not yet in the position to measure the symmetrical case, since the cross section is too low. A detailed discussion of our theoretical approach and a summary of all our experimental results to date are being prepared for publication.

The character of our measurements aims towards a thorough comparison with theory. From each *ab initio* calculation the theoretician should be able to extract differential and angular-correlation cross sections. Comparison of these data with experiments may be regarded as a test of the theory of higher order than the comparison with total cross sections. In addition,[4] measurements of this kind can be expected to provide new information on the momentum distribution and on the self-consistent field of the atomic electrons.

The authors acknowledge with pleasure the financial support of the Deutsche Forschungsgemeinschaft, the experimental contributions of Dipl. Phys. K. H. Hesselbacher, and the helpful discussions with Professor A. E. Glassgold, New York University, and Dr. A. Temkin, Goddard Space Flight Center in Maryland.

---

[1] The latest review on the theory of the ionization of atoms by electron impact has been published by M. R. H. Rudge, Rev. Mod. Phys. **40**, 564 (1968).

[2] For example, energy loss or differential cross sections. Up to now nearly exclusively the energy dependence of the total cross section has been measured, which represents an integration over several collision parameters.

[3] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England 1965), 3rd ed.

[4] A. E. Glassgold and G. Ialongo, Phys. Rev. **175**, 151 (1968).

DEPENDENCE OF PITCH ON COMPOSITION IN CHOLESTERIC LIQUID CRYSTALS

J. Adams, W. Haas, and J. Wysocki
Research Laboratories, Xerox Corporation, Webster, New York 14580

(Received 14 November 1968)

Two-component cholesteric liquid crystal films have been observed to exhibit a remarkable structural dependence on composition. There is evidence that the relationship of color and temperature in these films is connected with this dependence.

Dispersive scattering, and other anomalous optical properties of cholesteric liquid crystal films, can be explained in terms of Bragg-like scattering[1] from regions of local order which have an internal helical structure.[2] The basic optical parameters which characterize these films are the index of refraction n, and the pitch p of the helical arrangement. It is well known that the pitch is sensitive to temperature,[3] shear,[4] and organic vapors.[5] It is the purpose of this Letter to report the unusual effect of chemical composition on pitch in two-component mixtures.

The liquid crystal sample was mounted on a spectrometer stage. A monochromator was used as a source and a photodiode as a detector. The pitch was determined by measuring the angle of incidence φ_i and the angle of reflection φ_s as a function of scattered wavelength λ, according to

$$\lambda = 2np\cos\tfrac{1}{2}\left\{\sin^{-1}\left(\frac{\sin\varphi_i}{n}\right)+\sin^{-1}\left(\frac{\sin\varphi_s}{n}\right)\right\}. \quad (1)$$

This formula was derived by Fergason on the basis of a model of regions of local order imbedded in a material with refractive index n. These regions exhibit Bragg-like scattering in the optical regime. The appropriate geometry and definition of symbols are shown in Fig. 1.

The liquid crystal ingredients, all of which were crystalline at room temperature, were first weighed and dissolved in petroleum ether.

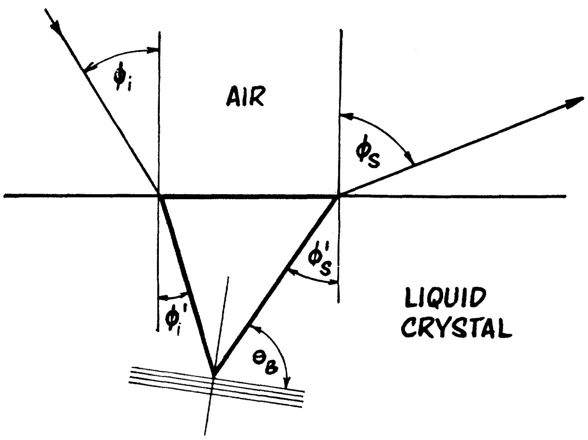

FIG. 1. Details of scattering geometry.

The mixture was deposited on a substrate, and after solvent evaporation, the films adopted the focal-conic texture. The films were then disturbed by a cover slip displacement; the resulting films exhibited the bright colors characteristic of the Grandjean plane texture. All measurements were taken with disturbed films at room temperature.

In all three systems studied, cholesteryl chloride was one constituent. The symbol β is used to designate the molar percentage of cholesteryl chloride in the mixture. The other component was a carboxylic ester of the form $C_{27}H_{45}OCO$-$(CH_2)_LCH_3$ varying from cholesteryl nonanoate ($L = 7$) to cholesteryl laurate ($L = 10$). All chemicals were obtained from K&K Laboratories.

All systems studied had the same qualitative behavior regarding dependence of pitch and thus observed colors on β. Results are shown in Fig. 2. The pitch is very sensitive to composition for compositions substantially different from those which yield a minimum pitch. The value of β which corresponds to minimum pitch (β_0) increases monotonically with increasing ester chain length. It is interesting that this minimum pitch is essentially independent of chain length. An important qualitative feature of these materials is that the slope of pitch versus temperature changes sign at β_0. For $\beta < \beta_0$, $\partial p/\partial T < 0$ and for $\beta > \beta_0$, $\partial p/\partial T > 0$. We believe that this was first observed by B. Mechlowitz of our laboratories. Furthermore, whenever $\partial p/\partial \beta$ was large, $\partial p/\partial T$ was large. In particular, mixtures around β_0 were conspicuously insensitive to temperature. This kind of temperature insensitivity has been reported by Fergason.[5] Another qualitative feature of these systems is that the influence of certain solvent vapors on pitch also changes sign at β_0. An example is the exposure of films to $CHCl_3$. For $\beta < \beta_0$, $CHCl_3$ vapor causes a shift toward the blue. For $\beta > \beta_0$ the same vapor causes a shift toward the red. The strong dependence of pitch on β in certain regions was so interesting that it was decided to study one system in more detail. Thus, the cholesteryl chloride–cholesteryl nonanoate mixture was measured in 0.2% increments in the range $23.0 \leq \beta \leq 26.4$, and these results are shown in Fig. 3. Although the dependence of p on β is strong in this region, the behavior is monotonic and reproducible. Evidently, in this narrow range, small changes in composition have a profound effect on the structure.

Since the permanent electric dipole moments of the different esters are essentially the same, we attribute the observed dependence of pitch on ester chain length to geometric factors. Electric-field–induced cholesteric-nematic phase-transformation studies[6,7] indicate that the long-chain ester plays the dominant cohesive role in holding the cholesteric state together. This same work also shows that the ability of the ester to maintain the cholesteric structure against the competition of the electric field is weakened at higher temperatures. Therefore, although

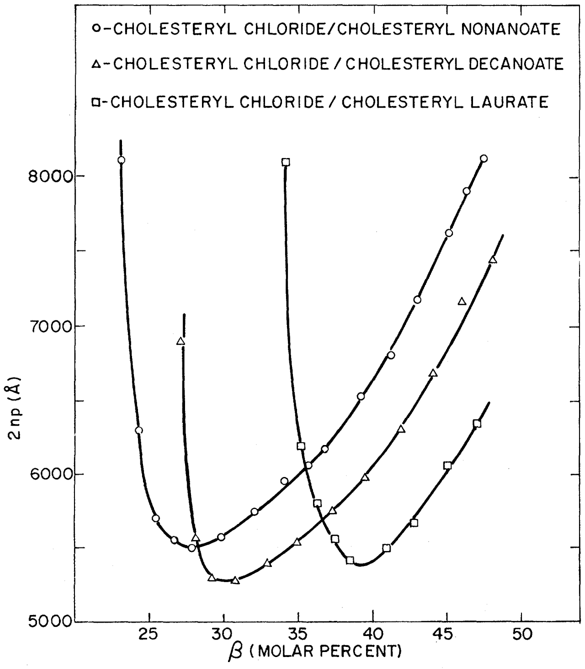

FIG. 2. Pitch versus chemical composition.

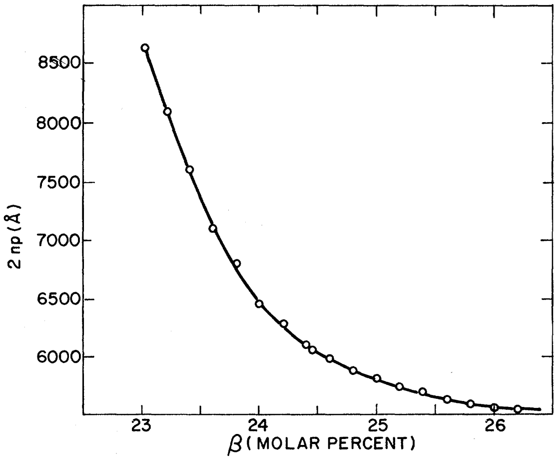

FIG. 3. An expanded view of pitch versus composition in a region of strong dependence in the cholesteryl chloride–cholesteryl nonanoate system.

we offer no explanation for the shape of the curves in Fig. 2, we are able to interpret the reversal of the sign of at β_0. If temperature reduces the effectiveness of the ester, then increasing temperature has the effect of increasing β. From Fig. 2 it is clear that for $\beta<\beta_0$, increasing β decreases λ; i.e., films should shift toward blue upon heating. In the region $\beta>\beta_0$, increasing β increases λ; i.e., films should shift toward red with heat. These shifts are, in fact, those that we observed. Furthermore, the inversion of solvent effect on pitch suggests that exposure to solvent effectively changes β (in the case of $CHCl_3$ it increases β). Figure 2 shows that the effect of a change in β on color inverts at β_0.

The nonmonotonic behavior of color versus composition, combined with the sign inversion of color change with temperature and color change in response to organic vapor, suggests that pitch may not be the best choice of a fundamental parameter in phenomenological theories.[8-10] Both ingredients of the liquid crystal mixtures have large permanent electric dipoles, the orientation of which relative to the molecular axis is quite different in the two molecules. We believe this must be taken into account. It is possible that the pitch is not an independent variable and is in fact determined uniquely by some combinations of other hidden variables but no such microscopic theory exists as yet.

The authors wish to thank James Becker for many interesting discussions and Bela Mechlowitz for technical support.

---

[1] J. L. Fergason, Mol. Cryst. 1, 293 (1966).

[2] H. L. deVries, Acta Cryst. 4, 219 (1951).

[3] J. L. Fergason, Sci. Am. 211, 77 (1964).

[4] G. Friedel, Ann. Physik 18, 273 (1922).

[5] J. L. Fergason *et al.*, Mol. Cryst. 1, 309 (1966).

[6] J. J. Wysocki, J. Adams, and W. Haas, Phys. Rev. Letters 20, 1024 (1968).

[7] J. J. Wysocki, J. Adams, and W. Haas, "Effects of dc Electric Fields Upon Cholesteric Liquid Crystals," in Proceedings of the Second International Conference on Liquid Crystal, Kent, Ohio, 12-16 August 1968 (to be published).

[8] P. Keating, "A Theory of the Cholesteric Mesophase," in Proceedings of the Second International Conference on Liquid Crystal, Kent, Ohio, 12-16 August 1968 (to be published).

[9] R. B. Meyer, Appl. Phys. Letters 12, 281 (1968).

[10] P. G. de Gennes, Solid State Commun. 6, 163 (1968).

MECHANISM OF ABSORPTION OF LIGHT BY FREE CONTINUUM POLARONS

E. Kartheuser
Institut de Physique, Universite de Liege, Sart Tilman, Liege, Belgium

and

R. Evrard*
Institut de Physique, Physique Theorique, Universite de Liege, Sart Tilman, Liege, Belgium

and

J. Devreese
Faculty of Science, University of Antwerp, Antwerp, Belgium, and Solid State Physics Department,
Studiecentrum voor Kernenergie, Mol-donk, Belgium

(Received 4 December 1968)

The absorption of light by free continuum polarons is treated in the framework of the Landau-Pekar approach which for this problem is not restricted to strong coupling but gives at least the qualitative behavior for intermediate coupling ($\alpha \approx 3$ to 6). The absorption curve consists of a relatively narrow zero-phonon peak and a broad sideband showing a multiphonon structure. The zero- and one-phonon contributions and the low-energy part of the two-phonon contribution have been evaluated numerically.

In the continuum polaron theory, the adiabatic strong-coupling method developed by Landau and Pekar[1] leads to two kinds of internal excited states: the "Franck-Condon"-like (FC) states and the "relaxed excited states." In the former, the polarization remains adapted to the initial electronic configuration whereas in the latter, the ionic polarization of the lattice is adapted to the final electronic configuration.

The purpose of this Letter is to explain how these two types of internal excited states which we studied in previous work[2,3] could be revealed