Magneto-optical effect in the weak ferromagnets LaMO$_3$ (M= Cr, Mn, and Fe)

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It is shown that antiferromagnetic spin order coupled through the spin-orbit interaction with the lattice distortion can lead to a nonvanishing ferromagnetic component of the orbital magnetization and strong optical nonreciprocity in transition-metal perovskite oxides with orthorhombic structure. This magneto-optical effect is expected to display very peculiar orientation dependence and disappears for particular directions of the antiferromagnetic spin magnetization. Based on the first principles band structure calculations, elements of the conductivity tensor relevant for this phenomenon are evaluated for the series of LaMO$_3$ oxides with M=Cr, Mn, and Fe. [S0163-1829(97)06513-2]

Magneto-optical properties of various compounds have been a subject of very intensive study for the past couple of decades due to their potential applicability in the technology of high density data storage. Traditionally, the range of materials considered in this field was essentially restricted to ferro- and ferrimagnets. For the conventional antiferromagnets, the magneto-optical effect is averaged out as a consequence of the time-reversal symmetry (T), though destroyed microscopically, but restored on the macroscopic scale. However, for several classes of the antiferromagnetic (AFM) compounds T remains broken macroscopically, suggesting a nonreciprocity in optical phenomena.[1,2] Broad interest in this problem has been attracted recently in connection with spontaneous violation of T predicted by so-called anyon models of high-T_c superconductivity and discovery of the nonreciprocal optical effects in magnetoelectric Cr_2O_3.[3]

One of the modes of T violation in antiferromagnets gives rise to the phenomenon of the weak ferromagnetism.[1] Such breakdown is quite typical for many distorted perovskite transition-metal oxides.[4] Intuitively, the relationship between weak ferromagnetism and nonreciprocal optical behavior is straightforward: the net magnetic moment results in the famous Faraday and Kerr rotations, but the effect is believed to be small and proportional to the ''weak'' ferromagnetic magnetization.[5] However, such an intuitive picture is very incomplete. In the present work we show that local noncollinearity between spin and orbital magnetic moments proposed recently[6,7] for the ground state of compounds with relatively low symmetry is the crucial aspect of optical nonreciprocity in the weak ferromagnets.

First, we propose a simple scenario of this noncollinearity stressing the local environment of magnetic sites and interatomic spin coupling. Generally, the orbital magnetic moment at the site i is related with the direction of the spin magnetization $\mathbf{e}=(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta)$ as $\mathbf{M}_L^i=\hat{\mathcal{L}}^i\mathbf{e}$ and canted from $\mathbf{e}$ by the angle

$$\cos\Psi=(\mathbf{e},\hat{\mathcal{L}}^i\mathbf{e})/(\hat{\mathcal{L}}^i\mathbf{e},\hat{\mathcal{L}}^i\mathbf{e})^{1/2}. \quad (1)$$

$\hat{\mathcal{L}}^i$ can be found through the real space expansion[8] from which we hold only the local term:

$$\mathcal{L}^i_{\alpha\beta}\simeq-\frac{\xi}{2\pi}\sum_{s=\pm1} s\ \mathrm{Im}\int_{-\infty}^{E_F}dE\,\mathrm{Tr}_L\{L_\alpha G^s_{ii}L_\beta G^s_{ii}\}, \quad (2)$$

where G^s_{ii} is the site-diagonal block of the scalar-relativistic Green's function with the spin s, L_α are Cartesian components of the angular momentum, ξ is the spin-orbit interaction (SOI) parameter, and Tr_L runs over the orbital indices.

The simplest example when $\mathbf{e}$ and $\mathbf{M}_L^i$ can be noncollinear is a uniaxial specimen. Then, $\hat{\mathcal{L}}^i$ is defined by its longitudinal ($\mathcal{L}^i_\parallel$) and two transversal ($\mathcal{L}^i_\perp$) diagonal matrix elements and Eq. (1) becomes $\cos\Psi=(\sin^2\theta+r\cos^2\theta)/(\sin^2\theta+r^2\cos^2\theta)^{1/2}$, where $r=\mathcal{L}^i_\perp/\mathcal{L}^i_\parallel$ is the anisotropy of the orbital magnetization. If $r\neq1$, spin and orbital magnetic moments are collinear only in the high symmetry directions, $\theta=0°$ and $\theta=90°$, one of which corresponds to the ground state configuration due to the energy of perpendicular magnetocrystalline anisotropy (MA) proportional to $\sin^2\theta$. More generally, the collinear alignment of $\mathbf{e}$ and $\mathbf{M}_L^i$ is realized when they are parallel to the principal axes of $\hat{\mathcal{L}}^i$. This picture is known and has been considered recently in the context of both magneto-optical properties[9] and magnetic circular x-ray dichroism[10] of uniaxial compounds.

If a crystallographic cell contains several formula units, two factors might become additionally important: (i) orientational modulation, which makes the local directions to be different for different magnetic sites; (ii) interatomic spin coupling, which forbids independent rotation of each spin magnetic moment. Then, the collinearity condition between $\mathbf{e}$ and $\mathbf{M}_L^i$, though existing locally for individual magnetic site, cannot be preserved globally for the lattice built by such sites leading to the noncollinear alignment between spin and orbital magnetic moments in the ground state.

Both factors are present in the antiferromagnetic insulators LaMO$_3$ with M= Cr, Mn, and Fe. All of them have the orthorhombic D^{16}_{2h} structure characterized by substantial rotations of MO$_6$ octahedra relative to each other (a kind of ''orientational modulation'') and show strong Heisenberg coupling between spin magnetic moments leading to the AFM spin ordering of A type when M= Mn and G type when M= Cr or Fe (Fig. 1). The noncollinearity of the spin magnetic moments, arising from the antisymmetric

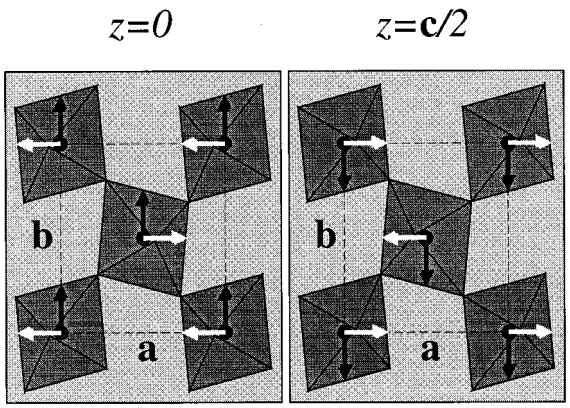

FIG. 1. Orientation of the MO_6 octahedra in two neighboring **ab** planes. Directions of the spin magnetic moments in $LaMnO_3$ and $LaFeO_3$ are shown by black and white arrows.

Dzyaloshinsky-Moriya (DM) exchange interaction, is suppressed by the strong Heisenberg term.[6,11] Thus, as a guideline for numerical calculations we employ a perturbative approach starting from the collinear spin arrangement.

Using the LMTO-Green's function technique based on the local-spin-density approximation,[12] and experimental parameters for the crystal structure,[13,14] we estimate $\hat{\mathcal{L}}^i$ characterizing the distribution of the orbital magnetization at the transition metal sites. Results are shown in Table I. Since inversion is only one local symmetry operation associated with the transition metal site, all elements of $\hat{\mathcal{L}}^i$ are generally nonvanishing. The relative orientation of **e** and $\mathbf{M}_L^i$ has to do with atomic Hund's third rule: Ψ is close to 180° (**e** and $\mathbf{M}_L^i$ are antiparallel) and 0° (**e** and $\mathbf{M}_L^i$ are parallel) for the less than half- and more than half-filled $3d$ states in $LaCrO_3$ and $LaFeO_3$. In $LaMnO_3$, which has the nearly half-filled $3d$ shell and largely distorted crystal structure, Ψ varies in the whole interval from 0° to 180°.

TABLE I. Local effect of the SOI on the orbital magnetization developed at the transition metal site: matrix $\hat{\mathcal{L}}^i$ given by Eq. (2) relative to the orthorhombic axes **a**, **b**, and **c** (in μ_B), and corresponding range of variations for the angles between **e** and $\mathbf{M}_L^i$ given by Eq. (1) (in degrees).

M	$\hat{\mathcal{L}}^i$	$\Psi_{\min}/\Psi_{\max}$
Cr	$\begin{pmatrix} -0.0377 & -0.0043 & 0.0002 \\ -0.0043 & -0.0396 & -0.0011 \\ 0.0002 & -0.0011 & -0.0404 \end{pmatrix}$	174 180
Mn	$\begin{pmatrix} -0.0027 & 0.0102 & 0.0006 \\ 0.0102 & -0.0112 & -0.0027 \\ 0.0006 & -0.0027 & -0.0021 \end{pmatrix}$	0 180
Fe	$\begin{pmatrix} 0.0499 & -0.0002 & -0.0006 \\ -0.0002 & 0.0527 & -0.0026 \\ -0.0006 & -0.0026 & 0.0503 \end{pmatrix}$	0 4

In order to obtain the net orbital magnetic moment given by the averaged matrix $\hat{\mathcal{L}}=\Sigma_{i=1}^{4}\hat{\mathcal{L}}^i$ we note that each of the four formula units in D_{2h}^{16} can be generated from that at the origin, say $i=1$, by the symmetry operations: (1) $\{E|\mathbf{0}\}$, (2) $\{C_{2\mathbf{a}}|\mathbf{a}/2+\mathbf{b}/2\}$, (3) $\{C_{2\mathbf{b}}|\mathbf{a}/2+\mathbf{b}/2+\mathbf{c}/2\}$, and (4) $\{C_{2\mathbf{c}}|\mathbf{c}/2\}$. In the notation $\{p|\mathbf{t}\}$, p is the point group operation, **t** is the translation, and $C_{2\alpha}$ is the 180° rotation around the orthorhombic axis α ($\alpha=\mathbf{a}$, **b**, and **c**).

A straightforward application of these symmetry operations to Eq. (2) in the case of ferromagnetic (FM) spin ordering yields

$$\hat{\mathcal{L}}^{\mathrm{F}}=4\begin{pmatrix} \mathcal{L}^1_{\mathbf{aa}} & 0 & 0 \\ 0 & \mathcal{L}^1_{\mathbf{bb}} & 0 \\ 0 & 0 & \mathcal{L}^1_{\mathbf{cc}} \end{pmatrix}, \tag{3}$$

as expected for the orthorhombic compound.

For the AFM spin ordering of A type, the symmetry operations (3) and (4) appear in combination with permutation of the spin indices $s\rightarrow -s$ in the scalar-relativistic Green's function. Then,

$$\hat{\mathcal{L}}^{A}=4\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \mathcal{L}^1_{\mathbf{bc}} \\ 0 & \mathcal{L}^1_{\mathbf{cb}} & 0 \end{pmatrix}, \tag{4}$$

and the net orbital magnetic moment is $\mathbf{M}_L=4(0,\mathcal{L}^1_{\mathbf{bc}}\cos\theta,\mathcal{L}^1_{\mathbf{cb}}\sin\theta\sin\phi)$. Therefore, $\mathbf{M}_L\|\mathbf{c}$ for $\mathbf{e}\|\mathbf{b}$, $\mathbf{M}_L\|\mathbf{b}$ for $\mathbf{e}\|\mathbf{c}$, and $\mathbf{M}_L=0$ for $\mathbf{e}\|\mathbf{a}$.

Similar calculations for the G-type AFM spin ordering, when the symmetry operations (2) and (4) are conjugated with $s\rightarrow -s$, give

$$\hat{\mathcal{L}}^{G}=4\begin{pmatrix} 0 & 0 & \mathcal{L}^1_{\mathbf{ac}} \\ 0 & 0 & 0 \\ \mathcal{L}^1_{\mathbf{ca}} & 0 & 0 \end{pmatrix}, \tag{5}$$

and $\mathbf{M}_L=4(\mathcal{L}^1_{\mathbf{ac}}\cos\theta,0,\mathcal{L}^1_{\mathbf{ca}}\sin\theta\cos\phi)$. Then, $\mathbf{M}_L\|\mathbf{c}$ for $\mathbf{e}\|\mathbf{a}$, $\mathbf{M}_L\|\mathbf{a}$ for $\mathbf{e}\|\mathbf{c}$, and $\mathbf{M}_L=0$ for $\mathbf{e}\|\mathbf{b}$.

The operation $s\rightarrow -s$ does not change the MA energy $E_{\mathrm{MA}}=(\mathbf{e},\hat{\tau}\mathbf{e})$,[17] which is an even order effect with respect to the SOI. Therefore, $\hat{\tau}$ has the same form as $\hat{\mathcal{L}}^{\mathrm{F}}$ both for FM and AFM spin ordering, and the easy magnetization direction is one of the **a**, **b**, and **c**.

Thus, using the symmetry arguments based on the local picture for the SOI we have shown that even when the spin magnetic moments are aligned antiferromagnetically, the orbital magnetization can exhibit a nonvanishing ferromagnetic component either in the **bc** plane or in the **ac** plane depending on the type of the spin ordering. This effect coexists with

TABLE II. Initial spin magnetic configuration S, induced orbital magnetic configuration L, angle between spin and orbital magnetic moments in the $M(3d)$ states Ψ (in degrees), and the one-electron magnetic anisotropy energy E_{MA} (in 10^{-5} Ry per formula unit measured from the most stable configuration) as obtained in the first principles band structure calculations.

M	S	L	Ψ	E_{MA}
	$G_{\mathbf{a}}$	Γ_4	173	0.29
Cr	$G_{\mathbf{b}}$	Γ_1	172	0.02
	$G_{\mathbf{c}}$	Γ_2	176	0
	$A_{\mathbf{a}}$	Γ_1	97	2.98
Mn	$A_{\mathbf{b}}$	Γ_4	134	0
	$A_{\mathbf{c}}$	Γ_3	95	2.71
	$G_{\mathbf{a}}$	Γ_4	1	0
Fe	$G_{\mathbf{b}}$	Γ_1	2	0.49
	$G_{\mathbf{c}}$	Γ_2	3	0.71

the antisymmetric DM exchange interaction. Both of them disappear in a higher symmetry. For example, tilting of MO_6 octahedra is a necessary condition for the DM interaction.[15] Without it, two neighboring **ab** planes shown in Fig. 1 become equivalent and the symmetry operation (4) transforms to $\{C_{2\mathbf{c}}|\mathbf{0}\}$. Then, $\mathcal{L}^1_{\mathbf{ac}}=\mathcal{L}^1_{\mathbf{ca}}=\mathcal{L}^1_{\mathbf{bc}}=\mathcal{L}^1_{\mathbf{cb}}=0$ and we have $\mathbf{M}_L=0$ always for the AFM spin ordering.

Appearance of the net orbital magnetization directly affects the propagation of polarized light in the medium.[16] Considering the polar Kerr effect, proportional to the antisymmetric component of conductivity tensor $\hat{\sigma}(\omega)$,[17,18] rotation of the polarization vector of linearly polarized light can be observed in the **c** direction for $\mathbf{e}\|\mathbf{b}(\mathbf{a})$, in the **b**(**a**) direction for $\mathbf{e}\|\mathbf{c}$, and the magneto-optical effect is prohibited when $\mathbf{e}\|\mathbf{a}(\mathbf{b})$ for the antiferromagnetic spin ordering of $A(G)$ type.[19]

Finally, we turn to the first principles calculations where we fix **e** sequentially along **a**, **b**, and **c** directions of the orthorhombic cell and evaluate the responding band structure after including SOI as a pseudoperturbation in the ASA-LMTO method.[20] We would like to stress again that while initial arrangement of the spin magnetic moments was totally collinear, the obtained distribution of the orbital magnetic moments (Table II) is noncollinear and, depending on the interatomic spin coupling and direction of the spin magnetization, belongs to one of the four types compatible with the space group D^{16}_{2h} (Ref. 4): $\Gamma_1(A_{\mathbf{a}}-G_{\mathbf{b}}-C_{\mathbf{c}})$, $\Gamma_2(F_{\mathbf{a}}-C_{\mathbf{b}}-G_{\mathbf{c}})$, $\Gamma_3(C_{\mathbf{a}}-F_{\mathbf{b}}-A_{\mathbf{c}})$, and $\Gamma_4(G_{\mathbf{a}}-A_{\mathbf{b}}-F_{\mathbf{c}})$.[21]

Then, the calculation of the interband optical conductivity is a matter of routine.[22] The diagonal part of $\hat{\sigma}(\omega)$ for the series of $LaMO_3$ has been discussed in Ref. 23. The antisymmetric component $\sigma^A(\omega)$ is shown in Fig. 2. For all compounds the main structure of $\sigma^A(\omega)$ around 4 eV corresponds to the charge-transfer excitations $O(2p)\rightarrow M(3d)$. It is instructive to compare this effect in the weak FM and in a saturated state where the spin magnetic moments are aligned ferromagnetically. A naive estimation for the reduction of $\sigma^A(\omega)$ in the weak FM state based on the assumption that the orbital magnetic moments always rigidly follow the spin ones might be the order of M^{WF}/M^T, where M^T is the magnitude of a magnetic moment and M^{WF} is the weak FM component. For $LaMnO_3$, where $M^T\sim 3.7\mu_B$ and $M^{\mathrm{WF}}\sim 0.1\mu_B$,[6,14] it gives $M^{\mathrm{WF}}/M^T<0.03$. Canting of the orbital moments renormalizes the magnitude of the magneto-optical effect dramatically. In $LaMnO_3$ the ratio of $\mathrm{Im}[\sigma^A(\omega)]$ obtained for the A-type AFM spin ordering with $\mathbf{e}\|\mathbf{b}$ to the one for the FM spin ordering with $\mathbf{e}\|\mathbf{c}$ is only about 0.5 at $\omega\sim 4$ eV. Thus, we expect essentially no difference in the magnitude of the magneto-optical effect in the normal FM and the weak FM states in $LaMO_3$. If the former is reachable for various ferromagnetically ordered films of the hole-doped $LaMnO_3$,[24] experiments for the antiferromagnetically ordered compounds are highly encouraged.

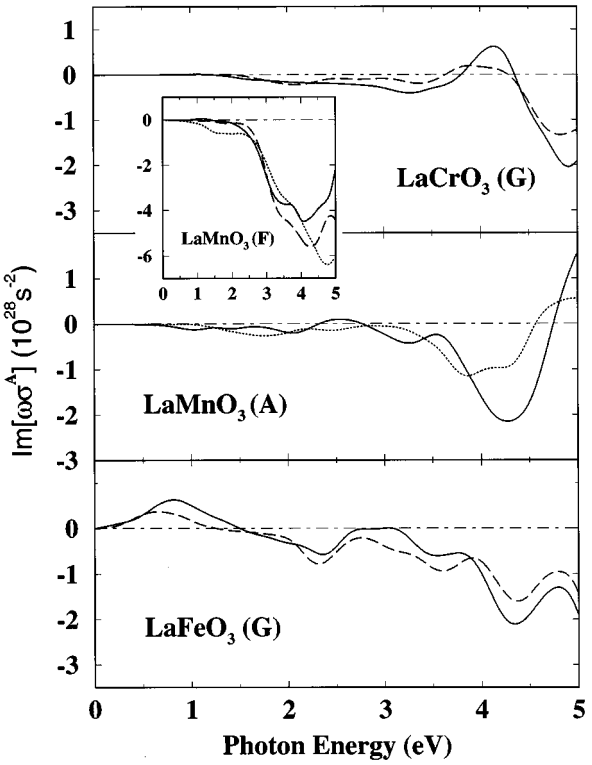

FIG. 2. Antisymmetric part of the conductivity tensor obtained for different magnetic configurations in $LaMO_3$: Γ_1 (dot-dashed), Γ_2 (dashed), Γ_3 (dotted), and Γ_4 (solid). AFM spin configuration used as a starting point is given in parentheses. Results for the FM spin ordering in $LaMnO_3$ are shown in the inset.

The analysis of the MA energy (Table II) shows that Γ_4 is the lowest energy configuration in $LaMnO_3$ and $LaFeO_3$. Thus the nonreciprocal optical rotation is expected in the **c** direction for both compounds. In $LaCrO_3$, two low energy configurations Γ_2 and Γ_1 are nearly degenerate. If the FM component along **a** is allowed in Γ_2, Γ_1 structure is totally AFM and excludes the magneto-optical effect.[25]

To summarize, the noncollinear magnetic ordering imposed by general symmetry rules has a different manifestation for the spin and orbital counterparts. Even if the spin noncollinearity is suppressed, the orbital magnetic moments can remain noncollinear. Appearance of the net orbital magnetization in the regime of weak ferromagnetism leads to the optical nonreciprocity which can be as large as in conventional spin ferromagnets. This is the new example of the

strong coupling between magnetic and lattice degrees of freedom observed in the transition-metal perovskite oxides[26] when this coupling is mediated by the spin-orbit interaction.

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[21] In these notations, the capital letters correspond to the type of the magnetic ordering (antiferro-*A*, *C*, *G* and ferro-*F*) for the **a**, **b**, and **c** projections of the magnetic moments.

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