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LETTERS TO THE EDITOR

Calorimetric evidence for two-step melting in graphite–bromine

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The melting transition in graphite–bromine intercalation compounds has lately become a subject of considerable scientific interest. The transition was first observed by electron diffraction at 379 ± 10 K[1]. Then it was observed by differential scanning calorimetry (DSC) at 373 K[2,3] and subsequently by X-ray diffraction at 373.7 K[3]. Most recently, X-ray diffraction results revealed anisotropic melting at 373.4 ± 0.1 K[4] and suggested the possibility that the fluid phase might be a two-dimensional realization of a smectic liquid crystal[4].

In this paper, the previously reported single DSC peak associated with the melting[2, 3] has been resolved into a doublet. The dominant doublet component occurs at 373.0 K; a secondary peak occurs at ~375.5 K. This observation provides evidence for the two-step nature of the melting process.

This study was performed using a Perkin–Elmer DSC–2 differential scanning calorimeter. A two-point temperature calibration of the calorimeter was performed by using the melting points of indium and tin, scanning at 5 K/min; enthalpy change calibration was performed by heating a known mass of indium through the melting point. The heat of fusion of indium was taken as 6.79 cal/g[5]. The transition temperature is defined as the temperature corresponding to the intersection of the leading edge of the DSC trace with the baseline.

Samples were obtained by desorbing saturated (~83 wt% bromine) graphite–bromine at room temperature in air. These saturated compounds were prepared by room-temperature vapor-phase intercalation of highly oriented pyrolytic graphite (HOPG) which had dimensions of ~4 × 4 × 0.5 mm. The sample weight was obtained both before and after heating in the DSC with a Perkin–Elmer AD–2Z microbalance, which had an uncertainty of ±0.002 mg. The sample was mounted in an unsealed platinum pan with a platinum cover and was purged with dry argon at 20 cc/min.

Figure 1 shows the experimental DSC recorder traces of a graphite–bromine sample scanned at various rates from 365 to 385 K. When the sample was first mounted in the calorimeter, it contained 25.6 wt% bromine. After 13 heating cycles through the melting transition, it lost less than 6% of its intercalate. The sample was heated to only slightly above the melting temperature (less than 385 K) for a total time of the order of tens of minutes. Trace 1 was scanned at 10 K/min with a sensitivity of 0.5 mcal/sec (full scale). Traces 2 and 3 were obtained by scanning at 5 and 2.5 K/min with sensitivities of 0.5 and 0.2 mcal/sec, respectively. All peaks were endothermic while heating. The first peak occurred at 374.3, 373.4 and 373.0 K for scan rates of 10, 5 and 2.5 K/min, respectively. The smaller, second peak was just noticeable at 10 K/min. At 20 K/min, only a single peak was observed. At 2.5 K/min, the second peak was distinctly resolved and is estimated to begin at 375.5 K. This behavior is reversible. Upon cooling, two exothermic peaks were observed: the first at 375.3 K and the second larger peak at 373 K.

The total enthalpy change (ΔH) associated with the melting, as determined from the peak area of the DSC thermogram, is 204 cal mole^{-1}Br$_2$: 178 cal mole^{-1}Br$_2$ for the first peak and 26 cal mole^{-1}Br$_2$ for the second peak. The value of 204 cal mole^{-1}Br$_2$ for the total energy of

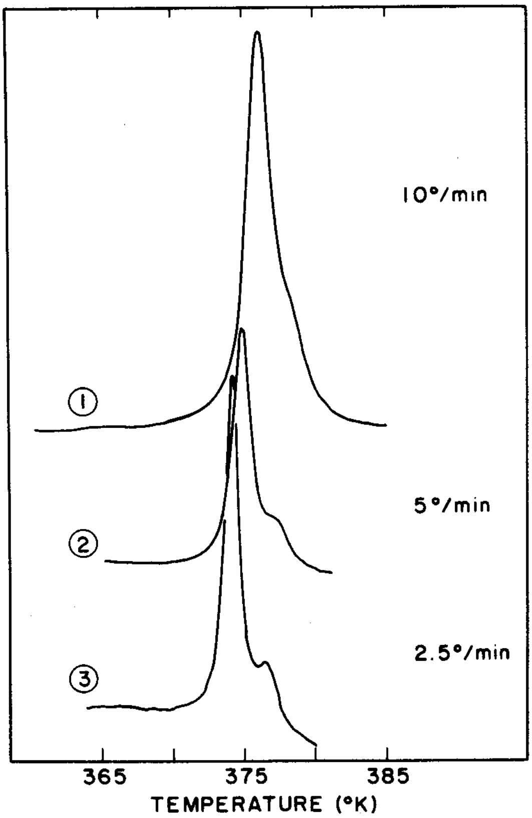

Fig. 1. DSC recorder traces of graphite–bromine taken at various heating rates. The doublet was revealed at the lowest heating rate.

the transition is in agreement with the previously reported value[3].

The entropy change (ΔS) can be determined from the enthalpy change and the transition temperature (T_c) by using the relation

$$\Delta S = \Delta H / T_c \qquad (1)$$

The entropy change of the first peak is approximately 0.48 cal mole^{-1}K^{-1}, while that of the second is only ~0.069 cal mole^{-1}K^{-1}.

There are at least two possible structural sources for the doublet in the enthalpy change of the melting transition. One is associated with the anisotropy in the melting[4], where the anisotropy stems from the correlation between the parallel polybromide chains[6, 7]. Another is associated with the multi-phase in-plane structure in the material[8]. However, the structural origin of this doublet will need to be determined by X-ray diffraction.

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REFERENCES

1. D. D. L. Chung, J. *Electron. Mat.* **7**, 189 (1978).
2. J. S. Culik and D. D. L. Chung, *Mater. Sci. Eng.* **44**, 129 (1980).
3. K. K. Bardhan, J. C. Wu and D. D. L. Chung, *Synth. Met.* **2**, 109 (1980).
4. A. Erbil, A. R. Kortan, R. J. Birgeneau and M. S. Dresselhaus, *Mat. Res. Soc. Symp. Proc.* (Intercalated Graphite), **20**, 21–26, Elsevier, New York, 1983.
5. *Perkin-Elmer DSC-2 Manual.*
6. D. Ghosh and D. D. L. Chung, *Mater. Res. Bull.* **18**, 1179 (1983).
7. D. Ghosh and D. D. L. Chung, *Mat. Res. Soc. Symp. Proc.* **20** (Intercalated Graphite), p. 15–20, Elsevier, New York, 1983.
8. D. Ghosh and D. D. L. Chung, *Synth. Met.* **7**, 283 (1983).