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Résumé. — Au moyen d’un microscope polarisant en configuration conoscopique on étudie pour la première fois les diagrammes de Kossel des phases chirales SmC* et SmM*. Dans le cas de la phase SmC* on observe un seul anneau de Kossel correspondant à la périodicité p/2 de la composante tensorielle \( |m| = 2 \) de la structure hélicoïdale du paramètre d’ordre \( g_3(r) \). La variation du pas \( p(T) \) en fonction de la température, obtenue à partir des diagrammes de Kossel, est en accord avec des mesures faites indépendamment par réflexion de Bragg en incidence normale aux couches smectiques. Le diagramme de Kossel de la phase SmM* comporte aussi un seul anneau central. En plus d’anneau de Kossel, dans le cas de la phase SmC* on observe des spirales d’Airy.

Abstract. — By means of optical microscopy, Kossel diagrams of chiral smectic phases are observed for the first time. Due to Bragg reflection, these diagrams occur in the focal plane of the microscope lens if the sample is illuminated with convergent monochromatic light. The Kossel diagram for the SmC* phase — observed for the chiral compound CE3 (BDH) — consists of a central ring corresponding to the periodicity \( p/2 \) of the \( |m| = 2 \) mode of the tensor order parameter \( g_3(r) \) describing the helical structure. The temperature dependence of the pitch \( p(T) \) determined by the Kossel method is in agreement with spectroscopic investigations of the Bragg scattering in back reflection. The Kossel diagrams of the unknown chiral smectic structure SmM* consist also of one central ring; no additional reciprocal lattice vectors are observed in the visible wavelength range for this phase. In addition to the Kossel diagrams, we report on the observation of Airy spirals in the SmC* phase.

1. Introduction.

Smectic liquid crystals formed by rodlike molecules are characterized by an orientational order of these molecules and by layer structure [1]. The density wave perpendicular to the layers can be described by a wavevector \( q_L \) with \( |q_L| = 2 \pi / \ell \), where the layer spacing \( \ell \) is of the order of several Å (1-2 molecular lengths). For some smectic phases, the director \( \mathbf{d}(r) \) indicating the preferred orientation of the molecular long axes is tilted by an angle...
with respect to the wavevector \( q_0 \). In the presence of chiral molecules, the tilted smectic phases SmC, SmI and SmF form a helix structure (Fig. 1). In terms of a tensor order parameter \( \xi(r) \), the helix structure of the SmC* phase corresponds to the following Fourier series:

\[
\xi(r) = \varepsilon_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + \varepsilon_{\pm 1} \begin{pmatrix} 0 & 0 & \pm \cos q_0 z \\ 0 & 0 & \sin q_0 z \\ \pm \cos q_0 z & \sin q_0 z & 0 \end{pmatrix} + \\
\varepsilon_{\pm 2} \begin{pmatrix} \cos (2q_0 z) & \pm \sin (2q_0 z) & 0 \\ \pm \sin (2q_0 z) & -\cos (2q_0 z) & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]

(1)

where non-zero coefficients \( \varepsilon_{+m} \) or \( \varepsilon_{-m} \) describe a righthanded and a lefthanded helix, respectively. Depending on the material, the pitch \( p = 2 \pi / |q_0| \) can exhibit a value between several hundreds of nm (for highly chiral systems) and infinity (for non-chiral systems). During the last decade, the theory and the application of chiral smectic phases have found remarkable interest, since their ferroelectric properties allow one to realize very fast bistable electrooptical devices [2].

Fig. 1. — Schematic representation for the structure of the cholesteric (a) and the chiral smectic phase SmC* (b, c). The director \( d \) representing the long molecular axes is given by \( d(r) = (\sin \tau \cos (q_0 \cdot r), \sin \tau \sin (q_0 \cdot r), \cos \tau) \). In the cholesteric phase (a), \( d \) is perpendicular to the helix axis, whereas the SmC* phase (b) shows a tilt angle \( \tau \) with \( 0 < \tau < 90^\circ \). In addition to the orientational order, the SmC* phase exhibits a layer structure of the molecules (c).
In this paper, a new alternative to investigate the pitch in smectic helix structures is presented. It is shown that the Kossel method which is a well known scattering technique to investigate solid crystals [3], colloidal crystals [4], liquid crystalline blue phases [5] and cholesteric phases [6], can be also applied to investigate helicoidal smectic phases.

So far, four different methods were used to investigate the pitch in these phases. According to the method by Martinot-Lagarde [7], the sample is contained between two glass slides. A uniform orientation of the helix axis parallel to the surface is obtained by slow cooling of the sample into the smectic phase while a magnetic field is applied. With this preparation, a parallel, straight fringe pattern occurs where the distance between the fringes is equal to the pitch [8]. If the pitch is larger than 1 \( \mu m \), it can be determined directly by observation in a polarizing microscope.

Another method to determine the spacing between the lines in a sample prepared in the same way is the diffraction method, where the sample is illuminated with a laser beam and the pitch is obtained from the distance between the interference maxima of the diffraction pattern. This method, initially used to investigate cholesteric phases [9] was applied to chiral smectic phases by S. A. Różański et al. [10, 11].

The Cano-method, which is very common to determine the pitch in cholesteric phases [12], was also used to investigate smectic helix structures [10]. In a wedge shaped sample with a strong anchoring of the molecules so that the wavevector \( \mathbf{q}_0 \) is oriententied perpendicular to the surface, the helix structure is distorted according to the conditions that the elastic free energy is minimized and that — at the same time — everywhere the sample thickness is equal to half of the pitch times an integer. For each change of this integer value by one, a disclination line occurs which can be observed in a polarizing microscope. The pitch can be obtained from the distance of these disclination lines.

Finally, selective reflection which is well known from cholesteric phases [13], was also observed for chiral smectic structures in the visible [14-16] and in the infrared wavelength range [10, 17, 18]. This phenomenon was predicted theoretically by D. W. Berreman [19] and the theory was developed also by other authors [20-22]. K. Hori [14] found that indeed two selective reflection bands can be observed in the SmC* phase, which correspond to the terms with the coefficients \( \varepsilon_{\pm 1} \) and \( \varepsilon_{\pm 2} \) in equation (1), respectively. The respective wavelengths are related to the pitch \( p \) by the Bragg condition

\[
\lambda = 2 \hat{n}d \cos \vartheta .
\]

Here, the spatial periodicity \( d \) can be either \( d = p \) (corresponding to the term with \( |m| = 1 \) in the tensor order parameter) or \( d = p/2 \) (corresponding to \( |m| = 2 \)). The mean refractive index \( \hat{n} \) in equation (2) appears due to refraction at the sample surface, the angle \( \vartheta \) describes the direction of light incidence with respect to the helix axis. The Bragg peak corresponding to \( d = p \) was found to exhibit a very weak intensity for light incidence along the reciprocal lattice vector \( \mathbf{q}_0 \) [14].

In conclusion, several methods which were developed in order to determine the pitch in cholesteric phases [9, 12, 13] were also applied to study chiral smectic phases [9-11, 10, 14-18]. Thus, it seemed of interest to see whether also the Kossel method is suitable to investigate smectic phases, since this method is well known for blue phases [5] and for cholesteric phases [6].

2. Kossel diagrams.

Kossel diagrams occur due to Bragg scattering if divergent or convergent monochromatic radiation is scattered by single crystals. These diagrams were detected in the year 1934 by W. Kossel et al. [3] who investigated the angular dependence of the characteristic X-radiation.
obtained by using a single crystal of copper as the anode in an X-ray tube. In this experiment, the crystal was a source of divergent radiation which was scattered by the cubic structure of this crystal. According to the Bragg condition, the radiation reflected by a family of planes described by the Miller indices $(hkl)$ forms a cone. This Kossel cone is perpendicular to the planes $(hkl)$ and exhibits an aperture angle $\vartheta$, given by the relation

$$\cos \vartheta = \frac{\lambda}{2d} \quad \text{or (in the reciprocal space)} \quad \cos \vartheta = \frac{|q_0|}{2|k|},$$

where $k$ is the wavevector of the incident radiation with $|k| = 2\pi/\lambda$. Consequently, W. Kossel et al. [3] observed dark and bright lines on a photographic plate, each of these Kossel lines being a cone section of a Kossel cone and thus representing the orientation and interplanar distance for the respective set of planes $(hkl)$.

Today, the principle of this method is used in order to investigate crystal structures with convergent electron beams [23], and for colloidal crystals using visible light [4]. Recently, it was shown that Kossel diagrams can be observed also in liquid crystals, namely in the cubic blue phases BPI [5] and BPII [24] as well as in the cholesteric phase [6]. In these applications, the crystal structures are illuminated with convergent monochromatic radiation by an external source. For the visible wavelength range, refraction at the sample surface has to be taken into account as in equation (2), and thus

$$\vartheta = \arccos \left( \frac{\lambda}{2nd} \right).$$

3. Experiment.

In order to investigate Kossel diagrams, a metallurgic microscope PME (Olympus) was equipped with an oil immersion objective exhibiting a large numeric aperture (1.3). The sample (Fig. 2a) was illuminated with convergent monochromatic light and observed in back reflection. As shown for blue phases [5], Kossel diagrams occurring in the visible range can be observed using this equipment. They occur in the focal plane of the microscope lens and can be observed by means of a Bertrand lens or just by removing the eye piece of the microscope.

The samples were prepared in two different ways. The substance was contained between a thin glass slide and the flat end of a glass cylinder which was transparent in one type of sample preparation or coated with an aluminium layer in the other type of samples. In the first case, only the light which is reflected due to Bragg scattering can be observed, whereas in the latter case also transmitted light can be seen due to reflection at the second interface of the sample. In both cases, the sample was illuminated with linearly polarized light and the analyzer was crossed with respect to the plane of polarization of the incident beam.

For chiral liquid crystal structures, Bragg scattering can be observed in back reflection if the respective reciprocal lattice vector $q_0$ is oriented along the direction of observation, i.e. perpendicular to the sample surface in our experimental setup. In the case of chiral smectic phases this orientation of $q_0$ corresponds to an alignment of the molecules perpendicular to the sample surface. In order to obtain such a homeotropic alignment of the liquid crystal, the inner glass surfaces were coated with lecithin. For the cholesteric phase, however, a planar (parallel) alignment of the molecules at the sample surface is required in order to get an orientation of $q_0$ perpendicular to the surface. This alignment could be induced by shear occurring when the glass cylinder was rotated with respect to the cover slide in the sample described above. The sample thickness was adjustable between about 5 $\mu$m and 50 $\mu$m. The temperature was controlled by means of Peltier elements using an AC bridge and measured separately by Pt 100 platinum resistors.
Fig. 2. — Experimental setup: (a) Kossel diagrams (Fig. 3) and conoscopic figures (Fig. 6) were observed in a polarizing microscope when illuminating the sample with convergent monochromatic light. (b) Reflection spectra were measured using a diode array spectrometer. The sample was illuminated with white, circularly polarized light under adjustable angle $\theta$. In order to cancel the light reflected at the sample surface, a circular analyzer was used.
For comparison of the results of the microscopic observation with spectroscopic data of the Bragg scattering, also the reflection spectra were measured (Fig. 2b). For this purpose, the sample was illuminated with white, circularly polarized light and the circularly polarized part of the reflected light with the same handedness was subjected to spectral analysis by a diode array spectrometer PR-702A (Photo Research). The angular dependence of the selective reflection was studied by adjusting the angle $\theta$ between the direction of light incidence and the surface normal of the sample. The position of the detector was adjusted as well, so that the reflection condition was fulfilled for each measurement.

The material under investigation was the well known compound (+)-4-n-Hexyloxyphenyl-4-(2-methylbutyl)biphenyl-4'-carboxylate (CE3)

\[
\text{C}_2\text{H}_5-\text{CH}-\text{CH}_2-\text{O}-\text{O}-\text{COO}-\text{O}-\text{C}_6\text{H}_{13}
\]

which was received by British Drug House (BDH) and used without further purification. This compound was studied previously by K. Hori [14, 15] and by P. Pollmann et al. [16]. CE3 exhibits a smectic SmC* phase as well as a cholesteric phase, both phases showing Bragg reflection in the visible wavelength range. The transition temperatures reported in reference [14] are: Cr 69.0 °C SmC* 80.0 °C N* 164.5 °C Iso.

Additionally, we investigated the following pyrimidine derivative

\[
\text{C}_6\text{H}_{13}\text{O} \quad \text{N} \quad \text{OOC} \quad \text{CH} - \text{CH}_2 - \text{CH}_3
\]

This compound was synthesized recently by D. Lôtzsch [27]. The compound (2) shows also selective reflection of visible light for a chiral smectic phase. However, X-ray investigations of this phase by D. Demus et al. [28] revealed a new smectic structure, called SmM*, which is different from the known smectic helix structures. According to reference [27], the transition temperatures are Cr 113.0 °C (SmJ 95.3 °C SmM* 102.0 °C) SmC* 154.5 °C Iso.

4. Results and discussion.

Kossel diagrams were observed in the phase SmC* (Fig. 3) as well as in the cholesteric phase of the chiral compound CE3. The Kossel diagrams for both phases consist of a single ring in the center of the diagram indicating the existence of a reciprocal lattice vector $\mathbf{q}_0$ oriented along the direction of observation. The diameter of the Kossel ring decreases continuously with increasing wavelength $\lambda$ of the incident monochromatic light. No Kossel line is observed if this wavelength exceeds the value $\lambda^*$, where the diameter of the central Kossel ring becomes zero. This wavelength $\lambda^*$ was measured as a function of temperature.

Additionally, the Bragg wavelength $\lambda_0$ of a macroscopic sample was measured in back reflection ($\theta = 5^\circ$) using the spectrometer. Comparison shows (Fig. 4) that the values $\lambda^*$ obtained by the Kossel method are about 15 to 20 nm higher than the values $\lambda_0$ measured spectroscopically. This can be explained by the linewidth of the Bragg reflection. The wavelength $\lambda_0$ represents the maximum intensity of reflected light whereas the value $\lambda^*$ obtained by the Kossel method corresponds to the maximum wavelength where the intensity is not zero. Indeed, the difference between these wavelengths corresponds to the halfwidth of the Bragg peaks.
Fig. 3. — Kossel diagrams of the SmC* phase observed with CE 3 for $t = 70.1 \, ^\circ\mathrm{C}$ for different wavelengths of the incident monochromatic light: a) 483 nm, b) 521 nm.
Fig. 4. — a) Temperature dependence of the Bragg wavelength $\lambda_0$ measured in back reflection (diamonds) and of the wavelength $\lambda_1$ (squares) where the central Kossel ring vanishes when the wavelength of the incident monochromatic light is increased. The two different types of squares corresponding to repeated measurements show that the results obtained by the Kossel method are good reproducible. b) Temperature dependence for the reciprocal values of the wavelengths represented in figure 2a.
Comparison of the values $\lambda_*$ and $\lambda_0$ measured in this work with the data given by K. Hori [14] shows that these wavelengths correspond to the spatial periodicity $d = p/2$ in equation (2). Consequently, the pitch $p$ of the helix structure is related to the wavelength $\lambda_*$ by

$$p = \frac{1}{n} (\lambda_* - \Delta\lambda) ,$$

(5)

where $\Delta\lambda \approx 15-20 \text{ nm}$ is the spectral halfwidth of the selective reflection band of the chiral smectic phase. The reflected light is right circularly polarized, indicating that the observed Kossel line represents a non-zero coefficient $\varepsilon_{+2}$ of the respective term in the expansion of the tensor order parameter (equation 1).

As expected, the values $\lambda_*$ and $\lambda_0$ for the Bragg wavelength show the same dependence on the temperature (Fig. 4a). A plot of the reciprocal values versus temperature (Fig. 4b) shows that the pitch does not diverge completely at the transition temperature SmC*-N*, indicating that this transition is of first order. This behaviour is in agreement with the observations by P. Pollmann and K. Schulte [16] that the transition temperature is shifted if the pressure is varied. This latter behaviour indicated that the transition SmC*-N* is also connected with a discontinuous change of the volume.

In order to compare the Bragg scattering of the smectic C* phase and the cholesteric phase more precisely, the angular dependence of the selective reflection was investigated in CE3 for two temperatures (65.4 °C and 81.6 °C) where these two phases show the same Bragg wavelength. As expected by the Bragg condition, this wavelength decreases in both cases with increasing angle $\theta$ of light incidence with respect to the surface normal (Fig. 5a). However, the dependence is slightly different for both phases, which can be explained by the difference of the effective refractive index $\bar{n}$ in both phases. Due to refraction at the sample surface, the angle $\theta$ between the wavevector $q_0$ and the direction of light incidence inside the sample is related to the angle $\theta$ measured outside the sample by

$$\sin \theta = \frac{1}{\bar{n}} \sin \theta .$$

(6)

Using this relation, equation (2) becomes

$$\lambda = \bar{n}p \sqrt{1 - \frac{1}{\bar{n}^2} \sin^2 \theta .}$$

(7)

Accordingly, a straight line is expected if $(\lambda/\lambda_0)^2$ is plotted versus $\sin^2 (\theta)$ (Fig. 5b):

$$\left(\frac{\lambda}{\lambda_0}\right)^2 = - \frac{1}{\bar{n}^2} \sin^2 \theta + 1 .$$

(8)

From figure 5b the values $\bar{n}_{N*} = 1.724$ and $\bar{n}_{SmC*} = 1.585$ were obtained for the refractive indices of the cholesteric and the smectic phase, respectively.

When investigating the Kossel diagrams on samples with a mirror at the second interface, Airy spirals (Fig. 6) were observed in addition to the Kossel line. These conoscopic figures occurring due to rotation of the plane of polarization are known for chiral solids such as quartz [25] and such spirals were also observed in cholesteric phases [26]. For a quartz plate observed in transmission with a circular analyzer, an Airy spiral with two branches can be observed, whereas Airy spirals with four branches occur if two quartz plates with the same thickness and opposite handedness are observed between crossed linear polarizers. In our experimental setup, the light passes the sample twice in the opposite direction due to
Fig. 5. — Angular dependence of the selective reflection of CE 3 for the chiral smectic phase SmC* 
(\(*, t = 65.4 ^\circ C\) ) and for the cholesteric phase (+, 81.6 \(^\circ\) C): a) Bragg wavelength \textit{versus} angle 
\(\theta\) of light incidence. b) Square of the reduced Bragg wavelength \textit{versus} \(\sin^2 \theta\) for the same data as 
represented in figure 5a. According to equation (8) the linear fit to this function allows one to determine 
the mean refractive index for light propagating along the helix axis.
Fig. 6. — Airy spiral observed in the SmC* phase of CE 3 for \( t = 60.1 \, ^\circ \text{C} \), \( \lambda = 430 \, \text{nm} \) \( \approx \lambda_0 \).

reflection at the second interface. This leads to the same conoscopic figure which is observed for two chiral plates of opposite handedness in transmission.

It should be stressed that we observed for the first time conoscopic figures which show the phenomena of optical rotation dispersion (Airy spiral) and of Bragg scattering (Kossel ring) simultaneously. According to the fact that the optical rotation changes sign at the Bragg wavelength [13], the Airy spirals exhibit opposite handedness for wavelengths larger and for wavelengths smaller than \( \lambda_0 \), respectively. However, the shape of the Airy spirals was found to depend also on the sample thickness.

Finally, we wish to report on the observation of Kossel diagrams in the unknown smectic phase SmM* occurring in the substance (2). This monotropic phase occurs at temperatures between 95.3 °C and 102.0 °C [27, 28]. In the SmM* phase, we observed a Kossel diagram consisting of a single central ring, as in the SmC* phase of CE3. This Kossel line corresponds to a reciprocal lattice vector along the viewing direction. Since no other Kossel lines were observed, it can be concluded that this unknown phase exhibits a helix structure only along one reciprocal lattice vector but no periodicities along other directions which are of the order of the wavelength of visible light.

5. Conclusions.

It has been shown that Kossel diagrams can be observed in chiral smectic phases exhibiting a helix structure. The Kossel diagrams investigated for the SmC* phase in CE3 and the SmM*
Phase in compound (2) consist of one circle in the center. This Kossel ring represents the mode with $|m| = 2$ in the tensor order parameter (Eq. (1)) and the diameter of this ring corresponds to a spatial periodicity of half of the pitch ($d = p/2$). According to previous observations, the occurrence of a second Kossel ring can be expected which corresponds to the term with $|m| = 1$ of the tensor order parameter and a spatial periodicity of $d = p$. However, this Kossel line should occur only for a very large aperture angle of the Kossel cone. It has not been detected so far.

The determination of the wavelength $\lambda$, where the diameter of the Kossel ring becomes zero on increasing wavelength allows one to determine the pitch of the helical structure. Although the accuracy of this method is limited by the half width of the selective reflection peak, the values are good reproducible and the temperature dependence of the pitch can be checked easily by this method. Additional information on the optical rotation dispersion might be obtained from Airy spirals observed in the same experimental setup. A more detailed analysis of the shape of these conoscopic figures is in progress.

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