Acoustical properties of *B*-modification smectic liquid crystals in static magnetic fields

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The temperature dependence of ultrasound velocity is studied for different orientation angles of the magnetic field and wave vector. A change is observed in the sign of anisotropy of ultrasound velocity in comparison with the nematic phase. Measurements are used as a basis for calculations of the temperature dependence of elastic constants.

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Investigation of the behavior of acoustical parameters for the ultrasonic waves propagating in liquid-crystal mesophases yields information about the molecular and thermodynamic properties of a given class of media of the condensed state of matter. Smectic *B* phases, which represent laminar structures with a hexagonal ordering of molecules in a layer,[1] have been studied less than the higher-temperature smectics *A* and *C* and a comparison of their properties with those of other mesophases, and also with solid bodies, is of interest from the standpoint of formulating a theory of the liquid-crystal state. In this work we report results of measurements of velocity of longitudinal ultrasound at the 3-MHz frequency in smectic *B* phases of butoxybenzylidene-butylanilene (BBBA) and butoxybenzylidene-octylanilene (BBOA). These materials have the following phase transition schemes: BBBA: crystal (Cr) $\xrightarrow{8^\circ C}$ smectic S_3

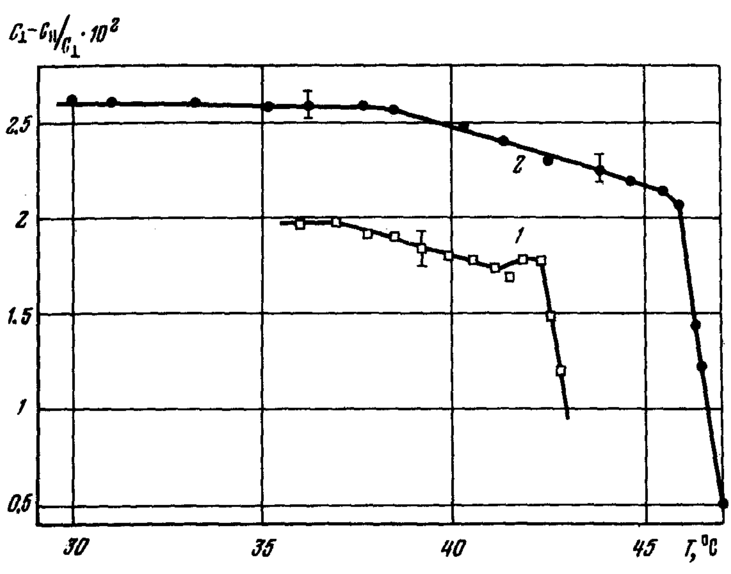

FIG. 1. Temperature dependence of ultrasound velocity anisotropy. 1—in BBBA; 2—in BBOA.

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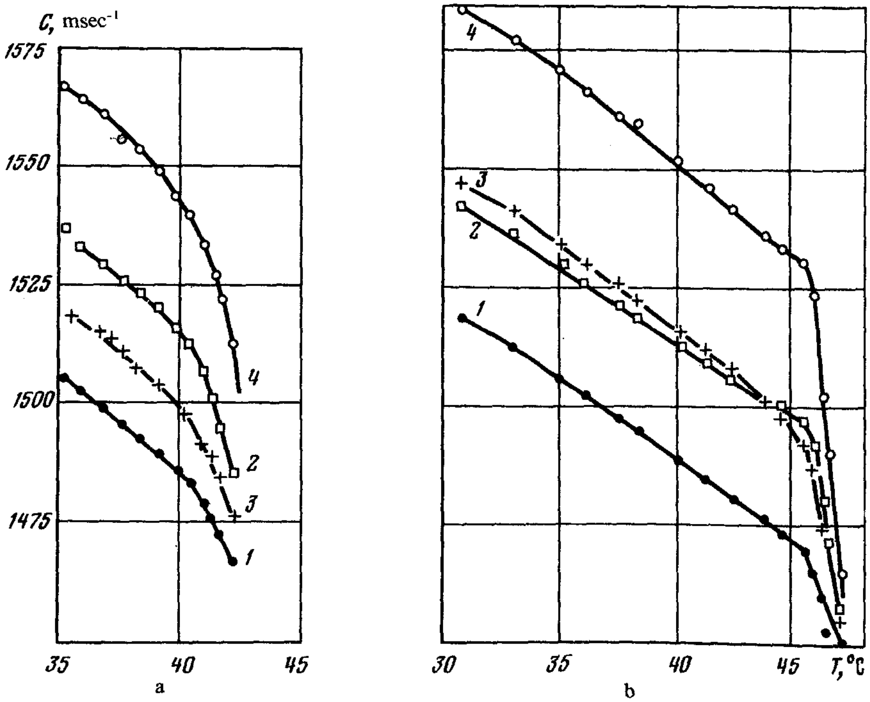

FIG. 2. Temperature dependence of ultrasound velocity anisotropy for different orientation angles θ: a—in BBBA; b—in BBOA; 1—$\theta = 30°$; 2—$\theta = 0°$; 3—$\theta = 60°$; 4—$\theta = 90°$.

$\xrightarrow{35°C}$ smectic $B\,(S_B)$ $\xrightarrow{42.5°C}$ smectic $A\,(S_A)$ $\xrightarrow{43.5°C}$ nematic (N) $\xrightarrow{70.9°C}$ isotropic liquid (I); BBOA: Cr $\xrightarrow{29.8°C}$ S_B $\xrightarrow{47.5°C}$ S_A $\xrightarrow{61.5°C}$ N $\xrightarrow{73°C}$ I. The phase classification corresponds to data in Ref. 2. Investigations were carried out in a 3-kGauss magnetic field by means of a pulsed-phase method involving a comparison of pulse fronts.[3] Errors in determining the velocity of ultrasound in a temperature range that exceeds the temperature of the phase transition S_A–S_B by 2 °C was 0.15%. As is known, variation in the magnetic field orientation in the smectic phases with respect to the direction of ultrasound propagation preserves the acoustical parameters and, therefore, the anisotropy of ultrasound velocity $\Delta C/C_\perp = (C_\parallel - C_\perp)/C_\perp$ was determined as the difference between the corresponding curves that were obtained during cooling from the nematic phase in a magnetic field directed parallel and normal to the wave vector. Here, $C_{\parallel,\perp}$ are the ultrasound velocities in the directions that are parallel with and normal to the magnetic field, respectively.

Figure 1 shows the temperature-dependent anisotropies $\Delta C/C_\perp$ in BBBA (curve 1) and BBOA (curve 2). In both materials, the absolute value of $\Delta C/C_\perp$ increases sharply for the phase transition S_A–S_B; this growth becomes smoother as the temperature decreases (the temperature coefficient of velocity anisotropy decreases 10–12-fold), and, subsequently, $\Delta C/C_\perp$ remains constant with the temperature, its value being $\sim 2\times10^{-2}$ for BBBA and $\sim 2.6\times10^{-2}$ for BBOA. While investigating the S_B

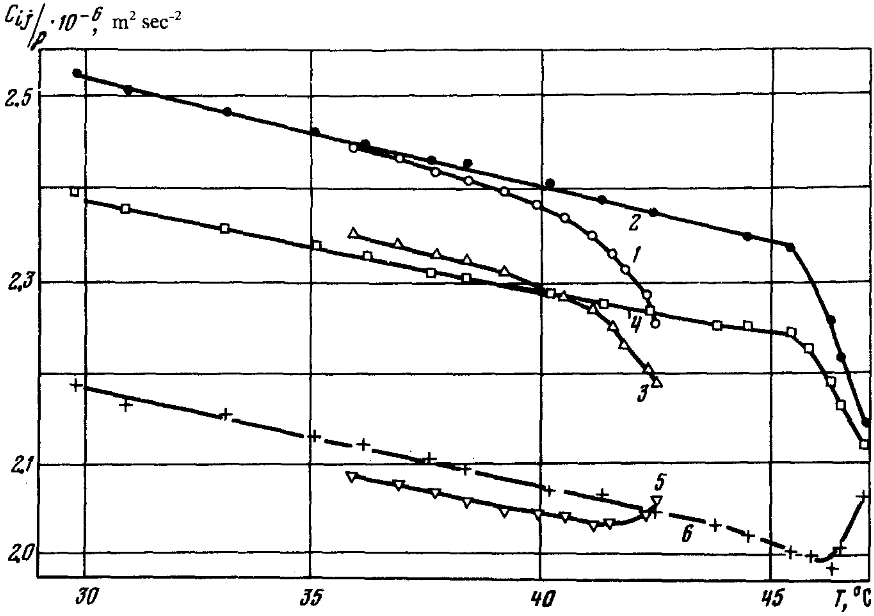

FIG. 3. Temperature dependence of elastic constants C_{11}—1,2; C_{33}—3,4; C_{13}—5,6 in BBBA (odd numbers) and BBOA (even numbers).

phases a change was observed in the sign of ultrasound velocity anisotropy with respect to the nematic phase, namely $C_{\perp} - C_{\parallel} > 0$.

Proceeding from the symmetry of B smectics,[4] the angular dependence of ultrasound velocity $C(\theta)$ is expressed as follows:

$$2\rho C^2(\theta) = C_{11}\sin^2\theta + C_{33}\cos^2\theta + C_{44} + \{[(C_{11} - C_{44})\sin^2\theta$$

$$-(C_{33} - C_{44})\cos^2\theta]^2 + 4(C_{13} + C_{44})^2\sin^2\theta\cos^2\theta\}^{1/2},$$

where C_{11}, C_{33}, C_{13}, C_{44} are the elastic constants and ρ is the density.

Figure 2 shows the results of measurements of ultrasound velocity for orientation angles of 0, 30, 60 and 90°. Based on these measurements, and using the foregoing relationship, we calculated the temperature dependence of the elastic constants C_{11}, C_{33} and C_{13} shown in Fig. 3. The elastic constants C_{11} and C_{33} increase with a decrease in the temperature. The C_{13} constants in both materials pass through a minimum near the phase transition S_A–S_B. The method used here does not permit the calculation of the shear modulus C_{44} from the angular dependence of ultrasound velocity since, in this case, error in C_{44} exceeds 100%. Based on the impedometric studies of the S_B phase in BBOA,[5] the shear modulus at frequencies below 5 MHz is below 10^7 dyn/cm². Inasmuch as the latter is three orders of magnitude smaller than the values of spatial elastic constants, the moduli reported in this paper were calculated under an assumption that C_{11}, C_{33}, $C_{13} \gg C_{44}$. The sign of ultrasound velocity anisotropy obtained in this work is in contrast with the results of Ref. 4 which show that in the S_B phase of ethyl-metoxy-benzylidene-aminocinnamate $C_{\parallel} - C_{\perp} > 0$. This difference may be associated with the use in Ref. 4 of an impure specimen of S_B-phase which, in contrast with the S_B phases of BBBA and BBOA, is naturally metastable and monotropic.

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