Pure and cascaded magnetochiral anisotropy in optical absorption

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(Received 18 March 1998)

In this paper we study the optical absorption of chiral media subject to a magnetic field parallel to the light. It is shown to exhibit pure and cascaded magnetochiral anisotropy. We present experimental evidence for the existence of pure magnetochiral anisotropy in absorption. [S1063-651X(98)08910-7]

PACS number(s): 42.25.Md, 78.20.Ls

The discoveries of natural optical activity by Arago (1811) in chiral (from the Greek *cheiros* for hand, meaning existing in two forms that can only be interconverted by parity reversal) crystals and of magnetically induced optical activity by Faraday (1846) in glass have contributed much to our understanding of the wave nature of light and of its interaction with matter. There is a strong phenomenological resemblance between the two effects. Both involve a difference in absorption and refraction between left and right circularly polarized light, the former in chiral media, the latter in media subject to a magnetic field **B** parallel to the wave vector of the light **k**. The physical origins, however, are completely different. Natural optical activity (NOA) is a result of a nonlocal optical response in media that lack all mirror symmetry (i.e., are chiral), whereas magnetic optical activity (MOA) results from the breaking of time-reversal symmetry by a magnetic field [1]. Under conditions where both symmetries are broken, an additional optical effect becomes possible. In 1962 an implicit prediction appeared of such a cross-effect between natural and magnetic optical activity, which discriminates between the two enantiomers (mirror images) of chiral molecules [2]. This was followed independently by a more general prediction of magnetospatial dispersion in noncentrosymmetric crystalline materials [3]. For reasons that will become clear below, this cross-effect has been called magnetochiral anisotropy and has since then been predicted independently several times [4–7]. Its existence can be appreciated by expanding the dielectric tensor of chiral media subject to a magnetic field to first order in **k** and **B** [3]:

$$\varepsilon_{ij}(\omega,\mathbf{k},\mathbf{B})=\varepsilon_{ij}(\omega)+\alpha_{ijl}(\omega)k_l+\beta_{ijl}(\omega)B_l+\gamma_{ijlm}(\omega)k_lB_m. \quad (1)$$

For the case that the magnetic field is parallel to the propagation direction of the light, the optical eigenmodes are right- and left-handed circularly polarized waves, denoted by $+$ and $-$. When considering only high symmetry media like gases, liquids, cubic crystals, or uniaxial crystals with their optical axis parallel to **B**, Eq. (1) can be simplified with the help of symmetry arguments and the circular eigenmodes to [3,4]

$$\varepsilon_{\pm}(\omega,\mathbf{k},\mathbf{B})=\varepsilon(\omega)\pm\alpha^{d/l}(\omega)k\pm\beta(\omega)B+\gamma^{d/l}(\omega)\mathbf{k}\cdot\mathbf{B}, \quad (2)$$

where $x^d(\omega)=-x^l(\omega)$ refers to right- (d) and left- (l) handed media, α describes natural optical activity, and β describes magnetic optical activity. The material parameters ε, α, β, and γ are all generally complex valued, and we will denote their real and imaginary parts by x' and x'', respectively. The essential features of magnetochiral anisotropy (MCA), represented by the fourth term on the right-hand side of Eq. (2), are (i) the dependence on the relative orientation of **k** and **B**, hence the name, (ii) the dependence on the handedness of the chiral medium, and, (iii) the independence of polarization. The existence of magnetochiral anisotropy is already important from the viewpoints of light-matter interaction and spectroscopy. It may even have far-reaching consequences, as it has been suggested as a possible explanation for the homochirality of life [8,9], because it enables enantioselective photochemistry in a magnetic field with unpolarized light. To assess the validity of this hypothesis, our microscopic understanding of MCA has to be developed. This paper is intended to make a contribution to this effort by providing quantitative experimental results for MCA in optical absorption.

An experimental indication for the existence of MCA was provided by Markelov *et al.* [10], who observed a difference in refractive index between light propagating parallel and antiparallel to the magnetic field in a chiral crystal of $LiIO_3$. Complete experimental evidence for MCA, confirming all features of the effect, was recently provided by Rikken and Raupach in emission [11], and by Kleindienst and Wagnière [12] in refraction, both obtained on liquid molecular systems. However, a quantitative analysis of the results in [11] is cumbersome because of the influence of nonradiative decay and the complexity of the luminescent molecules studied there. Absorption measurements do not suffer from nonradiative processes and allow reliable determination of the optical transition moments involved. The use of crystalline materials is to be preferred because of the absence of orientational averaging. Below we will present magnetochiral anisotropy measurements in optical absorption, on the well-characterized chiral crystal α-$NiSO_4\cdot 6H_2O$.

Symmetry arguments do not give any insight into the order of magnitude of the magnetochiral anisotropy. Baranova and Zeldovich presented a simple microscopic model [5] that can give an order-of-magnitude estimate. It is an extension of the classical Becquerel model for magnetic optical activity [1] and it interprets MCA as a result of the Larmor precession in natural optical activity. This approach is only valid if

the MOA is dominated by so-called A terms (derivative-type line shape of the dichroism), which is the case for all diamagnetic materials and for many paramagnetic materials. The well-known Becquerel result is (in cgs units)

$$\beta(\omega)=\frac{e}{2mc}\frac{\partial\varepsilon}{\partial\omega}, \tag{3}$$

where e and m are the electron charge and mass. Baranova and Zeldovich find analogously

$$\gamma(\omega)=\frac{e}{2mc}\frac{\partial\alpha}{\partial\omega}. \tag{4}$$

When studying natural circular dichroism (NCD) or magnetic circular dichroism (MCD), it is convenient to normalize the dichroism by the normal absorption in dimensionless dissymmetry factors;

$$g\equiv 2\frac{A_+-A_-}{A_++A_-}, \tag{5}$$

where $A_\pm$ is the optical extinction coefficient for right/left circularly polarized light. If $\varepsilon'_\pm \gg \varepsilon''_\pm$ (which is the case we studied experimentally), the dissymmetry factors for NCD and MCD can be simply expressed in the imaginary parts of the terms of Eq. (2):

$$g_{\mathrm{NCD}}=\frac{2\alpha''k}{\varepsilon''}, \tag{6}$$

$$g_{\mathrm{MCD}}=\frac{2\beta''B}{\varepsilon''}. \tag{7}$$

Here we define the magnetochiral anisotropy factor similarly:

$$g_{\mathrm{MCA}}\equiv 2\frac{A(\mathbf{B}\uparrow\uparrow\mathbf{k})-A(\mathbf{B}\uparrow\downarrow\mathbf{k})}{A(\mathbf{B}\uparrow\uparrow\mathbf{k})+A(\mathbf{B}\uparrow\downarrow\mathbf{k})}=\frac{2\gamma''kB}{\varepsilon''}. \tag{8}$$

The g_{NCD} is usually quite constant across one given optical transition. Then we can write $\alpha''(\omega)\equiv C\varepsilon''(\omega)$ where C is a constant, which leads to

$$g_{\mathrm{MCA}}=\frac{(e/mc)C(\partial\varepsilon''/\partial\omega)kB}{\varepsilon''}=g_{\mathrm{NCD}}\,g_{\mathrm{MCD}}. \tag{9}$$

This simple model therefore gives as an estimate for the relative strength of MCA in absorption the product of the relative strengths of NCD and MCD, a result that seems in line with physical intuition for a cross-effect. A detailed molecular theory for MCA in molecular liquids has been formulated by Barron and Vrbancich [13]. It requires complete knowledge of all molecular transition moments involved and therefore cannot be easily used to obtain quantitative predictions.

The absorption of unpolarized light by a medium with a dielectric constant as given by Eq. (2) is most readily calculated by considering linearly polarized light, which can be decomposed into two circularly polarized waves of the same amplitude and opposite handedness. If $\varepsilon'_\pm \gg \{\varepsilon''_\pm, |\alpha k|, |\beta B|, |\gamma kB|\}$ and neglecting reflection, the transmission coefficient T for linearly polarized light of such a medium with thickness L is found to be

$$T(\omega,\mathbf{k},\mathbf{B})=\exp\left\{-kL\left(2n''+\frac{\gamma''\mathbf{k}\cdot\mathbf{B}}{n'}\right)\right\}\times\cosh\left\{\frac{kL}{n'}(\alpha''k+\beta''B)\right\}, \tag{10}$$

where $n'+in''\equiv\sqrt{\varepsilon}$. This result holds for an arbitrary linear polarization, and therefore also for unpolarized light. The most straightforward method to measure γ'' would be to alternate the magnetic field direction at a frequency Ω and to do phase-sensitive detection of the transmitted intensity at Ω. Using Eq. (10), one finds for the ratio between the modulated transmitted intensity I_Ω and the static transmitted intensity I_0, for $I_\Omega \ll I_0$,

$$\frac{\langle I_\Omega\rangle}{I_0}=-\frac{kBL}{\sqrt{2}n'}\left(\gamma''k-\beta''\tanh\frac{\alpha''k^2L}{n'}\right). \tag{11}$$

The first term on the right-hand side represents the pure magnetochiral anisotropy in absorption. The second term stems from a cascading of natural and magnetic circular dichroism. Baranova and Zeldovich concluded that such cascading does not occur in refraction [5]. In our case, for absorption, it occurs due to the fact that NCD creates an excess of one circularly polarized component in the initially unpolarized light. Because of this excess, the MCD then leads to an intensity modulation at Ω. This cascaded MCA shows all the essential features of MCA given above, but can be discriminated from the pure effect by varying the sample thickness. A further difference is that the pure effect occurs only at an optical transition that shows both NCD and MCD, whereas the cascaded effect can also occur in composite media, of which one component shows MCD and another one shows NCD. In diluted systems, the pure effect is therefore linearly proportional to the concentration of active species, whereas the cascaded effect is proportional to the product of the concentrations of NCD-active species and MCD-active species. In the case that the latter two are the same, the cascaded effect is proportional to the square of the concentration of active species.

We have selected the chiral uniaxial crystal α-$NiSO_4\cdot 6H_2O$ as a good candidate to show a well-defined, strong MCA in absorption, because of a very large g_{NCD} [14] and a reasonably large g_{MCD} [15]. This material has been extensively studied in the past and its optical properties are well known. Because of the weakly allowed character of the visible and near-infrared optical transitions of the $[Ni(OH_2)_6]^{2+}$ complex, $\{\alpha' k, \beta' B, \gamma' kB\} \ll \varepsilon'$, which greatly simplifies the analysis, as shown above. Crystals of α-$NiSO_4\cdot 6H_2O$ were grown by slow evaporation from aqueous solutions at 40 °C. They are easily cleaved into platelets whose normal is along the optical axis [16]. Light transmitted perpendicularly through the platelets therefore showed no birefringence. The handedness of each crystal was determined by measuring its natural circular dichroism, which is shown in Fig. 1 together with the absorption and the magnetic circular dichroism. Within the experimental relative accuracy for the latter measurement ($\approx 5\%$), magnetic circular

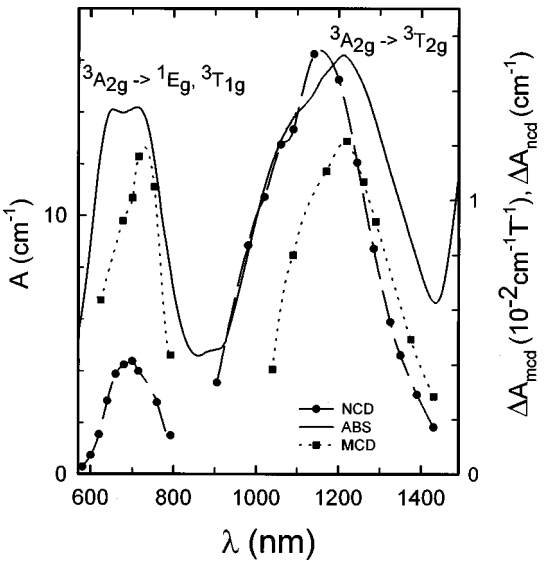

FIG. 1. Axial absorption, natural circular dichroism, and magnetic circular dichroism of an $(-)\alpha$-$NiSO_4\cdot 6H_2O$ crystal at room temperature. Dashed lines are only meant to guide the eye.

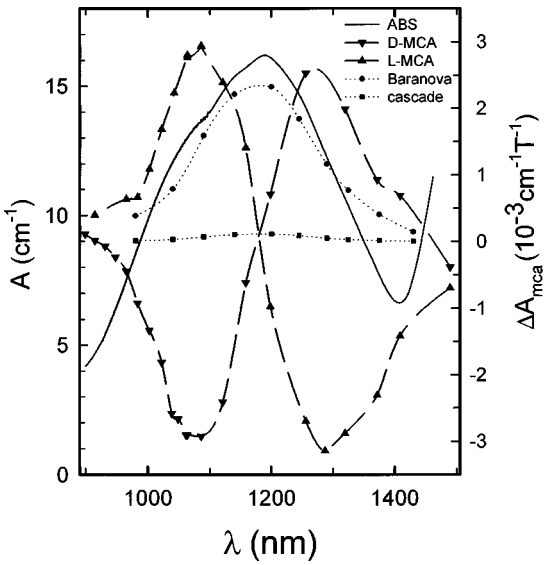

FIG. 3. Absorption (solid line) and magnetochiral absorption anisotropy of left- (L) and right- (D) handed α-$NiSO_4\cdot 6H_2O$ crystals (triangles). Dashed lines are only meant to guide the eye. Also shown are the calculated cascaded MCA effect (squares) and the prediction for MCA on the basis of the Baranova model Eq. (9) (circles).

dichroism was found to be the same for the two classes of crystals. Where comparison is possible, the results in Fig. 1 are in reasonable agreement with literature values [14,15]. From Fig. 1 it can be seen that the ratio of NCD over absorption is nearly constant across the transition, but that the MCD does not have a derivative line shape, so that the simple Baranova model that led to Eq. (9) does not strictly apply here.

Figure 2 shows the experimental setup to specifically measure magnetochiral anisotropy in absorption. Sample (S) consists of a cleaved platelet of α-$NiSO_4\cdot 6H_2O$ of a typical thickness about 0.6 mm, with its optical axis parallel to the externally applied magnetic field. The sample is illuminated with filtered (F), unpolarized light from an incandescent lamp (L) through a multimode optical quartz fiber (diameter

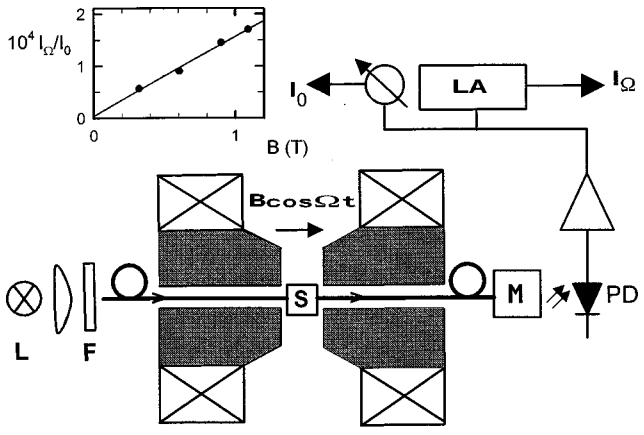

FIG. 2. Schematic setup to detect magnetochiral anisotropy in absorption, consisting of sample (S), an incandescent lamp (L) coarsely filtered by a color filter (F), multimode optical quartz fibers, a monochromator (M) with a photodiode (PD), and a lock-in amplifier (LA). Inset shows the magnetic field dependence of the MCA at $\lambda = 1066$ nm for a right-handed crystal. Straight line is a linear regression fit through the data points.

1 mm, numerical aperture 0.38). It was checked that the light incident on the sample was completely unpolarized. A similar fiber collects the transmitted light, from which specific wavelengths are selected by a monochromator (M) and detected by an InGaAs photodiode. The magnetic field is alternated at a frequency $\Omega = 0.9$ Hz and the transmitted intensity modulation is phase-sensitively detected at Ω by a lock-in amplifier (LA). As discussed above [Eq. (11)], the ratio between the modulated intensity and the static intensity is equal to $\Delta A_{\mathrm{MCA}} LB$, where $\Delta A_{\mathrm{MCA}} = [\gamma'' k^2 - \beta'' k \tanh(\alpha'' k^2 L/n')]/\sqrt{2} n'$. The inset of Fig. 2 gives a typical result of this setup, showing the existence of MCA and its expected linear magnetic field dependence.

Figure 3 shows the experimental spectra for ΔA_{MCA} for two crystals of opposite handedness, proving, within the experimental accuracy, the essential characteristic of MCA that ΔA_{MCA} should be of opposite sign for the two enantiomers. It was checked that reversing the direction of the optical axis of the crystals does not change the MCA and that the effect does not depend on the intensity of the light. Also shown is the cascaded MCA calculated from the second term in Eq. (11), using the observed natural and magnetic circular dichroism from Fig. 1. From both the magnitude and the line shape of this calculated cascaded contribution to the MCA, it is clear that α-$NiSO_4\cdot 6H_2O$ shows predominantly the pure effect. The prediction for MCA on the basis of the Baranova model is also shown in Fig. 3, although the MCD of α-$NiSO_4\cdot 6H_2O$ does not fulfill the validity requirements for this model. The line shape is evidently not correct, but the predicted magnitude agrees well with the experimental results. This simple model therefore seems to be useful to find order-of-magnitude estimates of MCA. A detailed analysis of our result in terms of the molecular theory for MCA by Barron and Vrbancich [13] is beyond the scope of the present paper.

Having now firmly established the existence of MCA in the optical properties of a solid state medium, it appears worthwhile to consider the existence of MCA in other physical properties of chiral systems in a magnetic field that involve (quasi)momentum, like electronic transport, heat conduction, etc. Furthermore, our results should give new impetus to the search for inverse magnetochiral anisotropy [17]. This predicted but never observed effect would imply the generation of a magnetization in a chiral medium by *unpolarized* light, the sign of which should depend on the handedness of the medium.

In conclusion, we have observed magnetochiral anisotropy in the optical absorption of chiral crystals. Analysis shows that we are dealing with a pure effect, but that also cascaded effects could occur in other materials.

We gratefully acknowledge H. Krath for technical assistance, Tamara Docters for crystal growth, and B. van Tiggelen and P. Wyder for a critical reading of the manuscript. Professor Wagnière kindly made his results available to us prior to publication. The Grenoble High Magnetic Field Laboratory is a ''laboratoire conventionné aux universités UJF et INP de Grenoble.''

[1] L. D. Landau, E. M. Lifshitz, and L. P. Pitaevski, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984).
[2] M. P. Groenewege, Mol. Phys. **5**, 541 (1962).
[3] D. L. Portigal and E. Burstein, J. Phys. Chem. Solids **32**, 603 (1971).
[4] N. B. Baranova, Yu. V. Bogdanov, and B. Ya. Zeldovich, Opt. Commun. **22**, 243 (1977).
[5] N. B. Baranova and B. Ya. Zeldovich, Mol. Phys. **38**, 1085 (1979).
[6] G. Wagnière and A. Meier, Chem. Phys. Lett. **93**, 78 (1982).
[7] G. Wagnière, Chem. Phys. Lett. **110**, 546 (1984).
[8] G. Wagnière and A. Meier, Experientia **39**, 1090 (1983).
[9] See, e.g., *Physical Origin of Homochirality in Life*, edited by D. B. Cline (AIP, New York, 1996).
[10] V. A. Markelov, M. A. Novikov, and A. A. Turkin, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 404 (1977) [JETP Lett. **25**, 378 (1977)].
[11] G. L. J. A. Rikken and E. Raupach, Nature (London) **390**, 493 (1997).
[12] P. Kleindienst and G. H. Wagnière, Chem. Phys. Lett. **288**, 89 (1998).
[13] L. D. Barron and J. Vrbancich, Mol. Phys. **51**, 715 (1984).
[14] K. Stadnicka, A. M. Glazer, and M. Koralewski, Acta Crystallogr., Sect. B: Struct. Sci. **B43**, 319 (1987), and references therein.
[15] A. J. McCaffery, P. J. Stephens, and P. N. Schatz, Inorg. Chem. **6**, 1614 (1967); and D. J. Hamm and A. F. Schreiner, Chem. Phys. Lett. **32**, 322 (1975).
[16] *Handbook of Chemistry and Physics*, 55th ed., edited by R. C. Weast (CRC Press, Cleveland, 1975); and *Crystal Structure Data of Inorganic Compounds*, edited by W. Pies and A. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 7, Pt. b (Springer, Berlin, 1982).
[17] G. Wagnière, Phys. Rev. A **40**, 2437 (1989).