A dielectric mode in electroclinic liquid crystals

A. K. Thakur, A. Choudhary, S. Kaur, S. S. Bawa, and A. M. Biradar[a)]
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India

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The dielectric properties of electroclinic and ferroelectric liquid crystal materials have been investigated in the frequency range of 100 Hz–10 MHz. A dielectric mode has been predicted in electroclinic liquid crystals near the transition temperature of Sm-C*–Sm-A phase. It has been observed that the investigated material has nonlayer shrinkage near the transition temperature of Sm-C*–Sm-A phase and shows anomalous behavior of dielectric spectra, tilt, and texture which is entirely different from the behavior of ferroelectric liquid crystals (FLCs). The dielectric relaxation frequency and tilt angle are almost constant with respect to temperature near the transition temperature under high bias field, which is characteristically different from FLCs. The high dielectric permittivity near T_c owing to the presence of mode contribution leads to the fact that there is an intralayer phason variation few degrees before transition. The mode has been named *random mode* due to its origin from randomization of tilt near T_c. Tilt randomization has been considered as an order parameter because in both the phases molecules are tilted but it is disordered in Sm-A phase making its intralayer polarization zero. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Since the discovery of electroclinic effect in ferroelectric liquid crystals (FLCs), efforts are underway to understand its properties near the transition temperature as well as its high potentiality in fascinating applications to optical signal processing and computing due to its fast electro-optical response in nanosecond range. This electroclinic effect is characterized by a coefficient $C_E = d\theta/dE$, called the electroclinic coefficient. Initially, the electroclinic effect was thought and observed on the basis of symmetry arguments by Garoff and Meyer.[1,2] It was predicted by Garoff and Meyer that the application of electric field parallel to the smectic layers in Sm-A phase biases the free rotation of the molecules and therefore produces a nonzero average of the transverse component of the molecular polarization and thus the electroclinic effect.

At the transition temperature the smectic layer structure undergoes folding into chevron structure due to layer stress, which degrades the contrast of the sample in the Sm-C* phase.[3] Later on it was found that the electroclinic effect could also be possible in tilted Sm-A phase in which although the molecules are tilted in Sm-A phase but the individual layer polarization is zero due to randomization of tilt in each layer.[4–8] These are the de Vries liquid crystals reported by Diele *et al.*,[9] and later explained by de Vries in 1974.[10] Diele *et al.* had obtained layer spacing, which was temperature independent for a number of compounds but at that time people failed to consider the wider implications of his findings. But as work was done, it was found that, in fact, it was the bending of the smectic layers at the transition which involve the zigzag defects at the domain boundaries. It is these zigzag defects which hinder the making of FLC displays with the best contrast. Since the last few years of 20th century much of the researchers thus have been working on these nonlayer shrinkage materials. One of the most appropriate and accepted explanation that is currently being exploited and applied in FLC samples was presented by the crystallographer de Vries.

Acccording to de Vries,[11] the average direction of long axis is perpendicular to the smectic planes, but the long axis of individual molecules makes large angles with the plane normal in random directions. So, we can say the material has a different type of Sm-A phase, where the molecules are tilted similar to those in Sm-C* phase. The tilted Sm-C* like smectic layers of Sm-A are stacked randomly, i.e., the molecules are tilted with respect to the smectic layer normal, similar to those in the Sm-C* phase but the tilt direction in different smectic layers are randomly oriented. In such materials tilt is not accompanied by layer stress,[3,12] due to which the value of electroclinic coefficient is more. In general, electroclinic effect is observed in both orthogonal as well as tilted Sm-A phase but there is an inherent characteristic difference between these two cases. In the former, the molecular symmetry as well as layer symmetry is D_∞ in Sm-A phase;[1,2] and in the latter though the individual molecular symmetry is C_2 yet the local layer symmetry is D_∞.[8,13] The only reason behind this is tilt randomization. Panarin *et al.* had also reported observation of a possible random mode in antiferroelectric liquid crystals.[14]

In this paper, we report the origin of a dielectric mode near the Sm-C*–Sm-A (tilted) phase in electroclinic liquid crystals (ELCs), which are the nonlayer shrinkage materials (more commonly called de Vries materials). The minimum tilt fluctuation near the transition, account for the nonappearance of soft mode in the studied material and the appearance of a random mode near T_c. It is the randomization of tilt in

a)Electronic mail: abiradar@mail.nplindia.ernet.in

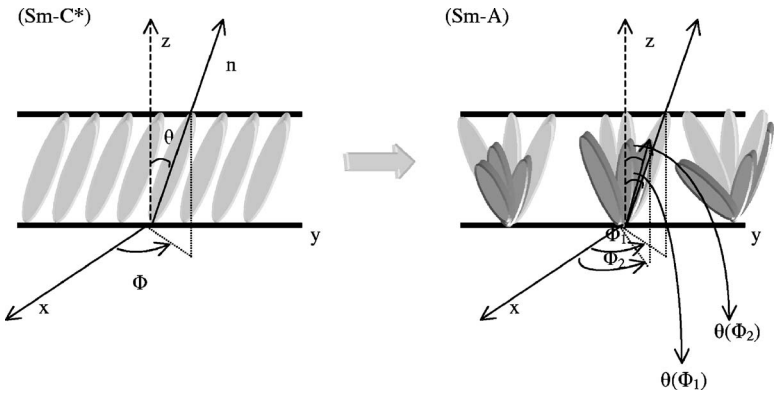

FIG. 1. Randomization in the Sm-A phase (right) distinguishes it from the constant tilt (with constant Φ) in the Sm-C phase. The variation in Φ makes the tilt in all directions.

Sm-A phase and even in Sm-C* phase near the transition temperature that explains the anomalous behavior of tilt and dielectric process in the material under investigation. Though it is an old material and lot of dielectric and x-ray data have been taken but no detailed studies have been done on the typical behavior of soft mode near and below the transition temperature, the high dielectric strength near the transition and constant tilt behavior in the vicinity of the transition temperature. It has also been qualitatively analyzed that tilt is not an order parameter in Sm-C*–Sm-A (tilted) phase transition. Moreover, the appearance of soft mode in such electroclinic liquid crystals has not been observed before the transition temperature in Sm-C* phase. Here an attempt has been made and presented to understand the dielectric modes near the transition temperature in de Vries material and its comparison with the conventional FLCs.

II. EXPERIMENT

Highly conducting ITO coated glass plates with a flatness of $\lambda/2$ have been used as electrodes. Both the electrodes of the cell were treated with adhesion promoter and nylon (6/6) and rubbed unidirectionally on both surfaces to get homogeneous alignment.[15] Thickness of the cells was maintained by means of photolithographic technique. The cells were calibrated using air and toluene as standard references. The phase sequence of electroclinic material 764*E* (BDH, England) is

$$\text{Cryst.} \overset{?}{\leftrightarrow} \text{Sm-C}^* \overset{28\ ^\circ\text{C}}{\leftrightarrow} \text{Sm-A} \overset{73\ ^\circ\text{C}}{\leftrightarrow} \text{N} \overset{89\text{–}92\ ^\circ\text{C}}{\leftrightarrow} \text{Iso.}$$

The phase sequence of the general FLC material CS-1026 (Chisso Corp., Japan) is

$$\text{Cryst.} \overset{-7\ ^\circ\text{C}}{\leftrightarrow} \text{Sm-C}^* \overset{64\ ^\circ\text{C}}{\leftrightarrow} \text{Sm-A} \overset{82\ ^\circ\text{C}}{\leftrightarrow} \text{N} \overset{91\ ^\circ\text{C}}{\leftrightarrow} \text{Iso.}$$

Samples of varying thickness (as thin as 2 μm to as thick as 20 μm) in the case of BDH-764E and (2–12 μm) in the case of CS-1026 were prepared. The present dielectric data is of 20 and 12 μm sample cells for BDH-764E and CS-1026, respectively. But the data reported here is independent of the thickness of the sample cells in both the cases. The filling was done through capillary action.

The dielectric measurements were carried out in an electrically shielded parallel plate condenser,[15] using HP 4192A impedance analyzer in the frequency range of 100 Hz–10 MHz. From the dielectric data Cole-Cole plots (ε', ε'') have been plotted for all temperatures with and without bias and the dielectric strength $\Delta\varepsilon$ (ε_0-ε_∞) has been calculated. The dielectric measurements were computer controlled and automated. The temperature stability was maintained at ±0.1 °C by INSTEC STC 200 temperature controller.

The optical tilt measurement was carried out using Carl-Zeiss polarizing microscope (Axioskop 40) and Linkam THMS 600 temperature controller. The homogeneously aligned cells maintained at the desired temperature were mounted on the polarizing microscope with crossed polarizers. A field high enough to unwind the helix is applied to the sample so that molecules in the whole sample are aligned uniformly with a tilt θ away from the layer normal. The sample is rotated on a microscope table to get minima in optical transmission. When the field is reversed the molecules rotate along the tilt cone so that the final tilt becomes $-\theta$ from the layer normal. Once again the microscope table is rotated to achieve the minimum transmission. The angle by which the microscope table was rotated from one minimum position to other minimum will be twice the tilt angle (2θ). The texture (500 times magnified) of the material BDH-764E too has been taken under the above-mentioned microscope and temperature controller.

III. RESULTS AND DISCUSSIONS

A. Tilt and textural study of electroclinic and ferroelectric liquid crystals

It is well established that electroclinic effect is present even in Sm-C* phase near the transition temperature which gives rise to soft mode (or amplitude mode) in the case of conventional Sm-C*–Sm-A (orthogonal) phase transition. It is also well known that electroclinic effect could be achieved by two different physical phenomenon, one which is based on symmetry arguments as predicted by Meyer,[1,2,16–18] near the Sm-C*–Sm-A (orthogonal) phase transition temperature. The second is based on changing the randomized tilt direction into ordered tilt, which is usually observed in chiral tilted Sm-A phase (de Vries materials) without changing the magnitude of tilt. In the latter case the magnitude of electroclinic coefficient is more because the tilt does not have to

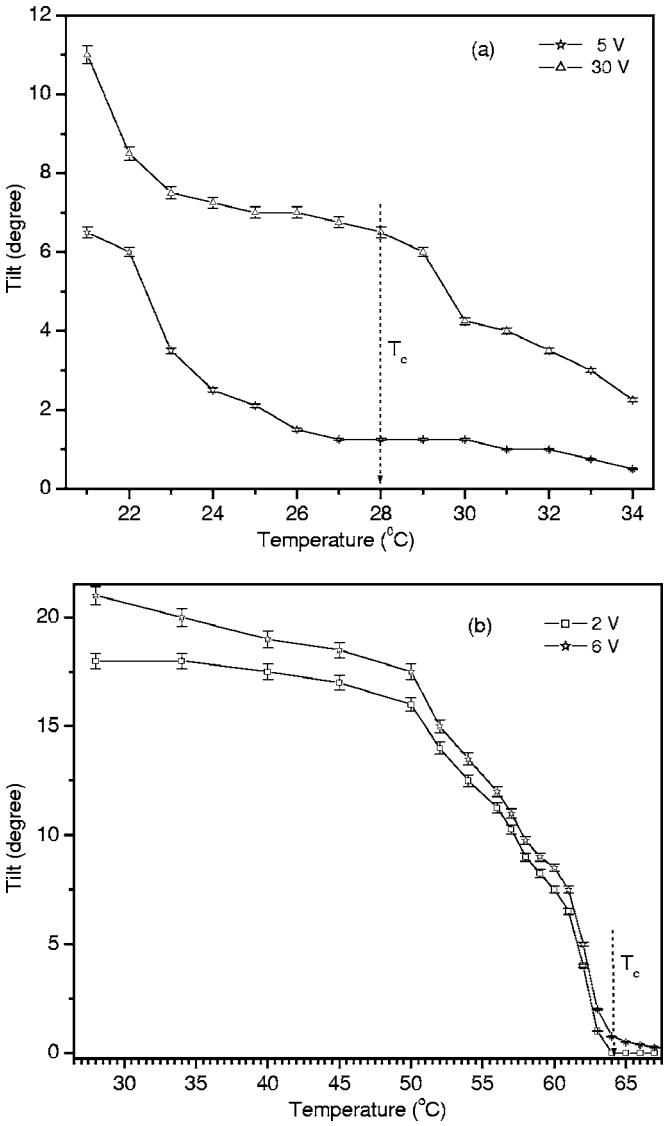

FIG. 2. (a) Temperature dependence of optical tilt (θ) at 5 and 30 V bias in Sm-C* and Sm-A phases near the transition temperature in ELC material BDH-764E of sample thickness 4 μm. (b) Temperature dependence of optical tilt (θ) at 2 and 6 V bias in Sm-C* and Sm-A phases near the transition temperature in FLC material CS-1026 of sample thickness 12 μm.

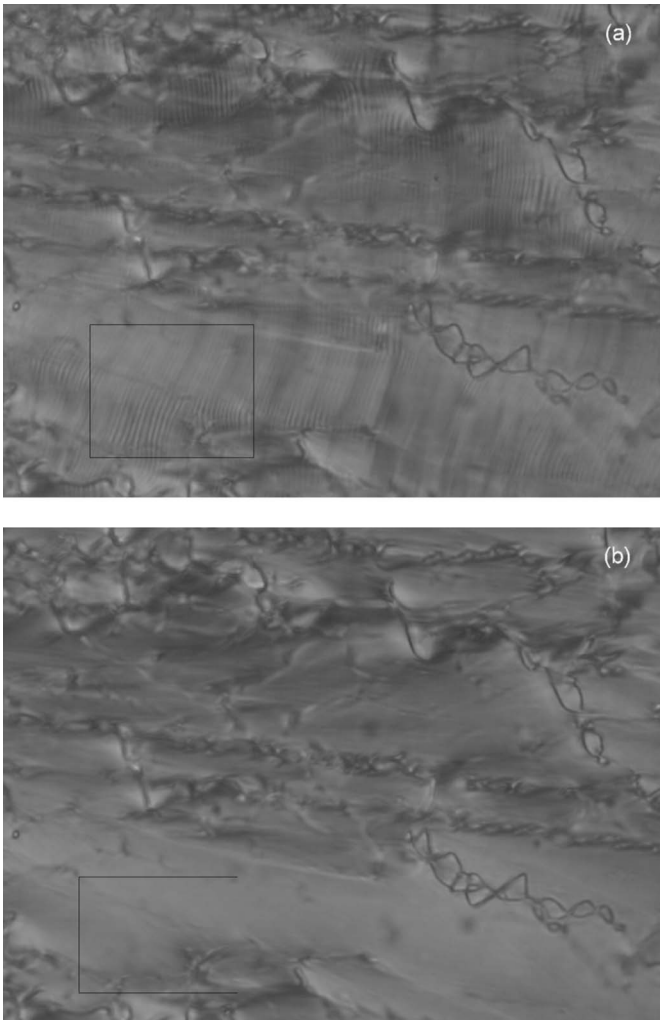

FIG. 3. Optical micrograph of ELC sample cells of 20 μm thickness at different temperatures of (a) 27 and (b) 29 °C. Dechiralization lines are visible at 27 °C (square marked) showing that the phase is Sm-C* but after T_c no lines are seen at 29 °C suggesting that change from Sm-C* to Sm-A phase has taken place.

resist layer compression.[3,8] These de Vries ELCs do not possess a long-range order of the direction of tilt. In the Sm-A phase, i.e., above the critical temperature T_c the molecular tilting direction is disordered with an azimuthal angle varying from 0 to 2π on the de Vries cone. Figure 1 clearly shows the de Vries Sm-A and Sm-C* phases.

Figure 2(a) shows the tilt behavior of an electroclinic liquid crystal under 5 and 30 V bias fields where one can clearly observe the almost constant tilt under high bias field of 30 V near the transition temperature. But in Fig. 2(b) no such behavior has been seen in FLCs at 6 V and it has also been checked that even increasing the bias voltage more than the threshold limit (6 V) the value of optical tilt does not change.[19] Now the basic question that arises is what type of material are we dealing with? It is established that there is a change in layer spacing as well as optical tilt during the transition from Sm-C* to Sm-A (orthogonal) phase in FLC materials but in the present study it remains almost constant in Sm-C* to Sm-A (tilted) phase [Fig. 2(a)]. The only difference as far as tilt is concerned in the case of chiral tilted Sm-A phase and Sm-C* phase is that in the former tilt is randomized within the layer but in the latter tilt is ordered near the transition temperature. The high bias voltage removes the intralayer randomization and the optical tilt remains constant near the transition temperature as seen in Fig. 2(a) for 30 V curve. Figures 2(a) and 2(b) clearly show the difference between the optical tilt in electroclinic and ferroelectric liquid crystals, respectively. In the case of de Vries electroclinic liquid crystals the optical tilt goes on increasing with respect to the bias voltage even before the transition temperature until it attains some constant value at a particular bias value as could be seen in Fig. 2(a). The abovementioned behavior of optical tilt under bias field is analogous to constant layer spacing in case of Sm-C*–Sm-A (tilted) transition.[4] The nature of transition has also been observed by texture which shows BDH-764E is having tilted Sm-A phase and CS-1026 is of orthogonal Sm-A phase. Figures 3(a) and 3(b) show the texture of BDH-764E 1 °C before and after the transition, respectively. The unchanging

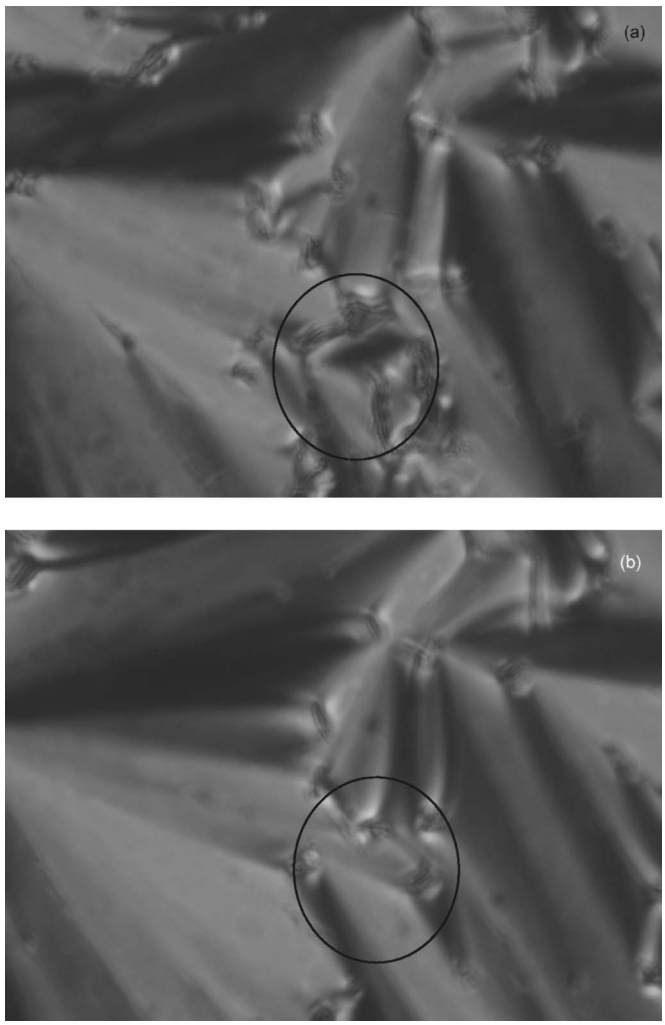

FIG. 4. Optical micrograph of FLC sample cells of 12 μm thickness at different temperatures of (a) 63 and (b) 65 °C. The encircled portion shows the change in the texture after the Sm-C*–SmA transition.

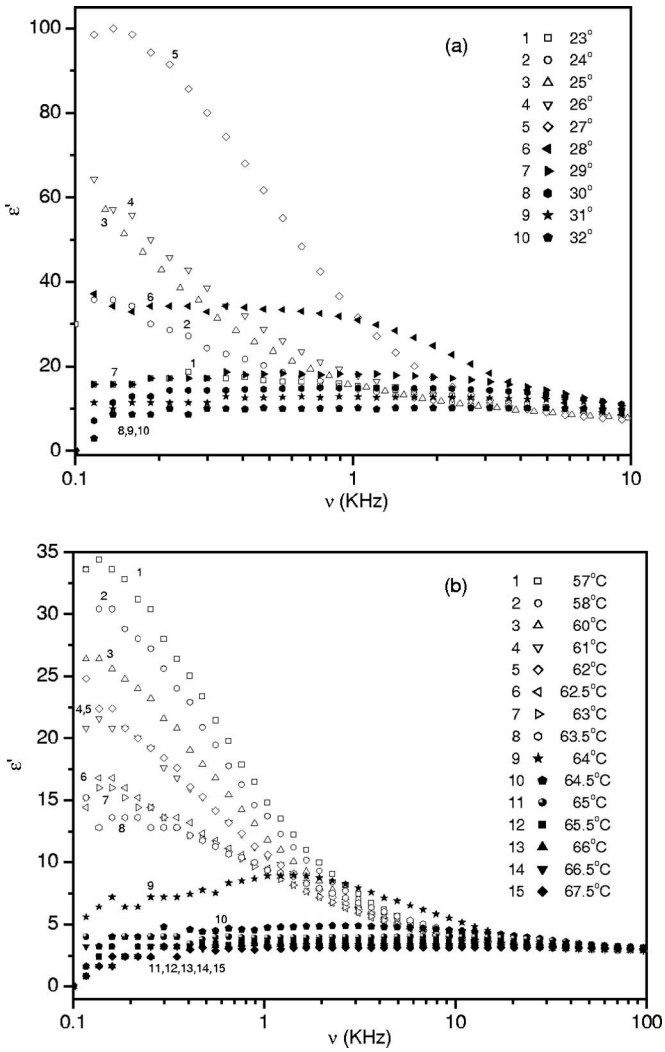

FIG. 5. (a) Dielectric dispersion as a function of frequency at different temperatures at 0 V bias in ELC sample of 20 μm thickness. Filled symbols have been used after T_c to distinguish the data before and after transition temperature. (b) Dielectric dispersion as a function of frequency at different temperatures at 0 V bias in FLC sample of 12 μm thickness. Filled symbols have been used after T_c to distinguish the data before and after transition temperature.

texture in BDH-764E both below and above the transition draws our attention to the same tilt exhibited in both the phases near T_c as shown in Fig. 2(a); which is the characteristic of nonlayer shrinkage (NLS) material. On the other hand, the texture of CS-1026 changes appreciably at the transition temperature (64 °C). The sharpness of texture appears suddenly at the transition temperature as depicted in Figs. 4(a) and 4(b) at 63 and 65 °C, respectively. This quick change at T_c can very well correlate the tilt behavior shown in Fig. 2(b), which comes to zero at T_c. In other words we can say that the tilt measurement and textural studies establish that the studied materials are of different geometry: one is de Vries and the other is the conventional FLC. The detailed studies of the texture of the de Vries material (BDH-764E) have already been carried out by us and would be published elsewhere. Moreover, texture studies in our case are similar to the texture in other materials exhibiting de Vries structure.[4]

B. Comparison of anomalous dielectric spectra of de Vries material with that of conventional FLCs

After confirming the nature of studied BDH 764 E and CS-1026 materials by tilt and texture observation, which shows one to be a de Vries type of ELC material and the other the conventional FLC, the dielectric spectra of these materials, has been taken which is shown in Fig. 5. Here the measuring electric field is perpendicular to the director. The director relaxation can be described in terms of the complex dielectric permittivity, which is given as

$$\varepsilon^*(\omega,T) = \varepsilon'(\omega,T) - i\varepsilon''(\omega,T), \tag{1}$$

where ε' denotes the real part of the complex dielectric permittivity and its spectrum is called dispersion curve, ε'' is the imaginary part and its spectrum is called the absorption (dielectric loss) curve, and ω is the angular frequency of applied electric field.

In order to characterize the temperature dependence of the observed dielectric relaxations, $\varepsilon^*(\omega)$ can be described by the Debye formula as follows:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)/(1 + \omega^2\tau^2) \quad (2)$$

and

$$\varepsilon''(\omega) = (\varepsilon_o - \varepsilon_\infty)\omega\tau/(1 + \omega^2\tau^2), \quad (3)$$

where ε_0 is the static dielectric permittivity, ε_∞ is the high frequency limit of dielectric permittivity, and τ is the relaxation time.

The generalization of Debye formulation describes a dielectric process with discrete distribution of relaxation time associated with a single dielectric process. Figures 5(a) and 5(b) show the dielectric dispersion curves at different temperatures in both ELCs and FLCs, respectively. In Fig. 5(a) it is observed that dielectric permittivity rises near the transition temperature in Sm-C* phase even at 0 V bias in ELCs whereas in FLCs the dielectric permittivity under 0 V bias is continuously decreasing as seen in Fig. 5(b). As we can see from Fig. 5(a), the dielectric permittivity (ε') has a low value at 23 °C. But as the temperature increases the dielectric permittivity increases up to the transition temperature and after that its value decreases. It is this increase in dielectric permittivity at 0 V which suggests that there are some local fluctuations other than the Goldstone mode. In other words, these local fluctuations are nothing but the random tilt fluctuations (θ) within layers and hence the increase shown in Fig. 5(a) is the contribution of the mode called *random mode*. On the other hand, in the case of FLC (CS-1026) one does not see any anomaly in the dielectric permittivity. It decreases right from the Sm-C* phase through the transition temperature to Sm-A phase as seen in Fig. 5(b).

The dielectric dispersion under bias field was also taken and a suppressed permittivity was observed in both the cases of ELCs and FLCs, respectively.[20–22] For a better differentiation between the two materials: ELCs and FLCs we have also taken Cole-Cole plots ($\varepsilon', \varepsilon''$) for presentation of dielectric spectra in a wide temperature range both in Sm-C* and Sm-A phases. The dielectric process exhibiting a continuous distribution of relaxation time, can be described by the Cole-Cole distribution of relaxation time as

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)/[1 - (i\omega\tau)^{1-\alpha}], \quad (4)$$

where α is the distribution parameter for a particular relaxation process.

Figures 6(a) and 6(b) shows the Cole-Cole distribution in BDH-764E at 1 °C below and above T_c, respectively. One can clearly see that there is no separation of the modes even at such high bias voltage. On the other hand, Cole-Cole plots of CS-1026 give a different picture. As could be seen, Fig. 7(a), which is the Cole-Cole at 62 °C (2 °C before T_c) shows that there are clearly two processes seen at this temperature on the application of 6 V bias. One is the Goldstone mode and other is the soft mode. As we increase the temperature after T_c only the soft mode contribution remains as clearly seen in Fig. 7(b), whereas no such separation of modes is seen in BDH-764E. The dielectric strength of BDH-764E and CS-1026, which has been calculated from

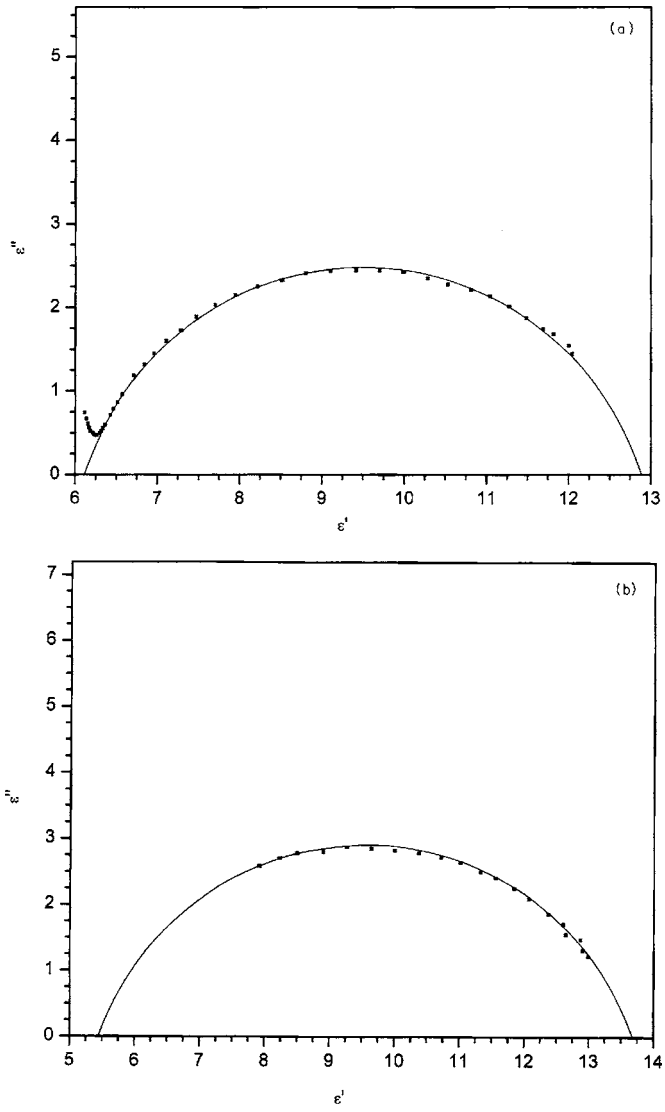

FIG. 6. Cole-Cole plot of ELC BDH-764E (20 μm thick) at 30 V bias voltage at different temperatures of (a) 27 and (b) 29 °C.

Cole-Cole plots is plotted in Figs. 8(a) and 8(b). One can clearly observe a very high dielectric strength in the case of BDH-764E and no separation of any modes there on the application of 30 V bias voltage. The dielectric strength in the case of CS-1026 has been segregated into that of Goldstone and soft mode at various temperatures at 6 V bias. The plotted graphs are under bias voltage in both the cases. One can clearly notice that in the case of BDH-764E the increase in the dielectric strength ($\Delta\varepsilon$) is over a wide temperature range until T_c where it is constant and then decreases as shown in Fig. 8(a). On the other hand, the increase in dielectric strength ($\Delta\varepsilon$) in CS-1026 is a steep one, within 2 °C of the transition temperature it attains a maximum value and thereafter drops to a low value immediately. Also a comparison of Figs. 8(a) and 8(b) shows that the dielectric strength ($\Delta\varepsilon$) in BDH-764E does not get separated in two modes as in the case of CS-1026 where we can clearly see the suppressed Goldstone mode (open square) and soft mode (open star) before the transition temperature. This shows that the de Vries ELC differs from the conventional FLC material near the transition temperature and even below T_c. Moreover, the

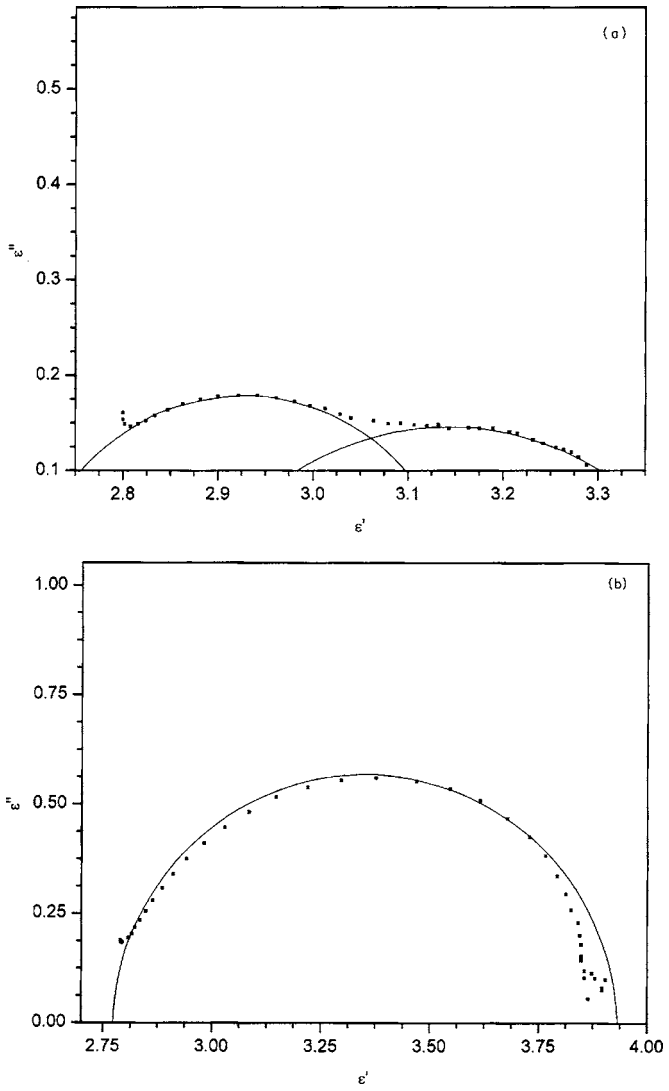

FIG. 7. Cole-Cole plot of FLC CS-1026 (12 μm thick) at 6 V bias voltage at different temperatures of (a) 62 and (b) 66 °C.

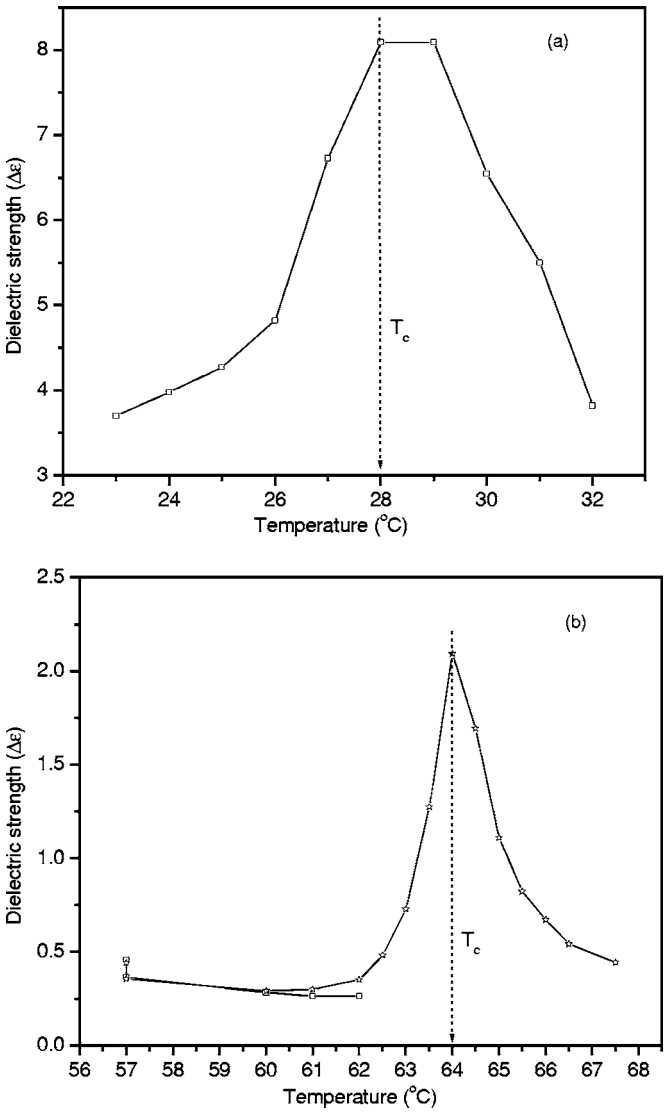

FIG. 8. (a) Dielectric strength as a function of temperatures at 30 V bias in ELC sample of 20 μm thickness. (b) Dielectric strength as a function of temperatures at 6 V bias in FLC sample of 12 μm thickness.

nature of dielectric relaxation with respect to temperature is showing very interesting results in the case of ELCs, as seen in Fig. 9(a). The constant behavior of relaxation frequency near the transition temperature with respect to temperature under 30 V bias field is not the behavior of conventional FLCs. In the general case, the bias application suppresses the phason variation (Φ) and the tilt variations (θ) become prominent near the transition temperature, which is temperature dependent, and falls with temperature just before T_c as could be seen in the case of conventional FLC (CS-1026) in Fig. 9(b). But this is not the case with ELCs. Instead of decreasing relaxation just before T_c we find a constant value of relaxation frequency under bias of 30 V. The relaxation frequency in FLCs under bias field clearly shows the soft mode relaxation and thus obeys the Curie-Weiss law as shown in Fig. 9(b). But ELCs are far off from this kind of behavior of obeying the Curie-Weiss law.[23] However, Krueger and Giesselmann,[22] reported the dielectric behavior in de Vries ELCs obeying the Curie-Weiss law in broad temperature range which might be due to the fact that the material has a very high spontaneous polarization of 185 nC/cm^2 as compared with the studied material which has a P_s of 39 nC/cm^2 as reported.[21]

C. Qualitative explanation of constant relaxation frequency in de Vries material

Now the question of immediate concern is that how is the behavior of dielectric relaxation related to the nature of transition in ELC materials? It could be qualitatively explained by considering the constant layer spacing at the Sm-C*–Sm-A transition temperature.

The change in layer spacing few degrees below and above T_c can be given as

$$\Delta d = L\cos\theta - L\cos(\theta + \Delta\theta), \tag{5}$$

where Δd is the change in layer spacing due to small change in tilt angle (θ) and L is the molecular length

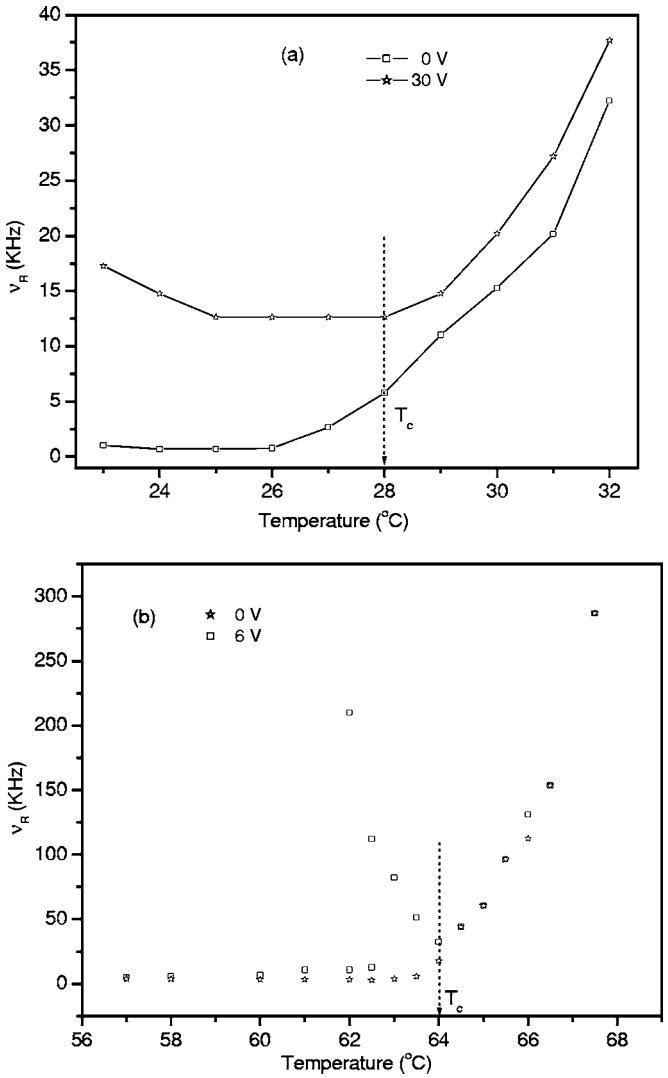

FIG. 9. (a) Temperature dependence of relaxation frequency (ν_R) at 0 and 30 V bias in Sm-C* and Sm-A phases in 20 μm thick ELC samples. (b) Temperature dependence of relaxation frequency (ν_R) at 0 and 6 V bias in Sm-C* and Sm-A phases in 12 μm thick FLC samples.

$$\Delta d = 2L \sin(\theta + \Delta\theta/2)\sin(\Delta\theta/2). \tag{6}$$

$\Delta\theta$ is an infinitesimal small change in tilt so $\sin(\Delta\theta/2) \approx \Delta\theta/2$. Hence,

$$\Delta d = L(\sin\theta)\Delta\theta. \tag{7}$$

Taking time dependency we get

$$\omega_s = \frac{(\Delta d/\Delta t)}{[L(\cos\theta\Delta\theta + \sin\theta)]} \tag{8}$$

$\Delta\theta$ is an infinitesimal small changes in tilt so $\cos\theta\Delta\theta$. is negligible as compared to $\sin\theta$. Hence,

$$\omega_s = \frac{(\Delta d/\Delta t)}{L\sin\theta} \tag{9}$$

where $\Delta\theta/\Delta t$ is being represented by ω_s which is the resultant frequency of soft mode. It is well established that soft (amplitude) mode is the time rate fluctuation of θ. So, to establish the correlation between soft mode and layer spacing the time dependence of Eq. (7) has been taken and it leads to nontrivial transition into Eq. (9). As in case of de Vries material layer spacing is strictly constant hence $\Delta d = 0$. This nonchanging layer spacing can be seen from the behavior of tilt as shown in Fig. 2(a) where it is constant in a wide range near the transition temperature. Thus this NLS material does not exhibit θ fluctuation. This implies that soft mode fluctuations are not possible in case of Sm-C*–Sm-A (tilted) transition near the transition temperature and if at all it exists then the amplitude is so small that it is difficult to be detected. In such transitions the Sm-C* and Sm-A phases are divided on the basis of ordered tilt and randomized tilt within layers, respectively.

D. Random mode and the order parameter

As mentioned in Sec. III C, the molecular arrangement in Sm-A phase of de Vries ELCs is random within a layer. In other words, in de Vries Sm-A phase, the optical tilt is a function of the azimuthal angle Φ within a layer. It is the randomized "θ" (having different azimuthal angle and thus resultant change in direction of vector θ) within layers that makes layer polarization zero inspite of the molecules exhibiting a local polarization in the Sm-A phase as shown in Fig. 1. It is due to the fact that polarization and direction of θ are strictly related. The change in the value of Φ within a layer makes the optical tilt θ to be a function of Φ. This variation in the original value of tilt θ to values varying from 0 to 2π (of Φ) gives rise to the mode named random mode. It is the intralayer azimuthal fluctuation, which gives rise to the random mode in the vicinity of transition temperature. It is worth mentioning here that, recently, experiments have been performed and has been observed that probably the randomization has its origin in the Sm-C* phase itself. The data will be published separately elsewhere.

This random mode is certain as soon as randomization in tilt appears within layers. Whenever randomization is removed under bias field, $\theta(\Phi)$ will attain its maximum value θ and relaxation process is constant with respect to temperature. Thus we can say that the constant relaxation frequency near T_c is due to the intralayer fluctuations in Φ. This behavior of relaxation frequency (ν_R) as shown in Fig. 9(a) is neither a characteristic of Goldstone mode nor soft mode. But the relaxation frequency is constant near T_c. That inspires us to think of some other process that is going on at that temperature. Thus, the de Vries geometry and the behavior of tilt, dielectric strength, and relaxation frequency near T_c points to the above intralayer phason fluctuation, which is nothing but the random mode. Even if there are tilt (θ) fluctuations in that randomized tilt near T_c then the process is too slow to be observed as compared to the amplitude of these intralayer Φ fluctuations. As we are talking about the tilt fluctuations θ we do not mean to change the layer spacing. These θ variations (if at all) are much small to cause any layer shrinkage.

As discussed earlier in the case of Sm-C* to Sm-A (tilted) transition, layer spacing remains constant as well as optical tilt shows almost constant value near the transition temperature. The basic question that now arises is that what are the basic differences in Sm-C* and tilted chiral Sm-A

phases? In the former, intralayer polarization is not zero but in the latter it is zero due to randomization of tilt within layers. As mentioned above the tilt as well as layer spacing remains constant during Sm-C* to Sm-A (tilted) transition then the question arises what should be considered as order parameter for such a transition? In summary only one factor, which is left, that can be considered, as a primary order parameter is "tilt randomization" as its magnitude is constant. The randomization of tilt is the only major factor, which changes at the transition point. Thus we abide by the facts to assume the presence of mode, which is named random mode due to its origin. It is the random mode, which shows its constant relaxation frequency near the transition temperature in Sm-C* phase in electroclinic liquid crystal under high bias field as shown in Fig. 9(a). As in deep Sm-C* phase the relaxation frequency is constant due to the phason fluctuations, similarly near the transition temperature it is the local phason fluctuations due to randomization within layers which as a result show a constant relaxation in these ELCs. Due to the second order nature of transition as observed by us, it is usual to think that randomization appears[21] slowly much before transition and leads to the origin of the random mode near the transition temperature in Sm-C* and Sm-A phases in ELC materials. It is worth mentioning here that the above all the results have also been confirmed in another electroclinic liquid crystal material, supplied by Hoechst, Germany (Felix 20).

IV. CONCLUSION

We have shown that the investigated material exhibiting constant tilt and same texture before and after T_c is the de Vries material. The dielectric spectra show its strikingly different characters as compared to the conventional FLCs. No separation of modes near T_c, constant relaxation just before transition temperature contradicts them with FLCs. This was explained on the basis of the intralayer fluctuations in Φ near T_c and thus we concluded that there is a mode, which is named as random mode near T_c. Moreover, the nonobeyance of the Curie-Weiss law prompted us to take another order parameter, which is the tilt randomization in ELC materials.

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[1] S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).
[2] S. Garoff and R. B. Meyer, Phys. Rev. A **19**, 338 (1979).
[3] F. Giesselmann, P. Zugenmaier, I. Dierking, S. T. Lagerwall, B. Stebler, M. Kaspar, V. Hamplová, and M. Glogarová, Phys. Rev. E **60**, 598 (1999).
[4] J. P. F Lagerwall and F. Giesselmann, Phys. Rev. E **66**, 031703 (2002).
[5] M. Rossle, R. Zentel, J. P. F. Lagerwall, and F. Giesselmann, Liq. Cryst. **31**, 883 (2004).
[6] J. Naciri, C. Carboni, and A. K. George, Liq. Cryst. **30**, 219 (2003).
[7] A. Tang, D. Konovalov, J. Naciri, B. R. Ratna, and S. Sprunt, Phys. Rev. E **65**, 010703 (2002).
[8] R. B. Meyer and R. A. Pelcovits, Phys. Rev. E **65**, 061704 (2002).
[9] S. Diele, P. Brand, and H. Sackmann, Mol. Cryst. Liq. Cryst. **16**, 105 (1972).
[10] A. De Vries, in *Abstracts of the Fifth International Liquid Crystal Conference, Stockholm*, edited by G. H. Brown (ILC Society, Kent, OH, 1974), p. 150.
[11] A. De Vries, Mol. Cryst. Liq. Cryst. Lett. **41**, 27 (1977); A. De Vries, A. Ekachai, and N. Spielberg, *ibid.* **49**, 143 (1979).
[12] M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt, and R. Shashidhar, Phys. Rev. E **61**, 1579 (2000).
[13] C. C. Huang *et al.*, Phys. Rev. E **69**, 041702 (2004).
[14] Yu. P. Panarin, V. Panov, O. E. Kalinovskaya, and J. K. Vij, J. Mater. Chem. **9**, 2967 (1999).
[15] M. Maeda, M. Miyamori, and I. Suzuki, Mol. Cryst. Liq. Cryst. **366**, 703 (2001).
[16] R. Blinc and B. Žekš, Phys. Rev. A **18**, 740 (1978).
[17] T. Carlsson, B. Žekš, C. Filipič, and A. Levstik, Phys. Rev. A **42**, 877 (1990).
[18] S. K. Kundu, E. Okabe, W. Haase, and B. K. Chaudhuri, Phys. Rev. E **64**, 051708 (2001).
[19] S. K. Prasad, V. N. Raja, D. S. S. Rao, and G. G. Nair, Phys. Rev. A **42**, 2479 (1990).
[20] A. K. Thakur, D. K. Sharma, S. P. Singh, S. S. Bawa, and A. M. Biradar, Ferroelectrics **289**, 63 (2003).
[21] A. K. Thakur, A. M. Biradar, S. P. Singh, D. K. Sharma, and S. S. Bawa, Jpn. J. Appl. Phys., Part 1 **43**, 1348 (2005).
[22] M. Krueger and F. Giesselmann, Phys. Rev. E **71**, 041704 (2005).
[23] S. Kaur, A. K. Thakur, A. Choudhary, S. S. Bawa, A. M. Biradar, and S. Annapoorni, Appl. Phys. Lett. **87**, 102507 (2005).