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M. G. Tomilin[a]; G. Yu. Ivanyuk[b]
[a] All-Russian Research Centre, S. I. Vavilov State Optical Institute, St. Petersburg, Russia [b] Kola Peninsula Research Center Geological Institute, Apatity, Russia

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The application of thin nematic liquid crystal layers to mineral analysis

by M. G. TOMILIN* and G. YU. IVANYUK†
All-Russian Research Centre, S. I. Vavilov State Optical Institute,
Birjevaya Line 12, 199034, St. Petersburg, Russia
† Kola Peninsula Research Center Geological Institute,
Fersmana 10, 184200, Apatity, Russia

A new method for visualizing inhomogeneous electric and magnetic field distributions on different mineral surfaces is discussed.

1. Introduction

Thin layers of liquid crystals (LCs) can be used as unusual recording media making it possible to visualize the distribution of different low power physical fields with sufficiently high optical resolution (approximately 1000 lines per mm) [1, 2]. The initial order in the LC is the physical basis for the visualization of the external fields. This order may be disturbed by various means, such as thermal, electric or magnetic fields, mechanical and intermolecular interaction forces or electromagnetic radiation. These LC properties are well known [3], but are commonly studied and used in the case of homogeneous external actions. In practice, however, the influence of spatially inhomogeneous fields on LC orientation is related to the distribution of the electric and magnetic fields on the objects' surface. This paper is devoted mainly to the application of LCs for the visualization of these fields on thin sections of different minerals. This LC method is also compared with traditional mineralogical methods.

The history of LC application in mineralogy dates back to 1916, when it was established [4], that LC molecules, when applied to a surface of orpiment, phlogopite, talc, halite, sylvite and some other minerals, were oriented spontaneously towards fixed crystallographic directions. It was demonstrated later [5–9] that the number of easily oriented directions is related to the substrate symmetry because of the LC molecules van der Waals interaction anisotropy with the substrate surface. This made it possible to observe the crystal growth zones and sectors, twins, blocks, mosaic and domain structures [5, 10–16]. This is best illustrated by the picture of an optically homogeneous ferroelectric GASH crystal (see figure 1). As soon as the theoretical basis for visualizing the inhomogeneous electrical and magnetic field distributions on the surfaces of different materials had been developed [17, 18] and experiments on obtaining the reproducible images of magnetic domains and other structural peculiarities of magnetic minerals were carried out, it became clear, that a novel method for obtaining new or even unique information was born.

The aim of this paper is to discuss possible LC applications to mineral analysis.

2. The essence of the method

The essence of the method consists of the application of LCs as recording media for visualizing electric or magnetic field inhomogeneities in the form of regions with local

* Author for correspondence.

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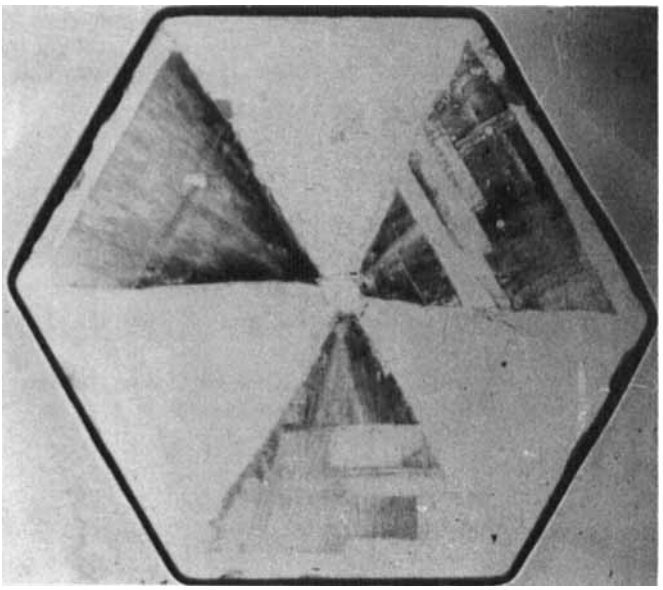


Figure 1. The growth sectors on the surface of an optically homogeneous GASH crystal, visualized by MBBA; $U = 50$ V, $T = 20°C$, $\times 5$ magnification.

reorientation of the LC molecules. The recording of these regions becomes possible when a LC deformed structure is illuminated in the transparent or reflective mode and the arising interference pattern is studied with crossed polarizers.

The light intensity over the layer I modulated by such a structure is described by the equation

$$I(x) = I_0 \sin^2 \frac{\delta(x)}{2}. \tag{1}$$

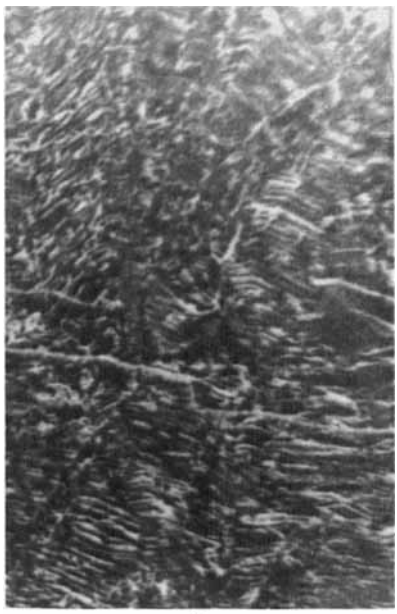
The phase delay $\delta(x)$, caused by the nematic liquid crystal (NLC) birefringence, is equal to

$$\delta(x) = \frac{2\pi}{\lambda}\left[-n_0 H + \int_0^H n(x, y)\, dy\right], \tag{2}$$

where H is the thickness of the NLC layer, $n(x, y)$ is the layer refractive index in the deformed zone, and n_0 is the refractive index in the non-deformed layer. If the orientation field has no twist, then only deformation bending occurs, hence

$$n(x, y) = [n_e^{-2} \sin^2 \varphi(x, y) + n_0^{-2} \cos^2 \varphi(x, y)]^{-0.5}. \tag{3}$$

Here $\varphi(x, y)$ is the tilt angle of the molecular long axes from the surface normal; n_e and n_0 are the refractive indices of the NLC layer for the extraordinary and ordinary rays, respectively. Thus, if a thin layer of the homogeneously oriented NLC (not thicker than 1 μm for realizing the interference conditions) is applied to a surface under study, the distribution of various physical fields can be observed through a polarizing microscope as different coloured surface regions. The LCs can record either static or dynamic fields. Moreover, the recording process is simple, clear and informative. This method is applied by depositing a uniform LC layer, a fraction of a micrometre thick on the surface under study. This layer is formed either by centrifuge or by dipping the surface



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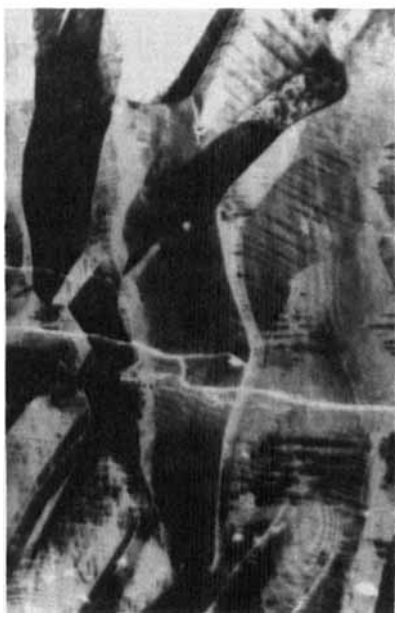

(*b*)

Figure 2. Pyrrhotite domains, visualized with magnetic emulsion (*a*) and MBBA (*b*); $T = 20°C$, × 300 magnification.

in a solution of a volatile solvent. In many cases it is enough to apply a LC with a brush, making the method ultimately simple and prompt. The application of a LC layer on the surface and removing it by solvents (alcohol, acetone and others) does not disturb the surface conditions, ensuring the non-destructive nature of the method [19].

3. The mineral magnetic field as visualized by NLC

The study of mineral magnetic field topography is commonly conducted using either magnetic emulsion or Kerr and Faraday effects [20]. Figure 2 shows the comparable images of the same sample magnetic domains, revealed by magnetic emulsion and NLC. Although both methods permit the visualization of the sample domain structure the character of the information obtained is essentially different. While the emulsion method produces an implicit picture of the domain distribution that requires additional laborious investigations for its interpretation, the NLC method, showing the magnetization direction at every surface point allows domain locations to be observed within the bounds of separate blocks, grains and their parts. The NLC method also shows higher resolution, allowing visualization of domains 0·5 mkm in size, whereas the emulsion method is unsuitable because of flocculi forming comparable in size. Besides visualizing domains in pyrrhotite, the NLCs also allow us to observe complex mosaic and labyrinthine domains in magnetite crystals, as well as striped and cylindrical domains in ferrogarten monocrystal films [25].

The theoretical aspects of the LC behaviour in inhomogeneous magnetic fields are discussed in [18, 21, 22]. As was established in [21] the NLC orientation in the magnetic field is determined by its diamagnetic susceptibility $\chi = [(\chi_{\parallel} + 2\chi_{\perp})/3] > 0$ described by the second order tensor

$$\chi_{ik} = \chi_{\perp}\delta_{ik} + \chi_a(L_i L_k), \tag{4}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are diamagnetic susceptibilities, respectively parallel or perpendicular to the NLC director $\mathbf{L}$, $\chi_a = \chi_{\parallel} - \chi_{\perp}$, and δ_{ik} is the Kroneker symbol. In NLCs the diamagnetic anisotropy has only positive values within the range from 0·3 to 1·04 $\times 10^{-9}$ m^3 mol^{-1} [22], though a magnetic field tends to orient the director along its lines of force. When the field strength $\mathbf{H}$ is enough to surmount the NLC elastic forces, the director reorients itself and a new stationary equilibrium is set (Freédericksz's transition). If the NLC molecules are orientated homeotropically to the substrate surface, the substrate magnetization vector will lie in the same plane with the director and only the bend deformations will be possible in accordance with the moments $\mathbf{L}$ and $\mathbf{H}$ equilibrium [18]

$$(k_1 - k_3)\mathbf{L} \times \operatorname{grad} \operatorname{div} \mathbf{L} + k_3 \mathbf{L} \times \nabla^2 \mathbf{L} + \chi_a(\mathbf{LH})(\mathbf{L} \times \mathbf{H}) = 0, \tag{5}$$

where k_1 and k_3 are NLC elastic modules along axes x, y. For many NLCs $k_1 = k_3$ (for MBBA $k_1 = 6 \times 10^{-7}$ dyne, $k_3 = 7 \times 10^{-7}$ dyne [3]. Let φ and ψ be the angles between y and $\mathbf{L}$, y and $\mathbf{H}$, respectively. Then the moment equilibrium equation can be written in the form [18]

$$\nabla^2(2\alpha) - (\chi_a/k\mathbf{H}^2) \sin 2\alpha = 0, \tag{6}$$

where $\alpha = \varphi + \psi$; $k = k_1 \cong k_3$. This equation is valid for fields of any strength which allow the NLCs to be considered as the media whose deformations unequivocally map the magnetic field topography at each point of the surface. Therefore the NLC technique besides the domain structure, also makes it possible to visualize other magnetic field inhomogeneities in minerals, such as crystal zones or mosaic structures, twins, blocks and so on. Figure 3 shows the growth zones in a magnetite crystal observed due to the

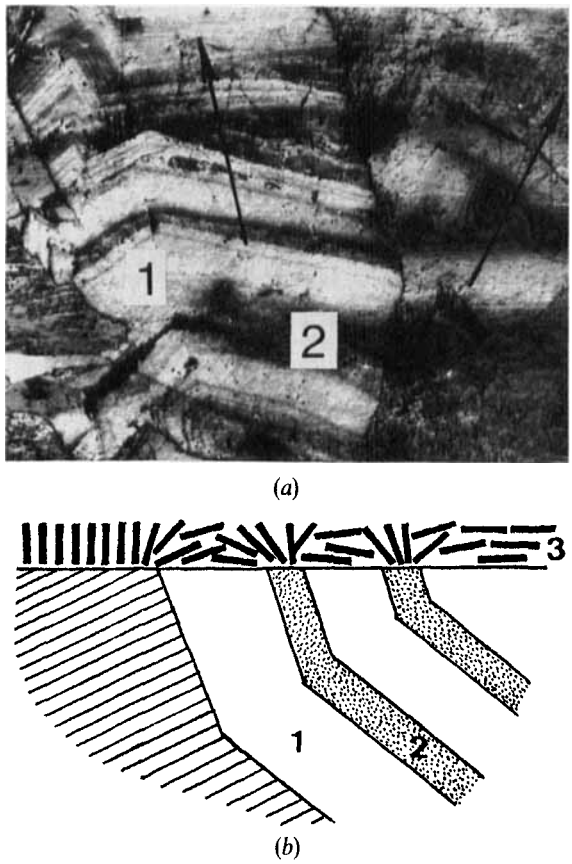

Figure 3. Growth zones in magnetite (*a*) and the scheme for their visualization by NLC (*b*). 1, 2—strong and weak magnetic field zones. Arrows show the grain magnetization directions.

residual magnetization difference, although the magnetization direction is the same for the whole crystal. In such cases the NLC technique can be applied to grain magnetic field parameter measurements. The paleomagnetic investigations may become a special field of application of this method, the orientation of the grain magnetization vector being determined with respect to the chosen directions in the sample, the geological structure or the Earth's magnetic pole.

4. Visualization of electric fields in minerals

A degree of torque moment, caused by the NLC van der Waals forces from intermolecular interaction with the substrate and seeking to orient the NLC molecules along the crystallographic direction of the mineral substrate always appears at the nematic–substrate interface [9, 23]. In particular, the MBBA director is oriented parallel to plane (001) on arbitrary grain sections of pyrrhotite, haematite and ilmenite; parallel to plane (111) in chalcopirite, and parallel to projection (001) on polished section planes of stibnite and goethite. The van der Waals interaction dependence on crystallographic direction allows us to apply the NLC technique to visualizing different

Figure 4. The visualization of twinning growth in Iceland spar by MBBA; $T=20°C$, $\times 100$ magnification.

crystal structure inhomogeneities: twins, blocks, etc. In particular, by using NLCs the twinning growth in Iceland spar and piezoquartz, that are not distinguished by standard optical methods, are observed (figure 4). Formerly this twinning growth was exposed by etching the samples. Using the NLC technique, the twin's boundary on the section surface is visualized due to the difference in molecular orientation energy on the two surfaces. Besides the van der Waals forces the NLC molecule's orientation is affected by electrostatic fields that are always present on the surface of a mineral grain contact. Since the electron or ion work function depends on crystallographic direction, particularly when the process is accompanied by ions absorption, the electrization must be characterized by anisotropy as was established for diamond spar [24]. As a result, the distribution of electric charges on a monomineral grain aggregate may turn out to be complicated.

The powder technique was used for the study of surface electrical fields inhomogeneities, which is similar to the magnetic emulsion technique, but instead of the ferromagnetic fractions the electrified dielectric fractions were applied, for example sulphur particles. These particles are attracted to oppositely charged surface areas exposing, for example, the domain distribution on ferroelectric crystal surfaces. But in order to obtain such an effect fairly strong fields are needed and it is also impossible to study vector parameters of the field. As was shown in [5, 10, 13, 14] the surface electric charges are able to affect the NLC molecule's orientation. Hence in the general case the NLC molecules with $\varepsilon_a > 0$ will be oriented with their long axes perpendicular to the surface of the electrostatically charged sample and with $\varepsilon_a < 0$ parallel to it (see figures 5 (*a*) and (*b*)).

The most illustrative example is that of ferroelectric crystal domains which visualizes the overall effect of the van der Waals forces and static electrization [5]. An advantage of the NLC technique is the possibility to observe not only the static distribution of physical fields, but also the dynamics of the process. The best example is the direct observation of the ferroelectric domain wall movement when the external electric field is applied [10]. Another factor that influences the NLC director distribution is a moisture layer adsorbed on the surface, which essentially enhances the process of electrostatic charging [5]. Such materials as quartz, glass and sulphur are able to be electrostatically charged after being kept for some time under atmospheric conditions [24]. All this opens possibilities for studying delicate physical and chemical processes (electrochemical reactions, corrosion, oxidation, etc.), that occur on the surface of materials in the course of time.

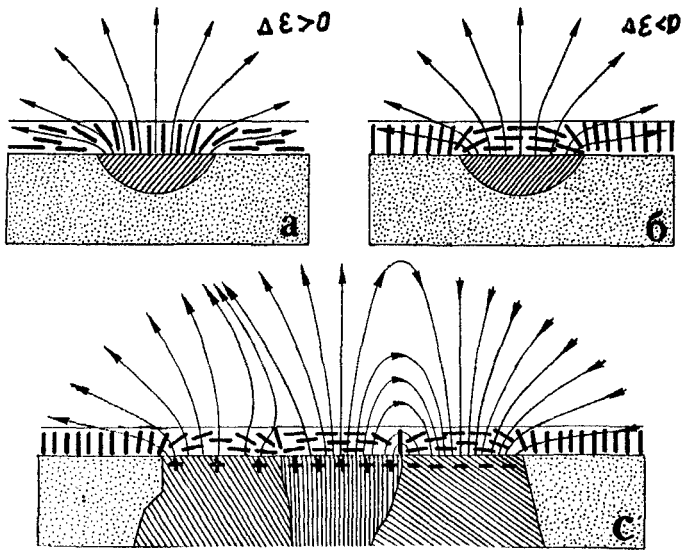

Figure 5. The orientation of NLC molecules in homogeneous (*a*), (*b*) and inhomogeneous (*c*) electrostatic fields.

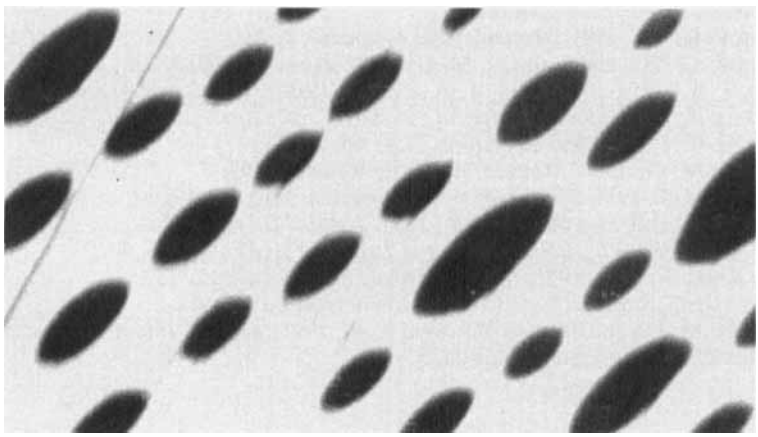

Figure 6. Domain structure in TGS crystal as visualized by NLC. $T=20°C$, $\times 100$ magnification.

5. Summary

The range of information obtained by the application of NLCs for the study of different minerals shows the efficiency of this technique. It permits visualization of the distribution of magnetic and electric fields either in static or dynamic cases. The future development is seen to involve optimizing the NLC parameters for solving specific problems, perfecting the process of surface coating by the NLC layer and to achieve more accurate thickness measurements. Further, the interpretation of the images is also a very important problem. It is also hoped to make the NLC technique become metrological and to reveal new fields of its application in minerology. It is already

possible to predict its efficiency in investigating thermal and acoustic field distributions, recrystallization and deformation processes, paleogeological studies of materials and in testing surface quality in precise analysis.

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