

**SYNCHROTRON X-RAY DIFFRACTION STUDY
OF THE INCOMMENSURATE GRAPHITE-BROMINE COMPOUND:
CHANGE IN THE *c*-AXIS REPEAT DISTANCE
DURING THE INCOMMENSURATE-COMMENSURATE TRANSITION ☆**

D. GHOSH and D.D.L. CHUNG

*Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University,
Pittsburgh, PA 15213, USA*

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Synchrotron X-ray diffraction showed that the incommensurate-commensurate transition of stage-2 graphite-bromine at 319 K involved a change of the *c*-axis repeat distance from 10.40 ± 0.01 Å to 10.22 ± 0.01 Å. This suggests that the transition is three-dimensional in nature and that the bromine atoms between two carbon layers in the incommensurate phase are not confined to a plane.

1. Introduction

In our previous papers [1,2] we had established a new phase transition in graphite-bromine intercalation compound. This transition is a structural transition in which the room-temperature incommensurate phase of the bromine superlattice assumes the commensurate configuration. We termed this transition an incommensurate-commensurate (I-C) transition, which was observed at 319 K. This phase transition was studied by the X-ray diffraction technique, and the resultant model of the incommensurate phase was investigated in a two-dimensional approximation, i.e. the in-plane peaks were studied. One important rationale for this is the fact that the bromine layers are uncorrelated along the *c* axis of the graphite. Nevertheless, the repeating unit along this direction has a fixed periodicity and thus the 00*l* reflections should give rise to Bragg peaks along the *c** axis of the reciprocal space. Along with the structural changes within the bromine layers during this transition, one should consider the possibility of a three-dimensional effect. More specifically, what happens to the sandwich thickness

during this transition? Intuitively, it is possible that this structural change may not be confined to the bromine layers only, especially if the transition is accompanied by the movement of the intercalate atoms in and out of the plane. Furthermore, a *c*-axis repeat distance of 10.39 Å for stage-2 graphite-bromine at room temperature had been reported [3,4] without giving any reference to the commensurate or incommensurate in-plane structure. It was, therefore, important to investigate the behavior of the 00*l* reflections during the I-C transition.

2. Experimental

The data collection was done at Cornell high-energy synchrotron source at the A-2 hutch on a Picker two-axis diffractometer fitted with a quarter χ -circle. Results from two different experiments are presented here. The beam (5.5 GeV and maximum current ≈ 45 mA in the three-bunch mode) was tuned to 10.0 keV in one occasion and 7.5 keV in the other. The crystal, ≈ 1.0 mm in diameter, was enclosed in a quartz capillary with liquid bromine and was surrounded by a microheater (Enraf-Nonius FR 559) which was heated by the power supplied through a temperature controller.

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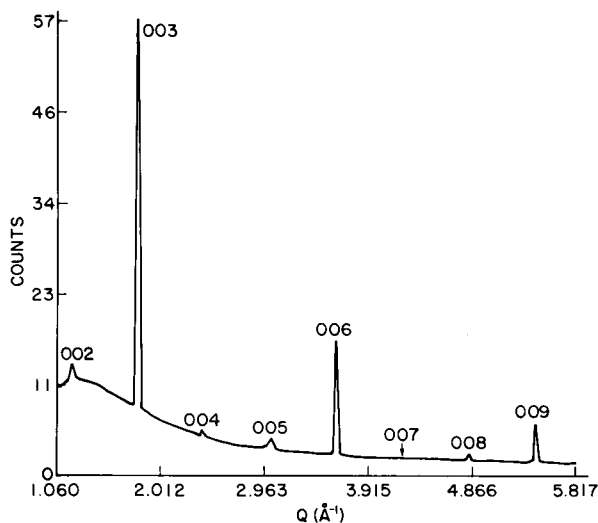


Fig. 1. 00 l X-ray diffraction pattern of stage-2 type B graphite-bromine at room temperature.

A second thermocouple measured the temperature on the outer surface of the capillary, in close proximity to the crystal. This temperature was later calibrated to account for the difference in temperature between the outer and inner surfaces of the capillary. Specimen orientation and data collection were carried out using the program XØPLUS. A step scan was used for the purpose.

Fig. 1 shows the 10 keV ($\lambda = 1.239 \pm 0.004 \text{ \AA}$) diffractogram which exhibits the 00 l reflections of the stage-2 type B graphite-bromine material at room temperature. (Type B refers to the material prepared by immersion in liquid bromine.) A $\theta/2\theta$ scan was used to record the spectrum. All the reflections above the noise level conform to the 00 l reflections, $l = 2, 3, \dots, 9$, of the lattice spacing of $10.40 \pm 0.01 \text{ \AA}$. The 001 reflection was too close to the direct beam and was hence washed away by it. Similar diffractograms were obtained from a number of identical samples and also with the 7.5 keV ($\lambda = 1.655 \pm 0.002 \text{ \AA}$) beam. The reflections 003, 006 and 009, which are close to the pure graphite 002, 004 and 006 reflections, respectively, are strongest of all. This is a typical phenomenon observed in all graphite intercalation compounds. These peaks are, however, downshifted in Q values from their corresponding pure graphite equivalents. The remaining reflections are solely due to the intercalation of bromine

layers and hence are loosely termed "superlattice peaks". These superlattice peaks are considerably weak and are mostly unobserved in diffractograms of small single-crystal materials taken with regular 1 kW sealed X-ray tubes. With synchrotron X-rays, however, these superlattice peaks are observed just above the noise level.

The complete diffractogram up to $l = 9$ was studied at each temperature. However, at temperatures higher than room temperature, the superlattice peaks became weaker and broader and gradually fell to the noise level as the temperature was raised; consequently they were unsuitable for quantitative evaluation of their position, size and shape. The graphite peaks, e.g., 003, 006 and 009, on the contrary, remained sharp and strong and were therefore suitable for the present study. Moreover, these graphite reflections have definite positions depending on the stage of the intercalated sample; hence the transitional behavior of their staging structure can be revealed by in situ study of these peaks.

Figs. 2a and 2b show the behavior of the 003 and 006 peaks at various temperatures above room temperature during heating. The solid lines through the data points represent smooth curves, independent of any particular shape of the peaks. The 003 peak, at $Q = 1.810 \pm 0.003 \text{ \AA}^{-1}$ moved almost continuously as the temperature was gradually raised. Beyond 325 K it assumed a Q value of $1.845 \pm 0.003 \text{ \AA}^{-1}$. Similarly the 006 peak, starting at $Q = 3.625 \pm 0.003 \text{ \AA}^{-1}$, assumed a Q value of $3.688 \pm 0.003 \text{ \AA}^{-1}$ beyond 325 K. The fractional shifts of these peaks are plotted versus the temperature during heating and cooling in fig. 3. The solid lines in these figures are smooth curves through the data points. These peaks, along with the other (weaker) ones in their maximally shifted positions, conform to a lattice spacing along the c direction of $10.22 \pm 0.01 \text{ \AA}$. Thus, there is a shrinking of 0.18 \AA of the c -lattice spacing during the transition. Fig. 3 also shows the reversibility of the peak shifts upon cooling.

The shifted 003 peak is close to the position for 006 of stage 5, while the shifted 006 peak is close to the position for 0012 of stage 5. However, the complete diffractogram at each temperature revealed no new peak, thus giving no evidence for a stage change. Furthermore, desorption of stage-2 graphite-bromine is expected to form stage 3 or a mixture of stages 3 and 4, rather than stage 5 alone. On the other hand,

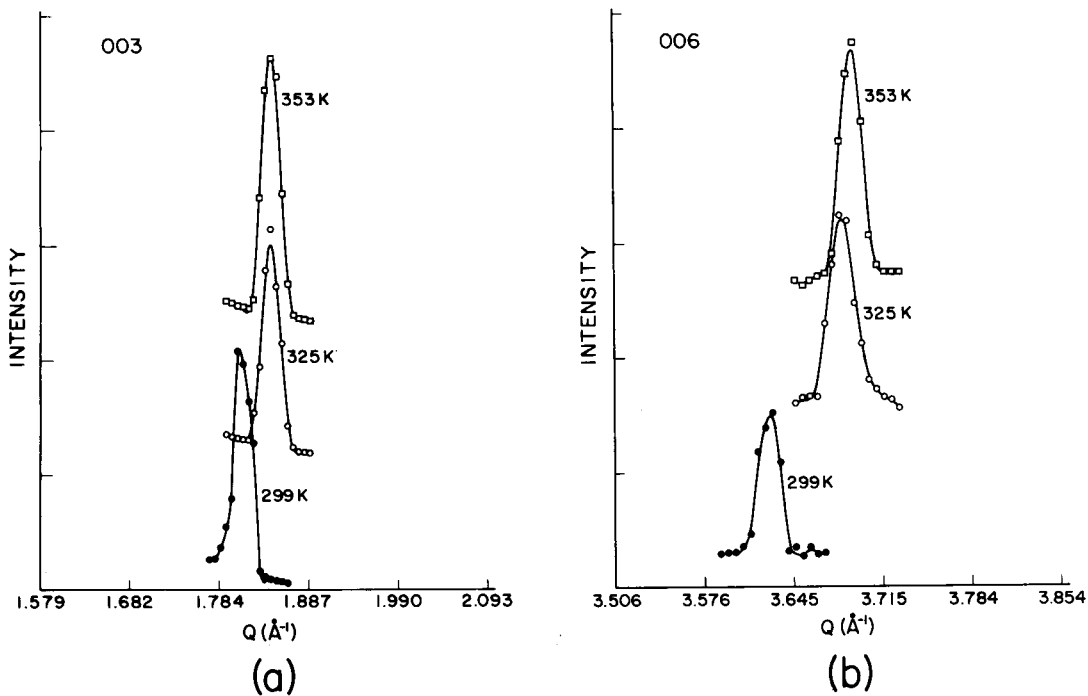


Fig. 2. Two 00 l X-ray diffraction peaks at various temperatures during heating: (a) 003, (b) 006.

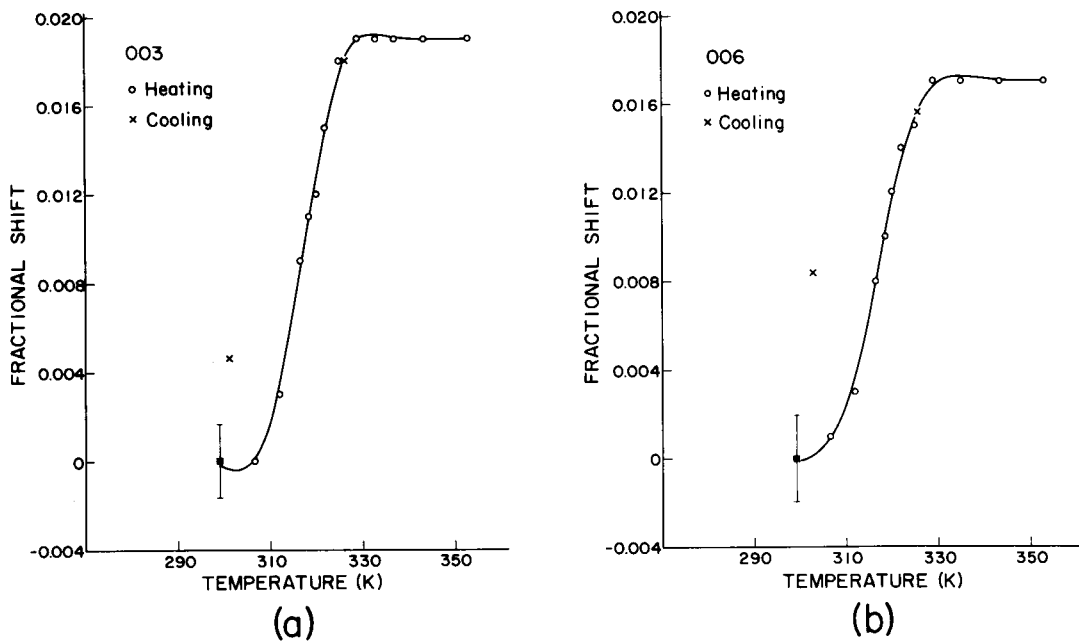


Fig. 3. Fractional shifts of two 00 l X-ray diffraction peaks versus the temperature during heating and cooling: (a) 003, (b) 006.

the fact that the superlattice lines gradually disappeared with increasing temperature means that a stage change cannot be ruled out. We conclude that the effect reported here is most probably due to a change of the carbon–bromine–carbon sandwich thickness rather than a change of stage. That the observed change took place at the I–C transition temperature further supports this interpretation.

That the commensurate (C) phase has a smaller sandwich thickness than the incommensurate (I) phase suggests that the bromine atoms are less coplanar in the I phase. This is consistent with the contention that the I phase has a smaller unit cell along the a axis [1].

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