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The existence of four dielectric modes in the planar oriented S_C^* phase of a fluorinated substance

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Soft mode and Goldstone mode properties have been studied for a fluorinated substance. The dielectric spectra have been measured on the planar oriented samples, in the frequency range from 10 Hz to 10 MHz. The thickness of the sample was 10 μm and two kinds of capacitors were used: (i) a low resistance EHC cell and (ii) gold coated electrodes. A bias field up to 10 kV cm^{-1} has been applied to show the existence of both the soft mode and domain mode in the S_C^* phase below T_C. In the S_C^* phase a strong Goldstone mode has been observed with a low critical frequency ($\nu_C^G = 15$ Hz). The high frequency side at the Goldstone mode spectrum is accompanied by a shoulder which consists of the soft mode and domain mode as well. In the vicinity of the S_A^*–S_C^* transition the dielectric parameters of the soft mode obey a Curie–Weiss law. The slope ratio is equal to $-1{\cdot}62$ for the inverse of dielectric increments ($\Delta\varepsilon^{-1}$) and $-1{\cdot}73$ for the critical frequencies (ν_C) obtained by using gold electrodes. The respective values received for the EHC cell are $-4{\cdot}14$ and $-2{\cdot}1$. The dielectric parameters of the domain mode have been obtained versus temperature and bias field. We can qualitatively show that a high frequency molecular relaxation is present in the S_A^* and S_C^* phases as the high frequency limit of dielectric permittivity is distinctly higher than the refractive index squared.

1. Introduction

Ferroelectric liquid crystals (FLCs) show a very rich dielectric spectrum. In addition to two molecular relaxation processes, connected with the reorientation of molecules around their long and short molecular axes, the S_C^* phase shows at least two collective processes, namely, the Goldstone mode and the soft mode [1]. The former originates from the phase deformation of the order parameter ξ ($\xi = \vartheta_0 \exp(i\phi)$) whereas the latter results from its amplitude fluctuation, which takes place in the vicinity of the S_C^*–S_A^* transition. Above this transition only the soft mode is present.

The theory worked out by Blinc and Žeks [1] predicts a Curie–Weiss behaviour of the soft mode dielectric parameters in the pretransition region. The inverse of the soft mode dielectric increment $[\Delta\varepsilon_\perp^s]^{-1}$ and the ν_C^S critical frequency should decrease linearly with temperature upon approaching the T_C transition temperature on both its sides. According to the theory the slope of the $[\Delta\varepsilon_\perp^S(T)]^{-1}$ straight line below T_C is by a factor of -2 greater than the adequate slope taken above T_C. The same relation is valid

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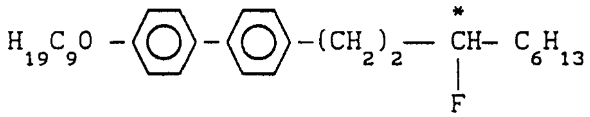
for the $\nu_C^S(T)$ dependence. On the other hand both $[\Delta\varepsilon_\perp^G]^{-1}$ and ν_C^G are temperature independent within the S_C^* phase.

Up to now many single component systems [2–14] and mixtures exhibiting ferroelectric phases have been studied by dielectric and electrooptic methods. The studies revealed that the dielectric spectrum in the S_C^* phase depends strongly on the bias field applied. At high bias fields the Goldstone mode contribution is suppressed, but there is always a residual spectrum which cannot be suppressed [9, 10, 14]. In one of our first papers devoted to this subject [9] the residual spectrum was called a new ferroelectric mode which can also be identified as a domain mode. However, there are some doubts if both modes are the same. In the S_C^* phase close to T_C the 'domain mode' overlaps the soft mode and we should decompose the spectrum into two separate contributions. It has also been found for many pure substances [4, 9] and for mixtures [14, 16] that the slope ratios for both dependencies $[\Delta\varepsilon_\perp^S(T)]^{-1}$ and $\nu_C^S(T)$ in the vicinity of T_C may vary from $-0{\cdot}2$ to -4.

In this paper a report on the dielectric studies of a fluorinated compound, showing the S_A^*, S_C^* and S_I^* phases, is given. The substance exhibits a high spontaneous polarization of *c.* 150 nC cm^{-2} [19] in the low temperature range of the S_C^* phase. The dielectric data obtained corroborate the theory quantitatively to some extent. However, in the S_C^* phase there is the domain mode, which influences the spectra at small bias fields and overlaps the soft mode. If we separate the soft mode spectrum from the composed relaxation peak in the S_C^* phase we can get better agreement between the experimental results and the mean field theory. As shown in this paper the domain mode depends strongly on the bias field and on the type of electrodes used.

2. Experimental

Dielectric spectra have been studied for the fluorinated substance showing the following phase sequence:



C 73°C S_I^* 76°C S_C^* 87°C S_A^* 90°C I*.

The perpendicular component of the complex electric permittivity ($\varepsilon_\perp^* = \varepsilon_\perp' - i\varepsilon_\perp''$) was measured on the planar aligned samples by using a HP impedance analyser. The measurements were carried out in the frequency range 5 Hz–13 MHz. Low resistance EHC-ITO and gold coated electrodes have been used to study some details of the dielectric spectrum in the pretransition region. In both cases the thickness of the sample was *c.* 10 μm. In the case of gold electrodes a planar alignment of the sample was obtained by slow cooling (-4 K h^{-1}) from the isotropic to the S_A^* and then to the S_C^* phase in a magnetic field of 1·2 T. The EHC cell gives a planar orientation similar to the surface treatment of ITO electrodes. The quantity of alignment was improved during the measurements by applying a low frequency AC field.

As the substance exhibits rather high spontaneous polarization the measuring electric field was equal to 0·1 V_{pp} to ensure a linear regime for complex electric permittivity measurements. The temperature was stabilized by means of an oil temperature controller and the accuracy of the relative temperature was of *c.* 0·02°C.

3. Results and discussion

3.1. *Phenomenological model*

The frequency dependence of the $\varepsilon_\perp^*$ complex electric permittivity in the S_C^* phase can be presented as follows [9, 13, 14]:

$$\varepsilon_\perp^*(\omega)=\varepsilon_{\perp\infty}+\frac{\varepsilon_{\perp 0}^{M}-\varepsilon_{\perp\infty}^{M}}{1+(i\omega\tau_M)^{1-\alpha_M}}+\frac{\varepsilon_{\perp 0}^{S}-\varepsilon_{\perp\infty}^{S}}{1+(i\omega\tau_S)^{1-\alpha_S}}+\frac{\varepsilon_{\perp 0}^{G}-\varepsilon_{\perp\infty}^{G}}{1+(i\omega\tau_G)^{1-\alpha_G}}, \qquad (1)$$

where the second term is connected with the molecular reorientation around the long axes, the third with the soft mode and the fourth with the Goldstone mode. For the S_A^* phase the last term is not present. The soft mode contribution shows up practically in the vicinity of the S_C^*–S_A^* transition. By splitting equation (1) into real and imaginary parts we obtain:

$$\varepsilon'(\omega)=\varepsilon_\infty+\frac{\varepsilon_{0S}-\varepsilon_\infty}{2}\left[1-\frac{\sinh A}{\cosh A+\sin(\pi\alpha_S/2)}\right]+\frac{\varepsilon_{0G}-\varepsilon_{0S}}{2}\left[1-\frac{\sinh B}{\cosh B+\sin(\pi\alpha_G/2)}\right], \qquad (2a)$$

$$\varepsilon''(\omega)=\frac{\varepsilon_{0S}-\varepsilon_\infty}{2}\,\frac{\cos(\pi\alpha_S/2)}{\cosh A+\sin(\pi\alpha_S/2)}+\frac{\varepsilon_{0G}-\varepsilon_{0S}}{2}\,\frac{\cos(\pi\alpha_G/2)}{\cosh B+\sin(\pi\alpha_G/2)}, \qquad (2b)$$

where $A=(1-\alpha_S)\ln(\omega\tau_S)$, $B=(1-\alpha_G)\ln(\omega\tau_G)$, $\varepsilon_{\perp 0}^{S}\equiv\varepsilon_{0S}$, $\varepsilon_{\perp 0}^{G}\equiv\varepsilon_{0G}$ and $\varepsilon_{\perp\infty}=\varepsilon_\infty$. It was assumed that the molecular term is included in ε_∞ as our measurements were done to 10 MHz only. Both the dispersion $\varepsilon'(\omega)$ and absorption $\varepsilon''(\omega)$ curves were fitted to the experimental points by a simplex method [15].

3.2. *Dielectric spectrum*

Figure 1 presents the dielectric spectra taken in the S_C^* phase of the substance studied. It can be clearly seen that the spectrum consists of two broad peaks (SM and GM). Both relaxation maxima exhibit big distribution parameters ($\alpha_S=0{\cdot}262$, $\alpha_G=0{\cdot}350$) which means that they are not single relaxation processes. In this case the SM spectrum is merged with other processes found before for another fluorinated substance [9]. Using a DC bias field we were able to suppress the low frequency (GM) contribution and under these circumstances the structure of the high frequency part of the spectrum was revealed (see figure 2). By fitting equations (2*a*) and (2*b*) to the experimental points we can split the spectrum into two contributions: the soft mode (SM) and the domain mode (DM). The former, with its distribution parameter $\alpha_S=0{\cdot}09$, seems to be a pure soft mode spectrum, the dielectric parameters of which fulfil the Curie–Weiss law (see figures 4(*a*) and (*b*)) in the vicinity of the S_C^*–S_A^* transition. The high frequency molecular relaxation contributes then to ε_∞ and its dispersion could be observed in the gigahertz frequency range [17, 18]. The dielectric spectrum obtained for the S_A^* phase is seen in figure 3. It is practically a Debye-type spectrum.

Figure 4(*a*) presents the inverses of the dielectric increment ($\Delta\varepsilon_\perp^{-1}$) for the Goldstone mode and soft mode as a function of temperature. The values were obtained by fitting equations (2) to the experimental points obtained with the ITO-EHC cell. The measurements for the Goldstone mode were taken in this case as $V_B=0$ V. The soft mode parameters presented in figure 4(*a*) for the S_C^* phase have been obtained at the bias field of 10 V. This figure presents the behaviour of the three dielectric modes (GM, SM and DM) in the vicinity of the S_C^*–S_A^* transition. It can be seen that the inverse of the Goldstone mode dielectric increment is practically constant within the S_C^* phase as

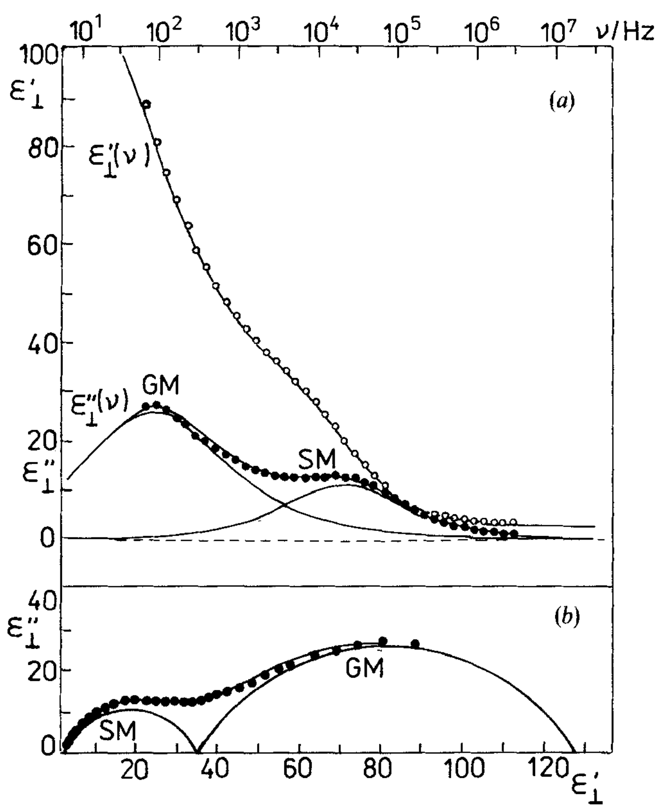


Figure 1. The dielectric spectrum obtained in the S_C^* phase of the substance studied. (*a*) Dispersion and absorption curves for the planar oriented sample; (*b*) Cole–Cole plot of the soft mode (SM) and Goldstone mode (GM) dielectric spectrum. $T=85{\cdot}4°C$, $\varepsilon_\infty=2{\cdot}445$, $\alpha_s=0{\cdot}262$, $\tau_s=7{\cdot}36\times10^{-6}$ s, $\varepsilon_{0S}=34{\cdot}651$, $\alpha_G=0{\cdot}350$, $\tau_G=1{\cdot}78\times10^{-3}$ s, $\varepsilon_{0G}=127{\cdot}059$.

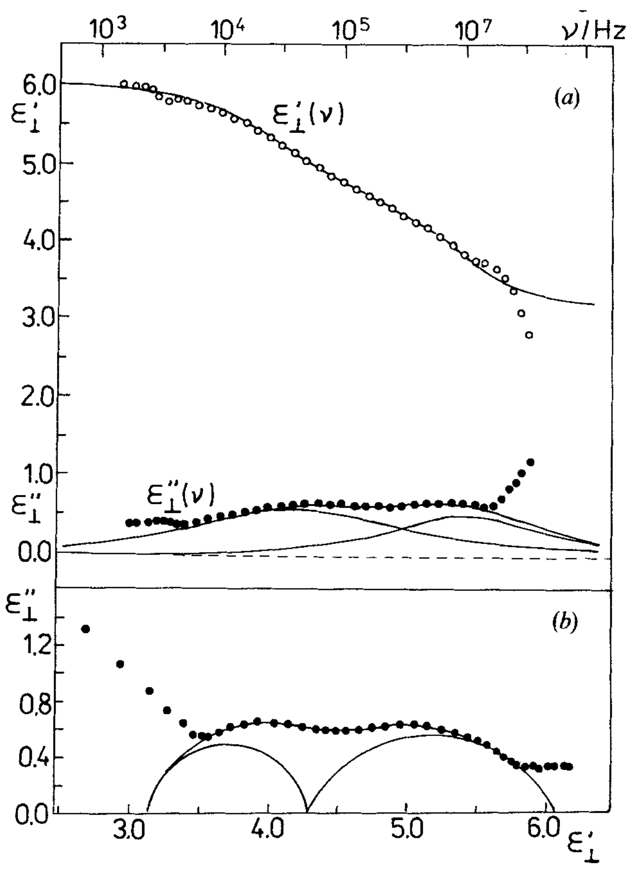


Figure 2. The dielectric spectrum taken in the S_C^* phase under the bias field voltage of 7 V. (*a*) Dispersion and absorption curves show the existence of at least two relaxation processes; (*b*) Cole–Cole plot of SM and DM mode spectrum. $T=84{\cdot}94°C$, $\varepsilon_\infty=3{\cdot}159$, $\alpha_s=0{\cdot}088$, $\tau_s=1{\cdot}53\times10^{-7}$ s, $\varepsilon_{0S}=4{\cdot}253$, $\alpha_D=0{\cdot}302$, $\tau_D=4{\cdot}06\times10^{-6}$ s, $\varepsilon_{0D}=6{\cdot}049$.

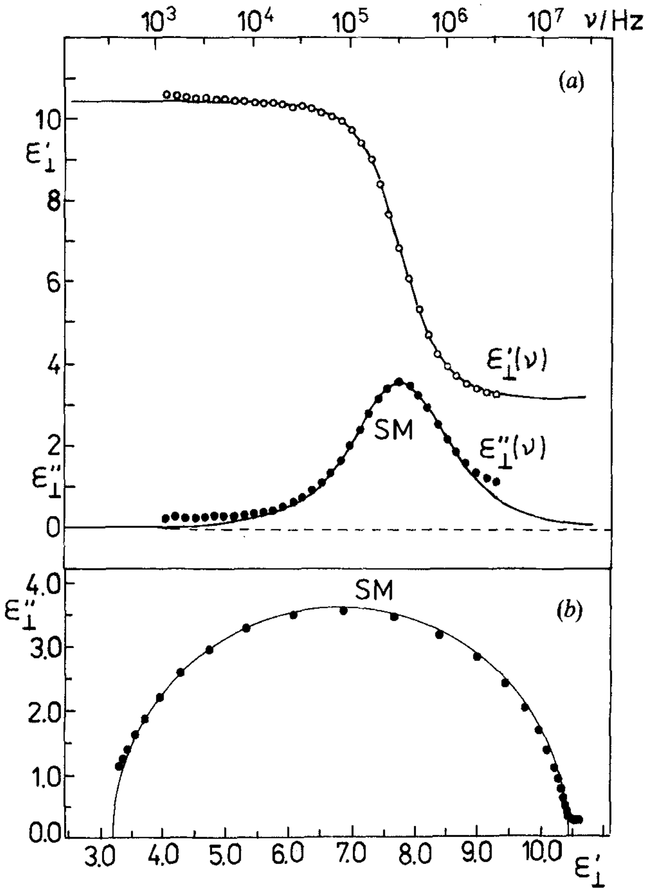
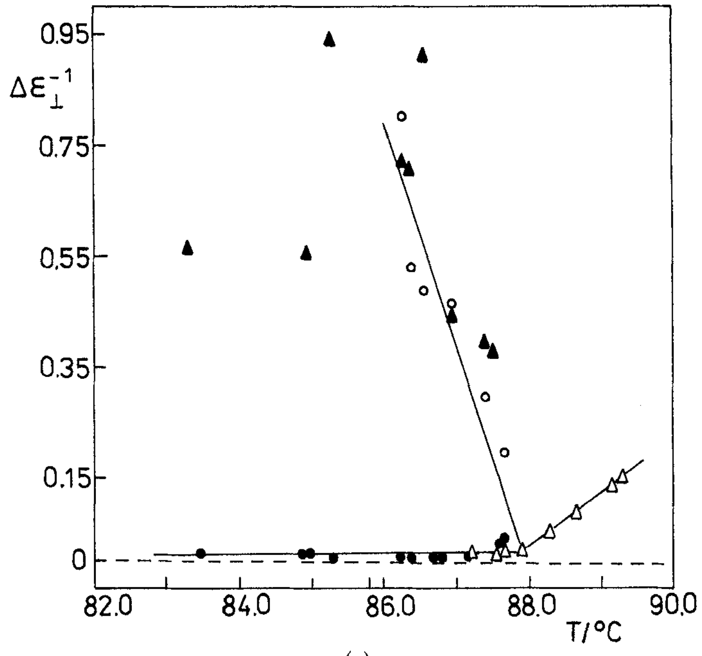


Figure 3. Dielectric spectrum obtained for the S_A^* phase. (*a*) Dispersion and absorption curves; (*b*) Cole–Cole plot of SM spectrum. $T=89.94°\mathrm{C}$, $\varepsilon_\infty=3.206$, $\alpha_s=0.002$, $\tau_s=4.76\times10^{-7}$ s, $\varepsilon_0=10.442$.

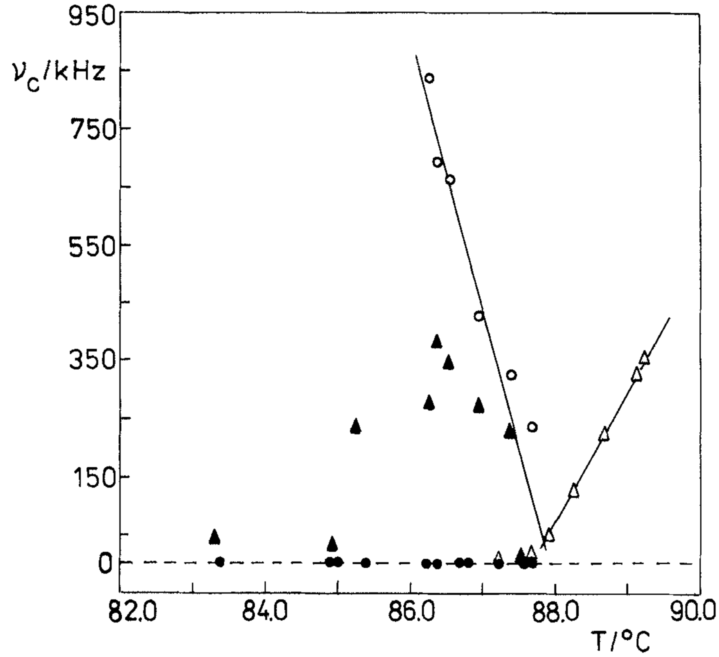
predicted by the theory. The points obtained for the soft mode show linear behaviour on both sides of the S_C^*–S_A^* transition and the slope ratio of the straight lines equals -4.14. As it is known from the Blinc and Žekš theory this ratio should amount to -2. Such a big discrepancy between the theoretical and experimental values is mostly caused by overlapping of the soft mode and domain mode at 10 V bias field.

Figure 4 (*b*) presents the temperature dependence of the critical frequencies obtained for the soft mode and Goldstone mode by fitting equations (2 *a*) and (2 *b*) to the experimental data obtained with the ITO-EHC cell. It can be clearly seen that the Goldstone mode critical frequency is also temperature independent in the S_C^* phase. The soft mode behaves also according to the Blinc and Žekš theory. The slope ratio of the straight lines is in this equal to -2.1, which is in very good agreement with the theoretical value. So, the difficulties connected with splitting the soft mode and domain mode do not influence the critical frequencies so much.

Figures 5 (*a*) and (*b*) present the same kind of dependencies as figures 4 (*a*) and (*b*) but the experimental data were in this case obtained with gold coated electrodes. The measurements for the Goldstone mode were performed at zero bias field. The soft mode

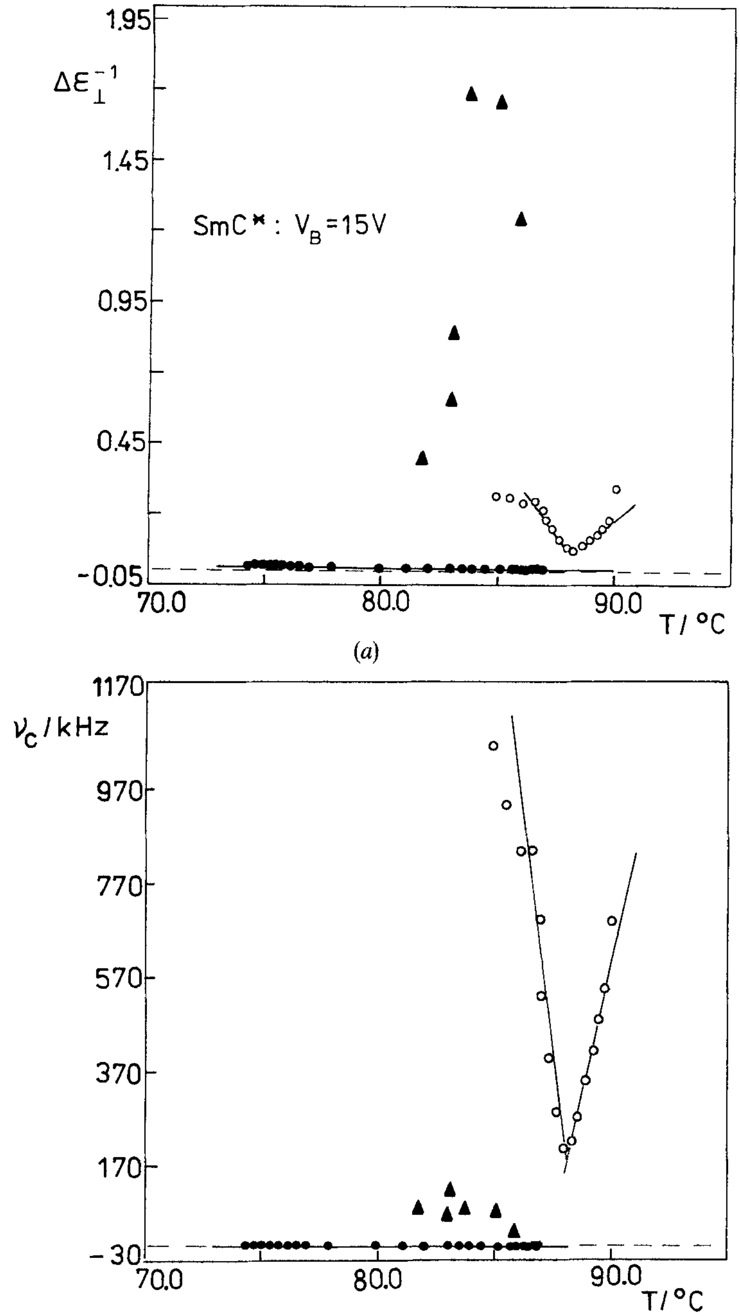


(*a*)



(*b*)

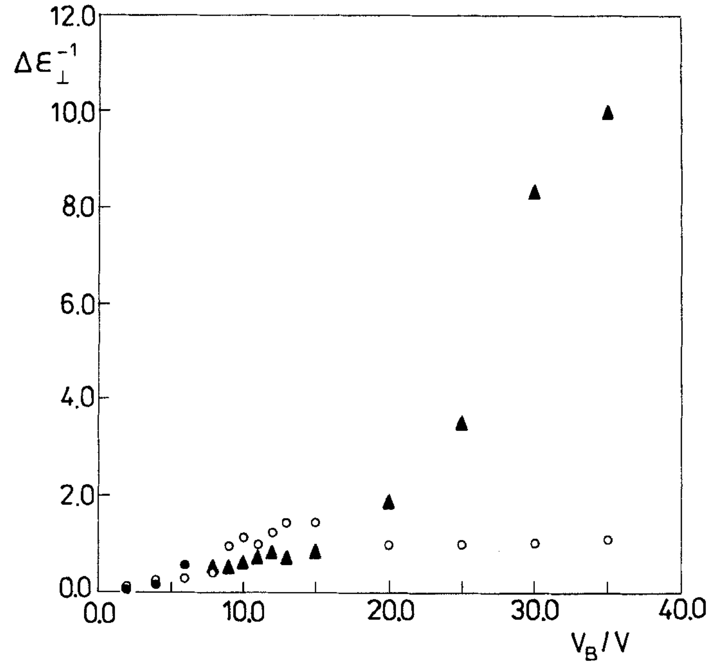
Figure 4. (*a*) Inverses of dielectric increments obtained for three dielectric modes. The data were obtained with the EHC cell. (*b*) Relaxation frequencies versus temperature for three dielectric modes observed for the substance under investigation. The data were obtained with the EHC cell. ▲, Domain mode; ●, Goldstone mode; ○, soft mode ($V_B = 10$ V); △, soft mode ($V_B = 0$ V).



(a)

(b)

Figure 5. (a) Inverses of the dielectric increments obtained for three dielectric modes observed with gold coated electrodes. (b) The temperature dependencies of the relaxation frequencies for the domain mode, Goldstone mode and soft mode. The data were obtained with gold coated electrodes. ▲, Domain mode; ●, Goldstone mode; ○, soft mode ($V_B = 10$ V).



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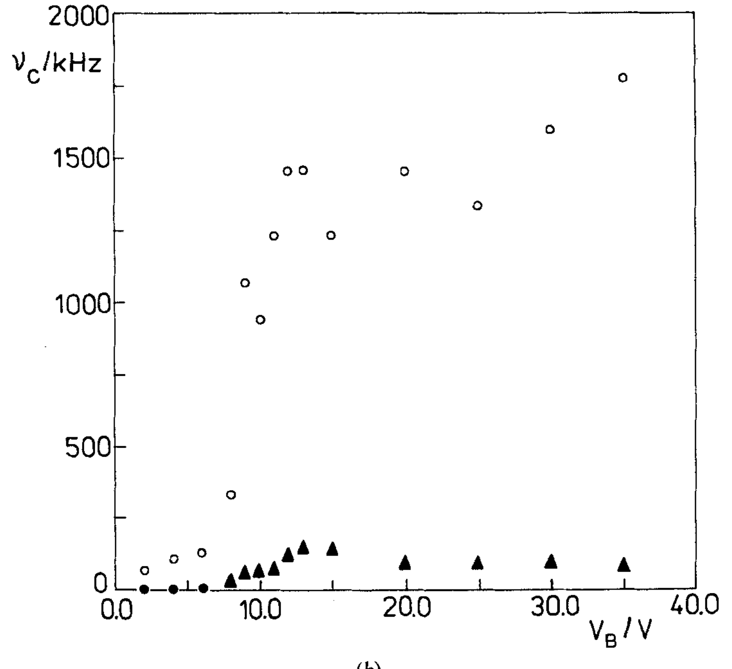

(*b*)

Figure 6. (*a*) The inverses of the dielectric increments as functions of bias fields for three collective modes: GM, SM and DM. ▲, Domain mode; ●, Goldstone mode; ○, soft mode. $T = 83°C$. (*b*) Bias field dependence of the relaxation frequencies for the GM, SM and DM.

data was obtained at $V_B = 10$ V. The slope ratio calculated for the data seen in figures 5 (*a*) and (*b*) are $-1{\cdot}62$ and $-1{\cdot}73$, respectively. Both values are by 25 per cent greater than the theoretical ones. We should explain that the data presented in this paper are in rather good agreement with the theory which is in contrast to the data acquired for the other systems [4, 9].

The domain mode exists in the S_C^* phase only. Its critical frequency depends on temperature; in the low temperature range it increases and then decreases with temperature upon approaching T_C. The bias field also influences the soft mode dielectric parameters. In figure 6 (*b*) the soft mode critical frequencies are presented as functions of the bias field, It can be seen that ν_C^S distinctly increases with the bias field. We should notice that the domain mode dielectric parameters are also bias field dependent. It can be seen that the domain mode shows up at a certain bias field ($V_B = 8$ V) and at higher voltages it slightly increases and eventually it becomes a constant. At the same time, the dielectric increment of the soft mode also decreases (see figure 6 (*a*)) whereas its critical frequency increases with bias field (see figure 6 *b*)) as was found before for other systems [6].

4. Conclusions

(1) The dielectric spectrum for the S_C^* ferroelectric phase consists of at least three collective modes: the Goldstone mode, the soft mode and the domain mode. Soft mode dielectric spectrum is a single relaxation process in the S_A^* phase. In the S_C^* phase it is also a Debye-type process provided it has been properly isolated from the low frequency contribution to the whole spectrum.

(2) The critical frequency of the Goldstone mode is temperature independent in the S_C^* phase, which means that in this case we are dealing with a non-activated process. The soft mode relaxation frequency and dielectric increments depend linearly on temperature in the vicinity of the S_C^*–S_A^* transition.

(3) The temperature dependencies of the critical frequencies and the dielectric increments of both soft mode and Goldstone mode confirm the theory worked out by Blinc and Žekš.

(4) The existence of the domain mode disturbs the soft mode spectrum, which is not easy to isolate at lower bias field. The domain mode spectrum shows up at high bias field and it may result from an interaction between the bias field and local polarization vector.

(5) The dielectric parameters of the modes observed are strongly dependent on the bias field. This means that physical properties of ferroelectric cells can be modified for practical purposes.

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