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EFFECT OF INTERCALATE DESORPTION ON THE TWO-DIMENSIONAL STRUCTURE OF GRAPHITE–BROMINE*

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Summary

By single crystal X-ray diffraction, the desorption of stage-2 C_7Br to an overall stoichiometry of $C_{35}Br$ was found to result in a change in the in-plane structure while the in-plane unit cell was maintained. The nearest-neighbor distances between the bromine atoms are 2.29, 2.43, 2.10 and 3.48 Å. The last distance is considerably larger than the corresponding one (2.86 Å) before desorption. The small distance of 2.10 Å suggests that the atoms may be in two layers or two phases, indicating that desorption decreased the in-plane bromine concentration to half of that of stage-2 C_7Br.

Introduction

Upon removal of the equilibrium with the intercalate vapor pressure, many intercalation compounds of graphite undergo intercalate desorption. Although the desorbed material is relatively low in intercalate concentration, its stability makes it attractive for technological applications.

By X-ray diffraction, Hennig [1] observed that the *c*-axis periodicities of desorbed compounds (termed residue compounds by Hennig) were almost identical to that of graphite and, hence, concluded that the bulk of the intercalate resided at defects rather than being in the form of layers between the graphite layers. Based on X-ray and electron diffraction results, Eeles and Turnbull [2] proposed a two-dimensional structural model of desorbed graphite–bromine (stage-4 $C_{28}Br$). However, the complicated nature of the in-plane diffraction pattern and the lack of high quality intensity data prevented any unambiguous determination of the structure. By electron and X-ray diffraction, we observed that desorbed graphite–bromine, with a nominal intercalate concentration as low as 0.2 mol% Br_2, contained intercalate layers with the same three-fold, twinned, monoclinic in-plane unit cell as concentrated well-staged compounds [3, 4]. Maire and Mering

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[5], based on X-ray diffraction results, suggested that the in-plane density of an intercalate layer decreased upon desorption from stage-2 C_7Br to stage-2 $C_{14}Br$. Consistent with this suggestion is the recent report of Simon *et al.* [6] that the desorption of stage-2 C_8Br resulted in stage-2 $C_{14}Br$, stage-3 $C_{21}Br$ and stage-4 $C_{28}Br$. The stage-2 $C_{14}Br$ compound was also reported by Moret *et al.* [7].

In this work, by single crystal X-ray diffraction, we found that the desorption of stage-2 C_7Br to an intercalate concentration of 19 wt.% Br_2 (overall stoichiometry of $C_{35}Br$) resulted in a change in the in-plane intercalate structure while the in-plane unit cell was maintained. In particular, evidence was obtained for the existence of one or two phases in which the in-plane intercalate density is half of that of stage-2 C_7Br.

Experimental

Single crystals of graphite (0.5 - 1.0 mm in diameter, ~ 0.05 mm thick) were examined before and after intercalation, using X-ray precession photographs (with filtered Mo Kα radiation). Intercalation and diffraction experiments were performed at room temperature (~24 °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 has the stoichiometry C_7Br and is the commensurate phase [8]. Type B, which probably has a higher intercalate concentration than Type A, is strongly incommensurate along the *a**-direction [9]. The two-dimensional arrangement of the bromine atoms had been determined in Type A by single crystal X-ray diffraction, as shown in Fig. 1 [8]. This paper reports on the two-dimensional structure of Type C (desorbed at room temperature in air for 20 days from Type A), which has a nominal overall stoichiometry of $C_{35}Br$, as determined by weight uptake measurement.

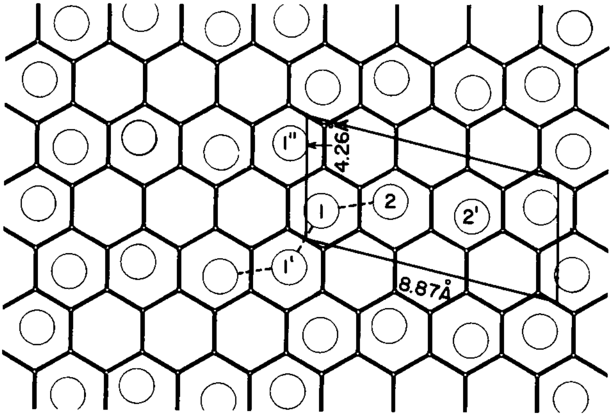

Fig. 1. Two-dimensional structure of Type A graphite–bromine at room temperature. The unit cell is indicated by the parallelogram. The interatomic distances are Br1–Br1′: 2.25 Å; Br1–Br2: 2.38 Å; Br1–Br1″: 2.55 Å; Br2–Br2′: 2.86 Å.

The X-ray diffraction experiment was performed with an Enraf–Nonius CAD-4 four-circle diffractometer in the Department of Crystallography of the University of Pittsburgh. Zirconium filtered Mo-radiation from a fine-focus, sealed X-ray tube was used. Integrated intensities were measured at 12 unique superlattice reciprocal points. In addition, six graphite reflections were measured away from the (*hki*0) graphite plane, at hypothetical *hk*1 ($l = 1$) positions, to avoid contamination from any pure graphite contribution. These were the only reflections with $F_{\mathrm{obs}} > 4\sigma(F_{\mathrm{obs}})$ 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. The sample was not in a capillary.

Analysis

The atomic positions were determined from the Patterson synthesis using the 12 superlattice reflections. This synthesis showed two peaks in the asymmetric part, Br1 and Br2, which established the structure (Fig. 2). 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. Structure factor calculations also showed that the occupancy factor of Br1 is twice that of Br2, in contrast to their equal occupancy in Type A. 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 final coordinates of the two bromine atoms were Br1: [0.059 (±0.002), 0.27 (±0.01)] and Br2: [0.300 (±0.004), 0.46 (±0.01)], which are slightly different from those of Type A. The Debye–Waller factors of the bromine

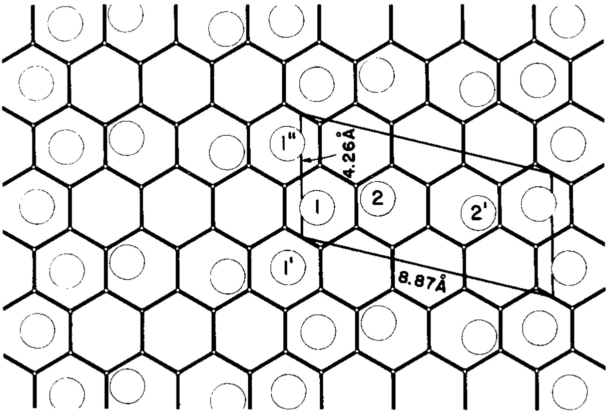

Fig. 2. Two-dimensional structure of Type C graphite–bromine at room temperature. The unit cell is indicated by the parallelogram. The interatomic distances are Br1–Br1′: 2.29 Å; Br1–Br2: 2.10 Å; Br1–Br1″: 2.43 Å; Br2–Br2′: 3.48 Å.

atoms were ~2.0 Å^2 (±0.5), which is smaller than those of Type A (~4.5 Å^2). The observed and calculated structure amplitudes of all 12 superlattice reflections are compared in Table 1. The nearest-neighbor distances between the bromine atoms are 2.29(±0.06), 2.43(±0.06), 2.10(±0.07) and 3.48 (±0.07) Å. The first two distances are close to the corresponding ones in Type A. The third distance is smaller than the corresponding one (2.38 Å) in Type A; it is even smaller than the intramolecular distance (2.28 Å) in

TABLE 1

Observed and calculated structure amplitudes

h, *k*	Obs. $\|F\|$	Calc. $\|F\|$	σ(Obs. $\|F\|$)
1, 0	55	54	1
2, 0	25	24	1
3, 0	45	44	1
5, 0	36	30	3
6, 0	27	17	2
0, 1	26	34	1
2, 1	17	19	3
−1, 1	26	29	1
−3, 1	18	23	3
−8, 1	22	19	1
0, 2	18	27	3
4, 2	27	16	4

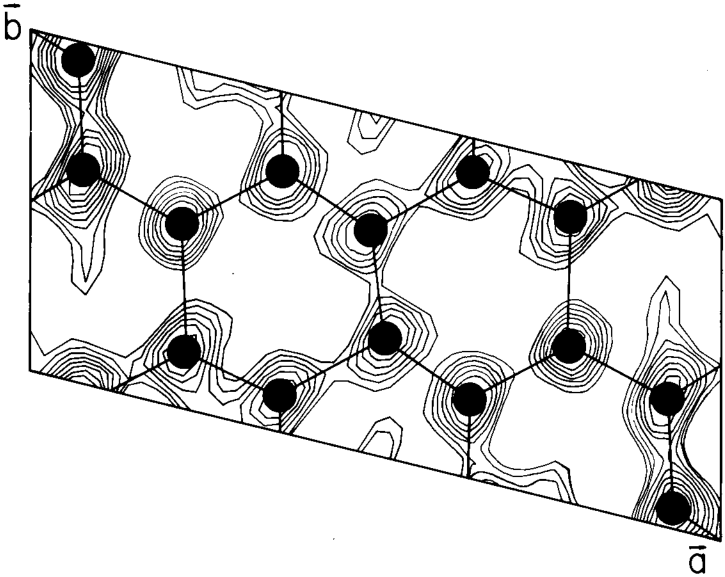

Fig. 3. Difference electron density map calculated with all reflections, revealing the graphite structure of Type C graphite–bromine in two-dimensional projection.

solid bromine. The fourth distance is considerably larger than the corresponding one (2.86 Å) in Type A; it is even larger than the smallest intermolecular distance of 3.34 Å in solid bromine.

A difference Fourier synthesis was made with all the reflections to reveal the graphite structure in two-dimensional projection. This map, shown in Fig. 3, exhibits essentially a single position of the carbon plane, and thus suggests an A–A stacking of the carbon layers, as in Type A [8].

The final structure factor calculation with two bromine atoms gave a disagreement factor R of ~18% and a weighted factor R_w of ~6%.

Discussion

That the distance between Br1 and Br2 is less than the intramolecular distance in solid bromine suggests the possibility that Br1 and Br2 do not coexist in the same intercalate layer, but belong to two different phases. If this is the case, the phase with Br1 and the phase with Br2 have in-plane intercalate densities that are half of that of stage-2 C_7Br. Furthermore, that Br1 has an occupancy factor that is twice that of Br2 means that the phase with Br1 is twice as abundant. The phase with Br1 consists of bromine chains along the *b*-axis, whereas the phase with Br2 consists of atomic Br. That the phase with Br2 is less abundant might be due to the relative ease of desorption of Br2 compared with Br1. The large distance between Br2 and Br2′ is consistent with the suggestion that the fractional charge transfer is higher for dilute compounds [10].

On the other hand, the coexistence of Br1 and Br2 in the same intercalate layer cannot be ruled out, especially since these atoms are not necessarily in the same plane (*i.e.*, the Br1–Br2 bond may tilt [11]). Such coexistence means the presence of a phase with the same in-plane intercalate density as stage-2 C_7Br. Because Br1 has an occupancy factor which is twice that of Br2, this phase would coexist with, and be as abundant as, the phase with only Br1. In the phase with both Br1 and Br2, the structure resembles that of Type A.

In conclusion, whether Br1 and Br2 coexist or not, a phase with an in-plane intercalate density which is half that of stage-2 C_7Br is present in Type C graphite–bromine.

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