Light scattering study of the smectic-C_α^* phase of a chiral liquid crystal

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(Received 26 November 1997)

Dynamic light scattering measurements have been performed on aligned bulk samples of the chiral liquid crystal MHPOBC in order to investigate the structure and dynamical properties of the smectic-C_α^* phase. Three different relaxation modes were observed: the amplitude and phase modes of the ferroelectric order parameter, and a very slow mode, which we associate with fluctuations in antiferroelectric order. The temperature dependence and dispersion of these modes is consistent with a crossover in the smectic-C_α^* phase from weakly ferroelectric near the smectic-C^* phase to antiferroelectric near the smectic-A phase, and with a director structure that contains both a helical antiferroelectric component of very long pitch and a possibly nonhelical ferroelectric component with much shorter period, comparable to the pretransitional pitch of the ferroelectric helix. [S1063-651X(98)06205-9]

PACS number(s): 61.30.Gd, 64.70.Md, 78.20.Ek

A large effort has been recently dedicated to the study of ferroelectric liquid crystals because of their unique physical properties and their increasing use in display technology. Even in pure compounds the balance between different types of intermolecular interactions is so delicate that multiple subphases, exhibiting ferro-(Sm-C^*), antiferro-(Sm-C_A), and ferrielectricity (Sm-C_γ) in addition to the paraelectric Sm-A phase, may exist over a narrow temperature range. Although numerous theoretical [1–3] and experimental [4–10] studies have established the basic nature of many of these phases, the structure of one of them—the Sm-C_α^* phase, which typically occurs between Sm-A and Sm-C^* or Sm-C_A phases—remains elusive. Early experiments [5,6] suggested the Sm-C_α^* is a tilted phase with small tilt angle, antiferroelectric pairing of the tilt directions between layers near the transition to the Sm-A phase, and antiferroelectric fluctuations extending above the transition. More recent studies have reached contrasting conclusions: the Sm-C_α^* has been reported [9] to have a helical director structure with very short (~100 nm pitch) or, alternatively, to be characterized [10] by a dynamic helical packing with very long (> several μm) average pitch.

The present dynamic light scattering study provides a possible clarification of this controversy. At the Sm-C^* to Sm-C_α^* transition, the phase fluctuations of the ferroelectric order parameter show a sharp drop in amplitude, and the amplitude fluctuations show anomalous slowing down from both sides of the transition. We also observe the appearance of a novel slow acoustic mode in the vicinity of the transition, whose amplitude relative to the ferroelectric modes increases monotonically in the Sm-C_α^* phase. The minimum frequency of this mode, which is observed even into the Sm-A phase, is centered at $\vec{q}=0$, the limit expected for a helical structure of infinite pitch. On the other hand, the dispersion minimum of the ferroelectric modes remains consistent with the pretransitional wave vector of the Sm-C^* helix, although the dispersion may no longer be parabolic. While not yet conclusive, our results suggest that the Sm-C_α^* phase *combines* features of an antiferroelectric structure with essentially infinite helical pitch and a ferroelectric structure with quite short pitch. We also discuss how this scenario is consistent with results [2] based on the Orihara-Ishibashi model [1] of the free energy for competing ferroelectric and antiferroelectric order parameters.

In our dynamic light scattering experiment, homeotropically aligned 25 μm thick samples of the liquid crystal R-MHPOBC were illuminated by 488 nm laser radiation. The homodyne intensity autocorrelation function was recorded for a depolarized, ordinary-extraordinary scattering process, with $\vec{q}\approx(0,0,q_z)$ in a back scattering geometry ($\hat{z}$ along the smectic layer normal) and $\vec{q}\approx(q_x,0,0)$ in a forward scattering geometry. In forward scattering, we probed a range $q_x=1-8\ \mu\mathrm{m}^{-1}$ with $q_z\leqslant 0.1\ \mu\mathrm{m}^{-1}$; because of refraction at the glass-air interface of our flat sample cells, our back scattering data are restricted to a narrow q_z range, 34–39 $\mu\mathrm{m}^{-1}$ with $q_x\leqslant 0.01\ \mu\mathrm{m}^{-1}$, plus a point at $q_z\approx 0$. The measured correlation functions were fit to multiple damped exponentials with the overall background always fixed to the measured value. Fluctuation mode amplitudes and frequencies were extracted from these fits.

Figure 1 shows typical correlation data in the Sm-C^*, Sm-C_α^*, and Sm-A phases observed in the back and forward scattering geometries. The solid lines are fits of the fast portion of the spectrum (i.e., $<10^{-4}$ sec) to two overdamped decays, while dashed lines are fits restricted to a single fast mode. Except for the vicinity of the Sm-A phase, it is clear that two fast modes, indicated by vertical arrows in the figures, are present. In the ferroelectric Sm-C^* phase, typical frequencies are $\omega_1=3\times10^5$ Hz and $\omega_2=3\times10^4$ Hz, and both modes scatter strongly near the transition to the Sm-C_α^* phase (T_{C^*,C_α^*}). We associate the faster mode (ω_1) with amplitude and the slower mode (ω_2) with phase fluctuations of the ferroelectric order parameter, which is equivalent to the in-layer director averaged over all the layers. In the Sm-C^* phase and for $q_z\sim 36\ \mu\mathrm{m}^{-1}$ (back scattering geometry), we also observe a mode with very low frequency, $\omega_4=5$ Hz. This mode is still evident just above T_{C^*,C_α^*}, but its scattering amplitude weakens significantly; it becomes unobservable at higher temperatures in the Sm-C_α^* phase. In the forward scattering geometry, where $q_z<0.1\ \mu\mathrm{m}^{-1}$, the pair

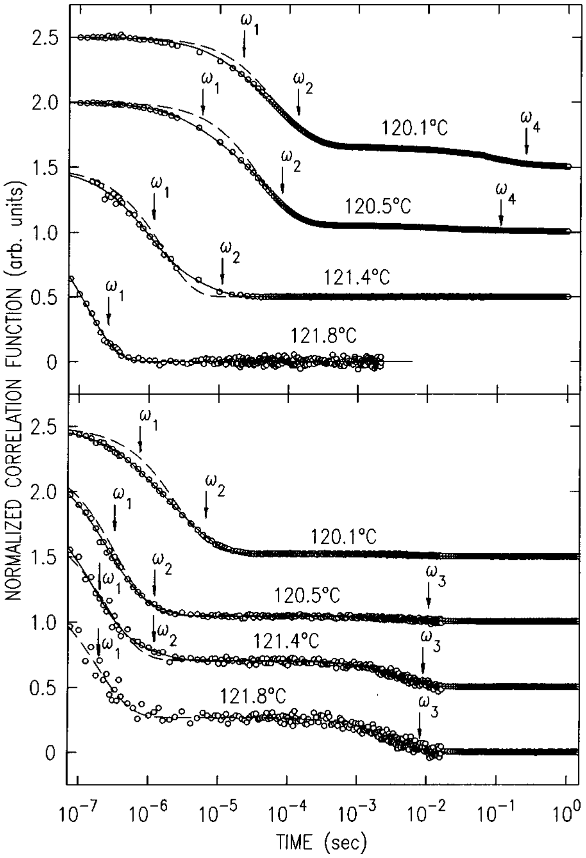

FIG. 1. Typical normalized time correlation functions in Sm-C^* (120.1 °C), Sm-C_α^* (120.5 and 121.4 °C), and Sm-A (121.8 °C) phases observed for $q_z = 36.0\ \mu\mathrm{m}^{-1}$, $q_x \approx 0$ (top) and $q_x = 5.0\ \mu\mathrm{m}^{-1}$, $q_z \approx 0$ (bottom). Arrows point to the characteristic decay times associated with each observed fluctuation mode. $T_{C^*,C_\alpha^*} = 120.3$ °C and $T_{C_\alpha^*,A} = 121.6$ °C.

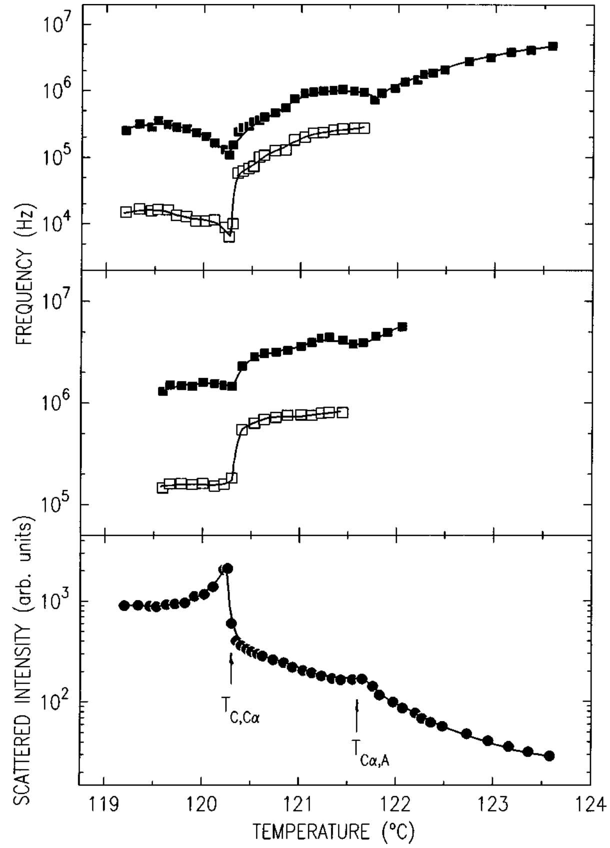

FIG. 2. Temperature dependence of the relaxation frequencies of the amplitude (filled symbols) and phase (open symbols) modes in Sm-C^*, Sm-C_α^*, and Sm-A phases for $q_z = 36.0\ \mu\mathrm{m}^{-1}$, $q_x \approx 0$ (top) and $q_x = 5.0\ \mu\mathrm{m}^{-1}$, $q_z \approx 0$ (middle). Bottom: Temperature dependence of the intensity of the scattered light for $q_x \approx 0$.

of fast modes shifts to higher frequency, and an additional mode (ω_3) appears in the slow part of the spectrum. Unlike the slow flucturations (ω_3) observed at large q_z, this mode *grows* in amplitude with increasing temperature, even into the Sm-A phase. Its frequency is found to be nearly temperature independent. Above the Sm-C_α^* to Sm-A transition $T_{C_\alpha^*,A}$ in both geometries, the fast spectrum contains only a single mode.

In Figs. 2–5, we present the results of our analysis of the correlation data. The presence of the Sm-C_α^* was clearly detected by our light scattering experiment. Figure 2 shows the temperature dependence of the frequencies of the two fast modes (ω_1 and ω_2) and the total scattered intensity at fixed scattering angles. Anomalous temperature dependence is observed in these quantities at the phase transitions, yielding $T_{C^*,C_\alpha^*} = 120.3$ °C and $T_{C_\alpha^*,A} = 121.6$ °C, in good agreement with published values [5] for MHPOBC. In particular, the amplitude mode shows an anomalous slowing down at T_{C^*,C_α^*}, and the scattered intensity exhibits a corresponding increase. Above the transition, the frequencies are significantly higher, and the overall scattering is weaker. These results are consistent with a decrease in the equilibrium value of the director tilt. The trend continues to the Sm-A phase, where only one fast mode (ω_1) is observed. The signature of the Sm-C_α^* to Sm-A transition is much weaker, but still evident.

We also measured the dispersion of the fluctuation modes at fixed temperatures. Figure 3 shows the dependence of the frequencies of the two fast modes on scattering wave vector q_z for three temperatures in the vicinity of and above the Sm-C^* to Sm-C_α^* transition. The point at $q_z = 0$ was obtained from the forward scattering geometry. The solid lines represent fits to quadratic functions in q_z. In the Sm-C^* phase, we find good agreement with the parabolic dispersion expected for a helical director structure along the layer normal; the fit yields a pretransitional gap $\approx 2 \times 10^3$ Hz for the amplitude mode, and $q_z \approx 20\ \mu\mathrm{m}^{-1}$ for the pretransitional helical wave vector, which corresponds to a pitch of 300 nm. This value is consistent with optical microscopy observations which show a shift to shorter wavelengths in the color reflected from the helical structure, as $T \to T_{C^*,C_\alpha^*}$ from below. On the other hand, in the Sm-C_α^* phase, fits to a simple quadratic dependence in q_z (dashed lines in the figure) are less satisfactory, and appear to break down at higher temperature. Although our analysis over such a limited range of q_z is not conclusive, it suggests a nonparabolic dispersion in the Sm-C_α^* phase, and indicates that a modulated component of the director structure remains, with a period roughly comparable to the pretransitional helical pitch.

Results for the frequency dispersion and relative amplitudes of the modes observed in forward scattering are shown in Figs. 4 and 5. The dispersion in q_x of all three modes

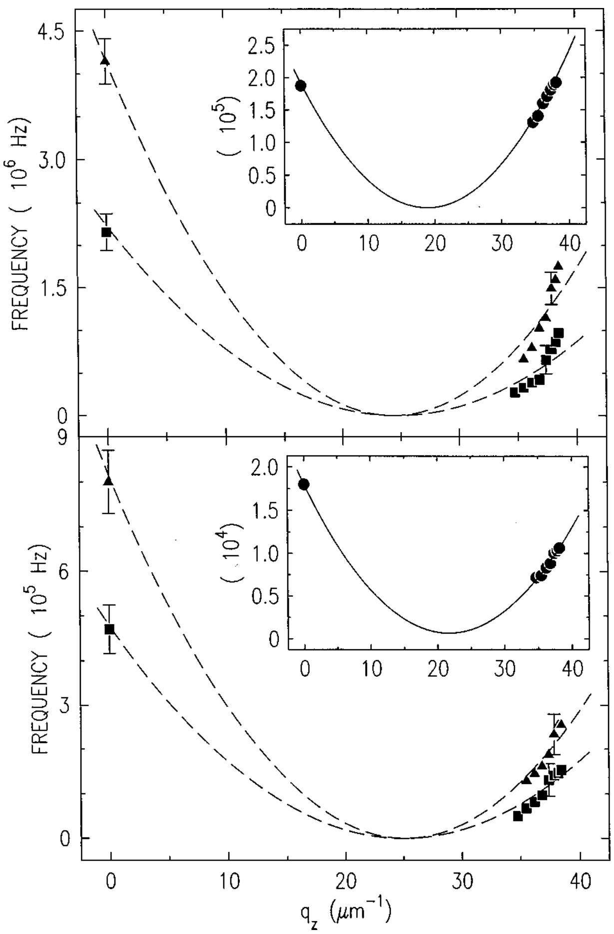

FIG. 3. Dependence of the relaxation frequencies on q_z ($q_x \approx 0$) for the ferroelectric amplitude (top) and phase (bottom) modes in the Sm-C^* (120.1 °C, circles) and Sm-C_α^* (120.5, squares and 121.4 °C, triangles) phases.

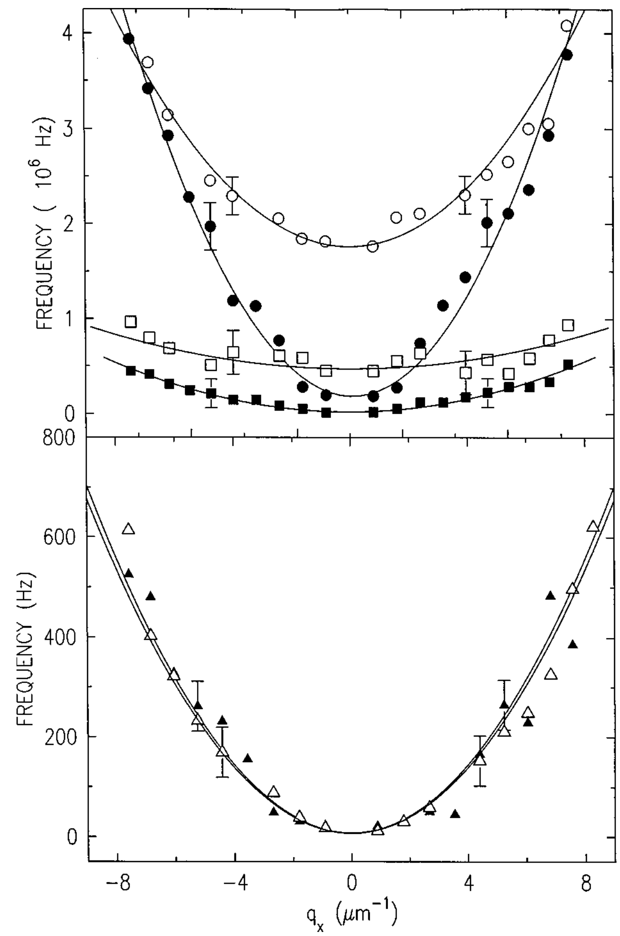

FIG. 4. Dependence of the relaxation frequencies on q_x ($q_z \approx 0$) for the ferroelectric amplitude and phase modes (top), and the slow mode (bottom), just inside the Sm-C^* (120.1 °C, filled symbols) phase and in the Sm-C_α^* (120.5 °C, open symbols) phase.

detected is parabolic on both sides of the Sm-C^* to Sm-C_α^* transition. The decrease in the relative amplitude of the ferroelectric phase mode at $T \sim T_{C^*,C_\alpha^*}$ again suggests a reduction in the equilibrium tilt angle. Above the transition, the relative scattering from the slow mode shows a steady increase as $T \to T_{C_\alpha^*,A}$, whereas the contribution from the remaining fast mode remains constant. Analysis of the dispersion of the slow mode in Fig. 4 indicates that it is gapless at $q_x = 0$. Since this mode is also not observed in the q_z scans at corresponding temperatures in the Sm-C_α^* phase, we conclude that it is an acoustic mode centered at $\vec{q} \approx 0$.

We now discuss these results in terms of the phenomenological model introduced by Orihara and Ishibashi [1], Zeks and Cepic [2], and Cepic and Zeks [3] (known as the OIZC model) to describe the competition between ferroelectric and antiferroelectric order in tilted chiral smectic liquid crystals. The ferroelectric and antiferroelectric order parameters are defined in terms of the in-plane component of the director in neighboring layers (labeled i and $i+1$) as, respectively, $\vec{\xi}_f = (\vec{\xi}_i + \vec{\xi}_{i+1})/2$ and $\vec{\xi}_a = (\vec{\xi}_i - \vec{\xi}_{i+1})/2$. The free energy density expanded in $\vec{\xi}_f$ and $\vec{\xi}_a$ is

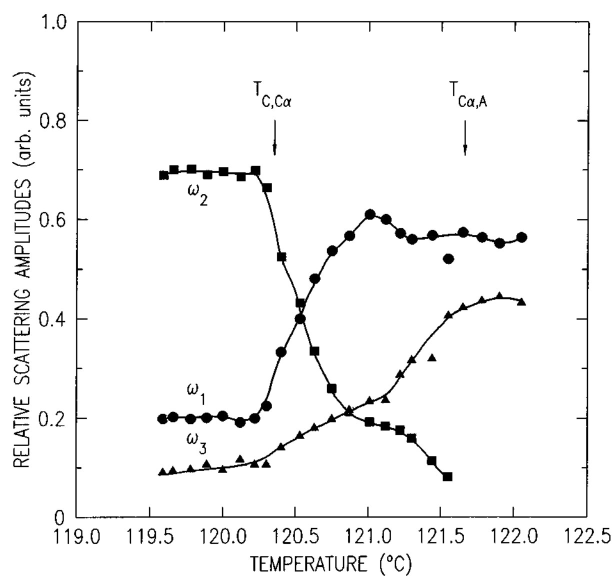

FIG. 5. Temperature dependence of the relative scattering amplitudes for the three modes observed for $q_z \approx 0$ in the Sm-C^*, Sm-C_α^*, and Sm-A phases.

$$\mathcal{F}=\sum_{\nu=f,a}\left\{\frac{\alpha_\nu^*}{2}\vec{\xi}_\nu^2+\frac{\beta_\nu}{4}\vec{\xi}_\nu^4+\delta_\nu\left(\vec{\xi}_\nu\times\frac{\partial\vec{\xi}_\nu}{\partial z}\right)_z+\frac{\kappa_\nu}{2}[(\vec{\nabla}\cdot\vec{\xi}_\nu)^2+(\vec{\nabla}\times\vec{\xi}_\nu)^2]\right\}+\gamma_1\vec{\xi}_f^2\vec{\xi}_a^2+\gamma_2(\vec{\xi}_f\cdot\vec{\xi}_a)^2, \quad (1)$$

where $\vec{\xi}_\nu$ lies in the x-y plane, and we have used a one elastic constant approximation in the derivative terms. Writing the order parameters in terms of an amplitude and phase, $\vec{\xi}_\nu=\theta_\nu(\cos\phi_\nu\hat{x}+\sin\phi_\nu\hat{y})$, assuming that the equilibrium values $\theta_{\nu,0}$ and $\phi_{\nu,0}$ are only functions of z (the coordinate along the layer normal), and minimizing the free energy, one finds one class of solution for the equilibrium structure that predicts a distinct phase between the Sm-C^* and Sm-A phases [2]. This class has $|\gamma_2|$ finite but sufficiently small so that the phases ϕ_f and ϕ_a—and the wave vectors of the associated director modulations—are not locked. If we then consider only solutions for which $\theta_{\nu,0}$ are independent of z, minimization of Eq. (1) gives $d^2\Delta\phi_0/dz^2=-\gamma_2(\theta_{\alpha,0}^2/2\kappa_f+\theta_{f,0}^2/2\kappa_a)\sin 2\Delta\phi_0$. Thus, the phase *difference* $\Delta\phi_0=\phi_{f,0}-\phi_{a,0}$ is a soliton along z. The fluctuation spectrum contains one acoustic and one weakly optic phase mode, and two amplitude modes. In the limit of weak coupling, one pair of phase and amplitude is associated with mainly ferroelectric fluctuations and the other with mainly antiferroelectric fluctuations.

Major features of our light scattering results may be explained by this solution together with the results of previous experiments [5,6], which suggest that the Sm-C_α^* phase is ferroelectriclike ($\theta_f>\theta_a$) near the Sm-C^* phase and antiferroelectriclike ($\theta_a>\theta_f$) near the Sm-A phase. This crossover, which implies a reduction in the scattering strength from the phase fluctuations ϕ_f and an increase in the frequency of the amplitude fluctuations θ_f, is consistent with the results in Fig. 2 obtained for the fast modes (ω_1 and ω_2) at $q_z\approx 36.0\ \mu\text{m}^{-1}$, and supports their assignment at large q_z in the Sm-C_α^* phase to fluctuations of the ferroelectric order parameter. As previously noted, the dispersion of these modes in q_z in the Sm-C^* phase is parabolic, with a pretransitional value of the helical wave vector $q_f\sim 20\ \mu\text{m}^{-1}$. Then the low frequency mode (ω_4) observed at $q_z\sim 36\ \mu\text{m}^{-1}$ *below* T_{C^*,C_α^*} can be assigned to the $2q_f\sim 40\ \mu\text{m}^{-1}$ branch of the ϕ_f fluctuations, which would be expected to be quite slow at this wave vector. Moreover, the scattering from this branch is expected to be weak and to drop when $T\to T_{C^*,C_\alpha^*}$, as evidenced in Fig. 1, since the fluctuation amplitude is proportional to θ_f^4 [8].

In the smectic-C_α^* phase, the additional slow model (ω_3) significantly increases in relative amplitude (Fig. 5) and evidently has zero frequency at $\vec{q}\approx 0$ (Fig. 4). These features suggest the presence of a macroscopic modulated structure, which fluctuates slowly about a very long average pitch. In fact, director fluctuations associated with a helicoidal superstructure with very long pitch have recently been reported in a circular dichroism study of the smectic-C_α^* phase [10]. Alternatively, the slow mode could arise from a macroscopic modulation of the smectic layer structure, which has been observed in homogeneously aligned chiral smectics [11]. Finally, the nonparabolic dispersion in q_z implied by our data in the smectic-C_α^* phase (Fig. 3) may reflect the contributions of both the acoustic and optic branches of the amplitude and phase modes, as predicted by the OIZC model. As noted above, the wave vectors corresponding to minimum frequency for weakly coupled modes are unlocked; thus, we could have an acoustic mode centered at high q_z (corresponding to the points with $q_z>30\ \mu\text{m}^{-1}$ in Fig. 3) and an optic mode which would be detected at substantially lower q_z (incorporating the single point at $q_z=0$ in Fig. 3). More complete measurements in q_z are clearly needed to confirm this scenario, and would be an important test of the OIZC model for the smectic-C_α^* phase.

To conclude, we have detected three modes in the spectrum of light scattered from the director fluctuations in the Sm-C_α^* phase of MHPOBC. Although a complete assignment of these modes cannot be made at present, our results indicate that the smectic-C_α^* phase is characterized by a small equilibrium director tilt and a dispersion of the out-of-plane order parameter fluctuations which contains more than a single acousticlike branch. These results are consistent with predicted behavior in the case of weakly coupled ferro- and antiferroelectric order. An additional, very slow mode suggests the presence of a macroscopic modulated structure in the smectic-C_α^* phase.

This research was supported by the NSF's Advanced Liquid Crystalline Optical Materials Science and Technology Center, under Grant No. DMR-8920147. We thank S. Keast and M. Neubert for the synthesis of the MHPOBC.

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