Observation of an Opticlike Phase Mode in an Antiferroelectric Liquid Crystal

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We have observed an acousticlike and an opticlike branch of phase excitations in a quasielastic light-scattering experiment performed in the antiferroelectric smectic-C_A^* phase of 4-(1-ethylheptyloxycarbonyl)phenyl-4′-alkylcarbonyloxy biphenyl-4-carboxylate. In contrast to the nearly gapless acoustic phason branch, the opticlike phase excitations always have a finite relaxation rate. The phenomenon is a direct consequence of a doubling of a smectic unit cell at the transition from the smectic-*A* phase and is in remarkable agreement with a Landau-type model. [S0031-9007(96)01043-5]

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The onset of the antiferroelectric liquid crystalline order at the smectic-*A*–smectic-C_A^* phase transition is characterized by the condensation of a nonpolar soft mode with the wave vector at the edge of the Brillouin zone $(-\pi/d, \pi/d)$ of a smectic-*A* liquid crystal with a smectic layer thickness d. As a result, the so-called alternating-tilt structure is formed in the antiferroelectric smectic-C_A^* phase, the nature of which is by now fairly well understood [1–4]. The antiferroelectric phase can be considered as a stack of tilted ferroelectric smectic layers. The direction of the molecular tilt and therefore also the direction of the local spontaneous polarization $\vec{P}_i$ of the neighboring layer reverses by nearly 180°, as we move along the layer normal. Two neighboring layers thus form an antiferroelectric unit cell with two nearly antiparallel electric dipoles and a very small value of the equilibrium electric polarization $\vec{P}_0(\vec{r}) = \vec{P}_i + \vec{P}_{i+1} \cong 0$. Because of chirality, the directions of the local electric polarization precess slowly around the layer normal, as one moves in a direction perpendicular to the smectic layers. This causes a helical modulation of the smectic-C_A^* phase with a wave vector $\vec{q}_a$ on a mesoscopic scale and leads to the so-called double-twisted helical structure, where two ferroelectric helices in fact gear into each other.

The condensation of the zone-boundary antiferroelectric soft mode has some fascinating implications for the spectrum of collective excitations of the antiferroelectric phase [5]. Similar to the phonon spectrum of a monatomic linear chain, we have in the smectic-*A* phase of an antiferroelectric liquid crystal a single, doubly degenerate branch of *overdamped collective orientational excitations* that critically slows down at the zone boundary, as shown in Fig. 1(a). At the phase transition, the original Brillouin zone is reduced because of a doubling of a unit cell, and the zone-boundary modes appear as the zone-center modes of the low-temperature phase. There are, therefore, four dispersion branches in the smectic-C_A^* phase, as shown schematically in Fig. 1(b). The lowest branch is a gapless phason branch [6] with a zero-frequency, symmetry restoring Goldstone mode that is analogous to the acoustic phonon branch of a diatomic lattice. In addition to the two high frequency amplitude branches that are strongly temperature dependent, an opticlike branch of phase excitations is expected to appear in the smectic-C_A^* phase. Similar to the optical phonon branch in a diatomic solid crystalline lattice, the appearance of this optical phason is here a direct consequence of a doubling of the originally monomolecular unit cell.

In this Letter, we report the first simultaneous observation of the dispersion relations of the opticlike and acousticlike phase excitations in an antiferroelectric smectic-C_A^* phase. As expected for an optic-like phason, the dispersion has a finite gap and is centered at $\vec{q}_a$. We have also observed a gapless branch of the zone-center phase modes, which have a minimum relaxation rate at $2\vec{q}_a$. From the measured temperature dependencies of the relaxation rates of both modes, we give a first consistent set of the coefficients of the Landau–de Gennes free-energy expansion

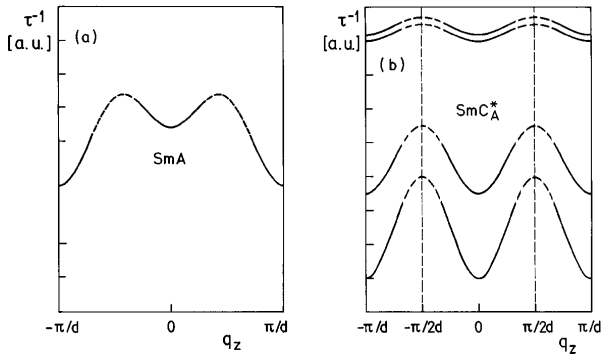

FIG. 1. The dispersion relation for the order parameter excitations in the smectic-*A* (a) and a homogeneous smectic-C_A^* phase (b) of an antiferroelectric liquid crystal [5].

for the antiferroelectric smectic-C_A^* phase [7,8] and find a remarkable agreement with theory.

The order parameter dynamics of the antiferroelectric smectic-C_A^* structure can be conveniently derived within the Orihara-Ishibashi [7,8] nonequilibrium free energy density, expanded in terms of the ferroelectric and antiferroelectric order parameters $\vec{\xi}_f$ and $\vec{\xi}_a$:

$$g = g_A + \sum_{\nu=a,f}\Big[\frac{1}{2}a_\nu|\vec{\xi}_\nu|^2 + \frac{1}{4}b_\nu|\vec{\xi}_\nu|^4 + \Lambda_\nu(\vec{\xi}_\nu \times \partial\vec{\xi}_\nu/\partial z)_z + \frac{1}{2}K_{3\nu}(\partial\vec{\xi}_\nu/\partial z)^2\Big] + \frac{1}{2}\gamma_1\vec{\xi}_a^{\,2}\cdot\vec{\xi}_f^{\,2} + \frac{1}{2}\gamma_2(\vec{\xi}_a\cdot\vec{\xi}_f)^2 . \quad (1)$$

Here, g_A is the equilibrium free-energy density of the smectic-A phase, $\vec{\xi}_{a,f} = \frac{1}{2}(\vec{\xi}_i \mp \vec{\xi}_{i+1})$, and the molecular tilt of the ith smectic layer is described by a two-component tilt vector $\vec{\xi}_i = (n_{ix}n_{iz}, n_{iy}n_{iz})$, where $\vec{n}_i$ is the corresponding director. It is easy to see from the structure of Eq. (1) that we have, in fact, two competing structures, i.e., ferroelectric and antiferroelectric helix, where the coupling between them is described by the coefficients γ_1 and γ_2. Here only $a_\nu = \alpha(T - T_\nu)$ $(\nu = a, f)$ are temperature dependent, whereas the rest of the coefficients are constant. Similar to the smectic-A–smectic-C^* transition, T_a and T_f are here the phase transition temperatures into the homogeneous antiferroelectric or ferroelectric phases, respectively, Λ_ν are the two Lifshitz coefficients, and $K_{3\nu}$ are the twist-bend-like elastic constants. For $T_a > T_f$ we have a second-order smectic-A–smectic-C_A^* transition into the antiferroelectric phase with the tilt angle $\theta_a(T) \approx (T_a^* - T)^{1/2}$ and the wave vector $q_a = -\Lambda_a/K_{3a}$ of the double-helical modulation, which is here temperature independent.

The phase-mode dynamics is analyzed within the Landau-Khalatnikov equations of motion of the free-energy density in a "twisted" reference frame [9,10], which follows the uniformly twisted structure of a double-antiferroelectric helix. A straightforward calculation leads to four dispersion branches in the antiferroelectric phase, as shown schematically in Fig. 1(b). The two high-frequency branches represent here helically modulated tilt excitations which are strongly temperature dependent and are observable only very close to the phase transition T_a^*. The other two, low-frequency dispersion branches are the acoustic-like phason branch

$$\tau_a^{-1}(q) = K_{3a}q^2/\eta , \quad (2)$$

and the optic-like phason branch

$$\tau_f^{-1}(q) = \Delta(T) + \frac{K_{3f}}{\eta}q^2 - \frac{\sqrt{\frac{1}{4}\gamma_2^2\theta_a^2 + 4K_{3f}^2(q_a - q_f)^2q^2}}{\eta} . \quad (3)$$

Here, $\Delta(T) = [a_f(T) + (\gamma_1 + \frac{1}{2}\gamma_2)\theta_a^2(T) + (2\Lambda_f + K_{3f}q_a)q_a]/\eta$ is a temperature dependent frequency gap and $q_f = -\Lambda_f/K_{3f}$. For simplicity, the two viscosity coefficients $\eta_{a,f}$ have been set equal, and we have considered only the plane-wave excitations with the wave vector $\vec{q} = (0, 0, q)$ along the double-helical axis.

The lower dispersion branch $\tau_a^{-1}(q)$ is gapless in the long-wavelength limit; i.e., $\tau_a^{-1}(q \to 0) \to 0$ and represents therefore the *gapless phason branch* with a zero-frequency, symmetry restoring Goldstone mode, which was observed recently [6]. On the other hand, the second branch of excitations [Eq. (3)] has a *finite frequency* for all wave vectors. This is therefore *the optic-like phason branch*, which emerges in the smectic-C_A^* phase due to a doubling of the smectic unit cell. A further insight into the physical properties of these two phason branches is given by analyzing the structure of the corresponding eigenvectors, as shown schematically in the insets to Fig. 2(a) and 2(b). Whereas the Goldstone mode represents for $q = 0$ a uniform rotation of a sample as a whole [inset Fig. 2(b)], the optic-like phason represents here an out-of-phase local rotation of the two neighboring layers [inset Fig. 2(a)]. It is straightforward to see that

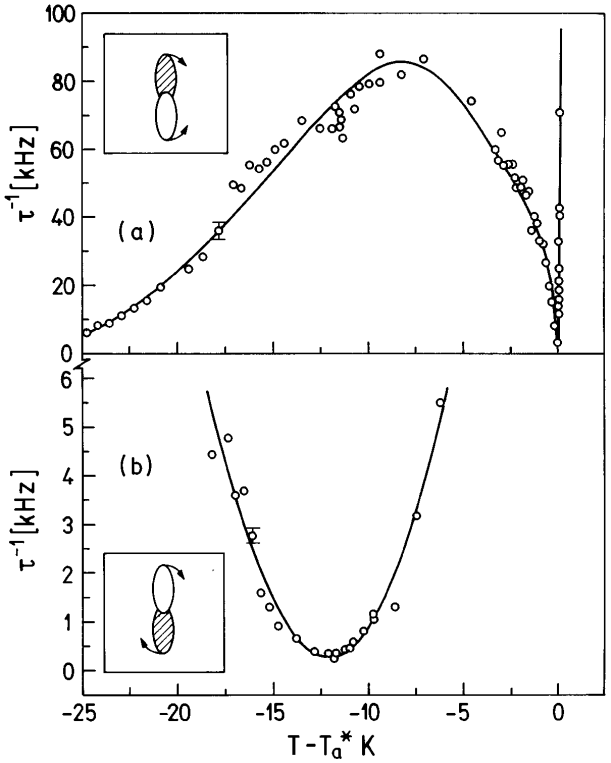

FIG. 2. Temperature dependence of the (a) optic-like phase mode and (b) acoustic-like phason in the smectic-C_A^* phase of EHPOCBC at $q_z = 2.8 \times 10^7\ \mathrm{m}^{-1}$. The soft mode in the smectic-A phase is shown at the far-right side of (a). The solid lines represent for $T < T_a^*$ the best fit by Eqs. (2) and (3), with $K_{3a}/\eta = 2.2 \times 10^{-11}\ \mathrm{m^2\,s^{-1}}$, $K_{3f}/\eta = 2 \times 10^{-10}\ \mathrm{m^2\,s^{-1}}$, $\alpha/\eta = 1.1 \times 10^6\ \mathrm{s^{-1}\,K^{-1}}$, $\gamma_1/b_a = 0.9$, $\gamma_2/b_a = 0.1$, and $q_f = 1 \times 10^7\ \mathrm{m^{-1}}$.

the Goldstone excitation is a nonpolar, whereas the zone-center optic phason is a polar mode, and can therefore couple to a homogeneous external electric field.

The quasielastic-scattering cross section for the acousticlike and the opticlike phasons can be evaluated within the perturbative approach to the optics of inhomogeneous liquid crystalline structures. Because the unit cell of the smectic-C_A^* phase is much smaller than the wavelength of visible light, the dielectric tensor, which determines the local optical properties, is an average over a unit cell

$$\varepsilon(\vec{r},t) = \frac{1}{2}(\varepsilon_i^0 + \varepsilon_{i+1}^0) + \frac{1}{2}[\delta\varepsilon_i(t) + \delta\varepsilon_{i+1}(t)]. \tag{4}$$

Here ε_i^0 and $\delta\varepsilon_i(t)$ are the static and the time-fluctuating parts of the dielectric tensor of the ith smectic layer, respectively. Because the symmetry of $\varepsilon_{jz}(\vec{r})$, $j = x, y$, is the same as the symmetry of $\vec{\xi}(t)$ [11], a straightforward calculation shows that in the Born approximation both phason branches are observable when an ordinary wave is scattered by the order parameter fluctuations into an extraordinary wave or vice versa. The scattering cross section for the acousticlike phason is proportional to the fourth power of the tilt angle, and is therefore smaller than the scattering cross section for the opticlike phason, which is quadratic in the tilt angle. Furthermore, due to their different coordinate dependencies, the acoustic phason branch is centered at the scattering wave vector $\vec{q}_s = 2\vec{q}_a$, whereas the opticlike phason branch is centered at $\vec{q}_s = \vec{q}_a$ in the *laboratory reference frame.*

The quasielastic light scattering experiment was performed in the smectic-A and smectic-C_A^* phases of 4-(1-ethylheptyloxycarbonyl)phenyl-4′-alkylcarbonyloxy biphenyl-4-carboxylate (EHPOCBC), which was aligned homeotropically in 50 μm glass cells. The experiment was performed in an ordinary-extraordinary scattering geometry with a wave vector $\vec{q} = (0, 0, q)$ [6,12]. Very close ($\approx$100 mK) to the antiferroelectric phase transition, we observe a very weak and a very fast single-exponential signal, which critically slows down at T_a^*, as shown at the far-right side of Fig. 2(a). This is therefore the soft mode of the transition. A finite value of the soft mode relaxation rate at T_a^* indicates that the scattering wave vector is far from the critical wave vector of the transition. In the antiferroelectric phase and close to T_a^*, this signal is masked by a much stronger, single-exponential signal. The relaxation rate of this signal first increases gradually by decreasing temperature, reaches a maximum at $T_a^* - T \approx 7$ K, and then gradually decreases by lowering the temperature. Then, at $T_a^* - T \approx 7$ K, a single-exponential signal changes into a double-exponential signal, clearly indicating the presence of a second eigenmode. There is an order of magnitude difference in the relaxation rates of both modes, whereas their intensities are almost the same. The second mode [see Fig. 2(b)] shows a very strong, parabolic temperature dependence, reaches a minimum rate at $T_a^* - T \approx 12$ K, and then increases again to higher relaxation rates.

The nature of both modes that were observed in the antiferroelectric smectic-C_A^* phase was further clarified by measuring their dispersion relations at a given temperature, as shown in Fig. 3(a) and 3(b). One can clearly see from Fig. 3(a) that the dispersion of the faster modes is centered close to $q_s = 1.6(1 \pm 0.1) \times 10^7$ m^{-1} and has a finite gap, whereas the dispersion of the low-frequency modes [Fig. 3(b)] is nearly gapless and centered at $q_s = 2.4(1 \pm 0.01) \times 10^7$ m^{-1}. As it is not possible to measure at the Bragg peak, where the relaxation rate should vanish, the observed small gap of 400 Hz is due to a small q_x component of the scattering wave vector. A nearly factor of two between the two wave vectors corresponding to the minima of the two dispersions indicates that the faster modes represent the *optical-like phason* excitations, whereas the slower branch corresponds to the *acousticlike phason* modes. This is also confirmed by the predictions of the Landau theory: Whereas the acoustic branch [Eq. (2)] is expected to be gapless, the optic branch should have

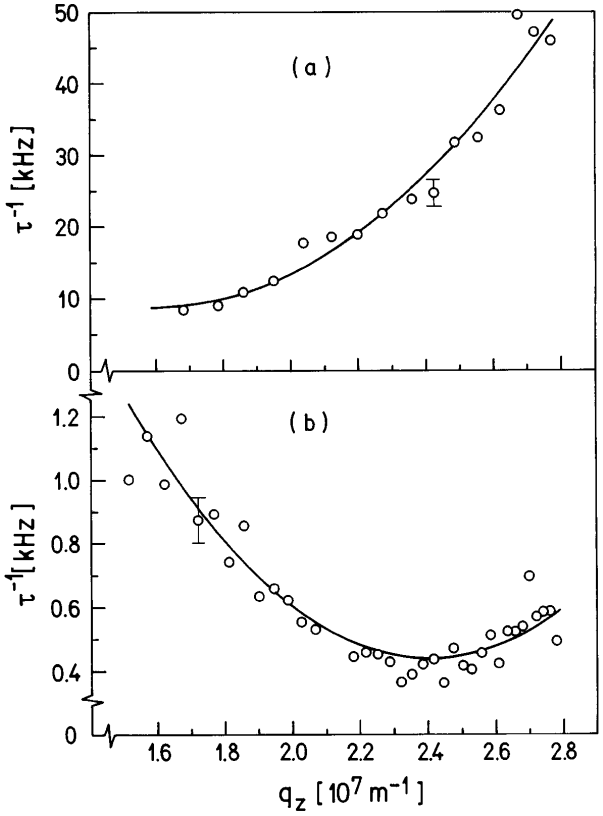

FIG. 3. (a) The dispersion relation of the optic-like phase mode in the smectic-C_A^* phase of EHPOCBC at $T_a^* - T \approx 10$ K. The solid line is the best parabolic fit with $K_{3f}/\eta = 2.9 \times 10^{-10}$ m^2 s^{-1}, $q_a = 1.6 \times 10^7$ m^{-1}, and a gap of 9.4 kHz. (b) The dispersion relation of the slow, acoustic-like phase mode in the smectic-C_A^* phase of EHPOCBC at $T_a^* - T \approx 14$ K. The solid line is the best fit to Eq. (2) with $K_{3a}/\eta = 1 \times 10^{-11}$ m^2 s^{-1}, $q_a = 1.2 \times 10^7$ m^{-1}, and a residual gap of 400 Hz due to a small mismatch of $\vec{q}_s$ and $\vec{q}_a$.

a finite relaxation rate for all wave vectors [Eq. (3)]. Indeed, the optical branch has a minimum frequency gap of approximately $\approx 9.4(1 \pm 0.2)$ kHz [see Fig. 3(a)], and no static Bragg scattering is observed at $\vec{q}_a$, whereas the acoustic phason branch is nearly gapless at $2\vec{q}_a$, where the Bragg peak appears. The observed intensities are also in agreement with expectations: The acoustic branch has a smaller cross section and is therefore observable only in the region of slow relaxation. The observed values of $\vec{q}_a$ are also consistent with infrared selective reflection measurements.

The measurements were fitted to the predictions of a simple Orihara-Ishibashi model [Eqs. (2) and (3)], where the temperature dependence of the helical period was measured with infrared selective reflection and included into analysis. This explains one part of the unusual temperature dependence of the observed relaxation rates, and we find a very good global agreement of the fitting parameters. The observed values of the coefficients, averaged over different samples and experimental runs, give $K_{3a}/\eta = 1.6(1 \pm 0.3) \times 10^{-11}\ \mathrm{m^2\,s^{-1}}$, which is an order of magnitude smaller than in MHPOBC [6,13] and $K_{3f}/\eta = 2(1 \pm 0.5) \times 10^{-10}\ \mathrm{m^2\,s^{-1}}$. For the rest of the coefficients we obtain $\alpha/\eta = 1.1(1 \pm 0.1) \times 10^{6}\ \mathrm{s^{-1}\,K^{-1}}$, $\gamma_1/b_a = 0.9(1 \pm 0.2)$, $\gamma_2/b_a = 0.1(1 \pm 0.2)$, and $q_f = 1(1 \pm 0.5) \times 10^{7}\ \mathrm{m^{-1}}$. The results clearly indicate that only one coupling term ($\gamma_1 \gg \gamma_2$) is dominant in the expansion (1).

The experiment leads to yet another observation, which is very important for the understanding of the nature of the antiferroelectric order in liquid crystals. The frequency gap of the optic-like phason branch is exceptionally small in the smectic-C_A^* phase i.e., it is of the order of 10 kHz. This indicates that the ferroelectric correlations are very soft in the antiferroelectric phase, or, in other words, the zone-center ferroelectric soft mode has nearly condensed at the phase transition point. This is consistent with our understanding of the nature of the long-range orientational order in tilted smectics, which tells us that the phase transition into the tilted smectic is driven by the in-plane, short-range van der Waals forces. In this context, there should not be much difference between the dynamics of the ferroelectric and antiferroelectric correlations in the smectic-*A* phase of an antiferroelectric liquid crystal, because they both imply spontaneous and collective tilting of the molecules. The only difference is that in zone-center, ferroelectric fluctuations, the molecules spontaneously tilt in the same direction, whereas in the antiferroelectric, zone-boundary fluctuations, the molecules fluctuate in a herring-bone-like, alternating fashion. The present experiment clearly indicates that there is not much energy difference between these two collective motions and directly confirms the Orihara-Ishibashi model of the smectic-*A*–smectic-C_A^* transition.

In conclusion, we have observed for the first time two dispersion branches in the smectic-C_A^* phase of an antiferroelectric liquid crystal, which have been identified as the acousticlike (nonpolar) and the opticlike (polar) phase excitations. The appearance of two distinct dispersion branches of phase excitations is here a direct consequence of a doubling of the originally monomolecular smectic unit cell at the phase transition point. The observed phenomenon is a direct analog to the phonon spectrum of a diatomic solid crystalline lattice, where, in addition to the gapless acoustic phonon branch, an optical phonon branch is observed. The difference is that in antiferroelectric liquid crystals the frequency gap between these two branches is many orders of magnitude smaller than in solids and can be easily observed.

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