Magnetochiral Anisotropy in Bragg Scattering

C. Koerdt,[1] G. Düchs,[1] and G. L. J. A. Rikken[1,2]

[1]*Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung/CNRS, BP 166, 38042 Grenoble, France*

[2]*Laboratoire National des Champs Magnétiques Pulsés, CNRS/INSA/UPS, BP 4245, 31432 Toulouse, France*

(Received 12 March 2003; published 12 August 2003)

We show experimentally that light scattering in cholesteric liquid crystals shows strongly resonant magnetochiral anisotropy near the Bragg resonance; the optical transmission of unpolarized light depends linearly on an external longitudinal magnetic field and on the handedness of the medium.

DOI: 10.1103/PhysRevLett.91.073902 PACS numbers: 42.70.Df, 78.20.Ek, 78.20.Ls

Recently a new polarization-independent optical effect was discovered: magnetochiral anisotropy (MChA). It is observed as a spatial anisotropy in the luminescence [1], refraction [2,3], absorption [4], and photochemistry [5] of chiral media subject to a magnetic field. The analogous effect for electronic magnetotransport in chiral conductors has also been reported [6,7]. The existence of MChA in optics can easily be rationalized by symmetry arguments that require that the dielectric constant is invariant under time reversal and parity. These arguments show that in the dielectric constant of a chiral optical medium, a polarization-independent term proportional to $\mathbf{k} \cdot \mathbf{B}$ is allowed ($\mathbf{k}$ is the wave vector of the light and $\mathbf{B}$ is the external magnetic field) [8–10]. For high symmetry chiral media like gases, liquids, or uniaxial crystals, this leads to a dielectric constant $\varepsilon_{\pm}(\omega, \mathbf{k}, \mathbf{B})$ for the $\pm$ circular eigenmodes, propagating parallel to the symmetry axis, of the form

$$\varepsilon_{\pm}(\omega, \mathbf{k}, \mathbf{B}) = \varepsilon(\omega) \pm \alpha^{d/l}(\omega)k \pm \beta(\omega)B + \gamma^{d/l}(\omega)\mathbf{k} \cdot \mathbf{B}, \tag{1}$$

where the superscripts refer to right (d)- and left (l)-handed media and $\alpha^d(\omega) = -\alpha^l(\omega)$, $\gamma^d(\omega) = -\gamma^l(\omega)$. The material parameters α, β, and γ are in general complex valued, where α and β describe natural and magnetic optical activity, respectively, and γ describes MChA. The essential features of MChA, as expressed by Eq. (1), are as follows: (i) the dependence on the relative orientation of $\mathbf{k}$ and $\mathbf{B}$, (ii) the dependence on the handedness of the chiral medium (enantioselectivity), and (iii) the independence of the polarization state of the light.

The MChA luminescence and absorption experiments measure $\mathrm{Im}\,\gamma$ and are intrinsically resonant with electronic transitions in the medium. Fairly large effects, with relative anisotropies up to 10^{-3} T^{-1} were reported [1]. In contrast, in the nonresonant MChA refraction experiments, which measure $\mathrm{Re}\,\gamma$, only refractive index anisotropies of 10^{-10} T^{-1} were found [2,3]. For both cases, the observed orders of magnitude agree with those predicted by simple models. One may wonder whether under resonant conditions the refractive MChA effect could be much larger. Such a situation was considered theoretically by Eritsyan [11], who calculated the transmission through a cholesteric liquid crystal in a magnetic field parallel to the helix axis for wavelengths close to the cholesteric Bragg resonance. In this work, only the α and β terms of Eq. (1) were taken into account, but nevertheless a strongly resonant transmission anisotropy of the order of 10^{-4} T^{-1} was predicted. It had already been pointed out that in absorption [4] and photochemistry [12], these two terms together can lead to a cascaded form of MChA, proportional to $\alpha \cdot \beta$, that has phenomenologically speaking the same properties as the genuine MChA, proportional to γ. The experimental verification of the existence of such a resonant enhancement of MChA in Bragg scattering is the subject of this Letter. Note that the existence of such an enhancement is not trivial, as the Bragg resonance involves forward and backward traveling waves of amplitudes determined by the chiral medium, and the MChA has opposite signs for these two propagation directions.

Cholesteric liquid crystals (ChLC) show a helical structure in their collective molecular orientation with a pitch that can be in the visible wavelength region [13,14]. By a proper choice of ChLC mixtures, both left- and right-handed helices and, consequently, both signs of α and γ can be realized. Around wavelengths resonant with the cholesteric pitch, αk can reach values up to 0.5, whereas βB will be 10^{-5} for normal laboratory fields [14]. In the isotropic phase, these materials have typically $\alpha k \simeq 10^{-5}$, implying an enhancement of 5 orders of magnitude of the optical activity. Intuitively, one could expect a similar enhancement of the MChA near the Bragg resonance.

The sample cells used consisted of two glass plates separated by a spacer with a thickness that can be chosen between 10 μm and 1 mm. The cells were filled with the LC mixture in the isotropic phase, and alignment of the helix axis perpendicular to the plates was obtained by gently shearing the plates or by a capillary flow of the isotropic phase between the glass plates. Since we worked in the visible wavelength range, the good crystalline quality could be easily verified by visual inspection. Different mixtures of cholesteryl chloride (ChCl) and

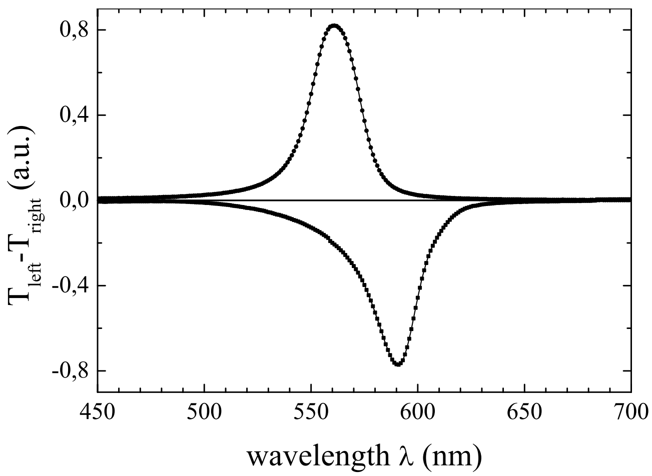

FIG. 1. Transmission difference between left- and right-circularly polarized light for two different ChLC mixtures (both ChCl/ChOC, in different weight ratios, sample thickness: 50 μm). Top: left-handed ChLC (weight ratio 1:3) at room temperature. Bottom: right-handed ChLC (weight ratio 4:1) at 343 K.

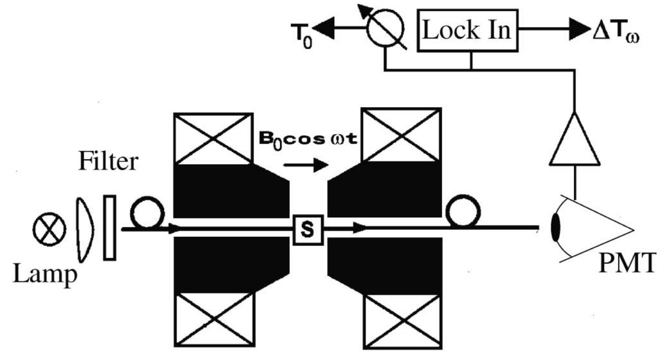

FIG. 2. Schematic setup of the magnetochiral anisotropy measurement. Filtered light is guided through an optical fiber (⌀ 1 mm, numerical aperture NA = 0.47) to the ChLC. Transmitted light is collected by a similar light guide and detected by a photomultiplier tube PMT. The alternating magnetic field is applied parallel to the axis connecting the fibers.

cholesteryl oleyl carbonate (ChOC) (Sigma-Aldrich) were used, two with a left-handed helix consisting of 1:3 (1:5) ChCl/ChOC and one with a right-handed helix (4:1 ChCl/ChOC), at temperatures of 300 and 343 K, respectively. Figure 1 shows the transmission difference between left- and right-circularly polarized light, for a left- and a right-handed sample. The maximum (Fig. 1, top) and the minimum (Fig. 1, bottom) in the circular differential spectra coincide with the Bragg resonances of the respective ChLCs. The magnetochiral anisotropy of such ChLCs was measured by applying an alternating magnetic field of about 0.5 T parallel to the helix axis. Unpolarized, incoherent light from a lamp, filtered by interference filters with a typical transmission bandwidth of 10 nm, was guided to the cell by means of an optical fiber (diameter 1 mm, numerical aperture 0.45). The light transmitted through the ChLC, parallel to the magnetic field direction, was collected by a similar fiber, which guided it to a photodiode detector. The magnetic field induced transmission changes were phase-sensitively detected by a lock-in amplifier (see Fig. 2). We define the relative transmission anisotropy Δt as

$$\Delta t \equiv \frac{T(B) - T(-B)}{T(B) + T(-B)}. \quad (2)$$

The inset of Fig. 3 shows the relative transmission anisotropy Δt for a left-handed sample as a function of magnetic field. A clear linear relation is found. The observed order of magnitude agrees reasonably well with the predictions by Eritsyan [11] and illustrates that under resonant conditions, refractive MChA can be quite strong. By rapid cooling to liquid nitrogen temperatures, we could freeze the cholesteric structure. We observed approximately the same MChA as at room temperature, thereby excluding magnetic realignment of the molecules as cause for the MChA that resulted.

Figure 3 shows the wavelength dependence of the MChA in the form of the relative transmission anisotropy normalized for the magnetic field $\eta = B^{-1}\Delta t$ for a left-handed ChLC. A clear resonance is observed that is close to the Bragg resonance. This is completely different from the wavelength dependence predicted by Eritsyan, which has a derivative-type line shape, with a zero crossing at

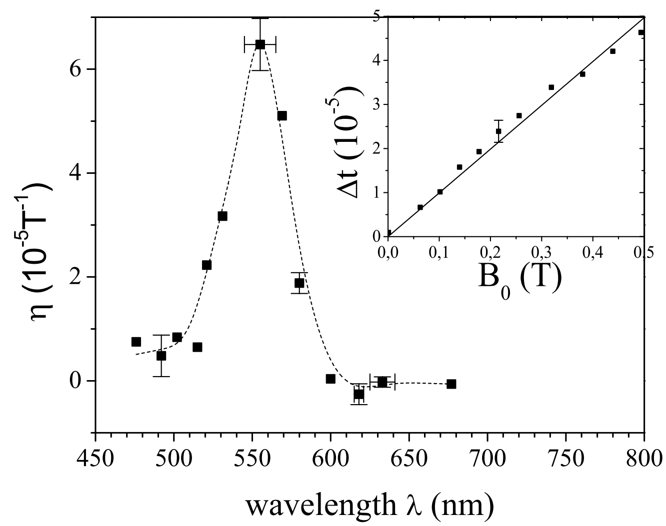

FIG. 3. Inset: Relative transmission anisotropy $\Delta t = \eta B$ versus magnetic field for a left-handed sample consisting of 1:5 ChCl/ChOC at room temperature, layer thickness $d =$ 500 μm, $\lambda = 481$ nm $\approx \lambda_{\rm Bragg}$. Main figure shows the wavelength dependence of the normalized relative transmission anisotropy η for a left-handed sample consisting of 1:3 ChCl/ChOC at room temperature, $d = 500$ μm, $B = 0.38$ T (line is guide to the eye). The maximum observed corresponds approximately to the Bragg resonance of the sample.

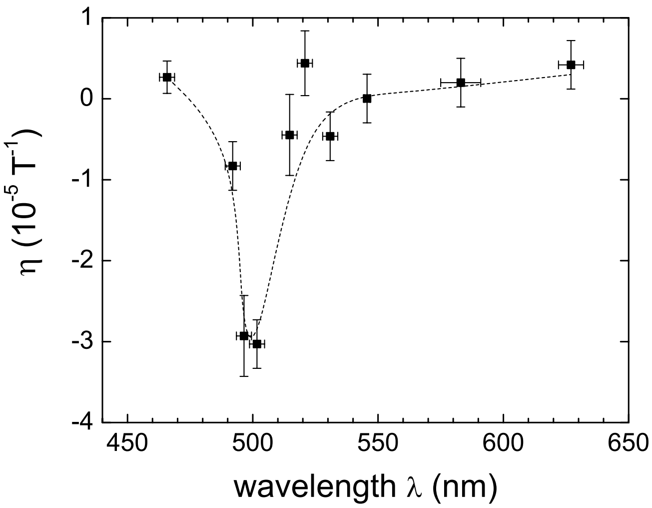

FIG. 4. Wavelength dependence of η for a right-handed sample consisting of 4:1 ChCl/ChOC at 343 K, $B = 0.37$ T, $d = 50$ μm (line is guide to the eye). The maximum in negative sense observed corresponds approximately to the Bragg resonance of the sample. The order of magnitude is similar to that in Fig. 3, whereas the sign has changed.

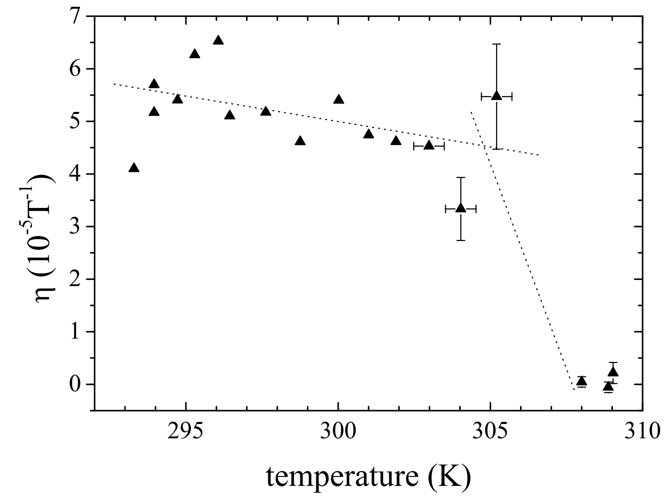

FIG. 5. Temperature dependence of the normalized relative transmission anisotropy η. The anisotropy vanishes at the cholesteric-isotropic phase transition temperature that was at 306 K for this sample, consisting of 1:5 ChCl/ChOC, $d = 500$ μm, $\lambda = 481$ nm $\approx \lambda_{\text{Bragg}}$. No stable data points could be obtained in the vicinity of the transition temperature itself.

the Bragg resonance, and large and opposite values in the two opposite wings of the Bragg band [11]. This large discrepancy suggests that the theoretical treatment in Ref. [11] is incomplete and that the γ terms of Eq. (1) play a dominant role in the observed MChA. A similar dominance of γ terms over $\alpha \cdot \beta$ terms was found in the absorption and photochemistry experiments [4,12]. Clearly, the development of a theory for light propagation in ChLC, involving the γ terms of Eq. (1) is called for.

The wavelength dependence of MChA for a right-handed sample is depicted in Fig. 4. The negative peak corresponds to the Bragg resonance [15], and in comparison with Fig. 3, one can see that by changing the handedness of the medium, the MChA changes its sign as was demanded for γ in Eq. (1). The MChA of both types of handedness is of the same order of magnitude. Note that the two types of samples are not enantiomers (mirror images), and therefore MChA strength, linewidth, etc., need not be identical. However, as the chiroptical properties of the two types of samples are of similar magnitude but opposite sign (Fig. 1), the magneto-optical properties should be similar on the basis of the close chemical similarity of their components. Similar magnitudes and opposite signs should be expected for the MChA of the two types of samples, as observed.

Measurements in the range between 18 and 500 μm proved η to be independent of sample thickness. There is at this moment no detailed theory that allows one to draw conclusions from this observation.

The dependence of the effect on the orientations of $\mathbf{k}$ and $\mathbf{B}$ was investigated by simply interchanging the light source and detector at the ends of the optical fibers. Thus the flow of light is inversed ($\mathbf{k}$ to $-\mathbf{k}$). We found that the anisotropy Δt (phase-sensitively measured with respect to an alternating magnetic field B) changes sign, whereas the absolute value was not affected. This proves the dependence of η on the direction of $\mathbf{k}$ and on the direction of $\mathbf{B}$.

Figure 5 shows the measured temperature dependence of η for the left-handed ChLC. The observed MChA clearly vanishes upon approaching the cholesteric-isotropic phase transition temperature, which was at 306 K for this sample. This behavior confirms that the MChA is related to the collective, cholesteric supermolecular structure.

Our results show that resonant enhancement of MChA around the Bragg resonance exists. The theoretical description by Eritsyan (Ref. [11]) was found to be incomplete. Our observation suggests that it should be possible to observe MChA in Bragg scattering of unpolarized, or linearly polarized x rays by chiral crystals. Thereby one could obtain specific chiral information of crystal structures, as an alternative to x-ray natural circular dichroism measurements by use of polarization modulation of synchrotron radiation [16].

We gratefully acknowledge stimulating discussions with Ernst Raupach and Georges Wagnière, as well as Bart van Tiggelen for a critical reading of the manuscript. The Grenoble High Magnetic Field Laboratory is a "laboratoire conventionné aux universités UJF et INP de Grenoble."

[1] G. L. J. A. Rikken and E. Raupach, Nature (London) **390**, 493 (1997).

[2] P. Kleindienst and G. Wagnière, Chem. Phys. Lett. **288**, 89 (1998).
[3] M. Vallet, R. Ghosh, A. Le Floch, T. Ruchon, F. Bretenaker, and J.-Y. Thepot, Phys. Rev. Lett. **87**, 183003 (2001).
[4] G. L. J. A. Rikken and E. Raupach, Phys. Rev. E **58**, 5081 (1998).
[5] G. L. J. A. Rikken and E. Raupach, Nature (London) **405**, 932 (2000).
[6] G. L. J. A. Rikken, J. Fölling, and P. Wyder, Phys. Rev. Lett. **87**, 236602 (2001).
[7] V. Krstic and G. L. J. A. Rikken, Chem. Phys. Lett. **364**, 51 (2002).
[8] D. L. Portigal and E. Burstein, J. Phys. Chem. Solids **32**, 603 (1971).
[9] N. B. Baranova, Yu.V. Bogdanov, and B. Ya. Zel'dovich, Opt. Commun. **22**, 243 (1977).
[10] O. S. Eritsyan, Sov. Phys. Usp. **25**, 919 (1982).
[11] O. S. Eritsyan, J. Exp. Theor. Phys. **90**, 102 (2000).
[12] E. Raupach, G. L. J. A. Rikken, C. Train, and B. Malézieux, Chem. Phys. **261**, 373 (2000).
[13] D. Dennis, J.W. Goodbye, G.W. Gray, H.W. Spiess, and V. Vill, *Handbook of Liquid Crystals* (Wiley VCH, New York, 1998).
[14] H. Kelker and R. Hatz, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim, 1980).
[15] Although the samples in Fig. 4 and Fig. 1 bottom are characterized by the same parameters, they differ quite a lot in their Bragg resonance positions. This is due to the very critical dependence on concentration and temperature typical of liquid crystals and, in particular, of our right-handed samples.
[16] L. Alagna, T. Prosperi, S. Turchini, J. Goulon, A. Rogalev, C. Goulon-Ginet, C.R. Natoli, R.D. Peacock, and B. Stewart, Phys. Rev. Lett. **80**, 4799 (1998).