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<sup>2</sup>"Proceedings of the NATO Advanced Study Institute on Anharmonic Lattices, Structural Transitions and Melting, Geilo, Norway, 24 April-1 May 1973," edited by T. Riste (Plenum, to be published).

<sup>3</sup>"Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

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<sup>16</sup>F. Borsa, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti, (Academic, to be published), has most recently observed the critical slowing down in one-dimensional ferromagnets at several NMR frequencies.

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<sup>19</sup>The constancy of the ratios  $\Delta\omega/B^2$  is good except for  $\theta = 45^\circ$  which is a factor of 1.3 too high. The deviation becomes more pronounced for smaller  $B$ 's and is not understood.

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## Optical Kerr Effect, Susceptibility, and Order Parameter of Plastic Succinonitrile

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The high-frequency electro-optic tensor of succinonitrile is measured throughout the plastic crystalline phase. Its strength, due to cooperative molecular response to the orienting optical field, is a generalized susceptibility increasing rapidly near the plastic-solid transition. Its anisotropy describes long-range cubic order of the average molecular orientation. This orientational order parameter decreases rapidly near the plastic-liquid transition, suggesting that the hitherto neglected average orientational order is essential to the plastic phase stability.

The plastic ( $P$ ) phase of molecular crystals is characterized by continuous reorientation of molecules which form on the average a regular lattice.<sup>1</sup> It is a common intermediate phase between liquid ( $L$ ) and solid ( $S$ ) phases for "globular" molecules. Succinonitrile ( $\text{CN-CH}_2\text{-CH}_2\text{-CN}$ ), though not strictly globular, exhibits an extended  $P$  phase melting at  $T_M = 331.3^\circ\text{K}$  and solidifying orientationally at  $T_S = 233.3^\circ\text{K}$ .<sup>2</sup> The lattice is

bcc in the  $P$  phase.<sup>3</sup> The molecules isomerize by rotation around the central C-C bond. The concentration of isomers is known<sup>4</sup> and their average position has recently been worked out.<sup>5</sup> A relatively strong depolarized Rayleigh wing has been measured<sup>6</sup> which suggests that the optically induced birefringence should also be large. The present Letter reports the measurement of the optical Kerr susceptibility  $\overline{\chi}^{\text{NL}}$  on oriented

succinonitrile single crystals<sup>7</sup> throughout the  $P$  phase. This tensor is related to the dielectric tensor  $\vec{\epsilon}$  by

$$\epsilon_{ij} = \epsilon_p \delta_{ij} + 4\pi\chi_{ijkl}^{\text{NL}} \langle F_k F_l \rangle + \dots, \quad (1)$$

where  $\epsilon_p$  is the low-level dielectric constant at the frequency of the probing field  $\vec{E}$ , whereas  $\vec{F}$  is the strong orienting laser field; the bracket is an average over the optical period. Hereafter the abbreviated subscript notation whereby each pair  $ij$  and  $kl$  is represented by one subscript is used. To our knowledge it is the first time that a nonisotropic optical Kerr tensor has been measured.

This tensor turns out to be particularly meaningful in the  $P$  phase if one makes the reasonable assumption that the main contribution of  $\vec{F}$  to the system's Hamiltonian is of the form  $-\frac{1}{2} \sum_a \langle \vec{F} \cdot \vec{\alpha}^a \cdot \vec{F}^{\text{loc}} \rangle$ , where the sum is over all molecules, or rigid molecular segments, or even single bonds, denoted by  $a$ ,  $\vec{\alpha}^a$  is the polarizability of these segments, and  $\vec{F}^{\text{loc}}$  is the local field corresponding to  $\vec{F}$ . The assumption neglects nonlinear molecular polarizability and electrostriction, but the present birefringence measurement is insensitive to the isotropic part of these nonlinearities. By use of methods similar to those used for Kerr liquids,<sup>8</sup> the assumption leads to

$$\vec{\chi}^{\text{NL}} = \beta N \left( \frac{\epsilon_p + 2}{3} \right)^2 \left( \frac{\epsilon_0 + 2}{3} \right) \vec{G}, \quad (2)$$

where  $\beta$  is  $1/kT$ ,  $N$  is the density of segments, the factors in parentheses are local field corrections for the probing and orienting fields, respectively, and  $\vec{G}$  is a tensorial polarizability correlation function. Under neglect of polarizability dispersion,  $\vec{G}$  can be written as

$$\vec{G} = \frac{1}{2\mathcal{N}} \sum_{a,b} \text{tr} \rho \vec{A}^a \vec{A}^b, \quad (3a)$$

with

$$\vec{A}^a \equiv \vec{\alpha}^a - \left( \frac{1}{3} \text{tr} \vec{\alpha}^a \right) \vec{\delta}. \quad (3b)$$

In (3a) the sum is over all rigid segment pairs in the sample,  $\mathcal{N}$  is the total number of segments, and the trace is over all possible orientations whose probability distribution is represented by the density  $\rho$ . The traceless second-order symmetric tensor  $\vec{A}^a$  is defined by (3b), where  $\vec{\delta}$  is the unit tensor of second rank. In the cubic phase  $\vec{G}$  has only two independent components since the trace over the first two subscripts vanishes in view of (3b), leading to  $G_{11} + 2G_{12} = 0$ . The particular significance of  $\vec{\chi}^{\text{NL}}$  lies in the fact

that the two independent components of  $\vec{G}$  are a measure of (i) the short-range correlation of molecular orientations, and (ii) the long-range average cubic anisotropy of these orientations.

A group-theoretical analysis of  $\vec{G}$  shows that the tensor decomposes into two irreducible tensorial sets which are written in terms of two independent quantities

$$U \equiv \frac{1}{6\mathcal{N}} \sum_{a,b} \text{tr} \rho \sum_i \vec{A}_{ii}^a \vec{A}_{ii}^b = G_{11}, \quad (4a)$$

$$V \equiv \frac{1}{6\mathcal{N}} \sum_{a,b} \text{tr} \rho \sum_{i < j} \vec{A}_{ij}^a \vec{A}_{ij}^b = G_{44}. \quad (4b)$$

The first irreducible set transforms as the representation  $\mathcal{D}^{(0)}$  of the full rotation group, and is proportional to  $Q \equiv U + 2V$ , which we call the tensor strength. The second irreducible set transforms as  $\mathcal{D}^{(4)}$ , and is proportional to  $C \equiv U - \frac{4}{3}V$ . One finds that (i) uncorrelated pairs  $a-b$  do not contribute to the trace in (4); (ii) correlated pairs contribute to  $Q$  independently of whether  $\rho$  has cubic or spherical symmetry; (iii) correlated pairs contribute to  $C$  only to the extent that  $\rho$  has cubic symmetry. Therefore  $Q$  measures the correlation range; as the transition to the  $S$  phase at  $T_s$  is characterized by long-range orientational order,  $Q$  is a generalized susceptibility that announces the  $P$ - $S$  transition. The relation  $C = 0$  amounts to  $2G_{44} + G_{12} - G_{11} = 0$ , which is the Cauchy relation characterizing the  $L$ -phase isotropy. As defined,  $C$  is sensitive both to long-range anisotropy and to short-range correlation; intuitively,  $C/Q$ , which is a dimensionless normalized quantity, should depend little if at all on the short-range correlation. It is an orientational order parameter of the  $L$ - $P$  transition. Instead of  $C/Q$  we use an order parameter  $\zeta$  that has the advantage of being simply related to  $\vec{G}$  (and  $\vec{\chi}^{\text{NL}}$ ):

$$\zeta \equiv \frac{1}{2} - G_{44}/(G_{11} - G_{12}) = 5C/(4Q + 6C), \quad (5)$$

and which we call the tensor anisotropy. The  $L$ - $P$  transition is characterized by the onset of both long-range orientational anisotropy and long-range translational order. Whereas the latter has been considered in current theories,<sup>9</sup> the former has so far been ignored. One essential result of our investigation is that  $\zeta$  shows remarkable pretransitional effects on the approach of the  $L$  phase, suggesting that the orientational anisotropy is essential to the  $P$  phase stability.

The quantities  $\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}}$  and  $\zeta = \frac{1}{2} - \chi_{44}^{\text{NL}} / (\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}})$  have been measured using a single transverse and longitudinal mode  $Q$ -switched

ruby laser as orienting field  $\vec{F}$ , and its second harmonic as probing field  $\vec{E}$ . The beams are linearly polarized at  $45^\circ$  from each other, superposed, and incident perpendicularly to a (110) cut of a 8-mm-long crystal contained between two thin Schlieren free quartz windows. Good optical quality is achieved by using a drop of octane on the crystal faces. The probing field is then passed through a compensator and an analyzer, and is detected with a fast photodiode. The compensator is carefully adjusted for no depolarized signal in the absence of  $\vec{F}$ . The depolarized power  $P_{\text{dep}}$  is normalized to the square of the orienting laser power  $P_0$  and to the probing power  $P_p$  which are simultaneously recorded and measured at pulse peak. The result is corrected for the relatively small window contribution.<sup>10</sup> With the known orientational relaxation times,<sup>6,11</sup> and for our pulse duration of  $\sim 30$  nsec, the steady-state assumption is well verified throughout the  $P$  phase. The crystal is rotated around the beam direction, and the measurement is repeated as a function of the angle  $\theta$  between  $\vec{F}$  and the [001] axis. For retardations much smaller than a quarter wave, one obtains from (1)

$$\frac{P_{\text{dep}}}{P_0^2 P_p} = (g/\lambda_p^2 c^2 \epsilon_0 \epsilon_p) (\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}})^2 f(\theta, \xi), \quad (6a)$$

with

$$f(\theta, \xi) \equiv [1 - \xi(1 + 6 \cos^2 \theta) \sin^2 \theta]^2, \quad (6b)$$

where  $g$  is a geometrical factor with the dimensions of an inverse area,<sup>12</sup> and  $\lambda_p$  is the vacuum wavelength of  $\vec{E}$ .

Figure 1 shows such a measurement at fixed

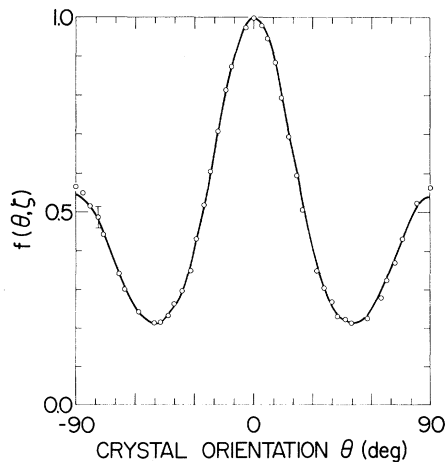


FIG. 1. The angular dependence of the normalized depolarized signal at  $19.9^\circ\text{C}$ . The solid curve corresponds to Eq. (6b) with  $\xi = 0.265$ .

$T$ . Each point is an average derived from at least four laser shots. The plot is normalized so that the ordinate is  $f(\theta, \xi)$ . The solid curve is given by (6b) and is obtained by a least-squares fit of the normalization constant and of  $\xi$ . From the shape of the curve, the sign of  $\xi$  and the direction of the [001] axis are determined unambiguously; the latter was also determined independently.<sup>7</sup> The square root of the normalization constant gives the relative value of  $\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}}$ . From a series of similar measurements, with six points between  $\theta = 0$  and  $\pi/2$  and five shots per point, we obtained the results of Fig. 2. The calibration of the left ordinate was made against  $\text{CCl}_4$  whose induced birefringence value is well known.<sup>10</sup> A direct calibration of our ruby power and beam cross sections led to an identical result within our experimental uncertainty. For the record, the square root of the signals obtained with the same thickness of some common nonlinear liquids are shown on the same scale, after window correction. Since  $\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}}$  is expected to be positive, it follows from the value of  $\xi$  that  $\chi_{44}^{\text{NL}}$  is positive throughout.

Since  $Q$  is proportional to  $(\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}})(\frac{5}{3} - 2\xi)$  it follows from Fig. 2 that the generalized susceptibility becomes very large on the approach of  $T_S$ , indicating an increased correlation range. An estimate of the correlation near  $T_M$  is obtained by comparing the experimental  $\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}}$

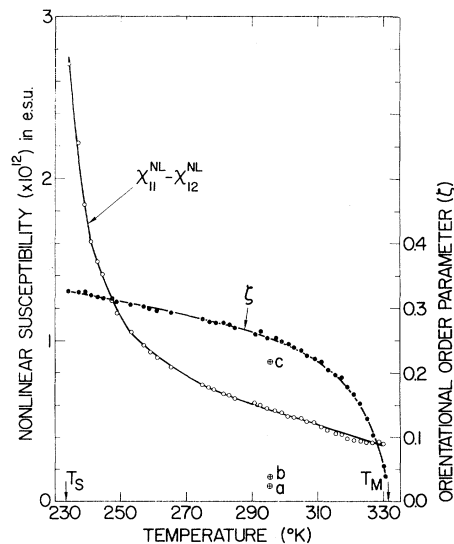


FIG. 2. The measured susceptibility and anisotropy. The solid curves are guides to the eye. Also shown are the susceptibilities of  $\text{CCl}_4$  (a), acetone (b), and benzene (c).

to a calculated value that assumes self-correlation only. The latter is obtained by calculating the isomers' polarizability as a sum over bonds,<sup>13</sup> using the known isomer concentrations,<sup>4</sup> and summing in (4a) with  $a = b$  only and isotropic distribution. The result is  $1 \times 10^{-13}$  esu, which is less than a third of the measured value. This would indicate that there is already correlation near  $T_M$ . The considerable decrease of  $\zeta$  near  $T_M$  indicates the progressive setting in of orientational isotropy in spite of the fact that the average molecular positions do form a regular lattice. This behavior is similar to that of the elastic-tensor anisotropy.<sup>14</sup> Unfortunately in this latter case detailed measurements near  $T_M$  are not available, and the relation to a correlation function is not expected to be nearly as simple as (2) and (3). The present results suggest that as the temperature is raised the molecules rotate more and more freely, to the point where their average orientation is almost isotropic and melting occurs. This interpretation is substantiated by the low entropy of melting,<sup>2</sup>  $\sim R \ln 4$  per mole; this value is consistent with a cell model in which each molecule can occupy any one of four cells in the disordered phase, but only one of them in the ordered phase. It is expected that Kerr-effect measurements will prove very fruitful for many plastic crystals, and that a microscopic model can be developed in those cases which are not complicated by molecular isomerism.

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