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Elastic constants at the smectic A-crystalline smectic B phase transition of the compound 5O.8

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We measured the velocity and absorption of the longitudinal sound waves in different phases of the compound 5O.8 at 2 MHz. Attention is given particularly to the smectic A-crystalline smectic B phase transition. We found that the jumps in the elastic constants at this transition are: $\Delta C_{11} > 0$, $\Delta C_{33} > 0$ and $\Delta C_{13} < 0$. The velocity anisotropy reverses its sign throughout this transition. Concerning the absorption, we found, in addition to an anomalous peak at this transition temperature, a broad maximum in the crystalline smectic B phase which was interpreted as due to the Landau-Khalatnikov mechanism, for which the relaxation time is anisotropic. We present a Landau type free energy, which includes a new term linear in the order parameter and quadratic in the strain field, in order to account qualitatively for the results.

1. Introduction

Although the nematic-isotropic (NI) [1], smectic A-nematic ($S_A N$) [2] and the smectic C-smectic A ($S_C S_A$) [3, 4] phase transitions have been the subject of intense study, there are very few [5] concerning the smectic B-smectic A ($S_B S_A$) phase transition. This motivates us to undertake ultrasonic studies of this transition. There are two kinds of smectic B phases: the crystalline smectic B [6] and the hexatic smectic B [7]. Our case here examines the crystalline smectic B and we shall refer to it, hereafter, as smectic B (S_B).

Ultrasound measurements at the NI transition show a downward bend of the velocity (dip) and a nonsymmetric sharp peak of absorption in the vicinity of the transition [8]. In spite of the great amount of theoretical and experimental work done on the $S_A N$ transition, its real nature is still controversial [2].

Ultrasonic measurements throughout the $S_A N$ transition show the same effects as in the NI transition with the additional appearance of velocity anisotropy in the smectic A phase [9, 10]. The $S_C S_A$ transition was found to have similar features with a downward bend of the velocity when approaching the transition temperature from above [3]. Another feature of this transition is the reverse of the sign of the velocity anisotropy [3].

As already mentioned, very few works have examined the $S_B S_A$ transition. To the best of our knowledge, only one work was carried out on this transition using the ultrasonic technique [11]. The results are inconclusive bearing in mind that they were analysed in the framework of the two dimensional melting theory [12]. Instead, it is well established now that this transition is a first order [13] phase transition to a true

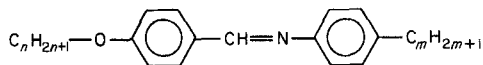
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crystalline phase with three dimensional order [6] and with the possibility of shear wave propagation at low frequencies [14]. The shear elastic constant, C_{44} , in this smectic B phase is five orders of magnitude smaller than the other elastic constants. This shows that the smectic B phase corresponds to a very soft crystal. The dielectric studies [15], which show that the molecules are mobile in this phase, are in agreement with the soft nature of this phase.

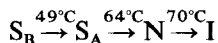
In this paper we present the results obtained from ultrasonic measurements of sound velocity and absorption in different phases of the compound 5O.8 at 2 MHz frequency. We shall emphasize here only the $S_B S_A$ transition aspects at a frequency of 2 MHz. Moreover, a Landau type free energy, to account qualitatively for some of the results, will be developed.

2. Experimental

The material used in the present investigation is 4-*n*-pentoxybenzylidene-4'-*n*-octylaniline or 5O.8 which belongs to the family of compounds: *N*-(4-*n*-alkoxybenzylidene)-4'-alkylanilines or in short *nO.m*. These compounds have the following general chemical structure:



They have a true crystalline structure [6] in the smectic B phase. For our compound 5O.8, we found the following transition temperatures:



The ultrasonic measurements were performed at a frequency of 2 MHz, by the standard echo technique and the phase difference method (for more details see [16]). Since the absorption is relatively large, we observed only the transmitted pulse, the echos being too small to get a reliable value of the absorption. The sample was slowly cooled from the isotropic phase at a rate of 5 min/ $^\circ\text{C}$ in a magnetic field of 10 kg which was sufficient for the sample alignment. Each cooling run was performed with fixed angle θ , between the magnetic field direction and the wave vector. By making cooling runs at different angles, we were able to measure the relative absorption, $\alpha(\theta)$, and the velocity, $V(\theta)$, simultaneously, as a function of θ .

3. Results and discussion

The variation of the velocity V with temperature T at 2 MHz is shown in figure 1. V_{\parallel} and V_{\perp} are the velocities when the wave vector is parallel and perpendicular to the director respectively. In this figure we observe the well known features of the NI (a dip in the velocity) and the $S_A N$ (appearance of the velocity anisotropy) phase transitions. The downward bend of the velocity in the smectic A when approaching the $S_B S_A$ transition temperature from above is, probably due to order parameter fluctuations [4]. At the $S_B S_A$ transition there are relatively large jumps in the velocities in the two directions; this characterizes a solid-fluid phase transition and moreover, the velocity anisotropy sign is reversed throughout the transition. This reversed anisotropy increases as the temperature decreases in the smectic B phase. In the vicinity of the $S_B S_A$ transition there is a range of coexistence of the two phases as expected for a first order phase transition. This coexistence range is about 1°C in accordance with previous X-ray measurements [5]. The experimental data belonging to this region were omitted. In

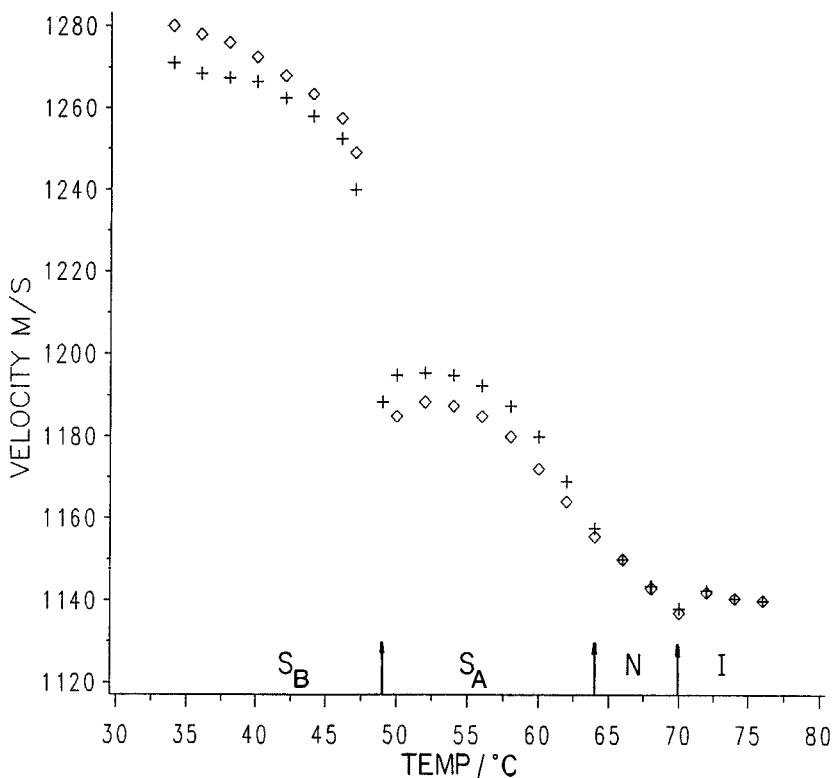


Figure 1. Sound velocity versus temperature at 2 MHz in the two main directions, (+) $\theta = 0^\circ$ and (\diamond) $\theta = 90^\circ$.

the smectic B phase we see that the velocity in both directions is about half of that found in the glass phase of glycerol [17]. This fact reflects the soft nature of this crystalline phase.

In figure 2 we show the temperature dependence of the relative absorption at $\theta = 0^\circ$, $\theta = 60^\circ$ and $\theta = 90^\circ$ directions. Concerning the $S_B S_A$ transition, we observe a small anomalous peak at the transition temperature. We think that this results from the order parameter fluctuations, since it is also observed at high frequencies, and this is in accordance with the bend in the velocities already mentioned. In addition, we notice another broad peak deep in the smectic B phase. The maximum of this broad peak occurs at different temperatures depending on the direction of propagation with respect to the director. The temperature at which this broad maximum occurs as a function of the angle θ is shown in figure 3. We believe that this anomalous absorption is due to the Landau-Khalatnikov [18] mechanism which results from the order parameter relaxation, since it appears in the smectic B phase only. Figure 3 reflects the anisotropy in the relaxation time of the order parameter in the smectic B phase.

In figure 4 we show the variation of the velocity with the angle θ between the wave vector and the symmetry axis at two temperatures in the smectic A and the smectic B phases. From this figure, we observe that the two curves have different shapes. Two main differences between the smectic A and the smectic B phases should be noticed here. Firstly, the velocity anisotropy $\Delta V = V_{\parallel} - V_{\perp}$ is positive in the smectic A while it is

negative in the smectic B phase. This is in agreement with previously reported results [11]. Secondly, the velocity anisotropy is larger in the smectic B than in the smectic A phase. The lines drawn are obtained from least squares fits to the data using the following equation [19]

$$V^2(\theta) = A - 2C \cos^2(\theta) + B \cos^4(\theta), \tag{1}$$

where $V(\theta)$ is the velocity at angle θ and A, B and C are the de Gennes elastic coefficients defined as

$$A = C_{11}/\rho, \quad B = (C_{11} + C_{33} - 2C_{13})/\rho, \quad C = (C_{11} - C_{13})/\rho. \tag{2}$$

Here, C_{ij} are the proper elastic tensor components and ρ is the density. Equation (1) is appropriate for the uniaxial symmetry, assuming small anisotropy ($C_{11} \simeq C_{13} \simeq C_{33}$) and $C_{44} = 0$. The fits of the data to equation (1) is very good so that the results are consistent with the symmetry of the two phases.

Figure 5 shows the temperature dependence of the elastic constants C_{11}, C_{13} and C_{33} . These were obtained, using equation (2), from least squares fits of the data with equation (1). From this figure we see that there are discontinuous jumps in C_{ij} at the $S_B S_A$ phase transition temperature, T_C . Here $\Delta C_{11} > 0, \Delta C_{33} > 0$ while $\Delta C_{13} < 0$, where we define $\Delta C_{ij} \equiv C_{ij}(T_C^-) - C_{ij}(T_C^+)$. These different signs of ΔC_{ij} have never been reported before, where at phase transitions negative ΔC_{ij} were generally found [20].

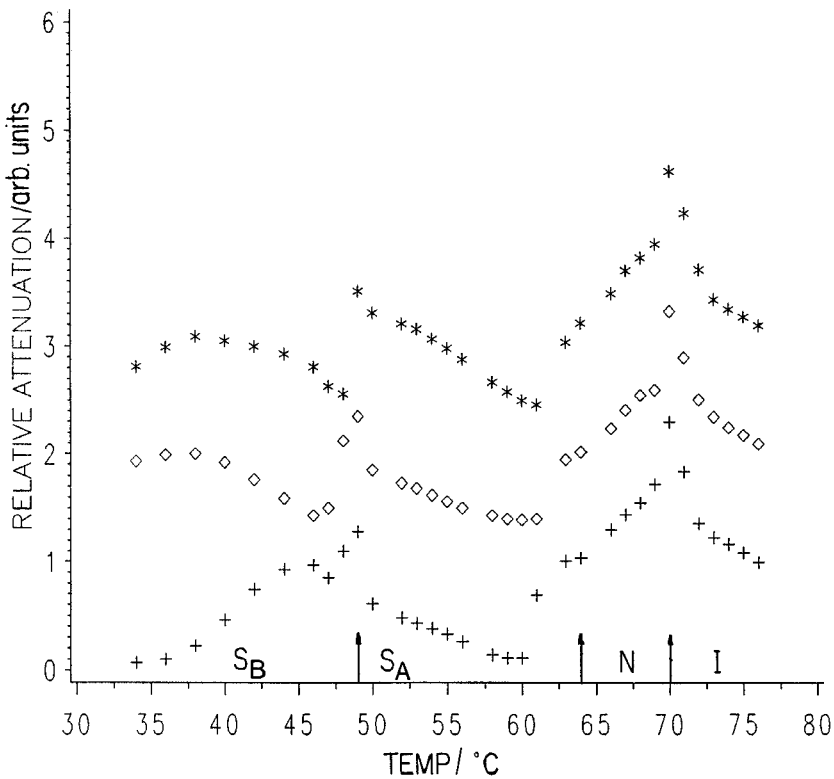


Figure 2. The relative absorption in the (*) $\theta = 0^\circ$, (\diamond) $\theta = 60^\circ$ and (+) $\theta = 90^\circ$ directions versus temperature T (the curves are displaced parallel to the relative attenuation axis).

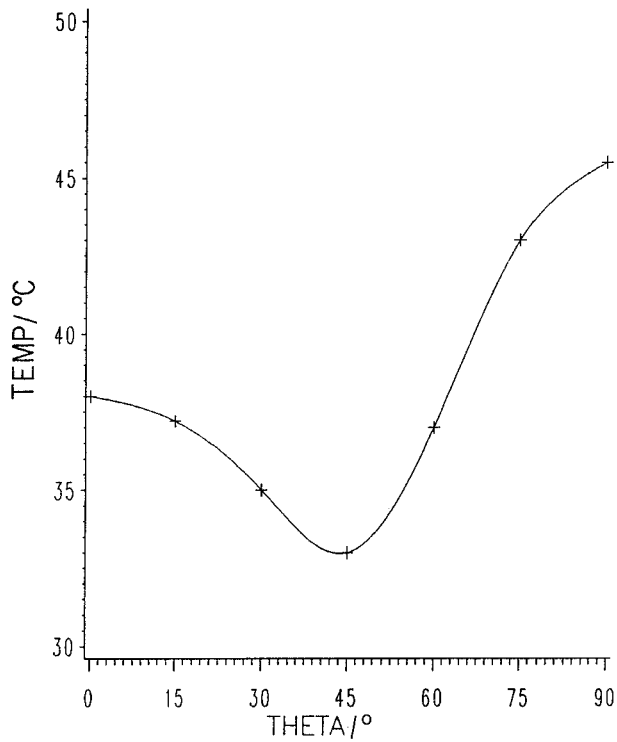


Figure 3. The temperature at which the maximum of the broad peak, due to the Landau-Khalatnikov mechanism, occurs versus θ .

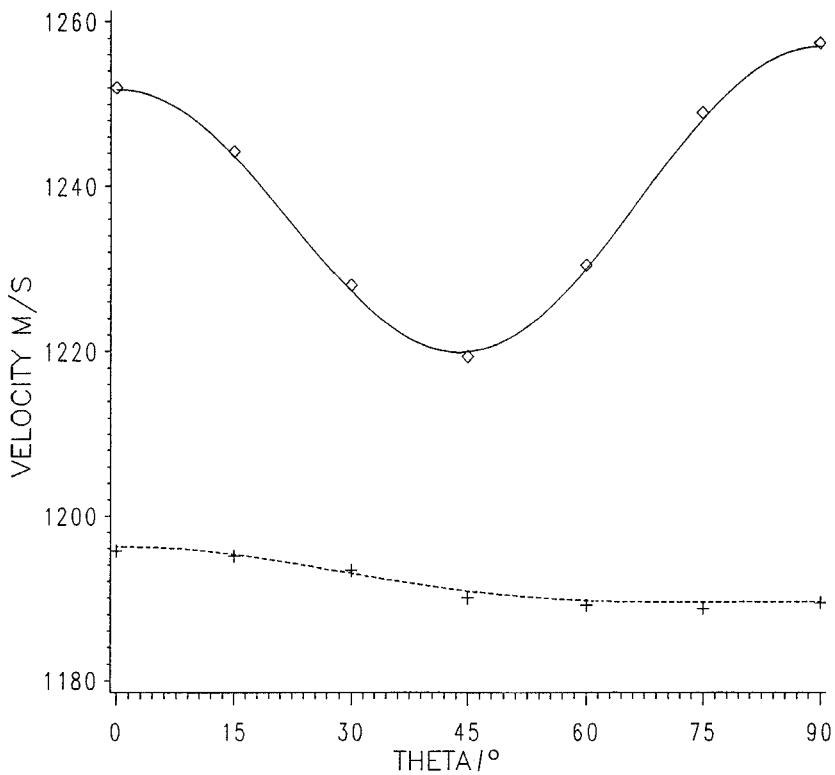


Figure 4. Velocity versus θ , for two temperatures: (+) 53°C (S_A) and (◇) 46°C (S_B).

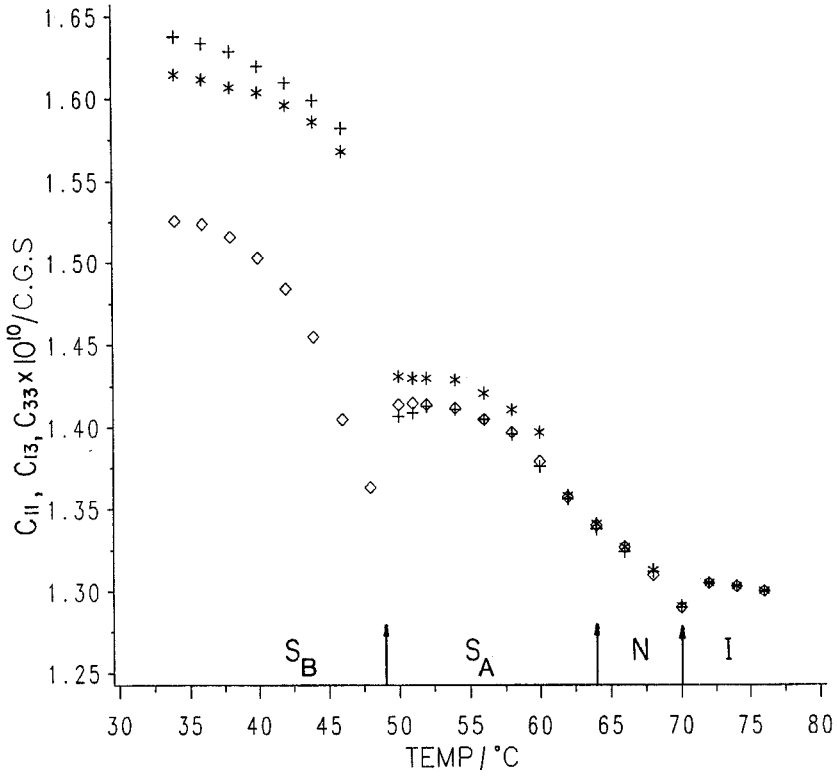


Figure 5. The measured elastic constants: (+) C_{11} , (◇) C_{13} , (★) C_{33} versus temperature.

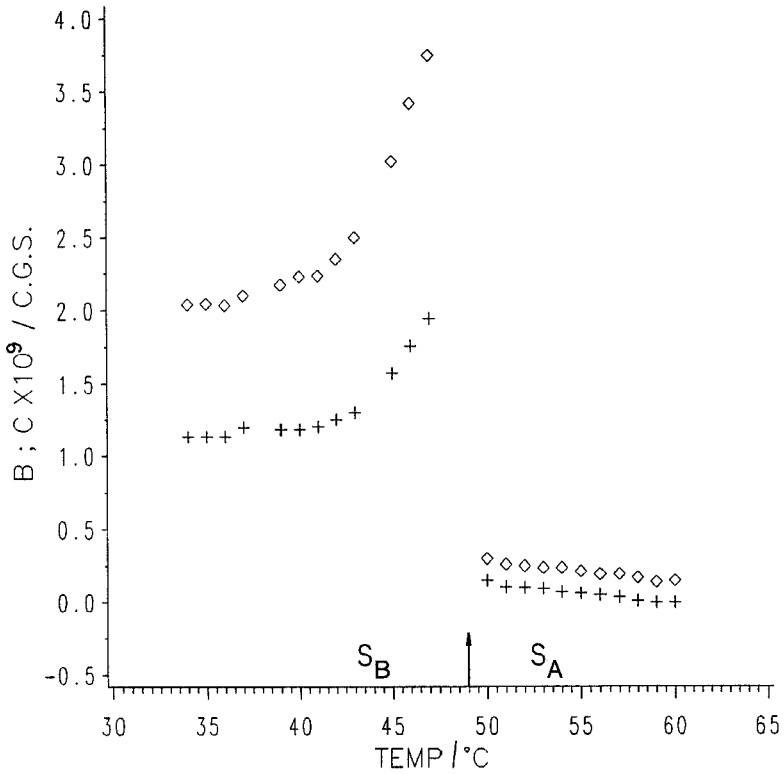


Figure 6. The de Gennes elastic constants B and C versus temperature.

Figure 6 shows the temperature dependence of the de Gennes elastic coefficients B and C . In the smectic A phase B and C increase gradually as the temperature decreases in accordance with previously reported works [10]. In the coexistence region there is a large jump in these coefficients. However, in the smectic B phase B and C , unexpectedly, decrease as the temperature decreases causing an unusual apparent softening of the sample as the temperature decreases. We shall come to this point later.

Returning to the discontinuous jumps in C_{ij} , we think that they result from the discontinuity in the static order parameter at the $S_B S_A$ transition temperature. To see this we propose a Landau type free energy of the form

$$F = F_1(\eta) + F_2(\chi_1, \chi_2, \chi_3) + F_3(\eta, \chi_1, \chi_2, \chi_3), \quad (3)$$

where η is the order parameter, χ_i ($i = 1, 2, 3$) represents the strain field components and the third axis is the symmetry axis. $F_1(\eta)$ is the Landau type free energy for the first order phase transition given by

$$F_1(\eta) = \frac{1}{2}\epsilon\eta^2 + \frac{1}{3}\beta\eta^3 + \frac{1}{4}\gamma\eta^4 + \frac{1}{5}\delta\eta^5 + \frac{1}{6}\lambda\eta^6, \quad (4)$$

where, $\epsilon = \epsilon_0(T - T_C)$ and β , γ and δ are constants. The η^3 and η^5 terms are allowed in solid-liquid phase transitions [21] while the η^6 term is necessary in order to have a stable solution [22]. F_2 is the ordinary elastic part given by

$$F_2 = \frac{1}{2}C_{11}(\chi_1 + \chi_2)^2 + \frac{1}{2}C_{33}\chi_3^2 + C_{13}(\chi_1 + \chi_2)\chi_3. \quad (5)$$

F_3 accounts for the coupling between the strain field and the order parameter. We suggest the following form which includes two kinds of couplings

$$F_3 = D_1(\chi_1 + \chi_2)\eta^2 + D_2\chi_3\eta^2 + E_1(\chi_1 + \chi_2)^2\eta + E_2\chi_3^2\eta + E_3(\chi_1 + \chi_2)\chi_3\eta. \quad (6)$$

The terms proportional to E_i ($i = 1, 2, 3$) (with coupling quadratic in strain field) are less familiar but allowed by symmetry considerations. Making the general minimization procedure of the total free energy, we get the isothermal elastic constants

$$C_{ij} = \frac{\partial^2 F_2}{\partial \chi_i \partial \chi_j} + \frac{\partial^2 F_3}{\partial \chi_i \partial \chi_j} - \frac{\partial^2 F_3}{\partial \chi_i \partial \eta} \frac{\partial^2 F_3}{\partial \chi_j \partial \eta} \left(\frac{\partial^2 F}{\partial \eta^2} \right)^{-1}; \quad C_{ij} \equiv \frac{\partial^2 F}{\partial \chi_i \partial \chi_j}. \quad (7)$$

For simplicity we use a one dimensional model obtained by omitting the indices, thus we may write the renormalized elastic constant in this case C^* , as

$$C^* = C_0 + 2E_\eta - \frac{\eta(2DC_0 + 2ED\eta)^2}{\mathcal{F}}, \quad (8)$$

where

$$\mathcal{F} = \beta C_0^2 + (2\gamma C_0^2 + 4C_0\beta E)\eta + (4E^2\beta + 8EC_0\gamma + 3C_0^2\delta - ED^2)\eta^2 + (8E^2\gamma + 12EC_0\delta + 4\lambda C_0^2)\eta^3 + (12E^2\delta + 16\lambda E)\eta^4 + 16E^2\lambda\eta^5.$$

C_0 is the bare elastic constant and β , γ and δ are defined in equation (4). To get C_{ij} (instead of C^*), one has to replace E and D that appear in equation (8) with the proper coefficients that appear in equation (6).

Figure 7 shows the variation of C^* with the normalized order parameter $\eta_n \equiv \eta/\eta_C$ (η_C is the value of the order parameter at the $S_B S_A$ transition), for three different values of E ($E = 0.31, 0.80, 1.50$) keeping the other constants at the same fixed values ($\lambda = 0, -\beta = \gamma = \delta = D = C_0 = 1.0$). The discontinuity in the static order parameter at the transition temperature results in a discontinuous jump up or down in C^* according to

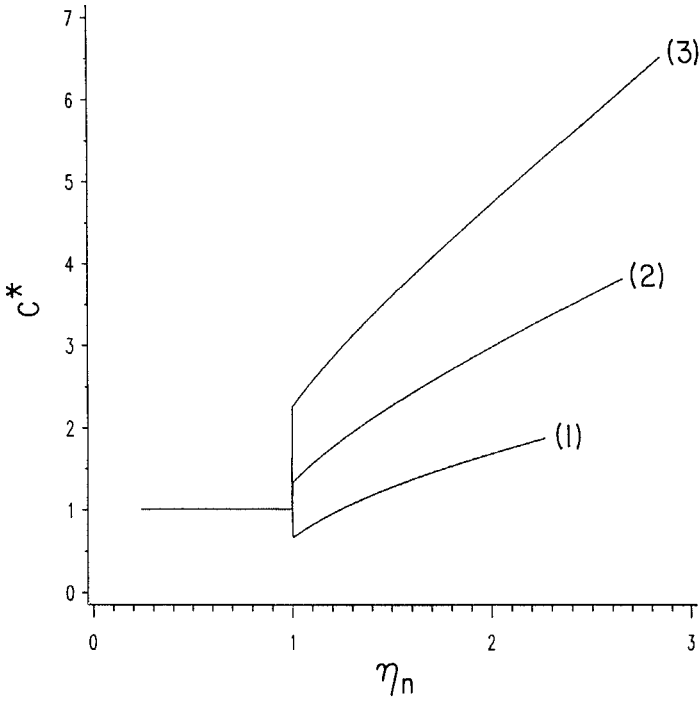


Figure 7. The elastic constants, C^* , versus the normalized order parameter $\eta_n \equiv \eta/\eta_c$ (η_c is the value of the order parameter at the $S_B S_A$ transition), predicted from a Landau type free energy for different values of E (see text): (1) $E = 0.31$, (2) $E = 0.80$ and (3) $E = 1.50$. To see the temperature dependence of C^* notice that η_n increases as T decreases.

the value of E . For the stated fixed values we found that for $E > 0.56$ $\Delta C^* > 0$ while for $E < 0.56$ $\Delta C^* < 0$. This behaviour shows the necessity of the coupling terms quadratic in strain field (see equation (6)) in order to have a case with $\Delta C_{ij} < 0$ or $\Delta C_{ij} > 0$. It is important to note that the Landau theory used here is a mean field one which corresponds to the case $\omega\tau \ll 1$ (far from the phase transition), where ω is the frequency of the applied harmonic sound wave and τ is the relaxation time. However, near the phase transition $\omega\tau \gg 1$. Because of the inequality [20]

$$\Delta C(\omega\tau = \infty) > \Delta C(\omega\tau = 0),$$

the measured $\Delta C_{ij} < 0(\omega\tau \rightarrow \infty)$ should correspond to the calculated $\Delta C^* < 0(\omega\tau \rightarrow 0, E < 0.56)$ while for the measured $\Delta C_{ij} > 0(\omega\tau \rightarrow \infty)$ the two calculated possibilities $\Delta C^* < 0$ or $\Delta C^* > 0$ could occur, and they correspond to $E < 0.56$ or $E > 0.56(\omega\tau \rightarrow 0)$ respectively. Consequently, the calculated jumps in C^* shown in figure 7 cover all the measured cases shown in figure 5.

Now, to obtain the temperature dependence of C^* we first have to solve numerically for $\eta(T)$ (to do so, one has to first find the solution $\eta \neq 0$ which minimizes the total free energy at each temperature and then to compute C^* for this temperature using the corresponding value of η found). This is not necessary for our purpose since we are mainly interested in ΔC_{ij} . However, $C^*(T)$ should have similar shape as shown in figure 7, but its value increases as the temperature decreases in the smectic B phase since C^* increases as η increases, while η increases as the temperature decreases.

Using equation (2), the temperature dependence of the elastic coefficients B and C in the smectic B phase could be calculated from the temperature dependence of C_{11} , C_{13} and C_{33} shown in figure 7. B and C calculated in this way have similar shapes to the corresponding experimental ones shown in figure 6. In spite of this similarity, based on static mean field arguments, we believe that this is not the case here but that the dynamics is responsible. To see this, we note that C_{ij} given by figure 7 represents the isothermal mean field values that are applicable far from the phase transition where $\omega\tau \ll 1$. On the other hand, the dynamics manifests itself through the absorption given in figure 2 and the anisotropy of the relaxation time of the order parameter observed in figure 3. To account qualitatively for the dynamical effects, we notice that increasing the frequency of the sound waves generally increases the hardness of the system. Assuming a single relaxation process with a time constant τ_B , we may write for the elastic coefficient B , which expresses the stiffness of the smectic layers [20]

$$B(\omega) = B(\omega = \infty) - \frac{B(\omega = \infty) - B(\omega = 0)}{1 + (\omega\tau_B)^2}. \quad (9)$$

Thus, passing from near the $S_B S_A$ phase transition, where $\omega\tau_B \gg 1$, to the region, where $\omega\tau_B \ll 1$, (in the smectic B phase) will decrease the hardness of the system. This explains, qualitatively, the apparent softening of the B coefficient. The same argument should work for the elastic coefficient C .

In conclusion, we measured discontinuous jumps in the elastic constants, $\Delta C_{11} > 0$, $\Delta C_{33} > 0$ and $\Delta C_{13} < 0$ through the $S_B S_A$ phase transition. Using a Landau type free energy, we found that these jumps can result from a coupling of the strain field to the order parameter in different ways at the transition temperature. The new coupling term, quadratic in the strain field and linear in the order parameter, is necessary in order to have $\Delta C_{ij} > 0$ or $\Delta C_{ij} < 0$. Moreover, we suggest that the apparent softening of the system results, at least in part, from the dynamics of the $S_B S_A$ phase transition. For the attenuation of sound waves, we found a sharp peak at the transition temperature which results from the fluctuations of the order parameter and a broad maximum deep in the smectic B phase which is thought to be due to the Landau-Khalatnikov mechanism. The relaxation time τ is found to be anisotropic in the smectic B phase. The different signs of ΔV in the smectic A and smectic B phases uncover the qualitatively different molecular interactions in the two phases. Studies at higher frequencies and by Brillouin scattering are currently being performed and will be the subject of another publication.

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