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## Slow mode of the smectic-A–smectic- $C_{\alpha}^*$ phase transition

Abbas Rastegar and Theo Rasing

*Research Institute for Materials, University of Nijmegen, 6525 ED Nijmegen, The Netherlands*

Igor Muševič

*Jožef Stefan Institute, Jamova 39, 1111 Ljubljana, Slovenia*

Gerd Heppke

*Iwan-N-Stranski-Institute, Technische Universität Berlin, Sekr. ER 11, Str. des 17. Juni 135, D-10623 Berlin, Germany*

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Unusual slow fluctuations as revealed recently by dynamic light scattering close to the Sm-A–Sm- $C_{\alpha}^*$  phase transition in the antiferroelectric liquid crystal 4-(1-methylheptyloxy-carbonyl)phenyl 4'-octyloxy biphenyl-4-carboxylate can be explained by the electrostatic coupling between impurity ions and director fluctuations. Within the vicinity of Sm-A–Sm- $C_{\alpha}^*$  transition, the relaxation rate of the slow mode depends linearly on temperature, but with a different slope in each phase. The square root of its intensity shows a clear Curie-Weiss divergence at the phase transition, which is a direct confirmation of the electrostatic coupling mechanism. [S1063-651X(99)06511-3]

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The study of the phase transitions in chiral smectics is fascinating due to the interesting symmetry changes between their subphases [1–5]. Simply by changing the temperature one can observe in one and the same material all para, ferro, ferri, and antiferroelectric phases and the transitions between them. Among them is the Sm-A–Sm- $C_{\alpha}^*$  phase transition which can be observed in the antiferroelectric liquid crystal 4-(1-methylheptyloxy-carbonyl)phenyl 4'-octyloxy biphenyl-4-carboxylate (MHPOBC) [6]. It has been shown by independent NMR [7] and optical experiments [8,9] that the Sm- $C_{\alpha}^*$  phase is a tilted smectic phase. From the very small value of the optical rotation in this phase [8,9], it was conjectured and later proved [10] that Sm- $C_{\alpha}^*$  is in fact ferroelectric with a very short helical period. It shows anti-ferroelectric properties close to the Sm-A phase and changes to a ferrielectriclike structure on approaching the Sm- $C^*$  phase [11,12].

Isozaki *et al.* and Sun *et al.* [13,14] developed the discrete Landau model of the Sm- $C_{\alpha}^*$  phase, which was based on competing interactions between the nearest- and next-nearest layers. The dynamics of the Sm- $C_{\alpha}^*$  phase was then described by Čepič and Žekš [15] in a simple discrete phenomenological model in which the next-nearest-neighbor inter-layer interactions play an important role. In their model, the order-parameter fluctuation spectrum of the Sm-A phase consists of a single, doubly degenerate branch of excitations with two minima that appear close to the center and close to the boundary of the Brillouin zone, respectively. They also predicted that the Sm- $C_{\alpha}^*$  phase is a tilted, short period ferroelectric phase. The order-parameter fluctuations can therefore be decomposed into the fluctuations of the phase and the magnitude of the tilt angle which are called phase and amplitude modes, respectively.

In a recent work we have reported the first dynamic light-scattering measurements in the vicinity of the Sm-A–Sm- $C_{\alpha}^*$  phase transition [16]. In addition to the

phase and amplitude modes we have observed unusual and very slow fluctuations in both Sm-A and Sm- $C_{\alpha}^*$  phases. This slow mode with a relaxation rate of the order of 50–200 Hz was not predicted in the model of Čepič and Žekš and could not be attributed to pure director modes. On the other hand, such a slow mode was observed in the Sm- $C^*$  phase by Lu *et al.* [17]. They attributed this slow mode to the electrostatic coupling of the impurity ions with the electric polarization of the sample.

In this paper we present a simple model that explains the origin of the slow fluctuations by taking into account the coupling (via the Coulomb interaction) of the director with the fluctuations of the local concentration of ionic impurities. We use a simple perturbation approach to calculate first-order corrections to the relaxation rates and scattering intensities of the director modes. We find a linear temperature dependence for the modes and a Curie-Weiss divergence for the square root of the intensity. We show our dynamic light-scattering measurements to be in excellent agreement with these calculations.

Consider a Sm- $C_{\alpha}^*$  system with the smectic layers normal to the  $z$  axis and the average molecular direction  $\mathbf{n}(\mathbf{r})$  tilted by an angle  $\theta$  from the  $z$  axis and with ionic impurities that follow a Brownian motion. The projection of the director  $\xi$  on the smectic plane makes an angle  $\phi$  with respect to the  $x$  axis and can be considered as the order parameter to describe the Sm- $C_{\alpha}^*$  phase. We assume that the equilibrium concentration of the ionic impurities is  $c_i$  and the local concentration fluctuation is  $\delta c_i$ . The total free-energy density of the fluctuations in this system is

$$f(\mathbf{r}) = f_d(\mathbf{r}) + f_c(\mathbf{r}) + f_e(\mathbf{r}). \quad (1)$$

Here  $f_d$  is the contribution of the director fluctuations to the total free energy,  $f_c$  results from the ionic impurities, and  $f_e$  is the electrical contribution of the total charge density to the total free energy.

The director contribution to the free energy density is [15]

$$f_d = \sum_{j=\text{All layers}} \frac{1}{2} a (\delta\xi_x^{j2} + \delta\xi_y^{j2}) + \frac{1}{2} a_1 (\delta\xi_x^j \delta\xi_x^{j+1} + \delta\xi_y^j \delta\xi_y^{j+1}) + \frac{1}{8} a_2 (\delta\xi_x^j \delta\xi_x^{j+2} + \delta\xi_y^j \delta\xi_y^{j+2}) + \frac{1}{2} f (\delta\xi_x^{j+1} \delta\xi_y^j - \delta\xi_y^{j+1} \delta\xi_x^j). \quad (2)$$

Here  $\delta\xi_x^j$  and  $\delta\xi_y^j$  are the components of the order-parameter fluctuations in the  $j$ th layer and  $a = \alpha(T - T_c)$  with  $\alpha > 0$  and  $T_c$  the transition temperature.  $a_1$  and  $a_2$  are coefficients that represent the strength of the achiral bilinear interaction between nearest and the next-nearest neighbors, respectively. The last term describes the chiral interaction.

The free-energy density  $f_c$  of the impurity ions can be calculated from the chemical potential of the ionic impurities:

$$f_c(\mathbf{r}) = \frac{1}{2} k_B T \frac{[\delta c_i(\mathbf{r})]^2}{c_i}. \quad (3)$$

Here  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\delta c_i(\mathbf{r})$  is the fluctuation of the local impurity concentration  $c_i$ .

The electrical contribution to the free energy  $f_e$  originates from the electrostatic Coulomb interaction of both real charges  $\rho_i(\mathbf{r})$  (ionic impurities) and fluctuation-induced polarization charges  $\rho_p = -\nabla \cdot \mathbf{P}(\mathbf{r}, t)$  and is given by

$$f_e = \frac{1}{2} \rho(\mathbf{r}) V(\mathbf{r}). \quad (4)$$

Here,  $\rho(\mathbf{r}) = \rho_i(\mathbf{r}) + \rho_p(\mathbf{r}) = e \delta c_i(\mathbf{r}) - \nabla \cdot \mathbf{P}$ ,  $V(\mathbf{r})$  is the local electric potential that satisfies the Poisson equation

$$\sum_{\alpha, \beta} \delta_\alpha [\varepsilon_{\alpha\beta} \delta_\beta V(\mathbf{r})] = -\frac{\rho(\mathbf{r})}{\varepsilon_0}. \quad (5)$$

$\varepsilon_{\alpha, \beta}$  is the dielectric tensor for high frequencies and  $\varepsilon_0$  is the permittivity of free space. The spontaneous polarization is  $P(x, y) = -P_0 \xi_y(\mathbf{r}) \hat{x} + P_0 \xi_x(\mathbf{r}) \hat{y}$  and  $P_0$  is the magnitude of the spontaneous polarization in the Sm- $C_\alpha^*$  phase. Note that  $P_0$  is replaced by the fluctuation-induced polarization  $P_0 = C\varepsilon$  in the Sm-A phase.  $C$  is the flexoelectric coefficient and  $\varepsilon$  is dielectric constant of the Sm-A phase.

Due to the helical symmetry of the Sm- $C_\alpha^*$  phase it is more convenient to expand the fluctuations of the order parameter as helicoidal fluctuations with wave vector  $\mathbf{q} = (q_x, q_y, q_z)$

$$\delta\xi_x^j(\mathbf{r}) = \sum_q \delta\xi_{q,x} e^{iq_z j d} e^{iq_x x} e^{iq_y y}, \quad (6)$$

$$\delta\xi_y^j(\mathbf{r}) = \sum_q \delta\xi_{q,y} e^{iq_z j d} e^{iq_x x} e^{iq_y y}.$$

Here  $d$  is the layer thickness. The total free energy of the fluctuations  $F = \int f(\mathbf{r}) d^3 \mathbf{r}$  with a wave vector  $\mathbf{q}$  is then given by  $F(\mathbf{q}) = F_d(\mathbf{q}) + F_c(\mathbf{q}) + F_e(\mathbf{q})$  and can be represented as

$$F(\mathbf{q}) = \frac{1}{2} \sum_q \delta\xi_{-q} \underline{D}(\mathbf{q}) \delta\xi_q, \quad (7)$$

where  $\delta\xi_q = [\delta\xi_{q,x}, \delta\xi_{q,y}, \delta c_i(q)]$  and  $F_c(q)$  and  $F_e(q)$  are the corresponding Fourier transforms. The dynamical matrix  $\underline{D}(\mathbf{q})$  is

$$\underline{D}(\mathbf{q}) = \begin{bmatrix} A & -B & iD \\ -B^* & A' & -iD' \\ -iD & iD' & E \end{bmatrix} \quad (8)$$

with the elements

$$A = a + a_1 e^{iq_z d} + \frac{a_2}{4} e^{i2q_z d} + \frac{P_0^2}{2\varepsilon\varepsilon_0} \frac{q_y^2}{q^2},$$

$$A' = a + a_1 e^{iq_z d} + \frac{a_2}{4} e^{i2q_z d} + \frac{P_0^2}{2\varepsilon\varepsilon_0} \frac{q_x^2}{q^2}, \quad (9a)$$

$$D = \frac{e_i P_0}{2\varepsilon\varepsilon_0} \frac{q_y}{q^2}, \quad D' = \frac{e_i P_0}{2\varepsilon\varepsilon_0} \frac{q_x}{q^2}, \quad (9b)$$

$$B = \frac{P_0^2}{2\varepsilon\varepsilon_0} \frac{q_x q_y}{q^2} + i2f \sin(q_z d), \quad E = \frac{1}{2} \frac{k_B T}{c_i} + \frac{e_i^2}{2\varepsilon\varepsilon_0 q^2}. \quad (10)$$

We use the Landau-Khalatnikov equations for director fluctuations to study the dynamics of the system

$$\frac{\partial \bar{F}_d(q)}{\partial \delta\xi_{-q}} = -\gamma \frac{\partial \delta\xi_q}{\partial t}, \quad (11)$$

where  $\gamma$  is the rotational viscosity and  $\bar{F}_d$  is the contribution of the director fluctuations to the dynamical tensor. For the dynamics of the ionic impurities we use the continuity equation

$$\frac{\partial \delta c_i(q)}{\partial t} = -\nabla \cdot \mathbf{J}_i = -\nabla \cdot \left[ m_i c_i \nabla \left( \frac{\partial F(q)}{\partial \delta c_i(-q)} \right) \right], \quad (12)$$

which can be rewritten in the form of a generalized diffusion equation for charge:

$$\frac{\partial \bar{F}_c(q)}{\partial \delta c_i(-q)} = -\gamma' \frac{\partial \delta c_i(q)}{\partial t}, \quad \gamma' = \frac{1}{m_i c_i q^2}. \quad (13)$$

Here  $\bar{F}_c$  is the contribution of the ionic impurities to the free energy. Note that the  $m_i$  of the impurity mobility is connected to the ionic mobility  $\mu_i$  in an external electric field by the equation  $\mu_i = e_i m_i$  where  $e_i$  is the electric charge of an ion.

After considering the time dependence of the fluctuations as  $\delta\xi_q = \delta\xi_{q,0} \exp[-t/\tau(q)]$ , the dynamics of the system reduces to a set of coupled linear equations. These have non-trivial solutions if the corresponding determinant vanishes:

$$\begin{vmatrix} A - \frac{\gamma}{\tau(q)} & -B & iD \\ -B^* & A' - \frac{\gamma}{\tau(q)} & -iD' \\ -iD & iD' & E - \frac{\gamma'}{\tau(q)} \end{vmatrix} = 0. \quad (14)$$

For a given wave vector we obtain three relaxation rates, which represent three branches of the excitation spectrum. In the absence of coupling ( $D=D'=0$ ), the determinant [Eq. (14)] gives us two director (phase and amplitude) modes and a single diffusion mode of the ionic impurities:

$$\begin{aligned} \frac{1}{\tau_{\text{am}}} &= \frac{1}{2\gamma} \left( a + a_1 e^{iq_z d} + \frac{a_2}{4} e^{i2q_z d} + 2f \sin(q_z d) \right), \\ \frac{1}{\tau_{\text{ph}}} &= \frac{1}{2\gamma} \left( a + a_1 e^{iq_z d} + \frac{a_2}{4} e^{i2q_z d} - 2f \sin(q_z d) \right), \\ \frac{1}{\tau_{\text{ion}}} &= \frac{1}{2} m_i k_B T q^2 + \frac{e_i^2 m_i c_i}{2\epsilon \epsilon_0}. \end{aligned} \quad (15)$$

The intensities of these modes can be calculated from the equipartition theorem. This gives a Curie-Weiss law for the intensity of the soft (and amplitudon) mode and a slight temperature dependence of the amplitude of the fluctuations of the impurity concentration. It is important to note that in this limit of uncoupled modes, we can observe only the two director modes in a light-scattering experiment because the ionic modes cause no fluctuations of the direction of the optical axis.

The situation is completely different when we include an electrostatic interaction. This has two consequences: (i) the eigenfrequencies are renormalized due to the coupling and (ii), the director and ionic modes become mixed such that the latter become visible in light-scattering experiments.

The general problem of diagonalizing the dynamical matrix is rather cumbersome. We have chosen a perturbation approach because there is a large difference in the relaxation rates: around 1 MHz for the relaxation rates of the soft mode and around 100 Hz for the ionic mode. Furthermore, one can choose the scattering geometry such that only fluctuations in the direction of  $q_x$  can be observed. Therefore, we can safely let  $q_y = q_z = 0$  (and therefore  $B=D=0$ ) without losing the generality of the problem. Equation (14) then reduces to

$$\left( A - \frac{\gamma}{\tau(q)} \right) \left[ D'^2 - \left( A' - \frac{\gamma}{\tau(q)} \right) \left( E - \frac{\gamma'}{\tau(q)} \right) \right] = 0. \quad (16)$$

Now  $D'$  is the only coupling coefficient which we assume to be small enough that it can be considered as a perturbation. The unperturbed solutions ( $D'=0$ ) are given by

$$\frac{1}{\tau_{\text{am}}^0} = \frac{A}{\gamma}, \quad \frac{1}{\tau_{\text{ph}}^0} = \frac{A'}{\gamma}, \quad \frac{1}{\tau_{\text{ion}}^0} = \frac{E}{\gamma'}. \quad (17)$$

To obtain the slow fluctuations we insert the unperturbed solutions for the director modes into the dynamical equation above [Eq. (16)]. After taking into account  $(A/\gamma) \gg (E/\gamma')$

[see Eqs. (9), (10), (14)], we find the perturbed relaxation rate of the ionic impurity mode:

$$\frac{1}{\tau_{\text{ion}}} = \frac{1}{2} \frac{k_B T \mu_i q_x^2}{e_i} + \frac{e_i \mu_i c_i}{2\epsilon \epsilon_0} - \frac{e_i P_0^2 \mu_i c_i}{4\epsilon^2 \epsilon_0^2 \gamma} \tau_{\text{am}}^0. \quad (18)$$

The dispersion relation for the ionic diffusion shows a finite gap in the limit of small wave vectors, which is characteristic for the Coulomb interaction. The third term in the right-hand side of Eq. (18) gives the correction due to the electrostatic coupling to the director fluctuations. This term is most significant for wave vectors that are parallel to the smectic planes and is proportional to the relaxation time of the fast director modes. A similar correction, only with an opposite sign, can be obtained for the fast director modes. Note that as soon as the polarization disappears (i.e.,  $P_0=0$ ) the ionic impurity mode is decoupled and unobservable. Note also that for paraelectric systems, like the Sm-A phase, this term is replaced by  $P_0=C\epsilon$ , reflecting the polarizability of this phase.

We have performed the perturbation analysis of the eigenvectors of the fluctuations in a similar way. After a straightforward calculation, we obtain the first-order correction  $\delta\xi_y^{(1)}$  to the amplitudes of the coupled director-ionic fluctuations:

$$\delta\xi_y^{(1)} \approx \frac{D'}{A(T)} |\delta c_i^{(0)}| \approx \frac{1}{\alpha(T-T_c)} |\delta c_i^{(0)}|. \quad (19)$$

Note that now the Curie-Weiss law for the soft director modes is also reflected in the amplitude of the slow ionic mode. This can be easily understood by remembering that the dielectric susceptibility of the system increases close to the Sm-A–Sm- $C_\alpha^*$  transition. This results in an increased intensity of the slow ionic mode. One should also note that the intensity of light scattered by this mode [ $I \approx (\delta\xi)^2$ ] is proportional to the inverse square of  $(T-T_c)$ .

In our experiments we used 50  $\mu\text{m}$  thick homeotropic cells filled with the antiferroelectric liquid crystal MHPOBC. Experiments in MHP8CBC showed similar results. A good homeotropic alignment was achieved using silane surfactants and was checked by a polarization microscope. The dynamic light-scattering experiments were performed by measuring the heterodyne autocorrelation functions of the intensity of the scattered light with a multi-tau ALV-5000E autocorrelator. We used a doubled-YAG ( $\lambda=532\text{ nm}$ ) laser to expand the experimental range to large scattering wave vectors. The scattering geometry was chosen such that the scattering wave vector remained either close to the plane of the smectic layers ( $q\parallel q_x$ ) or close to the normal to the smectic layers ( $q\parallel q_z$ ), depending on the required measurements. Ordinary polarized light ( $S$  polarized) was incident on the sample and extraordinary light ( $P$  polarized) was detected. The temperature was controlled with a resolution of 5 mK throughout the experiments. The measured autocorrelation functions of the scattered light intensity were in the heterodyne regime and were then fitted to exponential decay functions. The fit parameters give the amplitude and relaxation rate of the fluctuations in these phases.

Figure 1 shows the critical temperature dependence of the relaxation rate of the soft and slow modes in the Sm-A phase of MHPOBC over a wide temperature range. The slope of

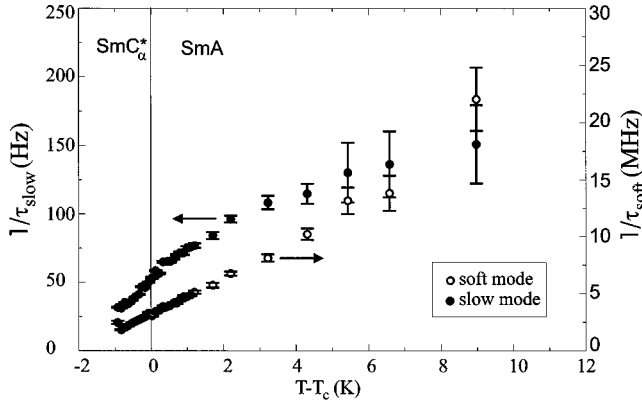


FIG. 1. Temperature dependence of the relaxation rate of the soft mode (open circles) and slow mode (solid circles) in the Sm-A and Sm- $C_{\alpha}^*$  phases of MHPOBC.  $T_c = 396.5$  K.

the temperature dependence of the soft mode is 1.6 MHz/K, which is a characteristic value for the soft mode in most ferroelectric liquid crystals like DOBAMBC and CE-8. At  $T_c = 396.5$  K, the relaxation rate of the soft mode is close to 3 MHz, which is a clear indication that the experiment was performed at a noncritical wave vector. It is known that for a chiral (helical) system, the relaxation rate of the soft mode at  $T_c$  and at a small wave vector is proportional to  $\tau_{\text{soft}}^{-1}(T_c, q \approx 0) \approx (K_3/\gamma)q_c^2$ . Here,  $K_3$  is the torsional elastic constant and  $q_c = 2\pi/p_c$  is the wave vector of the helix. By taking a typical value for  $K_3/\gamma \approx 3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , we obtain an approximate value for the helical period in the Sm- $C_{\alpha}^*$  phase  $p_c \approx 60$  nm, which is indeed a very short helix. The temperature dependence of the relaxation rate of the slow mode far above the transition tends to a saturated value of  $\approx 200$  Hz, whereas it nearly critically slows down at the transition. Figure 2 shows the temperature dependence of the relaxation

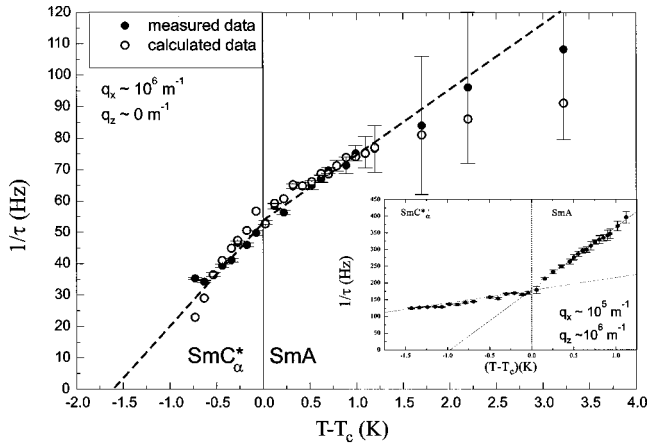


FIG. 2. Temperature dependence of the relaxation rate of the slow ionic mode near the Sm-A and Sm- $C_{\alpha}^*$  transition. Note the change of the two slopes (dashed lines), which is due to the emergence of spontaneous polarization. Open circles show the calculated relaxation rates of the slow mode using Eq. (20) with parameters  $C_1 = 0.54 \text{ s}^{-1} \text{ K}^{-1}$ ,  $C_2 = 45 \text{ s}^{-1}$ ,  $C_3 = 1.8 \times 10^8 \text{ s}^{-2}$ ,  $q_x \sim 10^6 \text{ m}^{-1}$ ,  $q_z \sim 0 \text{ m}^{-1}$ ,  $T_c = 396.5$  K, and  $\tau_{\text{Am}}^0(T)$  as determined from the experiment. Dashed lines are guides to the eye. The inset shows the experimental result at  $q_x \sim 10^5 \text{ m}^{-1}$ ,  $q_z \sim 10^6 \text{ m}^{-1}$  displaying a very sharp kink at  $T_c$ .

rate of the slow mode close to the Sm-A–Sm- $C_{\alpha}^*$  phase transition. It can be seen that the relaxation rate of the slow mode has a nearly linear temperature dependence both in the Sm-A phase and Sm- $C_{\alpha}^*$  phase. This is a unique characteristic of these slow fluctuations and can be used to determine the Sm-A–Sm- $C_{\alpha}^*$  phase transition temperature rather precisely, as illustrated even more clearly in the inset of Fig. 2. The open dots in Fig. 2 show the calculated relaxation rate of the slow mode using the following function:

$$\frac{1}{\tau} = C_1 T + C_2 - C_3 \tau_{\text{Am}}^0(T). \quad (20)$$

Here  $\tau_{\text{Am}}^0(T)$  is the measured soft mode relaxation time from Fig. 1 and  $C_1$ ,  $C_2$ , and  $C_3$  are parameters given by [see Eq. (18)]

$$\begin{aligned} C_1 &= \frac{1}{2} \frac{k_B \mu_i}{e_i} q^2, \\ C_2 &= \frac{e_i \mu_i c_i}{2 \varepsilon \varepsilon_0}, \\ C_3 &= \frac{e_i \mu_i c_i P_0^2}{4 \varepsilon^2 \varepsilon_0^2 \gamma}. \end{aligned} \quad (21)$$

One can see that the calculated relaxation times describe the decreasing of the slow relaxation rate with decreasing temperature quite well. Knowing the scattering wave vector  $q$ , we can calculate the mobility of the impurity ions from  $C_1 = 0.54 \text{ s}^{-1} \text{ K}^{-1}$ . If we assume that the ions possess a single elementary charge, the calculated electric mobility is  $\mu_i = 8.5 \times 10^{-1} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This is in excellent agreement with typical ionic mobilities reported by other authors [18]. Further, we can use this mobility to obtain an estimate of the ionic concentration of  $7 \times 10^{26}$  ions/m<sup>3</sup> from  $C_2 = 45 \text{ s}^{-1}$ . This roughly corresponds to one ion per  $10^7$  liquid crystal molecules, and is of reasonable magnitude. We also calculated the contribution of the first two terms in Eq. (18) for high temperatures. This gives a relaxation rate of 250 Hz, which is very close to the observed high-temperature limit of the slow relaxation rate, shown in Fig. 1. As predicted by theory [Eq. (18)], the third (correction) term vanishes in the high-temperature limit, because the relaxation time of the fast director fluctuations becomes very small.

As a second independent way of checking whether the slow mode indeed originates from the coupling between the ionic and director modes, we analyzed the measured temperature dependence of the intensity of light, scattered by the slow fluctuations. The theory predicts [Eq. (19)] that the *inverse square root* of the measured scattering intensity is proportional to  $(T - T_c)$ . This is in contrast to the director soft modes in ferroelectric liquid crystal, where the *inverse of the scattering intensity* is proportional to  $(T - T_c)$ . The results are shown in Fig. 3 and are in excellent agreement with the predicted inverse square root dependence. This clearly confirms the origin of the slow fluctuations in the vicinity of the Sm-A–Sm- $C_{\alpha}^*$ : the slow mode arises due to the electrostatic coupling of Brownian ionic motion with the collective excitations of the Sm- $C_{\alpha}^*$  order parameter.

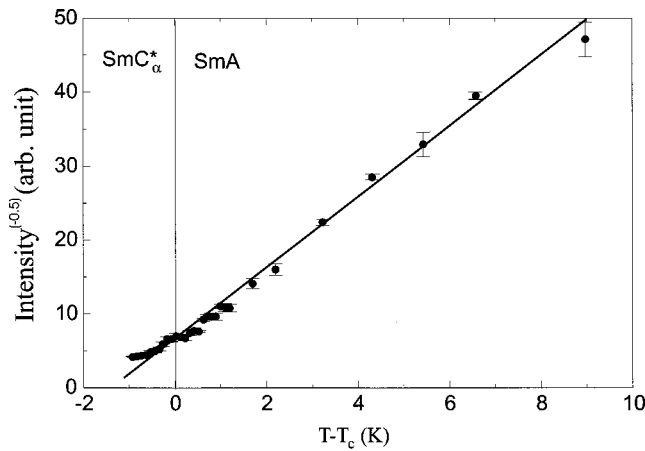


FIG. 3. The inverse square root of the intensity of the slow ionic mode as a function of temperature, showing nearly perfect Curie-Weiss law behavior.  $T_c = 396.5$  K.

In conclusion, we have observed slow fluctuations close to the Sm-A–Sm- $C_\alpha^*$  phase transition in MHPOBC. This mode represents ionic motion, coupled to the polarization field and is similar to the ionic modes observed in ferroelectric Sm- $C^*$  phases by Lu *et al.* [17]. By considering Brownian motion of ionic impurities which are present in this system, we have developed a theoretical description based on

the discrete model of the Sm-A–Sm- $C_\alpha^*$  phase transition [15], taking into account the electrostatic interaction between charges induced by fluctuations of the electric polarization and the impurity ions. These polarization charges originate either from flexoelectric effects in the Sm-A phase or from ferroelectricity in the Sm- $C_\alpha^*$  phase and are significant in materials with a high spontaneous polarization and a high dielectric susceptibility. These theoretical calculations are confirmed by our dynamic light-scattering measurements.

Due to the coupling to the soft director modes, the relaxation rate of the slow ionic mode is linearly temperature dependent in the vicinity of the Sm-A–Sm- $C_\alpha^*$  phase transition in both Sm-A and Sm- $C_\alpha^*$  phases. We have calculated the average mobility of the impurity ions in this system and our results are in good agreement with other experiments. As a final proof, we have presented the nearly Curie-Weiss behavior of the measured intensity of light, scattered by slow ionic modes. This behavior is typical for a noncritical mode, which is linearly coupled with a critical soft mode of the transition and fully supports our theoretical considerations.

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