Behavior of the Goldstone mode in smectic-C^* phase and the soft mode in the smectic-C^* and smectic-A^* phases of a ferroelectric liquid-crystal mixture

T. Pal Majumder, S. Sinha Roy, and S. K. Roy*
Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
(Received 12 July 1995; revised manuscript received 4 March 1996)

The complex dielectric permittivity has been measured as a function of temperature, and the bias electric field for a ferroelectric liquid-crystal mixture having low spontaneous polarization. By applying the bias electric field we have been able to measure the soft mode 2 °C inside the smectic-C^* phase. From the experimental results, relaxation frequency and dielectric strength of the Goldstone mode in the Sm-C^* phase and soft mode in the smectic-C^* and smectic-A^* phases have been determined. The parameter β, which determines the importance of biquadratic coupling compared to the bilinear coupling of extended Landau model near to the transition temperature in the Sm-C^* phase, has been determined from known values of spontaneous polarization and tilt angles at various temperatures. The experimental results have been compared to those of numerically calculated values and a good agreement between the results has been obtained. The Sm-C^*–Sm-A^* transition temperature T_C has been determined from the dielectric results. The deviation between the T_C determined experimentally and the T_C observed from texture studies is around 0.3 °C for the ferroelectric liquid-crystal mixture studied in this paper. [S1063-651X(96)05107-0]

PACS number(s): 61.30.−v, 77.84.Nh, 77.90.+k

I. INTRODUCTION

Many theoretical and experimental studies have been carried out on tilted chiral smectic phases of the molecule after the discovery of ferroelectricity in such phases by Meyer *et al.* [1] and the research works have been further accelerated particularly on the chiral smectic-C (Sm-C^*) phase after finding its applications in fast electro-optical devices. The thermodynamic behavior of the system can be best understood by the measurement of complex dielectric permittivity at various temperatures. It is now well established both theoretically [2–4] and experimentally [4–10] that the Goldstone mode observed in smectic-C^* phase arises due to the phase fluctuation and soft mode observed both in Sm-C^* and Sm-A^* phases and arises due to the tilt fluctuation of the ferroelectric liquid-crystal (FLC)-molecules. Carlsson *et al.* [4] also observed that the soft mode in the Sm-C^* phase appears a few degrees below the Sm-C^*–Sm-A^* transition temperature without a bias field for high P_S FLC material. Zeks [2] added another term to the classical Landau model when it fails to describe some of the experimental results. This term represents a biquadratic coupling (Ω) between tilt (θ) and polarization (P_S). The polarization dependent part of the free energy density in the extended Landau model is given by

$$g_P = 1/(2\epsilon)P_S^2 - CP_S\theta - 1/2\Omega P_S^2\theta^2 + 1/4\eta P_S^4, \qquad (1)$$

where η is a constant, ϵ the high temperature dielectric constant, C the piezoelectric bilinear coupling coefficient, and Ω the biquadratic coupling coefficient inducing a transverse quadrupole ordering.

The importance of the biquadratic coupling term has been verified from nuclear magnetic resonance (NMR) measurements by Lugar *et al.* [11]. It is the purpose of the present paper to investigate the temperature variation of the Goldstone mode and soft mode response in Sm-C^* and Sm-A^* phases and also to study the importance of biquadratic coupling between tilt and polarization for the interpretation of the experimental result near the Sm-C^*–Sm-A^* transition temperature. The effect of the bias field on the soft mode response in Sm-C^* phase has also been studied.

The material selected for the above studies is a ferroelectric liquid-crystal mixture Merck ZLI-4655-100, obtained from E. Merck. The sample possesses low spontaneous polarization ($=+22.6$ nC cm^{-2} at 20 °C). The phase sequences of the sample are as follows (Ch denotes cholesteric, I isotropic, and K crystal):

$$K \underset{-10\ ^\circ\mathrm{C}}{\leftrightarrow} \text{Sm-}C^* \underset{61\ ^\circ\mathrm{C}}{\leftrightarrow} \text{Sm-}A^* \underset{72\ ^\circ\mathrm{C}}{\leftrightarrow} \text{Ch} \underset{76\ ^\circ\mathrm{C}}{\leftrightarrow} I.$$

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

The dielectric studies have been carried in a planar aligned Indium-tin oxide (ITO) coated glass cell. The thickness is maintained by keeping a 100 μm Mylar spacer in between the coated plates. A well aligned planar geometry has been achieved by cooling down the temperature very slowly (0.2 °C/min) keeping it in a Mettler hot stage and simultaneously applying a low frequency (20 Hz) field to the cell. The simultaneous cooling and application of the ac field help to grow a monodomain planar structure and which is checked by a polarizing microscope. A detail experimental procedure and the theoretical background was given in our earlier paper [12].

A Hewlett-Packard impedance analyzer HP 4192A working in the frequency range of 5 Hz to 13 MHz has been used for the complex dielectric permittivity measurements. Before filling the sample, the cell has been calibrated using specpure benzene for the measurement of absolute value of the

*Author to whom correspondence should be addressed.

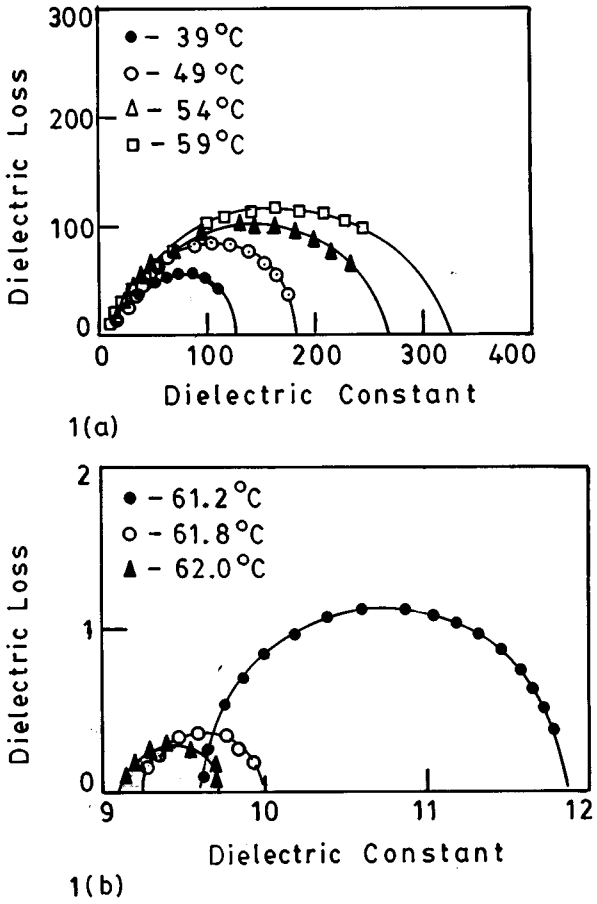

FIG. 1. (a) Cole-Cole plots for Goldstone mode at different temperatures. (b) Cole-Cole plots of soft mode in the Sm-A^* phase.

dielectric constant. A measuring voltage of 1 V peak to peak was applied in a direction parallel to the smectic layers.

By plotting ϵ' (the real part of the dielectric permittivity) vs ϵ'' (imaginary part of the dielectric permittivity) in a Cole-Cole diagram [Figs. 1(a) and 1(b)] at different temperatures, the relaxation frequency as well as the dielectric strength has been determined. The soft mode in the Sm-C^* phase is measured by complete unwinding of the helicoidal structure with an application of the dc bias field along with the ac probe field parallel to the smectic layer plane. In Fig. 2(a), it is observed that relaxation frequency of the Goldstone mode in the broad temperature range from 40°–60 °C very weakly depends on temperature. At this 20 °C temperature interval, the relaxation frequency increases from 800 Hz to 1 KHz and at the transition temperature, the observed relaxation frequency is 2 KHz. The Goldstone mode relaxation frequency of a structurally similar FLC material ZLI-4655-000 is of the same order of magnitude, but its Goldstone mode dielectric strength, as observed by Majumder, Mitra, and Roy [12], is one order of magnitude smaller than the presently studied molecule [Fig. 2(b)]. Inspite of their structural similarity the greater lowering of dielectric strength in ZLI-4655-000 is not only due to the lower spontaneous polarization of the molecule but also due to the suppression of the Goldstone mode in a thinner cell. In the presently studied molecule we have done the measurement in 100 μm cell, but Majumder, Mitra, and Roy [12] have done it in 8 μm cell where a possibility of the suppression of the Goldstone mode is quite obvious. The

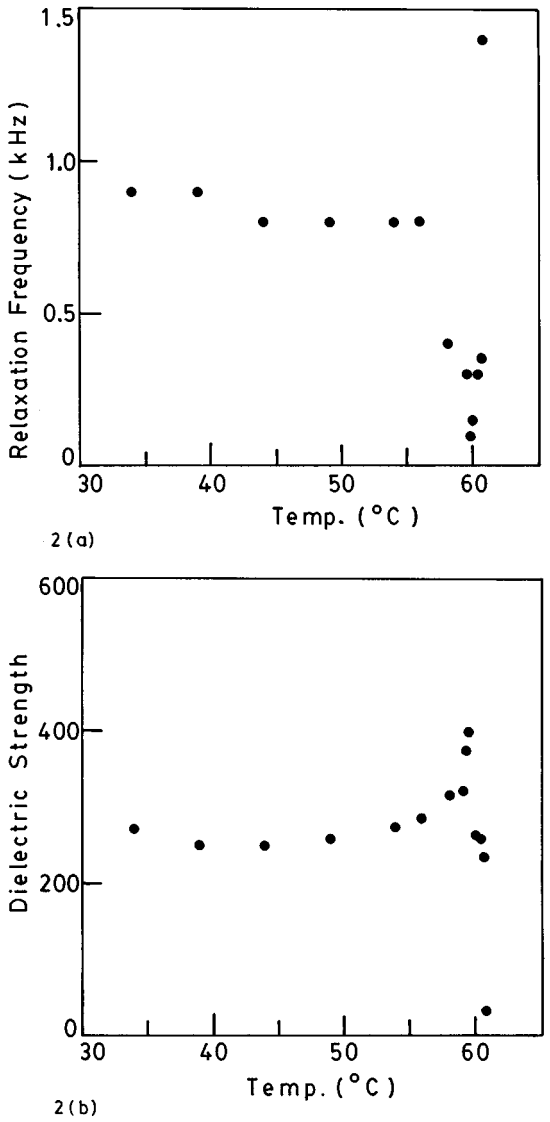

FIG. 2. (a) Variation of relaxation frequency of Goldstone mode with temperature. (b) Temperature dependence of the Goldstone mode dielectric strength ($\Delta\epsilon_G$).

Goldstone mode dielectric strength of the presently studied molecule, however, is of the same order of magnitude with similar types of molecules investigated by Biradar, Wrobel, and Haase [13] at the same $T_C - T$ and this is due to the similar P_S value of both molecules. The soft mode arises from the fact that on approaching the Sm-A^*–Sm-C^* transition, the elastic constant gets soft for this particular mode of vibration and dielectric strength diverges at the transition temperature. In Figs. 3 and 4, the relaxation frequency and dielectric strength of the soft mode both in Sm-A^* and Sm-C^* phases sharply vary with temperature. On approaching the Sm-A^*–Sm-C^* transition temperature, the relaxation frequency (Fig. 3) is found to decrease to a minimum value and dielectric strength (Fig. 4) increases to a maximum value at the phase transition temperature.

The inverse of the dielectric strength of the soft mode is, however, decreased to a minimum value at the transition temperature (Fig. 5). Soft mode data for the relaxation frequency and dielectric strength in the Sm-C^* phase, however,

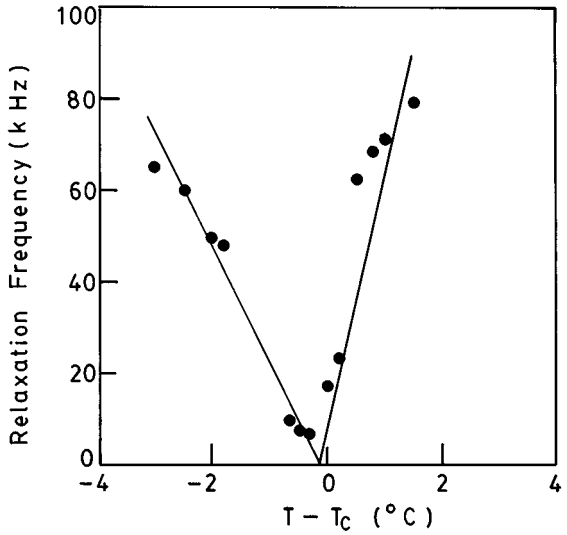

FIG. 3. Variation of relaxation frequency of soft mode in Sm-A^* and Sm-C^* phases with temperature.

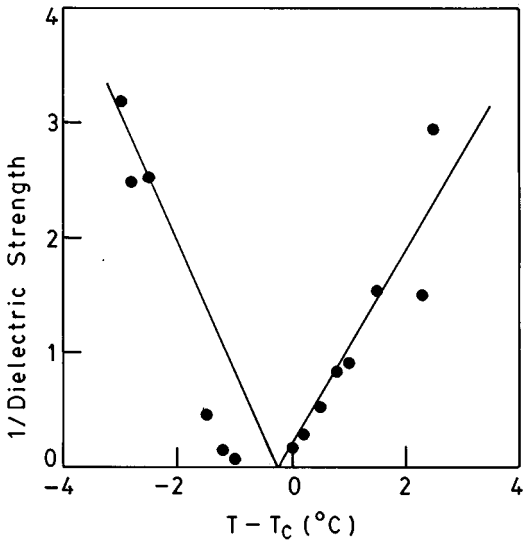

FIG. 5. Plot of inverse of dielectric strength $1/\Delta\epsilon_S$ vs temperature in Sm-C^* and Sm-A^* phases.

are obtained after quenching the helicoidal motion with the bias electric field.

In order to compare the temperature dependence dielectric strength and relaxation frequency curves with those of numerically calculated curves [4] both in Sm-C^* and Sm-A^* phases, it is essential to know a dimensionless parameter β, defined by Levstik *et al.* [3] and which is given as

$$\beta = \frac{\eta^{1/2} C \epsilon}{\Omega^{1/2}}. \tag{2}$$

This parameter indicates the importance of biquadratic coupling compared to the bilinear coupling, i.e., the smaller β means the importance is the biquadratic coupling. Carlsson *et al.* [4] numerically calculated the values of β which is found as $0<\beta<1$ and $\beta=1$ for the classical Landau model. The dimensionless parameter β has been determined using the following relation [16]:

$$\beta = \frac{\lim\limits_{T_C - T \Rightarrow 0} (P/\theta)}{\lim\limits_{T_C - T \Rightarrow \infty} (P/\theta)}. \tag{3}$$

The values of spontaneous polarization P_S and tilt angle θ at different temperatures are taken from the Merck Ferroelectric data sheet. The calculated β value for our FLC mixture is around 0.7, indicates a less biquadratic coupling between tilt and polarization. The less biquadratic coupling may be due to low spontaneous polarization of this FLC mixture. Carlsson *et al.* [4] using the extended Landau free energy equation numerically calculated the relaxation frequency, dielectric strength, and other parameters as a function of temperature and has shown the nature of the curves of relaxation frequency, dielectric strength, etc., against temperature for various β values.

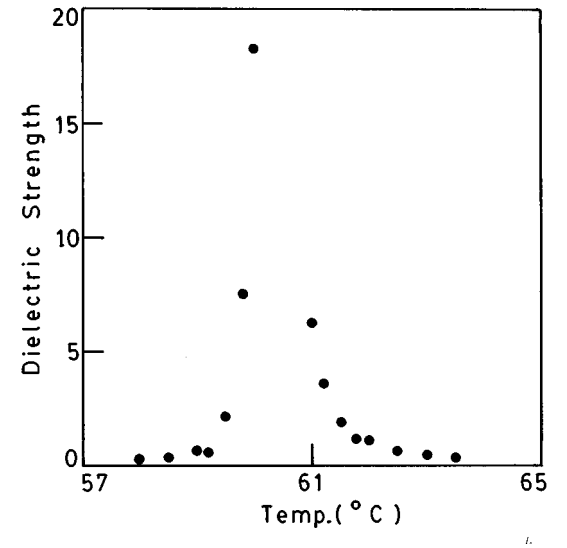

FIG. 4. Temperature dependence of the soft mode dielectric strength in Sm-A^* and Sm-C^* phases.

The temperature dependence of the Goldstone mode relaxation frequency and dielectric strength [Figs. 2(a) and 2(b)] of the presently studied system corresponds well to the nature of the numerically calculated curves of relaxation frequency and dielectric strength with a similar β value. Similarly the soft mode branch of the relaxation frequency and dielectric strength both in Sm-C^* and Sm-A^* phases (Figs. 3 and 4) shows the typical ''V'' shape behavior in the vicinity of the transition temperature which corresponds well to those of the numerically calculated curves with the same β value [3]. Our dielectric results can thus nicely be described by the extended Landau model.

The plot of relaxation frequency and the inverse of dielectric strength of the soft mode in the Sm-A^* phase as shown in Figs. 3 and 5 vary linearly with temperature and obey the Curie-Weiss law. The extrapolated curve cut the temperature axis at the Curie point which is in accordance with theoretical description [14,15]. The two soft mode branches of re-

laxation frequency in Sm-C^* and Sm-A^* phases in the present study meet the Curie temperature at $T_C = 60.8$ °C as shown in Fig. 3 and which is only 0.2 °C below the T_C observed from the texture studies under a polarizing microscope. The soft mode relaxation frequency and dielectric strength in the Sm-C^* phase has been determined under a bias field and as is observed from the experimental results that the perturbation on the relaxation frequency due to the bias field does not effect much in determining T_C by the extrapolation method. This was also observed earlier by Gouda, Skarp, and Lagerwall [16,17]. The inverse of dielectric strength of the two soft mode branches in Sm-C^* and Sm-A^* phases also gives a linear relation with temperature and two extrapolated branches meet at $T_C = 60.7$ °C, if we disregard the experimental data very near (within 1 °C) to the transition temperature in the Sm-C^* phase (Fig. 5), as the soft mode dielectric strength near the transition temperature is perturbed very much under the bias field [18]. T_C thus obtained from the extrapolation of two soft mode branches of dielectric strength without considering the data near to transition is consistant with that obtained from the extrapolation relaxation frequency. In the presently studied FLC mixture it is observed that the T_C obtained from the extrapolation of the two relaxation frequency branches and extrapolation of two $1/\Delta\epsilon_S$ branches of the soft mode in Sm-C^* and Sm-A^* phases are almost equal within experimental error and it is $\cong 0.3$ °C less than the T_C obtained from the texture studies. Sometimes the difference (ΔT_C) between the T_C determined from the dielectric method and the T_C obtained from texture studies is as much as around 1 °C–2 °C observed by other authors [8,11] for relatively high P_S materials but in the present study the difference of T_C (ΔT_C) is only around 0.3 °C. The small difference of T_C (ΔT_C) between texture and dielectric studies may be due to the less biquadratic coupling in the presently studied compound.

ACKNOWLEDGMENTS

The authors would like to thank E. Merck (Germany) for donating the sample. We are also thankful to the members of the MLS Laboratory of our Institute for providing the HP Impedance analyzer for the measurements.

[1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. J. Keller, J. Phys. (Paris) Lett. **36**, L-69 (1975).
[2] B. Zeks, Ferroelectrics **53**, 33 (1984).
[3] A. Levstik, T. Carlsson, C. Filipic, I. Levstik, and B. Zeks, Phys. Rev. A **35**, 3527 (1987).
[4] T. Carlsson, B. Zeks, C. Filipic, and A. Levstik, Phys. Rev. A **42**, 877 (1990).
[5] C. Filipic, T. Carlsson, A. Levstik, B. Zeks, R. Blinc, F. Gouda, S. T. Lagerwall, and K. Skarp, Phys. Rev. A **38**, 5833 (1988).
[6] K. Yoshino, T. Uemoto, and Y. Inuishi, Jpn. J. Appl. Phys. **16**, 571 (1977).
[7] J. Hoffman, W. Kuczynski, and J. Malecki, Mol. Cryst. Liq. Cryst. **44**, 287 (1978).
[8] M. Glogarova and J. Pavel, Mol. Cryst. Liq. Cryst. **114**, 249 (1984).
[9] C. H. Bahr, G. Heppke, and N. K. Sharma, Ferroelectrics **76**, 151 (1987).
[10] J. Zubia, A. Ezcurra, M. R. De La Fuente, M. A. Perfz Jubindo, T. Sierra, and J. L. Serrano, Liq. Cryst. **10**, 849 (1991).
[11] M. Lugar, V. Rutar, Z. Zeliger, and R. Blinc, Ferroelectrics **58**, 115 (1984).
[12] T. Pal Majumder, M. Mitra, and S. K. Roy, Phys. Rev. E **50**, 4796 (1994).
[13] A. M. Biradar, S. Wrobel, and W. Haase, Phys. Rev. A **39**, 2693 (1989).
[14] Ph. Martinot-Legard, and G. Durand, J. Phys. **42**, 269 (1981).
[15] R. Blinc and B. Zeks, Phys. Rev. A **18**, 740 (1977).
[16] F. Gouda, K. Skarp, and S. T. Lagerwall, Ferroelectrics **113**, 165 (1991).
[17] F. Gouda, G. Andersson, S. T. Lagerwall, K. Skarp, B. Stebler, T. Carlsson, B. Zeks, C. Filipic, and A. Levstik, Liq. Cryst. **6**, 219 (1989).
[18] F. Gouda, G. Andersson, S. T. Lagerwall, K. Skarp, B. Stebler, T. Carlsson, B. Zeks, C. Filipic, and A. Levstik, Mol. Cryst. Liq. Cryst. **6**, 151 (1989).