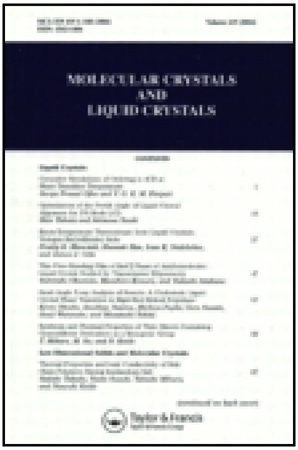

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NMAR Study of Short Range Smectic A Order iln the Nematic Phase of CBOOA

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NMR Study of Short Range Smectic A Order in the Nematic Phase of CBOOA†

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The proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) was measured in *n*-*p*-cyanobenzilidene-*p*-*n*-octaloxyanaline (CBOOA) doped with several weight percent cholesterol decanoate (CD). These measurements were made as a function of temperature and applied electric field intensity. Near the critical electric field for a cholesteric–nematic phase transition, order fluctuations are enhanced. In particular, at temperatures slightly above the smectic A-nematic phase transition and for electric fields near the critical field, there are large fluctuations in the short range order.

INTRODUCTION

The theory of the smectic A-nematic phase transition has been studied recently by deGennes[1] and McMillan.[2] In analogy to the susceptibility of superconductors, deGennes[1] postulated that the twist and bend elastic constants of the nematic phase should show an anomolous pretransitional effect just above the transitional temperature, T_{AN}. Applying Landau theory, deGennes shows that order fluctuations above T_{AN} will lead to the formation of ordered droplets. X-ray scattering data reported by deVries[3] has indicated the presence of small domains with smectic ordering in the nematic phase. In a smectic phase twist and bend deformations are forbidden,[4] so that the presence of short range smectic order in the nematic phase would lead to an increase in the elastic constants.

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In this paper we show the results of an experiment to determine whether the effects of short range order could be detected in the cholesteric ordering of a cholesteric-nematic mixture. The distortions of the angular distribution of the cholesteric structure due to an applied field are dependent on K_{22}, the twist elastic constant. An increase in this elastic constant will be reflected in the spin-lattice relaxation rate. Moreover, as the critical field for unwinding the nematic–cholesteric mixture is reached short range order fluctuations should be enhanced, which could lead to a further increase in the spin lattice relaxation rate.

SPIN-LATTICE RELAXATION IN NEMATIC-CHOLESTERIC MIXTURES

The theory of nuclear spin-lattice relaxation in nematics may be easily extended to the case of nematic–cholesteric mixtures. This is done by calculating the time dependence of the magnetization, taking into account angular dependent relaxation terms by including the angular distribution of molecular orientation along the pitch axis. The effective relaxation rate may then be extracted numerically from the time dependent integrals which describe the relative magnetization. A discussion of this technique has been given elsewhere.[5]

In the present work the relaxation time is calculated from the recent theory of Ukleja, Pirs, and Doane (UPD)[6] which we have extended to account for the full time dependence of the relaxation time in the rotating frame ($T_{1\rho}$).[5] We have chosen to measure $T_{1\rho}$ in preference to the spin-lattice relaxation time in the laboratory frame (T_1), as $T_{1\rho}$ shows a much larger angular dependence than does T_1.

The UPD theory takes into account collective order fluctuations, diffusion, and cross terms arising from mixing of these two effects. For $T_{1\rho}$ the most important terms in the angular dependence are those due to order fluctuations. These terms vanish for parallel alignment of the molecular axis with the magnetic field.

Thus, there are three principal reasons that the measurement of $T_{1\rho}$ in a nematic–cholesteric mixture as a function of temperature and applied electric field should provide a means of observing the effects of pre-transitional smectic order. First, the temperature dependence of the elastic constants and viscosities will affect the cut-off in the collective order modes. Second, the angular dependent terms in $T_{1\rho}$ will contribute strongly because of the twisted structure. And, third, fluctuations in the order modes will be enhanced near the critical field for unwinding the nematic–cholesteric mixture.

EXPERIMENTAL PROCEDURE

The compound CBOOA has a second order smectic A-nematic phase transition at 82.8°C in the pure state. Several researchers[7–13] have investigated the physical properties of this material near the transition temperature, T_{AN}. Anomolous increases have been reported for the bend elastic constant,[9,10] the twist elastic constant,[11,12] and the twist viscosity.[13]

A nematic–cholesteric mixture of CBOOA doped with 2.23 wt.% of cholesteryl decanoate (CD) was prepared in a standard sample cell.[14] The CD has a cholesteric mesophase between 83°C and 91°C. The mixture displays a cholesteric phase from 82.6°C to 95.1°C and has a smectic A phase below the cholesteric.

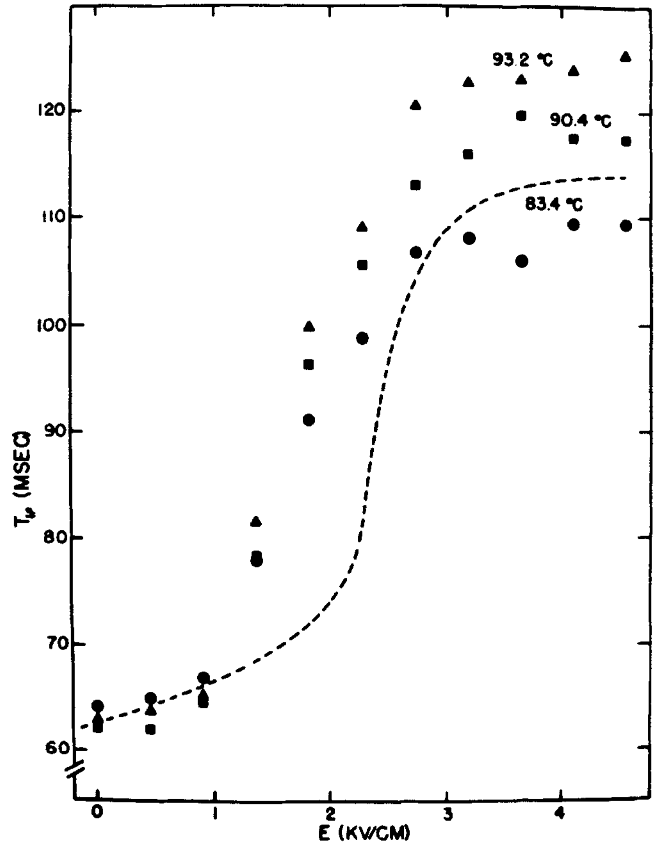

FIGURE 1 Rotating frame nuclear spin-lattice relaxation time as a function of applied electric field. The dashed line is a best fit of a calculation based on reference 6 (see text).

The rotating frame spin-lattice relaxation time was measured as a function of constant amplitude electric field. A 5 Khz ac electric field was used. The experiment was repeated at several temperatures through the cholesteric range. The electric field amplitude was varied from zero field to a value exceeding the critical field for a cholesteric-nematic phase transition. The electric field was applied parallel to the static magnetic field H_0 so that the total effective field was a combination of the two.

The $T_{1\rho}$ measurements were made at a spin-locking field strength $H_1 =$ 3.0 Gauss. The sample was allowed to come to thermal equilibrium before measuring each point eliminating the possibility of heating due to impurity conduction. The sample temperature was electronically controlled and was stable to within ±0.2°C.

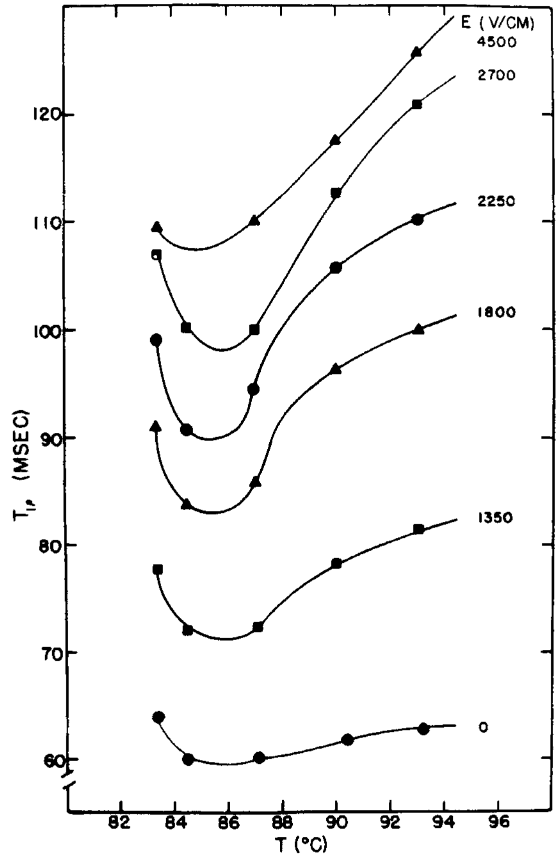

FIGURE 2 Temperature dependence of $T_{1\rho}$ at constant electric field.

The data plotted in Figure 1 show $T_{1\rho}$ as a function of electric field. Results are shown for three selected temperatures. All data in this figure display the same general structure. The relaxation time is monotonic in field strength increasing from a zero field value to a maximum which occurs at the critical field of 2700 V/cm. Above this field $T_{1\rho}$ rises slightly and then levels off.

Figure 2 shows the experimental results plotted as a function of temperature. The solid lines show the relationship between points taken at the same electric field strength. The effect of short range order is shown by the change in the shape of the curves in the temperature region between 83°C and 85°C.

To remove the effect of other temperature dependent factors, the data has been replotted in Figure 3 with a reduced relaxation time. The temperature dependence of the cholesteric phase has been removed by defining a reduced $T_{1\rho}$ as $\delta T_{1\rho}(E) = T_{1\rho}(E) - T_{1\rho}(E = 0)$.

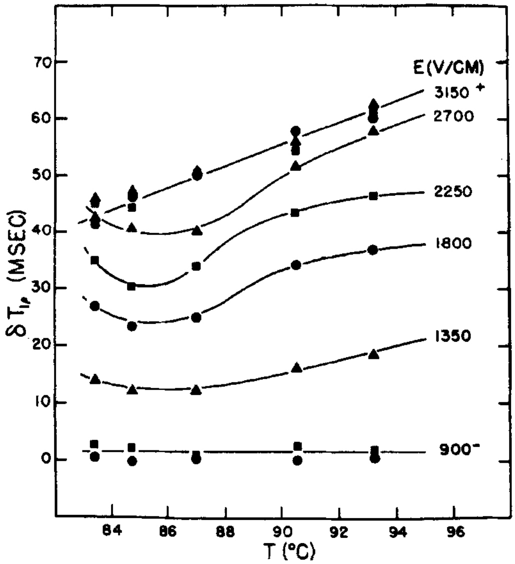

FIGURE 3 Reduced rotating frame nuclear spin-lattice relaxation time as a function of constant electric field intensity. Here $\delta T_{1\rho}(E) = T_{1\rho}(E) - T_{1\rho}(E = 0)$.

DISCUSSION

It can be seen from Figure 3 that $T_{1\rho}$ in the nematic–cholesteric mixture has a local minimum above the nematic–smectic A phase transition in CBOOA. The variations with temperature are particularly prominent near the critical field for the cholesteric–nematic phase transition, where the fluctuations are enhanced by that phase transition.

Using the method of reference 5 for computing the average relaxation along the cholesteric twist axis, the UPD theory yields a curve in which the relaxation time diverges logarithmically with increasing field strength up to the critical field strength. At the critical field the sample is assumed to be completely aligned and nematic in texture. Thus, no further change in the relaxation time would be expected above the critical field. This form does not adequately fit the observed behavior as is shown by the dashed line in Figure 1.

CONCLUSION

The rotating frame nuclear spin lattice relaxation in a nematic–cholesteric mixture of CBOOA/CD shows a temperature and electric field dependence which exhibits a local minimum above the nematic–smectic A phase transition of CBOOA. This behavior appears to be attributable to the onset of short range smectic A order in the nematic phase of CBOOA.

References

1. P. G. deGennes, *Solid State Comm.*, **10**, 753 (1972).
2. W. L. McMillan, *Phys. Rev.*, **A6**, 936 (1972).
3. A. deVries, *Mol. Cryst. Liquid Cryst.*, **10**, 219 (1970).
4. P. G. deGennes, "The Physics of Liquid Crystals,", (Clarendon Press, 1974).
5. C. E. Tarr and M. E. Field, *Mol. Cryst. Liquid Cryst.*, **30**, 143 (1975).
6. P. Ukleja, J. Pirs, and J. W. Doane, *Phys. Rev.*, **A14**, 414 (1976).
7. B. Cabane and W. G. Clark, *Solid State Comm.*, **13**, 129 (1973).
8. W. L. McMillan, *Phys. Rev.*, **A7**, 1419 (1973).
9. L. Cheung, R. B. Meyer, and H. Gruler, *Phys. Rev. Lett.*, **31**, 349 (1973).
10. P. E. Cladis, *Phys. Rev. Lett.*, **31**, 1200 (1973).
11. N. V. Madhusudana, P. P. Karat and S. Chandrasekhar, *Pramana Suppl.*, **1**, 225 (1975).
12. M. Delaye, R. Ribotta and G. Durand, *Phys. Rev. Lett.*, **31**, 443 (1973).
13. C. Huang, R. S. Pindak, P. J. Flanders, and J. T. Ho, *Phys. Rev. Lett.*, **33**, 400 (1974).
14. T. E. Kubaska, C. E. Tarr, and T. B. Tripp, *Mol. Cryst. Liquid Cryst.*, **29**, 155 (1974).