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Thermodynamic and Structural Studies of Polymorphism in 1,1,1-trichloroethane and 2,2-dichloropropane[†]

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Optical birefringence measurements have been made on the different solid phases of 1,1,1-trichloroethane and 2,2-dichloropropane with the object of establishing their ranges of stability and their interrelationships. The nature of the solid phase that is contiguous to the liquid seems to depend upon the amount of impurities present in the specimens. This result is confirmed by an extensive calorimetric investigation of two specimens of 1,1,1-trichloroethane containing 0.31 and 0.82 mol % of impurity respectively. A comparison of the calorimetric data with results published in the literature suggests that one or the other of two distinguishable phases I of solid 1,1,1-trichloroethane is stable in the phase I region. While some apparently conflicting results obtained previously are thus rationalized, it is not certain that still other phases I cannot be formed.

1 INTRODUCTION

Orientational disorder in crystals is usually found when molecules of nearly spherical or cylindrical shape are packed in lattices of high symmetry. The solids, which are also called plastic crystals, are characterized by low enthalpies and entropies ($\lesssim 2.5$ R) of melting, by high melting points relative to those of non-spherical homologues, as well as by high plasticity, flow under gravity having been observed in some cases.[1,2] These properties can be

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rationalized in terms of considerable orientational freedom coupled with transient short range ordering of the molecules,[3] but quantitative details of the subtle directional nature of the intermolecular forces are, at present, unavailable. At lower temperatures, the plastic phases normally transform into less symmetric, brittle solid phases.

The methylchloromethane (MCM) compounds (i.e. $(CH_3)_n\ CCl_{4-n}$ with $0 < n < 4$) are known to form a number of phases in the solid state, the higher temperature ones being plastic in nature. Properties and structures of various phases of the MCM compounds have been investigated extensively by R. Rudman and coworkers[4] using the techniques of X-ray crystallography and differential scanning calorimetry (DSC). They concluded that the phases I[5] of CCl_4, CH_3CCl_3 and $(CH_3)_2CCl_2$ exhibit polymorphism and they labelled the phases Ia and Ib, with Ia being the more highly symmetric. The general sequence of transformations from one phase to another was surmised to be liquid → Ia → Ib → II → Ib → liquid for a cycle of decreasing and then increasing temperature.

While the existence of polymorphism has been firmly established for CCl_4, subsequent measurements have shown that the strict order of transitions postulated by Silver and Rudman[4] is not necessarily followed. For instance, it has now been found[6,7] that phases Ia and Ib can both be formed directly from the liquid. Moreover, a birefringence study[8] established that Ib could transform into Ia, although the probable reason was a stabilizing effect of a glass surface upon phase Ia.[7,9] The thermodynamic properties show unambiguously that phase Ib should be the more stable.[7]

The situation with respect to 1,1,1-trichloroethane has not been so clear cut. Andon *et al.*[10] studied calorimetrically a very pure sample and found only well-defined single phases I and II and no evidence for polymorphism in phase I. They also did not detect a phase III about which there have been conflicting reports.[11-13] Rudman reported[14] the discovery of phase Ia, analogous to that in CCl_4, followed by the deduction from both X-ray and DSC measurements[4] that phases Ia and Ib of 1,1,1-trichloroethane were cubic.

In the experiments to be described in this paper, two samples of 1,1,1-trichloroethane, fortuitously containing appreciable and different amounts of impurity, have been studied by the techniques of optical birefringence and adiabatic calorimetry. Two different phases I have been characterized. If, as seems probable, they are the same as phases Ia and Ib defined by Silver and Rudman,[4] the conclusions to be drawn are that (i) phase Ib is not cubic, and (ii) the analogy of the sequence of phase transitions to that found in CCl_4 is imperfect.

Much less extensive studies of 2,2-dichloropropane were made but birefringence measurements show that it forms three solid phases and only one of them is cubic. As with CCl_4, either of two phases I can be formed from the liquid. The transition from non-cubic phase I to cubic phase I is slow but it appears that the single phase I reported in a calorimetric study[15] is the cubic one.

2 EXPERIMENTAL

(i) Materials

A commercial grade, 1,1,1-trichloroethane (Chemicals Procurement Laboratories, Inc.) was purified by preparative vapor phase chromatography. Two specimens were prepared, one with a column of XF-11-50 fluorinated Carbowax and the other with a column of SE30 on Chromosorb W. The original material contained about 4% total of three impurities which was reduced to 0.31 mole % of impurity in specimen X and to 0.82 mole % in specimen Y, as estimated by analytical chromatography. These estimates are consistent with the melting behavior of the specimens, as will be described later.

Both calorimetric specimens contained the same principal impurity which displayed a chromatographic peak extremely close to that of 1,1,1-trichloroethane. An unsuccessful attempt was made to identify the impurity with nmr techniques but all that could be deduced was that it contained a methyl group. During the heating of phase II of specimen Y, a small extra absorption of energy was observed at a temperature of about 223.7 K. If, as seems probable, the impurity is not solid soluble, this might be interpreted as its melting temperature.

CP grade 2,2-dichloropropane was obtained from J. T. Baker & Co. Several specimens of about 1 cm^3 each were further purified by gas chromatography using a column of XF-11-50 fluorinated Carbowax. Since a calorimetric study of 2,2-dichloropropane was not made, the purities of the specimens were not further investigated.

(ii) Calorimetry

The adiabatic calorimeter was previously used[7] for measurements on CCl_4. Degassed specimens were sealed in a copper vessel that was placed in good thermal contact with a tray carrying a platinum resistance thermometer and a heater.

Adiabatic conditions were maintained manually because, over most of the temperature range studied, the equilibrium times were not more than a few minutes. It was only in the immediate vicinity of the transitions that equilibrium times became uncomfortably long. In the latter stages of the phase II → I transition (>75% transformed), equilibrium temperatures were not determined because of this.

(iii) Optical birefringence

Two methods of estimating the birefringence of the crystal phases were employed using an apparatus[16] which had been slightly modified[8] for measurements on CCl_4. One technique (method A), which has been fully described,[16] was used to measure birefringence in the range $5 \times 10^{-6} < |n_e - n_0| < 1 \times 10^{-3}$, where n_e and n_0 are the refractive indices for the extraordinary and ordinary rays respectively. The aim was to verify the existence of cubic phases, although there was always slight ambiguity resulting from small birefringences caused by strain and other imperfections in the measuring system.

In method B, which was used for $|n_e - n_0| > 10^{-3}$, advantage was taken of a scheme widely used in mineralogy. The dimensions of crystallites in the optical field were estimated and $|n_e - n_0|$ determined from the maximum interference color at an angle of 45° off extinction, with the aid of an Interference Color Chart.[17]

3 RESULTS AND DISCUSSION

(i) 1,1,1-trichloroethane (MCF)

The freezing behavior as observed with the calorimeter at a cooling rate of approximately 2 J min^{-1} is shown in Figure 1. The typical cooling curves for MCF(X) and MCF(Y) can be seen to be quite different. MCF(X) froze at about 234 K (although very fast cooling depressed the freezing point by as much as 20°). The temperature of the calorimeter rose by about 0.7°, but, usually, the cooling rate did not return to its original value for an hour or more, thus indicating a very slow release of energy during the freezing. By contrast, MCF(Y) froze at a somewhat lower temperature ($\sim$229 K) but much more sharply; the cooling rate returned to its original value within a few minutes. On only one occasion, MCF(X) froze in its normal fashion with a small temperature rise but then, after 20 min, showed a sharp temperature rise not unlike that exhibited by MCF(Y). This example is illustrated as *b* in Figure 1.

The overall freezing behavior of CH_3CCl_3 shows a striking resemblance[7] to that of CCl_4, where the formation of phase Ia caused a small temperature rise followed by liberation of energy over a period of 2 or more hours. Sometimes, a spontaneous transformation from Ia to Ib gave a sharp temperature rise of the magnitude of 2° or more which was very similar to that for direct freezing to phase Ib.

The obvious conclusion to be drawn from these observations is that MCF(X) usually formed phase Ia and MCF(Y) phase Ib. Where both Ia

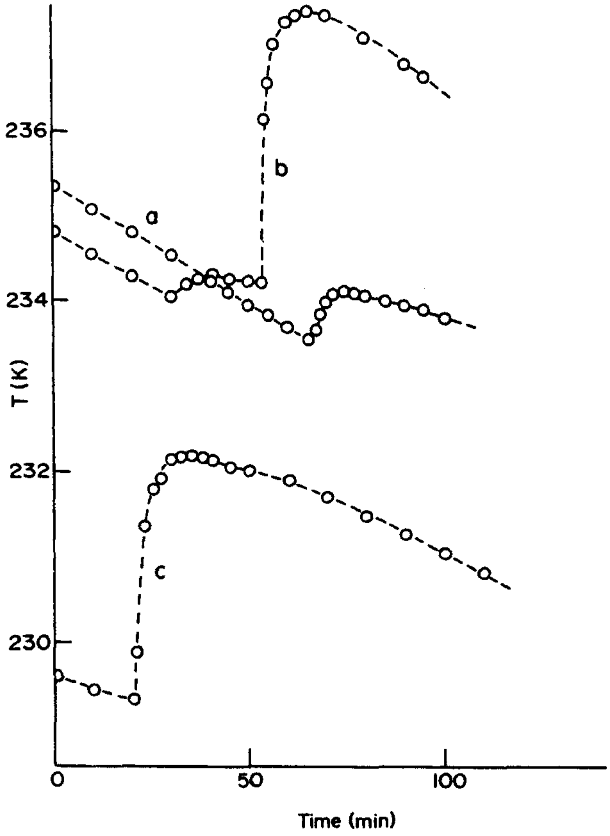

FIGURE 1 Cooling curves for 1,1,1-trichloroethane. a—Typical freezing curve for MCF(X). b—Only freezing curve for MCF(X) that showed two transitions. c—Typical freezing curve for MCF(Y).

and Ib were formed in MCF(X), which is the most reasonable interpretation of curve *b* in Figure 1, Ib has the higher freezing point which suggests that it is the more stable.

Table I shows transition temperatures, heats of transition, melting temperatures and heats of fusion for MCF(X) and MCF(Y) as well as values reported by other workers. The melting point and heat of fusion of MCF(X) agree closely with the values reported by Andon *et al.*[10] who used a very pure sample (~99.99 mole % pure). The limits given for our results are rather large because 0.32 mole % of impurity causes considerable premelting, as we shall discuss below. The lower melting point of MCF(Y) agrees fairly well with the results of most of the earlier workers who, presumably, also used less pure

TABLE I

Summary of thermodynamic measurements on 1,1,1-trichloroethane

	$T_{tr}(\text{II} \rightarrow \text{I})$ (K)	$\Delta H_{tr}(\text{II} \rightarrow \text{I})$ (J mole^{-1})	T_m (K)	ΔH_m (J mole^{-1})
Henne and Hubbard[18]	—	—	242.8	—
Rubin *et al*[11]	224.2 ± 0.03	7473 ± 8	240.2 ± 0.03	1883 ± 1255
Crowe and Smyth[12]	223.6	7448	240.1	1859
Clemett and Davies[19]	—	—	238.7	—
Silver and Rudman[4]	220.5	5134	231.9 (Ia → L)	908 (Ia → L)
			239.2 (Ib → L)	1887 (Ib → L)
Andon *et al.*[10]	224.80	7490 ± 5	243.1	2350 ± 5
Meijer[20]	224.7	7640 ± 30	243.3	2315 ± 15
Present measurements				
MCF(X)	224.3[a]	7450 ± 75	243.0 ± 0.3	2380 ± 45
MCF(Y)	223.9[a]	7715 ± 100	240.9 ± 0.3	2125 ± 50

[a] Equilibrium temperatures for 2/3 of transformation.

materials. It appears therefore that all of the available calorimetric results for 1,1,1-trichloroethane can be considered in two groups, fortuitously represented by MCF(X) and MCF(Y).

The depression of the freezing point and associated premelting phenomena are well-known in calorimetric studies. If the liquid phase is treated as an ideal solution and if the impurity is insoluble in the solid phase, the fraction of solid melted is related to the equilibrium temperature by

$$(T_m - T_{\text{obs}}) = \frac{RT_m^2 X_2}{\Delta H_m f} \tag{1}$$

where T_{obs} = equilibrium temperature, T_m = melting temperature of the pure solid, X_2 = mole fraction of impurity, ΔH_m = heat of fusion and f = fraction melted. From this, an expression for the excess heat capacity can be derived easily:

$$\Delta C = \frac{RT_m^2 X_2}{(T_{\text{obs}} - T_m)^2} \tag{2}$$

Figure 2 shows a plot of the excess heat capacities of MCF(X) and MCF(Y) versus temperature in the premelting region. For MCF(Y), it was possible to supercool the solid phase I below the phase II → phase I transition temperature (~223.9 K), thus making it possible to follow the entire premelting without the necessity of estimating the energy contribution of the solid/solid

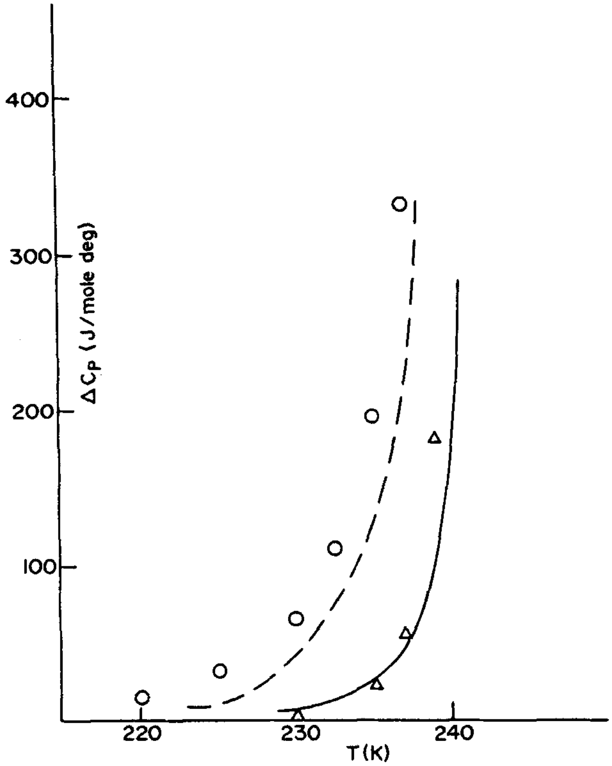

FIGURE 2 Excess heat capacity of melting as a function of temperature. △—MCF(X); ○—MCF(Y); — — calculated ideal excess heat capacity with $T_M = 243.0$ K, $X_2 = 0.0031$; ---- calculated ideal excess heat capacity with $T_M = 240.9$ K, $X_2 = 0.0082$.

transition. The curves shown were calculated using Eq. (2) and the following:

	T_m (K)	X_2 (mole %)
MCF(X)	243.0	0.31
MCF(Y)	240.9	0.82

It is clear that the observed premelting behavior corresponds reasonably closely to the level of impurity determined by gas chromatography. Two conclusions may be drawn from the comparison:

i) there seems to be no possibility that ΔH_m and T_m deduced for MCF(X) can explain the course of melting of MCF(Y);

ii) for both MCF(X) and MCF(Y), very little impurity is dissolved in the solid phases.

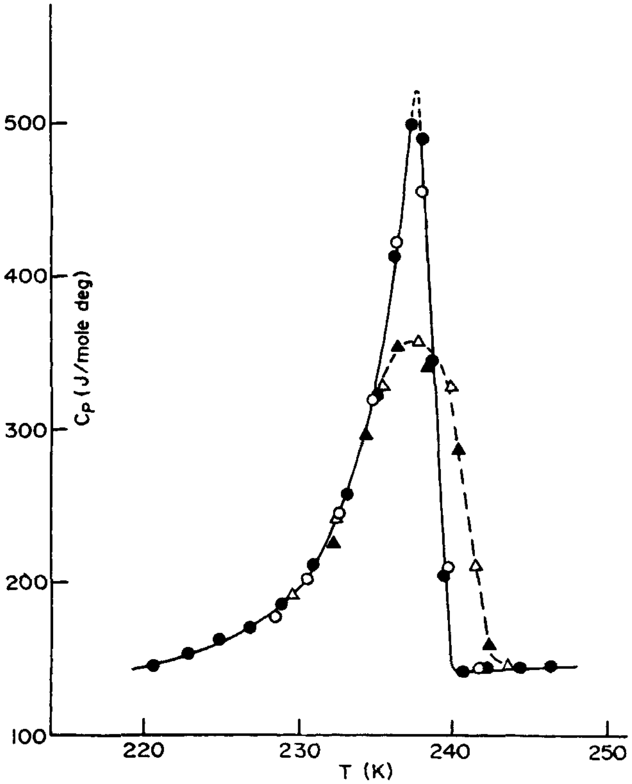

FIGURE 3 Total heat capacity of MCF(Y) through the melting region. ● ○ – duplicate measurements phase I → liquid for the sequence L → I → L; △ ▲ – duplicate measurements phase I → liquid for the sequence L → I → II → I → L.

In spite of ii), an additional interesting feature of melting of MCF(Y) was observed that may be related to the solubility of the impurity in the solid phases. As is illustrated in Figure 3, the detailed dependence of the total heat capacity on temperature through the melting region for $T > 235$ K seems to depend on whether or not the specimen had been previously transformed into phase II. The heats of fusion were, however, identical within the limit shown in Table I.

If we conclude that MCF(X) and MCF(Y) form different phases I, then, for thermodynamic consistency, the changes in enthalpy for the path phase II → liquid must be the same for the two specimens. Since we find that the heat capacities of the phases I of MCF(X) and MCF(Y) are very similar, it follows that $\Delta H(\mathrm{II} \rightarrow \mathrm{I})$ for MCF(X) must be less than that for MCF(Y) by 200 to 300 J/mole—the magnitude of the difference in the heats of fusion. As shown in Table I, this requirement is met.

In the thermal measurements on both MCF(X) and MCF(Y), no evidence was found for a possible phase III that was thought to exist because of the observation[11,12] of a heat capacity anomaly at about $T = 206$ K. Our results are therefore consistent with the recent calorimetric work of Andon *et al.*[10] and with the X-ray studies of Silver and Rudman.[13]

Birefringence studies of MCF(X) and MCF(Y) confirmed that two phases I form. MCF(X) showed a phase I that was non-birefringent, except for a small strain birefringence of the magnitude of 10^{-5}. This implies a cubic structure which is most probably the phase Ia identified by Silver and Rudman.[4] A birefringent phase I was never observed with MCF(X). By contrast, MCF(Y) always froze into a non-birefringence phase I which then transformed spontaneously into a birefringent phase with a consistent birefringence of the magnitude of 10^{-3} at a lower temperature. The actual numerical values of the birefringence of the different phases are given in Table II.

TABLE II

Observed optical birefringence

Phase	1,1,1-Trichloroethane	2,2-Dichloropropane
Ia	$<4 \times 10^{-5}$	$<1 \times 10^{-5}$
Ib	0.003 ± 0.001	0.011 ± 0.006
II	$\gg 10^{-2}$	$\gg 10^{-2}$

That the freezing behavior of MCF(X) or MCF(Y) differs in the birefringence apparatus from that displayed in the calorimeter is not surprising in view of the sensitivity of the polymorphs to the materials of construction. For instance, phase Ia of CCl_4 was clearly stabilized by a glass surface.[8,9] Nevertheless, the calorimetric and birefringence measurements on MCF(X) and MCF(Y) agree in showing that different *equilibrium* phases I form in the two specimens.

The sequence of phase changes as observed in the birefringence apparatus are displayed in Fig. 4. Average observed temperatures of the transitions are indicated and they differ somewhat from the values given in Table I. But, in the glass birefringence cell, a temperature gradient was unavoidable and so there was always a temperature difference of a few degrees between the crystal element being viewed and the copper thermometer. However, it should be noted that the melting point of MCF(Y) is shown to be less than that of MCF(X) by several degrees—in qualitative agreement with the calorimetric observations.

The structure of phase II of CH_3CCl_3 is known as a result of detailed X-ray measurements by Silver and Rudman.[13] It is orthorhombic with space group

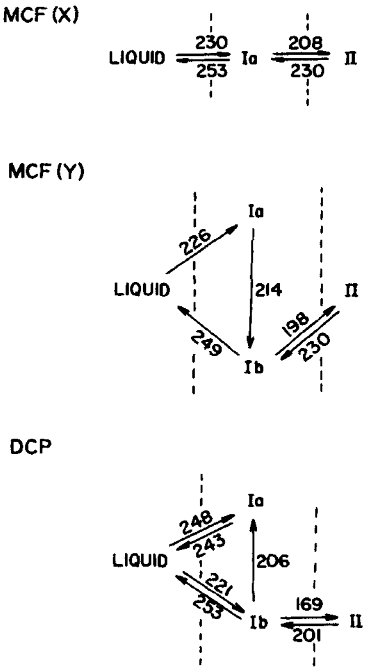

FIGURE 4 Phase transitions in MCF(X), MCF(Y) and DCP as deduced from birefringence observations. The numbers are temperatures in kelvins.

Pnma and four molecules per unit cell. Using the parameters of the structure as given by Silver and Rudman and taking the polarizability of the MCF molecule to be 104 × 10^{-25} cm^3 (as determined from bond polarizabilities[21]), we have calculated the birefringence of the phase following the method of Cowley.[22] The result, $|n_e - n_o| = 0.1$, is consistent with the observed birefringence (Table II).

(ii) 2,2-dichloropropane (DCP)

Much less is known about solid polymorphs of this compound. A calorimetric study has been made[15] but only a single phase I was observed. But, Silver and Rudman[4] described phases Ia and Ib occurring "nearly simultaneously". Very extensive investigations of birefringence made in the present work are summarized in the diagram at the bottom of Figure 4. The sequence of transitions is different from that of either MCF(X) or MCF(Y) and of carbon tetrachloride.[8] However, the times involved are not indicated and require some discussion.

When phase Ib ($|n_e - n_o| \sim 0.011$) was formed from the liquid, it could be maintained if it was cooled to a temperature of 200 K or less. On the other hand, if it were held at just below the melting temperature, it always transformed into Ia within a day or two. Once formed, phase Ia never was observed to transform into Ib or II even at temperatures as low as 120 K. However, as with CCl_4, it is possible that the stability of phase Ia is enhanced by the glass surface of the birefringence cell.

If the comparison of transition temperatures of MCF(X) and MCF(Y) observed in the calorimetric and birefringence experiments is used as a guide, we deduce from the birefringence observations (Figure 4) that, in his calorimetric work, van Miltenburg[15] measured the properties of phase Ia.

The birefringence of phase II of DCP was calculated by the method used for MCF (vide supra), using the structural data of Rudman and Post[23] and the assumption that the space groups of the phases II of MCF and DCP are the same. With a polarizability of 105×10^{-25} cm^3 for the DCP molecule (from bond polarizabilities[21]), $|n_e - n_o| = 0.05$ which, as with MCF, is consistent with a measured value of $\gg 10^{-2}$. Of course, the phases Ia, Ib and II of the MCM compounds need not be isostructural.

4 CONCLUSIONS

The fact that the first three members of the series of methylchloromethane compounds show polymorphic plastic phases is of considerable interest since, although the molecules are all approximately spherical in shape, the directional nature of the molecule/molecule forces must vary in detail as the symmetry of the molecules changes. However, the factors that govern the relative stabilities of phases Ia and Ib cannot be properly understood until the detailed structures of the phases Ib are known for all of the compounds. Only then can the distortions necessary to transform Ia into Ib be delineated.

The role of the impurities in stabilizing phase Ib in MCF(Y) deserves comment, especially since the heat capacity measurements show from the premelting behavior that the impurities are essentially insoluble in the solid phase. Possibly, in the liquid state, a critical impurity concentration exists for clusters of MCF and impurity molecules to form nuclei for the crystallization of Ib, but with only a small fraction of the impurity being incorporated into Ib. To account for the fact that the transformation of phase II into phase Ib occurs, one has to suppose that the small impurity centres remain in the solids.

The calorimetric and birefringence results described here, together with results obtained by others, indicate that, for the pure compounds, phase Ib is the more stable for CCl_4 and phase Ia for MCF and DCP. This is consistent with the higher melting points of Ib of CCl_4 and Ia of MCF but the birefringence data for DCP indicate that Ib rather than Ia is the higher melting. But the fact that MCF(X) showed a spontaneous transformation from Ia to Ib in one calorimetric experiment suggests that caution should be exercised in drawing sweeping conclusions. In any case, the differences between the Gibbs energies of the alternate plastic crystal polymorphs must be very small and thus it is not unreasonable that they may be changed in sign through interactions with surfaces or with small amounts of impurity. Moreover, it is probable that such effects are to be found in other systems. For example, a recent paper[24] reports a marked dependence of polymorphic behavior in cesium nitrite on small amounts of impurity.

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