

X-Ray Magnetochiral Dichroism: A New Spectroscopic Probe of Parity Nonconserving Magnetic Solids

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We report the first experimental detection of x-ray magnetochiral dichroism in magnetoelectric Cr_2O_3 . This dichroism, which does not require any polarized x-ray beam, is related to the time-reversal *odd* part of the optical activity tensor dominated by electric dipole-electric quadrupole $E1E2$ interference terms. The experiments were carried out using either a single crystal or a powdered pellet required to grow a *single* antiferromagnetic domain by magnetoelectric annealing. This new element (edge) specific spectroscopy offers unique access to the atomic *orbital* anapole moment Ω_z^- .

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Natural optical activity (OA) was discovered in the visible by Arago [1] early in the 19th century. In the x-ray range, OA has long been ignored but x-ray *natural* circular dichroism (XNCD) has now been detected in quite a few noncentrosymmetric crystals [2–5]. Unlike *magneto-optical* effects [e.g., Faraday rotation, magnetic circular dichroism (MCD), magnetic linear dichroism (MLD)] which refer to electric dipole transitions, the transitions related to OA mix multipole moments of opposite parity and thus requires *odd space parity*. By tradition, time-reversal *even* OA properties such as XNCD are called *natural*, whereas time-reversal *odd* OA properties are called “non-reciprocal.” This is precisely where one should be very careful not to confuse *nonreciprocal* OA with magneto-optical effects which are also time-reversal odd but have a different origin. In optics, the existence of *nonreciprocal birefringence* was questioned for approximately 30 years until Krichevstov *et al.* [6] finally discovered in 1993 the nonreciprocal reflectivity of a Cr_2O_3 single crystal below the Néel temperature. In the x-ray range, we already reported recently the observation of a *nonreciprocal* x-ray magnetic linear dichroism (XMLD) for a Cr doped V_2O_3 single crystal in which inversion symmetry was broken by magnetoelectric ordering [7]. We introduce below another nonreciprocal effect which we called *x-ray magnetochiral dichroism* (XM χ D) by analogy with a long expected optical effect [8–10] that was finally observed in 1997 in the visible by Rikken and Raupach [11]. It will be shown that, unlike XNCD which requires single crystals, XM χ D can be detected in powders.

In the optical theory of refringent scattering, OA is associated with a complex *gyration* tensor $\zeta_{\alpha\beta\gamma}^*$ which mixes electric (E) or magnetic (M) multipole components of opposite parity. In the x-ray range, $\zeta_{\alpha\beta\gamma}^*$ is largely dominated by electric dipole-electric quadrupole $E1E2$ interference terms. Recall that, in core spectroscopies, magnetic dipole ($M1$) transitions are forbidden and the

$E1 \cdot M1$ interference terms (responsible for OA in optics) vanish or contribute to second order effects [2,12]. In short, *natural* OA refers to the anti-Hermitian *imaginary part* [13,14]: $\zeta_{\alpha\beta\gamma}' = \text{Re}(E1_\alpha E2_{\beta\gamma}) - \text{Re}(E1_\beta E2_{\alpha\gamma})$ which has *even* time-reversal symmetry as required to induce a differential absorption of light [10,13]. Nonreciprocal OA will refer to the Hermitian *real part*: $\zeta_{\alpha\beta\gamma} = \text{Im}(E1_\alpha E2_{\beta\gamma}) + \text{Im}(E1_\beta E2_{\alpha\gamma})$ which has *odd* time-reversal symmetry [10,13]. For each component of the Stokes polarization vector, there is thus a specific dichroism $\Delta\sigma$ related to OA [14]. For x rays propagating along the z direction, (i) $S_0 \Rightarrow$ nonreciprocal XM χ D: $\sigma^{I_0}(H^+) - \sigma^{I_0}(H^-) \propto [\zeta_{yyz} + \zeta_{xxz}]$; (ii) $S_1 \Rightarrow$ nonreciprocal XMLD: $\sigma^{90^\circ}(H^\pm) - \sigma^{0^\circ}(H^\pm) \propto [\zeta_{yyz} - \zeta_{xxz}]$; (iii) $S_2 \Rightarrow$ nonreciprocal (Jones) cross XMLD: $\sigma^{135^\circ}(H^\pm) - \sigma^{45^\circ}(H^\pm) \propto 2\zeta_{xyz}$; (iv) $S_3 \Rightarrow$ XNCD: $\sigma^L - \sigma^R \propto 2\zeta_{xyz}'$.

Hereafter, we will focus on XM χ D which *does not require any polarized incident x-ray beam* since it is a property of the Stokes component S_0 . Magnetoelectric (ME) solids are good candidates to detect it since the magnetoelectric tensor is *odd* with respect to parity (P) and time reversal (Θ) but is left invariant in the product $P\Theta$ [15]. Up to 58 Shubnikov space-time groups are compatible with the linear ME effect [16] but we will see below that only 31 are compatible with XM χ D. The generic ME example is Cr_2O_3 : it has a centrosymmetric corundum structure (space group: $R\bar{3}c$) but a noncentrosymmetric $\bar{3}m'$ *space-time* group below the Néel temperature. In antiferromagnetic (AFM) Cr_2O_3 , the easy magnetization direction is along the trigonal axis \mathbf{c} and the magnetoelectric tensor is *uniaxial*. Since $\zeta_{xxz} = \zeta_{yyz}$, the nonreciprocal XMLD (S_1) should vanish for an x-ray beam propagating along \mathbf{c} . In Cr_2O_3 the spin moments can order in either one of two 180° domains which differ because the Cr spin moments have opposite direction with respect to the arrangement

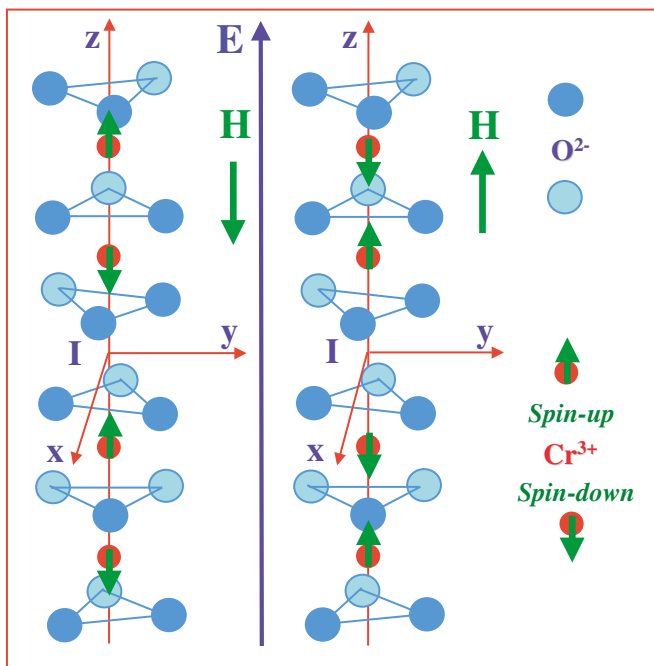


FIG. 1 (color). Schematic representation of the two 180° AFM domains grown by ME annealing with (left panel) antiparallel and (right panel) parallel electric (E) and magnetic (H) fields.

of the oxygen ligands: such domains can only be transformed in each other by a time-reversal operation (see Fig. 1). In equidomain states, there is no ME effect nor any XM χ D. *Magnetolectric annealing* makes it possible to grow single domain states and to switch from one domain to the other: it consists of heating the crystal in the paramagnetic state far above the Néel temperature and of applying simultaneously along the c axis a modest electric field E (5 kV/cm) plus a weak magnetic field H (± 0.5 T) before cooling down the crystal well below the phase transition ($T = 50$ K $\ll T_N = 310$ K). Depending on whether E and H are *parallel* or *antiparallel*, the free energy of the system is different and a single domain of well-characterized sign will grow [17]. The electric field was systematically switched off during the XM χ D measurements. Our crystal was cut parallel to the (001) plane and the incident x-ray beam was aligned parallel to the c axis.

For highly absorbing crystals, x-ray absorption near-edge structure (XANES) spectra are most conveniently recorded in the fluorescence excitation mode using a backscattering configuration [14], the detector being directly inserted inside the cryomagnet containing the sample [18]. Since XM χ D is an intrinsic property of S_0 , one should minimize any residual contribution of polarization dependent dichroism. For a *uniaxial* magnetic system such as Cr_2O_3 , it is most convenient to use a circularly or elliptically polarized x-ray beam propagating along the optical axis c , and to add incoherently spectra recorded with orthogonal polarization: $F_0 = F[RCP] + F[LCP]$. For a biaxial system featuring some magnetic anisotropy in the $\{x, y\}$ plane, it would have been nec-

essary to rotate the crystal around the c axis and to add the spectra recorded at $\{0^\circ, 45^\circ, 90^\circ, \text{ and } 135^\circ\}$ just as for XNCD experiments on biaxial crystals [5]. XM χ D spectra were simply calculated from F_0 spectra recorded with the sample either in equidomain states or in one single domain grown by ME annealing. Although the experiment looks trivial, it proved to be delicate because a fairly high angular beam stability ($< 0.1 \mu\text{rad}$) is required over long periods of times since inverting the domains by ME annealing is very time consuming. The beam stability was thus carefully monitored for each individual scan using an “internal standard” reference sample. XM χ D is nevertheless much more demanding from the beam stability than nonreciprocal XMLD in which the dichroism is measured for each data point, taking advantage of the fast $\pi \leftrightarrow \sigma$ flipping rates that can be achieved with a quarter-wave plate.

The Cr K -edge XM χ D spectra displayed in Fig. 2 were obtained by collecting XANES spectra *after* magnetolectric annealing but on subtracting — as reference — XANES spectra recorded with the crystal heated up to 370 K and

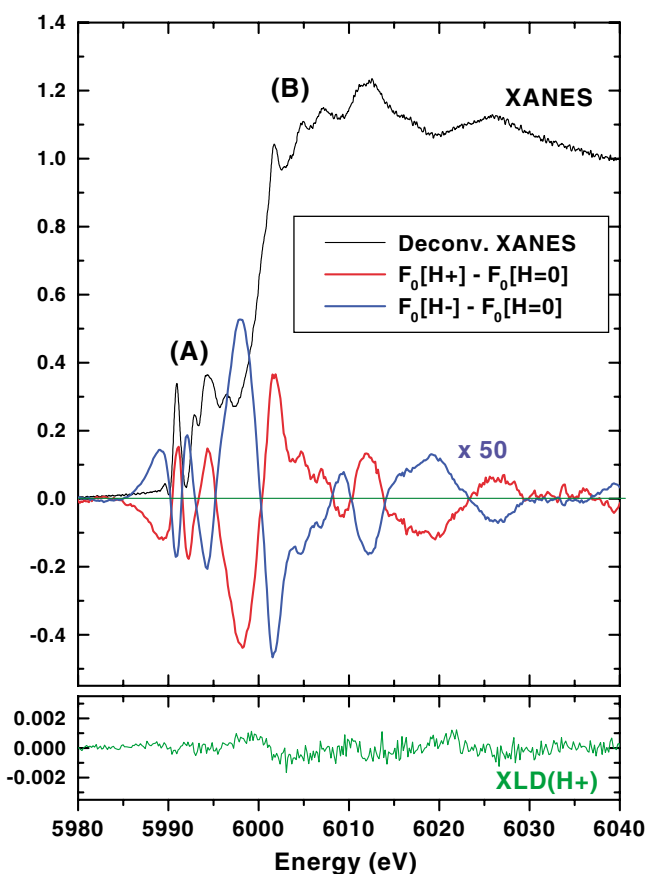


FIG. 2 (color). XM χ D spectra of a (001) Cr_2O_3 single crystal for $k \parallel c \parallel E \parallel H$. Equidomain states were taken as reference. A numerically deconvolved XANES spectrum of the same crystal in equidomain states is shown: pre-edge structures (A) can be assigned to $1s \rightarrow \{3d, 4p\}$ transitions; near-edge structures (B) to $1s \rightarrow \{nd, mp\}$ shape resonances. The bottom trace reproduces the measured linear dichroism spectrum including both reciprocal and nonreciprocal parts for domain $H(+)$.

cooled down to 50 K *without* magnetoelectric annealing so that the system should have returned to nearly equidomain states. The nonreciprocal nature of XM χ D is nicely illustrated by the inverted sign of the XM χ D spectra obtained when single domains of opposite time reversality are grown by ME annealing. A numerically deconvolved XANES spectrum recorded in equidomain states is also shown; the price to be paid for its improved energy resolution is an artificial increase of the noise level [19]. The uniaxial character of the magnetic structure is proved by the lack of significant structure in the linear dichroism spectrum (XLD) also reproduced in Fig. 2; the weak residual signatures shown result from a never perfect alignment.

It was very attractive to try to record next the XM χ D spectrum from a powdered pellet of Cr₂O₃. Recall that, in the early 1960s, Al'shin and Astrov [20] measured the linear ME effect of a powdered sample of Cr₂O₃ and reported a reduction factor 1:3 with respect to the same measurement performed on a single crystal. Such a reduction factor is fully consistent with the theory of the magnetoelectric effect [21]. As shown in Fig. 3, the XM χ D spectra recorded with the powdered sample and the single crystal look fairly similar but differ by an approximately 1:6 scaling factor. Such a larger reduction factor compared to the linear ME effect was not unexpected since, in the case of the paramagnetochoiral effect investigated by Barron and Vrbancich [10], a scaling factor 1:5 was derived which is consistent with the different natures of the tensor properties associated with the ME effect and the nonreciprocal OA. One may explain our slightly lower scaling factor by arguing that the ME annealing process is less effective in a powder than in a crystal [20]. Although the maximum amplitude of the dichroism measured with a powdered pellet is only of the order of 0.26%, Fig. 3 shows that such a small effect can well be measured with a very good *S/N* ratio at third generation synchrotron radiation sources. Note that Fig. 3 displays “full” XM χ D spectra, i.e., differences between XANES spectra recorded with single domains of opposite time reversality.

Since there is no *ab initio* code yet available to simulate XM χ D spectra, we tried to exploit an edge selective XM χ D sum rule. Recall that an XNCD sum rule had already been derived [12,22] which gave access to a *local* effective operator mixing orbitals of different parity (e.g., the 3*d*(Cr) and 4*p*(Cr) orbitals). This approach has recently been extended to the case of XM χ D [23]:

$$\begin{aligned} \Sigma_{E1E2} &= \int_{\text{edge}} \frac{\sigma_{E1E2}(\omega)}{(\hbar\omega)^2} d(\hbar\omega) = \frac{8\pi^2\alpha_0}{\hbar c} (2\ell_c + 1) \\ &\times \sum_{\ell=\ell_c \pm 1, \ell'=\ell \pm 1} D_\ell Q_{\ell'} a_{\ell'}^1(\ell_c, \ell) b^1(\mathbf{k}) \\ &\times \langle g | [\Omega_z^-]^{\ell \leftrightarrow \ell'} | g \rangle, \end{aligned}$$

in which $\ell_c = 0$ for a *K*-edge absorption spectrum, D_ℓ and $Q_{\ell'}$ are the dipole and quadrupole radial integrals associated with 4*p* and 3*d* final states, whereas $a_{\ell'}^1$ and b^1 are tabulated numerical factors which depend on the nature

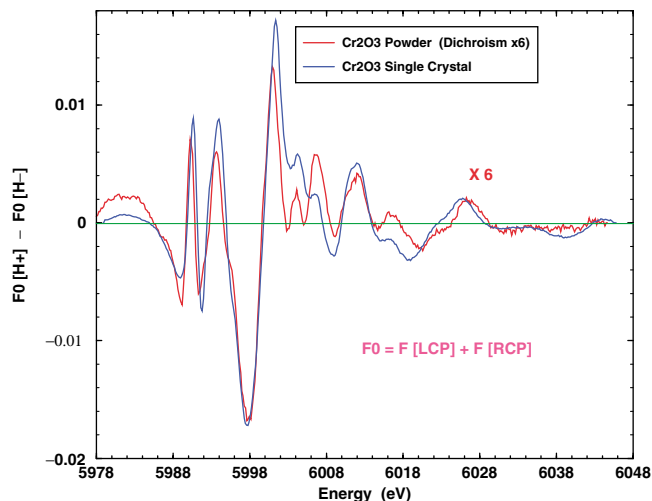


FIG. 3 (color). XM χ D spectra recorded with a single crystal and a powdered pellet for $\mathbf{k} \parallel \mathbf{E} \parallel \mathbf{H}$. Differential absorption spectra refer to the 180° domains grown by magnetoelectric annealing.

of the final state and on the experimental geometry, respectively. Interestingly, the operator $\Omega_z^- = i[\mathbf{n}, \mathbf{L}^2]/2$ describing the orbital mixing in the ground state *g* was identified with the *orbital anapole moment* [24].

A classical picture for anapoles was proposed long ago by Zel'dovich [25]: a toroidal solenoid generating an annular magnetic field $H_a(\mathbf{r})$ also produces an axial current $J_z(\mathbf{r})$ which has the peculiarity to be *odd* with respect to both parity and time reversal. The (toroid) anapole moment is the rms radius of this current $J_z(\mathbf{r})$. In solid state physics, such annular magnetic fields can be associated with either spin or orbital currents. That a spin anapole is inherently *magnetoelectric* is illustrated in Fig. 4. In the presence of a *magnetic* field *H*, the energy of each spin carrier (electron) depends on its location on the annular orbit on which the electrons are constrained: thus the electron distribution is no longer uniform and induces an *electric* polarization *P* orthogonal to *H*. This classic picture could be extended implicitly to orbital anapoles as well.

Not all ME groups admit the anapole moment as an irreducible representation: it was established by Ascher

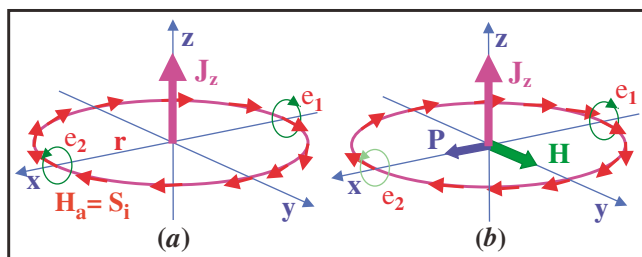


FIG. 4 (color). Classical picture for a ME spin anapole. (a) No external magnetic field: the charged spin carrier (electron) distribution is uniform on the annular orbit. (b) With the external magnetic field *H*: since electrons e_1 and e_2 no longer have the same energy, the electron distribution is not uniform and induces an electric polarization *P* orthogonal to *H*.

and others [26,27] that 31 Shubnikov groups satisfy this condition and thus make it possible to detect $\text{XM}\chi\text{D}$ spectra. As a puzzling paradox, the magnetic group $\bar{3}'m'$ is not one of them. In fact, this universally cited magnetic group was derived from early neutron diffraction data [28] and refers basically to the *spin* configurations of Fig. 1. Group theory implies that the corresponding *spin anapole* moment should vanish. There was, however, no experimental evidence as yet that *orbital* magnetism did or did not exist in Cr_2O_3 : our $\text{XM}\chi\text{D}$ signal reveals that there should exist an *orbital* anapole moment but it cannot tell us anything about the spin anapole moment. Our experiment nevertheless implies that the *overall* magnetic symmetry (including orbital + spin magnetism) has to be lower than $\bar{3}'m'$. It is our suggestion that the true space-time symmetry is most probably only $\bar{3}'$ since this ME group admits the anapole moment Ω_z^- as irreducible representation. The rather small orbital anapole moment (0.02 a.u.) which we derived from the $\text{XM}\chi\text{D}$ sum rule would suggest that the electronic structure is only affected by *weak* perturbations of lower symmetry. Our deductions match perfectly the conclusions of a recent theory developed by Muto *et al.* [29]: these authors had to introduce an odd parity, trigonal *twist field* of the successive layers of oxygen atoms located above and below the metal in order to explain the nonreciprocal polarization dependence of the second harmonic generation (SHG) spectra recorded with a Cr_2O_3 single crystal cooled below the Néel temperature [30]. Such a C_3 perturbation indeed would lower the overall magnetic symmetry to $\bar{3}'$. We found recently that Vallade [31], who was interested in magnetic SHG experiments, had already argued in 1968 that the local symmetry at the Cr atoms should be C_3 and that the magnetic group could not be $\bar{3}'m'$. Finally, it is worth noting that ME measurements cannot discriminate between spin and orbital anapole contributions and do not seem to be accurate enough to detect such small perturbations.

In conclusion, $\text{XM}\chi\text{D}$ appears as an attractive, element selective, new probe of parity nonconserving magnetic solids. It offers an elegant way to unravel hidden space-time symmetry properties of a ME crystal. Unlike XNCD spectra which require single crystals, $\text{XM}\chi\text{D}$ spectra can be measured with *powdered* samples at the expense of a 1 : 5 amplitude reduction factor.

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