

Three states of a cholesteric liquid crystal in micropores

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Three states of a cholesteric liquid crystal in pores 80 \AA in size have been observed: a transparent state (*A*), a turbid state (*B*), which exists at the same temperature as state *A*, and a transparent state (*C*), which exists at higher temperatures. An anomalous scattering of light is observed for state *B*.

The effect of surfaces on the physical properties of the condensed state of matter has recently been the subject of active research. Surface effects can give rise to new phases and to various transitions between these phases.¹ Particularly promising systems for this research are liquid crystals in the pores of a fine-pore quartz matrix, with a pore surface area reaching 10^5 cm^2 per 1 cm^3 . In this case we are dealing with an ordered system in the bounded volume of the pores, in which stable structural defects of the liquid crystals can arise.²

A study of cholesteryloleate, a cholesteric liquid crystal, which undergoes a tran-

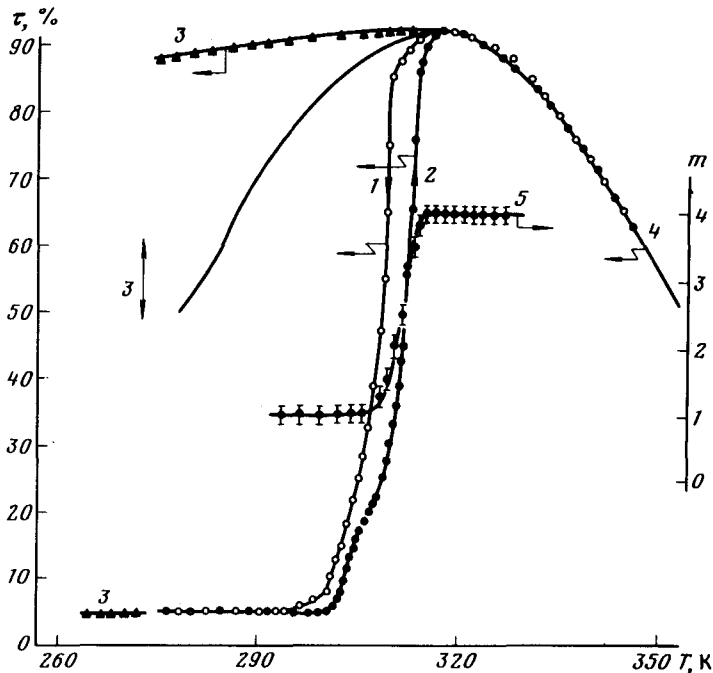


FIG. 1. Temperature dependence of the optical transmission τ (curves 1–4, scale at the left) and of the exponent m in the expression $I \sim \lambda^{-m}$ (curve 5, scale at the right).

sition to the isotropic phase at $T_{is} = 299.5$ K in bulk form, reveals the existence of three states of this liquid crystal in pores at $T > 295$ K.

The liquid crystal is injected into the pores of a rectangular porous plate $l = 0.1$ cm thick. The density of pores in the matrix is $2 \times 10^{18} \text{ cm}^{-3}$; the size (d) distribution of the pores has a sharp peak at $d = 80 \text{ \AA}$; and the total volume of the pores is 27% of the volume of the sample.³

Curves 1–3 in Fig. 1 show the light transmission τ at the wavelength $\lambda = 560 \text{ nm}$ versus the temperature T . At this wavelength there is no absorption in the matrix or in the liquid crystal, and the observed attenuation of the light is a consequence of scattering. At $T = 316 \text{ K}$ the sample is in a state with a maximum τ ($\tau = 92\%$); this is transparent state C . When the system is cooled at a rate higher than 0.1 K/min , τ varies in accordance with curve 1. At $T < 300 \text{ K}$ the transmission τ reaches its lowest value ($\tau = 5\%$) and is essentially independent of T ; a turbid state B forms. Curve 2 corresponds to the transition from B to C with increasing T . Each point on curve 2 was measured after ample time was allowed for temperature transients to die out.

Upon cooling from state C at a rate less than 0.1 K/min , the sample remains transparent in the interval $273 \text{ K} < T < 316 \text{ K}$, and τ depends only slightly on T (curve 3). Another transparent state, A , forms, and we will call it the “low-temperature” transparent state since it occurs at a temperature below that of state C . With a further reduction of T , state A is disrupted, because of crystallization of the liquid crystal in

the pores. This transition is reversible, and state *A* is restored when *T* is raised.

States *A* and *B*, which exist in the same temperature interval in the absence of an external agent, persist for a long time (thousands of hours), and transitions from one to the other can be caused by changing the temperature.

The observed changes $\tau = f(T)$ cannot be explained on the basis of a trivial scattering of light due to a difference between the refractive indices of the matrix (n_M) and the liquid crystal (n) and a dependence $n(T)$.

If the attenuation of the light flux were due exclusively to the scattering of light by optical inhomogeneities due to the difference between $n(T)$ and n_M , the extinction coefficient would be $\sigma \sim [n_M - n(T)]^2$. Curve 4 in Fig. 1 is a curve of $\tau = f(T)$, calculated with allowance for reflection of the light on the basis of a temperature coefficient $\alpha = 2.64 \times 10^{-4} \text{ K}^{-1}$ for the refractive index of the liquid crystal in the isotropic phase. At $T > 315 \text{ K}$ the experimental points agree with curve 4, and the liquid crystal in the pores exhibits the properties of an isotropic liquid. At $T < 315 \text{ K}$ the change in τ stems from the appearance of two different supermolecular structures of the liquid crystal in the pores.

The pores disrupt the spiral structure of the cholesteric liquid crystal, induce an optical anisotropy, and change^{4,5} the temperature of the phase transition. For the particular liquid crystal of these experiments, we have $|\Delta n| = |n_e - n_o| = 1.55 \times 10^{-2}$ in the volume at $T = 293 \text{ K}$ and $|\Delta n| = 3 \times 10^{-7}$ in the pores in state *A*.

Figure 2 shows σ spectra for states *A* and *B* at $T = 290 \text{ K}$. For state *A* we observe $\sigma \sim \lambda^{-4}$, which implies a Rayleigh scattering. For *B* there is an anomalous scattering by scattering centers with dimensions comparable to λ , and we observe a behavior $\sigma \sim \lambda^{-1}$. Curve 5 in Fig. 1 shows the results of a spectral study of the light scattering intensity ($I \sim \lambda^{-m}$) as a function of T at the transition from state *B* to state *C*. We see from this figure that m decreases from 1 to 4 with increasing T , in the same T interval in which τ changes from its minimum value to its maximum.

Measurements of the degree of depolarization of the scattered light⁶ for state *A* yield $\Delta_V = 0.22$, $\Delta_u = 0.5$, and the nontrivial value $\Delta_h = 1.8$. For state *B* we find $\Delta_V = 1$, $\Delta_h = 1$, and $\Delta_u = 1$, implying multiple scattering.

To determine the state of aggregation of the cholesteric liquid crystal in the pores,

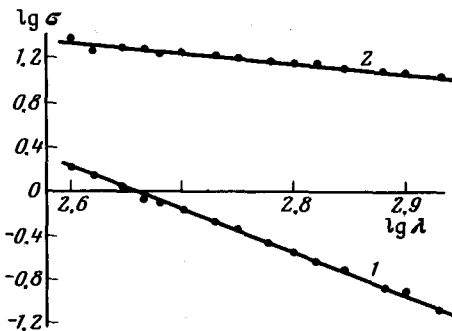


FIG. 2. The extinction coefficient σ (cm^{-1}) versus the wavelength λ (nm) in log-log scale. 1—Transparent state *A*; 2—turbid state *B*. $T = 290 \text{ K}$.

we compared the spectra and the degree of depolarization (P) of the fluorescence for the following systems: 1) the cholesteric liquid crystal in the pores, activated with rhodamine 6-G molecules (R6G), in state A ; 2) in state B ; 3) an ethanol solution of R6G; 4) R6G adsorbed on the walls of the pores of the dry matrix and in a matrix impregnated with ethanol; 5) at an R6G concentration of $2.7 \times 10^{16} \text{ cm}^{-3}$ and $T = 293 \text{ K}$. The corresponding positions of the peaks of the fluorescence band, λ_m , and of P are $\lambda_{1m} = \lambda_{2m} = \lambda_{3m} = \lambda_{5m} = 552 \text{ nm}$, $\lambda_{4m} = 538 \text{ nm}$ and $P_1 = 0.36$, $P_2 = 0.08$, $P_3 = 0.05$, $P_4 = 0.29$, and $P_5 = 0.1$. The value $P_2 = 0.08$ results not from an increase in the rotational mobility of the R6G molecules but from a depolarization due to scattering of the fluorescence by the turbid medium in the sample. Working from the measured values of P_1 and P_3 and the Levshin-Perren formula,⁷ we can estimate the ratio of the viscosity of ethanol (η_0) to the effective viscosity (η) of the cholesteric liquid crystal in the pores: $\eta = 21\eta_0 = 0.25 \text{ P}$; then the energy of the potential barrier obstructing the free rotation of the R6G molecules is $W = 11.5 \text{ kJ/mole}$, in order-of-magnitude agreement with the typical values of η and W for liquid crystals.

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¹V. L. Pokrovsky, Adv. Phys. **25**, 595 (1979).

²G. E. Volovik and O. D. Lavrenovich, Zh. Eksp. Teor. Fiz. **85**, 1997 (1983) [Sov. Phys. JETP **58**, 1159 (1983)].

³V. I. Zemskii, I. K. Meshkovskii, and A. V. Sechkarev, Dokl. Akad. Nauk SSSR **267**, 1377 (1982) [Sov. Phys. Dokl. **27**, 882 (1982)].

⁴M. Kuzma and M. Labes, Mol. Cryst. Liq. Cryst. **100**, 103 (1983).

⁵F. M. Aliev, I. K. Meshkovskii, and V. I. Kuznetsov, Dokl. Akad. Nauk SSSR **279**, 848 (1984) [Sov. Phys. Dokl. **29**, No. 12 (1984)].

⁶I. L. Fabelinskii, Molekulyarnoe rasseyanie sveta (Molecular Scattering of Light), Nauka, Moscow, 1965.

⁷A. M. Sarzhevskii and A. N. Sevchenko, Anizotropiya pogloshcheniya i ispuskaniya sveta molekulami (Anisotropy of Optical Absorption and Emission of Molecules), BGU, Minsk, 1971.

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