

Elasticity of Blue Phase I of Cholesteric Liquid Crystals

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(Received 28 November 1983)

Normal shear modes of axial symmetry were excited in polycrystalline samples of blue phase I. An average shear modulus, E , is determined from the frequencies of these modes. E is found to vary by nearly two orders of magnitude throughout the blue-phase temperature range. The authors report the first observation of faceted single crystals of blue phase I growing from the isotropic phase. These have enabled them to determine the blue phase I lattice constant.

PACS numbers: 61.30.-v, 62.10.+s, 64.70.Ja, 64.80.-v

Cholesteric blue phases are those mysterious intermediate phases which appear in the $\sim 0.5^\circ\text{C}$ temperature range between the cholesteric liquid-crystal phase of some short-pitch materials and the isotropic liquid phase. Although blue phases are the first example of thermotropic liquid-crystal phases (i.e., obtained by varying the temperature) ever to be observed, it is only in the last few years that serious attempts have been made to understand them.¹

In the nematic liquid-crystal phase, rodlike (or disclike) molecules move freely in three directions but tend to align along a unique direction denoted by a unit vector, n , called the director. If the molecules are chiral, cholesteric liquid-crystal phases may occur where the director rotates with constant pitch, p , about an axis perpendicular to n . The nematic phase is, thus, the special case of a cholesteric phase with infinite pitch. A cholesteric reflects light the same wavelength as its pitch and polarized circularly in the same sense as its helical structure, e.g., a right-handed cholesteric reflects right circularly polarized light.

Cholesteric liquid crystals undergo a first-order transition to the isotropic phase which, when the pitch is less than $\sim 4000 \text{ \AA}$, is often, but not always, accompanied by the appearance of blue phases. Blue phases are optically active but isotropic and reflect several wavelengths all of which are circularly polarized in the same sense as the cholesteric phase.² These lengths can be indexed according to a cubic lattice. There are currently three kinds of blue phases: I, II, and the blue fog. When all three phases are present,

blue phase I (BPI) is closest in temperature to the cholesteric phase and the fog is closest to the isotropic phase. In some cases, only one or two blue phases may occur. BPI is believed to be bcc (an I lattice); BPII, simple cubic (a P lattice); and no lattice is associated with the fog.¹

Under the assumption that BPI is bcc, its lattice constant, a , turns out to be somewhat greater than the pitch, p , for a 2π rotation of the director in the cholesteric phase. The lattice constant decreases as one approaches the transition to BPII and is very nearly, but not exactly, commensurate with p at the transition BPI-BPII.^{2,3} If one assumes that BPII is simple cubic, " a " is about $p/2$. Thus, blue-phase lattice constants are the same magnitude as those of colloidal crystals made of charged polymer particles dispersed in water. In this last case, several techniques have recently been developed to study the unusual physical properties that result from the shift to colloidal scales.⁴

The purpose of this Letter is to report the results of our measurements of the elastic shear modulus of BPI using the "oscillating cylinder" method.⁵ The method is similar to the one used by Clark, Vohra, and Handschy⁶ to measure the elastic modulus of BPI in a pure compound. Our method⁵ imposes a few requirements which we now discuss.

Axially symmetric normal modes in an elastic medium can be detected provided that their period, τ_1 , is larger than $\tau = \eta/E$, where η is an average shear viscosity and E , an average shear modulus. The period of the first mode⁵ is $\tau_0 = 1/f_0 = (2\pi/\mu)R(\rho/E)^{1/2}$ (where R is the radius of

the cylinder, $\rho \approx 1 \text{ g/cm}^3$ is the density, and μ is the first zero of the first Bessel function). As a result of its large unit cell the elastic modulus of the blue phase is expected to be rather weak (between 1000 and 1 dyn/cm^2). Hence, a large sample radius is needed to satisfy $\tau_1 > \tau$. In addition, the expression for τ_0 above assumes a BP cylinder much longer than a diameter. Our first requirement, then, is the availability of 10–20 g of material. Next because of rather crude (0.1°C) temperature regulation and measurements we required a blue-phase range much larger than the usual 0.5°C . Finally, because of some details of construction, we wanted a blue phase that occurs below 50°C .

In general, the second point can be satisfied by going to mixtures, and the others by using CB15 (cyano-4-methylbutyl-biphenyl) as a chiral agent since its blue-phase-isotropic transition temperature is -25°C . We chose ZLI1840 as the nematic mixture. It is obtained from Merck and has a 5°C nematic-isotropic two-phase transition region without CB15. We also made a nematic mixture of 75% 6OCB (cyano-hexyloxybiphenyl) and 25% T4 (cyanobutylterphenyl). To these two nematic mixtures we added 58% and 55% of CB15, respectively, to create the tight pitch favorable to blue phases. We refer to these two preparations as *A* and *B*.

With decreasing temperature, both mixtures exhibited a blue phase (first, coexisting with the isotropic liquid, and then, alone) in a large temperature interval ($\sim 5^\circ\text{C}$). With use of a reflecting metallurgical microscope, large, polyhedra-shaped monocrystals with well-defined facets were observed (for the first time) in this coexistence region (Fig. 1). The crystal habits had obviously a cubic point symmetry and, in fact, were found to be superpositions of two forms: a $\{211\}$ icositetrahedron and a $\{110\}$ rhombic dodecahedron. It can be shown that the occurrence of such crystal forms is characteristic of a centered (*I* type) lattice, and more precisely, of the $O^8(I4_132)$ space symmetry.^{7,8} On the basis of this microscopic examination, we can identify the blue phase observed in both mixtures as BPI.

With use of a small monochromator, the wavelength λ_{110} of the (110) Bragg reflection was determined and, consequently, the cubic-lattice constant $a = \lambda_{110}/n\sqrt{2}$ ($n \sim 1.5$ is an index of refraction) of blue phases in both mixtures *A* and *B*. We found $a_A = 251 \text{ nm}$ and $a_B = 302 \text{ nm}$.

For the shear-modulus measurements, sample *A* was a cylinder 1.22 cm in radius and 10 cm



FIG. 1. Photomicrograph of monocrystals of BPI (in equilibrium with isotropic liquid) in monochromatic illumination. The crystal habit indicates cubic point symmetry, *O*.

long. The shear deformation of this sample was detected simply by monitoring the intensity of light scattered by a He-Ne laser beam crossing the cylindrical sample off its axis. The sample was cooled from the isotropic phase until resonances were observed, and then measurements were made both on cooling to the cholesteric phase and heating until resonances disappeared. At say, 23°C , several harmonics were observed and their half-width $\Delta f_{1/2}$ was $< 1 \text{ Hz}$. At 26.0°C , the resonances broadened ($\Delta f_{1/2} \cong 5 \text{ Hz}$) and disappeared above 26.3°C even though the sample still appeared to be in the blue phase. It was isotropic at 27°C .

The frequency of the first mode, plotted as a function of temperature, T , in Fig. 2, shows a nearly linear dependence. We call T^* the extrapolated value of T where $f_0 = 0$. A linear fit to the points above 24°C yields $T^* = 27^\circ\text{C}$. With use of this value, a log-log plot of E ($E = 4.0f_0^2$) vs $T - T^*$ can be made and a best fit to this functional form is $E(\text{dyn/cm}^2) = 3.87(T - 27^\circ\text{C})^{2.1}$. In particular at $T - T^* = 3^\circ\text{C}$, $E = 376 \text{ dyn/cm}^2$. Assuming the elasticity of blue phases is due to gradients on a scale of the order of the lattice constant, a , in the director configuration, we find $K = Ea^2 = 2.4 \times 10^{-7} \text{ dyn}$. From Fig. 2, K sat-

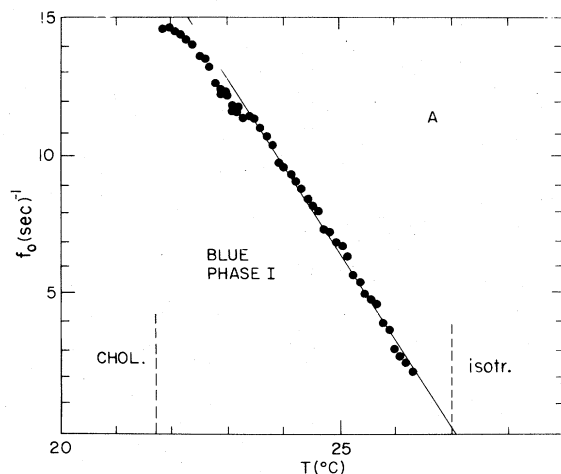


FIG. 2. The resonance frequency vs temperature for mixture A.

urates at a maximum 3×10^{-7} dyn in the vicinity of the cholesteric phase. The minimum measured value of K is 1×10^{-8} dyn at $T - T^* = 0.7^\circ\text{C}$. Independent measurements⁹ of the Frank twist constant in a similar material yield 2×10^{-7} dyn for the cholesteric phase and about 10^{-7} dyn in BPI and BPIL. Thus for $T - T^* \geq 2^\circ\text{C}$, K is in pretty good agreement with a Frank constant. It continues to decrease, however, when $T - T^* < 2^\circ\text{C}$ by another order of magnitude.

We proceeded in a similar manner for sample B which was 7 cm long with a 0.6-cm radius. Shearing this sample resulted in the deformation of a Debye-Scherrer ring which we detected by a photodiode situated at its edge. No resonance was observed above 44.5°C . In the light microscope we observed upon heating that the isotropic phase first appeared at 44°C and by 46°C , the sample was entirely isotropic. A plot of the resonance frequency as a function of temperature gave $T^* = 45.9^\circ\text{C}$. Figure 3 shows the log-log plot of E vs $T - T^*$. The best fit to these data is $E(\text{dyn}/\text{cm}^2) = 29.1(T - 45.9^\circ\text{C})^{1.9}$. At $T - T^* = 3^\circ\text{C}$, $E = 230 \text{ dyn}/\text{cm}^2$; thus, again, $K = 2.3 \times 10^{-7}$ dyn, identical to what is found in the first mixture with much the same temperature dependence.

Below 44°C , the quality of the resonance was very sharp ($\Delta f_{1/2} \lesssim 1 \text{ Hz}$). Even at 44.1°C , the signal was very good, but at 44.7°C it was no longer observed even though the sample seemed still in the blue phase.

In both samples, T^* corresponds to the disappearance of the blue phase upon heating and in both samples, resonance is no longer observed upon the nucleation of macroscopic isotropic re-

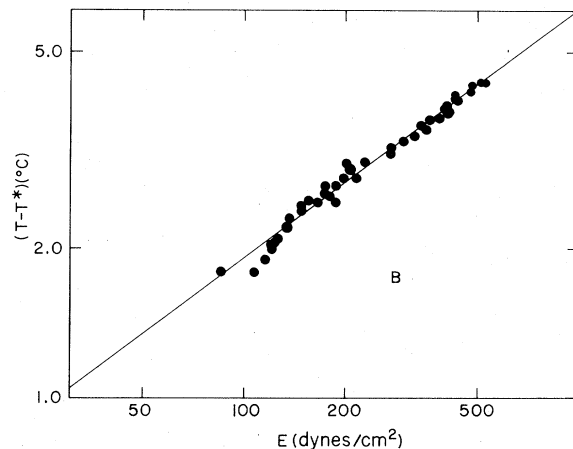


FIG. 3. Log-log plot of the elastic modulus vs $T - T^*$ for mixture B.

gions. The order of magnitude of the blue-phase elastic modulus is similar to colloidal crystals where E does not vary with temperature but is very sensitive to particle concentration and ionic purity of the suspension. Typically,⁵ the elastic modulus of a suspension of polystyrene spheres $0.1 \mu\text{m}$ in diameter is about $80 \text{ dyn}/\text{cm}^2$ when the particle density $n_s = 6 \times 10^{13}/\text{cm}^3$ and $5 \text{ dyn}/\text{cm}^2$ when $n_s \cong 1.3 \times 10^{13}/\text{cm}^3$. Thus, in colloidal crystals, E decreases with increasing lattice constant. Since the blue-phase lattice constant does not change much with temperature, at least not in the range where we could measure E , how can we account for such a dramatic dependence of E on temperature?

The interpretation is complicated by the fact that the coexistence of blue phase and isotropic liquid in both samples is relatively large. When isotropic regions completely surround the blue phase, no shear is transmitted and we are unable to observe resonance. Once the blue phase is established and extended isotropic regions (i.e., visible to the eye) are no longer apparent, we measure a shear modulus whose magnitude increases dramatically with decreasing temperature even though the mass of the sample is fixed. This suggests a strengthening of the effective "spring constant" of the blue-phase lattice. Since neither the Frank constant nor the lattice constant changes enough in a 5°C temperature range to account for a one or two order of magnitude change in E , an interpretation would be that the "number of springs" participating in resonance increases as the temperature decreases because, for example, microscopic regions of isotropic liquid are

being replaced by blue phase.¹⁰ Once there is no longer any isotropic region of any size left, E levels off. Such appears to be the case but only very close to the cholesteric phase.

One of us (P.E.C.) thanks L'Ecole Pratique des Hautes Etudes (Troisième Section, Science de la Vie) for support during a part of this work.

¹See, for example, R. M. Hornreich and S. Shtrikman, Phys. Rev. A 28, 1791 (1983), and references therein.

²P. L. Johnson, J. H. Flack, and P. P. Crooker,

Phys. Rev. Lett. 45, 641 (1980).

³P. Pieranski, Contemp. Phys. 24, 25 (1983).

⁴J. Hern, B. B. Rao, and J. T. Ho, Phys. Rev. A 24, 3272 (1981).

⁵E. Dubois-Violette, P. Pieranski, F. Rothen, and L. Strzelecki, J. Phys. (Paris) 41, 369 (1980).

⁶N. A. Clark, S. T. Vohra, and M. A. Handschy, Phys. Rev. Lett. 52, 57 (1984).

⁷F. C. Phillips, *An Introduction to Crystallography* (Longmans, Green, London, 1969), p. 306.

⁸P. E. Cladis, R. Barbet-Massin, and P. Pieranski, to be published.

⁹P. L. Finn and P. E. Cladis, Mol. Cryst. Liq. Cryst. 84, 159 (1982).

¹⁰See, for example, P. G. de Gennes, J. Phys. (Paris), Lett. 37, L-1 (1976).

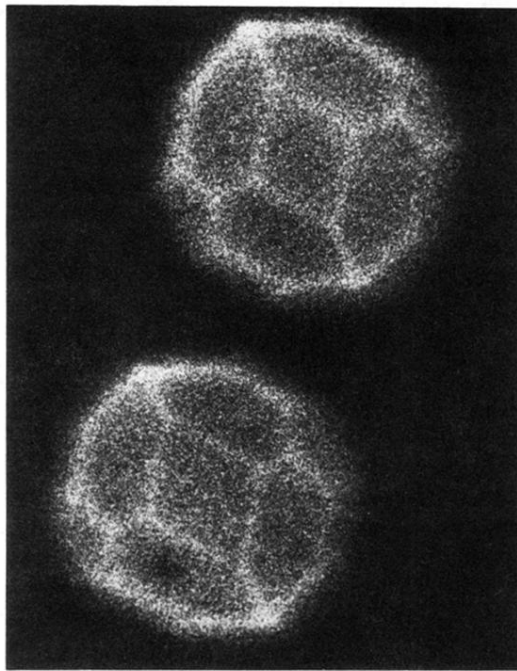


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