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Lev Mikhaylovich Blinov

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Lev Mikhaylovich Blinov
Institute of Crystallography, USSR Academy of Science, Moscow

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In this book the author presents a complete and readily understood treatment of all the known phenomena occurring in liquid crystals under the influence of electrical and magnetic fields. The first section of the book (Chapters 1–3) presents the physics of liquid crystals and the second section (Chapters 4–8) examines in detail the orientational and electrohydrodynamic effects in nematic phases and texture changes and instabilities in cholesteric and smectic liquid crystals. Major emphasis is given to explaining the qualitative aspects of the phenomena and to portraying their physical basis. The prospects for the practical application of electro-optical effects are also discussed.

Foreword

The number of publications devoted to the study of liquid crystals is increasing rapidly. According to LOCUS, the publishers of the abstracts journal *Liquid Crystals Abstracts*, approximately 180 works were published in 1968, whereas in 1975 about 800 abstracts and patents appeared. In parallel, the number of publications on the electro-optical and magneto-optical properties of liquid crystals is growing proportionally, if not at a faster rate, and their total number had reached about 500 by 1976. However, no book concentrating on this topic has appeared to date either in the USSR or elsewhere, although individual chapters of books by Kapustin[1] and Chistyakov[2] have concentrated on some electro-optical and magneto-optical phenomena. The need for such a book is felt to be particularly strong now, since electro-optical effects in liquid crystals have begun to be used extensively in technology and since the circle of those interested in this topic has expanded rapidly to include those engineers and scientists interested in electronics.

This book was conceived as a more extensive version of an earlier published survey,[3] and is based on a series of lectures on the electrical and optical properties of liquid crystals delivered by the author to his colleagues at the Organic Intermediates and Dyes Institute, Moscow. Although the opinion exists that 'a monograph expounds' but 'a textbook explains,'[4] this book attempts to give a graphic account of the phenomena with explanations of their physical bases. With this in mind, the author has endeavoured not to overlook the quantitative aspects of the subject matter, drawing upon De Gennes' theoretical development.[5] Thus, the aim of the book is to systematize the experimental and theoretical material relating to electro-optical and magneto-optical phenomena in liquid crystals, illustrating these phenomena from a solely physical point of view.

The book consists of two sections. The physical bases of the molecular–statistical and continuum theory of liquid crystals are presented in the introductory section without mathematical complexities, a subject which has been scarcely treated in the literature so far. The second section is devoted to the various electro-optical and magneto-optical effects. Their interpretation is given within the theoretical framework presented in the introductory section. The author has attempted to present a full bibliography only in the second section of the book; in the first section references are given only to those works which are primarily concerned with the underlying physical principles of the phenomena. The monograph is intended for a wide spectrum of scientists, including experimental physicists, electronic engineers, and physical chemists. University research workers and students specializing in the physics of dielectrics and crystals will also find useful material here. Some of the data on liquid crystal materials may also be of interest to theoretical physicists.

All the material in the book relates essentially to thermotropic liquid crystals since the electro-optics and magneto-optics of lyotropic mesophases have not yet developed into independent fields. The information on nematic and cholesteric materials is presented in more detail since smectic liquid crystals were not previously within the author's sphere of interest.

The book is not without its imperfections, and the author would be most grateful for any critical remarks which might prove useful in a subsequent publication.

The author expresses his grateful thanks to his colleagues in the field of the electro-optical properties of liquid crystals—M. I. Barnik, E. I. Balabanov, S. V. Belyayev, M. F. Grebenkin, I. N. Kompanets, V. G. Rumyantsev, S. A. Pikin, V. G. Chigrinov and V. M. Shoshin, E. I. Kovshev and V. V. Titov—in discussions with whom many physical and chemical problems were resolved. He also thanks V. A. Kizel' for his valuable advice.

L. M. BLINOV

Introduction

Liquid crystals are fluids in which there occurs a certain order in the arrangement of the molecules. As a result, there is anisotropy in the mechanical, electrical, magnetic, and optical properties. Although liquid crystals, or mesophases, combine the properties of a solid and an isotropic liquid, they exhibit very specific electro-optical and magneto-optical phenomena. As a rule these have no corresponding analogues in solids or in isotropic liquids.

On the one hand, liquid crystals exhibit all the effects characteristic of liquid dielectrics (such as the Kerr effect and electrohydrodynamic instabilities). On the other hand, many of the effects which are characteristic of a solid have not been detected in liquid crystals. This relates in particular to effects which depend on injection and motion of the charge carriers, the presence of unpaired electrons, special symmetry conditions (for example, the Pockels effect), and so forth. Liquid crystals are diamagnetic and therefore all their known magneto-optical phenomena have corresponding electro-optical analogues. Generally, the electro-optical properties of liquid crystals are more widely exploited than their magneto-optical properties for two reasons. Firstly, the molecules have permanent electric dipoles, but they do not have magnetic ones,† and hence there are possibilities for changing the sign of the dielectric anisotropy through variations in molecular geometry. In addition, there exist other dipole-induced effects, such as the flexo-electric effect and ferro-electricity. Secondly, a number of electro-optical effects arise because of the electrical current (electrohydrodynamic instabilities), and these phenomena do not have magnetic analogues. Nevertheless, we did not want to ignore in the title of the book the magneto-optical properties since many of the theoretical and experimental results had been obtained specifically for the case of the influence of a magnetic field on the mesophases, and besides, in some cases we consider the effects in crossed magnetic and electron fields (for brevity, we shall sometimes refer in detail only to the electro-optical properties, noting the corresponding magnetic analogues).

The basis of the majority of specific liquid crystal electro-optical and magneto-optical effects is found in the reorientation of the director (the axis of preferred orientation of the molecules) in the macroscopic volume of the

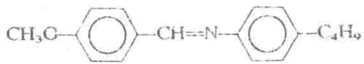
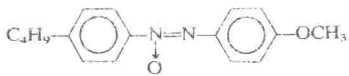
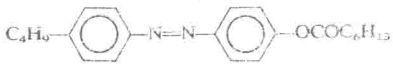
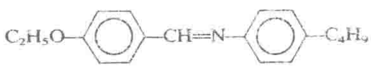
† Recently synthesized liquid crystals from the azoxy compound class with paramagnetic NO groups[13] form an exception.

material under the influence of an externally applied field or the flow of the liquid. Anisotropy of the electrical and magnetic properties of the medium (of the dielectric and diamagnetic susceptibilities and the electrical conductivity) controls the extent, in equilibrium, of the reorientation, whereas the dynamics of the process also depend on the anisotropy of the visco-elastic properties and the initial orientation of the director of the mesophase relative to the field. The optical properties of the medium, which reflect its local optical anisotropy, are changed as a result of this reorientation. This process of reorientation of the director (either occurring locally or throughout the whole of the sample) underlies all the electro-optical and magneto-optical effects. As an example we can take the Frederiks transition, dynamic scattering in which localized orientation of the director is caused by turbulence in the liquid, the cholesteric to nematic phase transition in a magnetic field in which the director is reoriented during the process of untwisting of the cholesteric helix, an undulation instability of smectic A with spatial-periodic variations of the director in a layer of the material, etc. This fundamental process of reorientations of the director on the one hand underlies the characteristic behaviour of liquid crystals in external fields, and on the other hand it can be accommodated in a continuum approach to the theoretical examination of the related phenomena.

Studies on the magnetic and electro-optical properties of liquid crystals have a short history, during which two stages can be traced. The slow process of collecting experimental data continued during the period beginning with Bjornstahl's work in 1918[6] up to 1968–70, although during this stage many of the currently well known effects were discovered (reorientation in a magnetic field,[7] light scattering,[8] the formation of domain structures,[9] the influence of a field on smectic[10] and cholesteric[11,12] mesophases, etc.). During this stage a major contribution was made by the Soviet school of researchers, Frederiks, Tsvetkov, and Kapustin.

In the 1970s the prospect of the wide application of liquid crystals in devices for the display of information encouraged the synthesis of a whole series of new classes of materials with a range of mesophases at room temperature. In this period also theoretical physicists who had previously been working with solids showed increased interest in liquid crystals, and thanks to the work of Leslie, De Gennes, Helfrich, Pikin, and others, a whole range of electro-optical effects came to be well understood. This is the period in which experimental efforts were directed towards precise control of experimental conditions, rigorous determination of the orientation of the molecules in liquid monocrystals, independent determination of the structure of a material and the measurement of the basic physical parameters which determine its electro-optical behaviour, etc. As a result, it can be stated that the physics of the majority of electro-optical and magneto-optical phenomena in nematic and cholesteric liquid crystals is fairly well developed, although this cannot yet be said for the various smectic mesophases. Moreover, electro-optical and magneto-optical measurements form the basis of a number of precise methods of determining the physical parameters of a material, such as its elastic constants, viscosity, optical anisotropy, and piezo-coefficient. All these advances have made the electro-optical and magneto-optical properties of liquid crystals an area of the physics of condensed matter which is independent, extremely interesting, and of practical use.

Table 1. Some physical parameters of low-temperature nematic liquid crystals as required for the calculation of electro-optical characteristics†

Abbreviation	Formula	Nematic range, (°C) Δt	Density, ρ ($g\,cm^{-3}$)	Dielectric permittivities $\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	Optical anisotropy, Δn ($\lambda = 6328$ nm)	Elastic constants (dynes $\times 10^{-7}$) K_{11}	K_{22}	K_{33}	Twist viscosity, (P) γ_1	Self-diffusion coefficients ($cm^2\,s^{-1} \times 10^{-7}$) $D_{\parallel}$	$D_{\perp}$
MBBA		21–45	1.054	4.58	5.17	−0.59	0.212[68]	5.8[69]	3.4[16]	7[69]	1.2[34]	6.9[46]	4.6[46]
BMAOB		20–74	1.117	5.08	5.34	−0.22	0.273[70]	6.9	5.5	10.5	1.1	—	—
Mixture A	$\frac{2}{3}$BMAOB + $\frac{1}{3}$ of compound 	0–75	1.108	4.85	5.25	−0.4	0.238	8.5	7.2	10.3	1–1.3	—	—
Mixture B	$\frac{2}{3}$MBBA + $\frac{1}{3}$ of compound (EBBA) 	−12–54	1.053	4.58	5.02	−0.46	—	6	3–4	7	1–1.3	—	—

† Reference numbers relate to Chapter 3. All other data obtained from refs. 71 and 78 in Chapter 3.

Table 2. Physical constants of p-azoxyanisole (PAA) (at 125 °C) and MBBA (at 25 °C)

Constant	PAA	MBBA
Density ($g\,cm^{-3}$)	1.168	1.088
Melting point (°C)	117.5	16
Clearing point (°C)	135	46
Diamagnetic anisotropy, $\Delta\chi$ (cgs units $\times 10^{-7}$)	1.18	0.97
Dielectric permittivities when $\omega = 0$:		
$\varepsilon_{\parallel}$	5.538	4.7
$\varepsilon_{\perp}$	5.705	5.4
Refractive indices for Na D-line:		
n_0	1.565	1.54
n_e	1.829	1.75
Surface tension ($dyn\,cm^{-1}$)	38	40
Velocity of sound ($cm\,s^{-1} \times 10^5$)	1.34	1.54
Elastic constants ($dyn \times 10^{-7}$):		
K_{11}	4.5	6
K_{22}	2.9	4
K_{33}	9.5	7.5
Coefficients of viscosity* (cP):		
γ_1	6.7; 5.8	77
γ_2	−7.0	−80
α_1	4.3	6.5
α_2	−6.9; −6.4	−77.5
α_3	−0.2; −0.6	−1
α_4	6.8; 8.3	83
α_5	4.7; 2.5	46
α_6	−2.3; −4.5	−35
η_2†	2.4; 1.5	16.3; 24
η_1†	9.2; 8.6	25.2; 103
η_3	3.4; 4.1	16.1; 41
Angle of orientation in the flow, Θ_0 (°)	9.1; 20	7 ; 19
Thermal conductivity ($cal\,cm^{-1}\,s^{-1}\,°C^{-1} \times 10^{-4}$):		
$\beta_{\parallel}$		5
$\beta_{\perp}$		3

* Different values of the coefficients for the same material are obtained from different published sources.

† Coefficients η_1 and η_2 are here defined according to Gahwiller (equation 3.37).

Note—The table was drawn up following the review paper by Stephen and Straley, *Rev. Mod. Phys.*, **46**, 617 (1974). The bibliographic references are cited therein.

Contents

B. ELECTRO-OPTICAL AND MAGNETO-OPTICAL EFFECTS IN LIQUID CRYSTALS