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Proton Spin-lattice Relaxation Near a Weak First Order Smectic A-Nematic Phase Transition

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The proton spin-lattice relaxation time T_1 in the nematic and smectic A phases of the liquid crystal *N*-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline was measured at several Larmor frequencies in the range of 5 to 30 MHz. By extrapolating to infinite Larmor frequency in the plots of T_1^{-1} versus the reciprocal of the square root of Larmor frequency, the relaxation rates due presumably to molecular diffusion were obtained at various temperatures. An activation energy for molecular diffusion in the mesophases was determined to be 3.4 Kcal/mole from these extrapolated values. At a low Larmor frequency (e.g. 5.5 MHz), the observed relaxation rate just above the smectic A-nematic (SN) transition can be attributed to the following relaxation mechanisms: molecular diffusion, long range nematic director fluctuations and short range smectic order fluctuations. The calculated relaxation rate due to the short range smectic order fluctuations in the nematic phase was found to depend critically on temperature with a critical temperature close to the SN transition temperature.

INTRODUCTION

In a smectic A phase, rod-like molecules are stacked in a layered structure with their long axes preferentially aligned perpendicular to the planes of the layers. de Gennes[1] has defined an order parameter for this phase as a complex quantity $\Psi(r)$, the modulus of which determines the density of the layers and the phase of which determines the position of the layers. A smectic A-nematic (SN) transition is characterized by a change in the translational order,

viz. from a phase with both an orientational order and a one dimensional smectic order to one of orientational order only. That the SN transition at temperature T_{SN} may be of second order was noted by Kobayashi[2] and McMillan.[3] de Gennes[1] further drew an analogy between the normal state diamagnetic susceptibility near a superconducting transition and the nematic bend (K_3) and twist (K_2) elastic constants near a SN transition. These predictions have immediately prompted many experimental investigations.[4-8] McMillan[4] has also found that the compound *N*-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline[9] (CBOOA) shows no detectable latent heat at T_{SN} and therefore presumably exhibits a second order SN transition. Recent experiments with this compound,[8] however, show that the transition at T_{SN} is first order. This agrees with the calculations of Halperin *et al.*,[10] which indicate that the SN transition should at least be weakly first order in all compounds. We report in this paper a proton spin-lattice relaxation time (T_1) study as a function of Larmor frequency ($\omega_L/2\pi$) and temperature in the nematic and smectic A phases of CBOOA. This work was undertaken because of the possible second order phase transition at T_{SN} and because of the recent T_1 calculations above and below a second order SN transition by Brochard.[11] Above a SN transition, according to Brochard, certain fluctuations in the nematic director fluctuations become restricted as the lower temperature smectic A phase is approached. This is revealed in T_1 through the singularity in the temperature dependence of the nematic bend and twist elastic constants and of the effective rotational viscosity γ_e. Brochard's T_1 calculations just above T_{SN}, however, do not take into account the short range fluctuations in the amplitude ($|\Psi|$) of the density wave. In the nematic phase, the short range smectic order ($|\Psi|$) relaxes in a finite lifetime τ_m as given by[11]

$$\tau_m^{-1} \sim \frac{K_{2,3}}{\gamma_e \xi^2}$$

where ξ is the coherence length of the short range smectic order (or the size of the cybotactic groups). It will be shown how one may use the proton T_1 to study the short range smectic order fluctuations just above T_{SN} in CBOOA by subtracting the relaxation rate due to other mechanisms, such as translational diffusion, from $1/T_1$. A determination of the critical exponents of K_2, K_3 and γ_e may be possible from the T_1 measurements above T_{SN} when either the director fluctuations become limited or the short range smectic density wave fluctuations are effective.

EXPERIMENTAL

The liquid crystal CBOOA was obtained from Eastman Kodak. The sample was used without further purification and sealed in a vacuum by the freeze-

melt method. The transition temperatures from isotropic to nematic, nematic to smectic A, and solid to smectic A were measured with a polarizing microscope equipped with a Mettler FP52 hot stage as 380.7, 355.8 and 346.2°K respectively. T_{SN} is reported[8] to be > 356.4°K in purified CBOOA samples.

The proton T_1 measurements were made with a Bruker B-KR 322S variable frequency pulsed spectrometer using $180° - \tau - 90°$ pulse sequences. The accuracy in our T_1 measurements is better than 5%. The temperatures of the sample were maintained by an air flow with a temperature gradient across the sample of the order of 0.5° C.

RESULTS AND DISCUSSION

The proton T_1 were measured at 5.5, 6.5, 8, 14 and 30 MHz in the smectic A and nematic phases of CBOOA. The data are presented in Figures 1 and 2. The proton T_1 in the smectic A phase measured by cooling from the nematic phase was found to be higher than that obtained by heating from the solid phase. It is believed that the cooling curve for T_1 (indicated by dashed lines)

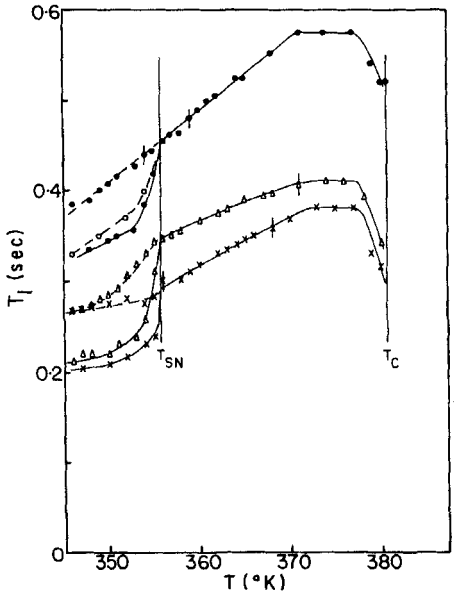

FIGURE 1 Proton spin-lattice relaxation time T_1 versus temperature. ×, △ and ● denote measurements at 5.5, 8 and 30 MHz respectively. ○ denotes measurements at 30 MHz while the sample was rotated through the magic angle. Dashed and solid lines in the smectic A phase represent cooling and heating curves respectively.

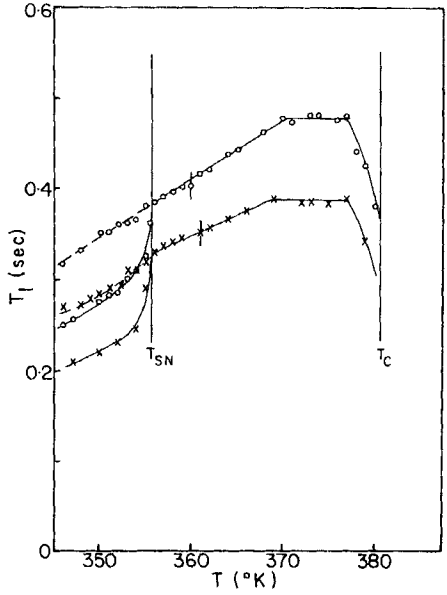

FIGURE 2 Proton spin-lattice relaxation time T_1 versus temperature. × and ○ denote measurements at 6.5 and 14 MHz respectively. Dashed and solid lines in the smectic A phase represent cooling and heating curves respectively.

in the smectic A phase would be more appropriate for data analysis, as the long molecular axes of rod-like molecules are "frozen-in" along the external magnetic field by cooling through the nematic phase to form a single domain sample of smectic A phase. We found this to be true even at the lowest field ($\sim$ 1.3 k Gauss) used in the present study. This was checked by observing the broadening of the free induction signal after the sample was rotated through the magic angle ($\sim$ 54°) to eliminate the dipolar broadening. T_1 was also measured at the magic angle at the above Larmor frequencies, but only the 30 MHz data are presented in Figure 1. It is therefore seen that the proton T_1 depends on the angle of rotation of the sample in the smectic A phase of CBOOA. It is also of interest to note that at all the Larmor frequencies studied the T_1 measured by cooling shows no apparent discontinuity at T_{SN}. This is in contradiction with the calculations of Brochard[11] in which T_1 was shown to depend critically on temperature both above and below a second order SN transition at T_{SN} if the Larmor frequency is sufficiently low (i.e. $\omega_L/2\pi \ll |T - T_{SN}|/T \cdot 10^5$ MHz). The difficulty in using proton T_1 to study order fluctuations (both short range and/or long range) in liquid crystals is that other relaxation mechanisms, such as molecular diffusion, also contribute significantly to the observed relaxation rate. It is now evident that diffusion[22] definitely contributes to the proton spin-lattice relaxation in liquid crystals.

The activation energy for diffusion can be easily obtained in the isotropic phase of liquid crystals by measuring the diffusion coefficient, but little or no information on diffusion is available in the liquid crystalline phases. Consequently, it is not a straightforward matter to interpret proton T_1 data in these mesophases.

In nematic liquid crystals, if the long range orientational order (director) fluctuations are responsible for the spin relaxation T_1 has been shown to follow the characteristic frequency dependence[13]

$$\frac{1}{T_1} = A(T)\omega_L^{-1/2} + R_0(T) \tag{1}$$

where $A(T)$ is weakly temperature dependent and $R_0(T)$ is the spin-lattice relaxation rate due to all other relaxation mechanisms, such as diffusion. Above a second order SN transition and at a Larmor frequency smaller than τ_m^{-1}, the director fluctuations still give a spin-lattice relaxation rate given by Eq. (1) except that $A(T)$ has the following critical behavior[11] owing to the singularity in K_2, K_3 and γ_e

$$A(T) \propto (T - T_c)^{1/2} \tag{2}$$

where the critical temperature T_c is T_{SN}. If the SN transition is weakly first order, T_c will be slightly below T_{SN}. Since the singularity in K_2, K_3, and γ_e occur very close to T_{SN},[8,14] one expects T_1 to behave critically within $\sim 3°$ above the phase transition provided the long range director fluctuations are only observed. Below T_{SN}, T_1 has a nematic type behavior in the limit of large Larmor frequency. When the Larmor frequency is small T_1 is calculated to be frequency independent and follows the relationship[11]

$$T_1 \propto (T_c - T)^{1/3} \tag{3}$$

Indeed our experiments show that T_1 is frequency independent in the low temperature end of the smectic A phase at $\omega_L/2\pi < 8$ MHz (Figures 1 and 2). $R_0(T)$, according to Eq. (1), can be obtained at various temperatures in the nematic and smectic A phases by extrapolating to infinite Larmor frequency in the plots of $1/T_1$ versus $(\omega_L/2\pi)^{-1/2}$ (Figure 3). As discussed above, Eq. (1) holds in the smectic A phase at large frequency (i.e., ≥ 8 MHz in CBOOA) and hence the extrapolation remains valid. In Figure 4, a semi-log plot of $(T_1)_0$, which is the reciprocal of R_0, versus$1/T$ is shown to give an activation energy $E_a = 3.4$ Kcal/mole. If R_0 arises mainly from molecular diffusion, a value of the activation energy for diffusion is therefore determined in the mesophases of CBOOA. The above E_a value assigned tentatively to molecular diffusion is lower than the E_a values for diffusion in the isotropic phase of nematics,[15] and is non-zero in contrast with the earlier measurements of

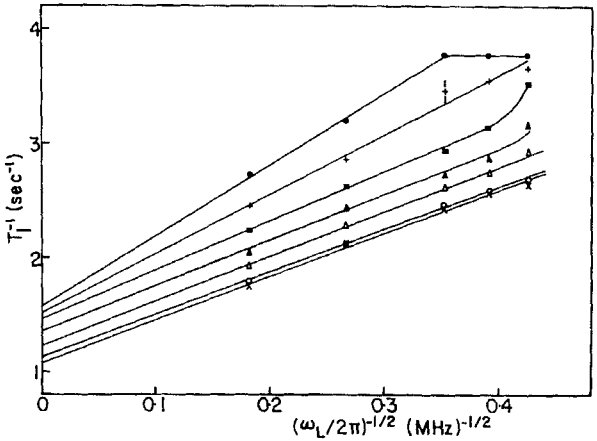

FIGURE 3 Proton spin-lattice relaxation rate versus $(\omega_L/2\pi)^{-1/2}$. ●, +, ■ denote measurements by cooling from the nematic phase at 345°, 350° and 355°K respectively. ▲, △, ○ and × denote measurements at 360°, 364°, 370° and 375°K respectively. The plot at 379°K is not shown for the sake of clarity.

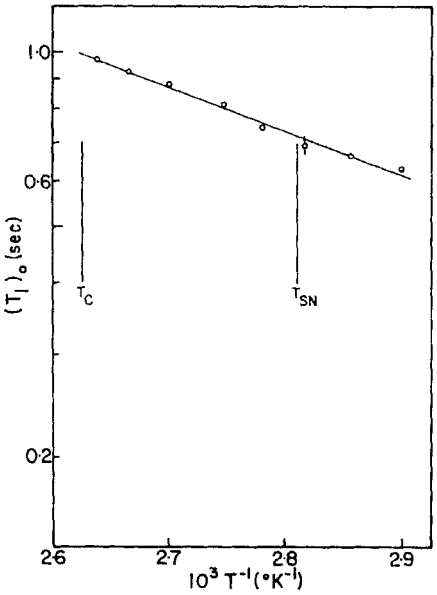

FIGURE 4 Plot of $(T_1)_0$ (see text) versus reciprocal temperature.

temperature independent diffusion coefficients in the mesophases of liquid crystals by neutron scattering.[16] It is not understood why R_0 shows no apparent discontinuity at T_{SN} since there is a change in the translational order at this temperature. It may be that R_0 is mainly ascribed to fast two dimensional diffusion within smectic layers below and not far above T_{SN}.

Knowing $R_0(T)$, one can calculate the relaxation rate $1/T_1'$ due to the long range orientational order fluctuations and the short range smectic density wave fluctuations by writing

$$\frac{1}{T_1} = \frac{1}{T_1'} + R_0 \tag{4}$$

A plot of $1/T_1'$ versus temperature at various ω_L is shown in Figure 5. At 30 MHz, $1/T_1'$ is temperature independent within experimental error in the entire nematic phase and increases gradually near and below T_{SN}. Similar behavior is observed at 14, 8 and 6.5 MHz except that $1/T_1'$ tends to increase farther above T_{SN} at lower frequency. At high Larmor frequency, the spin relaxation rate is insensitive to the local fluctuations in the short range smectic order. The temperature independent T_1' in the nematic phase is therefore consistent with relaxation by the long range orientation order fluctuations as described by $A(T)$ in Eq. (1). At 5.5 MHz, $1/T_1'$ remains almost constant in the smectic A phase but increases in the nematic phase as the temperature is

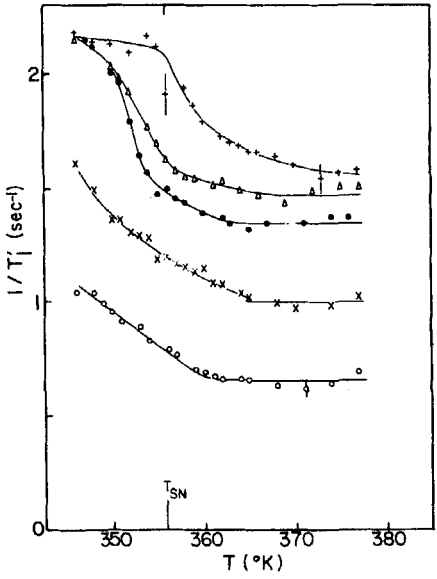

FIGURE 5 Plot of $1/T_1'$ (see text) versus temperature. +, △, ●, × and ○ denote data at 5.5, 6.5, 8, 14 and 30 MHz respectively.

lowered towards the SN transition. It has a temperature dependence opposite to that described by Eq. (2). Thus it is likely that restriction in certain director fluctuations due to the short range smectic ordering is not detected in the present T_1 study. However, the peculiar behavior in $1/T_1'$ at low frequency near T_{SN} must be caused by short range fluctuations in the smectic density wave. It therefore appears that an alternative to its intramolecular effects as calculated by Brochard [see Eq. (2)] is to consider as a spin relaxation mechanism the modulation of intermolecular dipolar interactions by such one dimensional density wave fluctuations above T_{SN}.

To study the intermolecular effects of short range smectic order fluctuations on the spin-lattice relaxation rate $(1/T_1'')$, one has to further subtract from $1/T_1'$ the rate due to the long range orientational order fluctuations of the nematic phase. In other words, one needs a value for $A(T)\omega_L^{-1/2}$ at 5.5 MHz. This value is calculated to be 1.52 $\sec^{-1}$ in the entire range of nematic phase using the fact that in the nematic phase, $1/T_1'$ at 30 MHz arises mainly from the term $A(T)\omega_L^{-1/2}$ in Eq. (1). Hence the values of T_1'' above T_{SN} are obtained as follows,

$$\frac{1}{T_1''} = \frac{1}{T_1'} - 1.52 \text{ sec}^{-1} \tag{5}$$

and are given in Table I. Knowing that T_c is approximately equal to T_{SN} in CBOOA,[8] a log–log plot of T_1'' versus $(T - T_c)$ was first made to give an approximate slope of 3/4. A plot of $(T_1'')^{4/3}$ versus T is presented in Figure 6. A linear curve is seen in a temperature range of about 12° above T_{SN}. Hence the spin-lattice relaxation time due to the short range smectic order fluctu-

TABLE I

Analysis of the proton T_1 measurements at 5.5 MHz

T (°K)	$(T_1)_{expt}$ ($\times 10^{-3}$ sec)	$\left(\frac{1}{T_1}\right)_{expt}$ ($\sec^{-1}$)	$\left(\frac{1}{T_1'}\right)$ ($\sec^{-1}$)	$\left(\frac{1}{T_1''}\right)$ ($\sec^{-1}$)	$(T_1'')^{4/3}$ ($\sec^{4/3}$)
356	300	3.33	1.91	0.39	3.5
358	300	3.33	1.94	0.42	3.2
359	310	3.23	1.86	0.34	4.2
360	318	3.14	1.79	0.27	5.6
362	330	3.03	1.73	0.21	8.0
363	335	2.99	1.70	0.18	9.8
364	340	2.94	1.69	0.17	10.6
365	345	2.90	1.66	0.14	13.7
366	349	2.87	1.66	0.14	13.7
368	358 ± 10	2.79	1.64	0.12	16.3 ± 40
370	367	2.72	1.60	0.08	29

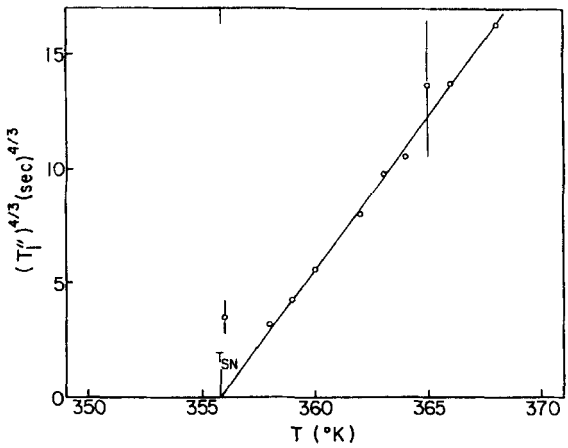

FIGURE 6 Plot of $(T_1'')^{4/3}$ versus temperature at 5.5 MHz.

ations in the nematic phase of CBOOA as determined experimentally follows a critical temperature behavior as given by

$$T_1'' \propto (T - T_c)^{3/4} \tag{6}$$

with $T_c \approx T_{SN}$. At present, the intermolecular effects on T_1 as a result of short range smectic order fluctuations have not been calculated theoretically. These effects must reflect the lifetime τ_m of the smectic order above T_{SN}. Thus if a suitable theory is available, Eq. (6) will provide an indirect determination of the critical exponent for γ_e using the known critical exponents of K_2 and K_3. ${}^{8}\gamma_e$ has been predicted to diverge as $\xi^{1/2}$,[11] and recently verified in CBOOA by two groups.[14] To test whether the assumptions and approximations used in the above analysis of the proton T_1 data are valid, the Brochard's T_1 calculation must be extended to include modulation of intermolecular dipolar interactions by the one dimensional density wave fluctuations. It also remains to be seen why the proton T_1 above a weak first order SN transition of CBOOA does not show the intramolecular effects of Pincus as a result of short range smectic order fluctuations. It is interesting to note that the restriction of certain director fluctuations has been observed in the isotropic phase of a smectic *A* liquid crystal diethylazoxybenzoate by means of the proton T_1 measurements[17] at a low Larmor frequency.

In conclusion, we have shown how one may study the influence of short range smectic order fluctuations on the intermolecular dipolar interactions near a weak first order SN transition using the proton spin-lattice relaxation time measurements at several Larmor frequencies.

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