

CALORIMETRIC STUDY OF THE PHASE TRANSITIONS IN GRAPHITE INTERCALATED WITH IODINE MONOCHLORIDE [☆]

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Differential scanning calorimetry on graphite-ICl intercalation compounds of stages 1–4 showed that the melting temperature of graphite-ICl increases with stage, such that the melting temperature is 305, 309, 311, 312 and 315 K for stages 1, 2, 3, 4, and the residue material, respectively.

1. Introduction

Graphite intercalated with iodine monochloride (ICl) has recently received considerable attention. Interesting new observations include that the electrical conductivity is ≈ 70 –80 times that of graphite [1] and the pressure-induced change from second-stage $C_{16}ICl$ to third-stage $C_{24}ICl$ at <12 kbar [2]. Much of this progress was made possible by the establishment of a two-bulb method for preparing graphite-ICl of stages 1 to 5 [3]. By using this method we prepared graphite-ICl of stages 1 to 4 and then we investigated the melting transition as a function of stage.

The melting transition in graphite-ICl (dilute) was first observed by electron diffraction as the disappearance of all the in-plane superlattice lines at 316 ± 10 K [4]. The observation was confirmed by X-ray diffraction, which gave a transition temperature of 315 K [5,6] for dilute graphite-ICl.

Differential scanning calorimetry (DSC) of graphite-ICl had been previously performed for different intercalate concentrations which were obtained by desorption of stage 1 compound for various lengths of time. It revealed two endothermic peaks during heating. The peak at 314 K was large at low intercalate concentrations and was attributed to stages ≥ 2 . The

peak at 307 K was large at high intercalate concentrations and was attributed to stage 1 [5]. In this work, DSC was performed on graphite-ICl of stages 1–4, which were found to correspond to four different peaks, such that the transition temperature increases with increasing stage.

2. Experimental techniques

The graphite material used was highly oriented pyrolytic graphite, which was kindly provided by Union Carbide Corporation. Graphite-ICl compounds of stages 1–4 were prepared by using a two-bulb method in which the ICl liquid was at temperature T_0 while the graphite sample was at temperature T [3]. T_0 was $25 \pm 2^\circ\text{C}$ (room temperature) for all stages; T was $25 \pm 2^\circ\text{C}$ (room temperature) for stage 1, $60 \pm 5^\circ\text{C}$ for stage 2 (together with a smaller amount of stage 1), $70 \pm 5^\circ\text{C}$ for stage 3, and $75 \pm 5^\circ\text{C}$ for stage 4. The ICl liquid and graphite were in different ends of a sealed glass tubing, which was not evacuated.

The stage was evaluated by 001 X-ray diffraction, using a Siemens diffractometer system with Cu K α radiation. Immediately (<1 min) after removing the sample from the reaction vessel, the sample was sealed without evacuation in a teflon sample holder and then observed by X-ray diffraction.

Calorimetry was performed by using a Perkin–

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Elmer DSC-2 differential scanning calorimeter. The heating rate used was 10 K/min. Immediately (<1 min) after removing the sample from the reaction vessel, the sample was sealed without evacuation in a stainless-steel DSC pan (with an O-ring). The sample holder was purged with dry nitrogen during the DSC measurement. The temperature had an accuracy of ± 1 K. The differential power sensitivity was 1 mcal/s full scale.

Diffraction and calorimetry were performed on different samples prepared under the same conditions.

3. Experimental results

Fig. 1 shows X-ray diffraction patterns of pristine

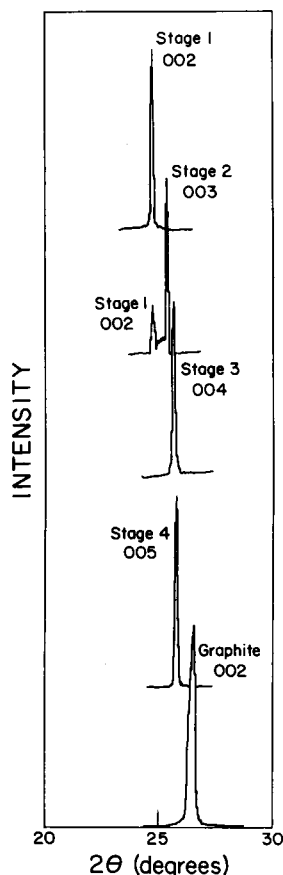


Fig. 1. X-ray diffraction patterns of graphite-ICl of stage 1 (top), stage 2 (together with a smaller amount of stage 1), stage 3 and stage 4, and pristine graphite (bottom). The vertical scales are not all the same for the five traces, which are intended to show the shifts in the peak positions.

Table 1

Calculated d values of various 00 l lines of stage 1 to stage 5

00 l	d (Å)				
	stage 1	stage 2	stage 3	stage 4	stage 5
001	7.200	10.550	13.900	17.250	20.600
002	3.600	5.275	6.950	8.625	10.300
003	2.400	3.517	4.633	5.750	6.867
004	1.800	2.637	3.475	4.312	5.150
005	1.440	2.110	2.780	3.450	4.120
006	1.200	1.758	2.317	2.875	3.433
007	1.029	1.507	1.986	2.464	2.943

graphite and graphite-ICl of stage 1, stage 2 (together with a smaller amount of stage 1), stage 3 and stage 4. Table 1 lists the calculated d values of various 00 l lines of stage 1 to stage 5. These values were calculated by using a carbon-carbon layer spacing of 3.350 Å and a carbon-intercalate layer spacing of 3.600 Å. For a given stage n , the strongest 00 l line is the 0, 0, $n + 1$ line (a well-known fact for many intercalation compounds). The calculated and experimental d values of these strongest lines for stages 1–4 are listed in table 2. Thus, the indexing of the lines in fig. 1 is firm and thereby the stage assignment is also firm.

Fig. 2 shows DSC thermograms of samples prepared as for those of fig. 1. Stage 1 shows a single peak at 305 K. Stage 2 (with some stage 1) shows a peak at 309 K and a smaller peak at 303 K (due to stage 1). Stage 3 shows a single peak at 311 K. Stage 4 shows a single peak at 312 K.

The DSC thermograms of fig. 2 were obtained dur-

Table 2

Calculated and experimental d values of the strongest 00 l lines of stages 1–4

Stage	00 l	d (Å)	
		experimental	calculated
1	002	3.60	3.600
2	003	3.52	3.517
3	004	3.47	3.475
4	005	3.45	3.450
graphite	002	3.36	3.350

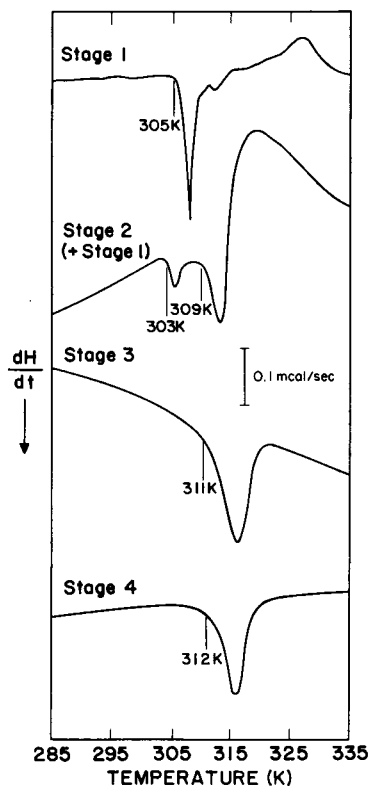


Fig. 2. DSC thermograms of samples prepared as for those of fig. 1.

ing the first heating. Due to intercalate desorption, subsequent heating cycles yielded peaks corresponding to higher stages. Fig. 3 shows DSC thermograms of the initially stage 1 sample during first, second and third heating. During the first heating beyond the melting temperature, a broad exothermic peak was observed. This exothermic peak is attributed to intercalate desorption, which is faster beyond the melting temperature, as had been shown by thermogravimetric analysis [7]. Intercalate desorption caused a decrease in sample weight, thereby causing a decrease in the sample's heat capacity, and thus resulted in an apparent exothermic effect. Although a single peak at 305 K was obtained during first heating, four peaks were obtained during second and subsequent heating. This means that desorption caused stage 1 to change to a mixture of stages 1–4. Fig. 4 shows DSC thermograms of the initially stage 4 sample during first, second and

Fig. 4. DSC thermograms of the initially stage 4 sample during first, second and third heating.

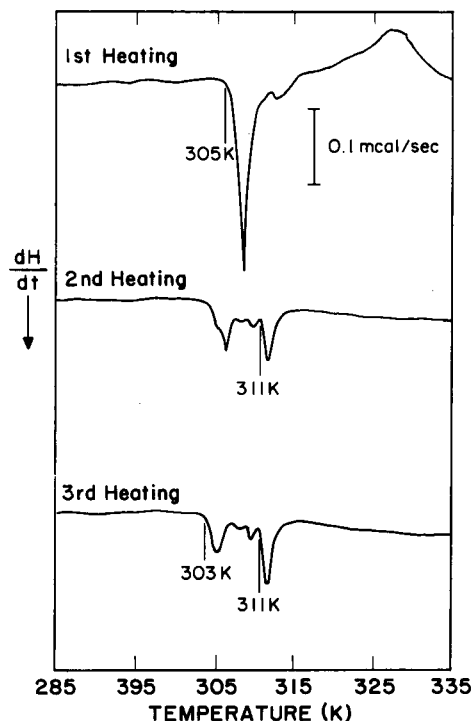
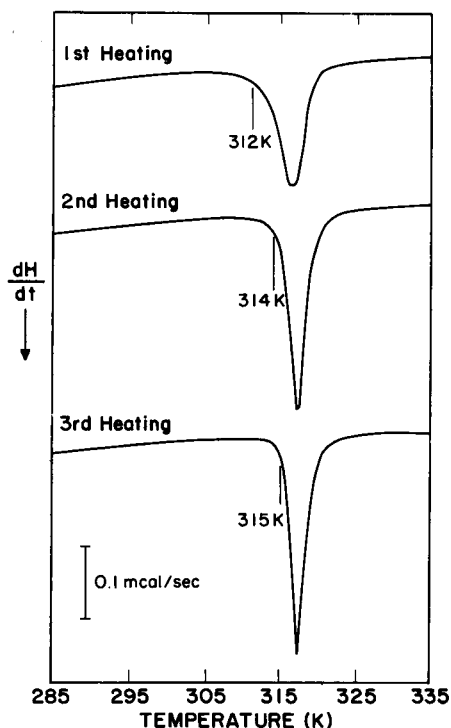


Fig. 3. DSC thermograms of the initially stage 1 sample during first, second and third heating.



third heating. A single peak at 312 K was observed during first heating; a single peak at 314 K was observed during second heating; a single peak at 315 K was observed during third heating. This means that desorption from stage 4 caused an increase of stage beyond 4 and the transition temperature continued to increase with stage beyond that of stage 4. Similar upshift of the transition temperature was observed for the other samples upon second heating. The highest transition temperature of 315 K is in agreement with the melting temperature observed in residue graphite-ICl by X-ray diffraction [6].

4. Discussion

The DSC results previously reported for graphite-ICl [5] were obtained with partially desorbed (initially stage 1) samples contained in unsealed Al sample pans. The improved DSC data reported here are due to the use of sealed sample pans and well-staged compounds. The old DSC data [5] resemble the second and third traces of fig. 3, although the two small peaks between the two big peaks are much clearer in the new data. Thus the new and old data are consistent with one another. The new data clearly show that the melting temperature of graphite-ICl increases with stage, such that the melting temperature is 305, 309, 311, 312 and 315 K for stages 1, 2, 3, 4, and the residue material, respectively.

The increase of the melting temperature of graphite-ICl with stage is analogous to the increase with stage of the temperature of the order-disorder transition (which may not be distinguishable from the commensurate-incommensurate transition) of graphite-bromine. The order-disorder transition temperature of graphite-bromine is 333 ± 3 , 337 ± 2 , 343 ± 2 and 350 ± 2 K for stages 2, 3, 4 and the residue material, respectively [8].

In contrast, an order-order transition temperature of graphite-Rb decreases with increasing stage [9]. Furthermore, the melting temperature of graphite-Cs

(stage 1) decreases with decreasing intercalate vapor pressure, so that the transition temperature was 608 K during first heating and 500 K during second heating [10]. These trends are opposite to that observed for graphite-ICl.

A higher stage number corresponds to a larger spacing between nearest intercalate layers and thus leads to less interaction between the intercalate layers. Hence, one intuitively expects that the in-plane melting temperature decreases with increasing stage. However, the opposite trend was observed for graphite-halogens. This unexpected trend is probably due to the dependence of the domain size on stage or the dependence of the in-plane intercalate concentration on stage. That the melting temperature of graphite-ICl and the order-disorder temperature of graphite-bromine vary with stage means that the graphite-halogens are not exactly two-dimensional, although X-ray diffraction study of graphite-bromine indicates a quasi two-dimensional structure [11].

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