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Ultrasonic study of the shear mechanical impedance of butyloxybenzylidene octylaniline near the crystalline-B-smectic-A phase transition (*)

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Résumé. — Nous présentons une étude détaillée de l'impédance mécanique de cisaillement du butyloxybenzylidène octylaniline (40.8) au voisinage de la transition cristal B-smectique A. Les mesures ont été effectuées à des fréquences comprises entre 5 et 85 MHz pour une onde de cisaillement se propageant perpendiculairement aux couches smectiques.

Dans les deux phases la réponse du matériau présente de grands effets de relaxation. Le changement de structure à la transition est indiqué par un accroissement de la partie réelle de l'impédance de cisaillement. Les résultats à 85 MHz sont ceux attendus pour une transition du 1^{er} ordre élargie par des effets d'impuretés, alors que les résultats à 5 MHz mettent en évidence un effet prétransitionnel dans un domaine de température de 2-3 °C en-dessous de la transition.

Abstract. — We report a detailed study of the shear mechanical impedance near the crystalline-B-smectic-A transition in butyloxybenzylidene octylaniline (40.8). The measurements were performed at various frequencies from 5 to 85 MHz for shear waves propagating along the normal to the layers.

In both phases the material response presents strong relaxation effects. The structure change at the transition is indicated by an increase in the real part of the shear impedance. The results at 85 MHz are those expected for a first-order transition broadened by impurity concentration, whereas the results at 5 MHz reveal a pretransitional effect in a temperature interval of 2-3 °C below the transition.

Certain liquid crystals, like butyloxybenzylidene octylaniline (40.8), have been the object, in recent years, of considerable interest because of theoretical speculations about the structure of the B phase and a possible connection to two-dimensional melting [1-4].

Recent X-ray measurements on thin films [5] or on bulk samples [6] demonstrated that the B phase of 40.8 does not present the characteristics expected for the hexatic model, but those of a three-dimensional (3D) solid.

On the other hand, mechanical experiments using shear waves propagating along the normal

(*) A preliminary account of this work was presented at the 8th International Liquid Crystal Conference, Kyoto, Japan (1980).

to the layers were performed to observe the shear of one layer relative to another [7-9]. However, some confusion has surrounded the nature of the response — elastic or viscoelastic — and the value of the associated elastic constant C_{44} [6-8].

Earlier we reported measurements at $\nu = 15$ MHz of the real part R and the imaginary part X of the shear mechanical impedance [8]. These measurements showed that the response of the B phase is not elastic, but viscoelastic at this frequency and that C_{44} must be necessarily below 10^7 dyn./cm². These results have been confirmed by Cagnon and Durand [9], who have shown that the material response becomes elastic only in the very low frequency range ($\nu \sim$ few Hz) and that the value of C_{44} is of the order of 10^6 dyn./cm², which is consistent with our estimation.

Another aspect of the problem concerns the existence of a pretransitional effect at the smectic-A to B (A-B) transition. Indeed the X-ray experiments [6] revealed no indication of pretransitional effects, whereas such effects were observed for the specific heat [14].

We present here a detailed study of the shear mechanical impedance across the A-B transition in the frequency range 5-85 MHz, which, notably, allowed us to detect a pretransitional effect in the B phase which becomes smaller and smaller as the frequency is increased. An important experimental difficulty was to separate this pretransitional effect from spurious effects related to the existence of a two-phase region.

The complex acoustic shear impedance of a material at a frequency ω is given by

$$Z = \rho V^* = [\rho G(\omega)]^{1/2} = R + iX \quad (1)$$

where V^* is the complex shear wave velocity and $G(\omega) = G' + iG''$ is the complex shear elastic modulus. This equation allows one to relate G' and G'' to R and X by

$$G' = \frac{R^2 - X^2}{\rho} \quad \text{and} \quad G'' = \frac{2RX}{\rho}. \quad (2)$$

In the presence of a relaxation process characterized by a single relaxation time τ , $G'(\omega)$ and $G''(\omega)$ are given by [10] :

$$G'(\omega) = G(0) + [G(\infty) - G(0)] \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (3)$$

and

$$G''(\omega) = [G(\infty) - G(0)] \frac{\omega\tau}{1 + \omega^2 \tau^2},$$

where $G(0)$ and $G(\infty)$ are the shear elastic modulus at zero and infinite frequencies respectively.

If the B phase has 3D long range crystalline order, the elastic constant $G(0)$ is C_{44} . When $\omega\tau \ll 1$, $G' \rightarrow C_{44}$ and C_{44} is related to R by $C_{44} = R^2/\rho$. In this regime R is frequency independent and X is equal to zero. In the presence of a relaxation process R increases with increasing frequency and X becomes non-zero. Thus, in order to determine whether the regime is hydrodynamic or not, one must measure the real and imaginary parts of Z or, equivalently, the frequency dependence of R .

In the smectic-A phase $G(0) \equiv 0$. When $\omega\tau \ll 1$, $G' \rightarrow 0$ and $R = X$. We obtain a viscous-damped shear mode for which

$$R = X = \left(\frac{\rho \eta \omega}{2} \right)^{1/2},$$

where η is the viscosity.

In the presence of a relaxation process, R and X become different and the smectic-A phase presents an apparent shear rigidity G' . Here again, measurements of R and X , or measurements

of the frequency dependence of R , are necessary to determine whether the regime is hydrodynamic or not.

R and X were measured by a standard impedometric technique which is based upon the measurement of the complex reflexion coefficient of an incident shear wave at a solid/liquid interface. We used the inclined incidence method which is known to be more sensitive than the one at normal incidence [11]. In this method a pulse of shear waves propagates in a fused silica bar along the path indicated in figure 1 and is reflected from the test surface. When the liquid to be

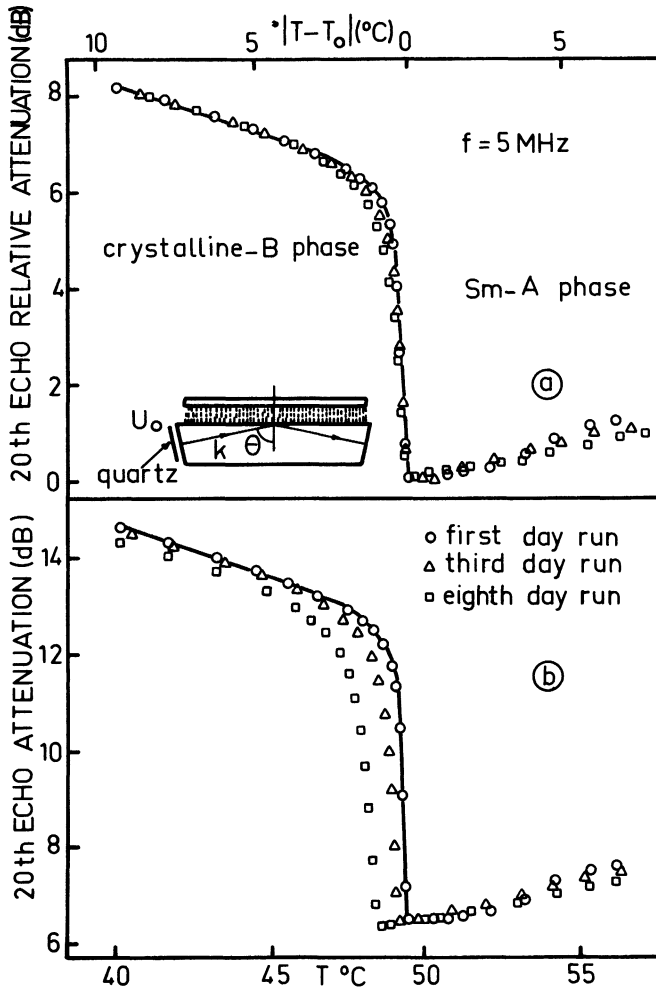


Fig. 1. — 20th echo attenuation *versus* temperature for fused silica-sample interface. The lower panel presents the data obtained during a week as described in the text. The attenuation corresponding to the fused silica-air interface, referred to as 0 dB, is constant within 0.1 dB. The upper panel presents the relative variation of the attenuation normalized at the temperature T_0 where the attenuation starts to increase. One can remark that the form of the curve is not changed whereas T_0 decreased by 1 °C. The continuous line represents the first day run. The increase in the attenuation at the transition shows that the reflection coefficient becomes smaller and correspondingly the shear modulus of 40.8 becomes larger. The figure shows also the schematic diagram of the acoustic system; the vibration u is parallel to the smectic layers, k is the wave vector and θ is the angle of incidence. The refracting angle ψ is very small ($\psi \sim 1^\circ$) so that the shear wave propagates in 40.8 practically along the normal to the layers.

studied is placed on this surface, a change in both the amplitude r and the phase ϕ of the reflected wave is produced. These changes are related to R and X by

$$R \simeq Z_s \cos \theta \frac{1-r}{1+r} \quad (4)$$

and

$$X \simeq Z_s \cos \theta \frac{2r\phi}{(1+r)^2}, \quad (5)$$

where Z_s is the shear mechanical impedance of the fused silica bar and θ is the angle of incidence. Equations (4) and (5) hold only for small ϕ ($\phi < 5^\circ$). In this limit, R is independent of ϕ .

The bar of fused silica was $7.65 \text{ cm} \times 1.60 \text{ cm} \times 2.15 \text{ cm}$ and θ was approximately 77° . The reflecting surface was optically polished to $\lambda/4$. The opposite surface was also polished to permit visual examination of the sample. We used a common transducer for generation and detection of the shear waves and we chose a low pulse-repetition rate of 50 Hz and a pulse length of the order of 5-10 μs . The transducer was an AT-cut quartz, gold plated, with a fundamental resonance of 5 MHz. It was oriented so that the shear vibration is parallel to the reflecting surface : this gives a pure shearing motion at the interface, and does not produce a longitudinal component on reflexion. The quartz was bonded to the bar by cooling a film of nematic liquid crystal into its crystalline phase. The nematic used was p-azoxyphenetole (P.A.P.) which becomes solid at $\sim 135^\circ\text{C}$. This bond presents the advantage of having a low loss and shear properties which are temperature-independent.

Because of impedance mismatch at the rod ends a train of echoes of decreasing amplitude was set up in the rod. As many as 50 echoes were observed in favourable cases. We thus were able to make measurements on signals which had undergone several reflexions at the interface, considerably increasing the accuracy of the method. The temperature of the bar was kept constant to within 0.01°C .

Experimentally r was determined by selecting a suitable echo in the echo train and by measuring its amplitude in decibels before and after the application of the sample to the bar. The difference Δ (dB) between the two values is related to r by :

$$\Delta \text{ (dB)} = 40 n \log r, \quad (6)$$

where n is the number of the echo. As the shear modulus of the test material approaches that of fused silica, r becomes small and Δ (dB) large.

Measurements of r were made at five frequencies, 5, 15, 25, 45 and 85 MHz, by comparing the selected echo against a reference signal. At each frequency the decibel loss was measured for the fused silica-air and fused silica-sample interfaces as a function of temperature, and values of R were computed from the Δ (dB) values using equations (6) and (4).

The period to obtain a fused silica-sample curve was typically 12 h and, as we shall see later, some experiments have required a week. To ensure adequate stability of the electronic system during this time it was necessary to regulate all power supplies and to derive the reference and the acoustic pulses from the same oscillator.

Phase measurements were obtained by superimposing the comparison pulse and the selected echo ; by appropriate adjustment of a variable delay line and the attenuator, the two pulses were made equal in amplitude and opposite in phase and therefore cancelled. After placing the liquid on the bar this process was repeated and the phase ϕ determined from the difference between the delay-line settings. Measurements of ϕ were made at 15 and 25 MHz. We have found that ϕ is always less than 3° . This justified the use of equation (4) in the determination of R . Other details of the set-up are given in reference [12].

Our sample of 40.8 was obtained from Dr. G. Lorenzo at Organix. Preliminary measurements

were performed using a sample made in Orsay by Dr. Germain, but the results which appear in this paper were obtained on the Organix sample. Apart from a slight difference in the values of the various transition temperatures, the ultrasonic behaviour of the two compounds was approximately the same.

The compound was placed between the reflecting surface of the bar and a coverglass both coated with a surfactant, and oriented in the homeotropic configuration. In this configuration the smectic layers were aligned in a direction parallel to the substrate, i.e. in a direction parallel to the shear displacement (Fig. 1). By reason of the oblique incidence, the transmitted wave propagates with an angle ψ with the normal to the layers. However, the value of ψ is very small because the shear mechanical impedance of fused silica is much higher than that of the B phase [13]. One may therefore consider that the shear wave propagates in a direction perpendicular to the layers.

The alignment was obtained by heating the sample into the nematic phase and then slowly cooling it down to the Sm-A and B phases. The quality of alignment was evaluated by examination between crossed polarizers. For each sample used it was possible to extinguish completely and uniformly the light transmitted between crossed polarizers. Since the compound is a Schiff's base which suffers from chemical instability the following precautions were taken ; before being placed on the bar the compound was first vacuum-pumped at $T \sim 80^\circ\text{C}$ for 12 hours to remove any residual solvent, and, once on the bar, it was maintained in a dry nitrogen atmosphere in order to prevent any contamination. Data obtained with samples prepared in this way were quite reproducible.

Most of the measurements were made using thin samples (no spacer between the bar and the coverglass). However, to check on a possible thickness dependence, preliminary measurements were carried out with thick samples (up to 0.2 cm). For these samples the alignment in the bulk was obtained by applying a magnetic field of 6 kG. Thin and thick samples gave identical results within experimental errors, which shows that the shear wave is strongly damped. Additional measurements were made without the coverglass to be certain that the pressure induced by the coverglass does not alter the smectic response.

All measurements were made by lowering the temperature, over a temperature range of about 20°C (from 60°C to 40°C), at intervals smaller than 0.1°C near T_{AB} . After a run, the sample was kept undisturbed at $T = 40^\circ\text{C}$ during at least two days, to test a possible influence of defects. No significant difference appeared in the measurements before and after this annealing procedure indicating that the quality of the sample is very good within the thickness « seen » by the shear wave. The transition temperature and the quality of the sample were verified by differential thermal analysis (DSC) before and after each experiment ; the width of the peak at the transition gave us an estimate of the temperature range where the B and the smectic-A phases coexist. Unless otherwise specified, all measurements presented here were carried out with silane as surfactant.

We have also tested the evolution of the sample as a function of time by performing measurements over a period of one week. For these particular measurements the following procedure was used. Each day, a run from 55°C to 40°C was made. During the night separating two runs the sample was kept undisturbed at 40°C . To avoid hysteresis effects related to the first-order character of the A-B transition, all the runs were made by lowering the temperature.

Since the measurements were made under an external field (shear stress), it is possible that the property we measured did not relate to thermal equilibrium. To be certain that this was not the case, we studied the response of the sample on the driving amplitude. We found no amplitude-dependent effect when the electric signal was varied from 2 to 200 V, which corresponds to an induced shear displacement varying from $0.1 \text{ \AA}$ to $10 \text{ \AA}$. This indicates that our measurements are in the linear response regime.

A typical result obtained at 5 MHz is shown in figure 1a. The curve represents the attenuation of the 20th echo measured for the fused silica-sample interface as a function of temperature.

As mentioned above the fused silica-air curve is temperature independent in this temperature range; therefore the curve in figure 1a directly yields the relative behaviour of the sample under shear. As the transition is approached from above, one observes that the attenuation of the reflected wave decreases slightly and then starts to increase very sharply at a temperature T_0 on entering the B phase. Deep in the B phase the attenuation increases monotonically with decreasing temperature. Although the transition is strongly first-order [6, 14], the form of the curve below T_0 suggests the existence of a pretransitional effect. The fact that this effect spreads over 2-3 °C while the width of the calorimetric peak measured by DSC on the same sample is only 0.7 °C confirms the pretransitional nature of the effect. Other arguments in favour of this pretransitional behaviour will be given in the discussion of results simultaneously obtained at 5 and 85 MHz.

Despite all the aforementioned precautions it was found that with the passage of time the sample would deteriorate. The deterioration was shown by a lowering of the temperature T_0 . This is illustrated in figure 1b where some of the results obtained over a period of a week have been reported. The important point to note, however, is that the form of the curve remains unchanged whereas T_0 decreases by ~ 1 °C during this period; this is shown in figure 1a where the results of figure 1b are normalized with respect to T_0 . The slight discrepancies which appear in the Sm-A phase and in the bend of the curve, and which are detected thanks to the extreme sensitivity of the technique, are likely due to subtle changes in the sample that are optically not detectable.

We repeated these measurements using lecithin coating. For the first day run the material response was roughly similar to that observed with silane coating, but it changed dramatically as a function of time; this change was evidenced by a faster decrease of T_0 , a softening of the system in the B phase and a reduction in the sharpness of the attenuation onset from one day to the next. Since our measurements were made in the linear response regime, we believe that this apparent softening was due to the diffusion of lecithin molecules through the planes of the B phase. Because of the diffusive nature of the shear mode in the Sm-A phase this diffusion effect should not strongly affect the response of the sample in this phase, as was observed.

Figure 2 shows the temperature dependence of R at various frequencies and figure 3 compares R and X values measured at 15 MHz; this allows the following remarks to be made:

(1) The large rise in R on entering the B phase exists for all frequencies and reflects the structure change of the A-B transition.

(2) In the B phase R increases with increasing frequency and X is non-zero. This is the behaviour expected in presence of dispersion. Therefore the measured shear modulus G' does not correspond to the hydrodynamic value ($C_{44} = R^2/\rho$). We find $G' \sim 10^7$ dyn./cm². Since $C_{44} < G'$, this value implies that C_{44} is at least more than an order of magnitude smaller than previously reported values of 10^8 dyn./cm²; this estimate is compatible with the value recently measured by Cagnon and Durand [9].

(3) In the Sm-A phase where $C_{44} \equiv 0$, R and X differ significantly. Since in the dispersionless regime R and X should be equal, this indicates the presence of relaxation processes. The Sm-A phase presents therefore an apparent shear modulus G' . We find $G' \simeq 3 \times 10^6$ dyn./cm². The low value of the dynamic viscosity ($\eta' \sim 6$ cp at 15 and 25 MHz) suggests that the data in the Sm-A phase are in the $\omega\tau \gg 1$ regime. The presence of dispersion in the Sm-A phase is not specific to 40.8 and has already been observed in Sm-A phase of other liquid crystals that do not have an A-B transition [15]. Two processes may contribute to the dispersion in the Sm-A and B phases: relaxation of dislocations which do not have enough time to migrate during the period when the film is sheared, and director fluctuations which are coupled to the shear flow.

(4) From our R and X measurements at 15 MHz we estimate the effective penetration depth l in the B phase to be ~ 1 μ m ($l = (R^2 + X^2)/\rho\omega X$). This length is small with respect to the thickness of the sample and is of the order of the wavelength of the shear mode [16].

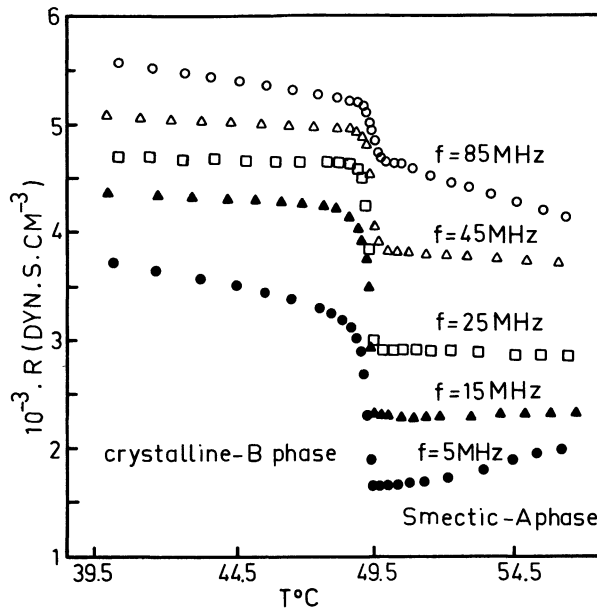


Fig. 2. — Temperature dependence of the real part R of the shear impedance at various frequencies.

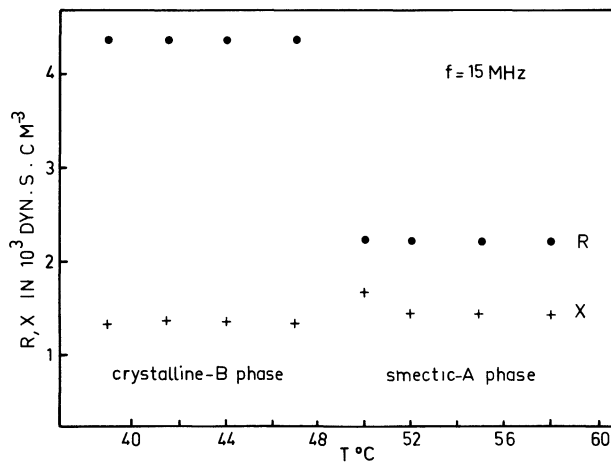


Fig. 3. — The real R and the imaginary X parts of the shear impedance in the smectic-A phase and solid B phase. The data show that relaxation effects are present in both phases.

(5) The difference between the value of R^2 measured in the B phase at a given frequency and the value of R^2 measured in the A phase at the same frequency shows again that $C_{44} \ll 10^7$ dyn./cm².

(6) A careful examination of figure 2 shows that the temperature T_0 for which R starts to rise, increases with increasing frequency. The simplest explanation is to admit that the effective penetration depth of the ultrasonic wave decreases with increasing ultrasonic frequency and that at very high frequency the wave detects only the coexistence region. This assumes that the coexis-

tence region is larger near the surface where each impurity (like the surfactant) may act as a nucleation centre.

During the latter part of this study we employed a device which allowed us to perform simultaneous measurements at 5 and 85 MHz in the same sample and thus at the same level of purity. These measurements are reported in figure 4. The results obtained at 85 MHz are those expected for a first-order transition that is broadened by impurities, whereas the results at 5 MHz show the existence of a pretransitional effect. Similar experiments were repeated with samples of different quality. Only for samples containing very little impurities, it is possible to separate the coexistence domain from the pretransitional effect domain. The results of figure 4 show that the temperature T_0 is high, 49.5 °C and 49.75 °C at 5 and 85 MHz respectively, but also that the width of the coexistence region determined in this way is already relatively large, of the order of 0.7 °C determined by X-ray techniques [17]. As the purity deteriorated, the variation in R at the transition for 85 MHz became softer and softer, and for « dirty » samples (in particular with lecithin) became virtually impossible to detect. In this latter case, one observed at 5 MHz a rounding in the variation of R at T_0 instead of the abrupt onset shown in figure 4.

In conclusion we have shown by two independent ways that 40.8 presents a viscoelastic behaviour in both smectic A and B phases between 5 and 85 MHz.

On the other hand we have observed on entering the B phase an increase in R for all frequencies which, taking account of the fact that this phase is a 3D-solid, marks the onset of the propagating regime for the shear wave. The value of G' at 15 MHz, the value of R^2 at 5 MHz and

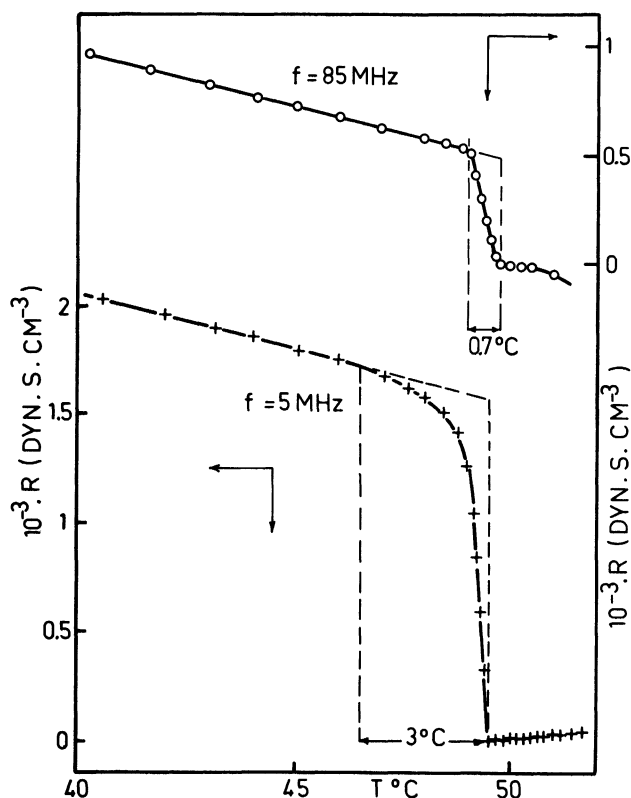


Fig. 4. — Relative variation of R simultaneously measured at 5 and 85 MHz near the A-B transition. The results at 85 MHz show the existence of a two-phase region, and those at 5 MHz reveal the presence of a pretransitional effect.

the variation of the R^2 value around the transition at a given frequency show by three different ways that $C_{44} \ll 10^7$ dyn./cm².

In addition, we have observed a pretransitional effect below T_{AB} in the real part of the shear impedance which reflects intrinsic properties rather than impurity-induced artifacts. This effect which becomes smaller and smaller as the frequency is increased, has a dynamical origin and is related to a high frequency relaxation process. The X-ray experiments [6] showing no indication of pretransitional changes in long range positional correlations, this effect could be due either to the director relaxation or to the changes in the defect structure *prior* to melting. However, the disappearance of this effect at high frequency suggests that it could be due to director relaxation rather than to the changes in the defect structure. The recent observation [18] in the very low frequency range by Cagnon and Durand of a pretransitional effect similar to the one we have observed at 5 MHz is in favour of this possibility.

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