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Remarks about the Phase Identification of Mesomorphic States

Reinhard D. Ennulat [a]

[a] U. S. Army Electronics Command, Night Vision Laboratory, Fort Belvoir, Virginia, 22060

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Remarks about the Phase Identification of Mesomorphic States

REINHARD D. ENNULAT

U. S. Army Electronics Command, Night Vision Laboratory,
Fort Belvoir, Virginia 22060

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Abstract—Experimental and conceptual problems associated with the identification of thermotropic mesophases are reviewed and discussed. Theories linking the observed optical properties of mesophases with their molecular building principle have considerable shortcomings. Therefore the identification of mesophases is mainly based on empirical rules pertaining to the optical behavior of characteristic textures. Certain ambiguities of a strictly optical approach may only challenge the ingenuity of the investigator, while other difficulties can prevent the determination of meso-mesophase and liquid-mesophase transition temperatures. Since phase transitions are defined by variations of more general thermodynamic quantities, thermal analysis is suggested as a remedy. The requirements on temperature scanning thermal analysis necessary to insure detection of all mesophases of a given sample are specified. The significance and the determination of sample impurities by thermal analysis are discussed. Comments are made on the correlation between characteristic textures and mesophases. The relevancy of uniaxial optical properties to phase identification and the homeotropic conditions of cholestreic mesophases are considered briefly.

Introduction

The classification and identification of mesomorphic states is based on the fundamental contributions by Friedel[1] and on a few more recent findings, reviewed by Gray.[2] In this system the type of a mesophase is defined according to the optical behaviour of its manifestations, the so-called textures. However, an exclusively optical approach to phase identification can yield ambiguous results. For example, characteristic textures may be suppressed due to adverse environmental influences. Furthermore the multiplicity of textures within a given mesophase, as well as the appearance of the same texture type in more than one mesophase, increase the likelihood of mis-identifications. This problem is aggravated by the occurrence of polymesomorphism of the smectic and possibly of other mesophases. The multitude of the optical appearances, their irregular emergence, and often the difficulty to visibly distinguish and identify a particular texture explain numerous controversies between investigations.

By X-ray diffraction and similar means attempts were made to directly determine the molecular arrangements that are characteristic for the various mesophases. Except for the smectic phase, little progress has been made in this work. For the other two mesophases and for the polymesomorphism of the smectic phase, only very general building principles were derived from the evaluation of all available physical and in particular optical data. As long as this state of affairs prevails, it seems to be irrelevant to seriously consider a better system of classification for mesophases or to decide on issues such as whether the cholesteric mesophase is closer related to the nematic or the smectic phase. One has to accept that we are still in the phenomenological state of the investigations with only a limited understanding of the structure and mechanism of thermotropic mesophases. Therefore it is important to classify the mesophases as carefully as possible in order to associate observations and data with the correct phase.

At present the scheme of phase identification is based primarily on optical evidence. Some, if not all, of the previously mentioned difficulties and ambiguities can be eliminated from exclusively optical investigations by also considering thermal analysis data. This experimental approach consists of determining the temperature range of the mesophases by inspection of the sample contained in the capillary of a melting point apparatus, recognizing the existence of mesophases and their sequences from temperature scanning thermal analysis data, and identifying the various phases by microscopic investigations. In this paper comments will be made on this procedure.

Capillary Method

In some cases the mesomorphic state and, in particular, the cholesteric mesophase can be recognized by merely observing the sample in the capillary of the melting point apparatus. The Thiele apparatus or its modification are used for this purpose.[3] The existence of mesomorphic states is deduced from the temperature reversible turbidity of the melt, while the cholesteric mesophase is inferred from the occurrence of the temperature dependent brilliant iridescent colors of the melted sample. However, in general, it is not possible to perceive with the naked eye temperature reversible changes of the turbidity level corresponding to phase transitions within the mesomorphic state.

Unfortunately, definite results cannot be obtained from other observations made within the capillary. Since the eye may be incapable of detecting the light scattered by the sample, the lack of turbidity does not necessarily imply the absence of a mesophase. This is a well-known fact for many nematic and cholesteric phases. Furthermore, the Bragg-like diffraction of light may not be perceived in the capillary, because either this effect may take place outside the visible spectrum or the material may exhibit the plane texture only under special circumstances. Last but not least, the cholesteric phase may not exist.

The temperature independent turbidity represents another ambiguous situation. A mesomorphic state which does not clear below the decomposition point, an ordinary material with a melting range up to the decomposition temperature, the scattering of light from air bubbles trapped in the melt during fusion,[4] or a melt which happens to be opaque for other reasons could possible explain this effect.

Gray[5] has briefly described a method to distinguish between smectic and non-smectic mesophases by observing the changes of the sample configuration on heating the capillary. As a rule, a sample in the smectic phase will stick to the capillary walls, while a sample in the nematic, cholesteric, or liquid state will fill the capillary because of the much lower viscosity. This effect is difficult to observe because of insufficient viscosity changes, interfering surface interactions, presence of air bubbles and their expansion, and so on.

From this it can be concluded that the capillary method only furnishes reliable melting and solidification points while additional information pertaining to the mesomorphic state cannot always be obtained.

Thermal Analysis

The transition temperatures for the various mesophases are thermodynamically defined quantities. The fact that particular physical effects may occur reversibly at such temperatures is to a certain degree incidental. These effects may depend on structural parameters of the compound, on impurities, on thermal history and on environmental conditions rather than on general thermodynamic quantities governing the phase transition. For example the latent heat of a transition can be generated by a multitude of changes of the molecular arrangement and in turn can be accompanied by a variety of physical effects. Therefore it must be concluded that the determination of the temperature range of a mesophase should be based on the observation of thermodynamic quantities such as latent heat and specific heat.† Since at this time it is impossible to relate this data to other physical properties with the aid of a proven theory, optically determined transition temperatures should be considered with caution. By the same token it is impossible to identify mesophases from exclusively thermodynamic data. At best, thermal analysis can furnish information about the existence of various phase regions of a given compound and provide a coarse classification into solid–solid,

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† Latent heats are generally observed at mesophase transitions. Arnold[6] reports a significant change of the specific heat in addition to the latent heat of a smectic to nematic transition.

solid–mesomorphic, solid–liquid, mesomorphic–mesomorphic, and mesomorphic–liquid phase transitions. The classification is judged by the relative magnitude of the latent heats and by the relative position of these transitions on the temperature scale. Last but not least, for reasonably pure materials the temperature reversibility of meso-mesophase transitions and clearing points[7] permits an easy distinction from the other type of phase changes.

The main condition to be met by thermal analysis investigations is to prevent the oversight of existing mesophases. With this method mesophases can only be recognized by thermal effects occurring at phase transitions. Since the temperature regions of mesophases were observed to range from a few degrees to 50°C and more, temperature scanning thermal analysis methods have to be employed in order to obtain an acceptable analysis time. Unfortunately neither the lowest limit of the variation of thermodynamic properties at mesophase transitions nor the smallest temperature separation of successive transitions are known. A scanning device with noise-limited sensitivity and temperature resolution is needed for the absolute detection of mesophases. O'Neil[8] found that high sensitivity and high temperature resolution lead to opposing design requirements for scanning thermal analysis devices and he proposed a certain type of temperature controlled scanning calorimeter which provides sensitivity and temperature resolution superior to ordinary differential thermal analysis instruments.

A differential scanning calorimeter of this kind, manufactured by the Perkin-Elmer Corporation, was modified to match the requirements for the investigation of mesophases. A factor of ten increase of the sensitivity without a significant sacrifice of accuracy was affected by a simple change of the output voltage divider furnishing the signal for the recorder. Any disturbing influence due to ambient temperature fluctuations was eliminated by enclosing the sample and reference holder of the device within an ice water cooled brass jacket. This also reduced the lower temperature limit for fast time linear cooling (10°C per minute and slower) from 90°C to 30°C. This temperature limit can, of course, be decreased further by simply using a coolant of a lower temperature. The modified instrument is capable of measuring 0.2 millicalories per second with a recorder deflection of 5 inches against a base line defined within ±5%. It should be possible with this device to detect the smallest latent heat reported for a mesophase transition[6] amounting to 24 cal/mole or 0.034 cal/g.

Such a general and simple specification cannot be formulated for the temperature resolution, i.e., the smallest recognizable temperature interval between two successive phase transitions. The instrument records the heat per unit time absorbed or expelled by the sample during the phase transition versus the sample temperature. The plots are approximately of triangular shape. The leading edge with its smaller slope occurs during the phase transition, while the trailing edge corresponds to a much shorter temperature range after the end of the transition. Thus the temperature resolution depends on height and width of the plots associated with successive transitions. For example, a resolution of 1 °C or less is obtained for peaks of equal height and a width of 1 °C. Because of the steepness of the trailing edge this resolution is also obtained when the peak height of the subsequent transition is about thirty times smaller. This is very important for phase identifications, since this case is usually realized by a melting process closely followed by a meso-mesophase transition or a clearing point.

The accuracy of the determination of mesomorphic temperature intervals depends on the error of the temperature measurement and on the purity of the sample. While the magnitude of the former is usually known, the influence of the latter is ordinarily not defined. Only few investigators used compounds of chromatographic or equivalent purity.[9] The resulting significant discrepancies of transition temperatures are often summarily dismissed as impurity effects. Unfortunately the problem is more serious than this, since mesophases can be either suppressed or induced by the presence of certain impurities.[10] By chromatographic purification and recrystallization the amount of impurities in the samples can be reduced to less than a few mole per cent. Since the melt of such compounds approximates an infinite dilute solution, the mole percentage x of the total impurity content can be determined from Van't Hoff's equation:[11]

$$x = \frac{\Delta H}{RT_m^2}(T_0 - T_m)$$

where R is the gas constant, T_0 the melting point of the major component, T_m the melting point of the mixture, ΔH the latent heat of transition and $T_0 - T_m$ the melting point depression. The quantities on the right side of this equation are either known or obtainable from scanning thermal analysis. The best method[12] to determine the melting point depression is to derive the melted fraction F of the sample and the corresponding equilibrium temperature T from the melting curve and to plot T versus $1/F$. For extremely pure samples a straight line results with a slope, which is equal to the depression $T_0 - T_m$. Impurity levels down to 0.05 mole per cent have been detected by this method.[11]

At present most mesomorphic materials cannot be sufficiently purified. Therefore their melting curves start with such a gentle slope, that the exact beginning of the melting process cannot be determined. This results in F-values, which are too small by a constant amount. While this discrepancy may not significantly effect the T versus $1/F$ curve for small $1/F$ values, a large upwards curvature of the plot is obtained for large values. The plot can be transformed into a straight line, if the F-values are corrected by the proper amount. The latter can be determined by successive approximation. So it is possible not only to deduce the depression $T_0 - T_m$ for mesomorphic materials, but also to correct the heat of fusion derived from the melting curve by adding the amount of heat corresponding to the initial melting. This correction can be as high as 10% or more.

The same kind of curvature of the T versus $1/F$ plot can occur, when the minor component forms a solid solution with the major component of the sample. Also in this case, the impurity content can be obtained according to Mastrangelo and Dornte[13] by linearization of the plot in a similar way as described above. However, there still remains the problem of deciding, which of the two causes is responsible for the curvature of the plot. This question cannot be resolved with only scanning thermal analysis data. But it is still possible to determine the impurity range of the sample. Let us assume that both effects originate the curvature. If one neglects the formation of solid solutions, the lower limit of the impurity concentration will be obtained. The upper limit of the impurity level will result, if the curvature of the plot is exclusively ascribed to the formation of a solid solution. Both of these conclusions can be directly derived from the paper of Mastrangelo and Dornte.[13] This statement cannot be extended to samples containing more than one solid solution, since no treatment is known. However, samples rarely exhibit this feature after extensive purification. Even a one component solid solution is usually not anticipated at lower temperatures under equilibrium conditions.[14] Nevertheless, thermal analysis tests should be performed only on slowly frozen samples. This will help to prevent even the partial formation of a solid solution during the freezing process as shown by Van Wijk and M. Smit.[15]

It can be concluded that temperature scanning thermal analysis is useful, if not indispensable for the phase identification of mesomorphic states. This approach not only furnishes information about existing mesophases and their temperature range, but also provides an impurity determination applicable for most of the cases. Samples, which do not contain solid solutions, permit an accurate impurity measurement, while samples with a one solid solution component allow only an estimate of the impurity content. But this method is not applicable for mixtures with more than one solid solution component.

Microscopic Investigation

Thermotropic mesophases are defined according to the existence of characteristic textures. Since the latter cannot be uniquely related to other physical properties, thermotropic mesophases must be identified by optical means. The main difficulties of this approach are the recognition and controlled formation of such textures. Generally mesophases appear as rather small and distorted elements forming fancy patterns and responding sensitively to environmental variations. It requires experience and patience to coax the material into exhibiting its characteristic textures by applying slow or fast temperature changes, by imposing or omitting mechanical disturbances, and so on. Unfortunately, the materials seem to react so differently to such treatment that only a few general rules are known for establishing certain well-developed characteristic textures.[16] In Table 1 a survey of the characteristic textures is presented with their important optical features. Since these textures are well described, by Friedel[1] and more recently by Gray,[2] the following will be restricted to comments pertaining to our experience with phase identifications.

Table 1 contains empiricial information obtained from data on thermotropic mesophases. Therefore, this phase identification scheme does not necessarily apply to lyotropic phases. A distinction between lyotropic and thermotropic phases is difficult in cases where the former exhibit thermotropic behavior.[17] At present a clear-cut decision cannot be obtained from the study of textures alone. Even the classification of lyotropic and thermotropic liquid crystals is subject to controversy. Friedel carefully defined the mesomorphic state as a molecular arrangement entirely different from that of the crystalline and the liquid state, and he carefully established that this new state of matter cannot be described by a three-dimensional lattice order. In particular Friedel distinguished this mesomorphic state from liquid crystals, which he defined as liquids with a three-dimensional lattice order. Therefore the difference between liquid crystals and solid crystals is only of quantitative nature, i.e. their structures are of the same type differing only in quantitative features, while the difference between the mesomorphic state and the other states of matter is of qualitative nature, i.e. their structures represent different types of molecular arrangements. Some authors use the words liquid crystal and mesomorphic state synonymously without providing a proper definition. Recently Gallot and Skoulios[18] pointed out the need to clarify

TABLE 1 *Characteristic Textures Suitable for Phase Identification*

Type of texture	Nematic	Smectic	Cholesteric	Reference direction
Birefringent textures	Homogeneous	Homogeneous	—	—
	Homeotropic O.S.$^+$	Homeotropic O.S.$^+$	See plane texture	O.S. optical sign; Optical axis normal to sample plane
	—	Focal conic (f.c.)	Focal conic (f.c.)	S.E. sign of elongation; Reference directions:
		1. f.c. domain SE$^+$	1. f.c. domain SE$^-$	Long axis of ellipse
		2. f.c. bands SE$^-$	2. f.c. bands SE$^+$	Length extension of band
		3. fan-shaped SE$^+$	3. fan-shaped SE$^-$	Rib of fan-shaped texture
	—	Batonnets	Batonnets	—
	Nematic droplets	—	—	—
	Centered texture	—	—	—
Optical active textures	—	—	Plane texture O.S.$^-$ color band	*Optical axis normal to sample surface*
Optical discontinuities	Threads	—	Threads	—

Sequence of *different* mesophases for rising temperatures:
Either solid–smectic–nematic–isotropic liquid
or solid–smectic–cholesteric–isotropic liquid

(For falling temperatures read sequence from right to left).

this situation. Mabis[19] even found an example, where the lack of the distinction between liquid crystals and mesomorphic state has lead to wrong conclusions. A certain lytropic compound was commonly considered to have a smectic phase because of its characteristic textures. According to general considerations valid for Friedel's mesomorphic state a structure of such a phase consists of parallel molecular strata. However, X-ray diffraction analysis of this material revealed a three-dimensional lattice order, which is not even of the layer type! So it must be concluded that Table 1 can only be used for the mesomorphic state as defined by Friedel. The empirical evidence seems to indicate that thermotropic phases represent true mesomorphic states. X-ray diffraction analysis or similar means should be used whenever necessary to verify the existence of the mesomorphic state and thus to ensure the applicability of Table 1.

Because of the empirical nature of Table 1, the data for phase identification may be incomplete and therefore subject to revision and refinement. For a given mesophase a complete set of characteristic textures can only be defined, if the molecular building principle of the mesophase is known and all textures compatible with it are derived.

This ideal situation is almost realized for single smetic mesophases. Its textures were explained in terms of molecular strata in which the long axis of the molecules are nearly aligned in a direction normal to the strata. The limiting surfaces of these strata form Dupin's cyclides, from which most likely all smectic textures are derived. This molecular model, ingeniously deduced by Friedel, was verified by X-ray diffraction analysis and optical studies.[20] For these reasons the identification criteria for single smectic mesophases rest on relatively safe grounds. However, the occurrence of smectic polymesomorphism presents a significant problem. More specific information about the mutual association of various strata or about the molecular arrangement within the strata or both may be required to derive all possible textures. Sackmann and co-workers[21] thoroughly investigated such multiple smectic phases and discussed their corresponding textures. These are not included in Table 1, since they are difficult to describe and not frequently encountered.

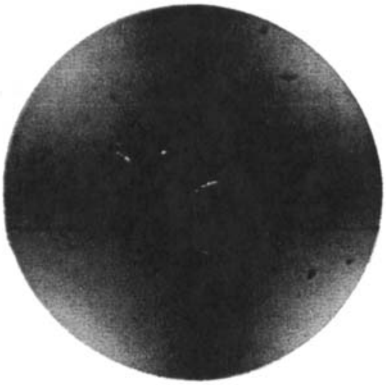
Much less is known about nematic mesophases. It is now established[2] that the molecules are oriented within a "swarm" about a preferred direction and that their centers of gravity are separated according to a certain distance statistics. Probably the lack of quantitative data such as distribution functions for molecular orientation and separation within a swarm, as well as the distribution functions describing size and direction of preferred orientation of the swarms themselves prevents the determination of all the textures which could exist in the nematic mesophase. Nevertheless the observed characteristic textures can be explained with the aid of this building principle, if not always in a unique way as in the case of the threads.[22]

Unfortunately even such a statement cannot be made with respect to cholesteric mesophases. X-ray studies[23] have yielded some limited data about the radial distribution function but have permitted only speculative rather than definite conclusions about the building principle of such phases. It is difficult to postulate a useful molecular arrangement for the cholesteric mesophase that would be compatible with its characteristic textures, the focal conic-like birefringent texture and the highly optical active plane texture, which also exhibits the Bragg-like diffraction of light. Some interesting speculations about this problem are reviewed by Gray.[24] Both textures should have about the same level of free energy in a finite temperature interval, although separated by a relatively small energy barrier. Fortunately the lack of understanding has not led to any difficulties with respect to phase identifications because of the unusual and unique optical features of the plane texture. It is not unlikely that further investigations, in particular on non-sterol derivatives, may result in a refinement of the classification of cholesteric phases.

In 1907 Vorländer[25] observed that the homeotropic texture of mesophases exhibit an optical behavior akin to uniaxial solid crystals. When observed through the Bertrand lens of a microscope in divergent light between crossed polarizers, such textures exhibit

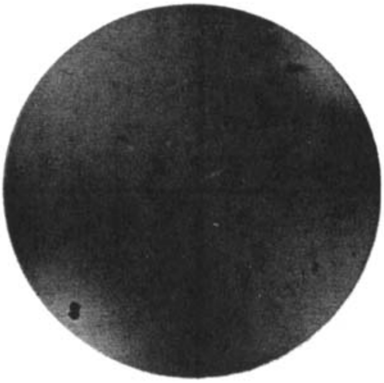
Figure 1: Interference Cross Exhibited by Homeotropic Textures of Cholesteryl Heptyl Thiocarbonate in Conoscopic Observation

1. Interference cross typical for the smectic and cholesteric mesophase of this material.

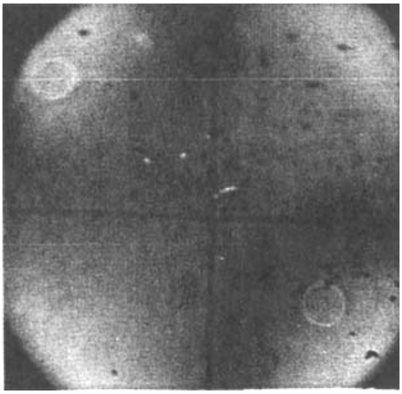


2. Identification of optical sign of homeotropic texture on account of interference colors induced by a subparallel waveplate (type Rot I, E. Leitz, Inc. N.Y.). This waveplate is placed between the sample and the analyser of the microscope. Its slow direction lies in the first and third quadrant of the cross shown in 1. and forms an angle of approximately 45° with the horizontal leg of the cross.

   a. Smectic phase:
      Positive Optical Sign

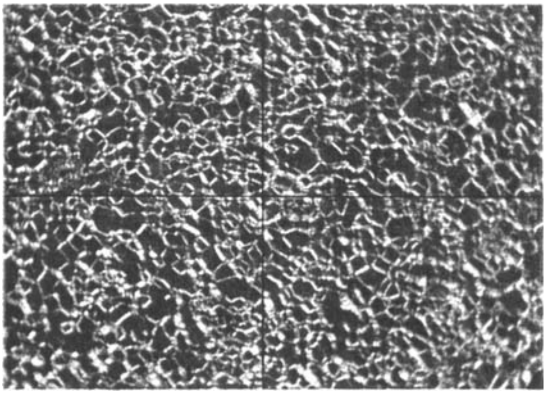


   b. Cholesteric Phase:
      Negative Optical Sign



Most of the dust particles shown in the microphotographs are deposited on the top surface of the lower lens inside the microscope condenser. Therefore, certain constellations of two or three of those particles can be used as reference points for the position of the blue or the yellow quadrants.

Figure 2: Sign of Elongation of Focal Conic Bands Exhibited by the Cholesteric Mesophase of Cholesteryl Nonanoate.



The polars are parallel to the cross hair. The subparallel gypsum waveplate (first order red) is inserted at an angle of 45° against the polars with its fast direction lying in the second and fourth quadrant. The sign of elongation is positive with respect to the length extension of the focal conic band, because the latter is yellow in the fast direction of the waveplate and blue for bands perpendicular to it.

an interference cross. It is possible to determine the optical sign of the texture from this cross with the aid of sub-parallel wave-plates[26] even for low birefringence. In Fig. 1 a sequence of photographs demonstrates the phase identification according to the optical sign.

In principle, this information could also be obtained from homogeneous and birefringent textures† if all the textures of a given mesophase would have the same uniaxial indicatrix. But even if the latter is established as a fact, it will be difficult to determine the optical sign. Since the orientation of birefringent regions within the sample can usually not be specified, the direction of the ordinary beam is not known and thus the optical sign cannot be obtained. The birefringent feature of such textures can be described by relating the direction of the slow and fast vibrations of polarized light with a reference direction of the texture that can be uniquely defined. Examples for such reference directions are the length extension of a focal conic band (often called oily streak) or a direction perpendicular to it, the radial or tangential direction of a spherulitic arrangement of birefringent elements, the direction of the rib of the fan-shaped texture and so on. Once the reference direction is defined a unique association can be made between it and the slow and fast vibrational directions of polarized light. The same approach proved to be useful in the field of optical crystallography, when the orientation of the ordinary beam of a crystal fragment cannot be determined. The direction of the slow or fast vibrational component in the crystal section is then determined with respect to a recognizable symmetry axis of the crystal habit. For example, the length extension of a crystal with a prismatic habit could provide such a reference direction. The term "sign of elongation" is used as a shorthand description for the birefringence of crystal sections.[27] This quantity is positive, when the slow vibrational direction is parallel to this elongation, or more general

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† The distinction between homogeneous and birefringent textures appears to be necessary, because they can be quite different manifestations of a given mesophase even in spite of the same molecular building principle. (For example, the homogeneous and the focal conic texture of the smectic mesophase.)

to the chosen reference direction, and negative in the opposite case. It is suggested to include in the definition of the "sign of elongation" also the birefringent mesomorphic textures, which have definable and reproducible reference directions. The use of such a quantity not only eliminates unnecessary confusion about the concept of the optical sign of a texture, but also provides quantitative criteria for the empirical phase identification scheme (see Table 1). Fig. 2 demonstrates the ease with which the sign of elongation can be determined. The insertion of a sub-parallel gypsum waveplate (first order red) at 45° against the crossed polars changes the color towards the yellow for focal conic bands approximately aligned along the fast direction of the waveplate and towards blue for bands perpendicular to it. This indicates that the slow vibration of polarized light in the focal conic band lies along its length extension and that the size of elongation is positive with respect to this direction. According to all previous experience, this result is characteristic for the cholesteric mesophase.

Friedel[1] derived the optical sign for most of the textures from partly assumed and partly known features of the mesomorphic building principle. Therefore, he does not distinguish between the optical sign of textures, for which the optical axis can be experimentally recognized, and the sign of elongation of textures, which do not have a discernible optical axis. Friedel's contribution significantly advanced the understanding of the mesomorphic state and led to fruitful hypothetical concepts about its molecular building principle. However, additional evidence is required to definitely establish the position of the optical axis for non-homeotropic textures. Until this is achieved, it appears to be necessary to distinguish between optical sign and sign of elongation.

The optical sign or sign of elongation have only an empirical significance for phase identifications, because of the lack of information about the molecular arrangement within a texture and the easy direction of polarization of the respective molecules. For example, the rule that a cholesteric mesophase should always exhibit a negative optical sign could be a dangerous generalization. With only very few exceptions, all known compounds exhibiting this mesophase are sterol derivatives and thus all have the sterane skeleton. Furthermore, the homeotropic behavior of this phase cannot be directly related to its birefringent textures, since this behavior is exhibited by the plane texture. In confocal observation the uniaxial-like interference cross of the plane texture can be seen from temperatures below the coherently scattered light region (i.e., Bragg-like diffracted light or the color band) up to the clearing point. In the color band the cross is observed when the narrow wavelength region of the diffracted light is filtered out. In this context, often a dull purple appearing texture is perceived above the color band. This is speculated to be a "homeotropic condition" caused by rapid coalescing of many small and undistinguishable particles.[28] The author believes that these particles are very small plane texture regions of various orientations. A mechanical disturbance such as the slip of the cover glass not only reduces the incoherent scattering but also appears to align these regions and thus induces the interference cross in confocal observation.

Conclusion

It must be admitted that the proposed experimental procedure for identification of mesophases is not perfect. It is still possible to overlook or mis-identify a mesophase. However, such errors can be made less likely by a combination of different methods: temperature scanning thermal analysis to recognize even small changes of thermodynamic quantities at phase transitions and careful microscopic investigation to identify the particular phases between the various transitions. There is no reason to doubt that further refinement of thermal analysis as well as an improvement of the optical investigation will permit the recognition of all enantiotropic phases. But monotropic phases may still be overlooked because of the shortness of the observation time due to interfering crystallization.[4]

The identification of mesophases is certain only to the extent that the classification of the mesomorphic state is defined. Due to shortcomings of the present theories of the structure of thermotropic mesophases, it is not possible to derive complete sets of characteristic textures for the various mesophases. As in the past, one has to rely on a purely empirical classification. (See Table 1.) Thus new findings can modify and refine empirical rules for phase identification. To support this development and to ensure unprejudiced experimental procedures, any phase identification scheme should be based on a minimum number of carefully chosen hypotheses. The proposed classification of mesomorphic phases is based on a molecular arrangement, which excludes a three-dimensional lattice order.[1] This is one of the reasons why this scheme does not generally apply to lyotropic phases. But it is valid for all thermotropic mesophases unless such a phase with a three-dimensional lattice order is discovered.

In the literature the concepts of mesomorphic and liquid crystal states are not always clearly defined partly because Friedel's original definition is disregarded. An attempt to find a general and more useful structural classification of these phases was made by C. Hermann,[29] who introduced statistical concepts of order to bridge the gap between the strictly ordered crystalline and the random gaseous state. In this connection the extension of crystalline to paracrystalline lattice order should be mentioned, which was proposed by Hosemann.[30] So valuable these concepts may be for the special case, they are not sufficient to cover the more general ordering principles which are realized in nature. A notable example for this may be the plane texture of the cholesteric phase. Although its structure is not known, certain of its dominant features are evident. These are the repeat distance of an unknown structural property of the magnitude of thousands of angstroms required to explain the Bragg-like diffraction of light and a special molecular arrangement with electrical features to account for the unusually high optical activity. Proposed structural models meeting both conditions are insufficiently described by either one of the two ordering concepts.

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