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Unusual melting behavior in a smectic liquid crystal

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Sound-velocity and attenuation measurements are reported for the smectic liquid crystal *p*-butoxybenzylidene-*p*′-octylaniline. At the smectic-*A* smectic-*B* transition temperature T_{AB}, v and α change rapidly, with a peak in α occurring below T_{AB}. A very small anomaly is also visible 2 to 2.5 degrees above T_{AB}. The data at T_{AB} are analyzed in terms of dislocation-mediated melting theories by assuming that the transition occurs at a crossover between two- and three-dimensional behavior. The low-frequency velocity change of $\Delta v/v = 0.047$ within the planes agrees well with the predicted value of 0.040.

I. INTRODUCTION

The smectic-*A* and smectic-*B* liquid crystalline phases both possess layered structures. The molecules within the planes in the S_A phase are isotropically distributed while in the S_B phase there is long-range crystalline order, generally with sixfold symmetry.[1] Correlations between the layers are expected to be weak in the S_A phase, but may be of long-range in the S_B phase.[2-5] Although recent theoretical work[6-8] suggests that two-dimensional melting may occur in a S_A-S_B system, the three-dimensional nature of the S_B phase must limit the applicability of these theories. Dislocation- (or vortex-) mediated melting has been reported in ^{4}He films,[9] He adsorbed on graphite,[10] and the electron solid,[11] but not in a system with weak commensuration forces. In that case a crossover behavior is expected below melting.[12] This behavior has not yet been observed for a liquid crystal system, although related behavior has been reported for Cs intercalated into graphite.[13] In order to test the theory of a crossover between 2D and 3D melting in smectic liquid crystals, we have measured the ultrasonic velocity and attenuation as a function of frequency and orientation in p-butoxybenzylidene-p′-octylaniline (BBOA or 40·8), which undergoes a S_A-S_B phase transition at 49.5 °C and a S_A-nematic transition at 63.7 °C.[14]

II. EXPERIMENT

Our acoustic cell is described elsewhere.[15,16] The bulk of the data was taken with a broadband acoustic spectrometer[16,17] which gave us the capability of making measurements at frequencies of $\omega/2\pi = 2$, 6, 10, and 14 MHz during a single run. Velocity resolution varied from 2×10^{-4} (at 2 MHz) to 5×10^{-5} (at higher frequencies) over a path length of 0.89 cm. Attenuation changes of 0.04 dB were reproducibly resolvable. Temperature was controlled to within 0.01 °C, but there were systematic errors of up to 0.5 °C. The liquid-crystalline material[18] was twice recrystallized from absolute ethanol. The samples were oriented in the nematic phase using a 17 kG magnetic field[19] which was maintained throughout the run. Separate runs were made at 0°, 45°, and 90° between the direction of propagation and the magnetic field (the director). In some later measurements a new multiple path cell was used,[16] allowing us to measure the orientation dependence in a single run.

III. RESULTS

We observed three distinct features in the sound absorption [Figs. 1(a) and 2(a)] which can be correlated with changes in the sound velocity [Figs. 1(b) and 2(b)]. As the temperature is raised within the smectic-*B* phase, the attenuation rises and reaches a peak just below the S_A-S_B transition temperature T_{AB}. The velocity decreases rapidly within the same temperature interval. Next, the attenuation drops sharply until T_{AB} is reached; here there is a clear break in the slope of α vs T, beyond which the attenuation continues to drop until it reaches a minimum deep within the S_A phase. The velocity also shows a discontinuity in slope at T_{AB}, especially at 2 MHz, where v is even seen to rise slightly just above the transi-

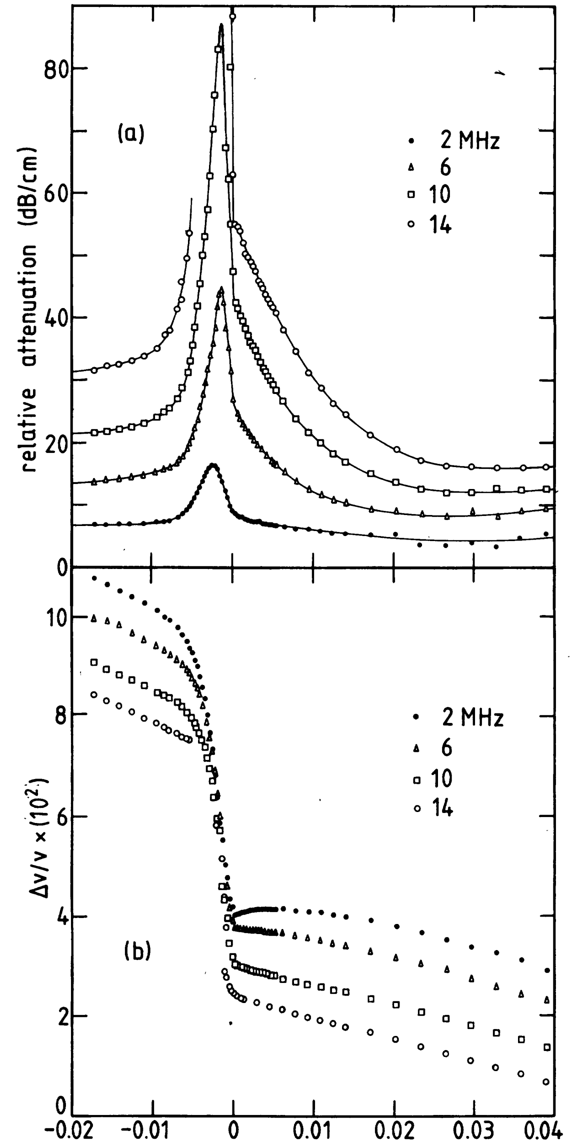

FIG. 1. The attenuation (a) and velocity (b) of sound in 40 • 8 at $\Theta=90°$ and several frequencies. The data have been arbitrarily displaced along the ordinate. $v_0=1060 \pm 40$ m/sec.

tion.

The third feature is only just visible within our resolution at a temperature T' given by $T' - T_{AB} \approx 0.006\ T_{AB}$. During some runs the data near T' were not closely spaced enough in temperature to resolve the anomaly (this is the case in Fig. 1). Other runs show a variety of small features here (Fig. 2—insets); therefore we took a closer look at the attenuation and velocity near T' using a high resolution pulse superposition method.[16] The anomaly is clearest in the attenuation data

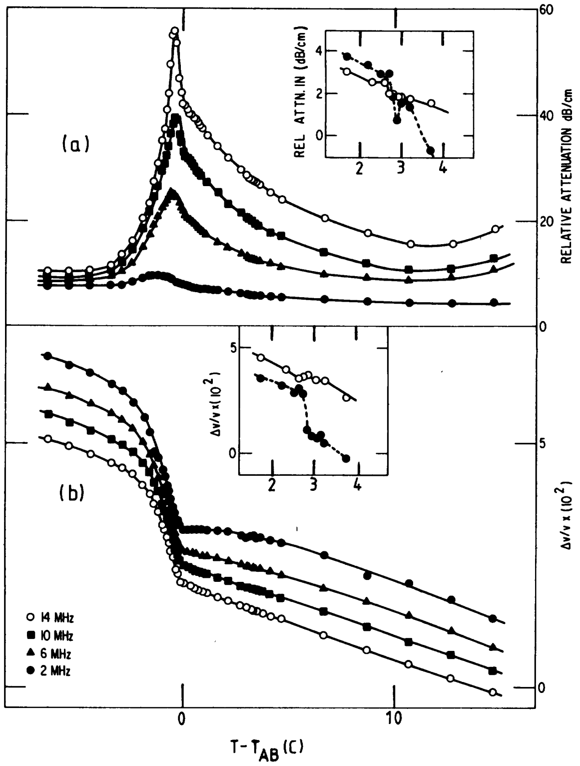

FIG. 2. The attenuation (a) and velocity (b) of sound in 40 • 8 at $\Theta=0°$ and several frequencies. The insets show typical anomalies observed at T' and compares their reproducibility upon lowering (○) and raising (●) temperature.

where a distinct change in slope is seen (Fig. 3), although this also was not totally reproducible (cf. inset). The velocity anomaly is less pronounced, but the lowest frequency (2 MHz) data always showed a broad maximum at T'.

We have measured the frequency behavior of the low-temperature attenuation peak. Its height scales approximately with ω, while it moves to *lower* temperatures at low frequencies. The size of the velocity reduction below T_{AB} becomes smaller at higher frequencies.

The velocity reduction and the absolute velocity in the S_B phase are largest at an orientation of 90° (propagation in the planes, Fig. 1) and least at intermediate angles (Fig. 2). The height of the attenuation peak also varies with orientation scaling approximately as 4 : 2 : 1 at 90°, 0° and 45°. The position of the attenuation peak appears to be independent of orientation (Fig. 4).

After recrystallization the transition temperature T_{AB} was 49.5 °C as judged by thermal microscopy measurements, but the elevated temperatures required to fill the cell and orient the sample reduced T_{AB} by 1–2°. (In the multipath cell, there was little change over long time periods in

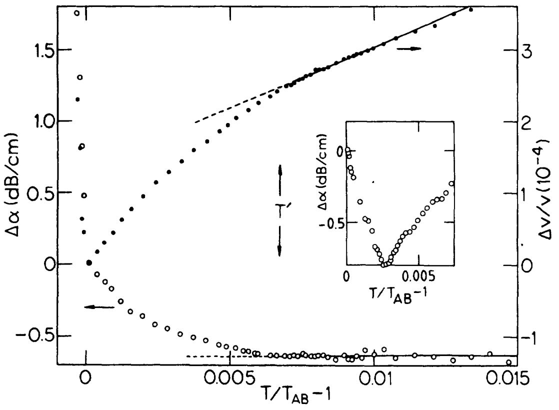

FIG. 3. High resolution measurements of the attenuation and velocity of sound in 40 • 8 at 2 MHz near T'. We have plotted α and v at $\Theta=90°$ minus their values at $\Theta=0°$. The lines are fitted to points above T' ($\simeq 51.6$ °C) as a guide to the eye. The inset shows data typical of runs where $\alpha(0)$ and $\alpha(90)$ had slightly different temperature dependences. T' is clearer, although the scatter is larger.

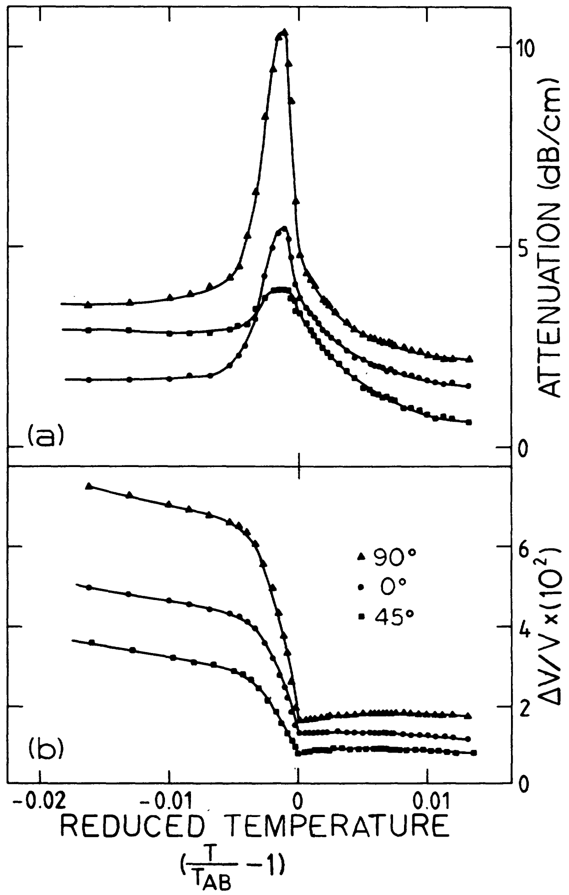

FIG. 4. The attenuation (a) and velocity (b) of sound in 40 • 8 at 2 MHz and orientations of 0°, 45°, and 90°.

the lower half since impurities were zone-refined to the top half where some degradation occurred.) Therefore we made *in situ* heating curve measurements which unambiguously determined T_{AB} in our samples. It was observed that only the temperatures of the anomalies and not their form depended upon these factors; similar behavior has been observed in other laboratories.[20] We have therefore plotted all our figures in terms of $T/T_{AB} - 1$.

The absence of a thermal anomaly at T' (Ref. 14) suggests that no first- or second-order phase transition exists there, although a transition of higher order is not ruled out. In one run we cycled the temperature and found temperature hysteresis of no more than 0.1 °C at T_{AB} or T'.

IV. DISCUSSION

From theoretical considerations, and because the effects are largest for in-plane propagation, it is natural to associate T_{AB} and possibly T' with phase transitions in the liquid-crystal layers. In particular, can we associate T_{AB} with dislocation-mediated melting? Since there exist finite, albeit very weak, correlations in the third dimension[4,21] the interaction energy between dislocation pairs can no longer be logarithmic at large separations[12] ("string" attachments in quark confinement language). This change permits the transition to become first order,[12] as is observed experimentally.[4] We shall assume however that the observed precursory behavior is similar to that expected for the second-order phase transition[22] of 2*D* melting; we can then answer the question within that framework.

There is a universal relationship between the 2D melting temperature T_M and the change in velocity at melting[6-8]:

$$\Delta v^2 = 4\pi k_B T_M/m\,, \tag{1}$$

where m is the mass of one molecule. For 40 • 8, we find that $(\Delta v/v)_{\text{theor}} = 0.040$, with $v_0 = 1070$ m/s. Operationally, we estimate the change at the (first-order) phase transition by extrapolating the behavior at some distance above and below T_{AB} back to the transition temperature. If we apply this procedure to Fig. 1(b), then we find $(\Delta v/v)_{\text{expt}} = 0.047$ at 2 MHz and $\theta = 90°$. This is very good agreement since we are observing the change in c_{11}, while the elastic constant combination that properly belongs in Eq. (1) is[8] $(c_{11}^2 - c_{12}^2)/4c_{11} \simeq (c_{11} - c_{12})/2$. This combination cannot be unambiguously determined from longitudinal sound measurements.

We can use the dynamical theory of the vortex-mediated transition in ^{4}He films[23] to estimate the affects of finite frequency on the sound propagation data. The attenuation peak should vary as the power dissipated, given approximately by

$$\alpha \propto P \propto \omega/\ln^2(\omega a^2/D)\,, \tag{2}$$

where a is the lattice constant and D is the diffusion constant. Our observation that the height of the peak varies linearly with frequency is consistent with Eq. 2. The shift of the attenuation peak to lower temperatures at lower frequencies is also consistent with the theory, but is opposite to the behavior predicted by the Landau-Khalatnikov theory. The velocity jump should be smaller at higher frequencies according to

$$1 - \Delta v/(\Delta v)_0 = 1/\ln(\omega a^2/D)\,, \tag{3}$$

again consistent with the data shown in Fig. 1. For these reasons, and because the observed effects are most pronounced for in-plane propagation, we then conclude that the transition at T_{AB} illustrates a crossover between 2D and 3D melting behavior, such that below T_{AB} we approach a second-order transition that becomes first order at T_{AB}.

The nature of the anomaly at T' is less clear. Figure 2 shows a detailed view of the attenuation and velocity from T_{AB} to above T', found by subtracting the 0° data from the 90° data in order to emphasize differences between in-plane and out-of-plane propagation. The anomaly in α at T' is coincident with a broad local maximum in v and a less distinct anomaly in Δv. Because the attenuation difference rises below T', we conclude that the anomalous nature of the region below T' shows up mainly within the layers. There is no obvious discontinuity in v, so that if there is a phase transition at T', it may be of third or higher order, in the Ehrenfest sense. We cannot, at this time, draw any other conclusions about the anomaly at T' (such as a description in terms of orientational order). Within the past year, measurements of viscosity,[24] birefringence,[25] and nuclear magnetic resonance[26] in 40·8 have been made, which also suggest that there is a 2–3° temperature interval above T_{AB} where the behavior of the material deviates measureably from that found deep within the smectic-A phase. We hope future theoretical work will point the way towards the most effective experimental probe for this interesting anomalous region.

V. CONCLUSIONS

We have observed strong pretransitional anomalies in sound propagation below the smectic-A–smectic-B phase transition in 40·8. We have found that the data are consistent with theories of dislocation-mediated melting, which may be applicable in a crossover region between two- and three-dimensional melting behavior. A second anomaly $2\text{–}2\frac{1}{2}$°C above the S_A-S_B transition has been observed but not explained.

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