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Interlayer molecular exchange in an anticlinically ordered chiral liquid crystal

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The interlayer molecular exchange has been determined in the antiferroelectric smectic-C_A^* phase of αd_2 deuterated 4-(1-methylheptyloxycarbonyl)phenyl4′-octyloxybiphenyl-4-carboxylate via quadrupolar deuteron NMR self-diffusion in the spatially varying electric field gradient produced by the anticlinic smectic layer structure. The interlayer self-diffusion coefficient is here by two orders of magnitude smaller than in synclinically ordered smectic phases. The results support the entropic suppression model of the origin of anticlinic smectic ordering. The applied technique could possibly allow for a new insight into the local structure of the intermediate ‘‘clock’’ phases.

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Ferroelectric (FE) chiral tilted smectic (Sm-C^*) liquid crystals [1] as well as most other tilted smectics exhibit synclinic ordering where molecules in adjacent layers tilt in the same direction. Because of chirality, both the average molecular tilt direction and the in-plane polarization in the Sm-C^* phase vary slowly in space as one goes from one smectic layer to another. The pitch P_0 of this helicoidal modulation is however large as compared to the interlayer spacing d. Recently tilted smectic phases have been discovered exhibiting anticlinic ordering [2]. In the Sm-C_A^* phase in particular, the tilt direction and the in-plane spontaneous polarization alternate from layer to layer, leading to antiferroelectric (AFE) ordering without intralayer positional ordering. Intermediate ‘‘clocklike’’ phases, where the angle between the tilt directions as well as between the directions of in-plane polarizations in two successive layers takes on intermediate values between 0 and π, have been discovered as well [3]. A variety of experimental techniques have been used to characterize these newly observed phases [4–6]. Most of them are macroscopic and, except for resonant x-ray scattering [7], do not provide for a direct insight into the structure on the molecular level.

The microscopic mechanisms leading to anticlinic respectively synclinic smectic ordering are still not well understood. One possibility is that the synclinic interlayer ordering is entropically favored [8] over the anticlinic one by molecular exchange between adjacent layers and out-of-layer fluctuations of the molecules. The existence of a bent tail configuration [9] found in 4-(1-methylheptyloxycarbonyl) phenyl4′-octyloxybiphenyl-4-carboxylate (MHPOBC) and other anticlinic liquid crystals could suppress this exchange, allowing weaker nonsteric interactions like dipole-dipole and quadrupolar ones, favoring anticlinic ordering, to take over. So far there has been no direct experimental evidence for this effect.

In this Rapid Communication we report that in the anticlinic AFE Sm-C_A^* phase of αd_2 deuterated MHPOBC liquid crystal a significant reduction of the interlayer molecular exchange process indeed takes place. The respective interlayer self-diffusion coefficient is here by two orders of magnitude smaller than the one found in synclinically ordered smectic phases [10]. The observed values are also significantly different from the ones obtained in the same system by forced Rayleigh scattering on tracer molecules [11] which did not show the expected reduction of the interlayer diffusion in the anticlinically ordered Sm-C_A^* phase. Our results, obtained by quadrupolar deuteron NMR (DNMR) self-diffusion measurements, give strong support for the abovementioned entropic suppression mechanism of the origin of anticlinic smectic ordering. In performing the experiments, we exploited the fact that the anticlinic layer structure provides for an intrinsic spatial modulation of the local electric field gradient (EFG) so that translational diffusion of quadrupolar nuclei such as deuterons can be detected on a microscopic level without the use of externally applied gradients. It should be stressed that the observed self-diffusion coefficients are so small that classical NMR pulsed magnetic field gradient self-diffusion measuring methods [12] fail because the pulsed gradients cannot be made large enough. In contrast to the time-domain quadrupolar diffusion methods introduced for incommensurate crystals [13,14] the full power of our technique rests on the use of the frequency domain and on the variation of the orientation of the sample with respect to the external magnetic field. We show that the obtained partially averaged DNMR spectra directly reflect the local structure and dynamics of the investigated liquid crystalline phase and allow for a discrimination between synclinic, anticlinic, or ‘‘clocklike’’ intermediate ordering.

To probe the self-diffusion of the anticlinically ordered MHPOBC in the Sm-C_A^* phase, we have performed a DNMR experiment in a 9 T ($\nu_L = 58.3$ MHz) superconducting magnet between 355 and 385 K. We have used a αd_2 deuterated sample in which the two aliphatic chain protons closest to the MHPOBC molecular core were replaced with deuterons. We have varied the angle θ_H between the normal to the smectic layers and the external magnetic field **H** in the range 0° to 90°. In order to prevent magnetic field-induced sample reorientation and layer destruction, the structure was stabilized by filling the sample into a multiple layer sandwich, made of thin glass plates. The layer thickness was 200 μm. The DNMR spectra were measured by a $90°_x - \tau - 90°_y - \tau$ solid echo pulse sequence at different sample orientations with a $\Delta\theta_H = 5°$ orientation interval.

For a sample at an orientation $\theta_H < \mathbf{H},\mathbf{z}$ where **z** points along the normal to smectic layers, the quadrupole-perturbed DNMR frequency shift from the Larmor frequency ν_L of a deuterated liquid crystal molecule with a molecular tilt θ_0 and an azimuthal angle ϕ is given by [15]

$$\nu(\phi)=\Omega(\phi)/2\pi=\pm 3/8\nu_Q S[3(\cos\theta_H\cos\theta_0 + \sin\theta_H\sin\theta_0\sin\phi)^2-1]. \tag{1}$$

Here $\nu_Q=e^2qQ/h$ is the quadrupole coupling constant. Because of rapid molecular reorientations around their long axes and the fluctuations of these axes around the average direction **n**, the largest principal axis of the C-D deuteron EFG tensor will point along the molecular director **n**. Due to the rather weak biasing of these motions, the time-average deuteron EFG tensor will possess cylindrical symmetry around this axis. S is the nematic order parameter which measures the degree of the orientational order of **n**. It should be stressed that the change in the orientation of the molecular director on going from one smectic layer to an adjacent one provides for an intrinsic spatial modulation of the orientation of the EFG tensor.

Expression (1) does not take into account intralayer and interlayer molecular diffusion. The former does not change the NMR absorption frequency $\Omega(\phi)$ since ϕ is constant within a smectic layer. Consequently, measurements of DNMR absorption spectra are insensitive to intralayer diffusion, macroscopically quantified by the intralayer component $D_\perp$ of the self-diffusion tensor. On the contrary, any interlayer molecular jumps, formally described as a one-dimensional random-walk process $z(t)$, and macroscopically by the interlayer self-diffusion component $D_\parallel$, demand a simultaneous change of the azimuthal angle $\phi=\phi(z(t))$, thus making $\Omega(\phi)$ time-dependent. In the Sm-C_A^* phase ϕ varies by π on going from one layer to an adjacent one. Self-diffusion thus results in a motionally altered spectrum if the motion is fast enough. The effect is only present at orientations where the magnetic field is not parallel to the normal to the smectic layers since at $\theta_H=0°$ interlayer jumps do not change the resonance frequency.

It should be pointed out that there exists a major difference between synclinic and anticlinic ordering, related to the impact of self-diffusion on the DNMR spectra. Synclinic ordering implies only a minute change in the DNMR frequency of two neighboring layers due to the infinitesimal change of the azimuthal angle $\Delta\phi=\phi(z+d)-\phi(z)=2\pi d/P_0 \ll 1$, as $P_0 \gg d$. For an anticlinic arrangement, on the other hand, $\Delta\phi=2\pi(d/P_0+1/n)$ is of the order of unity for small n. Here $n=2$ in the Sm-C_A^* phase and $n=3,4,\ldots$ in the clocklike phases. Consequently, the DNMR frequency changes significantly between adjacent layers in anticlinic systems. Motional averaging effects due to translational diffusion are thus negligible in synclinically ordered phases but all important in anticlinically and ‘‘clocklike’’ ordered ones.

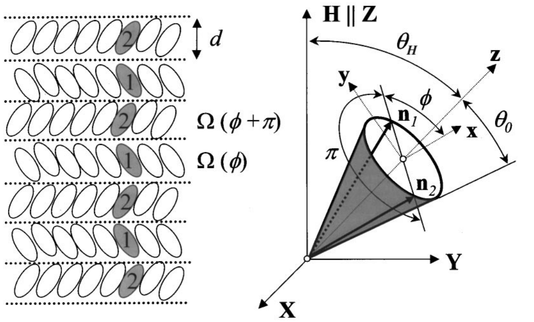

FIG. 1. Molecular director configuration in the Sm-C_A^* phase and the geometry of the DNMR experiment. **XYZ** is the laboratory frame, whereas the **xyz** frame is fixed to the LC smectic layers. $\mathbf{n}_1$ and $\mathbf{n}_2$ denote the directors in the neighboring layers, with the respective DNMR absorption frequencies $\Omega(\phi)$ and $\Omega(\phi+\pi)$.

The $n=2$ case of a Sm-C_A^* phase with $\Delta\phi\approx\pi$, in particular, corresponds to a two-site chemical exchange case where the molecule carrying the resonant nucleus performs stochastic jumps between to sites with resonances at $\Omega(\phi)$ and $\Omega(\phi+\pi)$, respectively (Fig. 1). This is so since DNMR does not resolve between the jumps into the upper and lower neighboring layers; that is, $\Omega(\phi+\pi)\approx\Omega(\phi-\pi)$. The absorption spectrum of such a system can be calculated by solving the Bloch master equation [16] for the nuclear magnetization $\mathbf{M}(t,\phi)=[M(t,\phi),M(t,\phi+\pi)]$ of the two sites,

$$\dot{\mathbf{M}}(t,\phi)=i\underline{\underline{\Omega}}(\phi)\mathbf{M}(t,\phi)-\mathbf{M}(t,\phi)/T_2+\underline{\underline{K}}\mathbf{M}(t,\phi), \tag{2a}$$

with

$$\underline{\underline{\Omega}}(\phi)=\begin{bmatrix}\Omega(\phi) & 0\\ 0 & \Omega(\phi+\pi)\end{bmatrix}, \quad \underline{\underline{K}}=2w\begin{bmatrix}-1 & 1\\ 1 & -1\end{bmatrix}. \tag{2b}$$

The elements of $\underline{\underline{\Omega}}(\phi)$ are defined with Eq. (1), T_2 is the spin-spin relaxation time, describing all contributions to the homogeneous line broadening apart from the diffusion, whereas $2w$ denotes the probability per unit time for the molecule to diffuse into one of the two neighboring layers. w, the interlayer jump probability, is related to the macroscopic diffusion coefficient via $w=D_\parallel/d^2$. The DNMR absorption spectrum, which is the real part of the Fourier-transformed sum of the magnetization components $M(t,\phi)+M(t,\phi+\pi)$, can be expressed analytically [16] as

$$I(\omega,\phi)\propto\frac{\delta\Omega^2(\phi)(T_2^{-1}+4w)+T_2^{-1}\{[\omega-\Omega_0(\phi)]^2+(T_2^{-1}+4w)^2\}}{\delta\Omega^4(\phi)-2\,\delta\Omega^2(\phi)\{[\omega-\Omega_0(\phi)]^2-T_2^{-2}-4T_2^{-1}w\}+\{[\omega-\Omega_0(\phi)]^2+T_2^{-2}\}\{[\omega-\Omega_0(\phi)]^2+(T_2^{-1}+4w)^2\}}. \tag{3}$$

Here $\Omega_0(\phi)$ is the averaged resonance frequency of two nuclear sites in adjacent, anticlinically ordered layers,

$$\begin{aligned}\Omega_0(\phi)&=[\Omega(\phi)+\Omega(\phi+\pi)]/2\\&=3\pi/4S\nu_Q[3(\cos^2\theta_H\cos^2\theta_0\\&\quad+\sin^2\theta_H\sin^2\theta_0\sin^2\phi)-1],\end{aligned}\tag{4a}$$

whereas $2\delta\Omega(\phi)$ represents the respective frequency separation,

$$\begin{aligned}\delta\Omega(\phi)&=[\Omega(\phi+\pi)-\Omega(\phi)]/2\\&=9\pi/8S\nu_Q\sin 2\theta_0\sin 2\theta_H\sin\phi.\end{aligned}\tag{4b}$$

If the exchange is neither fast nor slow with respect to $\delta\Omega(\phi)$, i.e., if we are in the intermediate exchange regime $w\approx\delta\Omega(\phi)$, the DNMR line shape is inherently non-Lorentzian, or equivalently, the solid-echo time-decay is not Hahn-like [16]. This makes the determination of w from the solid-echo decay rate rather tedious. Moreover, the response of the whole system is a linear superposition of contributions from all layers, so that one has to integrate over the distribution of phase angles $P(\phi)$. We therefore decided to consider the frequency domain response

$$I_{tot}(\omega)=\int_0^{2\pi}P(\phi)I(\omega,\phi)d\phi.\tag{5a}$$

The respective "fast motion" $(w=\infty)$ and "rigid lattice" $(w=0)$ limits are

$$I_{tot}(\omega)=P(\phi)|d\omega/d\phi|^{-1}*L(\omega),$$

$$\omega(\phi)=\begin{cases}\Omega_0(\phi); & w=\infty\\ \Omega(\phi); & w=0.\end{cases}\tag{5b}$$

Here $*$ denotes the convolution with the Lorentzian line shape $L(\omega)\propto(1+\omega^2T_2^2)^{-1}$. The big advantage of working in the frequency domain is the appearance of singularities at frequencies satisfying $d\omega/d\phi=0$. These singularities can be used to determine $\nu_QS(T)$ and $\theta_0(T)$, whereas the analysis of the line shape in the intermediate exchange regime yields w.

For a determination of the theoretical DNMR line shape as given by Eq. (5a), we have to know the distribution of the azimuthal angles $P(\phi)=dN/d\phi\propto|d\phi/dz|^{-1}$ in the presence of an external magnetic field, which introduces solitonlike distortion into the phase angle layer modulation. The spatial variation of $\phi(z)$ can be evaluated by minimizing the Landau free energy density [17] in the single elastic constant approximation $K=K_{22}\approx K_{33}$:

$$\begin{aligned}g=\sin^2\theta_0\Bigg\{&K\left[\frac{1}{2}\left(\frac{d\phi}{dz}\right)^2-\frac{2\pi}{P_0}\frac{d\phi}{dz}\right]\\&-\frac{1}{2}\chi_aH^2(\cos^2\theta_H\cot^2\theta_0+\sin^2\theta_0\sin^2\phi)\Bigg\}.\end{aligned}\tag{6}$$

Here χ_a is the anisotropy of the diamagnetic susceptibility. The fact that the critical magnetic field H^c for the unwinding of the modulated structure is inversely proportional to its pitch [18] implies that the anticlinic order is by far less sensitive to the external magnetic field than the superimposed chiral long pitch helicity. One can thus regard the $\Delta\phi\approx\pi$ anticlinicity of the two neighboring layers as fixed and then treat the chiral spatial modulation of this quasirigid double layer system in a continuous manner.

The theoretical DNMR line shape in the presence of diffusion can be rewritten as

$$\begin{aligned}&I_{tot}(\omega;\theta_H,\theta_0,h,w)\\&\quad\propto\int_0^{2\pi}\frac{E(k(h,\theta_H))}{\sqrt{1-k^2(h,\theta_H)\sin^2\phi}}I(\omega,\phi;\theta_H,\theta_0,w)d\phi,\end{aligned}\tag{7}$$

allowing for the determination of θ_0 and w by measuring I_{tot} at different sample orientations. Here $E(k)$ is the complete elliptic integral of the second kind and $k=k(h=H/H_0^c,\theta_H)$ is the respective modulus, given by the solution of the self-consistent equation $k=h\sin\theta_HE(k)$. $H_0^c=\pi^2/P_0\sqrt{K/\chi_a}$ is the critical field for the unwinding of the chiral helix at an orientation $\theta_H=90°$.

By a generalization of expression (7) it can be shown that the DNMR line shape angular patterns in the intermediate exchange regimes allow for a determination of the local structure, and more specifically, of the relative tilt direction arrangements in adjacent smectic layers in the general $n=3,4,\ldots$ case. DNMR can be thus used to discriminate

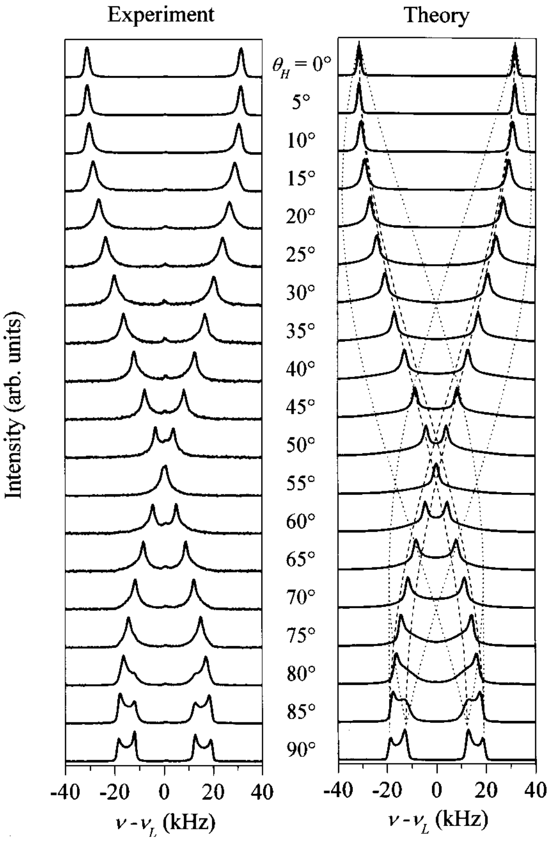

FIG. 2. Experimental and theoretical angular dependencies of the DNMR line shapes in the Sm-C_A^* phase of MHPOBC at $T=380$ K. The expected singularity positions in the "fast motion" limit $w=\infty$ and in the "rigid lattice" limit $w=0$ are shown as dashed and dotted lines, respectively.

between different ‘‘clocklike’’ smectic phases. The above method is not applicable to synclinic phases due to the absence of motional narrowing effects.

The experimental angular dependence of the DNMR spectra at $T=380$ K in Sm-C_A^* phase, where the molecular directors are known to be tilted with respect to the layer normals, is shown in Fig. 2. The results show that the averaged direction of the largest principal axis of the deuteron EFG tensor in the Sm-C_A^* phase is normal to the smectic layers. This is similar to the results found in the Sm-*A* phase where $\theta_0=0°$, i.e., where the molecular directors are parallel to the layer normals. The above result demonstrates the averaging of the anticlinically arranged deuteron EFG tensors in the Sm-C_A^* phase due to interlayer exchange. Nearly perfect theoretical line shape fits to Eq. (7) are obtained with $\nu_Q S=51\pm 2$ kHz, $\theta_0=20\pm 2°$, and $w=3.8\times 10^4(1\pm 0.2)$ s^{-1}. The value of the tilt angle θ_0 matches the one obtained by ellipsometry [3]. From the observed soliton-induced distortion of the spectra which is distinctively pronounced at $\theta_H=90°$ in the form of an asymmetry of the two spectral singularities, one finds a value of the critical field $H_0^c(380\,\mathrm{K})=18\,\mathrm{T}$. This is close to the critical field for the unwinding of the chiral helix measured via conoscopy [19]. By taking the distance between adjacent smectic layers as $d=3.4$ nm [8], one finds a surprisingly low value of the diffusion constant $D_\parallel=wd^2\approx 4.4(1\pm 0.3)\times 10^{-9}$ $\mathrm{cm^2\,s^{-1}}$. A variation of less than 20% about this value was detected at other investigated temperatures in the Sm-C_A^* phase. The observed value of $D_\parallel$ is significantly smaller than the values found in the synclinically ordered FE Sm-C^* phases, where $D_\parallel\approx 10^{-7}$ $\mathrm{cm^2\,s^{-1}}$ [10]. It is also much smaller than the values $D_\parallel\approx 6\text{–}8\times 10^{-8}$ $\mathrm{cm^2\,s^{-1}}$ found for tracer molecules [11] in the anticlinically ordered AFE Sm-C_A^* phase of MHPOBC. However, the diffusion of the tracer dye molecules may be considerably different from the bent MHPOBC molecules obeying different local ordering rules. Whereas the diffusion of tracer molecules gave no support for the anticlinic ordering induced reduction of the interlayer exchange rate, the direct measurement of the self-diffusion of the MHPOBC molecules definitely demonstrates the existence of this effect.

In conclusion we have shown that the measurement of quadrupolar self-diffusion induced motional averaging effects of the DNMR spectra at different orientations of the magnetic field with respect to the normal to the smectic layers allows for a determination of the local structure and dynamics of anticlinic smectic phases. We have also demonstrated the potential of this method in the investigations of ‘‘clocklike’’ and ferrielectric smectic phases. The extreme sensitivity of our technique is related to the large electric field gradient variations induced by different tilt direction arrangements in adjacent smectic layers. The results obtained in the antiferroelectric Sm-C_A^* phase of MHPOBC in particular support the entropic suppression mechanism model of the origin of anticlinic smectic ordering.

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