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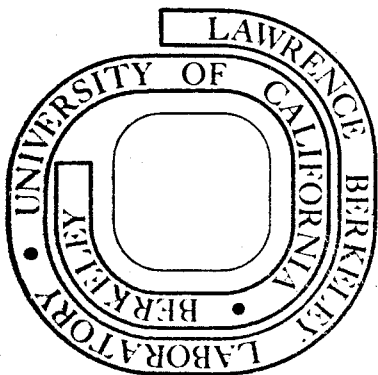
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Optical-Field-Induced Ordering in the
Isotropic Phase of a Nematic Liquid Crystal

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ABSTRACT

We have shown by measuring the field-induced refractive index that molecular ordering in the isotropic phase of MBBA can be induced by an intense laser field. We have also measured directly the ordering relaxation time as a function of temperature. The results are compared with the predictions of the Landau-de Gennes model.

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The linear optical properties of liquid crystalline materials have been the subject of extensive investigation recently. The nonlinear optical properties of the same materials, however, have not yet received much attention. In this paper, we report the first measurements on the optical-field-induced refractive index for a nematic substance in its isotropic phase. Ordering in the molecular orientation induced by the optical field is essentially responsible for this nonlinear refractive index. Field-induced ordering in the isotropic phase of a nematic system has been previously observed with an applied dc electric or magnetic field,¹⁻³ but the same effect obtained with an optical field has never been reported before. Using a Q-switched laser pulse, we have also been able to measure directly the relaxation time for the variation of the orientational order. Our results agree well with de Gennes' prediction.⁴

The present work was motivated by the idea that because of the strong molecular anisotropy, relatively weak laser field might be sufficient to induce an appreciable ordering in the isotropic phase of a liquid crystalline material. The resultant field-induced refractive index should increase strongly as the temperature approaches the isotropic-mesomorphic phase transition.⁴ For our case, we can write the free energy per unit volume for the isotropic phase as

$$F = F_0 + \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha}^* - \frac{1}{2} \chi_{\alpha\beta} E_{\alpha}^* E_{\beta} \quad (1)$$

$$A = a(T - T^*)$$

$$\chi_{\alpha\beta} = \bar{\chi} \delta_{\alpha\beta} + (2/3) \delta \chi_{\alpha\beta} (Q_{\alpha\beta}, T)$$

where E_{α} is the field component along $\hat{\alpha}$, $Q_{\alpha\beta}$ is the tensorial order parameter, a and T^* are constants, and $\delta \chi_{\alpha\beta}$ is the anisotropy in the

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susceptibility $\chi_{\alpha\beta}$ induced by the ordering $Q_{\alpha\beta}$ at the temperature T . We have neglected in the above expression terms of higher powers of $Q_{\alpha\beta}$ and terms describing the spatial variation of $Q_{\alpha\beta}$. The steady-state value of $Q_{\alpha\beta}$ induced by the field can then be obtained by minimization of F . For a given field, since the induced $Q_{\alpha\beta}$ is usually small such that $\delta\chi_{\alpha\beta} = \Delta\chi Q_{\alpha\beta}$ where $\Delta\chi \equiv (\partial\chi_{\alpha\beta}/\partial Q_{\alpha\beta})$ both $Q_{\alpha\beta}$ and $\Delta\chi_{\alpha\beta}$ should be proportional to $(T-T^*)^{-1}$.

However, if a short optical pulse is used to induce ordering, the ordering parameter may not be able to respond instantaneously. Then, the transient response of the order parameter is governed by the equation⁴

$$\nu \partial Q_{\alpha\beta} / \partial t + A Q_{\alpha\beta} = f_{\alpha\beta}(t) \quad (2)$$

$$f_{\alpha\beta} = \Delta\chi (3E_{\alpha}^* E_{\beta} - |E|^2 \delta_{\alpha\beta}) / 9$$

where ν is the viscosity coefficient. The solution of the above equation is

$$Q_{\alpha\beta}(t) = (1/\nu) e^{-t/\tau} \int_{-\infty}^t f_{\alpha\beta}(t') e^{t'/\tau} dt' \quad (3)$$

where $\tau = \nu/A = \nu/a(T-T^*)$ is the relaxation time. It is seen from Eq. (3) that long after the input pulse is over, $Q_{\alpha\beta}$ should decay as $\exp(-t/\tau)$. For an input laser pulse with a Gaussian pulse shape, $f_{\alpha\beta}(t) = C_{\alpha\beta} \exp(-a^2 t^2)$, we have

$$Q_{\alpha\beta}(t) = (C_{\alpha\beta}/\nu a) e^{-t/\tau} e^{1/4 a^2 \tau^2} \left[1 + \operatorname{erf}\left(at - \frac{1}{2a\tau}\right) \right] \quad (4)$$

which varies as $\exp(-t/\tau)$ when $at \gg 1$.

We can find $Q_{\alpha\beta}(t)$ by measuring the field-induced $\Delta\chi_{\alpha\beta}(t)$. For example, we can measure the birefringence $\chi_{\alpha\alpha} - \chi_{\beta\beta} = \Delta\chi_{\alpha\alpha}$ induced by a laser field linearly polarized along $\hat{\alpha}$. We have actually performed such measurements. We used the typical set-up for measurements of optical Kerr constants.⁵ A finite $Q_{\alpha\alpha}$ was first induced by a Q-switch ruby laser pulse of 10 nsec long and its subsequent variation was probed by a CW He-Ne laser beam.⁶ Results were obtained for MBBA at various temperatures in the isotropic phase. In every case, we obtained a perfect exponential tail for $Q_{\alpha\alpha}(t)$ from which we calculated the relaxation time τ . In Fig. 1, we present the experimental data τ as a function of T . They agree very well with the theoretical expression $\tau = \nu/a(T-T^*)$ of de Gennes⁴ if we assume $\nu = \nu_0 \exp(W/T)$ with $W = 2800^\circ\text{K}$ as suggested by Stinson and Litster³ and $T^* = 314.7^\circ\text{K}$. The clearing temperature of our material is $T_c = 315.5^\circ\text{K}$. The relaxation time varies from ~ 40 nsec at temperatures far above the phase transition to > 800 nsec near the transition. These results are in good agreement with those obtained from light scattering by Stinson and Litster.³

We have also measured the optical Kerr constant of MBBA as a function of temperature. Here, we define the Kerr constant as

$$\begin{aligned}
 B &= (\omega/cn) [(\Delta\chi_{\alpha\alpha} - \Delta\chi_{\beta\beta}) / |E_\alpha|^2]_{t=t_0} \\
 &= (\omega/cn) \Delta\chi(Q_{\alpha\alpha} / |E_\alpha|^2)_{t=t_0}
 \end{aligned}
 \tag{5}$$

where n is the refractive index and t_0 is the time at which $|E_\alpha|^2$ reaches its peak value. The results given as $2Bcn/\omega$ versus T are shown in Fig. 2. In comparison with CS_2 , we found $B(\text{MBBA})/B(\text{CS}_2) = 10$ at 326°K .

According to Owyong et al.,⁷ the optical Kerr constant can be written as $B = (\omega/cn)(\sigma + \beta)$, where σ and β are respectively the electronic and the nuclear contributions to the nonlinear refractive index. On the other hand, by measuring the field-induced rotation of the elliptical polarization of a laser pulse,⁸ one can obtain the quantity $D = (\omega/cn)(\sigma + 2\beta)$. If the electronic contribution is negligible, one should have $D = 2B$. This is what we would expect for liquid crystal-line materials. In order to show that this is indeed the case, we have conducted a separate experiment to measure the field-induced optical rotation of the polarization ellipse. Our experimental set-up was the same as the one used by Owyong et al.⁷ The results plotted as DCn/ω versus T are also shown in Fig. 2. It is seen in Fig. 2 that the two sets of data obtained from the two different experiments agree very well. This therefore indicates $\sigma \ll \beta$, i.e., the electronic contribution to the nonlinear refractive index is indeed negligible.

Both sets of results in Fig. 2 show that the nonlinear refractive index decreases strongly as the temperature approaches the phase transition. This is not in agreement with the simple theory which leads to Eqs. (2) and (3). We can approximate our input laser pulse by a Gaussian pulse. Thus, knowing τ , we can find from Eq. (4) $Q_{\alpha\beta}(0)$, and hence B or D , as a function of T . The theoretical curve thus obtained with $v = v_0 \exp(W/T)$ and $\Delta\chi$ independent of T is plotted in Fig. 2. The experimental data show clear deviation from the theoretical curve for $(T - T^*) < 5^\circ\text{K}$. We found that for $T - T^* \leq 3^\circ\text{K}$, our data can be fitted by assuming $\Delta\chi \propto (T - T^*)^\gamma$ with $\gamma = 0.3$ in Eq. (3). A similar discrepancy between theory and experiment has recently been observed

by Schadt and Helfrich¹ in their measurements on the dc Kerr effect.⁹ They also found a steady-state response of $(\Delta n/E^2) \propto (T - T^*)^{-\gamma}$ with $\gamma < 1$.

This discrepancy between theory and experiment is not clearly understood. We first thought that the higher-order terms which we had neglected in Eq. (1) might be important. However, the maximum field-induced Δn in our experiment with a field intensity of 0.3 MW/cm^2 was 5×10^{-7} which corresponds to $Q_{\alpha\alpha} = 1.2 \times 10^{-6}$. Using the coefficients determined by Stinson and Litster,³ we found these higher-order terms actually negligible. This conclusion was also supported by the fact that the results in Fig. 2 were independent of the laser intensity varied from 0.3 MW/cm^2 to 1 MW/cm^2 . It is of course possible that the mean-field theory may not be valid in this pretransitional region of $(T - T^*) < 5^\circ\text{K}$, yet the results of all other experiments except Ref. 1 seem to indicate that the mean-field theory holds for $(T - T_c) > 1^\circ\text{K}$.

Since our results of relaxation time measurements agree well with the prediction of Eq. (2), only the driving term in Eq. (2) should be modified in order to explain the discrepancy between theory and experiment in Fig. 2. In fact, the only difference between our work and the work of others on dc electric- and magnetic-field-induced birefringence is in the driving term. In the magnetic case, the induced anisotropy is $\delta\chi_{\alpha\beta}^H = \Delta\chi_{\alpha\beta}^H Q_{\alpha\beta}$. Since the magnetic interaction between molecules is small, the magnetic local-field correction in $\Delta\chi^H$ is negligible. However, in our case, because of the large electric interaction between molecules, the local-field correction in $\Delta\chi$ is important. Near the isotropic-nematic transition, the coherent length ξ for molecular

correlation varies as $(T - T^*)^{-1/2}$. The local field should change correspondingly, and hence $\Delta\chi$ may have a strong temperature dependence near the transition. Further theoretical investigation is needed to understand such an effect.

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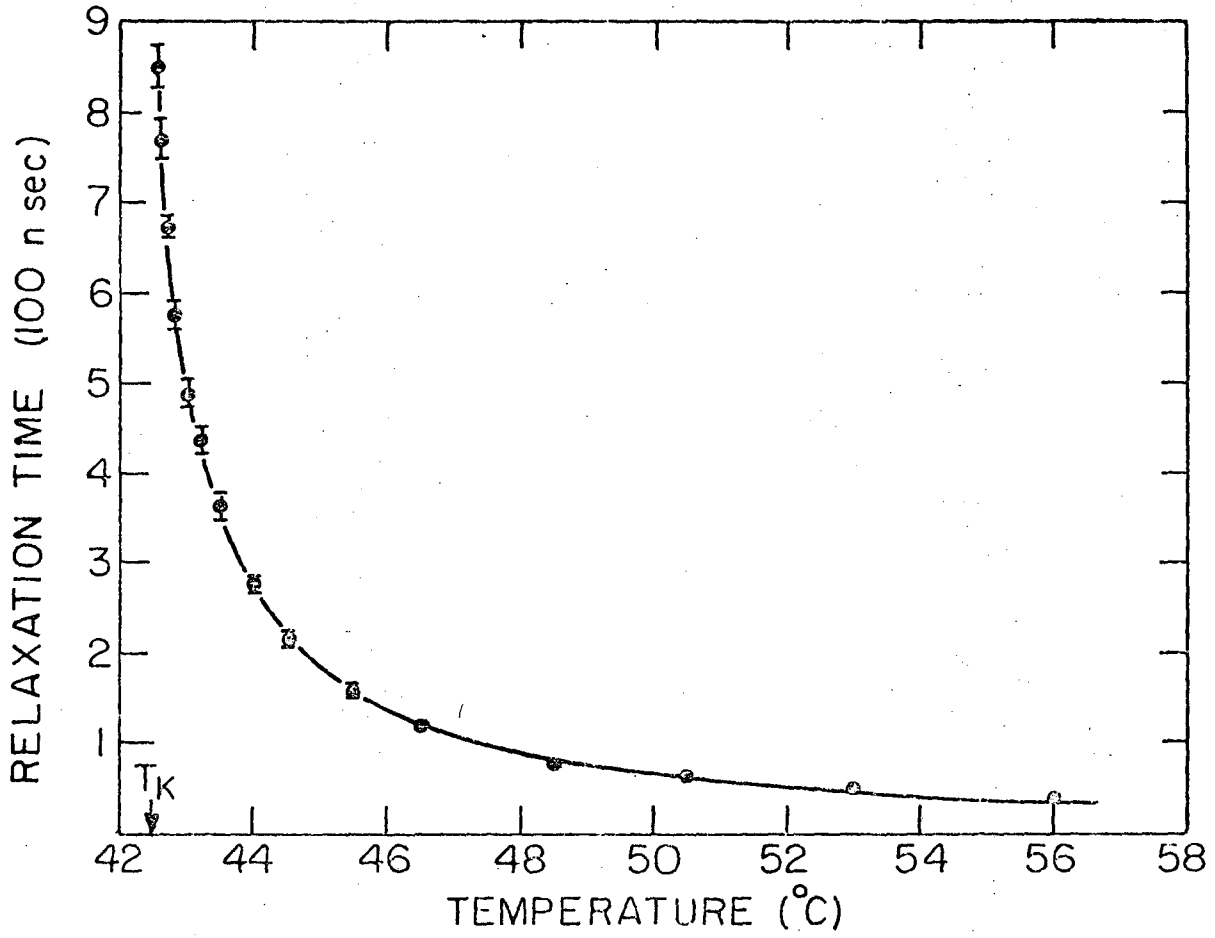
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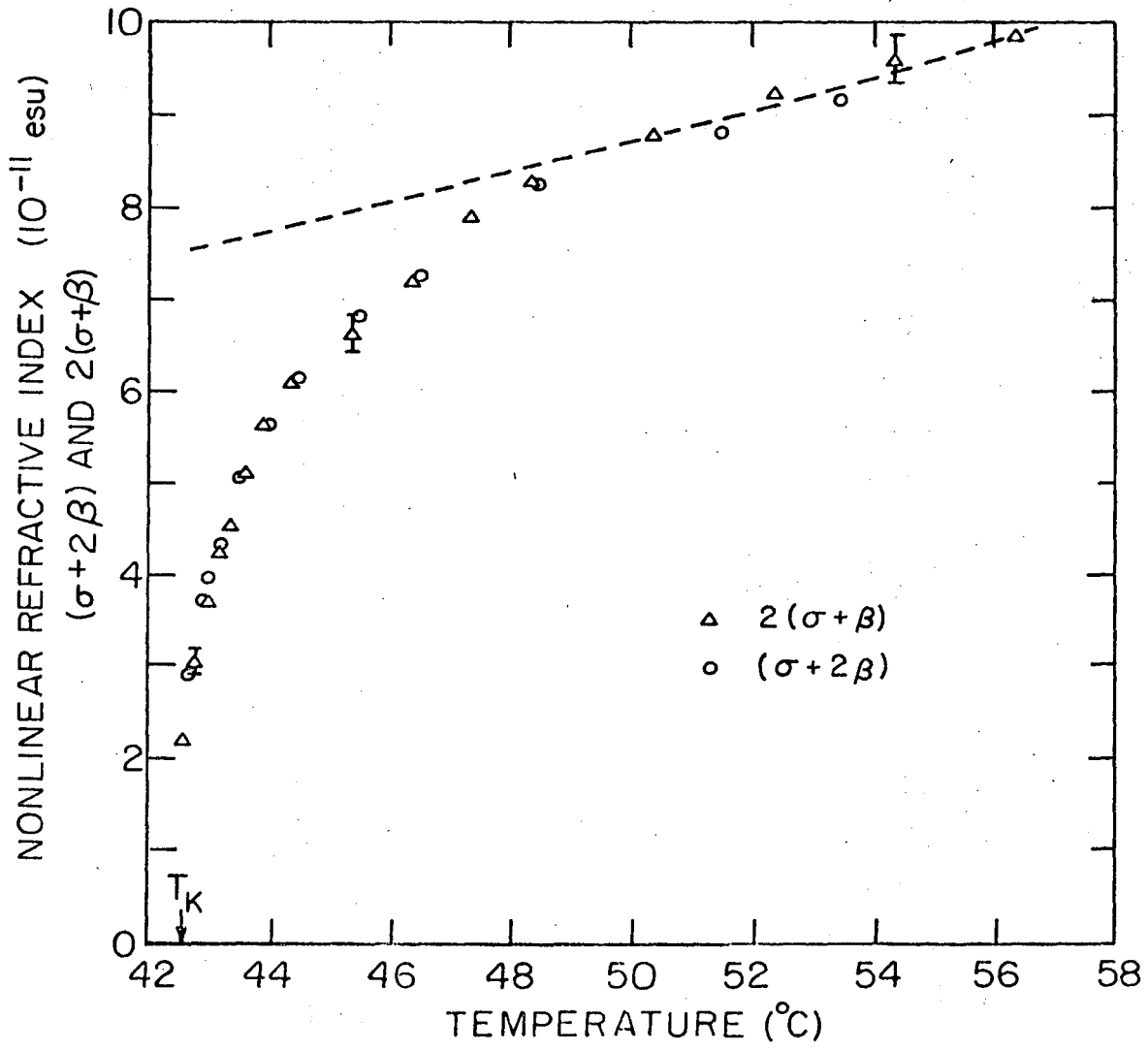
FIGURE CAPTIONS

Fig. 1. Relaxation time τ of the order parameter as a function of temperature. The solid curve is the theoretical curve obtained for $\tau = \nu_0^{\frac{1}{2}}(T - T^*)$ with $T^* = 314.7^\circ\text{K}$ and $\nu = \nu_0 \exp(2800^\circ\text{K}/T)$. The circular dots are the experimental data points.

Fig. 2. Nonlinear refractive indices $2(\sigma + \beta)$ and $(\sigma + 2\beta)$ as a function of temperature. The dashed curve is a theoretical curve obtained from Eq. (4) by assuming $\nu = \nu_0 \exp(2800^\circ\text{K}/T)$ and $\Delta\chi$ a constant.



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