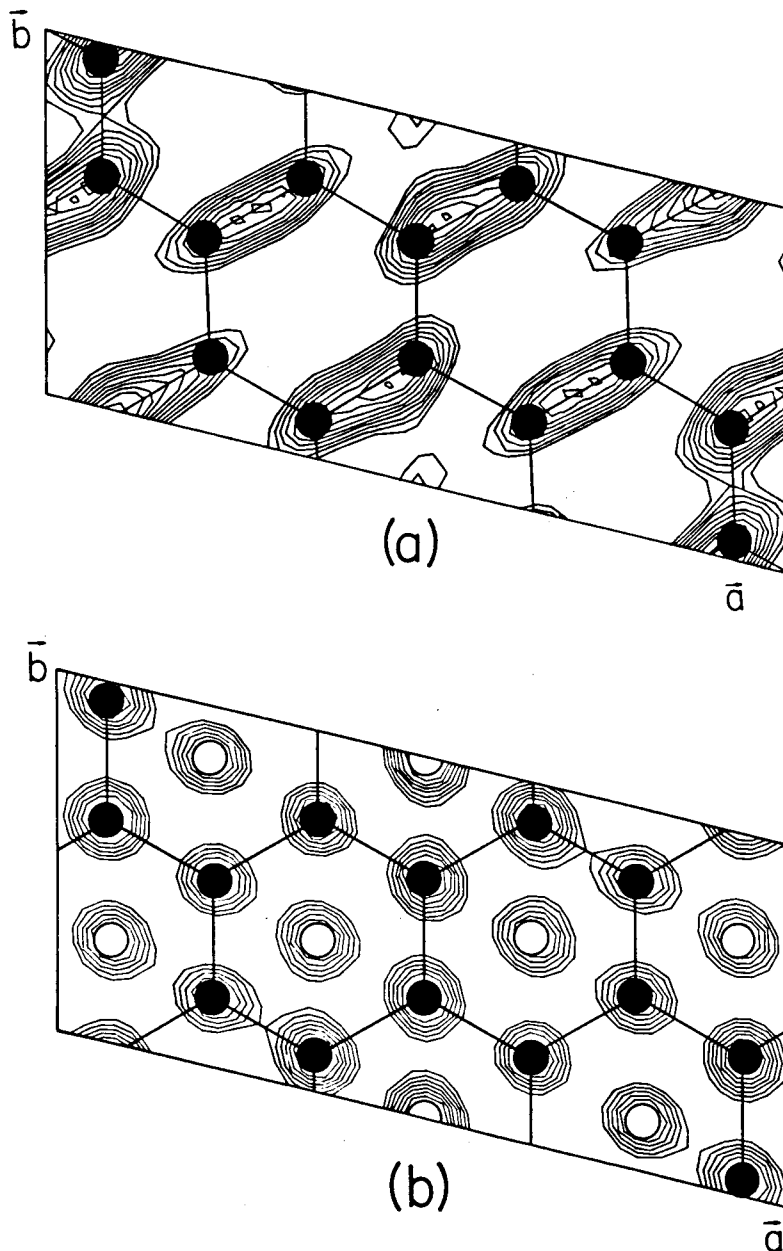


FIG. 2

Difference electron density map calculated with all reflections, revealing the graphite structure in two-dimensional projection. (a) From E1 data set, with off-plane graphite reflections. (b) From E2 data set, with in-plane graphite reflections.

it might also suggest that both A-A and B-B type stacking coexisted, possibly randomly, in the intercalation material. Final structure factor calculation with two bromine atoms and seven carbon atoms gave an R factor of $\sim 22\%$ and $R_w(15) \sim 15\%$. The difference map obtained with the E1 data shows weak additional electron densities which suggest the presence of a second phase in addition to the one of Fig. 1. However, no indication of this phase was obtained with the E2 data.

The Debye-Waller factors for the carbon atoms were fixed at 1.0 \AA^2 . The atom positions were already fixed from the difference map calculated with the bromine atoms and the 18 superlattice reflections. The two carbon atoms not located in the difference map were assumed to have very high Debye-Waller factors. The final co-ordinates of the two bromine atoms were [Br1:0.063 (± 0.003), 0.26 (± 0.01)] and Br2:[0.337 (± 0.004), 0.475 (± 0.01)]. The Debye-Waller factors were $\sim 4.5 \text{ \AA}^2$ (± 1.5). These numbers are quite similar to those obtained with the E1 data set. The observed and calculated structure amplitudes of all eighteen superlattice reflections are compared in Table 1. The nearest-neighbor distances between the bromine atoms are 2.25 (± 0.05), 2.38 (± 0.05), 2.55 (± 0.05) and 2.86 (± 0.06) Å. The first number is comparable to the intramolecular distance in solid bromine. Furthermore, Br1 makes close contacts with two other bromine atoms at distances of 2.38 and 2.55 Å; the smallest intermolecular distance is 3.34 Å in solid bromine. In our structure, the largest interatomic distance, 2.86 Å, is approximately along the direction perpendicular to the b-axis. Thus, approximately, the bromine atoms are distributed in zig-zag polymeric chains along the b-axis and the chains are spaced 8.61 Å apart. The cluster of four atoms, shown connected in Fig. 1 by dashed lines, forms one unit of a chain; the units are linked to each other through the 2.55 Å distance. On the other hand, the bromine atoms may not necessarily be all contained in a single plane; EXAFS analysis recently suggested a $\sim 20^\circ$ tilt between a bromine molecule and the graphite plane (16).

From the present analysis, we cannot rule out such a possibility. Nevertheless, results on the I-C-C-I thickness gave a distance of 3.5 Å between the bromine layer and the adjacent carbon layers. The bromine atoms, therefore, cannot significantly deviate from being planar without having a strong interaction with the carbon layers. Small deviation from planarity, however, would cause the interatomic distances to be larger than the ones resulted from the present two-dimensional picture.

Discussion

The existence of several polybromide ions are available in the literature. Two forms of Br_3^- had been reported in a variety of materials. One form is essentially symmetric, with the bond distances of 2.53 Å and 2.54 Å and the bond angle of 171° (17,18) (Fig. 3(a)). The other form (Fig. 3(b)) is asymmetric with the bond distances of 2.39 Å and 2.91 Å and the bond angle of 177.3° (19). The bond distances in the latter form of Br_3^- are close to the Br-Br distances in graphite-bromine. The Raman active Br-Br stretching modes for the asymmetric Br_3^- occur at 249 and 135 cm^{-1} in $\text{PBr}_4 + \text{Br}_3^-$ (20). The 249 cm^{-1} frequency is close to the main intercalate Raman mode frequency of 242 cm^{-1} in graphite-bromine; the 135 cm^{-1} frequency is not very far from the weak intercalate mode at $\sim 110\text{ cm}^{-1}$ (2). These frequency differences are probably due to the fact that the units that resemble Br_3^- in graphite-bromine strongly interact with one another.

In W_6Br_{16} , Br_4^{2-} interlinks $(\text{W}_6\text{Br}_{12})^{2+}$ units in a one-dimensional infinite polymer chain; the structure can be viewed as one-dimensional intercalation of Br_4^{2-} between $(\text{W}_6\text{Br}_{12})^{2+}$ (21). In W_6Br_{18} , such interlinking occurs in two directions, resulting in a two-dimensional network of Br_4^{2-} and $(\text{W}_6\text{Br}_{12})^{2+}$ units (22). The Br_4^{2-} ion (Fig. 3(c)) is linear, with the bond distances of 2.98, 2.43 and 2.98 Å (21). In our structure, the cluster of four Br atoms connected by dashed lines in Fig. 1 may resemble this species.

The Br_5^- ion (Fig. 3(d)) is also linear, with the bond distances of 2.38 and 2.82 Å (23). These distances are also close to the Br-Br distances in

graphite-bromine. The Raman-active vibrational stretching frequencies for Br_5^- occur at 245 cm^{-1} (intense) and 157 cm^{-1} (weak) in brominated nickel and palladium bis (diphenylglyoximates) (23). The 245 cm^{-1} frequency is very close to the main intercalate Raman mode frequency of 242 cm^{-1} in graphite-bromine (2).

The similarity in Br-Br distances with those of Br_3^- , Br_4^{2-} and Br_5^- suggests that the interacting Br_4^{x-} units in graphite-bromine have a character which resembles Br_3^- , Br_4^{2-} , Br_5^- , or other polybromide anions. Polymeric bromine with more than five bromine atoms in a chain and with all interatomic distances less than 3.0 Å, to our knowledge, has not been previously reported. The derived structure from the present investigation is much more complex in nature than the three simple polybromide anion structures referred to above. However, the existence of these polybromide ions and the possible hypervalency (trivalency) for bromine (24) support the chemical plausibility of our structure.

There is a possibility that the Br atoms in Fig. 1 belong to two correlated intercalate layers in two separate interlayer spaces, such that these layers are randomly stacked in pairs in stage-2 graphite-bromine, even though this possibility implies a stoichiometry of C_{14}Br , which is not consistent with weight uptake data.

Due to the complicated nature of the structural chemistry, it is difficult to estimate the value of x, which gives the charge transfer. A polybromide chain is probably a number of unit cells long, terminating at dislocations or at the interfaces between free graphite and graphite-bromine regions.

Acknowledgments

The authors are indebted to Professor W.R. Robinson of Purdue University for the use of his four-circle x-ray diffractometer system. They also thank Professor Robinson and Mr. S. Chang of Purdue University, and CHESS Staff members for their assistance with the intensity data collection.

References

1. W. T. Eeles and J. A. Turnbull, Proc. Roy. Soc. (London) A283, 179 (1965).
2. P. C. Eklund, N. Kambe, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. B18, 7069 (1978).
3. S. M. Heald and E. A. Stern, Phys. Rev. B17, 4069 (1978).
4. S. M. Heald and E. A. Stern, Synth. Met. 2, 87 (1980).
5. A. Frenzel, Diss. Tech-Hochschule, Berlin, 1933.
6. W. Rudorff, Z. Anorg. Allgem. Chem. 245, 383 (1941).
7. M. L. Saylor, M. H. Boca, D. S. Smith and P. C. Eklund, Ext. Abstr. Program - Bienn. Conf. Carbon 15, 117 (1981).
8. D. A. Platts, D. D. L. Chung and M. S. Dresselhaus, Phys. Rev. B15, 1087 (1977), and the references therein.
9. A. Erbil, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. B25, 5451 (1982).

10. R. W. G. Wyckoff, *Crystal Structures*, Vol. 1, Interscience, New York (1963).
11. D. Ghosh and D. D. L. Chung, *Mater. Res. Bull.*, 18, 727 (1983).
12. D. Ghosh and D. D. L. Chung, unpublished results.
13. D. Ghosh and D.D.L. Chung, *J. Physique Lett.*, in press.
14. Kindly provided by Professor R. Shiono of University of Pittsburgh.
15.
$$R = \frac{\sum ||F_{Obs}| - |F_{Cal}||}{\sum |F_{Obs}|} ; R_w = \left[\frac{\sum_w (|F_{Obs}| - |F_{Cal}|)^2}{\sum_w |F_{Obs}|^2} \right]^{1/2}$$
16. J. L. Feldman, E. F. Skelton, A. C. Ehrlich, D. D. Dominquez, W. T. Elam, S. B. Qadri and F. W. Lytle, *Bull. Am. Phys. Soc.* 28, 346 (1983).
17. C. Romers and E. W. M. Keulemans, *Proc. Ned. Acad. Sci.* B61, 345 (1958).
18. Halogen Chemistry, Ed. V. Gutmann, Vol. 1, Academic Press, London, 1967, p. 232.
19. G. L. Breneman and R. D. Willett, *Acta Cryst.* 23, 467 (1967).
20. W. Gabes and H. Gerding, *Recl. Trav. Chim. Pays-Bas* 90, 157 (1971).
21. R. Siepmann and H. G. von Schnering, *Z. Anorg. Allg. Chem.* 357, 289 (1968).
22. H. Schafer and R. Siepmann, *Z. Anorg. Allg. Chem.* 357, 273 (1968).
23. D. W. Kalina, J. W. Lyding, M. T. Ratajack, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.* 102, 7854. (1980).
24. K. M. Reese, *Mosaic* 14, 2 (1983).