Structure and Phase Transitions of Graphite Intercalated With Bromine

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Abstract. This paper reviews the current status of understanding of the structure and phase transitions of graphite-bromine intercalation compounds. Emphasis is given to the room temperature commensurate phase, the room temperature incommensurate phase and the high temperature incommensurate phase, together with the associated commensurate-incommensurate, incommensurate-commensurate and melting transitions.

Introduction

An attractive property of graphite intercalation compounds is the high electrical conductivity in the in-plane direction. The highest conductivities in these materials are found in acceptor compounds, e.g. $SbCl_5$, AsF_5, ICl[1] etc. However, that these intercalates are not pure elements complicates their structure. Bromine is practically the only elemental acceptor intercalate, so it is attractive for a fundamental study.

Synchrotron single crystal x-ray diffraction results have established the in-plane structure of the room temperature commensurate (β) phase of stage-2 graphite-bromine.[2,3] The solution of this structure has opened up new ground for understanding the behavior of this phase, for which much information is available in the literature. Furthermore, it sheds light on the structure of other graphite-bromine phases, such as the room temperature incommensurate (γ) phase[4,5] and the high temperature incommensurate (α) phase.[6,7] For these incommensurate phases, domain wall models have been found to agree with the experimental data, but the in-plane structures of these phases have not been fully established.[5,7] Other than the β, γ and α phases, three other phases (δ, ε, η) have been observed at lower temperatures, though their in-plane diffraction patterns have not been interpreted. Differential scanning calorimetry and x-ray diffraction showed that the δ-γ phase transition occurs at 297 K[6,8,9] and the ε-δ phase transition occurs at 277 K.[6,8-10] Moreover, x-ray diffraction[6] showed that the η-ε phase transition occurs at 226 K and that this transition corresponds to the change from streaks to spots in the electron diffraction pattern.[6,11] The various observed phase transition temperatures are summarized in Table 1, where Type B refers to stage 2 prepared in liquid bromine at room temperature, Type A refers to stage 2 prepared in vapor bromine at room temperature, and Type C refers to an indefinite stage(s) obtained by deintercalation (or desorption) of Type A.

The current status of knowledge on each phase is summarized in the following sections.

Phase β

Phase β refers to the room temperature commensurate phase. It is the most commonly seen phase of graphite-bromine, exhibiting a three-fold twinned monoclinic unit cell ($a = 8.87$ Å, $b = 4.26$ Å, $\gamma = 103.9°$)[2], with negligible correlation between the intercalate layers, as indicated by Bragg rods along the c*-direction.[12,13]

The in-plane structure of Phase β has been solved for Type A (stage-2 C_7Br)[3] and Type C (overall stoichiometry of $C_{35}Br$)[14] at room temperature.

Phase γ

Phase γ refers to the room temperature incommensurate phase. It had been observed in stage-2 graphite-bromine prepared in bromine liquid, i.e. Type B.[4,5] This phase was also observed in a saturated stage-2 compound (of nominal composition C_8Br) prepared by using the two-zone furnace technique.[9]

Table 1 Phase transition temperatures of graphite-bromine

Transition Type	Transition Temperature (K)				
	Stage 2		Stage 3	Stage 4	Type C (desorbed from Type A)
	Type B	Type A			
α-L				373[12]	374[6,8,10]
β-α	332[4]	333[4]	337[4]	342[4,7,12]	350[4]
γ-β	319[4,5]				
δ-γ	297[9]				
ε-δ	277[9]				
η-ε					226[6]

L: Liquid phase
β: Commensurate solid phase
α, γ: Incommensurate solid phases
δ, ε, η: Other solid phases

Fig. 1 of Ref. 4 and Fig. 5 of Ref. 9 show the in-plane diffraction pattern of Phase γ. It suggests that the bromine chains along the b-direction in Phase γ are periodically spaced along the a-direction, while the atom-to-atom correlation along the b-direction among the chains is limited.[4,5] The situation is thus quasi one-dimensional.[5] A one-dimensional analysis showed that Phase γ probably exhibits domains with Marti and Thorel type unregistry.[15]

Upon heating Type B, Phase γ transforms reversibly to Phase β at 319±1 K.[4,5] This is termed an incommensurate-commensurate (γ-β) transition.[4,5] Upon further heating Type B, Phase β transforms reversibly to Phase α at 332 K[4]; this is the commensurate-incommensurate (β-α) transition which was also observed in stage 2 (Type A)[4], stage 3[4], stage 4[4,7,12] and Type C.[4] Phase γ (the low temperature incommensurate phase) is much more incommensurate than Phase α (the high temperature incommensurate phase).[4] The γ-β transition is characterized by the disappearance of the incommensurate peaks at $Q_c(1-0.033)$ and $Q_c(1+0.058)$ and the appearance of the commensurate peak at Q_c,[5] in contrast to the slight shifts of the peaks in the β-α transition.[6,7] The critical exponent was 0.25. Moreover, the 00ℓ peaks shifted reversibly at the γ-β transition,[16] indicating a change of the sandwich thickness from 10.40±0.01 Å for Phase γ to 10.22 ±0.01 Å for Phase β.[16]

Phase α

Phase α refers to the high temperature incommensurate phase.[6,7,12] It is not as incommensurate as Phase γ. It had been reported to be a stripe domain phase of the Frank and van der Merwe type with 4π/7 phase shifts.[12] The incommensurability as a function of reduced temperature exhibits a power law with an exponent of 0.50±0.02.[12] Furthermore, power-law behavior at five harmonics ($\vec{G}$) of the mass density wave had been demonstrated and the scaling of the structure factor with G^2 had been confirmed.[17]

The β-α (commensurate-incommensurate) transition had been observed reversibly in stage 2 (Type B) at 332 K[4], in stage 2 (Type A) at 333 K[4], in stage 3 at 337 K[4], in stage 4 at 342 K[4,7,12] and in Type C at 350 K[4]. Thus, the β-α transition temperature appears to increase with increasing stage number.[4] Disordering was observed upon completion of the β-α transition, so the β-α transition is an order-disorder transition involving the change of an ordered commensurate phase to a disordered incommensurate phase.[4,18]

Upon heating Phase α undergoes a continuous melting transition[6,12,18-20] from a two-dimensional solid phase to an anisotropic liquid phase at 373.41 K.[12] Differential scanning calorimetry (DSC) revealed that the melting transition involves two steps. The first step gave a DSC peak at 373.0 K (enthalpy change = 178 cal $mole^{-1}$ Br_2); the second step gave a peak at 375.5 K (enthalpy change = 26 cal $mole^{-1}$ Br_2).[21]

Phase δ

Phase δ refers to the phase exhibiting the in-plane diffraction pattern shown in Fig. 6 (b) of Ref. 9. The phase was observed by x-ray diffraction upon cooling Phase γ below 297 K.[9] Differential scanning calorimetry revealed an endothermic peak at 297 K during heating.[6,8] Upon cooling, an exothermic peak was observed at 286 K.[6,8] Since the diffraction pattern has not been interpreted, neither the in-plane unit cell nor the in-plane atomic arrangement is known.

Phase ε

Phase ε refers to the phase exhibiting the in-plane diffraction pattern shown in Fig. 6 (c) of Ref. 9. The phase was observed by x-ray diffraction upon cooling Phase δ below 277 K.[9] Differential scanning calorimetry revealed an endothermic peak at 277 K during heating.[6,8,10] However, a corresponding exothermic peak at or below the transition temperature was not observed upon cooling.[6,8]

Phase η

Phase η refers to the phase exhibiting the diffraction pattern shown in Fig. 5 of Ref. 6. It was observed by x-ray diffraction upon cooling Type C below 226 K.[6] The transition corresponds to the change of streaks to spots in the electron diffraction pattern on cooling,[6,11] and it does not give rise to any calorimetry peak.[6] The appearance of sharp spots upon cooling $C_{14}Br$ between 240 and 230 K[22] is probably the same as the transition to Phase η observed in Type C at 226 K.[6]

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