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Detailed Refractive Index Measurement near Melting in a Plastic Crystal

Succinonitrile

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An interferometric measurement of the temperature derivative of the refractive index in succinonitrile is reported over a temperature range (30°C → 66°C) that includes melting. In pure material the behavior is clearly that of a first-order transition both on heating and on cooling. In impure material premelting effects are seen below fusion. In all cases appreciable supercooling can be observed.

Plastic crystals are molecular crystals whose molecules enjoy great freedom of reorientation.[1] Interest has recently developed in understanding their phase transitions and also, in general, in melting phenomena. Succinonitrile ($NC—CH_2—CH_2—CN$) has a plastic phase between 233.3 K and 331.3 K, in which the molecules execute step-wise isomerization by $2\pi/3$ about the central C—C bond, and rotation by $\pi/2$ around the four-fold crystalline directions for the trans-isomers.[2]

The orientational correlation function of succinonitrile in the plastic phase smoothly loses its anisotropy on the approach of melting.[3] A similar smooth disappearance of anisotropy occurs for the low-frequency elastic constants.[4] It is of interest to determine whether this behavior is reflected in the density ρ which is presumably related to an order parameter of the plastic–liquid transition. Density information in the plastic phase is already available from X-ray data,[5] but this information is not sufficiently detailed to ascertain the presence of any curvature in ρ as a function of temperature T. In non-polar cubic molecular crystals the Clausius–Mossotti relation[6]

$$\frac{4\pi}{3} A\alpha_0 \rho = M(n^2 - 1)/(n^2 + 2) \tag{1}$$

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is known to hold particularly well. Here α_0 is the mean molecular polarizability. A Avogadro's number, M the molecular weight, and n the refractive index. Hence a measurement of dn/dT gives a very good measure of the temperature dependence of the density. For these reasons we proceeded to an accurate interferometric measurement of dn/dT in succinonitrile in the region of the melting point T_M (= 58.2°C).

A Jamin–Pohl interferometer as shown in Figure 1 has been used. This instrument is a folded version of the Jamin interferometer which due to folding has excellent inherent stability to mechanical and thermal disturbances.[7] It consists of a large glass plate and a glass prism resting on an invar slab and placed in vacuum. A double set of fringes, one for measurement and one for reference, is formed by sending two beams through the instrument at different heights (only one beam path is shown in Figure 1 for clarity). These were derived from a He–Ne laser (6328 Å) with an inverted telescope and suitable masks. Each set of fringes had its own detection chain consisting of a pin hole, a photomultiplier, and an x-y recorder, the x axis monitoring the thermocouple voltage (i.e., proportional to temperature). This instrument is well suited to measure the temperature dependence of the refractive index

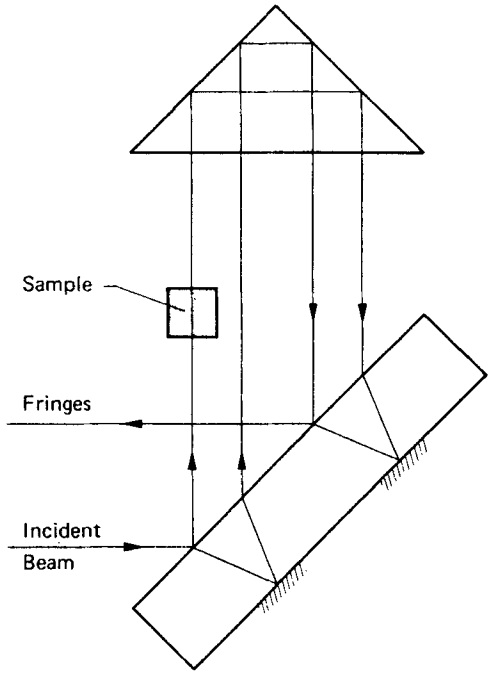

FIGURE 1 The Jamin–Pohl interferometer.

of isotropic materials, particularly liquids and gases, with very high accuracy —routinely 5 ppm. Succinonitrile of extremely high purity (zone refined more than 100 passes) was placed in a 10 × 10 mm quartz cell which was evacuated and sealed. Extreme care was taken in the transfer to the quartz cell in order to avoid contamination by water vapor or by air. The quartz cell had a conical bottom which allowed to grow a single crystal by the Bridgman–Stockbarger technique.[8] Growth rates of ~0.3 mm/hr were found to yield good quality crystals. A hollow quartz finger holding the thermocouple reached the upper region of the material from the top of the cell. This sample was placed in a temperature-controlled enclosure, whose temperature could be either stabilized or varied with an approximately constant heating or cooling rate (rates between 0.2 and 0.02°C/min were used).

Referring to Figure 1, the optical-path difference between the interfering beams due to the presence of the sample is $l(n-1) + l_q(n_q - 1)$ so the fractional fringe number N is given by

$$N = \lambda^{-1}[l(n-1) + l_q(n_q - 1)], \tag{2}$$

where λ is the wavelength in vacuum, l is the material thickness, $\frac{1}{2}l_q$ is the thickness of the quartz windows, and n_q their refractive index. In view of the extremely low resistance to deformation of the plastic crystal, and being given the slow temperature changes, it is reasonable to assume that no appreciable stress is built up in the sample and that the thickness l is set by the quartz cell. This is substantiated by our dn/dT results which at sufficiently high temperature (>30°C) appeared fairly independent of the heating rate provided this rate was sufficiently slow (<0.1°C/min). Differentiating Eq. (1) with respect to T, one obtains

$$\frac{dN}{dT} = \frac{l}{\lambda}\left\{\frac{dn}{dT} + \frac{l_q}{l}\frac{dn_q}{dT} + \alpha\left[(n-1) + (n_q - 1)\frac{l_q}{l}\right]\right\}, \tag{3}$$

where α is the linear expansion coefficient of the quartz cell. With $l_q/l = 0.2$, $\alpha = 0.5 \times 10^{-6}$/°C, and $dn_q/dT = 9.8 \times 10^{-6}$/°C the correction to dn/dT within curly brackets is $\simeq 2.2 \times 10^{-6}$/°C i.e., about 1%. The validity of this expression was checked by a calibration run on water (for which dn/dT is well known and rather small). The fractional fringe number obtained from the measurement beam has to be corrected for the changes in the reference fringes. This change was regular, and relatively small in the case of succinonitrile, giving a correction of the order of one to two percent.

The data obtained are summarized in Figure 2 and the actual values of dn/dT are given in Table I. These temperature coefficients are the average of three runs on two different crystals. The absolute refractive index scale in Figure 2 was obtained by extrapolation of the values given by Boyer *et al*,[9]

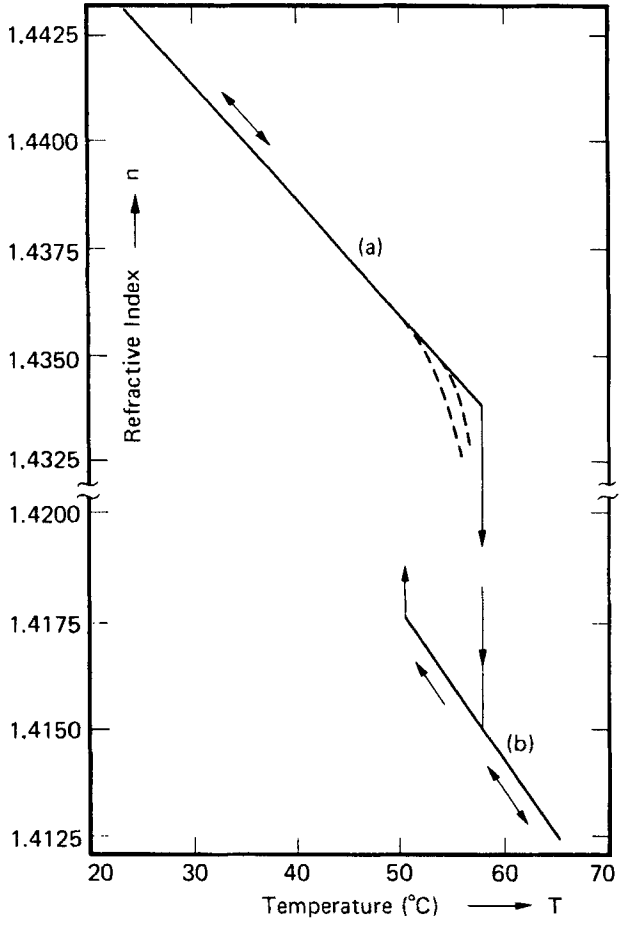

FIGURE 2 Summary of the refractive index data
(a) in the plastic phase
(b) in the liquid and supercooled liquid phases (note the break in vertical scale).
The dashed curves show the typical onset of premelting in impure samples. The solid lines were defined by taking one point per order of interference, i.e., approximately five points per °C, and the scatter is less than the thickness of the lines.

TABLE I

Experimental Results

State	Measured range	dN/dT (fringes/°C)	dn/dT (°C^{-1})
Plastic	32 to 58°C	−4.066	$(-2.64 \pm 0.06) \times 10^{-4}$
Liquid	50.5 to 66°C	−5.564	$(-3.52 \pm 0.02) \times 10^{-4}$

and should be considered as approximate compared to the highly accurate relative scale (about 10 ppm, see also Table I). The major statistical error is the thermocouple reading, accurate to ± 1 μV ($\sim \pm 0.02$°C). Systematic errors can be produced by material flow when the material is in the plastic phase. These will be discussed below. In the liquid phase it appears that the slopes have been determined to better than 2×10^{-6}/°C.

On heating a pure single crystal the refractive index decreases linearly on the scale of Figure 2. For impure samples (material which had been only partially zone-refined) the behavior is that shown by the dashed curves in Figure 2. The considerable bending occurring above ~ 52°C (which varies from sample to sample depending on purity), is accompanied by the development of opalescence which progressively reduces the fringe visibility and eventually prevents the measurement. Melting also occurs at a lower temperature for these samples. These effects are understood as caused by premelting: melted clusters forming in regions of higher impurity concentration scatter light strongly and produce a downward bend in $n(T)$, since the liquid has a lower refractive index and we measure an average over the light beam (~ 30 mm^2). It should be noted that the origin of loss in Kerr-effect anisotropy on the approach of melting[3] is not related to these premelting effects. Had premelting been responsible, the 1 cm thick sample used in the Kerr measurement would have become so opalescent that no measurement would have been possible a few degrees below T_M. Furthermore, the Kerr-effect strength would have shown a dip in the region of T_M due to the loss in transmitted light.

In pure samples there remains a small amount of curvature which typically starts in the region of 45°C and is too small to be distinguished on the scale of Figure 2. This curvature does not appear to be totally reproducible. In particular, it is not identical on heating and cooling and therefore might be related in all or in part to material flow effects. For these reasons the accuracy of dn/dT (Table I) is poorer in the plastic phase. The value quoted was obtained on a cooling run which showed relatively little curvature.

If we make the reasonable assertion that the temperature dependence of the refractive index is given by the Clausius-Mossotti relation [Eq. (1)], then a measure of the temperature dependence of α_0 is obtained. Differentiating Eq. (1) with respect to temperature, we find

$$\frac{1}{n}\frac{dn}{dT} = \frac{(n^2+2)(n^2-1)}{6n^2}\left(\frac{1}{\rho}\frac{d\rho}{dT} + \frac{1}{\alpha_0}\frac{d\alpha_0}{dT}\right). \tag{4}$$

From the linear expansion coefficient measured by X-ray diffraction[5] in the plastic phase, i.e., $1.85 \pm 0.01 \times 10^{-4}$/°C one obtains $(1/\rho)(d\rho/dT) = -5.55 \pm 0.03 \times 10^{-4}$/°C, where the possible increase in vacancies is neglected. Substituting this in Eq. (4) yields $(1/\alpha_0)(d\alpha_0/dT) \approx 0.4 \times 10^{-4}$/°C

for the temperature dependence of the polarizability in the plastic phase. This value is approximate as it is the difference of two large numbers. The positive coefficient reflects the greater occupancy of the (in general more polarizable) higher vibrational states with increasing temperature. The transition temperature in the purer sample is $T_M = 58.22°C$. On reaching T_M the fringes suddenly become fuzzy, and it is necessary to wait a long time to complete melting. This time was reduced by stabilizing the oven temperature at $\simeq 1°C$ above T_M. The slope obtained in the liquid region is the same on heating and cooling and also the same, within experimental accuracy, in the supercooled region. Again, from available thermal expansion data for the liquid phase[10] $(1/\rho)(d\rho/dT) = -8.2 \times 10^{-4}$. Substituting in Eq. (4) one obtains $(1/\alpha_0)(d\alpha_0/dT) \approx 0.7 \times 10^{-4}/°C$ which is in reasonable agreement with the value in the plastic phase being given the uncertainties of this calculation.

In the purer sample, the supercooled region terminates around 50.5°C. This temperature is only slightly higher for the impure samples. Upon crystallization the fringes suddenly disappear and the temperature probed by the thermocouple in the quartz finger jumps up by several degrees due to the release of the heat of crystallization.

In conclusion, the temperature derivative of the refractive index has been measured accurately in the region of melting. The transition is clearly first order. The loss of anisotropy seen in the Kerr-effect measurement is not clearly reflected in $n(T)$ below melting. Considerable supercooling is observed.

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