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Divergence of Cholesteric Pitch near a Smectic-*A* Transition*

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We have measured the detailed temperature dependence of the cholesteric pitch in cholesteryl nonanoate near the smectic-*A* transition. The data show a power-law behavior with an exponent $\nu = 0.675 \pm 0.025$, in agreement with theoretical prediction and with elastic-constant measurements in nematics.

Studies near the nematic or cholesteric to smectic-*A* transitions in liquid crystals have been of intense current interest[1-8] since the McMillan–de Gennes suggestion[9-11] that they may be second-order in nature, and that they are analogous to, but in many respects more tangible than, the superconducting transition. The buildup of short-range smectic order in the nematic or cholesteric phase is characterized by a coherence length ξ which diverges toward an apparent transition temperature T_c in the form

$$\xi = \xi_0 (T - T_c)^{-\nu}, \tag{1}$$

where the critical exponent ν is typically between 0.6 and 0.7 from model calculations and experiments on magnets and fluids.[12] This pretransitional behavior manifests itself in liquid crystals in the anomalous increase of the twist and bend elastic constants K_{22} and K_{33}, and of the cholesteric pitch p. Physically, the presence of short-range smectic order in a nematic makes twist and bend distortions energetically costly, and leads to additional contributions to the respective elastic constants which are expected to be proportional to ξ.[10] A similar situation applies to the elastic constants in a cholesteric. Furthermore, the "rotary" part of the free energy, proportional to K_{22}/p, is believed to depend mainly on the intermolecular interactions and therefore to be unaffected by the smectic transition. Hence K_{22} and p should have similar temperature dependences,[13] and the latter is expected to diverge like

$$p = p_0 + c(T - T_c)^{-\nu}, \tag{2}$$

where p_0 is the pitch in the absence of the smectic ordering. Experimentally, the untwisting of the cholesteric texture in the vicinity of the smectic-*A* transition, with the accompanying dramatic color changes, is well known,[14-16] but has not been studied carefully in the light of recent theoretical advances. In this paper we present the results of a detailed measurement of the temperature dependence of the pitch of cholesteryl nonanoate (CN) near the smectic-*A* phase and the first report of the value of a critical exponent for a cholesteric–smectic-*A* transition.

Our samples of CN were obtained from Vari-Light Corporation. On cooling from the isotropic liquid, CN forms a cholesteric phase at 91°C and a smectic-*A* phase at 74°C. We found using differential scanning calorimetry that the cholesteric–smectic-*A* transition entropy was $0.05R_0$, in agreement with previous measurements.[1,17] The samples were placed between glass slides separated by a 12-μm Mylar spacer. A planar structure with the helical axis perpendicular to the slides was formed by displacing the top slide when the liquid was in the cholesteric phase. Both untreated slides and slides coated with obliquely deposited SiO thin film[18] were used, the latter giving more uniform textures. The sample temperature was controlled to a stability of 0.003°C and measured with a platinum resistance thermometer. We used the rapid color changes near the smectic-A transition as a very sensitive indicator of sample defects and thermal gradients in our sample selection. The selective reflection technique was used to measure the pitch. Light from a modified Perkin-Elmer model 4000A spectrophotometer was focused on the sample at an angle of incidence θ of 10°, and the specularly reflected intensity was measured. Samples formed with coated slides gave stronger reflection intensities than uncoated ones, but otherwise the two types of slides yielded identical results. We obtain smooth and symmetric reflection peaks, and the wavelength λ_p of maximum reflection was resolvable with an accuracy of 0.5 nm in the violet and 1 nm in the red. The temperature dependence of λ_p in CN is shown in Fig. 1. The peak wavelength covered the entire visible range of the spectrophotometer in the temperature range of our measurement.

The peak wavelength λ_p is related to the pitch p by the Bragg-like expression[19-21]

$$\lambda_p = np(1 - n^{-2}\sin^2\theta)^{1/2}, \tag{3}$$

where $n = (n_e + n_o)/2$ is the average of the extraordinary and ordinary refractive indices, and the width $\Delta\lambda$ of the reflection peak is given by

$$\Delta\lambda = (n_e - n_o)p. \tag{4}$$

We found $\Delta\lambda$ to increase near the smectic phase, in qualitative agreement with Eq. (4), but with a somewhat more pronounced temperature dependence than that of the pitch. Between 75.0 and 74.5°C, while λ_p increased from 470 to 560 nm, $\Delta\lambda$ changed from 19 to 33 nm. This could be caused by the sample not being perfectly single domain, or by a slight temperature inhomogeneity. The former possibility means our data represent an average over the 1.5-mm × 4-mm illuminated area of the sample, and the latter allows us to estimate the temperature gradient to be no more than 0.01°C. Variations in n due to dispersion and temperature dependence in cholesterol esters are typically within 1% in the wavelength and temperature range of our measurement.[22] We could therefore neglect changes in n without significantly affecting the result of our analysis. With this approximation λ_p is a direct measure of p, and we fitted the data with the expression

$$\lambda_p = \lambda_0 + c'(T - T_c)^{-\nu}, \tag{5}$$

where λ_0 is the peak wavelength in the absence of the smectic transition.

To take into account the slight temperature dependence of λ_0, which affects principally the analysis of the few data points furthest from T_c, we measured the temperature dependence of the pitch in cholesteryl propionate (CP), a member of the same family of cholesterol esters as CN that does not have a smectic phase. We found that, except in the immediate vicinity of the isotropic phase, the pitch decreased almost linearly in temperature with an average slope of − 0.28%/°C. Practically identical temperature dependences have been reported for other cholesterics.[15,23] It is reasonable to expect P_0 in CN to behave similarly. We obtained additional evidence for this by doping CN with cholesteryl chloride (CC) to depress the smectic-A transition temperature and extend the cholesteric range. The temperature coefficient of the pitch was measured as a function of the concentration x of CC, and was found to extrapolate to a value at $x = 0$ very close to that obtained in CP.[24] We

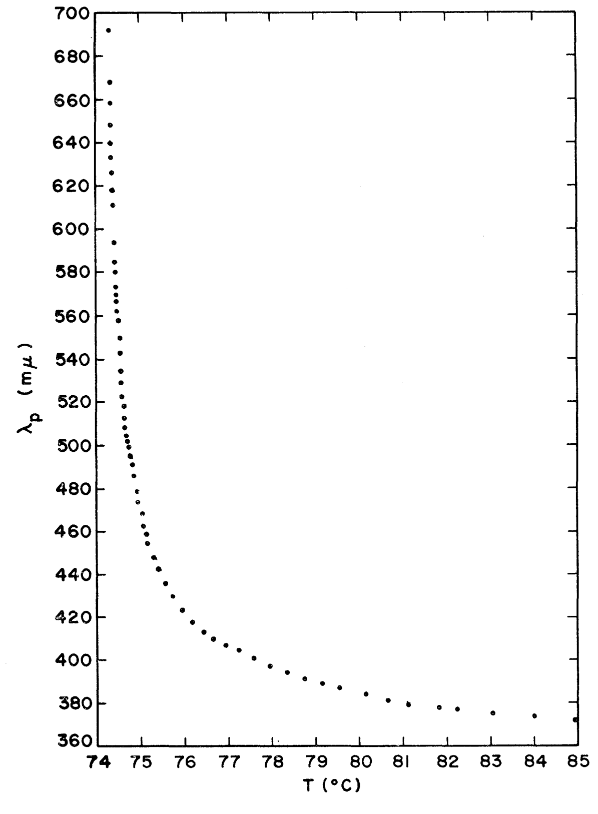

FIG. 1. Temperature dependence of the peak reflection wavelength λ_p in cholesteryl nonanoate.

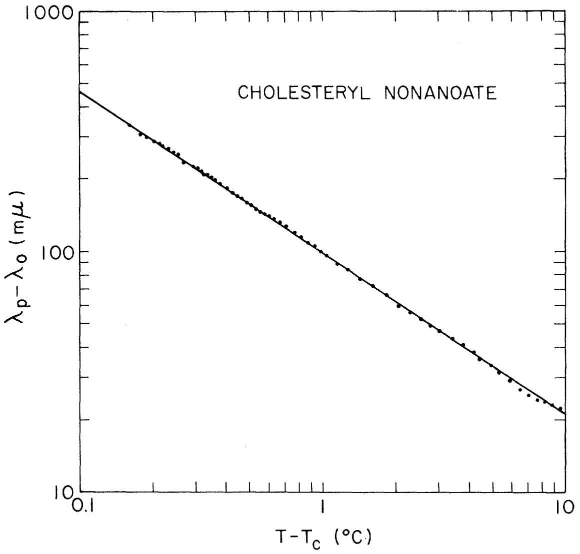

FIG. 2. Log-log plot of $\lambda_p-\lambda_0$ versus $T-T_c$. The straight line has a slope $\nu=0.675$.

therefore used the form

$$\lambda_0=\lambda_{00}[1+\alpha(T-T_c)] \tag{6}$$

for the peak wavelength in the absence of the smectic phase, where $\alpha=-2.8\times10^{-3}$/°C and λ_{00} is a constant.

A least-squares fit of the data by Eqs. (5) and (6) yielded the optimum parameters $\lambda_{00}=360$ nm, $T_c=74.14$°C, and $\nu=0.675\pm0.025$. A log-log plot of $\lambda_p-\lambda_0$ versus $T-T_c$ is shown in Fig. 2. The power law appears to be obeyed over nearly two decades in $T-T_c$. The value of ν is in excellent agreement with that predicted by de Gennes.[11] The error assigned to ν already includes the effect of allowing for reasonable variations in the value of α to be used in Eq. (6). Some questions have been raised about the possible effect of sample purity on the nature of the nematic-smectic-A transition.[8] The data discussed above were taken with an unpurified sample. We found that the apparent critical temperature T_c could range from 74.06°C in some aged samples to 74.25°C in samples purified by recrystallization with pentyl alcohol. The actual transition temperature is typically 0.05°C higher than T_c. However, the values of the exponent ν from the various samples agree with one another within the experimental uncertainty.

It would be interesting to see if the twist elastic constant K_{22} in CN exhibits a similar temperature dependence as that of the pitch. Unfortunately, the usual method of measuring K_{22} in cholesterics by untwisting the helical structure with an electric or magnetic field is not readily applicable to CN because its electric dipole moment is canted to the molecular axis and it has a negative magnetic anisotropy. However, Frank elastic-constant measurements have been made near the nematic-smectic-A transition in several materials. The value of ν obtained in p-cyanobenzylidene-p'-octyloxyaniline is 0.653 ± 0.015 for K_{33}[5] and 0.66 ± 0.05 for K_{22},[6] and that in p-butoxybenzylidene-p'-octylaniline is 0.65 ± 0.05.[7] The value we obtained for ν in CN is therefore consistent with these experiments on nematics and with theoretical expectation. Studies on other cholesterics and binary systems are in progress.

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Nuclear Acoustic Resonance of Liquid He^3 on a Metal Surface

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The nuclear acoustic resonance of He^3 spins has been excited and detected via Rayleigh waves on a metal surface. The signal is many orders of magnitude larger than the nuclear acoustic resonance signal detected in the bulk of solids. Its magnitude is very sensitive to surface damage. The effect has been observed with liquid He^3 in contact with gallium, aluminum, and gold.

Nuclear acoustic resonance (NAR) has been observed in solids. The resonance is excited either via the quadrupolar coupling[1] or via the dipolar one.[2,3] To my knowledge, NAR has not been observed in liquids. In this paper, I report the observation of the NAR of liquid He^3 in contact with a metal surface. The NAR is excited by forcing the solid surface to vibrate during a short time at a frequency and magnetic field which correspond to the resonance condition for the He^3 spins ($\Delta m = 1$ transition). The detection is made by recording the free decay of the surface vibration following the acoustic pulse. The experiment is similar to Hahn's experiment with radiofrequency waves.[4]

The observation conditions of this new effect are as follows: The sample is a metallic single crystal which has two faces flat and parallel. The area of these faces is about 1 cm^2 and the distance between them is 1 cm. The sample is in a liquid He^3 bath and has an X-cut quartz transducer bonded to one of its flat faces. The transducer diameter is 0.5 cm. An rf pulse of 1 μsec duration is applied to the transducer which converts it into a longitudinal acoustic wave train which propagates in the bulk and on the sample surface.[5] In the bulk, the wave is reflected successively on the two parallel sample faces and gives rise to acoustic echoes on the quartz transducer which are converted into rf pulses, then amplified and demodulated.

On the other hand, a Rayleigh wave propagates on the sample surface. Nevertheless, this wave does not return toward the transducer because the wave front (that one can consider circular in the simplest case of an isotropic medium) does not reach the different points of the sample edge (which is rectangular) at the same time. It is important to note at this stage that, except for the special case considered later, the vibrations of the quartz transducer are damped as soon as the rf pulse is removed (i.e., less than 0.5 μsec). As a result, the quartz vibrates only when an echo from the bulk reaches the sample surface. When the magnetic field is set up (normal to the sample faces in the present experiments), the echo amplitude varies because of all the magnetoacoustic effects. Nevertheless, one does not observe any change in the damping of the quartz transducer.

When the NAR condition is fulfilled for the He^3 spins (i.e., $\omega = \gamma H$, where ω is the acoustic angular frequency, γ the gyromagnetic factor, and H the magnetic field), one observes on the quartz transducer an acoustic free decay (AFD) following the acoustic pulse (i.e., the quartz does not stop vibrating as soon as the acoustic pulse is removed). The AFD is exponential (Fig. 1) and is quite similar to the nuclear induction signal induced in a coil following an rf pulse.[4] Furthermore, the AFD interfers with the echoes from the bulk. So, when the magnetic field is swept around the NAR, beats are observed.

Figure 2 shows the beat patterns obtained for the successive echoes. From the amplitude variation of the first echo (Fig. 2), one can see that the effect is very large. It gives an apparent attenuation variation of the order of 3×10^{-1} cm^{-1}. This value is to be compared with the usual attenuation vibration due to the NAR in the bulk which is of the order of 10^{-6} cm^{-1}.[1,3] Figure 2 shows also that the period δH_n of the beat pattern