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PHASE TRANSITIONS IN GRAPHITE–HALOGENS*

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Summary

X-ray diffraction and differential scanning calorimetry (DSC) were used to study the phase transitions in graphite–halogens (Br_2, ICl). In graphite–Br_2, a reversible transition associated with the melting of the ordered intercalate layers into liquidlike layers was observed at 373.7 K, and a transition corresponding to the change of streaks to spots in the (0001) zone electron diffraction pattern on cooling was observed at 226 K. Moreover, a transition at 277 K has been tentatively interpreted as being due to a phase transition associated with the stacking order of the intercalate layers. In addition, in graphite–Br_2, the first observation was made of a phase transition involving the shifting of various X-ray diffraction peaks in various directions at ~340 K. This transition is tentatively interpreted as being due to a commensurate–incommensurate phase transition. In graphite–ICl, reversible transitions were observed at 307 and 314 K. The 314 K peak is associated with the melting of the ordered intercalate layers into liquidlike layers; the 307 K peak is due to a phase transition associated with the stacking order of the intercalate layers.

Introduction

Graphite intercalation compounds exhibit phase transitions which affect the stability [1] and the properties [2, 3] of these compounds. Therefore, information on the phase transitions is essential for the application of graphite intercalation compounds at various temperatures.

This paper focuses on the use of X-ray diffraction and differential scanning calorimetry (DSC) to study the phase transitions in graphite–

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halogens (Br_2, ICl). Particular attention is given to the phase transition associated with the intralayer intercalate ordering.

Experimental

X-ray diffraction

Although considerable X-ray diffraction work has been done previously to study the crystal structure of graphite intercalation compounds, most of the information reported is concerned with the stage ordering (the stacking order of the carbon and the intercalate layers), as obtained from $00l$ diffraction lines. Information about the in-plane structure of the intercalate layers, as can be obtained from $hk0$ lines, is scant. This is because most of the X-ray diffraction work was conveniently performed by reflection of the X-ray beam off the c-face (the cleavage plane) of compounds based on highly-oriented pyrolytic graphite (HOPG). We report here a reflection geometry in which the X-ray beam is reflected off the a-face of compounds based on HOPG. This method is complementary to electron diffraction; the latter remains the most convenient method of observing the (001) reciprocal lattice plane [4], whereas the former provides quantitative intensity measurement.

In order to perform X-ray diffraction by reflection off the a-face, we used samples the surface area of which along the c-direction is much greater than that perpendicular to the c-direction. The samples were obtained from HOPG with a large thickness along the c-direction by cutting with a low speed diamond saw. Because optical flatness is not required for X-ray diffraction work, no subsequent surface preparation procedure [4] is necessary. The orientation of the sample with respect to the X-ray beam is illustrated in Fig. 1. Due to the texture of HOPG, all the diffraction vectors nearly lie on the basal plane, so the $hk0$ lines are observed. Of importance is that the geometry shown in Fig. 1 for an ideal HOPG sample does not permit the observation of any lines other than $hk0$ lines. This implies that this geometry yields $hk0$ lines that are more intense than the corresponding ones obtained on powder samples.

In this work, X-ray diffractometry was performed by using a Siemens diffractometer system with monochromated Cu Kα radiation. Data collection was carried out by using a multichannel analyzer.

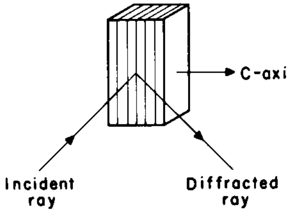

Fig. 1. X-ray diffraction geometry for observation of the intralayer ordering in samples based on highly-oriented pyrolytic graphite.

Differential scanning calorimetry

Calorimetry was performed by using a Perkin-Elmer DSC-2 differential scanning calorimeter, which is programmed to vary the average temperature of the sample pan and the reference pan (typically empty) at a constant rate, such as 10 K/min. Differential power is supplied to keep the temperature of the sample pan equal to that of the reference pan. As the average temperature changes, the power supplied to the sample with respect to the reference is constant, except when the sample undergoes a phase transition involving latent heat. When this occurs, the power supplied to the sample changes with respect to that supplied to the reference and results in a maximum or a minimum on the strip-chart recorder trace. The transition temperature is defined as the temperature corresponding to the intersection of the leading edge of the DSC trace with the baseline.

In order to determine the enthalpy change per mole of intercalate due to a phase transition, sample weight was obtained both before and after a DSC run with a Perkin-Elmer AD-2Z microbalance, which had an uncertainty of ±0.002 mg.

During the DSC measurement, the sample was mounted in an unsealed aluminum pan with an aluminum cover; the sample holder was purged with dry argon at 20 cm^3/min.

Sample preparation

Samples were prepared by vapor phase intercalation of highly-oriented pyrolytic graphite (HOPG). Graphite–ICl (graphite–Br_2) of various intercalate concentrations were prepared by using ICl–CCl_4 (Br_2–CCl_4) solutions. X-ray diffractometry was used to obtain information on the stage.

Because of intercalate desorption, which increases in rate as the temperature increases and becomes anomalously fast near the intralayer order–disorder transition [1], X-ray diffraction was performed as a function of temperature on samples which had been desorbed at a temperature above the temperature range of interest to the diffraction experiment. The use of desorbed samples minimised the variation of the intensity due to desorption. This is in contrast to earlier work on graphite–alkali metals [5] which used low stage samples without prior desorption. On the other hand, the use of desorbed samples restricts the investigation to relatively dilute (high stage) samples. However, because of the independence of the intralayer intercalate ordering on the intercalate concentration in graphite–halogens [4], this restriction is not of concern to the study of the in-plane phase transitions in graphite–halogens.

Results

Graphite–Br_2

The X-ray diffraction pattern of dilute graphite–Br_2 at 298.7 K is shown by a full line in Fig. 2. The pattern was obtained with the geometry

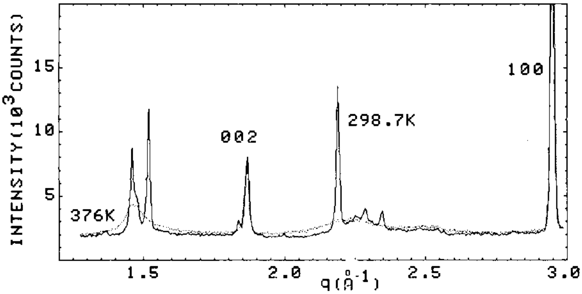

Fig. 2. X-ray diffraction pattern of graphite–Br_2 at 298.7 K (full line) and at 376.0 K (dotted line).

illustrated in Fig. 1, using Cu Kα radiation (λ = 1.542 Å). Besides the various $hk0$ intercalate peaks and the 100 graphite peaks, there is a relatively intense graphite 002 peak at q = 1.87 $\mathrm{\AA}^{-1}$, where q is defined as

$$q = \frac{4\pi \sin \theta}{\lambda}. \tag{1}$$

The 002 peak is observed in this geometry possibly because of scattering from the edge.

Similar measurements have been made on graphite–Br_2 compounds covering the entire range of intercalate concentration. The diffraction pattern was found to be qualitatively independent of the intercalate concentration, except that the relative intensities of the intercalate peaks and graphitic peaks increased with intercalate concentration. The observation that the in-plane diffraction pattern does not change with intercalate concentration is consistent with electron diffraction results [4].

As the sample temperature was raised, the intercalate peaks gradually decreased in intensity and finally vanished at 373.7 K, leaving diffused peaks characteristic of a disordered phase with a short-range order. Shown by a dotted line in Fig. 2 is the X-ray diffraction pattern of graphite–Br_2 at 376 K. This transition at 373.7 K corresponds to the melting of the intercalate layers. The transition temperature obtained is in agreement with the results of electron diffraction [4] and calorimetry [6].

Three intercalate peaks at different temperatures below 373.7 K are shown in Fig. 3. Of significance is that the peak positions shift as the temperature is changed. The variation of the positions of the peaks at $q \sim 1.46$ $\mathrm{\AA}^{-1}$ and $q \sim 2.2$ $\mathrm{\AA}^{-1}$ with temperature is shown in Fig. 4. Note that the peaks shift in opposite directions and the shift occurs for both peaks at ~340 K. This is interpreted as being due to a commensurate–incommensurate phase transition at ~340 K.

In addition, a structural transition was observed in graphite–Br_2 at ~226 K. Figure 5 shows the diffraction pattern obtained at ~80.0 K. In the range of q from 2.2 to 3.0 $\mathrm{\AA}^{-1}$, numerous small, sharp peaks appear on cooling below ~226 K. This transition involves only some of the in-plane superlattice peaks and corresponds to the change of streaks to spots in the (0001)

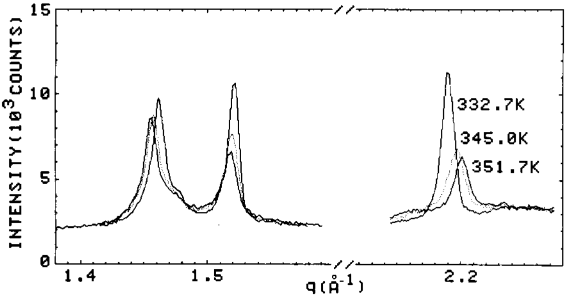

Fig. 3. A portion of the X-ray diffraction pattern of graphite–Br_2 at 332.7, 345.0 and 351.7 K. All three peaks are due to the intercalate.

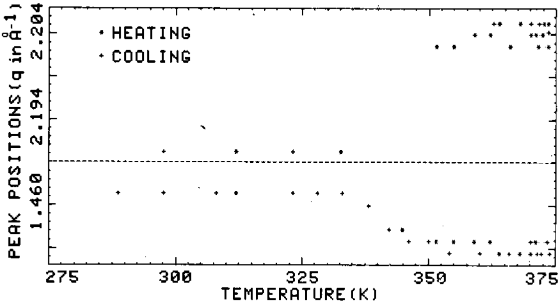

Fig. 4. Variation of peak position with temperature for the peaks at $q \sim 1.46$ Å^{-1} and 2.2 Å^{-1}.

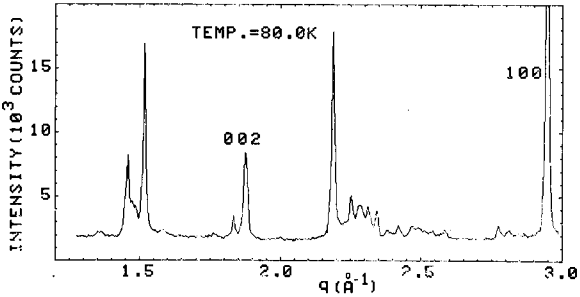

Fig. 5. X-ray diffraction pattern of graphite–Br_2 at 80.0 K.

zone electron diffraction pattern on cooling graphite–Br_2 from room temperature to liquid nitrogen temperature [4, 7]. This transition is probably associated with the orientation ordering of the intercalate molecules within an intercalate layer.

Figure 6 shows the integrated intensity of the intercalate peak at $q \sim 1.52$ Å^{-1} as a function of temperature. The intensity falls as the temperature increases and becomes zero at 373.7 K. In addition, a decrease in intensity was observed at ~340 K. This observation correlates with the appearance of

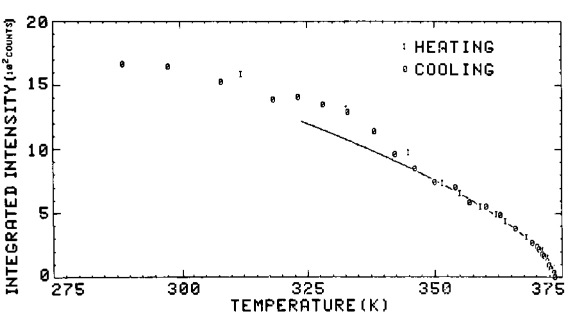

Fig. 6. Variation of the integrated intensity with temperature for the peak at $q \sim 1.52$ $Å^{-1}$.

an incommensurate phase at ~340 K. Also shown in Fig. 6 is the fit of the intensity *vs.* temperature curve to a power law, which gives the critical exponent $\beta \cong 0.32$ for the 373.7 K transition. Because of the incompletely known in-plane crystal structure of graphite–Br_2, the interpretation of this value of β is not pursued in this work.

Shown in Fig. 7 is the DSC thermogram of graphite–Br_2 obtained during heating. Three endothermic peaks are observed in the temperature range 220 - 390 K. They occur at 277, 297 and 373 K. On cooling, exothermic peaks were observed at 373 and 286 K. The 373 K peak has been identified as being due to the melting of the intercalate layers, as indicated by electron [4] and X-ray diffraction results.

The concentration dependence of the apparent enthalpy changes of the 277 and 373 K peaks is shown in Fig. 8. Because of exfoliation, which occurs at ~350 K for high concentration graphite–Br_2 [1], information relating to the 373 K peak could only be obtained on dilute samples. The data on the

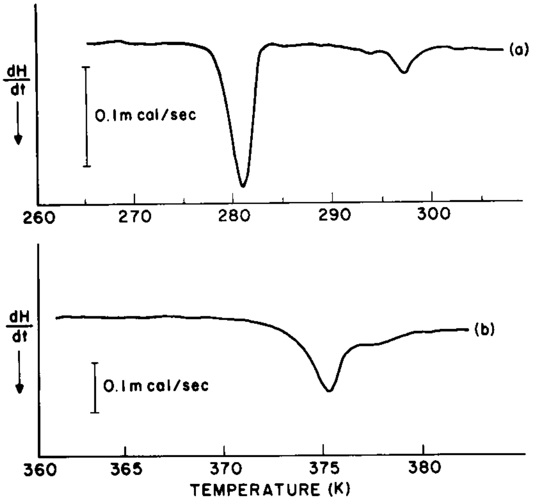

Fig. 7. DSC thermograms of graphite–Br_2 during heating.

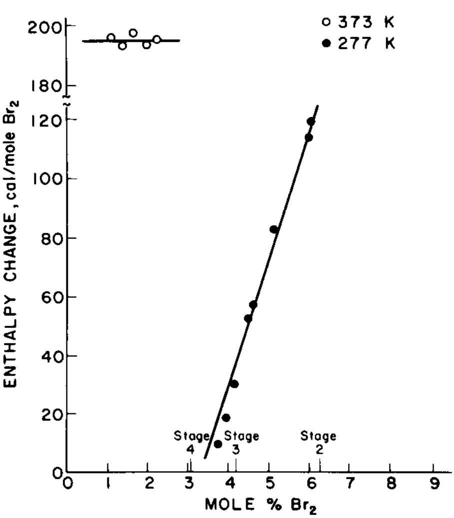

Fig. 8. Dependence of the apparent enthalpy change on intercalate concentration for the 277 and 373 K peaks of graphite–Br_2.

277 K peak were obtained during desorption of a stage 2 graphite–Br_2 compound. As shown in Fig. 8, the enthalpy change of the 277 K peak decreases as the Br_2 concentration decreases; the enthalpy change is 123 cal/mole Br_2 at ~6 mol% Br_2 (stage 2) and decreases monotonically to zero at ~3.5 mol% Br_2 (between pure stage 3 and pure stage 4).

In addition to measurement on graphite–Br_2 obtained by desorption from a stage 2 compound, we prepared a stage 3 graphite–Br_2 compound by using a Br_2–CCl_4 solution. X-ray diffraction indicated that no stage 2 component existed in the sample. No DSC peak was observed in this sample at 277 K. Therefore, only the stage 2 component contributes to the enthalpy change of the 277 K peak of graphite–Br_2.

We tentatively interpret the 277 K peak as being due to a phase transition associated with the stacking order of the intercalate layers and that only stage 2 exhibits such a transition. Due to exfoliation, the behavior of stage 2 at 373 K is not known. The three-dimensional ordering of stage 2 at 77 K is suggested by the X-ray diffraction results of Eeles and Turnbull [7].

Graphite–ICl

A similar X-ray diffraction investigation was carried out on dilute graphite–ICl in which one reversible transition was observed at 314 K, in agreement with electron diffraction [4] and calorimetry [6] results. Figure 9 shows X-ray diffraction patterns of graphite–ICl at 79.5 and 321 K, respectively. This transition is similar in nature to the 373 K transition of graphite–Br_2, *i.e.*, it involves the disordering of the intercalate layers on heating.

Shown in Fig. 10 are DSC thermograms obtained, during heating, for graphite–ICl of various intercalate concentrations. Two endothermic peaks were observed at 307 and 314 K. On cooling, exothermic peaks were ob-

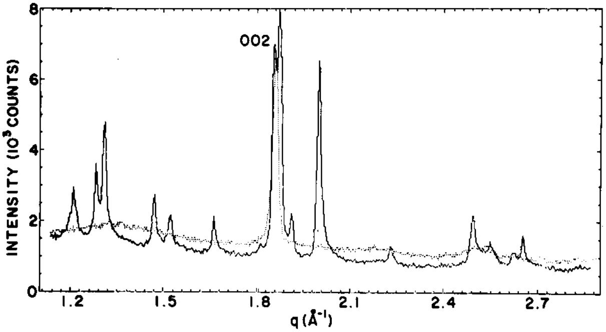

Fig. 9. X-ray diffraction patterns of graphite–ICl at 79.5 K (full line) and 321 K (dotted line).

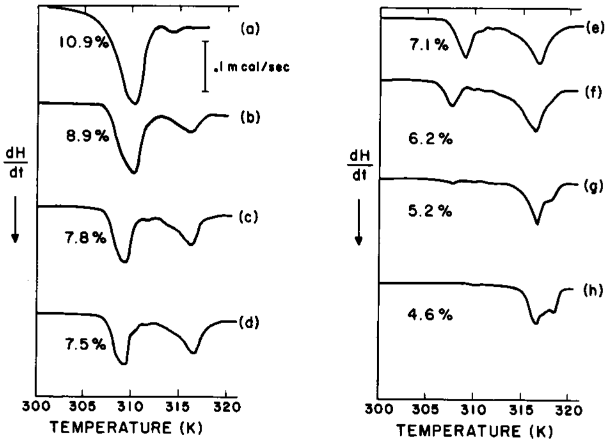

Fig. 10. DSC thermograms of graphite–ICl of various intercalate concentrations (in mol% ICl) during heating.

served at 310 and 302 K. The temperatures of both peaks are independent of the intercalate concentration, but the size of each peak is strongly dependent on the intercalate concentration. The different intercalate concentrations (in mol% ICl) were obtained by desorption of a stage 1 compound for various lengths of time. The size of the 307 K peak decreases as the ICl concentration decreases, whereas that of the 314 K peak increases as the ICl concentration decreases. The concentration dependence of the enthalpy change (in cal/mol intercalate) of each peak is graphically shown in Fig. 11. The apparent enthalpy change of the 307 K peak is 500 cal/mol ICl at 12.5 mol% ICl (stage 1) and decreases monotonically to zero at ~5 mol% ICl (stage 2 - 3). On the other hand, the apparent enthalpy change of the 314 K peak is zero at 12.5 mol% ICl, increases monotonically to 570 cal/mol ICl at ~4 mol% ICl, and is constant for concentrations less than ~4 mol% ICl.

To identify the two DSC peaks with structural transitions, consider the results of electron and X-ray diffraction. The X-ray diffraction results of

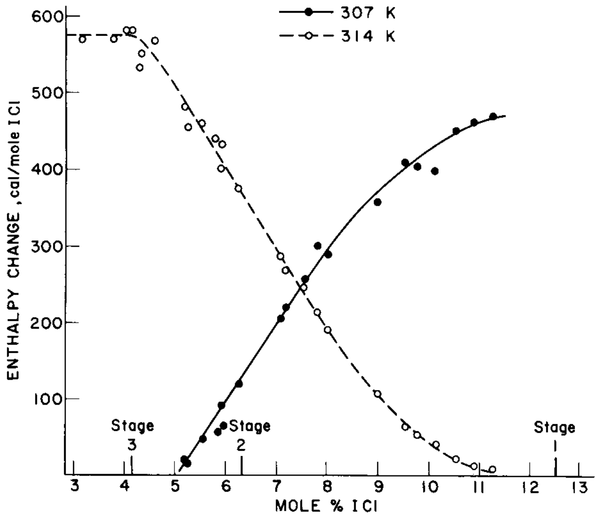

Fig. 11. Dependence of the apparent enthalpy change on intercalate concentration for the 307 and 314 K peaks of graphite–ICl.

Turnbull and Eeles [8] showed that graphite–ICl at 304 K has a three-dimensional crystal structure for stage = 1, but is nearly two-dimensionally ordered for stage ≥2. A two-dimensional ordering means that there is ordering within an intercalate layer but there is no correlation between different intercalate layers. The electron diffraction work of Chung [4] showed that graphite–ICl undergoes in-plane melting of the intercalate at 316 ± 10 K. This observation has been confirmed in this work by X-ray diffraction. Combination of the above diffraction results indicates that:

(i) for stage 1 graphite–ICl, there is a phase transition at a temperature between 304 and 316 K, because the ICl intercalate forms a three-dimensional structure at 304 K and is disordered at temperatures above 316 ± 10 K,

(ii) for graphite–ICl of stage ≥2, there is a change from nearly two-dimensional order to disorder at 316 ± 10 K.

Therefore, the 314 K DSC peak is identified as being due to the melting of the intercalate layers. Since the temperature of the phase transition associated with the stacking of the intercalate layers should be lower than that of the melting of the intercalate layers, we interpret the 307 K DSC peak as being due to a phase transition associated with the stacking order of the intercalate layers.

This interpretation of the 307 K DSC peak is consistent with the concentration dependence of the apparent enthalpy change (Fig. 11). The decrease of the apparent enthalpy change of the 307 K peak as the intercalate concentration decreases is expected, from the fact that no interlayer phase transition between 304 K and 316 K was observed for stage ≥ 2. As the originally stage 1 sample undergoes desorption, *i.e.*, as the intercalate concentration decreases, the sample becomes a mixture of stages. Since only stage 1 contributes to the 307 K peak's enthalpy change, which is normalized by the total ICl concentration to be in units of cal/mol ICl, the enthalpy change decreases as the concentration decreases and is zero when there is no stage 1 component in the sample. Since a partially desorbed sample of concentration corresponding to that of a pure stage 2 compound is a mixture of stages, and thus is partly stage 1, the stage 1 component vanishes at an overall sample concentration between that corresponding to a pure stage 2 compound and that of a pure stage 3 compound. This explains the fact that the extrapolation of the enthalpy change *vs.* concentration curve for the 307 K peak in Fig. 11 intersects the zero enthalpy change axis at a concentration between stage 2 and stage 3 rather than at the stage 2 concentration.

To give further evidence for the association of the 307 K peak with the stage 1 component of a sample, we prepared stage 2 graphite–ICl by using a solution of ICl in CCl_4. X-ray diffraction confirmed that there was no stage 1 component in the sample. Indeed, no DSC peak was observed in this sample at 307 K.

The interpretation of the 314 K DSC peak as the melting of the intercalate layers is also consistent with the concentration dependence of the enthalpy change (Fig. 11). Since the in-plane bonding is essentially not affected by the change in concentration, the enthalpy change of the intralayer phase transition should be independent of the concentration. Figure 11 shows that the enthalpy change of the 314 K peak is independent of the concentration for low concentrations and decreases to zero at high concentrations. This observation can be explained by assuming that the three-dimensional structure of the intercalate in a stage 1 compound is completely disordered on heating through 307 K. In other words, both the in-plane ordering and the stacking ordering of the intercalate layers are lost at 307 K. This assumption is suggested by the diffraction data of Turnbull and Eeles [8] but further X-ray diffraction work is needed for its verification. The assumption indicates that a completely stage 1 compound does not exhibit the 314 K DSC peak, but exhibits only the 307 K peak. Thus, only stages $\geqslant 2$ contribute to the 314 K peak's enthalpy change.

To give further evidence for the association of the 314 K peak with the components of stage $\geqslant 2$, we prepared stage 2 graphite–ICl, *i.e.*, no stage 1 component. The enthalpy change of the 314 K peak of this sample remained constant at ~570 cal/mole ICl as the sample desorbed. Thus the enthalpy change is indeed independent of the concentration for stage $\geqslant 2$.

Discussion

Diffraction and calorimetry have been found to be complementary experimental techniques in studying the phase transitions in graphite intercalation compounds. Calorimetry serves to detect phase transitions and to provide thermodynamic information on the transitions. On the other hand, diffraction is indispensable for identification of the phase transitions to certain structural changes.

The intensities of the various X-ray diffraction peaks have been found to vary rather smoothly with temperature before vanishing at 373.7 K, indicating that the 373.7 K transition is a continuous phase transition. This conclusion is consistent with the absence of a sharp ending of each DSC peak on completion of the phase transition. It is also consistent with the observed increase in specific heat (C_p) on disordering.

In this work, we have made the first X-ray diffraction observation of a phase transition involving an incommensurate phase in graphite intercalation compounds. This observation was made in dilute graphite–Br_2 at ~340 K.

Diffraction and DSC results strongly suggest that stage 1 graphite–ICl loses both interlayer and intralayer intercalate ordering at 307 K and that the intercalate in graphite–ICl of stage $\geqslant 2$ undergoes two-dimensional melting at 314 K.

Consider the interlayer and intralayer bonding between intercalate molecules. The distance between nearest intercalate layers in stage 1 graphite–ICl is ~7 Å. Although the in-plane crystal structure of graphite–ICl is not completely known, a rough estimate of the average in-plane distance between adjacant IC1 molecules is ~8.5 Å, which is the value in stage 1 graphite–K [9]. Thus the interlayer and intralayer spacings between nearest intercalate molecules are comparable in stage 1 graphite–ICl. This implies that, in stage 1 graphite–ICl, the intercalate layers are so close together that the bonding between ICl molecules in different layers is comparable with that between molecules in the same layer. Thus, when the interlayer bonding is broken as the temperature is raised, the intralayer bonding is broken too. This is a possible explanation for the fact that stage 1 graphite–ICl loses both intralayer and interlayer intercalate ordering at 307 K.

For stage 2 graphite–ICl, the distance between adjacent intercalate layers is 10.35 Å. This relatively large distance reduces the interaction between intercalate layers so that the intercalate ordering is nearly two-dimensional even at temperatures below 307 K.

Acknowledgements

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