Abnormal Behavior of Sound Velocity and Damping in the Vicinity of the Smectic-*A* –Smectic-*C* Transition in Terephthal-*bis*-*p*-*p*′-Butylaniline (TBBA)

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Sound velocity and damping measurements, taken at various angles θ between the normal to the smectic layers and the sound propagation direction, are reported for TBBA near its Sm*A*-Sm*C* transition. Both velocity and damping present marked pretransitional anisotropic effects above T_{AC}. The anisotropy of the transition also manifests itself on the positions of the damping peaks of which that for $\theta = 0°$ moves towards low temperatures as the frequency increases, whereas no displacement is observed for $0 = 45°$ and $90°$. The results are compared with the predictions of the current theories.

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Although the Sm*A*-Sm*C* transition has been widely studied in recent years, and with contradictory results as to its exact nature[1] (3D *XY*, or extended mean field), little work has been done on the dynamic behavior of this transition. More especially, ultrasound methods, which supply important information on phase-transition dynamics, have rarely been applied. However, one study,[2] carried out on $\bar{8}$S5 (4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate), has shown that velocity and damping anomalies occur *below* T_{AC}, which indicates that the dynamics of the transition in this compound is of the mean-field type.

In this Letter, we present a detailed study of the ultrasound velocity and damping behavior in the vicinity of the Sm*A*-Sm*C* transition in TBBA. The key result of this research is the fact that both velocity and damping present marked pretransitional effects *above* T_{AC}. The magnitude of these effects is a function of the angle θ between the sound propagation direction and the normal to the smectic layers. The anisotropy of the transition can also be observed in the positions of the damping peaks, of which the one for $\theta = 0°$ moves towards lower temperatures as the frequency increases, whereas their positions for $\theta = 45°$ and $90°$ do not move throughout the same frequency range. Analysis of the velocity measurements shows that the elastic constant B is higher than the elastic constant C in the Sm*A* phase, and that $B < C$ in the Sm*C* phase. This inversion of the B/C ratio, observed here for the first time, is also a direct consequence of the high degree of anisotropy of the transition. The Andereck and Swift (AS) fluctuation theory[3] explains all our observations above T_{AC} more satisfactorily than Liu's relaxation theory.[4] It is, however, possible that the AS theory is not efficient since recent results obtained on the same compound have shown that the specific heat does not appear to display any pretransitional effects above T_{AC},[5] and this is contrary to the theory's prediction.

The experiments were carried out with use of resonance and pulse techniques, with 3-MHz quartz crystals. The resonance technique has the advantage of being able to measure at the same time both damping and velocity in the megahertz range in which classic pulse techniques are known to be difficult to apply. The pulse device allowed the damping measurements to be extended to higher frequencies, i.e., 9, 15, 21, 27, and 33 MHz, and, by means of a simple switch, it was possible to take pulse and resonance measurements on the same cell. This enabled a significant comparison to be made between the two types of measurements, thus taken on the same sample.

These measurements were taken for the three orientations defined by $\theta = 0°$, $45°$, and $90°$. The Sm*A* phase samples for a given θ were prepared by our heating the compound into the nematic phase, and then cooling it gently in the presence of a 10-kG magnetic field. The Sm*C* phase samples were obtained by our switching off the magnetic field a few degrees before the compound was due to pass into the Sm*C* phase. These samples have randomly oriented molecules, but they do have a lamellar structure, as proven by the velocity measurements, which show marked anisotropy, as in the Sm*A* phase.

A fresh sample was used for each angle θ, and the measurements were taken under an inert atmosphere so as to avoid sample deterioration, which was always very slight, as can be seen from the high transition temperatures of the various samples studied (between 171 and 172° C). Temperature was controlled to within ±0.01 °C. A detailed description of the experimental method, the cell, and the precautions taken in order to guarantee a high degree of sample purity throughout the experiment are presented by Collin, Gallani, and Martinoty.[6,7]

Before presenting and discussing our results, we shall briefly review the ultrasound theories currently available. It is predicted that damping is the sum of two contributing factors. The first, coming from Sm*C* order-parameter fluctuations, was calculated for $T > T_{AC}$ by Andereck and Swift[3] (AS), who introduced into the free energy terms which couple the order parameter to the density variation (coupling constant γ_ρ) and to the layer-spacing gradient (coupling constant γ_u). AS predict that the critical effects on velocity and damping can be extremely anisotropic, the degree of anisotropy depending on the γ_u/γ_ρ ratio. Their calculation also predicts that α scales as $f^2(T-T_{AC})^{-(\bar{\alpha}+z\nu)}$ in the low-frequency regime, and as $(T-T_{AC})^{-2\bar{\alpha}}f^{1+\bar{\alpha}/z\nu}$ in the high-frequency regime. $\bar{\alpha}$ is the exponent of the specific heat and $z\nu$ that of the relaxation time τ of the order parameter $[\tau \sim (T-T_{AC})^{-z\nu}]$. Another interesting prediction states that the velocity V scales as $(T-T_{AC})^{-\bar{\alpha}}$; the behavior of V should therefore reflect that of the specific heat.

In addition to the contribution of the order-parameter fluctuations, which must occur on either side of the transition,[8] there also exists the so-called Landau-Khalatnikov contribution, coming from the relaxation of the order-parameter modulus.[9] The damping associated with this mechanism is given by

$$\alpha = \frac{V^2(\infty)-V^2(0)}{2V^3(0)}\,\frac{\omega^2\tau}{1+\omega^2\tau^2}, \tag{1}$$

where $V(\infty)$ and $V(0)$ are the high-frequency $(\omega\tau \gg 1)$ and low-frequency $(\omega\tau \ll 1)$ velocity limits. According to Eq. (1), α reaches its maximum $\alpha_{\max}$ when $\omega\tau=1$; $\alpha_{\max}$ scales as ω; and $\alpha_{\max}$ moves towards low temperatures as frequency increases.

The Landau-Khalatnikov mechanism appears in the low-temperature phase, where the mean value of the order parameter is nonzero. However, Liu[4] has pointed out that this mechanism should also appear in the high-temperature phase of the nematic–smectic-*A* and Sm*A*-Sm*C* transitions, as a result of a dynamic coupling, assumed to exist above the transition temperature, between the order-parameter and the hydrodynamic variables. Ultrasound damping and velocity could therefore present critical effects above the Sm*A*-Sm*C* transition, even when this transition is of the Landau type (no fluctuations). Liu's calculation shows that the strength of the relaxation is expressed as a function of the transport coefficients associated with the dynamic coupling mentioned above. This calculation does not, however, give any explicit information on the thermal variation of the relaxation strength, but does indicate that it is a function of the angle θ, which shows that the contribution of the relaxation, like that of the fluctuations, is anisotropic. One point of divergence between these two theories is high-frequency behavior, since Eq. (1) (valid for all frequencies) predicts that α is frequency independent, whereas the contribution of fluctuations gives $\alpha \sim f^{1+\bar{\alpha}/z\nu}$.

Figure 1 shows characteristic results of the behavior of ultrasound damping in the vicinity of the Sm*A*-Sm*C* transition. α/f^2 can be seen to present marked pretransitional effects on either side of the transition, effects which are anisotropic and which reach their maximum when $\theta=0°$. Figure 2 shows that velocity also presents pretransitional effects. These occur essentially in the Sm*A* phase, where velocity decreases as $T \rightarrow T_{AC}$, and, as with the damping, are much more marked for $\theta=0°$ than for $\theta=45°$ or $90°$. This anisotropy of the critical effects can be explained by both the Liu theory and the AS theory when $\gamma_u > \gamma_\rho$.

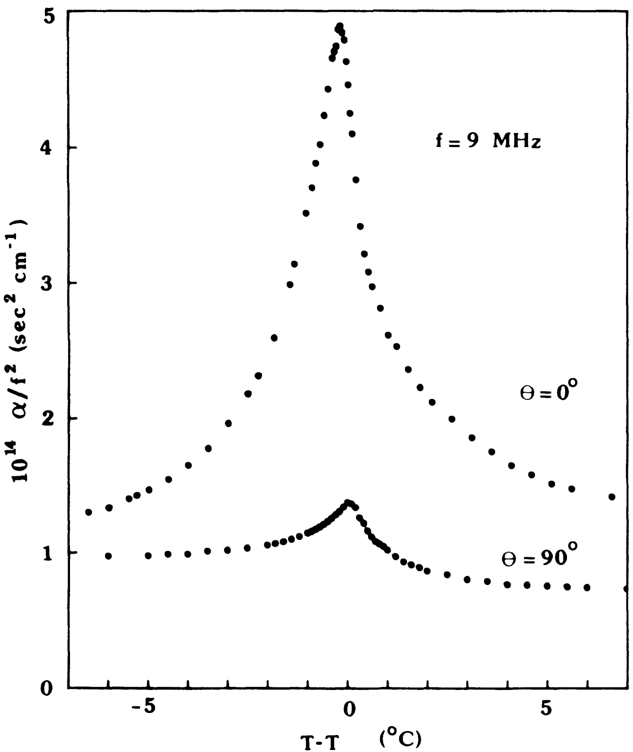

FIG. 1. Comparison between results for $\theta=0°$ and $90°$, showing that the critical effects on damping are anisotropic.

Analysis of the velocity measurements with use of the formula

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

allows the elastic constants A, B, and C of the compound to be determined, as well as the thermal variation of these constants. This analysis shows that B falls sharply in the Sm*A* phase when $T \rightarrow T_{AC}$, that this decrease is less marked for C, and that it is hardly visible in the case of A. This relative behavior of the elastic constants corresponds to that predicted by the AS theory when $\gamma_u > \gamma_\rho$. The same analysis shows that $B > C$ in the Sm*A* phase, which is the usual result, and that $B < C$ in the Sm*C* phase. This inversion of the B/C ratio is a direct consequence of the high degree of anisotropy of the Sm*A*-Sm*C* transition. It stems essentially from the fact that the velocity $V(0°)$ which is the highest of the three in the Sm*A* phase becomes the smallest in the Sm*C*

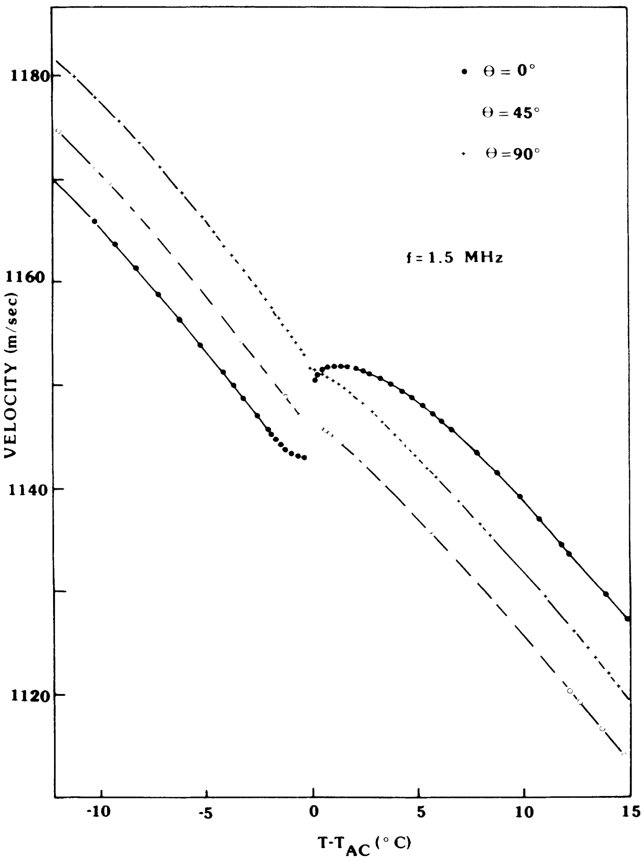

FIG. 2. Velocity curves for $\theta=0^\circ$, 45°, and 90°, at the smectic-A–smectic-C transition, showing inversion of velocity anisotropy between the two smectic phases. Detail of the measurements in the vicinity of T_{AC} is not shown.

phase.

Figure 3 shows the variation of damping as a function of frequency for $\theta=45^\circ$ at $T=T_{AC}$, i.e., in the $\omega\tau\gg 1$ regime. α/f^2 can be seen to obey a $1/f$-type variation.[10] This behavior is compatible with that predicted by the AS mechanism ($\alpha/f^2 \sim f^{-1+\bar{\alpha}/z\nu}$) when $\bar{\alpha}$ is near to zero, but cannot be explained by the Liu mechanism. In order for the Liu theory to give $\alpha/f^2 \sim 1/f$, the transport coefficients governing the relaxation amplitude would have to vary like $f^{0.5}$, and we can see no reason why this should be the case.

Figure 4 shows that the damping peak for $\theta=0^\circ$ moves towards low temperatures as frequency increases. On the other hand, no such shift was observed for $\theta=45^\circ$ and 90° within our experimental resolution (±0.01 °C). These differences in behavior are actual physical effects, since the measurements corresponding to a given angle θ were all taken simultaneously. The shift of the damping peak observed when $\theta=0^\circ$ corresponds to the behavior predicted by the Landau-Khalatnikov mechanism, which also predicts an f-type variation of the amplitude of the damping peaks [cf. Eq. (1)]. The experimental results show that this is roughly the case. A detailed analysis of these two effects would require us to know the contribution of both fluctuations and the background values, which varies from one frequency to another because of anharmonic effects.[7]

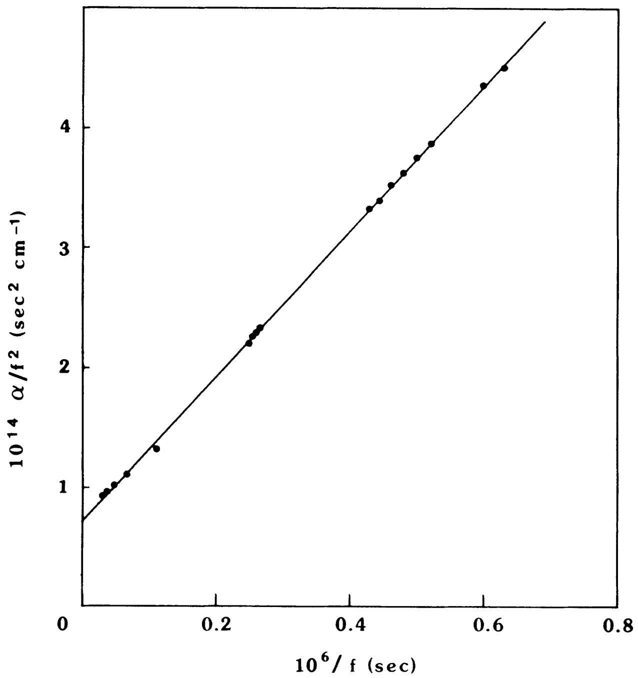

FIG. 3. Critical behavior of α/f^2 at $T=T_{AC}$ for $\theta=45^\circ$. The intercept of the straight line with the vertical axis gives the value of the background damping at T_{AC}.

It would be noted that the shift of the damping peak is not only linked to the thermal variation of τ^{-1}, since Liu's calculation[4] suggests that $V^2(\infty)-V^2(0)$ can be highly dependent on temperature. The absence of any

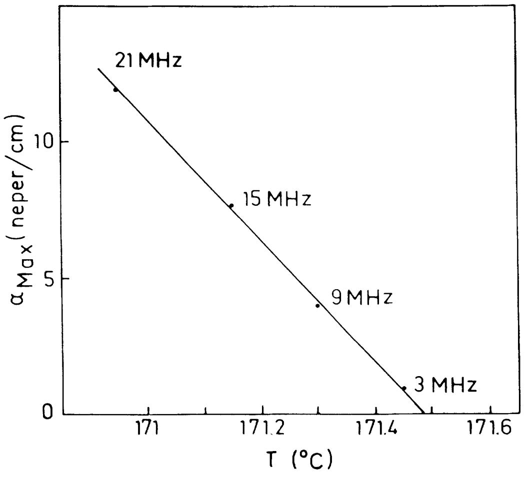

FIG. 4. Shift of damping peak as a function of temperature for various frequencies at $\theta=0^\circ$.

peak shift for $\theta = 45°$ and 90° indicates that relaxation amplitude, i.e., the $V^2(\infty) - V^2(0)$ term, is much smaller than for $\theta = 0°$, which is consistent with the estimations that can be made from the velocity measurements in Fig. 2. The fact that there was no shift of the ultrasound peak for samples relating to $\theta = 45°$ and 90° led us to take the temperature at which the peak occurs as the transition temperature T_{AC}. For $\theta = 0°$, T_{AC} was taken from the zero-frequency extrapolation from the position of the damping peak as a function of temperature (i.e., the extrapolation from the straight line in Fig. 4).

We return now to the pretransitional effects above T_{AC}. Liu's relaxation theory enables the velocity and damping anisotropies to be explained qualitatively. It does not, however, afford any explanation of the high-frequency behavior of α/f^2, which suggests that fluctuations do contribute to the critical effects. AS's fluctuation theory can explain, in qualitative terms, all our observations (i.e., the velocity anisotropy, the damping anisotropy, the more or less marked decrease of the elastic constants as $T \rightarrow T_{AC}$), and the high-frequency behavior of α/f^2 suggests that the transition is of a critical type. If this theory works, the thermal variation of velocity (or of the elastic constants) must reflect that of specific heat, which should therefore show critical effects above T_{AC}. Recent results, however, obtained on the same compound seem to show that this is not the case.[5] The apparent incompatibility between the ultrasound data and the specific-heat measurements could be explained by one of the two following possibilities: Either the specific heat is, in the present case, less sensitive to the order fluctuations than the ultrasonic techniques, or the critical effects observed on damping and velocity above T_{AC} are not due to the fluctuation mechanism suggested by AS. In this respect, it should be pointed out that coupling between the order-parameter fluctuations and velocity has so far been ignored. It could lead to anisotropic effects above T_{AC}. It is also possible that anharmonic effects are involved at this transition. Finally, we should point out that the behavior observed in TBBA is quite different from that in $\bar{8}$S5, since the ultrasound anomalies for the latter of these two compounds occur only below T_{AC}. This difference in behavior is even more surprising since the specific heat seems to show an extended mean-field-type behavior in both cases. It is at least clear that much work remains to be done before we fully understand the dynamics of this transition.

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[1] See, for example, R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. Goodby, Phys. Rev. A **27**, 1251 (1983). See also Y. Galerne, J. Phys. (Paris) **46**, 733 (1985).

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[6] D. Collin, J. L. Gallani, and P. Martinoty, Phys. Rev. A **34**, 2255 (1986).

[7] D. Collin, J. L. Gallani, and P. Martinoty, Phys. Rev. Lett. **58**, 254 (1987).

[8] The amplitude of this contribution is not necessarily the same in each of the two phases.

[9] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954), reprinted in *Collected Papers of L. D. Landau,* edited by D. Ter Haar (Gordon and Breach, London, 1967), p. 626.

[10] This behavior cannot be linked to anharmonic effects, since the latter do not contribute to damping for this orientation (see Ref. 6).