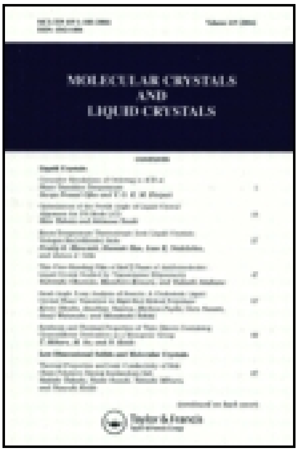

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DEUTERIUM NMR STUDY OF UNIAXIAL-BIAXIAL PHASE TRANSITIONS IN A SMECTOGEN

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Abstract The effects of uniaxial-biaxial phase transition on the spectral densities measured from the deuteron Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times are examined in two partially deuterated samples of 4-n-pentyloxybenzylidene-4′-heptylaniline (5O.7): one deuterated at the methine site (5O.7-d_1) and one with the aniline ring deuterated (5O.7-d_4). The deuterated sites are chosen so that their relaxation behaviours are not complicated by internal chain dynamics. It is found that the spectral densities show discontinuities at the $S_C - S_B$ phase transition, but show no discontinuity at the $S_A - S_C$ and $S_B - S_G$ phase transitions. Both the smectic C and G phases are biaxial. The results are discussed in terms of molecular reorientation and director fluctuations. Preliminary data for the sample director oriented at 90° with the external magnetic field are reported in the B and G phases of 5O.7-d_1.

INTRODUCTION

Nuclear spin relaxation measurements provide a powerful means of probing molecular dynamics in liquid crystals[1]. In recent years, many NMR studies of liquid crystals have employed the deuteron probe to measure the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times. These two relaxation times allow a separation of the two spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$, where $\omega_0/2\pi$ is the Larmor frequency. The temperature and frequency dependences of these spectral density parameters are useful to test different motional models in anisotropic media. Thus far most deuteron spin relaxation studies have been limited[1] to uniaxial nematic and smectic phases. S_C phase was probably the first mesophase to be recognized as biaxial. It was assumed[2] that the effects of phase biaxiality are small and may be neglected when treating spin relaxation in S_C phases. Biaxial smectic phases have been known for sometime, while biaxial nematic phases are now found in lyotropics[3] and thermotropics[4] including polymer liquid crystals. Deuteron NMR spectroscopy has played[5,6] an important role in detecting phase biaxiality through measuring a motionally-induced asymmetry parameter $\overline{\eta}$ in the quadupolar spin interaction. Similar information can be measured[7] from ^{14}N NQR spectra. The non-zero $\overline{\eta}$ gives a direct measurement of the ordering of transverse molecular axes, e.g. bipolar orientational order[8], when reasonable hypotheses regarding the motions involved are taken into account. It is noted that the effects of $\overline{\eta}$ on the deuteron NMR spectral patterns are only observed when the director is not aligned along the external magnetic field.

Recently Berggren et. al.[9] have examined rotational diffusion of uniaxial probes in biaxial liquid crystal phases. They have calculated orientational correlation functions and spectral densities that are needed to interpret spin relaxation data in biaxial phases. They showed that some spectral densities vanish, while others change continuously at the biaxial-uniaxial phase transition. The "biaxial" spectral densities are those which are non-zero in the biaxial phase and vanish in the uniaxial phase. By examining the orientation dependences of spin-lattice relaxation times, we found[10] that the "biaxial" spectral densities are not observed as long as the sample director is oriented along the external magnetic field. These findings provide the theoretical basis for the present study. The smectogen 4-n-pentyloxybenzylidene-4′-hetylaniline (5O.7) exhibits the following phase sequence: $N - S_A - S_C - S_B - S_G$, upon cooling from the isotropic phase. The high temperature "disordered" phases (N, S_A, S_C) have been studied[11] in a methine-deuterated (5O.7-d$_1$) and a ring-deuterated (5O.7-d$_4$) sample at 15.3 and 46 MHz. In this paper, we focus on the spectral density data in the "disordered" and "ordered" smectic phases, in particular the phase transitions among these smectic phases. We present the basic theory in the next section.

BASIC THEORY

As a first approximation, we treat 5O.7 as a uniaxial molecule. In a stochastic Markovian process, the orientational correlation function for a uniaxial molecule can be written as

$$G^{LL'}_{mm'n}(t) = \int\int d\Omega_0 d\Omega P(\Omega_0) D^{L*}_{mn}(\Omega_0) P(\Omega_0|\Omega t) D^{L'}_{m'n}(\Omega) \tag{1}$$

where m and n represent the projection index of a rank L tensor in the laboratory frame and in the molecular frame, respectively. $P(\Omega_0|\Omega t)$ is the conditional probability of finding a molecule with the orientation given by the Euler angles $\Omega \equiv (\alpha, \beta, \gamma)$ at time t if the orientation of the molecule was Ω_0 at $t = 0$, and $P(\Omega)$, the equilibrium probability, is given by the Boltzmann distribution:

$$P(\Omega) = \frac{\exp[-U(\Omega)/kT]}{\int d\Omega \exp[-U(\Omega)/kT]} \tag{2}$$

where $U(\Omega)$ is the potential of mean torque acting on the molecule due to its neighbours. For uniaxial molecules in biaxial mesophases of D_{2h} symmetry, the potential of mean torque depends[12] on two Euler angles β and α, and may be expanded in terms of Wigner rotation matrices as

$$\frac{U(\alpha,\beta)}{kT} = \sum_{Jp} a_{Jp} D^J_{p0}(\alpha,\beta) \tag{3}$$

Following the procedures and approximations used by Nordio et al.[13], Berggren et al. have solved the rotational diffusion equation with the above $U(\alpha, \beta)$ to give the conditional probability that is required for evaluating the orientational correlation functions. In general, these correlation functions can be written as sum of decaying exponentials:

$$G^{LL'}_{mm'n}(t) = \sum_K (\beta^{LL'}_{mm'n})_K \exp[(\alpha^{LL'}_{mm'n})_K \, t] \tag{4}$$

where $(\alpha^{LL'}_{mm'n})_K$, the decay constants and $(\beta^{LL'}_{mm'n})_K$, the relative weights of the exponentials can be found in ref. [9]. The spectral densities in deuteron NMR experiments ($L = L' = 2$) can be obtained by Fourier transforming $G^2_{mm'n}(t)$ to give

$$J_{m_L m'_L}(\omega) = \frac{3\pi^2}{2}(q_{CD})^2 \sum_{m_M} \left[d^2_{m_M 0}(\theta)\right]^2 \sum_K \frac{(\beta^2_{m_L m'_L m_M})_K (\alpha^2_{m_L m'_L m_M})_K}{(\alpha^2_{m_L m'_L m_M})^2_K + \omega^2} \tag{5}$$

where $q_{CD} = e^2qQ/h$ is the quadrupolar coupling constant and θ is the angle between the C-D bond and the molecular z axis. In uniaxial phases, eq. (4) reduces to

$$G^2_{m_L m_M}(t) = \sum_j a^{(j)}_{m_L m_M} \exp[-t/(b^{(j)}_{m_L m_M} \tau^{(2)}_{m_M})] \tag{6}$$

in the notation of Vold and Vold[14]. The j sums over one to three, the coefficients $a^{(j)}_{m_L m_M}$ and $b^{(j)}_{m_L m_M}$ depend on the nematic order parameter $< P_2 >$ and $\tau^{(2)}_{m_M}$ are the usual correlation times for diffusion of a molecule in an isotropic liquid. Hence the possibility of observing correlation functions with $m_L \neq m'_L$ exists in biaxial phases. For uniaxial molecules in phases of the D_{2h} symmetry, the correlation functions $G^2_{m_L m'_L m_M}$ are nonzero. Furthermore, the standard properties of Wigner rotation matrices give

$$G^2_{m_L m'_L m_M}(t) = (-1)^{-m_L - m'_L} G^2_{m_L m'_L -m_M}(t) \tag{7}$$

which indicate that the spectral densities $J_{m_L m'_L}(\omega)$ vanish as long as the sum of m_L and m'_L is an odd number.

Using the standard spin relaxation theory[15] for deuterons (I=1), the quadrupolar and Zeeman spin-lattice relaxation rates for the director oriented at Ω in the laboratory frame are given by

$$\begin{aligned} [T_{1Q}(\Omega)]^{-1} &= 3J_1(\omega_0, \Omega) \\ [T_{1Z}(\Omega)]^{-1} &= J_1(\omega_0, \Omega) + 4J_2(2\omega_0, \Omega) \end{aligned} \tag{8}$$

where $\Omega \equiv (\Theta, \Phi)$ denotes the polar angles of the director in the laboratory frame whose z_L axis is along the external magnetic field and $J_m(m\omega_0, \Omega)$ are the spectral densities that contain explicit orientational dependences on the director. Note that $J_m(m\omega_0, 0°) \equiv J_m(m\omega_0)$ when the director is aligned along the magnetic field ($\Theta = 0°$). In order to interpret the angular-dependent spin–lattice rates in eq. (8), explicit expressions for $J_m(m\omega_0, \Omega)$ are given[10] below in terms of $J_{m_L m'_L}(m\omega_0)$:

$$\begin{aligned} J_1(\omega,\Omega) &= \frac{3}{2}\cos^2\Theta\sin^2\Theta J_{0,0}(\omega)+\frac{1}{2}(1-3\cos^2\Theta+4\cos^4\Theta)J_{1,1}(\omega)\\ &+\frac{1}{2}(1-\cos^4\Theta)J_{2,2}(\omega)-\sqrt{6}\cos 2\Phi\cos^2\Theta\sin^2\Theta J_{2,0}(\omega)\\ &-\frac{1}{2}\cos 2\Phi\left[1-5\cos^2\Theta+4\cos^4\Theta\right]J_{1,-1}(\omega)\\ &-\frac{1}{2}\cos 4\Phi\left[1-\cos^2\Theta\right]^2 J_{2,-2}(\omega) \end{aligned} \tag{9}$$

$$\begin{aligned} J_2(2\omega,\Omega) &= \frac{3}{8}(1-\cos^2\Theta)^2 J_{0,0}(2\omega)+\frac{1}{2}(1-\cos^4\Theta)J_{1,1}(2\omega)\\ &+\frac{1}{8}(1+6\cos^2\Theta+\cos^4\Theta)J_{2,2}(2\omega)\\ &+\frac{\sqrt{6}}{4}\cos 2\Phi\left[1-\cos^4\Theta\right]J_{2,0}(2\omega)\\ &+\frac{1}{2}\cos 2\Phi\left[1-\cos^2\Theta\right]^2 J_{1,-1}(2\omega)\\ &+\frac{1}{8}\cos 4\Phi\left[1-\cos^2\Theta\right]^2 J_{2,-2}(2\omega) \end{aligned} \tag{10}$$

These two equations reduce to the familiar expressions[16] for uniaxial phases, using $J_{m_L,m_L}(\omega)\equiv J_{m_L}(\omega)$. The reason is that the "biaxial" spectral densities $J_{2,0}(m\omega)$, $J_{1,-1}(m\omega)$ and $J_{2,-2}(m\omega)$ are nonzero only in biaxial phases[9]. In particular, these spectral densities involve parameters that depend on the biaxial order parameters $\langle D^4_{2,0}\rangle$, $\langle D^2_{2,0}\rangle$ and/or $\langle D^4_{4,0}\rangle$. It is obvious from eqs. (9) and (10) that when the director is aligned along the external field ($\Theta = 0°$), the spin–lattice relaxation rates are independent of the "biaxial" terms even in biaxial phases.

EXPERIMENTAL AND INTERPRETATION

The 5O.7-d$_1$ sample is labeled at the methine site and has a nematic-isotropic transition temperature T_c = 77.6°C, while the 5O.7-d$_4$ sample is labeled at the aniline ring and has a T_c = 76.2°C. The transition temperatures of 5O.7-d$_1$ are close to the literature values[17] for 5O.7 ($S_G - S_B$ at 38°C, $S_B - S_C$ at 52°C, $S_C - S_A$ at 55°C, $S_A - N$ at 64°C and $N - I$ at 78°C). When comparing the data of 5O.7-d$_1$, and 5O.7-d$_4$, we scale the temperatures to give a common T_c of 77.6°C. Broadband Jeener-Broekaert (J-B) sequence[18] with the appropriate phase-cycling and T_{1Q}. In order to illustrate the marked differences in the behaviours of spectral densities between the disordered phases and the ordered smectic phases, we present in figure 1 the smoothed data[11,19] in all the mesophases of 5O.7-d$_4$. The smoothed data[19] in the ordered smectic phases of 5O.7-d$_1$ are shown in figure 2. It is clear from figure 1 that the spectral densities of the ring deuterons show discontinuities at the $S_C - S_B$ transition. This is also the case for the methine deuteron. We will see below that such discontinuities are not directly linked to phase biaxiality but to the nature of molecular motions.

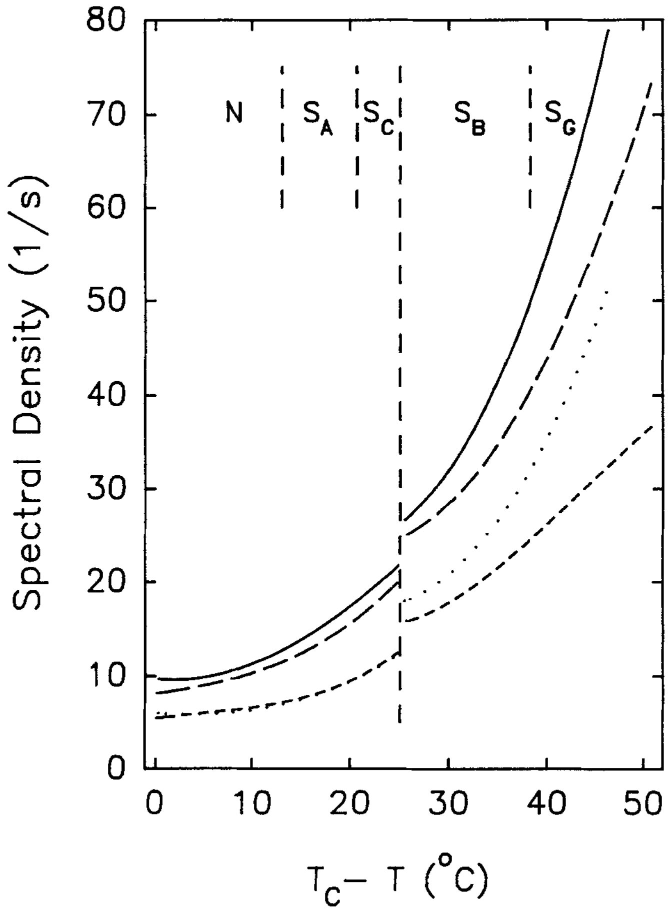

FIGURE 1 Smoothed spectral density data versus $T_c - T$ in the mesopases of 5O.7-d$_4$. Solid and dotted lines denote $J_1(\omega)$ and $J_2(2\omega)$ at 15.3 MHz, respectively, while long and short dashed lines denote $J_1(\omega)$ and $J_2(2\omega)$ at 46 MHz, respectively.

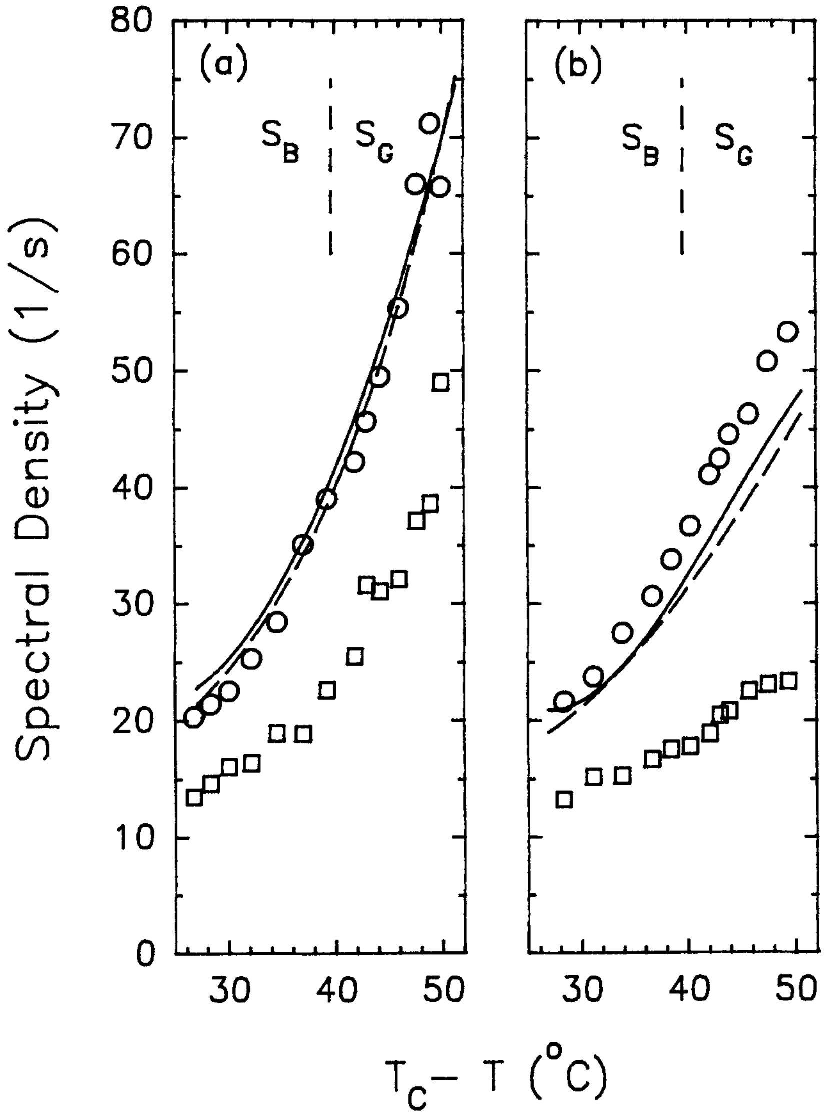

FIGURE 2 Smoothed spectral density data versus $T_c - T$ in the S_B and S_G phase of 5O.7-d$_1$ at 15.3 MHz (a) and 46 MHz (b). Solid and dashed lines denote $J_1(\omega)$ and $J_2(2\omega)$, respectively. ○ and □ represent respectively $J_1(\omega, 90°)$ and $J_2(2\omega, 90°)$, taken with the director normal to the external field.

From these figures, we see that no discontinuities are detected in the spectral densities of these sites at the $S_A - S_C$ and $S_B - S_G$ transitions. The observation is consistent with the fact that the director in the S_G phase of 5O.7 is aligned[20] along the external magnetic field ($\Theta = 0°$) while the layers are tilted, and in S_C phases the average director is also aligned[21] by the external field. Since uniaxial spectral densities for molecular reorientation vary continuously[9] at the unaxial-biaxial transition, the theory indeed agrees with the above experimental observation. It also suggests that spin relaxation in S_C and S_G phases of 5O.7 can be treated as that in a uniaxial phase. As seen in figures 1 and 2, the J_2's of both the deuterated sites show no frequency dependence[11] in the disordered phases, while in the S_B and S_G phases they show a large frequency dependence as do their corresponding J_1's. We also note that the J_1/J_2 ratios are quite different for the two deuterated sites in the ordered smectic phases. To explain the temperature and frequency dependences of the spectral densities, it is necessary to use models[11,19] to describe various motions that are responsible for the relaxation of methine and ring deuterons in the mesophases.

In the disordered phases, we have identified[11] director fluctuations and molecular reorientation as relaxation mechanisms for the methine deuteron. For the aniline ring deuterons, internal ring rotations must also be included for spin relaxation. A rotational diffusion constant D_R is used to describe free rotation of the aniline ring about its *para* axis. It was found that molecular reorientation can best be modeled by the "third rate" model[14]. In this model, the rotational diffusion tensor of a uniaxial molecule is chosen to be diagonal in the director frame with principal diffusion constants D_α and D_β, which describe rotational diffusion of the molecule around the director and about an axis perpendicular to the director, respectively. The third rate constant D_γ describes the fast rotation (γ-motion) of the molecule about its long axis. Director fluctuations can be characterized by a "material" prefactor A_{DF}. The A_{DF} value has been found[11] to be relatively constant at 1.38 $\times 10^6$ $s^{-3/2}$ for 5O.7. The reader is asked to refer to ref. [11] for the analyses. To give an idea of the quality of fit, we summarize in table I some representative results from quantitative fitting of the experimental spectral densities from the methine and ring sites at both Larmor frequencies. The derived diffusion constants all show Arrhenius temperature behaviours.

TABLE I: *Results in the disordered phases from a four-parameter minimization* of sum squared error[11] between experimental spectral density data (in parentheses) and those calculated with the third rate model and director fluctuations. At each temperature, first row gives data at 15.3 MHz and second row gives those at 46 MHz.

T(°C)	methine (s^{-1}) $J_1(\omega)$	methine (s^{-1}) $J_2(2\omega)$	ring (s^{-1}) $J_1(\omega)$	ring (s^{-1}) $J_2(2\omega)$	D (s^{-1})
72.5	19.1 (19.1)	7.5 (7.8)	9.92 (9.9)	6.0 (6.0)	$D_\alpha = 2.05 \times 10^9$
	14.0 (14.0)	7.4 (7.1)	8.98 (9.0)	6.0 (6.0)	$D_\beta = 1.14 \times 10^9$
					$D_\gamma = 7.25 \times 10^9$
					$D_R = 1.02 \times 10^9$
62.5	21.1 (21.1)	9.6 (9.6)	13.4 (13.6)	7.6 (7.6)	$D_\alpha = 1.63 \times 10^9$
	16.0 (16.1)	9.6 (9.6)	12.5 (12.3)	7.6 (7.6)	$D_\beta = 0.68 \times 10^9$
					$D_\gamma = 6.87 \times 10^9$
					$D_R = 0.44 \times 10^9$
52.5	25.8 (26.0)	14.5 (14.0)	21.4 (21.8)	11.4 (12.0)	$D_\alpha = 1.18 \times 10^9$
	20.7 (20.4)	14.5 (14.0)	20.4 (20.1)	11.4 (12.0)	$D_\beta = 0.45 \times 10^9$
					$D_\gamma = 4.71 \times 10^9$
					$D_R = 0.09 \times 10^9$

It is noted that D_R becomes small in the S_C phase and that ring rotations are ineffective for spin relaxation in the ordered smectic phases. Now director fluctuations are also ineffective in the ordered smectic phases. The remaining relaxation mechanism in these phases is the molecular reorientation. To describe molecular reorientation in the ordered smectic phases, we have modified[19] the third rate model to account for a biased γ-motion. The rotation of the molecule about its long axis is limited to a librational motion with a diffusion constant D_ϕ and an angular amplitude of $\pm\phi_0/2$. The model parameters $D_\alpha, D_\beta, D_\phi$ and ϕ_0 were again derived by minimizing the sum squared error. It was found that the D_β values are very small ($\leq 10^4\ s^{-1}$) and putting $D_\beta = 0$ makes trivial difference on the minimized sum squared errors. Also, the D_α value has a relatively large error because of its small magnitude. We summarize our representative results of the S_B and S_G phases in table II ($D_\beta = 0$). Finally, we present in figure 2 some preliminary data of 5O.7-d_1 in which the director has been oriented at 90° with respect to the external magnetic field. We found that at both frequencies,

$J_1(\omega_0, 90°) \simeq J_1(\omega_0, 0^0)$ while $J_2(2\omega_0, 90°)$ is roughly a factor of two smaller than $J_2(2\omega_0, 0^0)$ in the S_B and S_G phases. These data also show continuous change at uniaxial-biaxial phase transition. The interpretation of these interesting results awaits further investigation.

TABLE II: Results in the ordered smectic phases from a three-parameter minimization of sum squared error between experimental spectral density data (in parentheses) and those calculated by the third rate model with a biased γ-motion. At each temperature, first row gives data at 15.3 MHz and second row gives those at 46 MHz.

T(°C)	methine (s^{-1})		ring (s^{-1})		ϕ_0 (deg.)	D (s^{-1})
	$J_1(\omega)$	$J_2(2\omega)$	$J_1(\omega)$	$J_2(2\omega)$		
47.5	25.8 (26.0)	24.4 (25.0)	32.3 (32.0)	21.0 (20.3)	200	$D_\alpha = 2.2 \times 10^6$
	20.2 (21.3)	21.0 (20.6)	29.6 (28.3)	17.0 (17.6)		$D_\phi = 3.1 \times 10^9$
41.5	35.1 (34.3)	32.5 (33.0)	42.5 (44.0)	27.9 (28.2)	198	$D_\alpha = 3.4 \times 10^6$
	26.0 (27.2)	27.6 (26.7)	38.1 (36.3)	22.2 (22.4)		$D_\phi = 2.4 \times 10^9$
33.5	51.0 (53.2)	47.7 (51.7)	64.4 (68.2)	39.3 (44.2)	195	$D_\alpha = 4.7 \times 10^6$
	39.1 (38.3)	40.7 (36.9)	57.0 (53.3)	32.2 (30.2)		$D_\phi = 1.5 \times 10^9$

CONCLUSION

We have studied spin relaxation of two deuterated sites in the mesophases of 5O.7. Molecular reorientation and director fluctuations are important in the disordered phases, while biased γ-motion can account for the observed spectral densities in the ordered smectic phases. A change in the nature of γ-motion and the quenching of director fluctuations are responsible for the observed discontinuities in spectral densities at the S_C - S_B phase transition. We have shown that as long as the director is aligned with the external magnetic field, the "biaxial" spectral densities remain unobservable in biaxial phases. No discontinuity is observed in the spectral densities at the uniaxial-biaxial phase transition as long as the director is aligned along the external magnetic field and the relaxation mechanism(s) remains unchanged through the transition.

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REFERENCES

1. R. Y. Dong, Nuclear Magnetic Resonance of Liquid Crystals (Springer-Verlag, New York, 1994).
2. R. Y. Dong, Mol. Cryst. Liq. Cryst., 141, 349 (1986).
3. L. J. Yu and A. Saupe, Phys. Rev. Lett., 45, 1000 (1980).
4. J. Malthête, L. Liébert, A. M. Levelut, and Y. Galerne, C. R. Acad. Sci. Paris, 303, 1073 (1986); S. Chandrasekhar, B. R. Ratna, B. K. Sadashiva, and V.N. Raja, Mol. Cryst. Liq. Cryst., 165, 123 (1988); F. Hessel and H. Finkelmann, Polym. Bull., 15, 349 (1986).
5. J. W. Doane, in Nuclear Magnetic Resonance of Liquid Crystals, edited by J. W. Emsley (D. Reidel Publishing Co., Holland, 1985), chap. 18 and 19.
6. Z. Luz, D. Goldfarb, and H. Zimmerman, in Nuclear Magnetic Resonance of Liquid Crystals, edited by J. W. Emsley (D. Reidel Publishing Co., Holland, 1985), chap. 14.
7. R. Blinc, J. Dolinšek, M. Luzar, and J. Seliger, Liq. Cryst., 3, 663 (1988).
8. J. Seliger, V. Zagar, and R. Blinc, Phys. Rev. A, 17, 1149 (1978).
9. E. Berggren, R. Tarroni, and C. Zannoni, J. Chem. Phys., 99, 6180 (1993).
10. R. Y. Dong, Liq. Cryst., 16, 1101 (1994). Equations 4 and 5 were partly incorrect.
11. R. Y. Dong and X. Shen, Phys. Rev. E, 49, 538 (1994).
12. C. Zannoni and M. Guerra, Mol. Phys., 44, 849 (1981).
13. P. L. Nordio and U. Segre, in The Physics of Liquid Crystals, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979), chap. 4.
14. R. R. Vold and R. L. Vold, J. Chem. Phys., 88, 1443 (1988).
15. J. P. Jacobsen, H. K. Bildsoe, and K. Schumburg, J. Magn. Reson., 23, 153 (1976); R. R. Vold and R. L. Vold, J. Chem. Phys., 66, 4018 (1977).
16. G. R. Luckhurst and A. Sanson, Mol. Phys., 24, 1297 (1972); J. H. Freed, 66, 4183 (1977).
17. J. W. Goodby, G. W. Gray, A. J. Leadbetter, and M. A. Mazid, in Liquid Crystals of One- and Two-dimensional Order, edited by W. Helfrichand G. Heppke (Springer-Verlag, Berlin, 1980).
18. S. Wimperis, J. Magn. Reson., 83, 509 (1989); G. L. Hoatson, J. Magn. Reson., 94, 152 (1992); R. Y. Dong, Bull. Magn. Reson., 14, 134 (1992).
19. X. Shen and R. Y. Dong, to be published.
20. M. J. Vaz, Z. Yaniv, R. Y. Dong, and J. W. Doane, J. Magn. Reson., 62, 461 (1985).
21. S. Meiboom and Z. Luz, Mol. Cryst. Liq. Cryst. , 22, 143 (1973); R. A. Wise, D. H. Smith, and J. W. Doane, Phys. Rev. A, 7, 1366 (1973).