Observation of Phason Dispersion in a Ferroelectric Liquid Crystal by Light Scattering

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The phason dispersion relation has been measured in the smectic-C^* phase of the ferroelectric liquid crystal *p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl cinnamate (DOBAMBC), together with the temperature dependence of the phason and amplitudon excitations, by optical-mixing spectroscopy. The overdamped phason was found to be nearly gapless in contrast to crystalline incommensurate systems where the modulation wave is pinned by frozen defects. A theory of light scattering by phasons and amplitudons in ferroelectric liquid crystals has been developed.

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Whereas the presence of acousticlike phason modes[1,2] in structurally incommensurate (IC) crystals has been by now clearly demonstrated by inelastic neutron scattering,[3,4] NMR,[5] EPR,[6] and a variety of other techniques, no truly gapless phason seems to have been observed so far, and the question of the possible existence of such a mode is still open. The phason represents the sliding of the IC modulation wave recovering the broken translational high-temperature periodicity of the phase. Unlike true acoustic modes it becomes overdamped in the long-wavelength limit.[7] The theory of IC systems[1,2] predicts the existence of a gapless phason mode in the IC phase in addition to the opticlike amplitudon branch. Impurities[8] and higher-order commensurability effects[9] may produce a locking of the modulation wave to the underlying lattice and introduce a gap Δ_ϕ into the phason spectrum:

$$\omega_\phi^2=\Delta_\phi^2+K^2(\mathbf{q}-\mathbf{q}_0)^2. \tag{1}$$

NMR,[5,10] EPR,[6] and neutron-scattering data[3,4] have indeed shown that Δ_ϕ is of the order of 10^{10} Hz in solid IC dielectrics.

To resolve the question of the existence of a gapless phason we decided to look for a system with no frozen impurities and with negligible higher-order commensurability effects.[9] Ferroelectric smectic-C^*-type (Sm-C^*) liquid crystals,[11-13] where the periodicity of the helicoidal orientational ordering ($\simeq 10^3$ interlayer distances) is incommensurate to the periodicity of the one-dimensional density modulation, fulfill both the above conditions. Here we report on what we believe to be the first observation of the dispersion relation for a nearly gapless phason. The system investigated is the ferroelectric liquid crystal *p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl cinnamate (DOBAMBC),[11] where the periodicity of the IC helicoidal modulation wave is of the order of the wavelength of light (i.e., a few micrometers) and not in the x-ray region as in most IC solids. We determined by optical-mixing spectroscopy the phason dispersion as well as the temperature dependence of the phason and amplitudon excitations in the Sm-C^* phase in the vicinity of the first Bragg peak together with the temperature dependence of the soft mode of the smectric-A (Sm-A) phase.

In the Sm-A phase, the long axes of the molecules are oriented perpendicular to the smectic layers so that the molecular director is $\mathbf{n}=(0,0,n_z)$. Below T_c in the Sm-C^* phase the molecules tilt away from the normal to the smectic layers. The order parameter of the transition is a two-component tilt vector,[11,12] $\xi=(\xi_1,\xi_2)=(n_x n_z, n_y n_z)$. The direction of the tilt precesses on the surface of a cone as one goes from one smectic layer to another thus forming a helicoidal modulation wave:

$$\xi_1\approx\theta\cos(q_0 z+\varphi), \tag{2a}$$

$$\xi_2\approx\theta\sin(q_0 z+\varphi). \tag{2b}$$

Here the tilt angle θ describes the amplitude and φ the phase of the modulation wave, whereas $q_0=2\pi/p$ is determined by the pitch (p) of the helix. The order parameters (2a) and (2b) as well as the Landau thermodynamic potential

$$g=\tfrac{1}{2}a(\xi_1^2+\xi_2^2)\tfrac{1}{4}b(\xi_1^2+\xi_2^2)^4-\Lambda[\xi_1(d\xi_2/dz)-\xi_2(d\xi_1/dz)]+\tfrac{1}{2}K_3[(d\xi_1/dz)^2+(d\xi_2/dz)^2], \tag{3a}$$

$$a=\alpha(T-T_0),\quad b,\Lambda,K_3=\text{const}, \tag{3b}$$

describing the Sm-A-Sm-C^* transition[11-13] are completely analogous to those of solid crystals[2] near the normal (N) -incommensurate transition. The same is true for the main features of the order-parameter excitation spectra.[13] The amplitudon corresponds to a fluctuation in the magnitude of the tilt angle $\Delta\theta(t)=\theta-\theta_0$, whereas the phason corresponds to a fluctuation in the direction of the tilt vector, i.e., a fluctuation in the phase $\varphi=\varphi(t)$ of the modulation wave.

There are also important differences between IC phases in solids and Sm-C^* liquid crystals. Even a very small concentration of frozen-in "random field" defects pinning the phase of the modulation wave makes it practically impossible to observe light scattering due to phasons.[14] Such defects seem to be always present in solids, whereas they are absent in Sm-C^* liquid crystals. Another important difference is that in all known IC solids the coupling of the phason with light is described by a term that is proportional to the order parameter squared. As a result of that, the intensity of phason light scattering goes to zero as T_c is approached from below, even in the absence of frozen-in random-field defects. In Sm-C^* liquid crystals, on the other hand, the phason coupling with light is linear in the order parameter as $\xi_1=n_xn_z$ and $\xi_2=n_yn_z$ transform in the same way as the dielectric tensor components ϵ_{xz} and ϵ_{yz}. Thus

$$\epsilon_{xz}=A\xi_1,\quad \epsilon_{yz}=A\xi_2, \tag{4}$$

and the intensity of the phason light scattering does not go to zero at T_c. Similarly the intensity of soft-mode light scattering in the Sm-A phase above T_c is nonzero in contrast to light scattering from the soft mode in the N phase of IC solids.

In the Born approximation, i.e., with the neglect of multiple scattering, the spectral density of the scattered light is

$$I(\mathbf{q},\omega)\approx\langle|\Delta\epsilon_{ij}(\mathbf{q},\omega)l_{Ii}l_{Sj}|^2\rangle, \tag{5}$$

where $\mathbf{q}=\mathbf{k}_I-\mathbf{k}_S$ and $\omega=\omega_I-\omega_S$ represent the difference between the wave vectors and frequencies of the incident and scattered light, $\mathbf{l}_I$ and $\mathbf{l}_S$ are the corresponding unit polarization vectors, and $\Delta\epsilon_{ij}(\mathbf{q},\omega)$ is the Fourier transform of the dielectric constant fluctuation $\Delta\epsilon_{ij}(\mathbf{r},t)$. The angle brackets designate statistical averaging. It follows from Eqs. (4) and (5) that a change in the polarization of light takes place at scattering. In the following we shall assume that the incident light is polarized in the scattering plane—which is defined by the helical axis and the normal to the sample wall—and the scattered light is polarized perpendicular to the scattering plane, so that

$$I(\mathbf{q},\omega)=A^2\langle|\xi_2(\bar{q},\omega)|^2\rangle \tag{6}$$

and the scattering vector $\mathbf{q}$ is perpendicular to the smectic layers. If we introduce $\theta=\theta_0+\Delta\theta(t)$ and $\varphi=\varphi(t)$, we find with the help of (2a) and (2b) for the Sm-C^* phase,

$$\langle|\xi_2(\mathbf{q},\omega)^2\rangle=\tfrac{1}{4}\theta_0^2\langle|\varphi(\mathbf{q}_0+\mathbf{q},\omega)|^2\rangle+\tfrac{1}{4}\theta_0^2\langle|\varphi(\mathbf{q}_0-\mathbf{q},\omega)|^2\rangle+\tfrac{1}{4}\langle|\Delta\theta(\mathbf{q}_0+\mathbf{q},\omega)|^2\rangle+\tfrac{1}{4}\langle|\Delta\theta(\mathbf{q}_0-\mathbf{q},\omega)|^2\rangle. \tag{7}$$

Here the first two terms on the right-hand side correspond to phase fluctuations while the other two describe amplitude fluctuations.

With the help of expressions (3a) and (3b) and the dissipation function density

$$\rho=\tfrac{1}{2}\gamma(\dot{\xi}_1^2+\dot{\xi}_2^2) \tag{8}$$

appropriate for the description of relaxational modes, one gets

$$\langle|\varphi(k,\omega)|^2\rangle=T/\theta_0^2(\gamma^2\omega^2+K_3^2k^4) \tag{9a}$$

and

$$\langle|\Delta\varphi(k,\omega)|^2\rangle=T/\{\gamma^2\omega^2+[2a(T_c-T)+K_3k^2]^2\}, \tag{9b}$$

where $T_c=T_0+(1/a)\Lambda^2/K_3$ and $\theta_0^2=(\Lambda^2/K_3-a)/b$. The inverse phason and amplitudon relaxation times τ^{-1} are given by the poles of Eqs. (9a) and (9b) as

$$\tau_{\text{phas}}^{-1}(\pm\mathbf{q})=(K_3/\gamma)(\mathbf{q}_0\pm\mathbf{q})^2 \tag{10a}$$

and

$$\tau_{\text{ampl}}^{-1}(\pm\mathbf{q})=\gamma^{-1}[2a(T_c-T)+K_3(\mathbf{q}_0\pm\mathbf{q})^2]. \tag{10b}$$

Since we observe quasielastic scattering in the vicinity of the first Bragg peak, we may introduce $\mathbf{q}=\mathbf{q}_0+\mathbf{k}$ resulting in

$$I_{\text{inelast}}\approx A^2[\tfrac{1}{4}\theta_0^2\langle|\varphi(\mathbf{k},\omega|^2\rangle+\tfrac{1}{4}\theta_0^2\langle|\varphi(2\mathbf{q}_0+\mathbf{k},\omega|^2\rangle+\tfrac{1}{4}\langle|\Delta\theta(2\mathbf{q}_0+\mathbf{k},\omega)|^2\rangle+\tfrac{1}{4}\langle|\Delta\theta(\mathbf{k},\omega)|^2\rangle. \tag{11}$$

Here only the first term is the contribution of the gapless "Goldstone" phason,[1] whereas the second term corresponds to an "optic" phason. The relaxation rate of this phason does not go to zero as $k \rightarrow 0$ (and $q \rightarrow q_0$) unlike the Goldstone phason. It should be emphasized that the Goldstone phason is observable only near the first-order Bragg peak. If, for instance, $\mathbf{q}=3\mathbf{q}_0+\mathbf{k}$, there is no term in expression (7) corresponding to a gapless excitation for $\mathbf{k} \rightarrow \mathbf{0}$.

In the Sm-A phase, i.e., for $T > T_c$, one obtains the soft-mode scattering contribution as

$$\langle |\xi_2(\mathbf{q},\omega)|^2\rangle = \tfrac{1}{2}(T/\pi)\gamma\left\{\{\gamma^2\omega^2+[\alpha(T-T_c)+K_3(\mathbf{q}_0-\mathbf{q})^2]^2\}^{-1} + \{\gamma^2\omega^2+[\alpha(T-T_c)+K_3(\mathbf{q}_0+\mathbf{q})^2]^2\}^{-1}\right\} \quad (12a)$$

and the inverse soft-mode relaxation time as

$$\tau_1^{-1}(\pm q)=\gamma^{-1}[\alpha(T-T_c)+K_3(\mathbf{q}_0\pm\mathbf{q})^2]. \quad (12b)$$

At $T=T_c$, expression (12b) coincides with (10a) and (10b).

To check for phason and amplitudon fluctuations in the ferroelectric Sm-C^* phase we studied the wave vector and temperature dependence of inelastic laser light scattering in DOBAMBC in the vicinity of the first Bragg peak using optical-mixing spectroscopy. A He-Ne laser with 1-mW incident power was used. Because of the presence of static scattering, all the measurements were done in the heterodyne regime. 75-μm-thick samples were prepared between clean glass plates. The liquid crystal was aligned with the smectic planes perpendicular to the glass plates by slowly cooling (4°/h) from the isotropic phase to the Sm-A phase in a superconducting magnet with a magnetic field of 6.3 T. The positions of the diffraction spots gave the value of the pitch p of the helix and thus of $q_0=2\pi/p$. The temperature was stabilized to a few millikelvins. The drift in T_c due to the slow degradation of the sample was found to be about 50 mK/h. The scattering geometry was such (inset to Fig. 1) that only excitations with the wave vector parallel to the helical axis (z) were tested. Close to T_c the tilt angle is small and the Sm-C^* phase can be approximated by a modulated uniaxial system with the optic axis along the helix.[15] Fluctuations of ϵ_{xz} (or ϵ_{yz}) are then observable in a scattering geometry with the incident light polarized as an extraordinary wave and the scattered light as an ordinary wave. Because of the resulting difference in the indices of refraction, the first Bragg peak appears at an "asymmetric" position, i.e., the scattering angle is different from the incident angle.

The photon intensity correlation function shows in the Sm-A phase a fast one-exponential time decay and the corresponding relaxation time τ_1^{-1} exhibits a critical slowing down on approaching the Sm-A-Sm-C^* transition from above. It can be attributed to soft-mode-type fluctuations of the amplitude of the order parameter. The corresponding relaxation frequency $f=1/\tau_1$ is practically wave-vector independent and changes from 100 kHz at $T-T_c=40$ mK to 10 kHz at 10 mK above T_c. The value of the relaxation frequency drops to 100 Hz around T_c (Fig. 1).

Below T_c in the Sm-C^* phase, a slow mode (τ_2^{-1}) appears in addition to the fast mode (τ_1^{-1}). The slow mode is, close to T_c (where the pitch is constant), practically temperature independent, whereas the fast mode again shows a critical behavior. A typical value of the relaxation frequency of the fast mode 20 mK below T_c is 50 kHz, whereas the relaxation frequency of the slow mode is smaller by about 3 orders of magnitude and lies in the 10^2-Hz region. The fast mode (τ_1^{-1}) can be assigned to amplitude (τ_{ampl}^{-1}) and the slow mode (τ_2^{-1}) to phase fluctuations (τ_{phas}^{-1}).

The phason dispersion relation $\tau_2^{-1}=\tau_2^{-1}(q_z-q_0)$ measured at $T_c-T=0.1$ K is presented in Fig. 2. The data can be—except very close to q_0—well described by

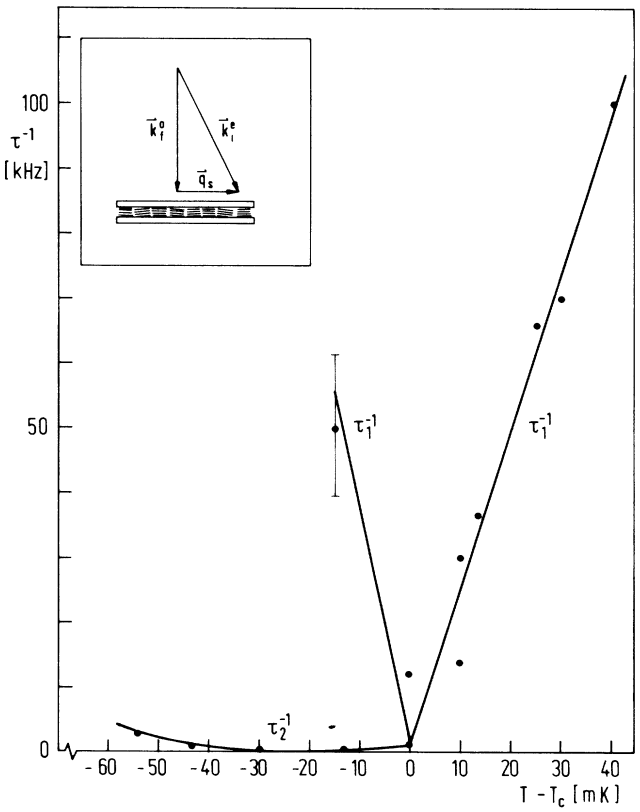

FIG. 1. Temperature dependence of the order-parameter relaxation frequencies τ^{-1} close to the Sm-A-Sm-C^* transition in DOBAMBC for $\mathbf{q}=(0,0,q_0)$. The soft-mode and amplitudon relaxation times are designated by τ_1, whereas the phason relaxation time is designated by τ_2. Inset: Scattering geometry.

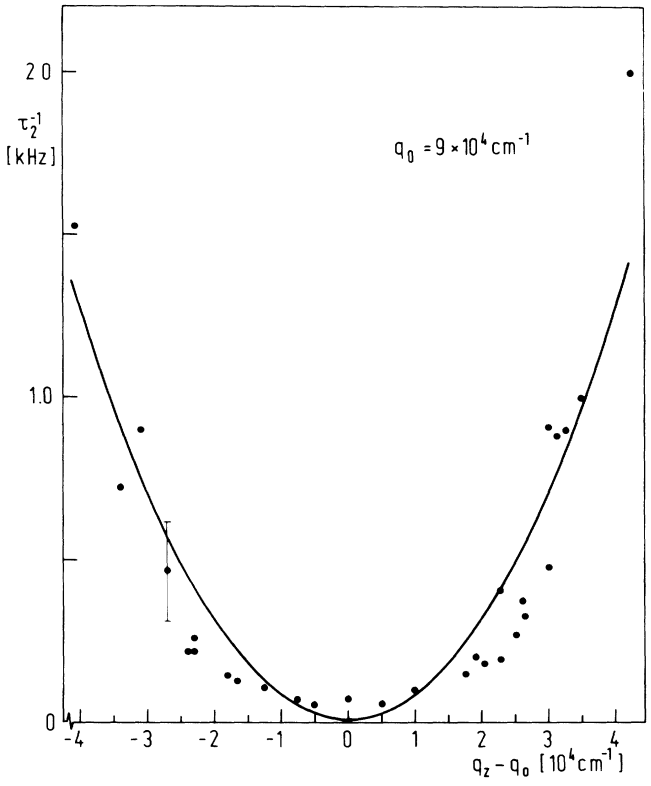

FIG. 2. Phason dispersion relation in DOBAMBC at $T_c - T = 0.1$ K. The scattering vector is parallel to the helical axis.

an overdamped gapless ($\Delta_\phi = 0$) phason where the relaxation rate depends quadratically on $(q_z - q_0)$. The full line in Fig. 2 shows the least-squares fit to the relation $\tau_{\text{phas}}^{-1} = (K_3/\gamma)(q_z - q_0)^2$, where $K_3/\gamma = 8 \times 10^{-7}$ cm^2/s. The deviations at $(q_z - q_0)/q_0 = 0$–0.2 seem to be caused by a small ($q_x/q_z \leq 10^{-2}$–10^{-1}) contribution of modes with wave vectors perpendicular to the helical axis which does not vanish for $q_z - q_0 \to 0$. We have found that the dispersion relation in the x direction is about 10 times steeper than in the z direction. An angular deviation of a tenth of a degree from the z direction is enough to introduce an apparent nonzero value of τ_2^{-1} of the order of 100 Hz as indeed observed.

It should be noted that the above deviations from the square-law fit cannot be explained by pinning defects. We have observed by polarized optical miscroscopy that there is less than one orientational defect per 100 pitches in our samples. If the deviations from the square-law fit of the dispersion relation were due to defects, they would thus occur at different $(q_z - q_0)/q_0$ values than observed.

We believe that the above results represent the first direct observation of phason excitations and phason dispersion in incommensurate crystals by optical spectroscopy. They show that in ferroelectric liquid crystals the phason excitations are of a much lower frequency than in incommensurate crystals. They seem to be nearly gapless as indeed predicted by theory for a system with no frozen defects and vanishingly small higher-order commensurability effects. The difference from crystalline incommensurate systems is dramatically demonstrated by the fact that in IC crystals, because of pinning to frozen defects, the phason gap Δ_ϕ is of the order of 10^{10}–10^{11} Hz, whereas in ferroelectric liquid crystals Δ_ϕ is smaller than 100 Hz.

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