positive Asymmetrie nur bei verhältnismäßig großem X $(> 0{,}3)$ auftritt, ist diese Spinfolge nicht sehr wahrscheinlich. Dagegen könnte nach Abb. 4 eine solche Asymmetrie leicht bei einem reinen Gamow–Teller-$5/2^+ - 7/2^+ - 7/2^+$-Übergang auftreten.

E. Schlußbetrachtung

Unsere Messung der Zirkularpolarisation der 498 keV-γ-Quanten des Rh^{103} kann nur dann eine definitive Entscheidung über den Spin des 538 keV-Niveaus bringen, wenn das Mischungsverhältnis der 498 keV-γ-Strahlung bekannt ist und außerhalb der Grenzen $0{,}4 < \delta < 2{,}6$ liegt. Unter der aus Messungen des K/L-Verhältnisses gestützten Annahme eines fast reinen E 2-Übergangs mit einer M 1-Beimischung $< 13\%$ folgt für das 538 keV-Niveau von Rh^{103} der Spin $5/2^+$. Die bei niedrigen v/c-Werten auftretenden Abweichungen der Polarisation lassen sich dahin deuten, daß das 650 keV-Niveau den Spin $7/2^+$ besitzt.

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Electric Field Effects in Cholesteric Liquid Crystals

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Several physical effects of strong electric fields upon a *cholesteric* liquid crystal have been found. While the alignment of nematic liquid crystals by electric and magnetic fields has been known for some time[1]; and various authors, particularly Friedel (ref. [1], p. 344), have classified the cholesteric phase as an alternate form to the nematic phase; we are not aware of any electric field effects upon cholesteric liquid crystals reported in the literature.

It might seem natural to examine optical effects in electric fields transverse to the viewing direction, in analogy with other electro-optic effects. However, one of our group[2] reasoning from the following considerations reached a different conclusion.

a) The intensity of the selectively reflected light in the plane cholesteric texture depends strongly upon the substrate material. E. g. Mylar plastic oriented by rolling and known for its strongly polar surface induces more reflection than glass, a comparatively amorphous material.

b) The model of de Vries[3] explains the strong reflection band and the high optical rotatory power of opposite sign on either side of that band by a screw structure. Even though only normal incidence and reflection is considered by this model, it suggests that there exists a preferred axis parallel to, and a preferred plane normal to the screw axis.

c) Hence the most sensitive effect might be observed by a field directed along such a screw axis and parallel to the viewing direction, for only in this direction would the field effect upon the individual molecular dipole axes be cumulative rather than periodic along the screw structure. We have therefore examined several cholesteric compounds in polarized light in a field parallel to the viewing axis. In this letter we wish to report on effects observed in cholesterol nonanoate, hereafter designated "CN".

Observations were made with a polarizing microscope using incident illumination, a transparent upper electrode of NESA glass, and an opaque, blackened, lower electrode of anodized copper. The microscope analyzer was crossed with the polarization of specularly reflected light, and magnifications of 30 to 250 were used.

Both instantaneous and time average light intensity were monitored by a photomultiplier on a third tube of the trinocular polarizing microscope. Readout was by means of a meter or oscilloscope.

The thickness of the sample was controlled with the aid of a mylar spacing sheet usually 15 microns thick between the electrodes. A circular hole of 3 mm dia. was cut in the mylar to accomodate the sample.

Fields up to 2.4×10^7 V./M. were monitored directly by a voltmeter connected to the electrodes. Near dielectric breakdown, a current of 3 microamperes was observed, but almost all measurements were taken under smaller fields at which the current leakage was less than 10^{-7} amperes.

Impurity effects can be ruled out by the following: The cholesterol nonanoate, (CN) used was chromatographically purified and checked. The behaviour of the sample did not degrade or alter with time or continued exposure to high electric fields. The zero field behaviour of the samples throughout was the same as that of samples exposed only to glass. Additionally, CN is known to be chemically stable at the temperatures used. All observations except as noted were made on the selectively scattered light from the cholesteric mesophase.

The twelve following main features have been observed in CN. The first five of these have mainly to do with D. C. fields, the last seven with A. C. fields.

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[1] M. G. Friedel, Ann. Physique **18**, 378 [1922].

[2] R. Ennulat, private communication.

[3] H. L. de Vries, Acta Cryst. **4**, 219 [1951].

1. Application of a strong D. C. field parallel to the viewing direction yields up to a five-fold increase in the intensity of reflected light.

2. When the liquid crystal is cooled from the clearing point with the field continuously applied, the intensity of reflected light is up to seven times greater than when the field is turned on only within the color temperature range.

3. The intensity of reflected light is an approximately linear function of applied voltage up to electrical breakdown of the material, providing, that the field is applied above the clearing point, and maintained while the material is cooled into the colored cholesteric range. Some slight saturation of the effect with field may take place, but is within experimental error.

4. A marked hysteresis is shown. The intensity does not return to its original value when the field is switched off, but remains nearly two-thirds of full intensity. Attempts to recover the original no-field intensity by use of A. C. fields are only partly effective. See below.

5. At fields near but below breakdown strength, approximately 2.4×10^7 V./M., perhaps ten to twenty small, dark points per square millimeter appear suddenly and just as rapidly disappear. Except for the color, the appearance under the microscope could be likened very much to a mud volcano, with bubbles bursting irregularly and repeatedly at the surface. Because we will deal with two other kinds of spots we will label these "type A".

Application of an A. C. field to CN gives a complicated frequency-dependant behaviour as follows: In general, the same type of behaviour occurs at higher frequencies for higher temperatures (blue); and at lower frequencies for lower temperatures (red). For a given behaviour, the A. C. field frequency is *more nearly* inversely proportional to visible color wavelength, rather than proportional to temperature.

6. Below 1 to 5 cycles per second, one sees primarily the D.C. behaviour with the added feature of switching transients. The transient consists of various dark spots of the order of $20-100$ microns dia. suddenly appearing in the field of view and then fading out. Two sets of spots appear alternately, one for each sign of polarity change. Such spots move about to some extent, and are well-defined at much lower fields than those which appear near breakdown. Additionally, these spots appear synchronously with polarity reversal so that we will call them "type B".

7. Between 1 and 35 cps, depending upon temperature, there is a very broad minimum in time average intensity of reflected light as a function of frequency. At this minimum, about 25 percent of the scattered light intensity of the D. C. case remains. The broad minimum is also found both for 30 micron and for 8 micron samples; but the intensity decrement is smaller for the very thin case. As freqency rises in the 1 to 35 cycle range, the spots grow in size and number until the field of view is mainly occupied by spots of the order of $100-200$ microns dia. nearly equal in size, and closely packed in an almost-hexagonal, irregular pattern. The edges of the dark spots have a definite color, characteristic of a lower temperature than the rest of the medium. These spots are in continual agitated movement. Since these spots have transformed continuously from the low-frequency regime, they are still "type B".

Also, for some samples there is a sharp temperature-independant minimum in the average reflected light intensity to as little as 13 percent of the D. C. case. This sharp minimum, however, seems to be dependant upon the gross dimensions of the samples, and furthermore, requires extended times of the order of ten minutes for the light intensity to fall after suitable temperature and frequency conditions have been initiated. No special visible structure seems to be associated with this minimum except for the already occurring spots.

8. As the frequency rises further in the 1 to 35 cycle range the spots move into irregular rows, and growing in size, amalgamate into heavy dark lines of the order of 20 to 100 microns wide and 100 to 500 microns long depending on temperature. It must be remarked that both these lines and the spots preceeding them are remarkably uniform in size in an isothermal field of view, varying at most 10 percent in thickness. Surprisingly, the average measured light intensity is starting to rise slowly again with the formation of these dark rows.

9. As the frequency increases further, now between 18 and 65 cycles, again depending upon temperature, the heavy bars begin to fade and grow thinner. The average light intensity rises until it returns to that of the D. C. case. The bars disappear completely, and other very thin lines appear. These give a threaded appearance reminiscent of a nematic liquid crystal.

10. In this regime, there can also be seen a few dark dots of about 10 microns apparent size. These are in continual irregular translation with velocities of the order of .5 mm/sec. A very high proportion of the motion is circular or spiral; often with several tens of consecutive orbits observed. There is no visual evidence that these spots are partaking of a gross vortex motion of the fluid, but it seems that these spots are following some sort of regular discontinuity within the liquid crystal. These spots are followed by a trail which fades out some 150 microns or so behind them. Such spots are sometimes "captured" at some fixed, visible, local discontinuity where they merge into the local detail; but they have not been seen to stop in the absence of a visible discontinuity. These dots are designated "type C".

11. The application of a strong A. C. field of 50 cps to a sample of CN which had been very rapidly cooled from above the clearing point, (especially if the "homeotropic"[4] texture remained into the usual color range) tended to generate large stable spiral structures within a minute. More than twenty complete turns could be counted in some instances; the nearly perfect spirals being up to 500 microns diameter and quite uniformly colored.

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[4] G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, New York 1962, p. 41.

Such spirals nucleated at the center of and were concentric with, maltese crosses of "spherulitic" structures observed growing in the homeotropic texture. Smaller spirals are observed otherwise in this and other materials, but we have never observed such extensive, rapid and repeatable development of these spirals as with high frequency A. C. electric fields.

12. Observation of the instantaneous intensity of reflected light indicated sharp spiked decreases in light intensity at twice the applied A. C. field frequency. These dips were approximately proportional to the average intensity and could be observed by the 1 P 21 photocell up to the clearing point, considerably warmer than the color temperature. The dips disappeared above 1000 cps applied A. C. frequency, but an A. C. component to the light reflected could be restored by applying a D. C. bias field equal to the peak A. C. field; the maximum instantaneous field remaining below breakdown. As one might suppose, this A. C. component was at the fundamental frequency, and could be observed up to 3000 cps.

Some regularities in the evidence suggest themselves.

1. The field seems to align the somewhat disoriented putative mesophase screw axes of de Vries' Theory[3] normal to the electrodes. The temperature dependance of reflection wavelength is not shifted, implying no change in the screw pitch.

2. The electric field effect depends, as in the nematic case, not only upon the individual molecular dipole moment, but also on the cooperative structure of the mesophase. This is shown by the relatively weak probable dipole moment of CN as compared to the supposedly strong dipole moments of certain other cholesteric compounds showing no detectable effect. Work in progress is expected to elucidate this matter.

3. Very crude calculations based on the observed time constants and estimated viscosity and density yield an electric dipole moment for CN of the order of .01 to 1 Debye molecule. The large uncertainties make agreement with a crude estimate based on molecular structure fortuitous.

4. In the colored cholesteric regime, the large spirals centered upon the "spherulitic" nuclei (ref. [1], pp. 364 to 373 and 386) lend more credence to a structure which has both an internal screw axis and a preferred plane of orientation parallel to the sample boundary, and which is consistent with the general picture presented, for instance by Gray (ref. [4], pp. 47 – 54).

5. No magnetic effects have been observed, and due to the smallness of the electric currents passing into the electrodes, none are expected here. Work is presently in progress to determine whether strong magnetic fields can affect cholesteric liquid crystals.

6. Since the liquid crystal was separated from the massive copper stage only by a very thin oxide layer, the liquid crystal could not have been at a very different temperature from the stage. The small electrical power, usually less than fifty microwatts, should not affect the very well heat-sinked microscope stage. Furthermore, since a careful study showed no displacement of the intensity as a function of temperature, temperature effects due to local heating are extremely unlikely.

7. Rectification due to the copper oxide blackening on the stage was suspected, but was found to be much less important as measured by the D. C. component of the A. C. current than the D. C. unbalance in amplifier output. Nevertheless even this unbalance could be kept under one percent.

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Dielektrische Relaxation von Toluolderivaten

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Bei aromatischen Molekülen mit polaren Gruppen läßt sich ein Zusammenhang zwischen der mesomeren Wechselwirkung dieser polaren Gruppe mit dem π-Elektronensystem und ihrer dielektrischen Relaxation in einem unpolaren Lösungsmittel aufzeigen: Mit zunehmender Wechselwirkung orientiert sich ein immer kleinerer Anteil der elektrischen Momentkomponente, die senkrecht zur Drehachse steht, durch Drehung der Gruppe allein, ohne Mitbewegung des Moleküls[1].

Mit dem hier mitgeteilten Meßmaterial soll nun geprüft werden, ob auch die dielektrische Relaxation der Methylen- und Methylgruppe am Benzolring entsprechende Gesetzmäßigkeiten erkennen läßt. Die Tabellen enthalten die charakteristischen Daten des jeweils durch zwei Debye-Kurven angenäherten Absorptionsverlaufs:

$$\frac{\varepsilon''}{\Delta\varepsilon_{\mathrm{S}}-\Delta n^2}=(1-G)\,\frac{\omega\,\tau_1}{1+\omega^2\,\tau_1{}^2}+G\,\frac{\omega\,\tau_2}{1+\omega^2\,\tau_2{}^2}\,.$$

Dazu wurde die dielektrische Absorption der untersuchten Moleküle in benzolischer Lösung von 20 °C bei fünf Wellenlängen zwischen 60 cm und 7 mm bestimmt und zusätzlich das molekulare Dipolmoment μ gemessen[2]. $\mu_2=\mu\cdot\sqrt{G}$ ist die Komponente des Moments, die sich mit der kurzen Relaxationszeit τ_2 durch Drehung der Gruppe orientiert.

In Tab. 1 sind Moleküle mit der Chlormethyl- bzw. Brommethylgruppe zusammengestellt, also mit Substituenten $-CH_2X$. Hier ist die mesomere Wechsel-

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[1] G. Klages u. P. Knobloch, Z. Naturforschg. **20 a**, 580 [1965].

[2] Meßmethode und Auswertung sind in [1] beschrieben. — Herrn P. Nehmiz sei für die Durchführung der Messungen bei 7 mm Wellenlänge sehr gedankt.