Experimental study of the critical dynamics in the vicinity of the smectic *A*–smectic *C* phase transition[1)]

V. A. Balandin, E. V. Gurovich, A. S. Kashitsyn, S. V. Pasechnik, A. A. Tabidze, and A. C. Gol'dberg

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The viscoelastic properties of a smectic over a broad range of developed fluctuations are described in detail on the basis of some theoretical concepts regarding the nature of the phase transition between the smectic *A* and *C* phases. The spectra of all acoustic modes are presented. The critical behavior of the shear waves is studied experimentally. The orientational dependence of the absorption is obtained. The orientational behavior of the absorption is observed and explained as a function of how close the smectic is to the critical temperature. The temperature dependence of the compression modulus of the smectic layers near the transition point is studied. The critical behavior of the velocity and absorption of longitudinal sound over a broad range of ultrasound frequencies is investigated by resonator and pulse-phase methods. The temperature-frequency dependence of all (three) elasticity moduli of the smectic and of the bulk viscosity coefficients are calculated. The universal relationships between the corrections to the various elasticity moduli among themselves and the corrections to the bulk viscosity coefficients are verified experimentally. The corrections to the bulk viscosity coefficients, associated with the strong fluctuations of the smectic layers, are investigated. The specific features of the corrections in the low-symmetry *C*-phase due to the appearance of an additional orientational mode are discussed. The experimental data in the crossover region are analyzed, and the explicit form of the dynamic correlators of the order parameter is derived.

1. INTRODUCTION

At the present time a large body of experimental data has been accumulated from ultrasound studies of the dynamics of various liquid-crystal phases.[1–6] The results of studies on the propagation and absorption of longitudinal and transverse waves has made it possible to determine various elastic moduli and kinetic coefficients in liquid crystals. The data obtained from these studies is in quite good agreement with contemporary theoretical ideas about the nature of acoustic modes in liquid crystals.[7–9]

However, numerous studies of the transitions between various liquid-crystal phases up until recently have been dedicated mainly to the study only of static critical phenomena, specifically: critical calorimetry,[10,11] the temperature dependence of the order parameter,[12] and the susceptibility.[13] The same is true of the theoretical description of critical phenomena in liquid crystals. There are several reasons for the difficulties, both experimental and theoretical, in the study of the critical dynamics. The first is the existence in liquid crystals of a strong anisotropy. Because of it universal models, which are the conventional models in the theory of critical phenomena, with a multicomponent order parameter, defined in the "isotopic" space, are inapplicable to the description of liquid crystals, or applicable only in a narrow region near the transition. This region is probably difficult to reach. Actual experiments are carried out in the transition (crossover) region and require a specific analysis in a situation with a strong initial anisotropy.

In addition, an experimental study of the critical phenomena in the presence of a strong anisotropy by means of ultrasound requires large quantities of a single-domain sample, precise orientation of the wave vector of the excited wave with respect to the director and an accurate account of the surface distortions of the latter.

The second reason for difficulties in an ultrasound study of critical phenomena in liquid crystals has to do with the fact that in the narrow temperature interval in which they exist they typically undergo numerous phase transitions. The pretransition regions, which are associated with various critical points, overlap each other. Therefore, in the interpretation of the results separating out the contributions from the various transitions becomes a quite complex problem.

Third, in the high-frequency region molecular dissociation processes, which are independent of the critical phenomena, begin to be manifested. Their frequency dependence also must be taken into account in the processing of the experimental data.

Finally, for the smectic phases ordinary hydrodynamics, strictly speaking, generally breaks down. This has to do with the strong fluctuations of the smectic layers. Even far from any transitions taking the fluctuations of the layers into account cause the sound absorption to have a nontrivial frequency dependence.[14]

Only in recent years has it been possible to overcome these difficulties. Mazenko, Ramaswamy, and Toner[14] have shown that critical fluctuations of smectic layers lead to the appearance of corrections to the bulk viscosity coefficients which diverge in the low-frequency limit as ω^{-1}. A consistent theory of dynamic effects, associated with the fluctuations of the smectic layers in the smectic *A* phase, was constructed in Refs. 15 and 16, and for the smectic *C* phases in Ref. 17. Almost simultaneous with these theoretical investigations experiments appeared confirming them, both on first[3,6,18] and second[5] sound.

As to the phase transitions themselves, one of the simplest of these from the point of view of a theoretical description turned out to be the smectic *A*–smectic *C* transition. The

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region of developed fluctuations in this transition has been sharply fixed in numerous experiments (see, e.g., Refs. 10–13). The thermodynamics of this transition with the strong anisotropy taken into account was constructed in Ref. 19, and its critical dynamics was studied theoretically in Refs. 20 and 21.

The present paper is dedicated to an experimental study of the dynamics of the smectic A–smectic C phase transition using ultrasound. The goal of this work is to confirm present theoretical concepts[19-21] about the nature of this phase transition, measure the material parameters of the substance (compressibility of the smectic layers, the viscosity coefficients, the elastic moduli) and their critical dependences on closeness to the transition point, and investigate the contribution to the viscosity coefficients of the critical fluctuations and the fluctuations of the smectic layers over a wide frequency range.

The critical dynamic effects, in spite of the difficulty in interpreting the experiment, turned out to be significantly more informative than the static effects.

2. THEORETICAL PART

2.1. Critical thermodynamics

In the present section we will briefly describe the critical behavior of the smectic phases near the temperature of the transition from the A phase to the C phase. Details of a calculational nature can be found in Refs. 19 and 20, which are specifically dedicated to a theoretical study of this transition. We note that the temperature region of the developed fluctuations near this transition is quite broad. It is comparable with the width of the existence region of the smectic phases themselves. By virtue of this, the conclusions obtained as a result of a consideration of the critical fluctuations are to a significant degree of a general nature since the smectic phases can almost always be considered as being near to the investigated transition.

In equilibrium smectics are systems of equidistant layers, whose normal vector we take to be directed along the z axis. To describe the deviation of the smectic layers from equilibrium, we introduce the smectic variable u, which plays the role of a displacement vector of the layers along the z axis. The elastic energy associated with the curvature of the smectic layers to first order has the standard form[8,9]

$$^1/_2B(\nabla_z u)^2+^1/_2K(\nabla_\perp{}^2u)^2. \tag{1}$$

Here B is the compression modulus of the smectic layers, and K is a coefficient analogous to the Frank modulus in nematics.

The average direction of the major axes of the anisotropic molecules of which the liquid crystal is composed is given by the unit vector $\mathbf{n}$—the director. The main term in the energy density associated with the inhomogeneous deformation of the director in space has the following form:

$$^1/_2K_1(\nabla\mathbf{n})^2+^1/_2K_2(\mathbf{n}[\nabla\mathbf{n}])^2+^1/_2K_3((\mathbf{n}\nabla)\mathbf{n})^2, \tag{2}$$

where K_1, K_2, and K_3 are the Frank moduli.

The various smectic phases differ from one another by the arrangement of the anisotropic molecules inside the smectic layer. Thus, in the smectic A phase the director is perpendicular to the layer, wherefore the vectors $\mathbf{n}$ and $\mathbf{e}$ (the unit normal vector of the layer) coincide. In the smectic C phase the director deviates from the normal to the layer by some angle. The intermolecular forces in this case determine only the projection of the director on the normal to the layer.

A natural order parameter for the phase transition between the smectic A and C phases described above is the vector introduced in Ref. 19

$$\boldsymbol{\psi}=[\mathbf{ne}]. \tag{3}$$

Its value is identically equal to zero in the smectic A phase and differs from zero in the C phase. Since the vector $\mathbf{e}$ is directed along the normal to the layers, the vector $\boldsymbol{\psi}$ lies in the plane of the smectic layer and has only two components.

In the energy expansion there are two terms which determine the relation between the orientation of the molecules (the director $\mathbf{n}$) and the normal to the layer $\mathbf{e}$:

$$^1/_2A\boldsymbol{\psi}^2+^1/_4U\boldsymbol{\psi}^4. \tag{4}$$

The parameter A characterizes the phase transition: when A is greater than zero the A phase is realized, and when A is less than zero—the C phase; U is a constant at the four-point vertex.

The density ρ and the specific entropy σ also enter into the complete set of thermodynamic variables of the smectic, in addition to the smectic variable and the order parameter $\boldsymbol{\psi}$. In the vicinity of the transition only the order parameter $\boldsymbol{\psi}$ fluctuates strongly; the remaining variables fluctuate weakly. Their deviations from equilibrium can be conveniently described by the components of the dimensionless vector $\boldsymbol{\varphi}$

$$\varphi_\nu=\begin{bmatrix}\varphi_\rho\\ \varphi_\sigma\\ \varphi_u\end{bmatrix}=\begin{bmatrix}\delta\rho/\rho\\ \delta\sigma/\sigma\\ \nabla_z u\end{bmatrix}. \tag{5}$$

Here $\delta\rho$ and $\delta\sigma$ are the deviations from the equilibrium values of the density and the specific entropy, respectively.

As usual, to investigate the peculiarities of the phase transition it is sufficient to keep the terms of lowest order in $\boldsymbol{\psi}$ in the energy density. In the interaction terms of the order parameter with the weakly fluctuating quantities φ_ν it is sufficient to keep the terms that are linear in the latter quantities. In the part of the energy that does not contain $\boldsymbol{\psi}$ it is sufficient to keep only the terms quadratic in the weakly fluctuating variables φ_ν. As a result the energy density in the vicinity of the smectic A– smectic C transition acquires the following form:

$$E=^1/_2A\boldsymbol{\psi}^2+^1/_2K_1(\mathbf{e}(\nabla\boldsymbol{\psi}))^2+^1/_2K_2(\nabla\boldsymbol{\psi})^2+^1/_2K_3((\mathbf{e}\nabla)\boldsymbol{\psi})^2 +^1/_4U\boldsymbol{\psi}^4+^1/_2\boldsymbol{\varphi}\mathbf{g}^-\boldsymbol{\varphi}+^1/_2\boldsymbol{\varphi}\boldsymbol{\psi}^2. \tag{6}$$

In expression (6) we have introduced the vector

$$D_\nu=\begin{bmatrix}D_\rho\\ D_\sigma\\ D_u\end{bmatrix}.$$

As follows from Eq. (6), the coefficients D_ν characterize the magnitude of the interaction of the order parameter with the fluctuations of the density, the specific entropy, and the displacement of the smectic layers, respectively. In expression (6) we have also introduced the elastic modulus matrix

$$g_{\mu\nu}^-=\frac{\partial^2E}{\partial\varphi_\mu\partial\varphi_\nu}, \tag{7}$$

where, in particular,

$$g_{uu}^{-}=\frac{\partial^2 E}{\partial(\nabla_z u)^2}=B, \tag{8}$$

$$g_{u\rho}^{-}=\rho\frac{\partial^2 E}{\partial\rho\partial\nabla_z u}=-B\left(\frac{\partial\ln l}{\partial\ln\rho}\right)_\sigma,$$

$$g_{\rho\rho}^{-}=\rho^2\frac{\partial^2 E}{\partial\rho^2}=\rho\left(\frac{\partial P}{\partial\rho}\right)_\sigma.$$

This notation, in contrast to the conventional notation[3,18,22] $g_{\rho\rho}^{-}=A$, $g_{uu}^{-}=B$, and $g_{\rho u}^{-}=C$ makes it possible to use matrix formalism, which simplifies the otherwise cumbersome formulas. In Eqs. (8) P is the pressure, g_{uu}^{-} is the compression modulus of the smectic layers B, which was introduced in Eq. (1), and the elastic modulus $g_{\rho\rho}^{-}$ is the inverse compressibility. The elastic moduli associated with the compression of the smectic layers satisfy the following relation:

$$\frac{g_{u\rho}^{-}}{g_{uu}^{-}}=-\left(\frac{\partial\ln l}{\partial\ln\rho}\right)_\sigma\sim -1, \tag{9}$$

where l is the equilibrium spacing between the smectic layers.

Before embarking upon an exposition of the critical behavior of the quantities introduced in expressions (6)–(9) in the vicinity of the A–C transition, we present typical values of the material parameters of a smectic:

—the compression modulus of the smectic layers has the typical value

$$g_{uu}^{-}=B\sim 10^8\ \text{erg/cm}^3, \tag{10}$$

—the compressibility of the smectic has a value of the same order of magnitude as in ordinary liquids:

$$g_{\rho\rho}^{-}\sim 10^{10}\ \text{erg/cm}^3. \tag{11}$$

It follows from this that in the smectic phases there exists a small parameter

$$g_{uu}^{-}/g_{\rho\rho}^{-}\sim g_{u\rho}^{-}/g_{\rho\rho}^{-}\sim 10^{-2}, \tag{12}$$

which shows that the density in the smectic is weakly modulated, because the latter is close to a nematic.

The components of the vector **D**, which figure in the energy density (6) and which describe the contribution to the energy from the interaction of the order parameter with the weakly fluctuating quantities, are equal in order of magnitude to the compression modulus of the smectic layers. The quantity U has the same order of magnitude:

$$U,\ D_\rho,\ D_\sigma,\ D_u\sim 10^8\ \text{erg/cm}^3. \tag{13}$$

Finally, the characteristic value of the Frank moduli in a smectic coincides with their value in a nematic:

$$K_{1,2,3},\ K\sim 10^{-6}\ \text{erg/cm}. \tag{14}$$

As the analysis of Kats and Lebedev[19] has shown, neither in the mean-field theory nor in the wide range of developed fluctuations does treating the fluctuations of the order parameter yield corrections to the gradient terms of the energy density (6). In the latter region the Frank moduli are not renormalized. Renormalization of the Frank moduli, corresponding completely to the universal behavior of the ψ^4 model with a two-component order parameter, does not take place in the real situation. In what follows, by the region of developed fluctuations we mean specifically the region of nonuniversal critical behavior. In this region the critical behavior is described by nonuniversal indices, which depend on the unrenormalized ratios of the Frank moduli K_1/K_2 and K_1/K_3.

In contrast with the Frank moduli the elastic moduli are very sensitive to how near the system is to the smectic A–smectic C transition. In the mean field theory these moduli undergo a jump at the transition

$$\delta g_{\nu\mu}^{-}=-D_\nu D_\mu/2U. \tag{15}$$

It follows from Eqs. (10) and (13) that the elastic moduli decrease by a jump at the transition from the A to the C phase of the order of magnitude of g_{uu}^{-}.

In the region of developed fluctuations critical corrections to the elastic moduli arise. The renormalized elastic moduli have the following form:[20]

$$\tilde{g}_{\mu\nu}^{-}=g_{\mu\nu}^{-}-\frac{D_\mu D_\nu F(\tau)}{1+(\mathbf{DgD})F(\tau)}, \tag{16}$$

where D and g^{-} are unrenormalized quantities, and the magnitude of F is determined by the correlator of the order parameter

$$F(\tau)=\int\frac{\langle\langle\psi^2(0)\psi^2(r)\rangle\rangle}{4T}d^3r, \tag{17}$$

where T is the temperature, τ is the dimensionless parameter of the nearness of the system to the phase transition of the form

$$\tau=(T-T_{AC})/T_{AC}. \tag{18}$$

The correlator (17) has a critical singularity $\sim\tau^{-\alpha}$ near the transition point. The specific heat index α is a small quantity. In the standard model[23] with a two-component order parameter it is close to zero. By virtue of the nonuniversality the index α lies within the limits 0.06–0.14.

The quantity A figuring in expressions (4) and (6) is $\sim\tau^{-\gamma}$ in the region of developed fluctuations. The susceptibility index γ varies, depending on the starting ratios of the Frank moduli, in the range 1–1.25.

In the mean field theory the order parameter behaves like $\tau^{1/2}$ with approach to the transition point, and in the region of developed fluctuations—like $\tau^{2\beta}$. The magnitude of the index β of the order parameter lies within the range $\sim$0.43–0.45, and the index of the correlation length $\nu\sim$0.58–0.62.

All the critical indices the nonuniversal region were calculated by the method of the renormalization group in three-dimensional space.[19] The essential results of the experiments[10–13] agree with the qualitative and quantitative characteristics of the A–C transition described above.

2.2. Dynamic viscoelastic properties of a smectic in the vicinity of the A–C transition

A consistent description of the dynamic effects associated with the fluctuations of the order parameter was made in Ref. 20. A nondissipative system of hydrodynamic equations for the long-wave variables of a smectic (the velocity v, the order parameter ψ, the density ρ, the specific entropy σ, and the smectic variable u) was obtained with the help of the Poisson bracket method.[24] The kinetic terms, which take dissipative processes into account, were then added to these

equations in the standard way. The eigenmode spectrum of the smectic with the fluctuations of the order parameter taken into account was calculated with the help of the diagram technique.[25] The technical details of the calculations can be found in Ref. 20 or in the review (26).

The theoretical scheme developed in Ref. 20 for the study of critical dynamics provides the basis for the idea of the effective exclusion of the weakly fluctuating variables. As a result of such an exclusion it was possible to obtain an "effective equation of the dynamics" of the order parameter itself:

$$\frac{\partial \psi}{\partial t} = \Gamma^{eff} \frac{\delta E^{eff}}{\delta \psi}. \tag{19}$$

Here Γ^{eff} and E^{eff} are, respectively, the effective kinetic coefficient and the effective energy associated with ψ. Equation (19) corresponds to the purely dissipative dynamics[27] of the two-component order parameter. As was shown by the renormalization group study in the scaling region, the kinetic coefficient depends on the wave vector q according to a power-law relationship:

$$\Gamma^{eff} \propto q^{z-2}, \tag{20}$$

where z is the dynamic index and is very close to 2.

Along with the thermodynamic critical indices introduced in Sec. 2.1, the index z determines the scaling laws of the behavior of the various dynamic correlators.

In what follows we will have need of the following irreducible dynamic correlator:

$$F = \int \frac{\langle\langle \psi^2(r,t)\psi^2(0,0)\rangle\rangle}{4T} e^{-i\omega t} \frac{d^3r\,dt}{(2\pi)^4} = F'(\omega,\tau) + iF''(\omega,\tau). \tag{21}$$

Here ω is the frequency. In the hydrodynamic and fluctuation regions the real functions F' and F'' behave in the following way:

$$\begin{aligned} &F' \propto \tau^{-\alpha},\ F''/\omega \propto \tau^{-(z\nu+\alpha)}; \\ &F' \propto \omega^{-\alpha/z\nu},\ F''/\omega \propto \omega^{-(\alpha/z\nu+1)}. \end{aligned} \tag{22}$$

Here α and ν are the above specific heat indices and the correlation length, respectively, and z is the dynamic critical index.[27]

The spectra of the noncritical modes were determined in Ref. 20 as the poles of the corresponding renormalized response functions. We will present at once results pertinent to the spectra of the acoustic modes.

The frequencies of first and second sound ω as functions of the wave vector $\mathbf{q}$ are determined in the vicinity of the A–C transition by solving the system of equations

$$\omega\rho\delta_{im} - f_{ip}^{\mu} q_p G_{\mu\nu}^{-}(\omega,\tau) q^l f_{lm}^{\nu} - i\eta_{iklm} q_l q_k \omega = 0. \tag{23}$$

Here η is the viscosity tensor of the smectic:[8,22]

$$\begin{aligned} \eta = {} & \eta_1(\delta_{il}^{\perp}\delta_{km}^{\perp} + \delta_{kl}^{\perp}\delta_{im}^{\perp}) + (\eta_2 - \eta_1)\delta_{ik}^{\perp}\delta_{lm}^{\perp} + \eta_5 e_i e_k e_l e_m \\ & + {}^1/_2\eta_3(e_i e_l \delta_{km}^{\perp} \\ & + e_k e_l \delta_{im}^{\perp} + e_i e_m \delta_{kl}^{\perp} + e_k e_m \delta_{il}^{\perp}) \\ & + \eta_4(e_i e_k \delta_{lm}^{\perp} + e_l e_m \delta_{ik}^{\perp}),\ \delta_{ik}^{\perp} = \delta_{ik} - e_i e_k, \end{aligned} \tag{24}$$

e is the equilibrium value of the unit normal vector of the smectic layers, and $\eta_{2,4,5}$ are the bulk viscosity coefficients and $\eta_{1,3}$ are the shear viscosity coefficients. In Eqs. (23) we have introduced the vector

$$f_{ik}^{\mu} = \begin{bmatrix} f_{ik}^{\rho} \\ f_{ik}^{\sigma} \\ f_{ik}^{u} \end{bmatrix} = \begin{bmatrix} \rho\delta_{ik} \\ 0 \\ e_i e_k \end{bmatrix}. \tag{25}$$

The complex quantities $\mathbf{G}^-$ figuring in Eq. (23) are the renormalized dynamic moduli $\mathbf{g}^-$. They have the following form:[20,26]

$$G_{\mu\nu}^{-}(\omega,\tau) = g_{\mu\nu}^{-} - \frac{D_\mu D_\nu F(\omega,\tau)}{1 + [\mathbf{DgD}]F(\omega,\tau)}. \tag{26}$$

It is precisely the components of matrix (26) that determine the dynamic viscoelastic properties of the liquid crystal. In particular, they determine the acoustic spectra studied in the ultrasound experiments. It follows immediately from Eqs. (23) that the renormalized viscosity tensor, which takes the critical fluctuations of the order parameter into account, is equal to

$$\tilde{\eta}_{iklm} = \eta_{iklm} + \delta\eta_{iklm}(\omega,\tau),$$

where the first term corresponds to the unrenormalized value, and the correction has the form

$$\omega\delta\eta_{iklm} = f_{ik}^{\mu}\,\mathrm{Im}\,G_{\mu\nu}^{-} f_{lm}^{\nu}. \tag{27}$$

Here Im G^- is the imaginary part of the dynamic renormalized matrix of the elastic moduli (26).

Making use of the explicit form of the viscosity tensor (24) and the components of the vector $\mathbf{f}^{\mu}$ figuring into Eq. (27), it is not difficult to calculate the values of the critical corrections to the viscosity coefficients:

$$\begin{aligned} {}^1/_2\omega\delta\eta_5 &= \mathrm{Im}\,G_{\rho\rho}^{-} - 2\,\mathrm{Im}\,G_{\rho u}^{-} + \mathrm{Im}\,G_{uu}^{-}, \\ {}^1/_2\omega\delta\eta_4 &= \mathrm{Im}\,G_{\rho\rho}^{-} - \mathrm{Im}\,G_{\rho u}^{-}, \\ {}^1/_2\omega\delta\eta_2 &= \mathrm{Im}\,G_{\rho\rho}^{-}. \end{aligned} \tag{28}$$

The imaginary part of the complex matrix (26) determines the fluctuational corrections to the sound absorption. Its real part determines the elastic dynamic properties of the smectic. In the vicinity of the phase transition the dynamic elastic moduli (7) and (8) are equal to

$$\tilde{g}_{\mu\nu}^{-}(\omega,\tau) = \mathrm{Re}\,G_{\mu\nu}^{-}(\omega,\tau) = g_{\mu\nu}^{-} + \delta g_{\mu\nu}^{-}(\omega,\tau). \tag{29}$$

The first term on the right-hand side of this equation corresponds to the unrenormalized value of the elastic moduli.

Let us consider the behavior of the viscosity (28) and the elastic moduli (29). In the region of universal critical behavior the fluctuational corrections to the compressibility are much greater than the unrenormalized values:

$$(\mathbf{DgD})F \gg 1. \tag{30}$$

After some elementary calculations which have to do with isolating the real part of the matrix (26), it is possible to find expressions that describe the behavior of the elastic moduli in the scaling region (the region of universal behavior). Taking Eq. (30) into account, we obtain

$$\delta g_{\mu\nu}^{-} = -\frac{D_\nu D_\mu}{(\mathbf{DgD})} + \frac{D_\nu D_\mu}{(\mathbf{DgD})} \frac{F'(\omega,\tau)}{F'^2 + F''^2}, \tag{31}$$

$$\nu,\ \mu = u,\ \rho,\ \sigma.$$

For the critical corrections to the bulk viscosity coefficients in the scaling region we find

$$\frac{\omega\delta\eta_5}{2}=\frac{(D_\rho-D_u)^2}{(\mathbf{DgD})}\frac{F''}{F'^2+F''^2}$$
$$\frac{\omega\delta\eta_4}{2}=\frac{(D_\rho-D_u)D_\rho}{(\mathbf{DgD})}\frac{F''}{F'^2+F''^2}, \qquad (32)$$
$$\frac{\omega\delta\eta_2}{2}=\frac{D_\rho^2}{(\mathbf{DgD})}\frac{F''}{F'^2+F''^2}.$$

The compressibilities in the scaling region near the transition diverge like $\tau^{-\alpha}$. The behavior of the elastic moduli has a more complicated character. In Eq. (31) the second terms vary like τ^α in the hydrodynamic limit and are, generally speaking, small in comparison with the first. However, they cannot be neglected, since in the opposite case the elastic modulus matrix $\tilde{\mathbf{g}}^-$ becomes degenerate.

From Eqs. (30)–(32) follow the laws of critical behavior in the scaling region. Using relations (22), we find in the hydrodynamic limit

$$\delta g^-(\tau)\propto\tau^\alpha+\text{const},$$
$$\delta\eta_{2,4,5}(\tau)\propto\tau^{\alpha-z\nu} \qquad (33)$$

and in the fluctuation limit

$$\delta g^-(\omega)\propto\omega^{\alpha/z\nu}+\text{const},$$
$$\delta\eta_{2,4,5}(\omega)\propto\omega^{\alpha/z\nu-1}. \qquad (34)$$

Note that since the finite frequency ω suppresses the critical fluctuations, the scaling behavior of the smectic, described by the laws (30)–(34), is apparently not realized experimentally. For the majority of real second-order phase transitions in liquid media at experimentally realizable frequencies and temperatures condition (30) is practically never satisfied. In other words, the critical corrections to the moduli $\mathbf{g}^-$ are less than their unrenormalized values.

As follows from an analysis of experimental results,[5,6] at the most commonly used frequency for ultraviolet measurements $\omega\sim10^6$ sec^{-1} the critical corrections are much smaller than the starting elastic modulus $g_{\rho\rho}^-$. Recall that the latter in smectics plays the role of the ordinary compressibility in liquids $\partial P/\partial\rho$ and amounts to $\sim10^{10}$ erg/cm^3. However, in the region of developed fluctuations the critical corrections δg^-, generally speaking, are not small incomparison with the small elastic compression modulus of the smectic layers $g_{uu}^-\sim10^8$ erg/cm^3. Thus, in smectics by virtue of Eq. (12) the width of the crossover region is broadened. In the crossover region the critical corrections become comparable to the unrenormalized values:

$$(\mathbf{DgD})F\sim\mathbf{D}^2F/g_{uu}^-\sim1. \qquad (35)$$

Calculating the real part of matrix (26), we obtain the following cumbersome formulas for the corrections to the elastic moduli in the crossover region

$$\delta g_{\nu\mu}^-=-\frac{D_\nu D_\mu}{(\mathbf{DgD})}\frac{[(\mathbf{DgD})^{-1}+F']F'+F''^2}{[(\mathbf{DgD})^{-1}+F']^2+F''^2}, \quad \nu,\mu=u,\rho,\sigma. \qquad (36)$$

The corrections to the bulk viscosity coefficients in the crossover region have the form

$$^1/_2\omega\delta\eta_5=(D_\rho-D_u)^2M,\ ^1/_2\omega\delta\eta_2=D_\rho^2M,$$
$$^1/_2\omega\delta\eta_4=(D_\rho-D_u)D_\rho M, \qquad (37)$$
$$M=\frac{(\mathbf{DgD})^{-1}F''}{[(\mathbf{DgD})^{-1}+F']^2+F''^2}.$$

From formulas (36) and (37) it is seen that in the transition region between the region of universal behavior and the region of weak fluctuations the behavior of the elastic moduli and the corrections to the viscosity coefficients already ceases to obey the simple critical dependences. This is because the unrenormalized moduli figure in formulas (36) and (37), along with the fluctuation terms.

Note that the elastic moduli and the corrections to the bulk viscosity coefficients in the crossover region behave in a very complicated manner. In particular, the absorption maximum and the minimum of the elastic moduli no longer need coincide at the phase transition point. Indeed, at the transition point the functions F' and F'' figuring in the critical corrections are extremal. However, the extrema of the quantities (36) and (37) can be shifted to one of the smectic phases. We emphasize that this effect is purely dynamical.

Let us consider, finally, the region far from the transition point, where the critical corrections can be assumed to be weak not only in comparison with the elastic compressibility modulus $g_{\rho\rho}^-$, which has a value of $\sim10^{10}$ erg/cm^3, but also in comparison with the elastic compression modulus of the smectic layers $g_{uu}^-\sim10^8$ erg/cm^3, i.e., where

$$F(\mathbf{DgD})\sim FD^2/g_{uu}^-\ll1. \qquad (38)$$

In this case from relations (28) it is possible to obtain

$$\delta g_{uu}^-=-D_u^2F'(\omega,\tau),$$
$$\delta g_{\rho u}^-=-D_uD_\rho F'(\omega,\tau), \qquad (39)$$
$$\delta g_{\rho\rho}^-=-D_\rho^2F'(\omega,\tau).$$

For the critical corrections to the viscosity in the region of weak fluctuations we obtain

$$^1/_2\omega\delta\eta_2=D_\rho^2F'',$$
$$^1/_2\omega\delta\eta_4=D_\nu(D_\rho-D_u)F'', \qquad (40)$$
$$^1/_2\omega\delta\eta_5=(D_\rho-D_u)^2F''.$$

The critical correction in relations (39) and (40) were first obtained in Ref. 21 by the method of interacting modes.

Making use of relations (22), we obtain the law of the critical behavior of the fluctuational corrections to the elastic moduli and to the bulk viscosity coefficients. In the hydrodynamic and fluctuation regions they have the following forms, respectively:

$$\delta g_{\nu\mu}^-\propto\tau^{-\alpha},\ \delta\eta_{2,4,5}\propto\tau^{-(z\nu+\alpha)},$$
$$\delta g_{\nu\mu}^-\propto\omega^{-\alpha/z\nu},\ \delta\eta_{2,4,5}\propto\omega^{-(1+\alpha/z\nu)}. \qquad (41)$$

We emphasize again that Eqs. (39)–(41) are valid as long as the critical corrections are small in comparison with the unrenormalized compression modulus of the smectic layers [as long as condition (38) is satisfied].

The critical corrections to the elastic moduli of a smectic satisfy the following relation:

$$\delta g_{uu}^-:\delta g_{\rho u}^-:\delta g_{\rho\rho}^-=(D_u/D_\rho)^2:(D_u/D_\rho):1. \qquad (42)$$

Here the critical fluctuations always cause the elastic moduli g_{uu} and $g_{\rho\rho}^-$ to decrease. The sign of the critical correction to the crossover elastic modulus $g_{u\rho}^-$ is determined by the sign of the quantity D_u/D_ρ and can be both negative and positive.

The corrections to the bulk viscosity coefficients are connected by the universal relation

$$\delta\eta_5 : \delta\eta_4 : \delta\eta_2 = (1-D_u/D_\rho)^2 : (1-D_u/D_\rho) : 1. \qquad (43)$$

The corrections to the bulk viscosity coefficients η_5 and η_2 are always positive, and the sign of the critical corrections to the bulk viscosity coefficient η_4 is determined by the sign of the quantity $1 - D_u/D_\rho$. This sign is not universal and can be both positive and negative.

2.3. Corrections to the viscosity coefficients connected with the fluctuations of the smectic layers

In the above examination of the critical dynamics of the A–C transition the fluctuations of the density ρ, the specific entropy, and the displacement of the smectic layers were taken into account in the first approximation. In the hydrodynamic equations only the terms linear in the deviations of these weakly fluctuating quantities (5) were kept, and in the energy expansion, the quadratic terms.

However, this approximation, which is valid for fluctuations of ρ and σ, is, generally speaking, invalid for fluctuations of the smectic layers. The point here is that although the smectics possess solid-state order in the direction perpendicular to the layers, the layers themselves can slip past one other. In such an infinite system the fluctuations destroy the long-range order.[28] In a real system an account of the interaction of the fluctuations leads to highly nontrivial corrections to the sound absorption. To obtain them in the expansion over the smectic variable (1) of the energy associated with the deformation of the layers, it is necessary to take into account not only the quadratic terms but also the cubic terms

$$-\varphi_\nu D_\nu' (\nabla_\perp u)^2, \qquad (44)$$

where

$$D' = \begin{bmatrix} D_\rho \\ D_\sigma \\ D_u \end{bmatrix} = \begin{bmatrix} g_{u\rho}^- \\ g_{u\sigma}^- \\ g_{uu}^- \end{bmatrix},$$

and φ_ν are the components of the weakly fluctuating quantities introduced in Eq. (5). In the thermodynamics taking the cubic term into account[29,30] leads to logarithmically weak (probably not experimentally observable) corrections to the elastic moduli. In the hydrodynamics the interaction of the fluctuations of the smectic layers leads to corrections to the bulk viscosity coefficients which are divergent in the low-frequency limit.[14]

A consistent calculation of the magnitude of these corrections, based on the hydrodynamic equations for the smectic A phase, was carried out in Ref. 15 by means of the diagram technique[25] and expounded in detail in Ref. 8. The interaction vertices in this technique are the nonlinear terms in the hydrodynamic equations proceeding from the cubic terms (44).

We present the results obtained in Ref. 15. The correction to the viscosity tensor due to the fluctuations of the smectic layers in the A and C phases has the following form [cf. Eq. (27)]:

$$\delta'\eta_{iklm} = f_{ik}^\mu D_\mu' D_\nu' f_{lm}^\nu A_{A,C}/\omega, \qquad (45)$$

and in the smectic A phase the coefficient A is equal to

$$A_A = \frac{T}{128K^{3/2}}. \qquad (46)$$

The dummy indices ν and μ run through the values ρ, σ, and u; and the components of the vectors $\mathbf{f}$ and $\mathbf{D}'$, figuring in Eq. (45), are given by Eqs. (25) and (44).

In the smectic A the corrections to the viscosity tensor also diverge in the low-frequency limit $\sim\omega^{-1}$. However, the coefficient A_C in the smectic C phase is different.[17] The reason for this is that in the smectic C, along with the slow fluctuations of the smectic layers, there appears an additional slow mode, the orientational mode. In the smectic C the orientational mode is strongly coupled to the mode associated with the oscillations of the smectic layers. Because of this coupling the coefficient A_C in the C phase is greater by a factor of Ξ than in the A phase:

$$A_C = \frac{T}{128}\frac{\Xi}{K^{3/2}}. \qquad (47)$$

The positive quantity $\Xi > 1$ depends on the material parameters of the smectic C (the Frank moduli and the elastic moduli). Numerical calculation[17] has shown that it can be much greater than unity ($\gtrsim 10$).

Making use of the explicit form of the viscosity tensor and the vector (25), we find that the fluctuations of the smectic layers lead to the following corrections to the bulk viscosity coefficients[2)]

$$\begin{aligned} \frac{\delta'\eta_5}{2} &= \frac{(g_{u\rho}^- - g_{uu}^-)^2}{(g_{uu}^-)^{1/2}}\frac{A_{A,C}}{\omega}, \\ \frac{\delta'\eta_4}{2} &= \frac{(g_{u\rho}^- - g_{uu}^-)g_{u\rho}^-}{(g_{uu}^-)^{1/2}}\frac{A_{A,C}}{\omega}, \\ \frac{\delta'\eta_2}{2} &= \frac{(g_{u\rho}^-)^2}{(g_{uu}^-)^{1/2}}\frac{A_{A,C}}{\omega}. \end{aligned} \qquad (48)$$

Here g^- are the elastic moduli, and the quantity A in the smectic A and C phases is given, respectively, by expressions (46) and (47). Note that the corrections to the bulk viscosity coefficients η_5 and η_2 are always positive. The sign of the correction to the bulk viscosity coefficient η_4 is indeterminate. Nevertheless, the universal relation

$$\delta'\eta_2\delta'\eta_5 = \delta'\eta_4^2,$$

which follows from Eqs. (48), ensures the growth of the entropy.

2.4. Spectra of the acoustic modes in the vicinity of the smectic A–smectic C phase transition

In general, even far from the transition temperature the spectra of second and first sound, obtained from the solution of system (23), are quite involved. Nevertheless, they can be written in explicit form using the condition for the existence of a small parameter (12).[3,8,14,19]

The ratios of the renormalized elastic moduli

$$\frac{\tilde g_{uu}^-}{\tilde g_{\rho\rho}^-} \sim \frac{\tilde g_{u\rho}^-}{\tilde g_{\rho\rho}^-} \sim \frac{\tilde g_{uu}^-}{\tilde g_{\rho\rho}^-} \sim 10^{-2} \qquad (49)$$

also remain small. By solving the system of equations (23) taking Eq. (49) into account, it is possible to obtain the spectra of first and second sound. In the vicinity of the transition they have the following form:

$$\frac{\rho\omega^2}{q^2}=\rho c_{(1,2)}^2-i\omega\eta_{(1,2)}, \tag{50}$$

$$\rho c_{(1)}^2=\tilde{g}_{\rho\rho}^{-}-2\tilde{g}_{\rho u}^{-}\frac{q_z^2}{q^2}+\tilde{g}_{uu}^{-}\frac{q_z^4}{q^4}, \tag{51}$$

$$\eta_{(1)}=[\eta_1+(\eta_2+\delta\eta_2+\delta'\eta_2)]\,q_\perp^4/q^4+(\eta_5+\delta\eta_5+\delta'\eta_5)\,q_z^4/q^4+2[\eta_3+(\eta_4+\delta\eta_4+\delta'\eta_4)]\,q_z^2q_\perp^2/q^4, \tag{52}$$

$$\rho c_{(2)}^2=\tilde{g}_{uu}^{-}q_z^2q_\perp^2/q^4, \tag{53}$$

$$\eta_{(2)}=\eta_3(q_z^2-q_\perp^2)^2/q^4+[\eta_1+(\eta_2+\delta\eta_2+\delta'\eta_2)+(\eta_5+\delta\eta_5+\delta'\eta_5)-2(\eta_4+\delta\eta_4+\delta'\eta_4)]\,q_z^2q_\perp^2/q^4. \tag{54}$$

Here q_z and $q_\perp$ are the components of the wave vector $\mathbf{q}$ along the normal $\mathbf{e}$ and perpendicular to it, respectively, η are the unrenormalized viscosity coefficients introduced in Eq. (24), $\delta\eta$ are the critical corrections to the bulk viscosity coefficients (28), (32), (37), and (40), $\delta'\eta$ are the corrections to the bulk viscosity coefficients associated with the fluctuations of the smectic layers (48), and $\tilde{\mathbf{g}}^-$ are the renormalized dynamic elastic moduli of the smectic (29), (31), (36), and (39).

The sound described by the spectrum (50)–(52) is analogous to ordinary sound in liquids or longitudinal sound in solids. The wave vector $\mathbf{q}$ coincides in this mode with the direction of the velocity vector. The mode (50), (53), (54) describes second sound, which is analogous to shear sound in solids. Second sound degenerates into the diffusion mode when the wave vector coincides with the normal to the layer or lies in it.

3. SHEAR WAVES (SECOND SOUND)

3.1. Experimental technique and results

We investigated the propagation of shear waves in the vicinity of the smectic *A*–smectic *C* phase transition. As the objects of our study we chose materials which undergo the following phase transitions:

pentyloxybenzylidene-hexylaniline (PBHA)—

$$I \xleftrightarrow{346{,}2\ \text{K}} N \xleftrightarrow{334{,}3\ \text{K}} S_A \xleftrightarrow{324{,}7\ \text{K}} S_C,$$

butyloxyphenyl-decyloxybenzoate (BOPDOB)—

$$I \xleftrightarrow{359{,}4\ \text{K}} N \xleftrightarrow{346{,}7\ \text{K}} S_A \xleftrightarrow{335{,}2\ \text{K}} S_C.$$

and butyloxyphenyl-nonyloxybenzoate (BOPNOB)—

$$I \xleftrightarrow{363{,}5\ \text{K}} N \xleftrightarrow{351{,}1\ \text{K}} S_A \xleftrightarrow{330{,}5\ \text{K}} S_C.$$

The smectic phases were oriented starting from the nematic phase by a magnetic field by means of a magnetic induction of 2.2 T with subsequent cooling. The study of second sound in the smectics was carried out by the acoustic shear impedance method. A detailed account of this method and a diagram of the experiment can be found in Ref. 31.

A quartz disk served as the measuring element. For some experimental geometries the working surface of the disk was treated with various surface-binding substances—silanes, which created a homeotropic or planar orientation of the molecules of the smectic. The measurement of the angular dependence was made at 5° intervals. The fundamental frequency of the experiment was 3 MHz. The absolute measurement error was at most 3–5%. The geometry of the experiment ensured propagation only of second sound.

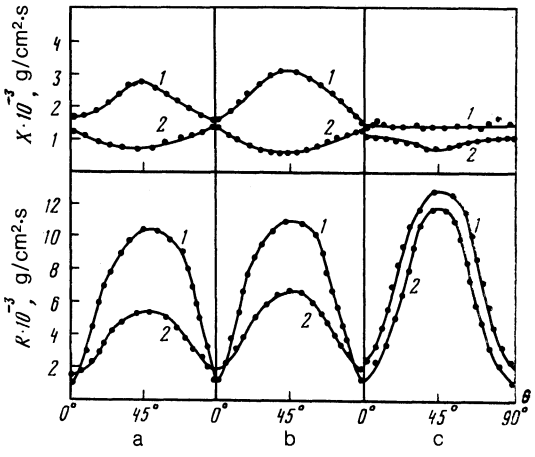

FIG. 1. Orientational dependence of the real (R) and imaginary (X) components of the impedance (the inverse wave vector) at $f=3$ MHz for various substances: a) BOPNOB: 1) A phase, $T-T_{AC}=4$ K, 2) C phase, $T-T_{AC}=-3$ K; b) PBHA: 1) A phase, $T-T_{AC}=4.3$ K, 2) C phase, $T-T_{AC}=-1$ K; c) BOPDOB: 1) A phase, $T-T_{AC}=12.5$ K, 2) A phase, $T-T_{AC}=3.5$ K.

During the course of the experiment the imaginary (X) and real (R) components of the acoustic shear impedance of the liquid crystal were measured using radio devices. These components are related in the following way with the inverse wave vector of the propagating second sound:

$$q^{-1}(\omega)=[R(\omega)+iX(\omega)]/\rho\omega. \tag{55}$$

Figure 1 shows the orientational dependence of the components of the impedance [or to within the constant factor $\rho\omega$ the inverse wave vector (55)]. In these figures and everywhere below θ is the angle between the normal vector to the smectic layer $\mathbf{e}$ and the wave vector $\mathbf{q}$.

3.2. Analysis of the experimental data

Solving Eq. (50) for the square of the inverse wave vector and using the definition of the components of the impedance (55), we obtain after separating the imaginary and real parts

$$g_{uu}^{-}(\omega,\tau)=\frac{4(R^2-X^2)}{\rho\sin^2 2\theta},$$
$$\eta_{(2)}(\theta,\omega,\tau)=\frac{2RX}{\rho\omega}. \tag{56}$$

The viscosity coefficient of second sound $\eta_{(2)}$, which depends on the direction of propagation and takes account of the critical corrections and the corrections associated with the fluctuations of the smectic layers, is given by Eq. (54). Equations (56) make it possible to express the material parameters of the smectic in terms of the experimental values of the components R and X of the shear impedance.

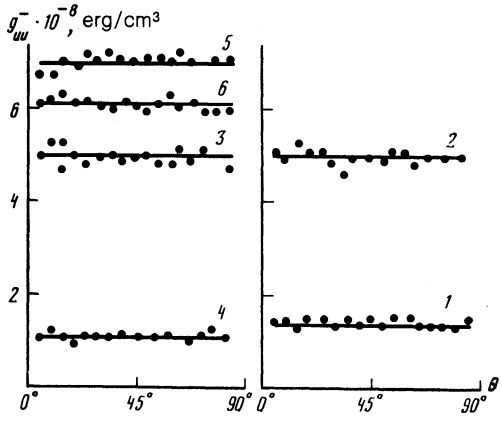

FIG. 2. Compression modulus of the smectic layers g_{uu}^{-} calculated according to Eqs. (56) ($f = 3$ MHz): 1) BOPNOB, A phase, $T - T_{AC} = 4$ K, 2) BOPNOB, C phase, $T - T_{AC} = -3$ K, 3) PBHA, A phase, $T - T_{AC} = 4.3$ K, 4) PBHA, C phase, $T - T_{AC} = -1$ K; 5) BOPDOB, A phase, $T - T_{AC} = 3.5$ K, 6) A phase, $T - T_{AC} = 12.5$ K.

Figure 2 shows the compression moduli of the smectic layers in the investigated substances for the smectic A and C phases. As also follows from the mean field theory [see Eq. (15)], in the transition from the smectic A to the smectic C phase the magnitude of this elastic modulus decreases by an amount comparable to itself: $\Delta g_{uu}^{-} \sim 10^8$ erg/cm³. The lack of dependence of the magnitude of the elastic modulus g_{uu}^{-} calculated according to Eq. (56) on the orientation confirms the single-domain character of the investigated sample and the form of the spectrum of second sound (50), (53), (54).

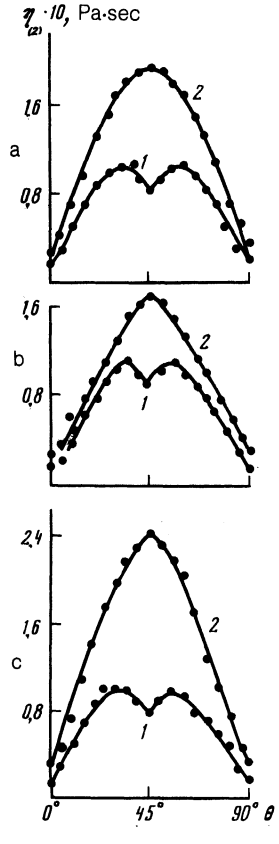

FIG. 3. Orientational dependence of the viscosity coefficient of second sound (54) calculated according to Eqs. (56) ($f = 3$ MHz): a) BOPNOB: 1) A phase, $T - T_{AC} = 4$ K, 2) C phase, $T - T_{AC} = -3$ K; b) PBHA: 1) A phase, $T - T_{AC} = 4.3$ K, 2) C phase, $T - T_{AC} = -1$ K; c) BOPDOB: 1) A phase, $T - T_{AC} = 12.5$ K, 2) A phase, $T - T_{AC} = 3.5$ K.

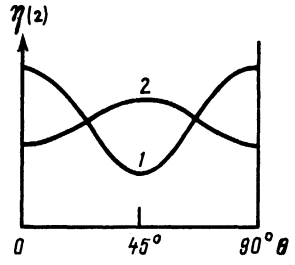

FIG. 4. Theoretical orientational dependence of the viscosity coefficient of second sound (54) for the two cases described by inequalities (57).

Figure 3 shows the orientational dependence of the viscosity of second sound (54). It can be seen that a changeover of regimes takes place in its orientational behavior: for the propagation angle $\theta = 45°$ the absorption maximum (curve 2) changes into a minimum (curve 1). The reason for this is the following. The theoretical orientational dependence of the viscosity of second sound, described by expression (54), is depicted in Fig. 4. Here curves 1 and 2 describe, respectively, the situations

$$^1/_2\eta_s \gtrless (\eta_1+\eta_2+\eta_5-2\eta_4)+\delta\eta_{(2)}(\omega,\tau)+\delta'\eta_{(2)}(\omega,\tau). \quad (57)$$

The last two terms on the right-hand sides of these inequalities describe the critical corrections (28) and the corrections associated with the fluctuations of the smectic layers (48). These corrections in the vicinity of the transition depend strongly on the frequency and the temperature. As the temperature of the transition from the smectic A to the smectic C phase is approached, the critical correction $\delta\eta$ grows strongly. Its growth with approach to the transition temperature leads to the changeover (57) of the regimes in the orientational behavior of the viscosity.

However, the agreement of the experimental orientational dependences (Fig. 3) with the theoretical (Fig. 4) breaks down in the propagation angle ranges 0–25° and 75–90°. This has to do with the fact that at $\theta = 0°$ and 90° second sound degenerates into the diffusion mode. The sound penetration depth in a sample of the investigated medium in this case is comparable with the depth of influence of the boundary conditions on the quartz disc. This may explain the difference between the experimental (Fig. 3) and theoretical

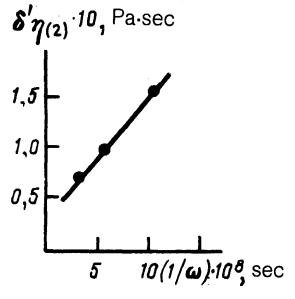

FIG. 5. Frequency dependence of the correction (48) to the viscosity coefficient of second sound (54) associated with the fluctuations of the smectic layers, calculated according to Eqs. (56); $\theta = 45°$.

(Fig. 4) orientational dependences of the absorption of second sound at these angles.

Unfortunately, we do not know of any other experimental data on the orientational dependence of the absorption of second sound in oriented smectic liquid crystals. (In Ref. 32 only the orientational dependence of the real component R of the impedance was measured.)

Let us turn now to the frequency dependence of the components of the impedance at constant temperature. The magnitudes of these components at the propagation angle $\theta = 45°$ were measured at three frequencies $\omega = 9.86 \cdot 10^6$ sec^{-1}, $1.88 \cdot 10^7$ sec^{-1}, and $3.14 \cdot 10^7$ sec^{-1}. The dependence of the viscosity coefficient of second sound on the inverse frequency is shown in Fig. 5.

Making use of Eq. (47), from the slope of the straight line depicted in Fig. 5 we can make the following estimate

$$K/\Xi^{2/3} \sim 2.7 \cdot 10^{-8} \text{ erg/cm}. \tag{58}$$

Ξ is a dimensionless quantity associated with the appearance in the smectic C phase of an additional orientational mode. From typical values of the Frank modulus (14) and the estimate (58) we get the following estimate

$$\Xi \sim 10. \tag{59}$$

Note that the treatment of the frequency dependence of the damping of the sound according to Eq. (46), which is valid only for the A phase, gives rise to the invalid conclusion that the Frank modulus K decreases in the transition from the A to the C phase. Estimate (59) agrees numerically with the experimental results of Ref. 18, in which, however, the increase of the fluctuational damping (47) by the factor Ξ in the smectic C was incorrectly interpreted as a decrease in the Frank modulus.

Finally, let us directly consider the smectic A–smectic C phase transition. The temperature dependences of the elastic modulus g_{uu}^- calculated according to Eqs. (56) and the viscosity of second sound $\eta_{(2)}$ are shown in Fig. 6. Far from the transition point the regular behavior of the absorption [of course, taking into account the temperature-independent corrections associated with the fluctuations of the smectic layers (48)] is determined by the unrenormalized viscosity coefficients.

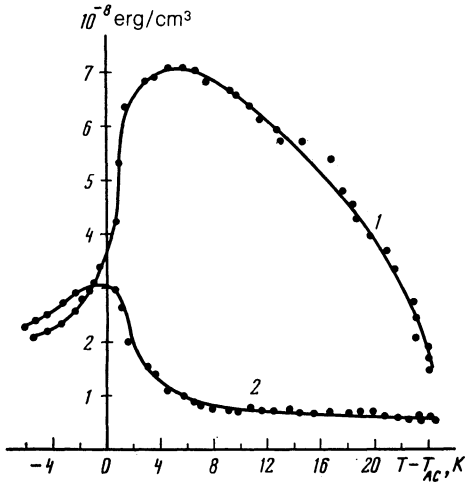

FIG. 6. 1) Temperature dependence of the compression modulus of the smectic layers (8), and 2) the viscosity $\omega\eta_{(2)}$ of second sound (54) in the vicinity of the smectic A–smectic C phase transition for BOPDOB, calculated according to Eqs. (56); $\theta = 45°$, $f = 3$ MHz.

Figure 6 shows convincingly that in the region of developed fluctuations the critical corrections are equal in order of magnitude to the unrenormalized value of the elastic modulus g_{uu}^-:

$$\omega\delta\eta_{(2)}(\omega) = \text{Im}\, G_{uu}^-(\omega) \sim \delta g_{uu}^- \sim g_{uu}^-.$$

This is because the latter is relatively small. Thus, in the frequency range investigated ($\omega \sim 10^7$ sec^{-1}) the critical fluctuational corrections, generally speaking, are not small. Therefore in the analysis of the critical behavior of the quantities $\tilde{g}_{uu}^-$ and $\eta_{(2)}$ it is necessary to use the cumbersome formulas (36) and (37). These formulas describe the temperature–frequency behavior of the viscosity and the compression modulus in the crossover region. The regular behavior of the compression modulus of the smectic layers is determined on the smectic A phase side by the nematic–smectic transition:[5]

$$g_{uu}^- \propto |T - T_{AN}|^{0.44}.$$

The value of the critical index coincides with that obtained experimentally in Ref. 4.

In the regions of developed fluctuations the absorption maximum (37) and the minimum of the value of the elastic modulus (36) do not necessarily correspond to the transition temperature. The fluctuations of the order parameter ψ are at their strongest, of course, at the transition point. However, the functions F' and F'', which have an extremum at the transition point, figure in a complicated way in expression (36) for the renormalized dynamic elastic modulus and in expression (37) for the fluctuational correction to the viscosity, shifting the extrema of these quantities away from the transition point. This is quite evident from the experimental temperature dependences of the compression modulus (Fig. 6). The minimum of the compression modulus is shifted into the C phase.

4. LONGITUDINAL WAVE (FIRST SOUND)

4.1. Experimental technique and results

During the course of the experiment the values of the velocity (c) and the absorption coefficient of ultrasound (α) were measured in the smectic A and C phases of ρ-(hexyloxy) phenylether ρ-(decyloxy) benzoic acid. This compound possesses the following polymorphism:[33]

$$S_X \overset{317\text{ K}}{\longleftrightarrow} S_C \overset{350.8\text{ K}}{\longleftrightarrow} S_A \overset{356.7\text{ K}}{\longleftrightarrow} N.$$

The orientational smectic phases were obtained by cooling the sample from the nematic phase in a magnetic field with a strength of 0.3 T for various angles between the wave vector and the magnetic field vector. Because of the large penetration depth of longitudinal sound (in comparison with second sound), the orienting influence of the surfaces of the measuring devices was negligibly small (the characteristic dimension of the sample was ~ 1 cm). The measurements were carried out over a wide range of ultrasound frequencies $f = 0.15$–27 MHz (in the frequency interval 0.15–1.3 MHz—by the resonator method[34] using a specially shaped resonator, and in the frequency interval 3–27 MHz—

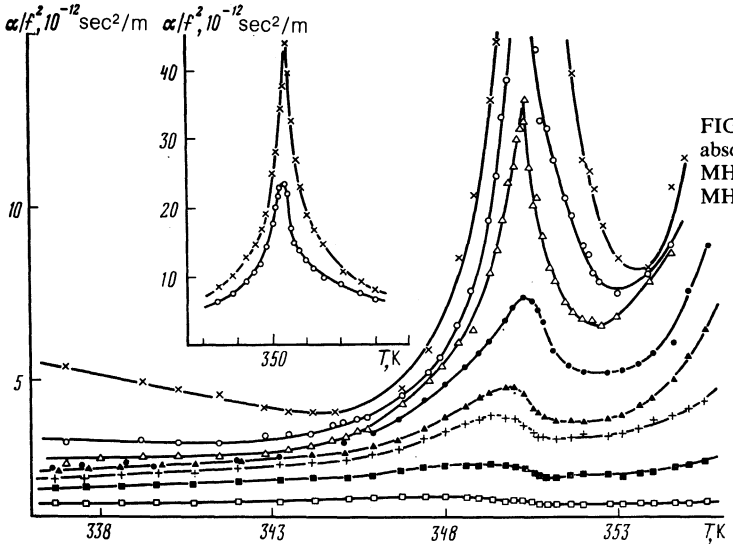

FIG. 7. Temperature dependence of the quantity α/f^2 (α is the ultrasound absorption coefficient) at $\theta = 0°$; ×—0.36 MHz, ○—0.69 MHz, △—1.2 MHz, ●—3 MHz, ▲—5 MHz, +—8.7 MHz, ■—15.8 MHz, □—27.7 MHz.

by the modified pulse–phase method with variable frequency).[35]

The temperature variations of the ultrasound velocity $c - c_0$ were determined by both of the indicated methods relative to the value of c_0, which was measured in the nematic or isotropic phase. The error of measurement of the quantity $c - c_0$ was less than 1%, which for characteristic temperature variations of the velocity, of the order of 100 m/sec, were less than 1 m/sec. Note that the results presented below for the ultrasound velocity can contain a measurement error of the magnitude of c_0 (less than 0.5%, or ~6 m/sec). However, it is of a systematic nature and does not influence the conclusions made in this paper.

The error in the measurement of the absolute value of the ultrasound absorption coefficient by the resonator method was less than 5%, and by the pulse–phase method, 10%. The latter method made it possible to determine the temperature variations of the magnitude of α with an error of ~2% relative to the absolute value of α. The measurements and their analysis were carried out with the help of an automated measuring–calculational complex.[36]

Figures 7 and 8 show the temperature dependence of the absorption coefficient for the angles $\theta = 0°$ and 90°, respectively. For a single-domain sample the angle θ coincides with the angle between the wave vector and the normal to the smectic surface. For the case $\theta = 0°$ a strong frequency dependence of the quantity α/f^2 is observed both in the A and C phases. In this case in the low-frequency region there is a substantial pretransition growth of the given parameter. At $\theta = 90°$ the frequency dependence of the absorption coefficient is weaker, and small anomalies in the vicinity of the A–C transition are observed only at low frequencies. The critical anomalies of the quantity α/f^2 grow as θ varies from 90° to 0° (Figs. 9 and 10) and decrease as the frequency increases. Figures 7–10 convincingly demonstrate the presence of a strong anisotropy in the critical absorption of ultrasound.

Note that the character of the critical anomalies of the acoustic parameters in the vicinity of the A–C phase transition does not vary substantially when a sample of oriented A phase is cooled either in the presence or the absence of the relatively weak magnetic field used in the experiment.

Figures 11 and 12 show the temperature dependence of the ultrasound velocity for various orientations at the frequencies 0.36 and 27 MHz. The minimum velocity, which takes place at low temperatures, in the region of the A–C transition, for θ near zero increases with increase in the frequency and at $f \geqslant 5$ MHz is practically absent. In this case the

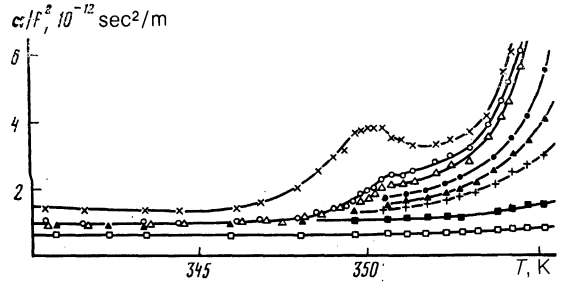

FIG. 8. Temperature dependence of the quantity α/f^2 at $\theta = 90°$ (notation the same as in Fig. 7).

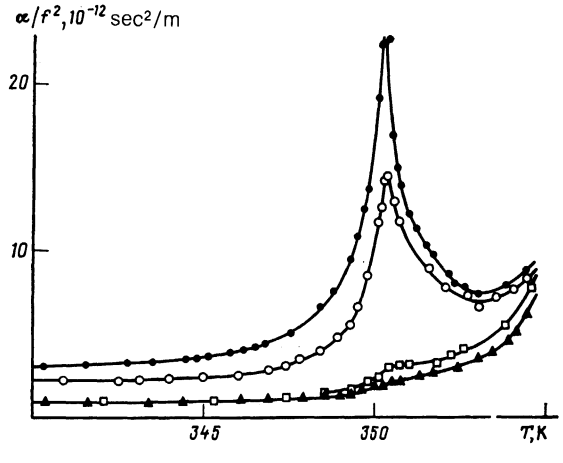

FIG. 9. Temperature dependence of the quantity α/f^2 at the frequency 0.6 MHz at $\theta = 0°$ (●), 30° (○), 60° (□), 90° (▲).

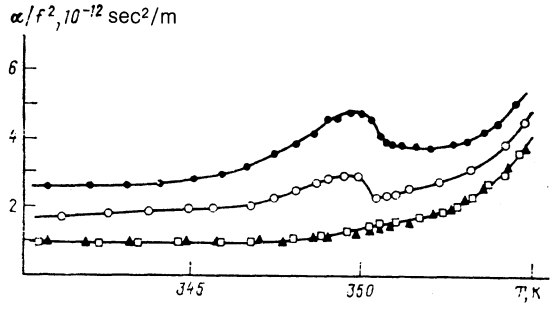

FIG. 10. Temperature dependence of the quantity α/f^2 at the frequency 5 MHz at $\theta = 0°$ (●), 30° (○), 60° (□), 90° (▲).

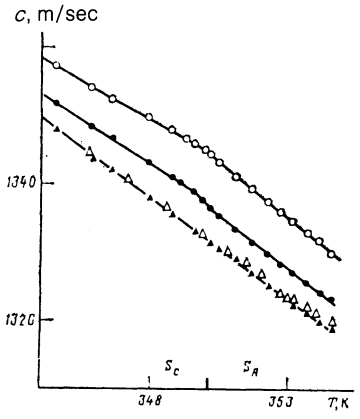

FIG. 12. The same as in Fig. 11, for $f = 27.7$ MHz.

phase transition is accompanied by a change in the velocity temperature coefficient (Fig. 12). At $\theta = 60°$ and 90° no significant changes in the nature of the temperature dependence of the ultrasound velocity are observed in the investigated frequency interval with the exception of the lowest frequencies, where only small changes in the velocity temperature coefficient are noted. At all of the investigated frequencies the values of the ultrasound velocity at $\theta = 90°$ and 60° differed by no more than 1 m/sec.

As can be seen from Figs. 11 and 12, the critical corrections to the sound velocity, like the corrections to the viscosity, are strongly anisotropic. The temperature dependence of the relative anisotropy $\Delta c/c = [c(0°) - c(90°)]/c(90°)$ is shown in Fig. 13 over the entire investigated frequency interval. Note the existence of a dependence of the anisotropy of the ultrasound velocity on the frequency in both smectic phases. In the smectic A at $|T - T_{AC}| \gtrsim 3$ K (T_{AC} is the A–C transition temperature) at frequencies < 5 MHz the frequency dependence of the indicated parameter is practically absent. This indicates that the low-frequency (hydrodynamic) limit has been reached.

To calculate the viscosity coefficients and the elastic moduli of the smectic, the temperature dependence of the density was determined experimentally. The measurements were carried out with the help of a pycnometer with an error $\lesssim 0.1\%$. Within the limits of the indicated error in the investigated temperature interval the density is described by a linear law $\rho(T) = 1.099 - 1.599 \cdot 10^3\, T$ (here T is in °C, ρ is in g/cm^3).

4.2. Analysis and discussion of the experimental results

Critical behavior of the ultrasound velocity

We begin our analysis of the experimental results with a discussion of the critical behavior of the sound velocity. Note that the nature of the temperature dependence of the acoustic parameters at $\theta = 90°$ (Figs. 9 and 11) indirectly indicates the preservation of the single-domain structure of the A phase in the transition to the C phase. In this case the orientational dependence of the velocity of longitudinal sound is described by Eq. (51).

From the frequency–temperature dependence of the velocity of first sound (Figs. 11 and 12) for the four orientations it is possible to calculate the elastic moduli of the smectic, renormalized by the critical fluctuations, figuring in Eq. (51). Figure 14 presents the temperature dependences of the elastic moduli of the smectic related to the compressibility of the smectic layers. With approach to the nematic phase they tend to zero in the low-frequency region. By virtue of the narrowness of the temperature interval of existence of the smectics, the given moduli remain small ($\sim 10^8$ erg/cm^3) in this interval, in agreement with Eq. (10).

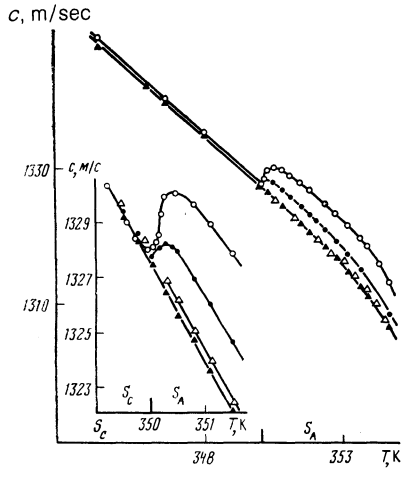

FIG. 11. Temperature dependence of the ultrasound velocity at the frequency 0.36 MHz at $\theta = 0°$ (○), 30° (●), 60° (△), 90° (▲).

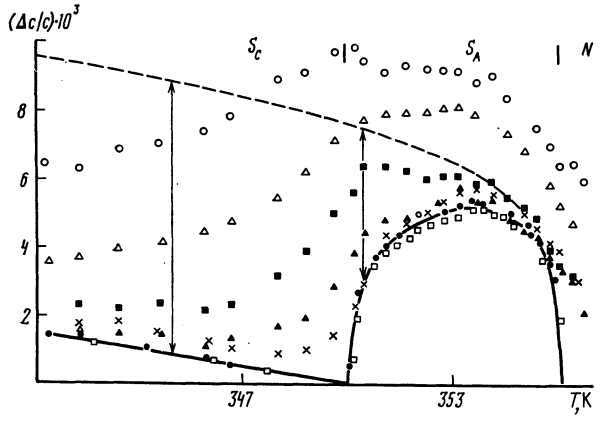

FIG. 13. Temperature dependence of the relative anisotropy of the ultrasound velocity: □—0.15 MHz, ●—0.36 MHz, ×—3 MHz, ▲—5 MHz, ■—8.7 MHz, △—15.6 MHz, ○—27.7 MHz. The arrows show the quantity $\delta\Delta c/c$.

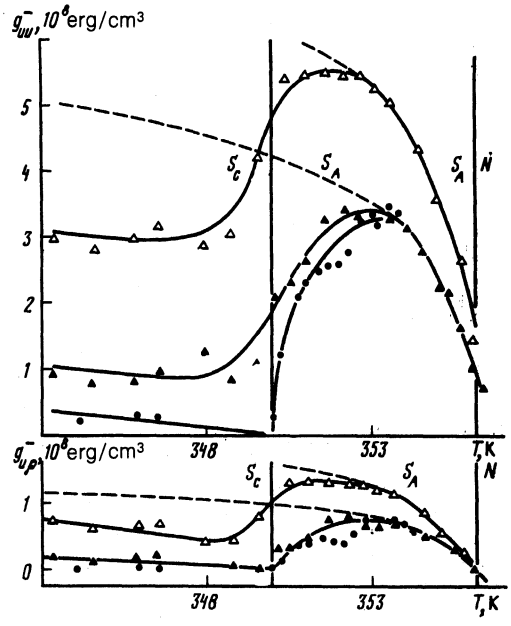

FIG. 14. Temperature dependence of the elastic moduli g_{uu}^- and g_{up}^-: ●—0.36 MHz, ▲—5 MHz, △—15.6 MHz.

The temperature dependence of the elastic modulus g_{pp}^- (the compression modulus at constant interlayer spacing l) is shown in Fig. 15. This elastic modulus has a magnitude $\sim 10^{10}$ erg/cm³, which agrees with Eq. (11). From the calculated values of the elastic moduli (Figs. 14 and 15) it can be seen that over the entire investigated frequency–temperature region the ratio (12) of the elastic moduli renormalized by the critical fluctuations remains small:

$$\frac{g_{up}^-}{g_{pp}^-} \sim \frac{g_{uu}^-}{g_{pp}^-} \sim \frac{g_{uo}^-}{g_{pp}^-} \sim 10^{-2}.$$

This makes it possible in the analysis of the results on the velocity of first sound in the vicinity of the A–C transition to use Eq. (51), which was obtained to first order in the small parameter (12).

The frequency dependence of the elastic moduli g_{uu}^- and g_{up}^- far from the transition is apparently related to the appearance at high frequencies of noncritical mechanisms of molecular dissociation. In addition, in the smectic A phase

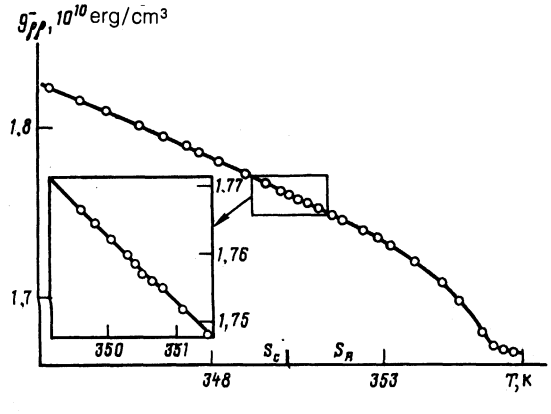

FIG. 15. Temperature dependence of the elastic modulus g_{pp}^- at the frequency 0.15 MHz.

the behavior of the elastic moduli is complicated by the proximity of the nematic–smectic A phase transition. The regions of developed fluctuations of these transitions overlap, hindering the analysis of the dispersion properties of the elastic moduli. Nevertheless, at low frequencies, as can be seen from Fig. 14, the frequency dependence disappears. This indicates the attainment of the hydrodynamic limit.

From Eq. (9) it is possible, using the starting values of the elastic moduli, to calculate the density (pressure) dependence of the interlayer distance l. The calculations show that as the density increases, the interlayer distance l decreases. In this case in the smectic A and C phases we obtain for the quantity (9)

$$\left(\frac{\partial \ln l}{\partial \ln \rho}\right)_\sigma \sim -0.2. \tag{60}$$

Generally speaking, it is quite possible that the interlayer distance also increases with an increase in the density. The magnitude of expression (60) does not depend on the temperature within the limits of measurement error and is the same in both phases.

If the smectic A–smectic C phase transition were absent, the behavior of the elastic moduli would be described by regular temperature dependence. To investigate the critical corrections to the elastic moduli associated with the fluctuations of the order parameter, it is necessary to know this regular dependence. To determine it (the dashed curves in Fig. 14), we have made use of experimental data on the total velocity anisotropy (Fig. 13). The velocity anisotropy in the vicinity of the A–N transition is quite well described by the following power law

$$\Delta c/c \sim (\Delta T_{AN})^{0.25}, \tag{61}$$

where $\Delta T_{AN} = |T - T_{AN}|$, where T_{AN} is the A–N transition temperature. The value of the critical index 0.25 is in agreement with the experimental results.[37,38]

Taking Eq. (12) into account, it is easy to show that the total velocity anisotropy is equal to

$$\frac{\Delta c}{c} = \frac{g_{uu}^- - 2g_{up}^-}{g_{pp}^-}. \tag{62}$$

From this relation it follows that in the vicinity of the nematic–smectic A phase transition the critical behavior of the elastic moduli g_{uu}^- and g_{up}^- and the total velocity anisotropy obey the same law. However, in contrast with the values of the elastic moduli (Fig. 14), which were obtained indirectly by an analysis of the orientational dependence of the velocity, the total anisotropy was measured (Fig. 13) directly and more precisely. The regular behavior in the vicinity of the smectic A–smectic C phase transition (the dashed curves in Fig. 14) was constructed by extrapolation of the experimental data near T_{AN} according to the law (61).

As can be seen from Fig. 14, in the transition from the smectic A to the smectic C phase the elastic moduli g_{uu}^- and g_{up}^- decrease dramatically. This decrease is manifested especially strikingly at low frequencies. In this case the difference between the regular dependence (the dashed curve) and the experimentally obtained values of the moduli is of the same order of magnitude as the compression modulus of the smectic layers itself g_{uu}^-. This fact in combination with the theo-

retical value (15) of the mean-field jumps of the elastic moduli which take place in the transition from the A to the C phase confirms the estimates (13)

$$D_u,\ D_\rho,\ U \sim 10^8\ \text{erg/cm}^3.$$

Recall that U characterizes the self-interaction energy of the order parameter (4), while the quantities D_u and D_ρ, introduced in Eq. (6), characterize the contributions to the energy density of the interaction of the order parameter with the deviation of the density ρ and the displacement of the smectic layers u from their equilibrium values, respectively.

It follows from Fig. 14 that the fluctuational decrease of the elastic moduli begins even in the smectic A phase. As long as the critical corrections are small [and satisfy conditions (38)], they are described by expressions (39) and (41) and

$$\delta g_{uu}^{-},\ \delta g_{\rho\rho}^{-} \propto |T-T_{AC}|^{-\alpha}. \tag{63}$$

Here α is the specific heat index, which, according to theoretical calculations,[9,27] is very small (~ 0.1). According to the experimental results we have $\alpha \lesssim 0.25$. Unfortunately, the numerical value of this index, obtained by an analysis of the experimental curves shown in Fig. 13, is very sensitive to the course of the extrapolated regular dependences and to experimental error.

It is interesting to consider the possibility of obtaining the universal relations (42) between the critical corrections to the various elastic moduli experimentally. In Sec. 2 of this paper it was shown that both in the region of weak fluctuations and in the crossover region the ratios of the corrections to the elastic moduli are equal to

$$\frac{\delta g_{uu}^{-}(\omega,\tau)}{\delta g_{u\rho}^{-}(\omega,\tau)} = \frac{\delta g_{u\rho}^{-}(\omega,\tau)}{\delta g_{\rho\rho}^{-}(\omega,\tau)} = \frac{D_u}{D_\rho} \sim 4. \tag{64}$$

From this it follows that the critical correction to the elastic modulus $g_{\rho\rho}^{-}$ (Fig. 15) is one order of magnitude less than the corresponding contribution to g_{uu}^{-} and lies at the limit of experimental accuracy. The values of the ratios (64), calculated using the values of the critical corrections to the elastic moduli g_{uu}^{-} and $g_{u\rho}^{-}$ plotted in Fig. 14, are given in Fig. 16. It can be seen that in the vicinity of the transition this quantity does not depend on either the frequency or the temperature.

Critical behavior of the viscosity

Let us turn now our attention to a discussion of the viscous properties of the smectic in the vicinity of the A–C transition. The orientational dependence of the coefficient of absorption α of first sound in a single-domain smectic sample is described by expression (52). Applying expression (52) to the four curves of the dependence of α/f^2 on T at the four orientations $\theta = 0,\ 30,\ 60,\ 90°$, we calculated the frequency–temperature dependences of the viscosity coefficients of the smectic. The results of this calculation are shown in Figs. 17–19.

The critical corrections to the bulk viscosity coefficients are significantly greater than the corresponding corrections to the elastic moduli. However, the analysis of the viscosity coefficients in the vicinity of the A–C transition is more complicated. First, as is quite clear from Figs. 17–19, on the smectic A phase side the fluctuation region of the investigated A–C transition substantially overlaps the region of developed fluctuations of the nematic–smectic A phase transition. Second, even far from the A–C phase transition in the smectic C phase there exists a frequency dependence of the viscosity coefficients in the hydrodynamic limit. This has to do with the fact that in the smectic phases strong fluctuations of the smectic layers lead to a highly nontrivial contribution to the bulk viscosity coefficients, which diverges like ω^{-1} (Ref. 14). This contribution is not related to the critical fluctuations of the order parameter and must be considered separately.

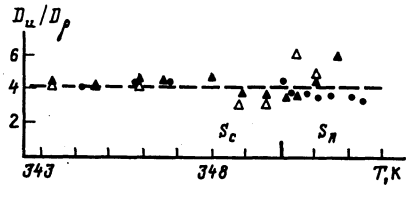

FIG. 16. Temperature dependence of the ratio D_u/D_ρ: ●—0.36 MHz, ▲—5 MHz, △—15.6 MHz.

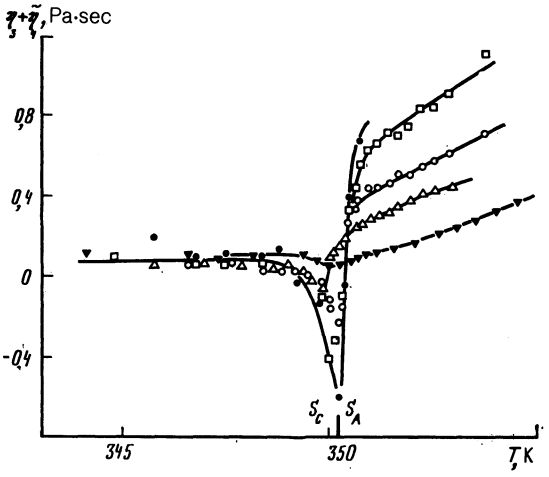

FIG. 17. Temperature dependence of the quantity $\eta_3 + \tilde{\eta}_4$: ●—0.36 MHz, □—0.47 MHz, ○—0.69 MHz, △—1.2 MHz, ▼—5 MHz.

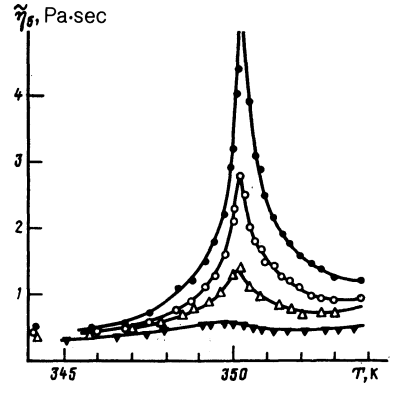

FIG. 18. Temperature dependence of the viscosity coefficients $\tilde{\eta}_5$. Notation the same as in Fig. 17.

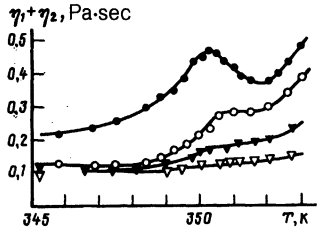

FIG. 19. Temperature dependence of the viscosity coefficient $\eta_1 + \eta_2$: ●—0.36 MHz, ○—0.69 MHz, ▼—1.2 MHz, ▽—5 MHz.

The fluctuations of the smectic layers lead to the appearance of the corrections (48) to the bulk viscosity coefficients (see Fig. 20). Using the values of the elastic moduli g_{uu}^{-} and g_{up}^{-} entering into Eqs. (48) and determining the slopes of the straight-line dependences of $\tilde{\eta}_5$ on ω^{-1} in the low-frequency region far from the transition, it is possible to determine the value of the parameter A_C figuring in Eq. (47). Calculation shows that

$$\Xi/K^{3/2} \sim 10^{10}\ (\text{erg/cm})^{-3/2}. \tag{65}$$

Taking into account that the critical fluctuations do not renormalize the elastic Frank modulus K and its values in the smectic A and C phases coincide, it is possible to describe the experimentally observed values of $\delta'\eta_5$ in the low-frequency region in the smectic A phase by an expression of the form (48) for $\Xi \sim 10$.

(Recall that the dimensionless positive parameter Ξ characterizes the increase of the fluctuational contribution associated with the oscillations of the smectic layers in the C phase in comparison with the A phase.)[17] Estimation of the Frank modulus then gives $K \sim 10^{-6}$ erg/cm, which corresponds to typical values for it in the smectic phases.

The numerical value $\Xi \sim 10$ agrees with the experimental results of Ref. 18. However, in this work the increase of the coefficient A was incorrectly interpreted as a decrease of the Frank modulus K in the transition from the A to the C phase.

In the vicinity of the smectic A– smectic C phase transition divergent critical corrections to the bulk viscosity coefficients appear (see Figs. 17–19). They are due to the fluctuations of the order parameter. As long as the critical corrections are small, they are described by Eqs. (40). With the growth of the critical fluctuations in the crossover region (35) it becomes necessary to use the cumbersome expressions (37) to describe the corrections to the bulk viscosity coefficients. As follows from these relations, the critical corrections to the viscosity coefficients η_5 and η_2 are positive. In smectics an interesting situation is possible in which the critical fluctuations cause the viscosity coefficient η_4 to decrease. It is specifically this situation that is reflected in Fig. 17. The bulk viscosity coefficient η_4 generally becomes negative in the vicinity of the transition. Over the entire region of developed fluctuations the critical corrections to the bulk viscosity coefficients are related with each other by the universal relation (43), i.e.,

$$\frac{\delta\eta_5(\omega,\tau)}{\delta\eta_4(\omega,\tau)} = \frac{\delta\eta_4(\omega,\tau)}{\delta\eta_2(\omega,\tau)} = \left(1-\frac{D_u}{D_p}\right) \sim -3. \tag{66}$$

Here D_u and D_p are the parameters introduced in Eq. (6).

The difference between the experimental values of the viscosity coefficients depicted in Figs. 17–19 and their regular dependence corresponds to the critical contribution $\delta\eta$. The regular dependence is constructed by direct extrapolation of the experimental data obtained for the smectic C phase far from T_{AC} and for the A phase in the vicinity of T_{AN}. In the region of developed fluctuations the ratio of critical corrections (66) is insensitive to the systematic errors associated with the determination of the regular dependence of the viscosity coefficients.[6] Note that, as follows from theory, the magnitude of the ratio D_u/D_p is not renormalized by the critical fluctuations. The numerical value obtained from the analysis of the critical corrections to the bulk viscosity coefficients agrees with the values (64) (see Fig. 16) obtained independently by an analysis of the critical behavior of the elastic moduli.

As long as the fluctuational corrections are small, the critical corrections to the bulk viscosity coefficients in the hydrodynamic and fluctuation regions are described by the laws (41). Figures 21 and 22 present the temperature and

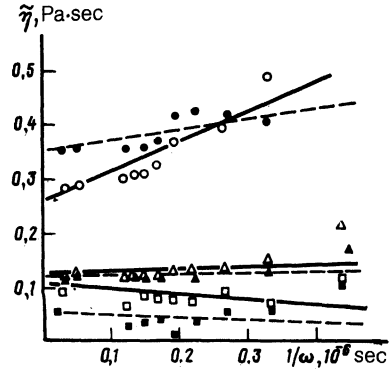

FIG. 20. Dependence of the quantities $\tilde{\eta}_5$, $\eta_1 + \tilde{\eta}_2$, and $\eta_3 + \tilde{\eta}_4$ in the S_C phase: ○—$\tilde{\eta}_5$, △—$\eta_1 + \tilde{\eta}_2$, □—$\eta_3 + \tilde{\eta}_4$ ($T = 337$ K), ●—$\tilde{\eta}_5$, ▲—$\eta_1 + \tilde{\eta}_2$, ■—$\eta_3 + \tilde{\eta}_4$ ($T = 344$ K).

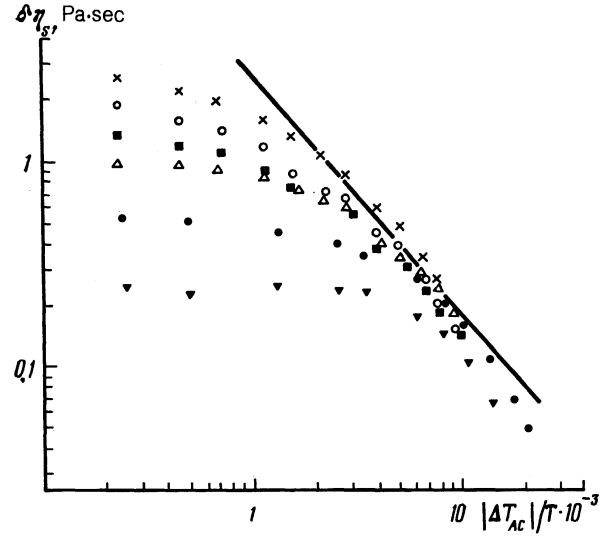

FIG. 21. Temperature dependence of $\delta\eta_5$ in the S_C phase: ×—0.36 MHz, ○—0.69 MHz, ■—1.2 MHz, △—3 MHz, ●—5 MHz, ▼—8.7 MHz.

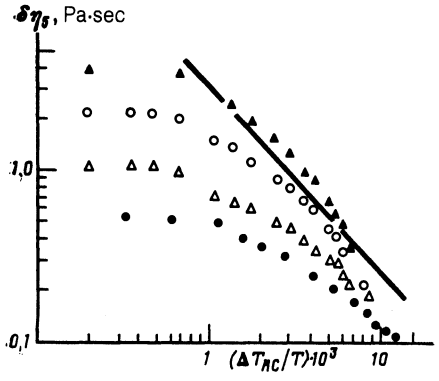

FIG. 22. Temperature dependence of $\delta\eta_5$ in the S_A phase: ▲—0.36 MHz, ○—0.69 MHz, △—1.2 MHz, ●—3 MHz.

frequency dependences of the critical correction $\delta\eta_5$. The solid line in Fig. 23 corresponds to the following value of the following combination of critical indices (see Sec. 2):

$$z\nu+\alpha\approx 1.1. \tag{67}$$

As might have been expected, the indices ν and α are the same in both smectic phases. Their numerical values agree with the theoretical values obtained in Refs. 9, 20, and 27. The deviation of the critical corrections from the power-law dependences (41) determines the boundary of the hydrodynamic and fluctuation regions.[6]

Analysis of the viscoelastic properties in the crossover region

With the approach to the transition temperature the fluctuations of the order parameter grow. However, for most real second-order phase transitions the critical corrections to the elastic moduli always remain small in comparison with their unrenormalized values. In other words, because of the large values of the unrenormalized elastic moduli the crossover region (35) is located in an experimentally unreachable range of temperatures and frequencies. The critical corrections can therefore always be taken to be small and can always be described by power laws of the type (41). In smectics the elastic moduli g_{uu}^- and $g_{u\rho}^-$, related to the compression of the smectic layers, are small. The critical corrections to the sound absorption, while remaining small in comparison with the ordinary compression modulus $g_{\rho\rho}^- \sim 10^{10}$ erg/cm^3, in the crossover region become comparable with the modulus $B\sim 10^8$ erg/cm^3. In this case in the analysis of the experimental data neither the fluctuational part nor the starting part can be neglected, and it is necessary to use Eqs. (36) and (37). According to these formulas the critical behavior of the viscoelastic properties in the crossover region is described by the imaginary (F'') and real (F') parts of the dynamic correlator (21). These functions figure in a complicated way in the expressions for the critical corrections.

It is interesting to extract the functions F' and F'' from the experimental data, and all the more so because according to current notions in the region of developed fluctuations these fluctuations should be universal. Solving the system of equations (36), (37) for the functions F' and F'', we obtain

$$F'+iF''=\frac{(DgD)}{D_u^2}\delta G_{uu}^-\left(1-\frac{(DgD)}{D_u^2}\delta G_{uu}^-\right)^{-1},$$
$$\delta G_{uu}^-=(\tilde{g}_{uu}^- - g_{uu}^-)+i\omega(\delta\eta_5-2\delta\eta_4+\delta\eta_3). \tag{68}$$

Here the compressibility matrix $\mathbf{g}$ and the vector $\mathbf{D}$ were defined in Eqs. (6) and (8); g_{uu}^- is the unrenormalized elas-

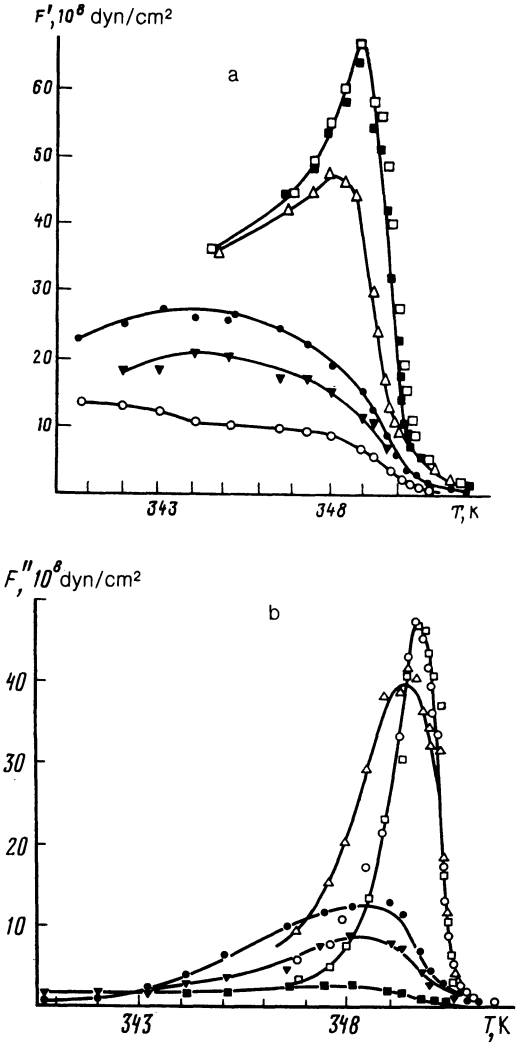

FIG. 24. Temperature dependence (a) of the function F' for $\omega = 0.36$ MHz (□); after Ref. 3 (■); after Ref. 5 (△); 8.7 MHz (●); 15.6 MHz (▼); 27.7 MHz (○), and (b) of the function F'' for $\omega = 0.36$ MHz (□); 3 MHz (○); 5 MHz (△); 8.7 MHz (●); 15.6 MHz (▼); and 27.7 MHz (□).

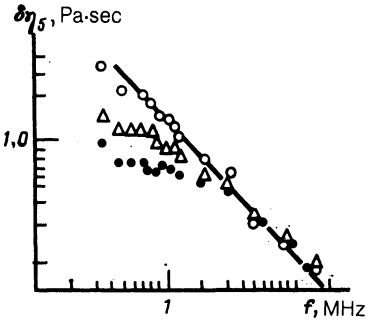

FIG. 23. Temperature dependence of $\delta\eta_5$ in the S_A phase at $T = 353$ K: ○—0.36 MHz, △—1.2 MHz, ●—3 MHz.

tic compression modulus of the smectic layers (the dashed curve in Fig. 14); $\bar{g}_{uu}$ is the elastic modulus renormalized by the critical corrections (the solid curve in Fig. 14); $\delta\eta_{2,4,5}$ are the critical corrections to the bulk viscosity coefficients (Figs. 17–19). We take the regular dependence of (**DgD**), figuring in expression (68), to be proportional to $1/g_{uu}^{-}$. The error associated with this is small of order (12).[3)] Figure 24 depicts the imaginary (F'') and real (F') parts of the correlator of the order parameter (21) constructed from the data according to Eqs. (68).

Functions of the form (21) were first calculated by Imura and Okano in Ref. 39 in the study of the nematic–isotropic liquid transition in the Ornstein–Zernike approximation. In Ref. 4 it was shown that the Ornstein–Zernike approximation describes the experimental situation quite well for a weak first-order transition.

The functions F' and F'' in the region of developed fluctuations, plotted in Fig. 24, differ from the Imura–Okano functions. This is not hard to understand if we take into account that the scaling value of the critical specific heat index for the A–C transition, which amounts to ~ 0.1, differs sharply from the value $\alpha = 0.5$, which corresponds to the Ornstein–Zernike approximation.

5. CONCLUSION

As the analysis of the experimental data for the frequencies $\omega \sim 10^7$ sec^{-1} showed, the damping of second sound is not small. In this case the measured components of the shear impedance (or to within a numerical factor the imaginary and real components of the inverse wave vector) are the most adequate parameters for the description of second sound. This follows strikingly from the formulas which were used in the analysis [Eqs. (56)].

The compression moduli of the smectic layers, calculated from the orientational dependence of the impedance (Fig. 1) confirm the form of the spectrum (50). However, the question of the orientational behavior of the viscosity coefficient of second sound (54) in its propagation along the smectic layers and perpendicular to them remains open.

The data on the frequency dependence of the impedance have made it possible to estimate the correction to the viscosity of second sound associated with the fluctuations of the smectic layers.[14] The estimates (58) and (59) do not contradict the increase predicted in Ref. 17 of the fluctuational damping of sound in the smectic C phase due to the appearance of an additional orientational mode.

Finally, it should be observed that at $\omega \sim 10^7$ sec^{-1} the critical corrections to the viscosity, to the second sound velocity, and to the compression modulus of the smectic layers are comparable with their unrenormalized values. In other words, the fluctuations of the order parameter, while strongly renormalizing the bare values, nevertheless lead to universal behavior.

The analysis of the experimental data shows that a study of longitudinal (first) sound affords the possibility of completely determining the critical behavior of all the viscoelastic properties of the smectic in the vicinity of the A–C transition.

The elastic dynamic properties are determined by the three moduli (8). Their temperature–frequency behavior is shown in Figs. 14 and 15. As can be seen from these figures, in the transition from the smectic A phase to the smectic C phase the elastic moduli cause the compression modulus of the smectic layers B to decrease by an order of magnitude. Over a wide frequency–temperature region the critical corrections to the elastic moduli have a magnitude of $\sim 10^8$ erg/cm^3. Thus, in smectic liquid crystals the very interesting situation is realized in which the critical corrections, while remaining small in comparison with the total compression modulus $g_{\rho\rho}^{-} \sim 10^{10}$ erg/cm^3, become comparable with the compression modulus of the smectic layers B. In this case the behavior of the elastic moduli of the smectic with the critical fluctuations taken into account is described by the complicated expressions (36) and (37). However, everywhere in the vicinity of the transition, including the crossover region, the corrections to the elastic moduli are related by the universal relations (42). This is strikingly demonstrated by Fig. 16.

The regular behavior of the elastic moduli far from the transition point makes it possible to investigate the pressure (density) dependence of the interlayer distance in the smectics.

The absorption of sound in smectics is determined by five viscosity coefficients. The fluctuational corrections to the shear viscosity coefficients are absent. The critical behavior of the bulk viscosity coefficients is depicted in Figs. 19–21. As long as the critical corrections are small, the corrections to the bulk viscosity coefficients $\sim |T - T_{AC}|^{-1.1}$. In the crossover region the corrections to these coefficients are described by the cumbersome formula (37).

The analysis of the frequency–temperature behavior in this case is quite complicated. Nevertheless, the critical corrections to the various bulk viscosity coefficients are related by the universal relation (43). Numerical analysis of the experimental data confirms this.

The frequency dependence of the viscosity far from the A–C transition makes it possible to investigate the breakdown of the hydrodynamics associated with the fluctuations of the smectic layers. For the smectic C phase there is a singularity in the fluctuational sound absorption due to the presence of the additional orientational mode. The coupling of the orientational mode with the mode associated with the oscillations of the smectic layers leads to an increase in the proportionality coefficient in from of ω^{-1} in the C phase in comparison with the A phase. In the present paper we have experimentally discovered an increase in the fluctuational correction to the viscosity in the smectic C in comparison with the smectic A by a factor of $\Xi \sim 10$.

From the critical behavior of the viscosity and the elastic moduli it is possible to extract information on the behavior of the dynamic correlator (21). This correlator determines the critical corrections to the viscosity coefficients and the elastic moduli. The frequency–temperature dependences of its imaginary and real parts are shown in Fig. 24. The analytic form of the function F in the Ornstein–Zernike approximation is determined by a function of the Imura–Okano type.[39] However, for the A–C phase transition the mean field approximation hardly applies. This is because the critical specific heat index $\alpha \sim 0.1$ for the two-component order parameter differs sharply from the value $\alpha = 0.5$ obtained in the Ornstein–Zernike approximation. It is for this reason that the experimental frequency–temperature dependences of F' and F'' in the region of developed fluctuations

are in poor agreement with the form of the Imura–Okano functions. In the region of developed fluctuations the error in determining the critical corrections and, consequently, the functions F is great. In addition, the exact form of the functions F is sensitive to the systematic errors associated with isolating the regular dependence of the elastic moduli and the kinetic coefficients.

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[1)] The present work is based on the experimental results of two independent experimental groups. The part of the work dedicated to second sound was written by E. V. Gurovich, A. A. Tabidze, and A. C. Gol'dberg. The second part (longitudinal waves) was written by V. A. Balandin, E. V. Gurovich, A. S. Kashitsyn, and S. V. Pasechnik.

[2)] In the vicinity of the A–C transition it is natural to expect that the elastic moduli g^- which figure in Eqs. (48) are replaced by their renormalized values $\tilde{g}^-$.

[3)] Generally speaking, for an exact calculation of F from Eq. (68), in addition to the values of $g^-_{\rho\rho}$, $g^-_{\rho u}$, and g^-_{uu} measured in the presence of ultrasound it is also necessary to know the regular temperature dependences of the specific heat $g^-_{\sigma\sigma}$ and the interlayer spacing l.

[1] A. P. Kapustin and O. A. Kapustina, *The Acoustics of Liquid Crystals* [in Russian], Nauka, Moscow (1986).
[2] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Nauka, Moscow (1987).
[3] S. Bhattacharya and J. B. Ketterson, Phys. Rev. Lett. **49**, 997 (1982).
[4] C. Baumann, J. P. Marcerou, J. Prost, and J. C. Rouillon, Phys. Rev. Lett. **54**, 1268 (1985).
[5] A. A. Tabidze, G. P. Abramkin, and N. I. Koshkin, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 386 (1988) [Sov. Phys. JETP Lett. **47**, 461 (1988)]. G. P. Abramkin, N. I. Koshkin, and A. A. Tabidze, *Applications of Ultra-Acoustics to the Investigation of Matter*, No. 37 [in Russian], VZMI, Moscow, p. 28.
[6] V. A. Balandin, E. V. Gurovich, A. S. Kashitsyn *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 30 (1989) [Sov. Phys. JETP Lett. **49**, 34 (1989)].
[7] V. De Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, New York (1980).
[8] E. I. Kats and V. V. Lebedev, *The Dynamics of Liquid Crystals* [in Russian], Nauka, Moscow (1988).
[9] P. De Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1974).
[10] C. C. Huang and S. C. Lien, Phys. Rev. Lett. **47**, 1917 (1981).
[11] M. A. Anisimov, V. P. Voronov, A. O. Kur'kov, and F. N. Kholmurodov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 248 (1985) [Sov. Phys. JETP Lett. **41**, 302 (1985)].
[12] G. R. Safina, H. Kaplan, J. Als-Nielsen *et al.*, Phys. Rev. B **21**, 4149 (1980).
[13] R. Schaetzing, Ph.D. Thesis, MIT (1980).
[14] G. A. Mazenko, S. Ramaswamy, and J. Toner, Phys. Rev. A **28**, 1618 (1983); Phys. Rev. Lett. **49**, 51 (1982).
[15] E. I. Kats and V. V. Lebedev, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 594 (1983) [Sov. Phys. JETP Lett. **37**, 709 (1983)]; Zh. Eksp. Teor. Fiz. **85**, 2019 (1983) [Sov. Phys. JETP **58**, 1172 (1983)].
[16] E. I. Kats and V. V. Lebedev, Zh. Eksp. Teor. Fiz. **88**, 823 (1985) [Sov. Phys. JETP **61**, 484 (1985)].
[17] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, Twelfth Int. Liquid Crystal Conference, Fraibyrg, 1988, p. 537, *Liquid Crystals 1990* (in press).
[18] J. L. Gallani and P. Martinoty, Phys. Rev. Lett. **58**, 254 (1987).
[19] E. I. Kats and V. V. Lebedev, Zh. Eksp. Teor. Fiz. **91**, 878 (1986) [Sov. Phys. JETP **64**, 518 (1986)].
[20] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, Zh. Eksp. Teor. Fiz. **94**, No. 4, 167 (1988) [Sov. Phys. JETP **67**, 741 (1988)].
[21] S. B. Andereck and J. Swift, Phys. Rev. A **25**, 1084 (1981).
[22] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 2nd. ed., Pergamon Press, Oxford (1970).
[23] K. G. Wilson, Phys. Rev. B **4**, 3174 (1971).
[24] I. E. Dzyaloshinskii and G. E. Volovick, Ann. Phys. **125**, 67 (1980). G. E. Volovik and E. I. Kats, Zh. Eksp. Teor. Fiz. **81**, 240 (1981) [Sov. Phys. JETP **54**, 122 (1983)].
[25] V. V. Lebedev, A. I. Sukhorukov, and I. M. Khalatnikov, Zh. Eksp. Teor. Fiz. **85**, 1590 (1983) [Sov. Phys. JETP **58**, 925 (1983)].
[26] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, Adv. Phys. 1990 (in press).
[27] P. C. Halperin and B. I. Hohenberg, Rev. Mod. Phys. **49**, 435 (1977).
[28] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part 1, 3rd. ed., Pergamon Press, Oxford (1980).
[29] G. Grinstein and R. A. Pelkovits, Phys. Rev. A **26**, 915 (1982).
[30] E. I. Kats, Zh. Eksp. Teor. Fiz. **83**, 1376 (1982) [Sov. Phys. JETP **56**, 791 (1982)].
[31] A. A. Tabidze and R. Kh. Kazakov, Izmeritel'naya Tekhnika (*Measurement Technique*) [in Russian], No. 1, 1983, p. 34.
[32] B. G. Cheng, B. K. Sarma, I. D. Calder *et al.*, Phys. Rev. Lett. **46**, 828 (1981). B. G. Cheng, B. K. Sarma, S. Bhattacharya, and J. B. Ketterson, Phys. Lett. **88A**, 70 (1982).
[33] D. Demus and H. Demus, *Flüssige Kristalle in Tabellen*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1973).
[34] V. A. Balandin, S. V. Pasechnik, V. I. Prokopiev, and O. Y. Shmelyoff, *Liquid Crystals 1988*, Vol. 3, p. 1319.
[35] V. A. Balandin, V. F. Nozdrev, and O. Ya. Shmelev, Proceedings of the Tenth All-Union Acoustic Conference, Moscow (1983), p. 52.
[36] O. Ya. Shmelev, Izmeritel'naya Tekhnika (*Measurement Technique*) [in Russian], No. 4, 1988, p. 157.
[37] P. Davidov, G. R. Safinya, M. Kaplan *et al.*, Phys. Rev. B **19**, 1657 (1979).
[38] V. A. Balandin, S. B. Kashitsyn, and O. Y. Shmelyoff, 8-LCCSC, Krakow, 1989, p. 54.
[39] H. Imura and K. Okano, Chem. Phys. Lett. **19**, 387.

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