

FIG. 3. The relative superelastic cross section for $v=5 \rightarrow v=0$ in N_2 calculated from electron excitation data.

$v=5$ level of N_2 yields a value approximately equal to the total quenching cross section.³ Because of the uncertainty in the distribution of excited rubidium atoms in the collision chamber, and to a lesser extent the uncertainty in the magnitudes of the Rb and N_2 superelastic cross sections, the estimate is reliable only to an order of magnitude. This result indicates that in not less than 10% of the quenching collisions, the Rb electronic energy is transferred into the $v=5$ vibrational level of N_2 . Excitation to this level represents the maximum possible transfer of the available electronic energy into vibration. This is in contrast with the quenching of excited Hg by CO. Karl, Kruus, and Polanyi,⁷ by direct observation of infrared emission from collisionally excited

CO, measured the distribution of vibrationally excited states and showed that levels lying higher than half the available electronic energy of Hg are not excited. That is, every quenching collision transfers at least 2 eV into kinetic energy. It is also interesting to note that the total quenching cross sections of excited Rb and the other alkali metals⁸ by N_2 are an order of magnitude larger than that of excited Hg by CO.

Information about the population distribution of remaining vibrational levels of N_2 will help to resolve the differences between the two quenching processes. Work along these lines with improved energy resolution is planned.

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RELATIONSHIP BETWEEN ELECTRIC FIELD STRENGTH AND HELIX PITCH IN INDUCED CHOLESTERIC-NEMATIC PHASE TRANSITIONS*

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A cholesteric-nematic phase transition can be induced by relatively weak electric fields, and the threshold field varies inversely with the pitch of the helix in corroboration of recent theoretical suggestions. The phase change is accompanied by a change in the activation energy for charge-carrier production and can easily be observed by both conductivity measurements and direct optical examination.

Recently Meyer¹ has presented a theory regarding the influence of electric and magnetic fields on the structure of cholesteric liquid crystals. He concludes that application of an electric field parallel to the helix axis should destroy the helical structure, and that the threshold field strength should be $F_c = (2\pi/Z_0)(k_{22}/\Delta\epsilon)^{1/2}$ where

Z_0 denotes the pitch of the undisturbed helix, $\Delta\epsilon$ the anisotropy of the dielectric constant, and k_{22} the modulus of torsional strain. Wysocki, Adams, and Haas² have indeed observed a field-induced phase transition in a mixture of cholesteryl chloride, nonanoate, and oleyl carbonate at a field of $(3-4) \times 10^5$ V cm⁻¹. They were unable to

decide unambiguously whether the final phase was smectic or nematic. For a conclusive check of Meyer's theory, it is necessary to determine whether F_c varies inversely with the pitch of the helix. The experiments herein reported were performed with a 1.75:1 mixture of cholesteryl chloride and myristate which has a strongly temperature-dependent helical pitch at temperatures $T \geq 43^\circ\text{C}$ and a nematic phase near 43° .³

The sample was placed between two conducting glass electrodes with a 10-mil Teflon spacer and was mounted in an optical cell which could be heated by a N_2 stream of controlled temperature. Detection of the phase transition could be achieved either electrically or by direct viewing under a microscope. Figure 1 shows a typical set of Arrhenius plots of the current at various field strengths. Each curve consists of four regions which are closely related to the optical behavior of the liquid crystal. Region I corresponds to the isotropic melt. The thermal-activation energy of the current is $E_{is} = 0.77 \pm 0.02$ eV. Below the sharply defined transition temperature $T_{is \rightarrow c1} = 61.3 \pm 0.3^\circ\text{C}$, a cholesteric phase is present (region II) characterized by an activation energy $E_{c1} = 1.30 \pm 0.05$ eV. Upon further cooling a phase

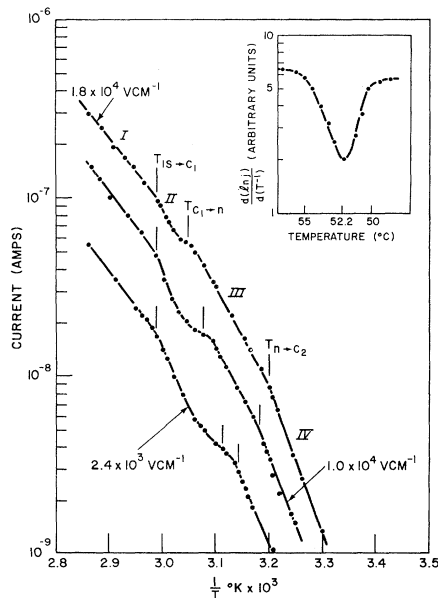


FIG. 1. Temperature dependence of the dark current (electrode area 1.4 cm^2). $T_{is \rightarrow c1}$, $T_{c1 \rightarrow n}$, and $T_{n \rightarrow c2}$ are the isotropic-cholesteric and the field dependent cholesteric \rightarrow nematic and nematic \rightarrow cholesteric transition temperatures. The curve in the upper right corner gives the derivative $d \ln j / d(1/T)$ near the cholesteric-nematic transition temperature $T_{c1 \rightarrow n}$ ($F = 3.94 \times 10^4 \text{ V cm}^{-1}$). The optically determined value of $T_{c1 \rightarrow n}$ is 52.2°C .

transition is observed at a well-defined temperature $T_{c1 \rightarrow n}$ which depends on the applied field. It is accompanied by a turbulence which becomes stronger with increasing field. The relaxation time for the transition is in the range 1-10 sec depending on the field. For $T > T_{c1 \rightarrow n}$ the material behaves like an uniaxial crystal, i.e., normally incident plane-polarized light now emerges plane polarized and thus can be extinguished (angle between polarizer and analyzer $\sim 85^\circ$). Visually the liquid crystal appears clear in region III.

Obviously an ordered phase has been induced by the field. If the temperature is near 47° it is possible to change the phase at relatively low fields, e.g., $F < 4 \times 10^3 \text{ V cm}^{-1}$. In this case the final phase is no longer completely ordered but displays an increasing rodlike texture with decreasing field under the microscope.⁴ This is typical for nematic liquid crystals. It can therefore be concluded that a transition from a cholesteric to a nematic phase occurred rather than to a smectic phase.² In the $j(1/T)$ curve the transition manifests itself as a shoulder. Figure 1(b) shows that $d \ln j / d(1/T)$ has a minimum at $T = T_{c1 \rightarrow n}$. This enables determination of the phase transition simply by current measurements.⁵ At a well defined temperature $T = T_{n \rightarrow c2}$, which again depends on F , a re-establishment of the cholesteric phase occurs (region IV). Electrically this corresponds to a change in the activation energy from 1.13 ± 0.05 eV, which is typical for the nematic phase, to 1.50 ± 0.05 eV. Again $T_{n \rightarrow c2}$ can be inferred from the condition

$$\left[\frac{d^2 \ln j}{d(1/T)^2} \right]_{T = T_{n \rightarrow c2}} = 0,$$

and coincides with the optically determined value.

Plotting the transition temperatures $T_{c1 \rightarrow n}$ and $T_{n \rightarrow c2}$ against the electric field yields a phase diagram (Fig. 2), which reveals a close similarity when compared with the temperature dependence of the helical pitch.³ If one shifts the $1/Z_0(T)$ curve by 4° to higher temperature, both curves coincide.⁶ This is a clear indication that indeed the threshold field varies as $F_c \sim Z_0^{-1}$. In order to evaluate k_{22} , it is necessary to know $\Delta\epsilon$. Assuming $\Delta\epsilon = 0.1$, one obtains the reasonable value $k_{22} = 3 \times 10^{-6}$ dyn. An experimental determination of $\Delta\epsilon$ is in progress. Under the present experimental conditions, discharge of carriers at the electrodes exceeds by far bimolecular recombination in the bulk. Therefore the current must be given by $j = e\dot{n}$, where $\dot{n}(F)$ is the carrier production rate. Note that the mobility does not en-

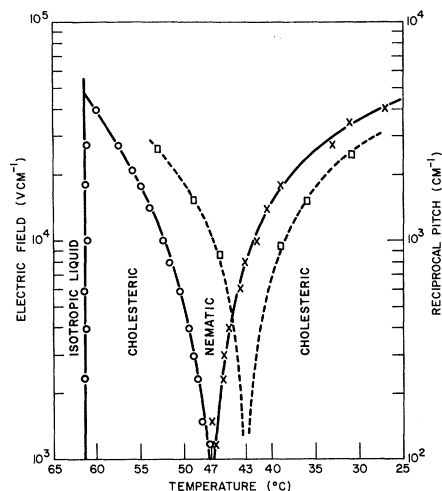


FIG. 2. Solid curve: phase diagram of a 1.75:1 mixture of cholesteryl chloride and myristate. Dashed curve: temperature dependence of the helical pitch (after Sackmann *et al.*, Ref. 3).

ter, i.e., the temperature dependence of the current must be essentially related to charge-carrier production. For $0.3 \times 10^5 < F < 1.8 \times 10^5$ V cm⁻¹, the current closely follows the law

$$j = j_0 \exp \left\{ \left[E - \left(\frac{eF}{\epsilon \epsilon_0 \pi} \right)^{1/2} \right] / kT \right\}$$

which is typical for volume ionization involving the Poole-Frenkel effect. From $d \ln j / d[(F)^{1/2}] \exp = 1.10 \times 10^{-2}$, a reasonable value for the dielectric constant of the material of 6.2 can be in-

ferred. This indicates that charge carriers are produced in the bulk rather than injected from the electrodes. The observed change of the activation energy of the current at the phase transition must therefore be due to a change of the energy levels involved in the ionization process.

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⁴In addition the angle between polarizer and analyzer at which the field has minimum brightness in transmitted light decreases to about 20° with decreasing applied electric field.

⁵This corresponds to the recent observation of S. Kusabayashi and M. M. Labes, *Proceedings of the Second International Conference on Liquid Crystals*, Kent, Ohio, August, 1968 (to be published), that the smectic-cholesteric transition in cholesteryl nonanoate is also accompanied by a conductivity change.

⁶The discrepancy between Sackmann *et al.*, Ref. 3, and the present measurements regarding the temperature at which the mixture is nematic at zero applied field is of minor importance since the Z_0 values of these authors are taken with an applied magnetic field. Furthermore, slight changes in the sample composition may have an influence.