Splitting Effect of Added Diamantan-4-ol on the First Pre-melting Transition of Diamantane

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Summary The rotational and lattice changes which coincide in the first of the two pre-melting transitions of pure diamantane are separated by making dilute solid solutions of diamantan-4-ol in the hydrocarbon.

IN a previous communication[1] we reported transitions involving plastically crystalline phases in diamantane (I) and several derivatives. We now report a novel effect observed when diamantan-4-ol (II) is admixed in dilute solid solution with (I). Transition temperatures previously observed by the d.s.c. technique in the pure compounds are given in the Table.

Whilst the T_2 and fusion peaks for (I) show only small changes in temperature and magnitude when small amounts of (II) are added, the T_1 transition is markedly changed by very low concentrations of (II). It splits into a broad peak which appears to be a lambda-point transition,[2] peaking at about 383 K, and a small, sharp transition, presumably first order (onset ~ 405 K) (Figure 1).† The peak size of the lambda-point transition does not significantly change in

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† Data were obtained with a Du Pont thermal analyser fitted with a d.s.c. cell; the rate of heating in sealed pans was 10 °C/min.

the range 0·28—10 mol % of (II). It begins to decrease below 0·1 mol %, and the first-order transition grows to the 4·48 ± 0·21 kJ mol^{-1} previously reported for pure (I).

TABLE. *Transition temperatures* T/K.

	T_1	T_2	T_{fusion}
(I)	415	447	524
(II)		448	484

Above 0·28 mol % (II), however, the enthalpy and entropy of the first-order transition decrease linearly with increasing concentration, disappearing completely at *ca.* 8 mol % (II) (Figure 2).† Extrapolation back to pure (I) gives a value of 4·80 J deg^{-1} mol^{-1} for the entropy of this transition. This value is 5·98 J deg^{-1} mol^{-1} lower than that obtained for the T_1 transition in pure (I), and the diffeence must be attributed to the entropy of the lambda-point transition. Since the lambda peak is broad, estimates of entropy from simple d.s.c. measurements are not very precise, but are in reasonable agreement with the above value.

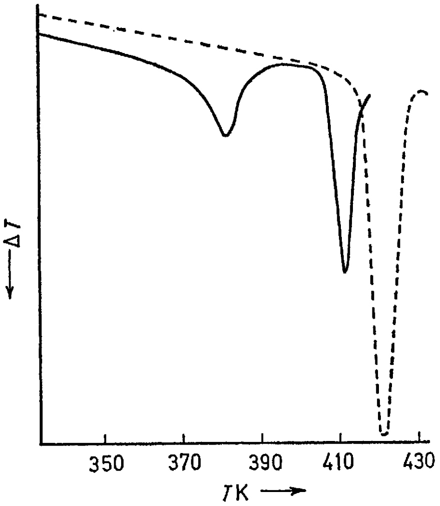

FIGURE 1. *Splitting of the* T_1 *transition of pure* (I) *found in a solid solution of* (II) (0·84 *mol* %) *in* (I). *The downward shift of this transition in going from pure* (I) *to the solution is probably due to lattice slackening.*

What are the molecular motions which occur separately in these two transitions of the solid solutions, but coincide in the original T_1 transition of pure (I)? The latter type of transition has been shown by *X*-ray investigations[3] to involve both a lattice rearrangement and the onset of orientational disorder. If such disorder is responsible for the lambda-point transition its ΔS value should be very close to $R\ln Q$, where Q is the ratio of distinguishable orientations allowed at temperatures immediately above the transition to those allowed immediately below the transition. As (I) shows two pre-melting transitions, orientational disorder at T_1 is very likely to be limited. Thus it is reasonable to associate the lambda-point transition with the onset of the easiest rotation,[4] which is that about the C(4)–C(9) axis in (I) [1]giving only two molecular orientations differing by 60°. ΔS should therefore be very close to $R\ln 2$ (5·74 J deg^{-1} mol^{-1}) as found.

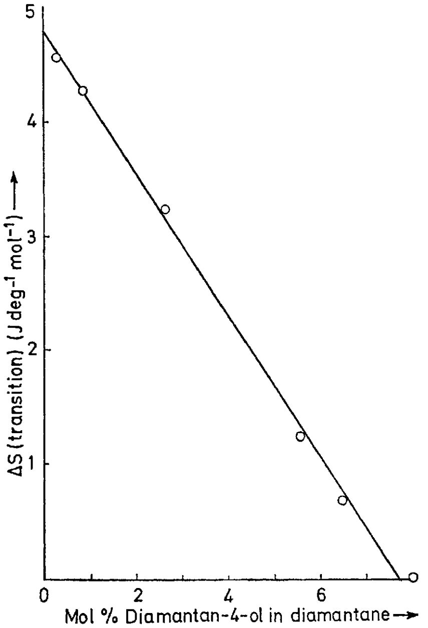

FIGURE 2. ΔS *for the* T_1 *transition as a function of concentration of* (II) *in* (I).

It is conceivable that very small concentrations of molecules of (II) are responsible for the onset of orientational disorder at *ca.* 110° because they either initiate or significantly shorten chains of co-operatively rotating molecules of (I) throughout the solution. Normally the lattice change simultaneously generates this disorder, giving a large first-order transition (T_1). Thus molecules of (II) may be regarded as lattice defects so that in those regions of the solid where pure (I) exists there is limited disorder but no lattice change at temperatures between the lambda-point transition and the first-order transition. It is significant that the magnitude of the first-order transition decreases linearly and disappears at *ca.* 8 mol % of (II). At this concentration every molecule of (I) should be in close proximity to a molecule of (II) in densely packed lattices. This result clearly indicates that molecules of (II) produce in their vicinity small regions of lattice similar to that existing in pure (I) between T_1 and T_2.

Separation has now been achieved for the first time, and the importance of this has been stressed by Westrum[5] as a method of studying the mechanisms of plastically crystalline phase changes. Knowledge of the lattice geometry of the solute[6] would further clarify that of different phases.

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[1] T. Clark, D. E. Johnston, H. Mackle, M. A. McKervey, and J. J. Rooney, *J.C.S. Chem. Comm.*, 1972, 1042.

[2] A. R. Ubbelohde, *J. Chim. phys.*, 1966, **63**, 33.

[3] See for example C. E. Nordman and D. L. Schmitkons, *Acta Cryst.*, 1965, **18**, 764.

[4] The onset of rotation alone has been observed to give a transition of this sort. See for example S. Glasstone, 'Textbook of Physical Chemistry,' 2nd edn., 1946, Macmillan, London, pp. 422—424.

[5] E. F. Westrum jun., *J. Chim. phys.*, 1966, **63**, 46.

[6] The crystal structure of (II) has not yet been determined; for the structure of (I) at room temperature see I. L. Karle and J. Karle, *J. Amer. Chem. Soc.*, 1965, **87**, 918.