

assumption that the "excited" beam consisted entirely of excited molecules. While it was argued that, on the basis of the almost resonant charge transfer, the excited $N_2 A^3\Sigma$ should be highly preferred, the possibility that some ground-state N_2 molecules are produced cannot be eliminated. It should be noted, however, that corrections for this effect would make the excited-state ionization-cross-section and emission coefficient even larger.

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¹N. G. Utterback and G. H. Miller, *Rev. Sci. Instr.* **32**, 1102 (1961).

²These arguments contain the implicit assumption that the N_2^+ ions were in the ground state. In order to verify that excited N_2^+ ions did not dominate the results, the ionizing electron energy was varied from 18 to 24 eV in the charge-transfer cross-section measurement (35-eV ion beam) and from 19.5 to 24 eV in

the ionization cross-section measurement (35-eV neutral excited beam). No change outside ± 5 and $\pm 10\%$, respectively, could be detected up to 22-eV electron energy. Above 22 eV, however, both cross sections increased markedly. This is interpreted as being due to the production of long-lived N_2^+ excited ions, which transfer charge with NO to produce highly excited metastable N_2 molecules.

³N. G. Utterback and G. H. Miller, *Phys. Rev.* **124**, 1477 (1961), and **129**, 219 (1963).

⁴N. G. Utterback and T. Griffith, Jr., *Rev. Sci. Instr.* **37**, 866 (1966).

⁵This result has immediate practical importance in calculation of bulk ionization rates through integration of cross sections over velocity distributions. It has been shown (C. F. Hansen, private communication) that if this result holds generally, bulk ionization rates can be dominated by collision between excited particles even though relatively few of these are present. It would then be essential to know the cross sections for collisions between all the excited-state possibilities in order to calculate reliable reaction rates.

⁶H. D. Hagstrum, *J. Appl. Phys.* **31**, 897 (1960).

ELECTRIC-FIELD-INDUCED PHASE CHANGE IN CHOLESTERIC LIQUID CRYSTALS

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Several workers¹⁻³ have reported the influence of electric fields upon the scattering of light by cholesteric liquid crystals. In this Letter, we wish to report a phase transition which was observed in cholesteric liquid crystals subjected to high dc electric fields. To our knowledge, a change of phase in these materials due to electric fields has not been previously identified.

Results were obtained as follows. A cholesteric liquid crystal was put between, and in contact with, tin-oxide-coated glass plates separated by 0.2 mm. The liquid-crystal materials were mixtures of cholesteryl chloride, nonanoate, and oleyl carbonate with typical proportions of 30, 56, and 14% by weight, respectively.⁴ The normal appearance of the layer was that of a milky white, opalescent sheet from which light was diffusely scattered. When plane-polarized light was normally incident on the layer, it was impossible to extinguish the field of view with a linear analyzer. When an average electric field of $\approx 10^5$ V/cm was applied, the liquid crystal assumed a clear, colorless appearance. Normally incident, plane-polarized light now emerged plane-polarized and thus could be extinguished. However, the material was not optically isotropic. Plane-

polarized light obliquely incident on the structure did not emerge plane-polarized, indicating that the film was acting as a birefringent material with an optic axis perpendicular to the surface of the film, i.e., parallel to the applied field.

The uniaxial character of the film and the sign of birefringence were determined in a second experiment using a Leitz Ortholux polarizing mi-

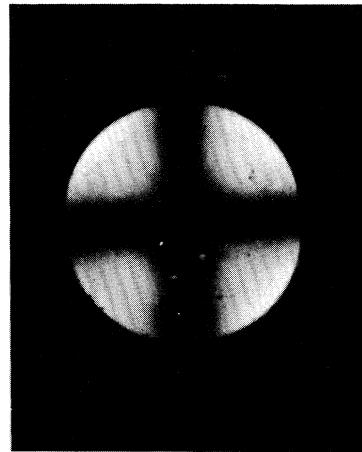


FIG. 1. Photograph of uniaxial conoscopic figure.

roscope with a $50\times$ objective and convergent light. Because of the short focal distance involved, a very thin upper electrode was required, and a 0.2-mm-thick microslide was used which had a conducting coating of evaporated chromium (optical density ≈ 0.3). The spacer in this cell was $\frac{1}{4}$ -mil Mylar. When no field was applied, conoscopic patterns which would have indicated optical alignment were not observed unless the sample was mechanically worked by slightly displacing the upper electrode in a shearing mode. In that case, optical alignment was achieved, and a uniaxial conoscopic figure such as shown in Fig. 1 appeared. Insertion of a gypsum first-order-red plate resulted in a color figure which is characteristic of optically negative uniaxial material⁵; i.e., the first and third quadrants were yellow while the second and fourth were blue. This result was not surprising since cholesteric liquid crystals have negative birefringence.⁶ When a field of $\approx 10^5$ V/cm was applied, the conoscopic color pattern inverted quickly to that characteristic of optically positive uniaxial material; i.e., the first and third quadrants became blue while the second and fourth became yellow. No change was observed in the black conoscopic cross. Since positive birefringence is only associated with nematic and smectic mesophases,⁶ it is clear that the electric field has induced either a cholesteric-nematic or a cholesteric-smectic phase transition. (A cholesteric-nematic transition induced by magnetic fields has recently been reported.⁷)

The phase transition is most likely due to interaction of the electric field with molecular dipole moments. The transition cannot be attributed to squeezing due to electrostatic forces on the condenser plates since purely mechanical pressure does not cause the transition.

The temperature dependence of the threshold field was measured in the latter structure. Results obtained are shown in Fig. 2. The threshold field falls rapidly with temperature up to the isotropic transition point, $\approx 57^\circ\text{C}$ for this material. At this temperature, and slightly above, the material can still be aligned in a positive birefringent state, but at fields in excess of 4×10^5 V/cm. Reproducible data in this temperature region were difficult to obtain, however, because of sample breakdown.

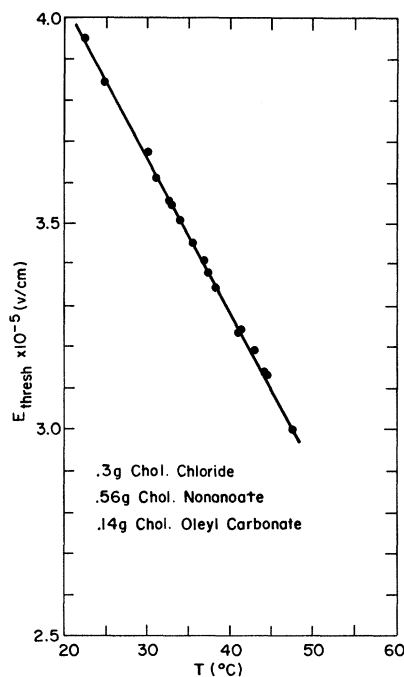


FIG. 2. Threshold field for phase transition versus temperature.

Further investigations of these effects are planned to clarify the high electric-field interactions with cholesteric liquid crystals.

¹J. H. Muller, *Z. Naturforsch.* **20a**, 849 (1965).

²W. J. Harper, *Mol. Crystals* **1**, 325 (1966).

³J. H. Muller, *Mol. Crystals* **2**, 167 (1966).

⁴Other mixtures in which the field-induced phase transition was observed are cholesteryl chloride and 35%/65% cholesteryl chloride/nonanoate. The purity of these compounds is reported to be 98–99% by the manufacturer, Distillation Products Industries, Division of Eastman Kodak Company. Since the peak value of transition temperature obtained from differential thermal analyses of these compounds agrees with the transition temperature specified by the manufacturer, we believe they are substantially as pure as when received.

⁵E. E. Wahlstrom, *Optical Crystallography* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 202.

⁶G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, Inc., New York, 1962), p. 40.

⁷E. Sackmann, S. Meiboom, and L. Snyder, *J. Am. Chem. Soc.* **89**, 5981 (1967).

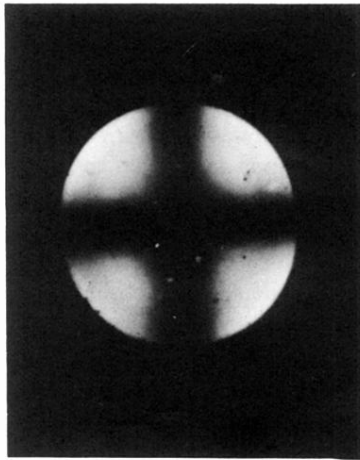


FIG. 1. Photograph of uniaxial conoscopic figure.