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Observation of magnetically induced changes in the phason band structure in a ferroelectric liquid crystal

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Fluctuations of the phase of the order parameter of a Sm C* (helicoidal) ferroelectric liquid crystal were measured by photon autocorrelation spectroscopy. Phason relaxation times near the modulation wave vector show a strong magnetic field dependence in the region where the helical pitch is field-independent, indicating a cross-over between the plane-wave and soliton like regime of the helicoidal structure of the Sm C* phase.

The ferroelectric smectic C* phase [1] is a spatially modulated, helicoidal phase, where rod-like molecules are arranged in liquid-like smectic layers. The director $\boldsymbol{n}(\boldsymbol{r})$ that describes the time averaged direction of the long molecular axis is tilted with respect to the smectic normal $\boldsymbol{e}_z$ and precesses around the normal going from one layer to another.

The time averaged value of the molecular transverse electric dipole moment is nonzero in the Sm C* phase and a local spontaneous polarisation $\boldsymbol{P}(\boldsymbol{r})$ appears along the C_2 axis.

The helical ordering of the director field $\boldsymbol{n}(\boldsymbol{r})$ in the Sm C* phase and the well known anisotropic properties of liquid crystalline molecules are responsible for some fascinating optical, dynamical and thermodynamical properties of this phase. In particular, the helical distribution of the director field $\boldsymbol{n}(\boldsymbol{r})$ induces helicoidal ordering of different susceptibility tensors such as the dielectric tensor $\boldsymbol{\varepsilon}(\boldsymbol{r})$ and the diamagnetic tensor $\boldsymbol{\chi}(\boldsymbol{r})$. It is well known that external fields couple strongly to the liquid crystalline director field, and large electro-optic and magneto-optic effects can be observed in these phases. As an example, an external magnetic field applied parallel to the smectic layers will tend to align the molecules in the direction of the field [2]. The director field will be distorted and the helicoidal structure will transform into a soliton-like structure with slightly different pitch. The distortion of the helix and the appearance of soliton-like structure strongly influence the form of susceptibility tensors of the Sm C* phase and this results in remarkable changes of the optical properties of the ferroelectric Sm C* phase.

The helicoidal Sm C* phase is not a static structure. As already mentioned, individual molecules undergo thermally excited rotations around the molecular axis. This motion is fast, with typical rates in the 100–1000 MHz range. Besides the individual molecular motion, collective fluctuations of the Sm C* order parameter are present as a result of long range order. In contrast to the fast individual molecular motions, the collective excitations are slow, with relaxation times in the millisecond range.

We shall consider fluctuations of the order parameter that propagate along the helical axis. The dynamics of these fluctuations can be derived from the Landau thermodynamic potential [3, 4], applied to the nonequilibrium value of the Sm C* order parameter [5]. As a result, one finds in the Sm C* phase two overdamped normal modes. The first mode corresponds to fluctuations of the magnitude of the tilt angle θ and is denoted as an amplitudon mode, while the second one is identified as a fluctuation of the

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phase of the tilt angle $\Phi(\boldsymbol{r})$ and is designated as a phason mode. These two modes have been observed in an inelastic light scattering experiment [6] and it has been confirmed that the Landau–Khalatnikov equations of motion for the Sm C* order parameter describe the Sm C* phase dynamics well. The phason mode can be considered as a small, plane-wave excitation of the director field phase, recovering the lost symmetry of the higher temperature, disordered phase. In the long wavelength limit $\boldsymbol{q} \to 0$, it represents a pure rotation of the helical structure and we expect that the relaxation rate for such a zero energy excitation would be equal to zero. As mentioned before an external magnetic field, applied parallel to the smectic layers, distorts the helix and induces a π-soliton lattice. We can expect that such a distortion of the director field strongly influences the dynamics of phason excitations.

Let us discuss briefly the predictions of the theory [7, 8]. Writing down the non-equilibrium value of the Sm C* order parameter as

$$\begin{aligned} \xi_1(z,t) &= n_x n_z = \theta \cos \Phi(z,t)\,, \\ \xi_2(z,t) &= n_y n_z = \theta \sin \Phi(z,t)\,, \end{aligned} \tag{1}$$

and taking the phase dependent part of the free energy density

$$\begin{aligned} g(\Phi) = -\Lambda\theta^2 \frac{\mathrm{d}\Phi}{\mathrm{d}z} + \tfrac{1}{2} K_{33}\theta^2 \left(\frac{\mathrm{d}\Phi}{\mathrm{d}z}\right)^2 \\ - \tfrac{1}{2}\,\Delta\chi\, \boldsymbol{H}_x^2 \theta^2 \cos^2 \Phi\,, \end{aligned} \tag{2}$$

one obtains after minimizing $g(\Phi)$ with respect to $\Phi(z)$ static solutions $\Phi_0(z)$ of the Sine-Gordon equation in the well known form of a π-soliton lattice. In eq. (2), Λ is the Lifshitz term, K_{33} is the torsional elastic constant and $\Delta\chi$ is the diamagnetic anisotropy. After expanding the free-energy density in terms of $\delta\Phi(z,t)$, where $\Phi(z,t) = \Phi_0(z) + \delta\Phi(z,t)$, and taking the Bloch expansion for the fluctuating part of the phase of the order parameter,

$$\delta\Phi(z,t) = \sum \Phi_q(z)\, \mathrm{e}^{-t/\tau(q)}\,, \tag{3}$$

one obtains after applying the Landau–Khalatnikov equations of motion, Lame's equation of order one for $\Phi_q(z)$:

$$\frac{\mathrm{d}^2\Phi_q}{\mathrm{d}u^2} + [h - 2k^2 sn^2(u,k)]\Phi_q = 0\,. \tag{4}$$

Here $u = z/\beta k$ is an argument of a Jacobian elliptic function of modulus k, $\beta^2 = K_{33}/\Delta\chi\, \boldsymbol{H}^2$, $h = k^2[(\beta^2\gamma/\tau(q)K_{33}) + 1]$ and γ is the viscosity of the Sm C* phase. It has been shown that for certain characteristic values of the wave vector q_z, the phason relaxation rates may be expressed as [8]

$$\tau_2^{-1}(q_z) \simeq \frac{K_{33}}{\gamma} \frac{(1-k^2)K^2(k)}{E^2(k)} (q_c - q_z)^2\,, \quad q_z \simeq q_c \tag{5}$$

$$\tau_{2-}^{-1}(q_z) \simeq \frac{K_{33}}{\gamma} \frac{(1-k^2)}{\beta^2 k^2}\,, \quad q_z \leqslant 2q_c \tag{6}$$

$$\tau_{2+}^{-1}(q_z) \simeq \frac{K_{33}}{\gamma} \frac{1}{\beta^2 k^2} \qquad q_z \geqslant 2q_c \tag{7}$$

Here $K(k)$ and $E(k)$ are complete elliptic integrals of the first and second kind, respectively, and $q_c = 2\pi/p$ is the wave vector of the helix. Modulus k defines the field regime and can be obtained from the equation

$$k = \frac{\boldsymbol{H}_x}{\boldsymbol{H}_c} E(k)\,, \tag{8}$$

where $\boldsymbol{H}_c$ is the critical field that completely unwinds the helical structure. In the limit of small field k goes to 0 and in the limit of high field k goes to 1.

Results (6) and (7) show that in an external field the phason mode splits into an acoustic-like and optic-like branch $\tau_{2-}^{-1}(q_z)$ and $\tau_{2+}^{-1}(q_z)$, respectively. These two branches are separated by a field dependent gap $\Delta G(\boldsymbol{H})$ that appears at the edge of the Brillouin zone at $q_z = 2q_c$.

In the experiment, we have used a photon autocorrelation technique to measure the autocorrelation function of the scattered light intensity. In the Sm C* phase, an overdamped phason mode will give rise to an exponentially decaying autocorrelation function of the scattered light intensity. An inelastic light scattering spectrometer was constructed, fitting into a 60 mm Bitter magnet. A helium-neon laser beam was slightly focused to a 50 μm spot, illuminating the liquid crystal sample in the center of the magnet. The sample was placed in a thermostated oven with better than 0.1 K temperature stability and could be rotated around the magnetic field direction. In this way, we could change the direction and magnitude of the scattering wave vector, keeping the scattering plane perpendicular to the magnetic field direction. The scattered light was collected with a lens and was focused to a 100 μm pinhole, etched in a chromium mirror. The mirror was inclined at 45° with respect to the axis of the light-collecting optics. Together with a microscope eyepiece, it allowed for visual inspection of the liquid crystal sample and fine adjustments of the illuminated spot to the pinhole center. The axis of the collecting optics was positioned at an angle 1° off the incoming light direction, thus always assuring a heterodyne detection. The scattered light, passing through the pinhole, was collected with a multimode fibre and led into the photomultiplier, placed far away from the magnet. The set-up is schematically shown in fig. 1. The same set-up was also used to measure Bragg diffraction angles, corresponding to elastically scattered light. For that purpose, angular scans of light intensity, transmitted through the sample, were recorded. Because of the relatively large pitch, Bragg diffraction occurred in the forward direction [9] and could be easily observed. In this way, we could measure the magnetic field dependence of the pitch of the helix.

A mixture, consisting of 35% of pure chiral liquid crystal 4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8) and 65% of racemic liquid crystal CE-8R was studied in the experiment. Samples of 120 μm thickness were prepared between clean glass slides, treated with dimethyloctadecyl-3-(trimethoxysilyl)propylammonium chloride (DMOAP). Good homeotropic alignment of the Sm C* phase was obtained. The sample was placed

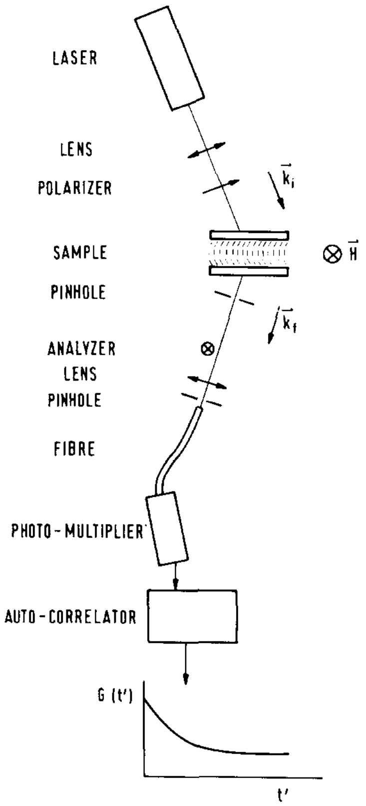

Fig. 1. Set-up for the inelastic light scattering experiment in high magnetic field.

between two glass half-cylinders, using a resin as an index-matching material. The cylinder was placed in the oven with the axis of rotation along the magnetic field direction. The whole configuration assured a light scattering geometry where the scattering plane was perpendicular to the field direction with the Sm C* helical axis lying in the scattering plane. In this way, the light scattering geometry was unaffected by sample rotation and the helical axis was always at right angles with respect to the field.

The measurements were taken 3 K below the λ-line. The magnetic field dependence of the pitch of the helix was measured in order to determine the critical magnetic field for helix unwinding. The field was increased at a very slow rate of 0.05 T/min. The pitch of the helix is almost field independent up to 6 T as shown in fig. 2. In the region above 6 T, one can see that

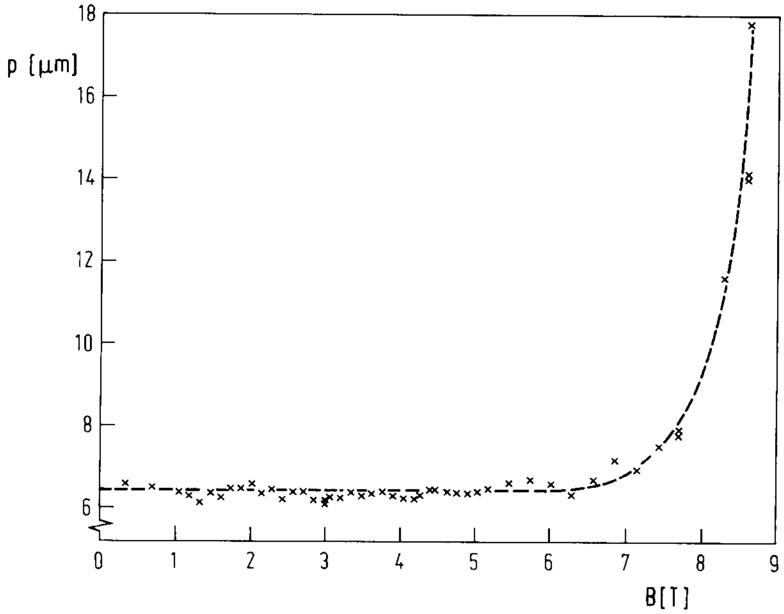

Fig. 2. Magnetic field dependence of the pitch of the helix in the Sm C* phase of a mixture of 35% pure and 65% racemic liquid crystal CE-8, at $T_c - T = 3$ K.

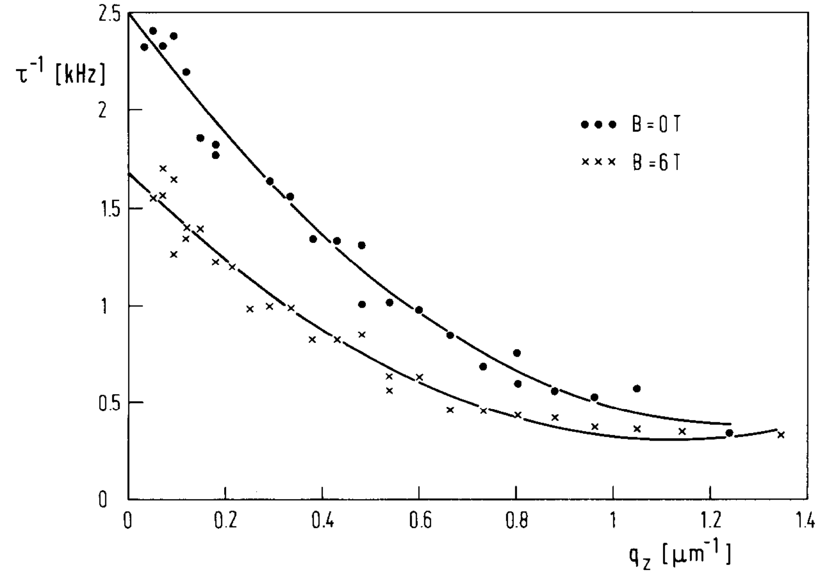

Fig. 3. Phason dispersions in a mixture of 35% pure and 65% racemic liquid crystal CE8 as measured at 0 and 6.0 T. (Note: these results contain a small perpendicular component of the phason wave vector $q_x \approx 0.1\ \mu m^{-1}$.)

the system behaves qualitatively different. By monitoring the scattering intensity, we have observed that it was necessary to wait as long as 10 min to reach the new equilibrium, even for 0.1 T steps. At 8.5 T a sudden divergence of the pitch of the helix was observed and we could not detect any diffracted light at higher fields. We thus conclude that the critical field for the Sm C* to Sm C transition is equal to $\boldsymbol{H} = 8.5 \pm 0.1$ T.

The phason dispersion relation was measured at 0 and 6.0 T. The magnetic field was swept slowly to the desired value, and then the system was left for 30 min to reach the equilibrium state. The results are shown in fig. 3. One can clearly observe the change in the shape of the phason dispersion relation. By fitting the dispersions at 0 and 6.0 T with a parabolic function, a decrease of the effective damping constant K_{33}/γ is observed and a very small shift of the center of the dispersion. This is just what one expects from eq. (5). In the high field limit, $\tau_2^{-1}(q)$ tends to zero for each q, and the dispersion becomes "flat" near the critical field.

These preliminary results give a strong indication for a possible magnetically induced gap in the phason dispersion relation as a result of a cross-over in the phason dynamics in the Sm C* phase of a chiral ferroelectric liquid crystal. The results are in agreement with the observed increase of higher-order Bragg peak intensities that indicate the appearance of a π-soliton structure in the Sm C* phase.

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