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Frequency Dependence of Rotating-Frame Nuclear Spin-Lattice Relaxation in Nematic-Cholesteric Mixtures†

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The frequency dependence of the rotating frame proton spin-lattice relaxation time $T_{1\rho}$ for a cholesteric structure was derived from a recent calculation of the angular dependence of $T_{1\rho}$ for nematic liquid crystals. The calculated frequency dependence is in good agreement with experimental studies of several nematic-cholesteric mixtures.

INTRODUCTION

Several investigators[1–3] have reported investigations of nuclear spin-lattice relaxation in cholesteric liquid crystals. In particular, it has been shown that some of these data are non-exponential and are adequately represented by a linear combination of two single exponential relaxation functions. The present work is an attempt to explain this non-exponential behavior in terms of a recent theoretical calculation[4] of spin-lattice relaxation in nematic liquid crystals. This theory of nematics is extended to cholesterics and predicts non-exponential relaxation in both the laboratory and rotating frames. These calculations are in good agreement with measurements in several nematic-cholesteric mixtures.

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CALCULATION OF SPIN-LATTICE RELAXATION

Let us consider a nematic material with a positive anisotropy in its magnetic susceptibility that is doped with a small amount of cholesteric material. In such a case the material takes on a helical structure whose pitch is a function of cholesteric concentration. If the mixture is placed in a magnetic field, the structure is distorted, and, in sufficiently large magnetic fields, goes into a well aligned nematic structure. If the helical axis is taken to be the z-axis, and ϕ is the angle between the preferred direction of the molecular axis and the magnetic field at some point z, then the relationship between ϕ and z is given by:[5]

$$d\phi/dz = (1 - k^2 \cos^2 \phi)^{1/2}/k\xi, \tag{1}$$

where ξ is a characteristic length, z is a distance along the twist axis, and k is the solution of the equation:

$$\frac{k}{E(k)} = \frac{H}{H_c}, \tag{2}$$

where $E(k)$ is a complete elliptic integral of the second kind, and H_c is the critical field for which the material unwinds to a nematic structure.

Now, since the spin-lattice relaxation in the nematic phase is angularly dependent, then the relaxation time in the cholesteric phase should depend upon molecular position along the z-axis. The relaxation times in the laboratory and rotating frames T_1 and $T_{1\rho}$ are given by:[4]

$$T_1^{-1} = \frac{A}{\sqrt{\omega_0}} \left[\left(\tfrac{1}{2} + \sqrt{2}\right) - \tfrac{3}{2}\cos^2 \phi + \left(2 - \sqrt{2}\right)\cos^4 \phi\right] + B, \tag{3a}$$

and:

$$T_{1\rho}^{-1} = \frac{A_\rho}{\sqrt{\omega_1}} \left(\frac{9}{2\sqrt{2}}(\cos^2 \phi - \cos^4 \phi) + \left[\left(\frac{5}{4} + \frac{1}{2\sqrt{2}}\right) - \frac{15}{4}\cos^2 \phi + \left(5 - \frac{1}{2\sqrt{2}}\right)\cos^4 \phi\right]\sqrt{\omega_1/\omega_0}\right) + B_\rho, \tag{3b}$$

where A, A_ρ, B, B_ρ are independent of ϕ and B and B_ρ are also independent of frequency, ω_0 is the Larmor frequency $\omega_0 = \gamma H_0$, and $\omega_1 = \gamma H_1$, where H_1 is the magnitude of the rotating r.f. magnetic field.

To calculate T_1 or $T_{1\rho}$ in a nematic-cholesteric mixture we begin by assuming that the magnetization at a time t following a 90° pulse is the sum of the magnetization due to spins distributed with uniform density along the

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z-axis. The total relative magnetization is then given by:

$$M(t) = \frac{1}{z_0} \int_0^{z_0} e^{-t/T_1(z)} \, dz \tag{4}$$

where $T_1(z)$ is the appropriate relaxation time at position z along the helical axis. Thus, by performing the integral of Eq. 4 with the aid of Eqs. 1 and 3, we obtain the total magnetization as a function of time t. It is possible to then extract the values of T_1 that should be observed experimentally. These integrations must be performed numerically and require a knowledge of the constants A and B in Eqs. 3 for the material under study.

EXPERIMENT

Several nematic-cholesteric mixtures have been investigated. Because of the rather large amount of information necessary to discuss each, however, we shall present detailed results for only one, a mixture of 1.75 wt% of cholesterol-nonanoate (CN) in *n*-*p*-cyanobenzilidene-*p*-*n*-octaloxyanaline (CBOOA). The samples used were obtained commercially (Eastman Organics) and were purified by recrystalization from ethanol. The sample cell geometry used has been described elsewhere.[6] Measurements of the proton relaxation times T_1 and $T_{1\rho}$ were made using standard n.m.r. techniques in a magnetic field of 7 kG. This field was well below the critical field of 12.1 kG for this mixture.

In order to obtain the constants A and B in Eqs. 3, the mixture was untwisted to a nematic texture using a low frequency electric field of sufficient magnitude to maintain the nematic structure for all angles θ between the electric and magnetic fields. Both T_1 and $T_{1\rho}$ were measured as a function of θ, and the constants A and B obtained by fitting Eqs. 3 to these data. The angular dependence of T_1 is much weaker than that of $T_{1\rho}$ in this mixture, and we shall concentrate our discussion on $T_{1\rho}$.

The results of the measurement of the angular dependence of $T_{1\rho}$ in a 5 kHz electric field of 3.8 kV/cm is shown in Figure 1. The solid line shows the best fit to the data using Eq. 3b for which $A_\rho = 2.34 \times 10^3\ \text{sec}^{-1/2}$ and $B_\rho = 4.00\ \text{sec}^{-1}$. These constants were then used to calculate $T_{1\rho}$ as a function of position along the cholesteric pitch axis using Eqs. 1 and 3b. The resulting function is periodic with a period of $z_0/2$ and is symmetric about $z = z_0/4$, where z_0 is the pitch length. To calculate the contributions to the magnetization from all molecules, it is then necessary only to consider those molecules from $z = 0$ to $z = z_0/4$. The dependence of $T_{1\rho}$ on z in this interval is shown in Figure 2, where $H_0 = 7.05$ kG, $H_0/H_c = 0.58$, and $H_1 = 5$ G.

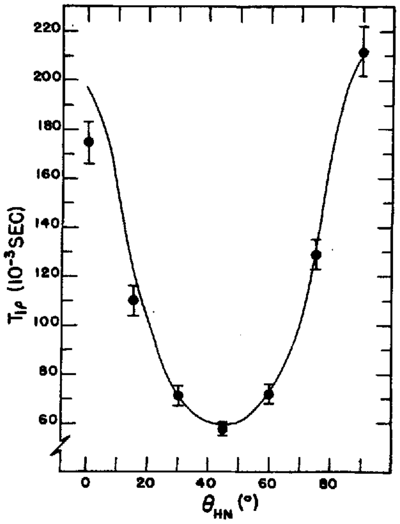

FIGURE 1 Angular Dependence of $T_{1\rho}$ for 1.75 wt %CN in CBOOA for H_1 = 5 G. Solid line is best fit of Eq. 3b to data.

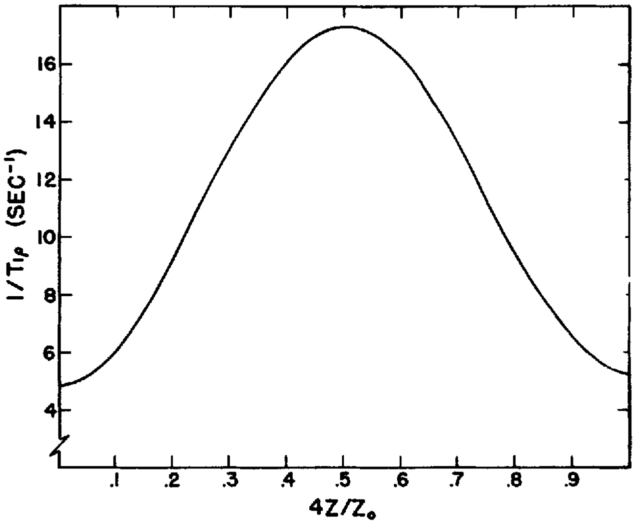

FIGURE 2 $T_{1\rho}$ as a function of position along the cholesteric pitch axis using parameters obtained from data in Figure 1.

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Finally, $T_{1\rho}$ was calculated as a function of H_1 using Eq. 3b and the constants A_ρ and B_ρ determined previously. The integration technique discussed above was used to generate the magnetization in the rotating-frame as a function of time. In Figure 3 this calculated dependence of $T_{1\rho}$ on H_1 is shown by the solid line and compared to several experimental values which are plotted with ±5% error bars.

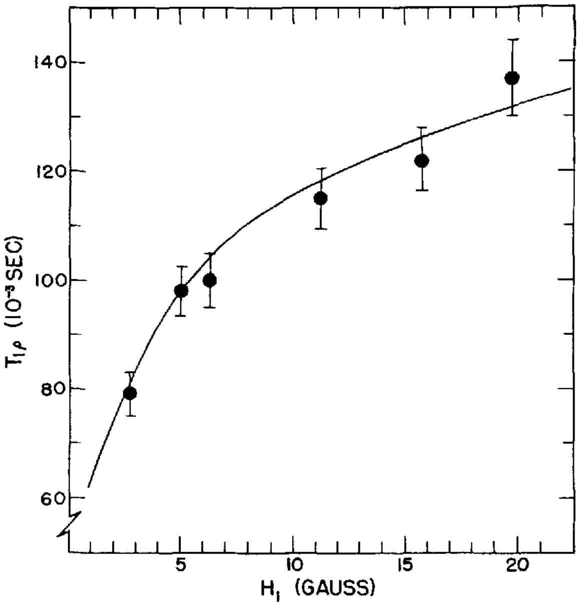

FIGURE 3 $T_{1\rho}$ as a function of H_1 for $H_0 = 7.05$ kG $= 0.58\ H_c$.

An iterative technique[7] was used to extract relaxation times from the calculated values of magnetization. In all cases, the theory predicts non-exponential relaxation for both T_1 and $T_{1\rho}$ which can be closely approximated by the sum of two exponential relaxation functions. The departure from single exponential relaxation is appreciable only for values of H_0 near the critical field H_c. For the data presented here ($H_0 = 0.58\ H_c$), the relaxation is nearly exponential, and only a single relaxation time is assumed in the solid curve in Figure 3 and in fitting the experimental data shown.

It should be noted that the angular dependence of $T_{1\rho}$ for the mixture treated here is the same as that measured in pure CBOOA. For somewhat higher concentrations of CN in CBOOA, however, the angular dependence of $T_{1\rho}$ was observed to differ noticably from that of the pure material, which suggests that the cut-off frequency[4] for short range order fluctuations is influenced by the dopant. Data from the more concentrated mixtures, however, did agree well with calculated values, provided that A_p and B_p were determined from measurements on the mixed sample.

CONCLUSION

The rotating-frame spin-lattice relaxation in nematic-cholesteric mixtures can be described by suitably averaging the relaxation mechanism due to short range order fluctuations for nematics over the angular distribution of molecular orientations along the cholesteric pitch axis. This result suggests several additional studies, for example, measurement of the cholesteric-nematic phase transition induced by an electric field, as well as magnetic field (H_0) and temperature dependences of T_1 and $T_{1\rho}$. The case of the electric field induced transition should be especially interesting as changes in the order fluctuations should be particularly noticable near the critical electric field intensity for the phase transition. These studies are currently underway in our laboratory.

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