Liquid crystalline "blue phases"

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HUNDRED YEARS after the discovery of thermotropic liquid crystals by Friedrich Reinitzer and Otto Lehmann these substances have found most important technological applications for displays, light-valves or color-television screens. Simultaneously they have remained objects of intensive basic research, in which many models of modern physics are realized (like solitons, instabilities, frustration). In this talk I concentrate on the blue phases. These are liquids, consisting of elongated molecules, whose long axes align and form three-dimensional orientation patterns, although the centers of mass remain distributed randomly. The patterns are periodic, most of them with cubic space-group symmetry. The unit cell, whose diameter are comparable to the wavelength of visible light, contains 10^7 molecules. The blue appearance stems from Bragg reflections in the visible. Single crystals can be produced with cubic morphology. Growth has been observed along screw dislocations according to a mechanism proposed 40 years ago by F. C. Frank. Within a temperature interval of 1K one finds up to three different phases. An electric field distorts the unit cell (electrostriction). When the field strength is increased, phase transitions take place to blue phase modifications of tetragonal and hexagonal symmetry. The patterns contain complex defect structures, which are analysed by Landau theory and by group-theoretical and topological tools. Of still unknown structure is the blue fog. It appears structureless amorphous, yet forms a thermodynamically distinct and stable phase. Several models are discussed, among them an icosahedral quasiperiodic structure.

1. Introduction

LIQUID CRYSTALS are states of matter, which consist of anisotropic organic molecules. The shapes of the molecules can be rodlike, disklike or bowllike and can be given a unique symmetry axis. The *centers of mass* of the molecules either do not show any long range order at all, as in a threedimensional fluid, or the order is reduced to a layer structure, i.e. to a stack of twodimensional fluids. The *axes* of the molecules, however, are aligned, yielding an anisotropic, birefringent and in some cases optically active liquid. Light wave interference in such a liquid leads to iridescence, which was observed frequently by natural scientists already in the second half of the 19th century.

At that time Friedrich Reinitzer, botanist at the Technical High School in Prague, investigated cholesterylacetate and benzoate under the polarizing microscope. He reported his observations in a letter of March 14, 1888, to Otto Lehmann in Aachen, who was known as expert in the crystallization microscopy. Therein Reinitzer describes the properties of a second liquid phase existing in a temperature interval between the solid phase and the isotropic melt, which displayed interference colours and birefringence. The following exchange of letters and publication of the results [1] count as discovery of the new "mesomorphous" phases. The hundredth anniversary of the event has been celebrated in August 1988 at the International Liquid Crystal Conference in Freiburg, and it is also one motivation for the present article.

Otto Lehmann, to whom the letter was addressed, was called to Karlsruhe in 1889 as successor of Heinrich Hertz and headed the Institute of Physics for 30 years. The new state of matter was investigated thoroughly by him. Lehmann also coined the name "Liquid Crystal", because he observed in a liquid what previously had been seen in solid crystals only and namely birefringence. So far the history.

2. Basic research and applications

Liquid crystals are usually divided into three classes. In *nematic* liquid crystals the preferred direction of the molecular axes is constant in space. It is marked by a line segment, denoted *director*. In *cholesteric* liquid crystals the director twists about an axis orthogonal to it as one proceeds in space. The helicoidal director field and its handedness are due to a chiral structure of the mesogenic molecules. The pitch of the screw ranges from about 100 nm to 1μm and can be tuned over a wide scale by admixture of a nematic liquid or a cholesteric phase of opposite handedness. In *smectic* liquid crystals the centers of mass of the molecules are concentrated in loose-packed layers. The axes are aligned either perpendicularly to the layers (SmA) or under a constant tilt angle (SmC). Other smectic systems possess further positional and orientational order within the layers. A single chemical composition can assume several liquid crystalline states between the solid and the isotropic-liquid phase. Due to this polymorphism liquid crystals offer a vast field for the investigation of phase transitions and critical phenomena. The spontaneously broken symmetries are described by hydrodynamic theories with additional — orientational — degrees of freedom. The equations of motion are nonlinear and give rise to solitons, topological defects and electro-hydrodynamic instabilities.

The direction of anisotropy — and hence the local optical axis — is easily controlled by external magnetic and electric fields. Therefore one hundred years after their disclosure the liquid crystals have found numerous technological applications as displays for digital watches, TV colour screens or laptop computers, or as light valves for optical computers.

3. The cholesteric phase

The molecules of a cholesterogenic material, for instance cholesterylbenzoate, are elongated and slightly twisted. Cooling them below 186°C changes the substance from an isotropic, optically active liquid to the anisotropic cholesteric phase. If for a volume element, whose diameter is much smaller than the cholesteric pitch, the orientational distribution function for the molecular axes is plotted in a polar diagram, one obtains a surface, which in good approximation represents an ellipsoid of three axes. Coarsly it is characterized by labeling the longest axis as the director. A measure for the degree of order in the volume element is the quadrupole moment of the ellipsoid, represented by a symmetric, traceless, second-rank tensor. Its main axes coincide with the axes of the ellipsoid, its eigenvalues describe the deviation of the ellipsoid from spherical form. The tensor varies in space, thus the molecular order is described by a quadrupole tensor *field*.

It is well known, that *vector* fields can be expanded into plane waves, and that for each wavevector q three polarizations are possible: one right- and one lefthanded transversal polarization of helicity $m = -1$ and $m = 1$, respectively, and one longitudinal polarization of helicity $m = 0$. Vector fields carry spin 1, and the helicity denotes the azimuthal quantum number with respect to the propagation direction as quantization axis. A quadrupole tensor field has spin 2. There are five polarizations per wave vector: four circular transversal of helicities $m = \pm2$ and $m = \pm1$, and one longitudinal of $m = 0$ (Fig. 1).

A right-handed cholesteric liquid crystal, which is aligned along the z-axis, is a superposition of a constant, uniaxially oblate quadrupole tensor field (of helicity $m = 0$ and wavevector q = 0) and an $m = -2$ mode of q $= q\hat{z}$, where $q = 2\pi/$pitch. The constant $m = 0$ part gives rise to a constant dielectric anisotropy and hence to birefringence. The
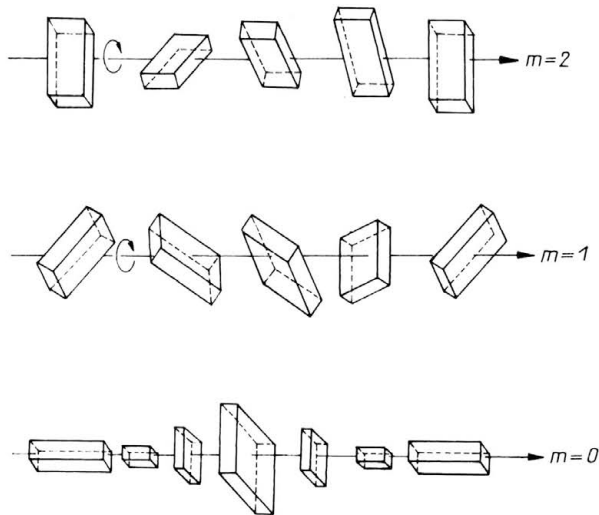
FIG. 1. Basic modes of a quadrupole tensor field: circularly transversal of helicity $m = 2$ and $m = 1$, respectively, longitudinal of helicity $m = 0$. The edges of the bricks are directed along the main axes of the tensor. The deviations of the edge lengths from those of a cube are a measure for the tensor eingenvalues.

tensor wave ($m = -2$, $q = q\hat{z}$) can be scanned by resonant circularly polarized light. When right-handed circularly polarized light ($m = -1$, $q = -q\hat{z}/2$), which has azimuthal quantum number $m = 1$ with respect to the positive z-direction as quantization axis, falls from above onto the helix, it does not only transfer its wave vector $q\hat{z}$, but also its azimuthal quantum number $m = -2$, so that the light is reflected in a right-handed polarized state ($m = -1$, $q = +q\hat{z}/2$). Left-handed circularly polarized light is not reflected. Thus there is selective reflection with respect to the wavevector (or wavelength) due to the presence of a periodic structure, but also selective reflection with respect to the polarization due to the presence of helical structure.

The pitch and therefore the selectively reflected wavelength (the *color* of the substance) are sensitively temperature dependent. Admixture of cholesteric liquid crystals to fluids allows not only visualization of the flow field, but also of the temperature distribution [2].

4. The "blue phases"

A detailed analysis proves that in many cholesterogenic chemicals the transition from the isotropic liquid to the cholesteric phase does not proceed in one step, but in up to four first-order phase transitions, with up to three stable intermediary states and in a temperature interval of 1°C. The bridging states are denoted blue phases (BP) I,II and III with increasing temperature. The third has a cloudy and amorphous appearence and is called "blue fog" [3]. BPI and BPII form soft, frequently coagulating platelets of micrometer to submillimeter size. They are optically isotropic (do not display birefringence), therefore their structure must be either also isotropic or at least cubic. Indeed, light is selectively reflected with scattering vectors forming a reciprocal lattice of a cubic periodic system. The Bravais lattice is body-centered for BPI and most probably simple cubic for BPII. The wavelength of the reflected light and hence the lattice constant is of the same order

of magnitude as the cholesteric pitch, mostly in the blue range. The periodic structure obviously has an almost macroscopic unit cell containing about 10^7 molecules. There are no hints, that the centers of mass of the molecules are ordered. The periodicity exclusively is due to a complex continuous orientational pattern of an anisotropic liquid. The polarization characteristics of scattered light reveal, what the pattern might look like. It is in backscattering geometry identical to the polarization characteristics of a single cholesteric helix. The quadrupole tensor field must be composed of helicoidal waves (m,q) of helicity $m = 2$ (or $m = -2$, dependent on the compound), and wave vectors q out of a cubic reciprocal lattice (the constant $m = 0$ contributions interfere destructively).

5. The defect lattice

Optical and morphological investigations (see Sect. 7) provide strong indications that the space group for BPI is O^8 ($I4_132$) and for BPII is O^2 ($P4_232$). The symmetry groups allow to extract systematic features from the confusing helicoidal texture of the tensor crystal. For each space group there are special symmetry sites. There are points, lines or planes associated with a group of point symmetry operations, under which the objects
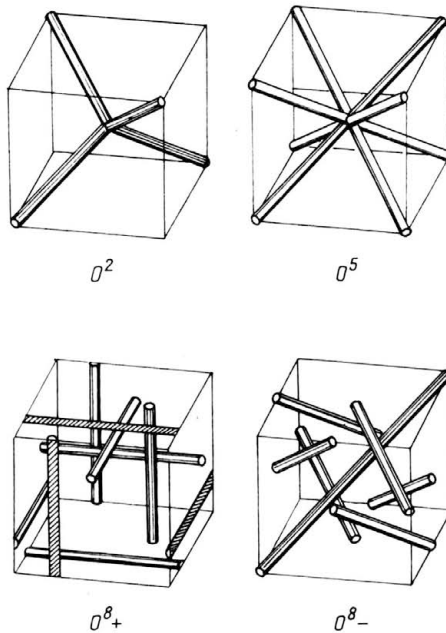

FIG. 2. Models of the defect lattice, which characterizes quadrupole tensor fields of space groups O^2, O^5 and O^8. For O^8 two modifications are presented, O^8_+ and O^8_-, which are related by an exchange of spiral cylinders and disclination lines (according to Ref.[12]).

affixed to the site — here the quadrupole tensors — must be invariant. If at a site this symmetry group is e.g. the cubic one, the three axes of the quadrupole tensor must be equal and of eigenvalue zero. Then the phase at this point is isotropic, giving rise to a *point singularity*. Along lines in space, which represent more than twofold axes of rotation, two of the eigenvalues of the tensor must coincide, thus giving rise to an ellipsoid

of rotation. Now there are two possibilities: For a *prolate* ellipsoid, the director is well defined. It turns out, that lines of prolate ellipsoids form the bores of "double-twist cylinders", from which the directors spiral away perpendicularly to all directions. Along lines with *oblate* ellipsoids of rotation the director (the longest axis) is ill-defined. The lines form singularities — disclinations — in the director field. Blue phases therefore can be interpreted as lattices of point singularities and disclination lines intertwined with double-twist cylinders (Fig. 2).

6. Theory

How can such complex patterns form? Hints are given by the Landau theory of phase transitions. It departs from a phenomenological free energy density, which is expanded into powers of the order parameter — here of the quadrupole tensor — and its derivatives. Since cholesterogenic compounds are optically active and lacking mirror symmetry in the isotropic phase, it suffices for the free energy density to be a pseudoscalar instead of a scalar. It can contain "chiral" terms, in particular those linear in the derivatives of the order parameter. The consequences of the presence of these linear terms are exposed most clearly, if the quadrupole tensor is represented in a spherical basis as five-component complex spin-2 vector

$$(1) \qquad Q^{(2)} = [Q_2^{(2)}, Q_1^{(2)}, Q_0^{(2)}, Q_{-1}^{(2)}, Q_{-2}^{(2)}] \, .$$

The chiral terms can be combined with other, quadratic terms, to a nonnegative contribution

$$(2) \qquad \frac{1}{2} K \sum_{r=1}^{3} |(\partial_r - iq J_r) Q^{(2)}|^2 \, .$$

K denotes an elastic constant, J_r a 5×5 angular momentum matrix acting on the spin-2 vector. The operator in round brackets generates a combined translation and rotation, i.e. a screw motion. Term (2) does vanish, if upon proceeding from a space point $\mathbf{x}$ along a direction $\hat{e}_r$ towards $\mathbf{x} + s\hat{e}_r$

$$(3) \qquad Q^{(2)}(\mathbf{x} + s\hat{e}_r) = \exp(iqs J_r) Q^{(2)}(\mathbf{x}) \, ,$$

i.e. if the tensor rotates rigidly about the axis $\hat{e}_r$ and by the angle qs [4]. Such a multiple twist , if supported to emanate from each space point, cannot be realized in flat space, only on a curved manifold. Just try to move about a square according to its initial position; the system is *geometrically frustrated*. Term (2) is very similar to the quadratic contribution in the Landau–Ginzburg theory of superconductors placed in a magnetic field

$$(4) \qquad \frac{1}{2} K \sum_{r=1}^{3} |(\partial_r - i\frac{q}{\hbar c} A_r) \psi|^2 \, .$$

A_r is component of the vector potential, ψ the complex order parameter, and q the total charge of the Cooper pair. The blue phases can be viewed as tensor fields in a uniform gauge field, however not with U(1) gauge symmetry as for the superconductor, but with an SO(3)-Yang–Mills gauge group. Type II superconductors in a magnetic field form regular flux-line lattices, i.e. defect lattices. Therefore it is plausible, if blue phases relieve the frustration by forming a defect lattice.
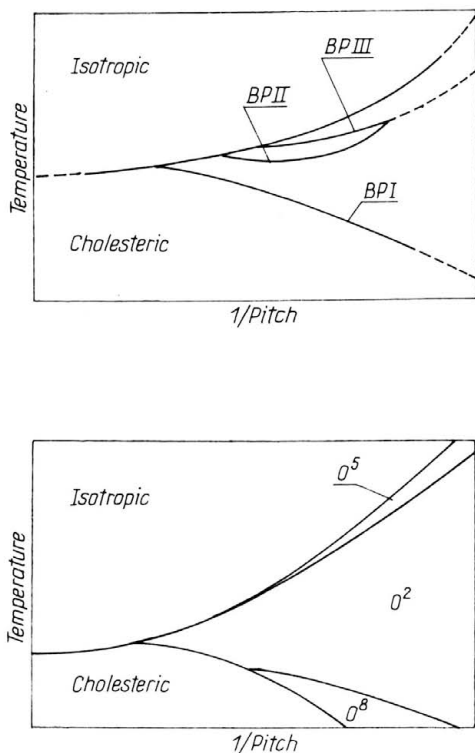
FIG. 3. Experimentally determined phase diagram (above) in comparison
with calculations (below, see for instance Ref.[5]).

To calculate the real orientation pattern and the phase boundaries several groups [5] have superposed helix tensor modes to form textures of different cubic space group symmetry. Amplitudes and phases were determined by minimization of the free energy. The symmetry of the minimal solution labels the phase. The phases are plotted in a temperature-chirality diagram (Fig. 3). Chirality is defined as the inverse pitch. It can be controlled by mixture of cholesterogenic compounds of opposite handedness or by addition of nematogens. The very costly calculations agree with experiment inasfar as the blue phases appear first at critical chiralities and that the correct symmetry is ascribed to BPI and BPII. In the region where BPIII is existing theory, however, places another cubic phase of space group symmetry O^5(I432).

7. Morphological investigations

In 1981 ONUSSEIT and STEGEMEYER [3] were successful in growing single blue phase crystals by slow cooling from the isotropic liquid or the blue fog. The liquid unit cells attach themselves along particular faces. For BPI these are the 110- and 211-planes, giving rise to rhombic dodecahedra up to 2 mm - "drops" of cubic morphology. In statistical theories of growth steps or kinks on the facets represent elementary excitations, which are proliferating at a roughening transition of well defined temperature. BARBET-MASSIN, CLADIS and PIERANSKI [6] have observed the steps on the facets of the Blue Phases.

They were able to confirm a growth process which has been proposed already in 1951 by BURTON, CABRERA and FRANK [7]: growth along a screw dislocation. The line defect (of a defect lattice!) could be monitored through the entire single crystal. The morphological investigations corroborate the space group assignments for the blue phases.

8. Field induced phases

The orientational order of liquid crystals responds even to very small external fields. Alternating electric fields reorient and deform blue phase single crystals (electrostriction, see [3]). With increasing field strength the lattice constant jumps discontinuously, and transitions occur to other phases, first to the cholesteric and then — by unwinding of the helix — to the nematic phase. In small regions of the temperature-voltage diagram new, field-induced phases have been spotted: a tetragonal phase, denoted BPX, two hexagonal ones, BPH, and a yet unidentified structure, BPE. In a temperature interval of 1°C thus up to seven phases can be detected between the cholesteric state and the isotropic fluid.

9. Elasticity and hydrodynamics

Blue phases are fluids with a threedimensional periodic structure. What is the nature of their hydrodynamic modes? Do they show elasticity? Several groups have ascertained, that the static shear modulus is finite [8,9]. Of very detailed nature are the data of KLEIMAN et al. [10]. The authors measured shear modulus G and viscosity η through a torsional oscillator figured as a cup viscosimeter with very small amplitudes (the shear distortion is less than 0.02 %). Both quantities generally are temperature dependent and peak or change steeply at the phase transition points. In the isotropic liquid, G is zero and η is frequency independent, which are the properties of a Newtonian fluid. In the cholesteric phase, G approaches a very small value as the frequency goes to zero. But the intermediary blue phases clearly possess a nonzero static shear modulus and a strong variation of the vicosity with frequency, thus comprising a *viscoelastic solid* with respect to their hydrodynamic properties.

10. The "blue fog"

This state of matter appearing amorphous and without structure displays a single broad reflection line. The phase definitely is thermodynamically stable. In the transition isotropic-BPIII almost all the latent heat of the total transition isotropic-cholesteric is produced. Thus in this transition the basic structure of all blue phases must be established. According to the BELL group [11] these basic units are the spiral cylinders, which are arranged regularly in the cubic phases, but are entangled like spaghettis in the blue fog. Electron microscopy of freeze-fractured samples indeed show irregular filaments [11]. An alternative model is the icosahedral blue phase. It combines aspects of the theory of quasi-crystals with those of liquid crystals and is managable analytically. The quadrupole tensor field proposed is a superposition of $m = 2$ (or $m = -2$) helicoidal modes with wavevectors, which point along edges and vertex directions of an icosahedron. The model explains the isotropy of the blue fog, since the icosahedron is of high point symmetry. Also the broad reflection maximum is plausible, since all wavevectors involved are of about the same length. Aspects of amorphicity are contained, because subsets of the wavevectors

are mutually incommensurate and forbid translational symmetry. Finally Landau theory places the icosahedral phase close to the O^5-structure in the calculated phase diagram. Those lines in space, where the quadrupole tensor is uniaxial prolate, are interpreted as cores of the spiral cylinders. Plots of these lines for the icosahedral phase also appear wormlike and irregular. There is no final clarity about the real nature of the blue fog.

11. A hundred years "blue phases"

We have gained some insight into a system, where due to geometrical frustration molecular axes are organizing themselves to complex threedimensional structures. The blue phases are a challenge to the experimentalists, since they require extreme temperature stabilization. Light-optical methods not only take advantage of selective reflexion with respect to the wavelength, but also with respect to polarization. The blue phases also are a challenge to the Landau theory of phase transitions of systems represented by inhomogeneous periodic (and quasi-periodic?) tensor fields. Why their growth is identical to that of atomic crystals is as unknown as are details about their hydrodynamic and viscoelastic behaviour.

In the initially cited letter of Reinitzer two color flashes are reported seen when cholesterylbenzoate was cooled from the isotropic fluid to the solid stage. STEGEMEYER and BERGMANN [3] have repeated the experiment and have discovered, that the second flash occurred in the transition cholesteric-solid, the first, however, in the transition from the isotropic melt to the blue phase. Thus the first documented observation of blue phase also is dating back to the year 1888.

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