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THERMAL CHARACTERIZATION OF THE PLASTIC CRYSTALLINE PHASE

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ABSTRACT

Differential scanning calorimetry provides a simple and rapid method for the identification and characterization of plastic crystalline materials. The methods used are illustrated by applying them to 2,2-dinitropropane.

INTRODUCTION

Plastic crystals were first recognized by Timmermans[1] as a distinct phase of matter. Most of the plastic crystals that have been identified are organic materials, and they can easily be confused with impure organic preparations. The materials are sticky and low-melting. Samples sublimed onto a cold surface often produce hard crystals that appear to have been purified, but they again become sticky on standing. A complete study of the purity of such a system can be time-consuming without providing direct evidence for the nature of the material. Differential scanning calorimetry provides a direct method for the identification and characterization of plastic crystalline materials.

Plastic crystals have one or more energetic solid-state transitions (of the order of 2–3 kcal/mole), a large heat-capacity discontinuity at the transition, and a very low entropy of fusion. The entropy of fusion of a plastic crystal will be of the order of R, the gas constant, and will be less than 5 eu[2]. Excellent surveys of the properties of plastic crystals are provided by Westrum and McCullough[3] and Aston[3].

Westrum and McCullough[3] state that "A plastic crystal is distinguished from the disordered crystals --- by the fact that the degree of disorder is significantly higher". For normal solid-state order–disorder transitions, $\Delta S_t = R \ln N_2/N_1$, where N is the number of nonequivalent states possible. At a plastic crystal transition, where molecular rotation about the molecular center of mass becomes important, N_2 should be very large. Therefore, a plastic crystalline phase can be identified unequivocally by making measurements of heat capacity, transition temperature, and transition energy through the solid-state and melting transitions of a suspected material.

EXPERIMENTAL

A Perkin–Elmer Differential Scanning Calorimeter, Model DSC-1B, was used to make all of the measurements. Heat capacities were measured by the method proposed by O'Neill[4]; however, granular NaCl was used as the reference material. The 2,2-dinitropropane was resublimed and was completely colorless, m.p. 53 °C. Samples were run in sealed cells (Perkin–Elmer Part Number 219-0062) to eliminate errors caused by the vaporization of the sample. Transition energies were measured with an analog computer–integrator designed and built by G. P. Watts and R. K. Spotts of this Laboratory. Since low-temperature operation was required, the average temperature and differential temperature functions of the DSC-1B were carefully recalibrated before and after making the measurements.

RESULTS AND DISCUSSION

2,2-Dinitropropane has been identified as a plastic crystalline material by Crowe and Smyth[5] on the basis of the large discontinuity in its dielectric constant at 266.1–268.1 °K. The X-ray disorder of the plastic phase of 2,2-dinitropropane has been studied by Abrahams[6]. None of the thermal properties of the compound have been reported.

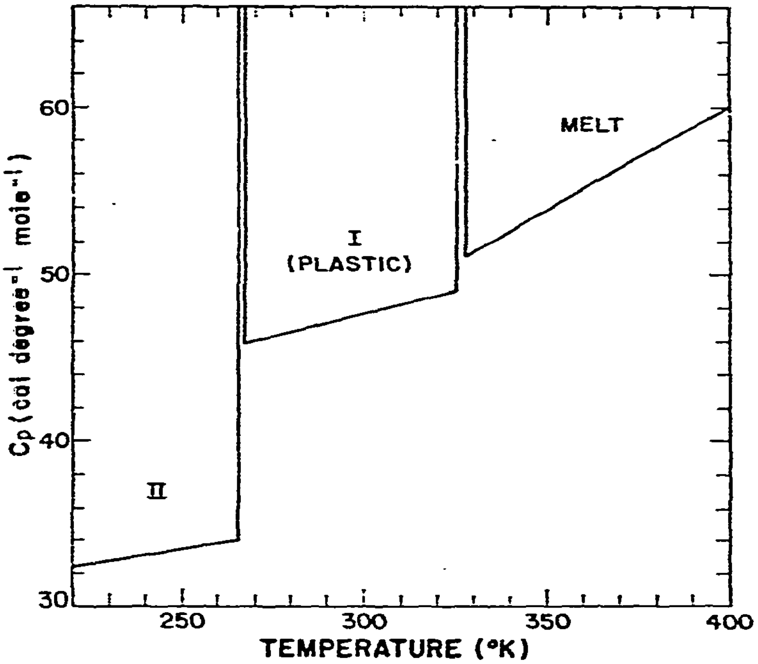

Fig. 1. Heat capacity of 2,2-dinitropropane as a function of temperature.

2,2-Dinitropropane shows a single crystal transition between −100 °C and its melting point. The transition exhibits considerable hysteresis, and it forms the boundary of a large heat-capacity discontinuity. The heat capacity as a function of temperature is shown in Fig. 1. The high-temperature modification (Fig. 1, phase I) has the mechanical properties of a classical plastic crystal and is optically isotropic; the low-temperature modification (Fig. 1, phase II) is anisotropic. Some thermal characteristics are presented in Table I. The precision of the measurements is estimated to be as follows: heating cycles, 0.8 cal/g at 95% confidence; cooling cycles, 0.5 cal/g at 95% confidence; and fusion, 0.2 cal/g at 95% confidence.

TABLE I

OBSERVED THERMAL PROPERTIES OF 2,2-DINITROPROPANE

	Transition	*Temperature (°K)*	*ΔH (cal/mole)*	*ΔS (eu)*[b]
Heating cycle	II–I	266.5[a]	2,492	9.4
Cooling cycle	I–II	~247[a]	2,372	9.6
Heating cycle	melting	326	576	1.8

[a]First appearance. [b]$\Delta S = \Delta H/T$.

The thermal data, therefore, prove that 2,2-dinitropropane forms a plastic crystalline phase. The large heat-capacity and entropy discontinuities at the transiton temperature show that a very large number of nonequivalent states of disorder appear ($N_2/N_1 \approx 119$). Since the entropy of fusion is approximately R, it is evident that fusion provides no more than the degrees of freedom of translation, *i.e.*, all of the degrees of freedom of rotation appeared in the energetic solid-state transition. Phase I in Fig. 1 is a solid with free molecular rotation.

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