~~been observed for metals other than noble metals, nor has the amplification of higher harmonics been observed.[10] With the sharp-point structures of the present experiments we were able to observe emission of a surface-enhanced third harmonic in silver and a surface enhancement of the second harmonic in aluminum.~~

~~We note with thanks that the idea for this experiment came from V. B. Braginskiĭ. We thank L. V. Keldysh, G. N. Flerov, and V. B. Braginskiĭ for assistance, discussions, and criticism. We thank É. I. Rau, B. V. Mchedlishvili, and V. I. Kuznetsov for assistance in fabricating and describing the samples.~~

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~~Translated by Dave Parsons~~
~~Edited by S. J. Amoretty~~

Division of drops of a liquid crystal in the case of a cholesteric–smectic-A phase transition

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(Submitted 27 July 1984)
Pis'ma Zh. Eksp. Teor. Fiz. 40, No. 6, 242–245 (25 September 1984)

The spontaneous division of liquid-crystal drops, suspended freely in an isotropic matrix has been detected following a cholesteric–smectic-A phase transition, caused by an anomalous increase of the surface area of the drops in the pretransitional region. It is suggested that the surface energy of the cholesteric–smectic-A interface can be negative.

1. It is known that a drop of liquid immersed in another liquid assumes a spherical shape in the absence of external fields and mixing. This example is the simplest illustration of the positiveness of the surface-tension coefficient.[1] For drops of a liquid crystal (LC) the situation is more complicated because of the presence of surface-tension anisotropy and the nonzero elastic energy of volume distortions. For this reason, not only spherical drops but also tactoidal drops[4] or drops shaped like two connected spherical segments[3] are also observed. However, the LC drops retain their cohesiveness under all possible changes in shape described in the literature.

In this letter we report an experimental observation of the division of liquid-crystal which occurs as a result of a cholesteric–smectic-*A* phase transition and which is associated with a change in the shape of the drop from a spherical to a cylindrical shape in the pretransitional region.

2. The liquid-crystal drops [a 7:3 (by weight) mixture of cholesteryl pelargonate (CP) and nonyloxybenzoic acid (NOBA)] were dispersed in glycerine with 0.1% lecithin. Far from the transition point the drops of cholesteric phase have a disordered texture (Fig. 1a). Their shape is spherical or flattened if the drops touch the glass walls of the cell. As the temperature is decreased, the shape of the drops changes within 1–2 °C of the transition point. At first, several small protuberances form (two, as a rule, but sometimes more) (Fig. 1b). The development of protuberances as the phase-transition point is approached leads to the appearance of cylindrically shaped drops (Figs. 1c and 1d). The cholesteric layers in such elongated drops are everywhere oriented perpendicular to the surface, as is evident in Figs. 1c and 1d, because of the sharp increase

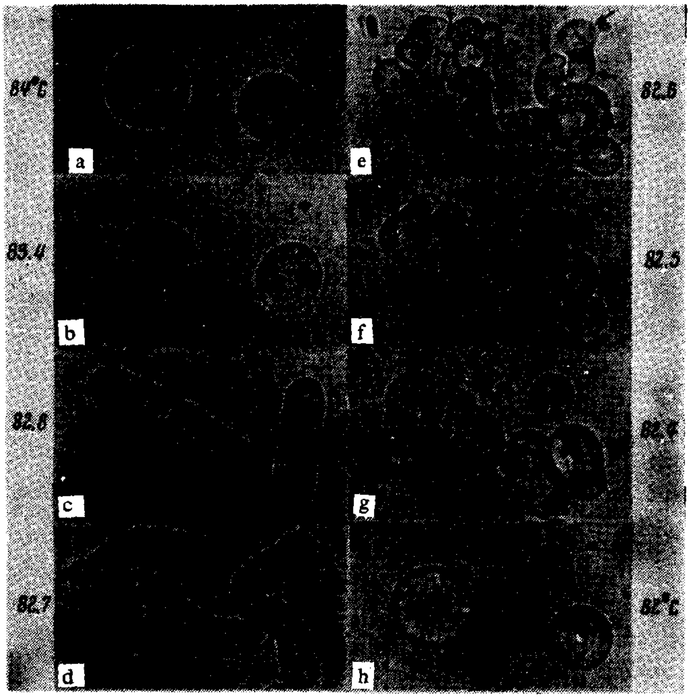

FIG. 1. The evolution of the shape of liquid-crystal drops in the case of a cholesteric–smectic-*A* transition. The values of the temperature are indicated on the right and on the left. The sizes of the drops in Fig. 1a are 60 and 50 μm. The arrows in Figs. 1d and 1e indicate the regions of the smectic phase in the cholesteric drop.

in the pitch of the spiral in the pretransitional region. Figure 1d also shows the appearance in different locations of cholesteric drops in the smectic phase, whose layers are oriented parallel to the surface. As they increase in size, the smectic sections assume the shape of the spherical sectors with a radial structure (Fig. 1e),[4] and then coalesce with each other, striving to form spherically shaped drops (Figs. 1f and 1g). Because of the pretransitional extension of the drops, however, not all of the smectic sections have time to coalesce. As a result, several separate "daughter" drops of smectic A are formed (Fig. 1h). As the temperature is further decreased, no changes occur in the system. Upon increasing the temperature the "daughter" drops may coalesce in the cholesteric phase (not necessarily near the transition point). We also note that if lecithin is not present in the glycerin matrix, there is no division of drops or change in their shape. Furthermore, a pure CP, without NOBA impurities, exhibits no division of drops, while their shape changes slightly.

3. Analysis of Fig. 1 shows that the division of the drops is a result of a pretransitional increase in the surface area of the drops (Figs. 1b–1d). As a result, the smectic nucleating centers move apart from each other. The stretching of the drops is associated with a decrease in the value of the coefficient of surface tension at the drop–matrix boundary. The transition from Fig. 1a to Fig. 1c is accompanied by a change in two contributions to the free energy of the drops. The first contribution, the exchange, which is associated primarily with the increase in the fluctuations of smectic order, is[1] $\Delta F_V = \frac{1}{2} K_2(q' - q)^2 V$; the surface makes the second contribution: $\Delta F_S = \sigma' S' - \sigma S$, where q is the wave number of the cholesteric spiral; σ is the coefficient of surface tension at the drop–matrix boundary; S is the surface area of the drop (all quantities are for drops in Fig. 1a); q', σ', and S' are the corresponding quantities in Fig. 1c; K_2 is the elastic twist constant; and V is the volume of the drop. From the condition $\Delta F_V + \Delta F_S = 0$ it follows that $\sigma' < \sigma$; more precisely,

$$k\sigma' = \sigma - \frac{1}{6}K_2(q' - q)^2 R, \tag{1}$$

where $k = S'/S$, and R is the radius of the drop in Fig. 1a. A decrease in the value of σ' with respect to σ can be qualitatively explained on the basis of an analysis of the structure of the drop–matrix interface.

It is first necessary to take into account that this interface contains a transitional layer (a "membrane"), which consists primarily of lecithin molecules (a surfactant). The lecithin molecules, as we know from numerous studies of analogous systems, permit the formation of a normal boundary orientation of the LC molecules (see, for example, Refs. 3–5). Since the spiral twisting of the cholesteric phase leads to a partial breakdown of normal orientation, for drops in Fig. 1a we have

$$\sigma \approx \sigma_0 + \sigma_{\|} + \Delta\sigma/2, \tag{2}$$

where σ_0 is the coefficient of surface tension at the matrix–membrane boundary, $\Delta\sigma = \sigma_{\perp} - \sigma_{\|} > 0$, $\sigma_{\perp}$ and $\sigma_{\|}$ are the corresponding coefficients for the membrane–LC interface when the molecules of the LC are oriented perpendicular and parallel to the normal to the interface. In order of magnitude, σ, σ_0, $\sigma_{\|} \sim 10^{-2}$–10^{-3} (N/m) (see, for example, Ref. 5). It is logical to expect that near the transition point the orienting effect of the membrane facilitates the formation of a thin layer of smectic phase on the

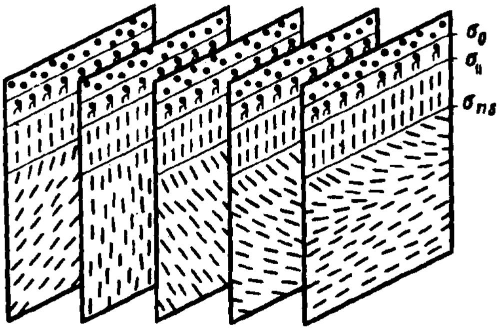

FIG. 2. A crude model of the surface of a liquid-crystal drop near a cholesteric–smectic-A transition. The circles denote glycerine molecules, the rods denote molecules of LC, and the symbol ꝭ denotes a lecithin molecule.

surface of the drops (Fig. 2). Consequently, for the drops in Fig. 1c we have

$$\sigma' \approx \sigma_0 + \sigma_\parallel + \sigma_{ns} , \tag{3}$$

where σ_{ns} is the energy per unit surface area of the cholesteric–smectic-A interface.

As follows from relations (1)–(3), the fact that σ' is less than σ can be explained by the contribution of $\Delta\sigma$ if $\Delta\sigma \sim \sigma_0$, $\sigma_\parallel$, $\dfrac{\Delta F_V}{S} \sim 10^{-2}$–$10^{-3}$ (N/m) and $\Delta\sigma > k\sigma_{ns}$.

4. It is of interest to discuss the quantity σ_{ns}. For the geometry of the system in Fig. 2 we have

$$\sigma_{ns} \approx \frac{1}{4}(K_2 + K_3)q^2(\zeta - \lambda), \tag{4}$$

where K_3 is the longitudinal-bending constant, λ is the depth of penetration of the deformations of the director into the smectic A, and ζ is the distance at which the order parameter of the smectic decreases to zero. Expression (4) is analogous to the expression for the energy of a metal–superconductor surface.[6] This suggests that there is a similarity in the description of a cholesteric–smectic-A phase transition and a metal–superconductor phase transition in a magnetic field.[7,8] Depending on the ratio $\kappa = \lambda / \zeta$, the quantity σ_{ns} will be either positive or negative. As exact calculations show,[6,7] the critical values of κ is $1/\sqrt{2}$. The value of κ estimated in Ref. 8 for a pure (without impurities) CP exactly coincides with the critical value.[2)] In the situation described, κ must be greater than the critical value, since, first of all, the presence of impurity NOBA molecules in the CP decreases ζ and, secondly, for thin smectic layers, the value of λ is expected to increase at the surface of the drops. If $K_2 + K_3 \approx 10^{-11}$ N, $q \approx 2 \times 10^7 \mathrm{m}^{-1}$, $\lambda \approx 10$ $\zeta \approx 10^{-7}$ m, we would have $\sigma_{ns} \approx (-10^{-4})$ N/m. Therefore, σ_{ns} can also facilitate the extension of the drops in the pretransitional region. It is important to confirm in further studies the existence of a negative surface energy of the cholesteric–smectic-A interface with accurate quantitative data, both theoretical and experimental.

We are deeply grateful to E. I. Kats, M. V. Kurik, V. M. Filev, and S. V. Shiyanovskiĭ for a discussion of the results.

[1)] The importance of this contribution was brought to our attention by V. M. Filev.

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Translated by M. E. Alferieff
Edited by S. J. Amoretty

Conductivity increase of a 2*D* electron gas with decreasing temperature in Si (100) metal-insulator-semiconductor structures

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(Submitted 30 July 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 6, 245–248 (25 September 1984)

A linear temperature dependence has been found for the conductivity σ of a 2*D* electron gas on a Si (100) surface at liquid-helium temperatures ($1.3\ \text{K} \leqslant T \leqslant 4.2\ \text{K}$): $\sigma(N_S, T) = \sigma_0(N_S) - \alpha T$. Under these particular experimental conditions the coefficient α depends only weakly on the electron density (N_S) in the inversion layer. At $N_S \approx 2 \times 10^{11}\ \text{cm}^{-2}$ the conductivity increases severalfold as the temperature is reduced from 4.2 to 1.3 K.

The temperature dependence of the conductivity of a 2*D* electron gas in a metal-insulator-semiconductor structure at low temperatures may be determined by several factors[1]: 1) localization effects, 2) scattering of electrons by phonons, and 3) a temperature dependence of the screening of charged static defects.[2,3] Strong-localization effects cause an exponential decrease in the conductivity with decreasing temperature and are seen at $\sigma \lesssim 10^{-5}$ S. We will not discuss this range of conductivities in the present letter. At higher conductivities, the weak localization of electrons gives rise to logarithmic corrections to the conductivity, $\Delta\sigma(T) \sim (e^2/2\pi^2\hbar) \ln T/T_0$, with a typical value $e^2/2\pi^2\hbar \approx 1.2 \times 10^{-5}$ S. Two other mechanisms lead to an increase in the conductivity with decreasing temperature. It should be noted that there has been essentially no study of how the temperature dependence of the screening affects the conductivity of a

0021-3640/84/181019-05$01.00