## Magnetic charge and the magnetoelectricity in hexagonal manganites $RMnO_3$ and ferrites $RFeO_3$

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The magnetoelectric (ME) effect is the phenomenon in which polarization  $\mathbf{P}$  is induced by a magnetic field  $\mathbf{H}$  or magnetization  $\mathbf{M}$  is induced by an electric field  $\boldsymbol{\mathcal{E}}$ . The ME coupling (MEC) between magnetic and electric properties has motivated intense experimental and theoretical investigations in bulk single crystals, thin films, composite layers and organic-inorganic hybrid materials in recent years[1].

The linear ME effect  $\alpha$  is defined as

$$\alpha_{\beta\nu} = \frac{\partial P_{\beta}}{\partial H_{\nu}} \Big|_{\boldsymbol{\mathcal{E}}} = \mu_0 \frac{\partial M_{\nu}}{\partial \mathcal{E}_{\beta}} \Big|_{\mathbf{H}}, \qquad (1)$$

where indices  $\beta$  and  $\nu$  denote the Cartesian directions and  $\mu_0$  is the vacuum permeability. From a theoretical point of view, the linear ME effect can be decomposed into electronic (frozen-ion), ionic (lattice-mediated), and strain-mediated responses [2]. Each term can be further subdivided into spin and orbital contributions based on the origin of the induced magnetization. As the orbital moment is largely quenched on transition-metal sites, most phenomenological and first-principles studies focus on the spin-electronic [6] and the spin-lattice [3, 4] contributions. Following [5], the latter can be written as

$$\alpha^{\text{latt}} \propto Z^{\text{e}} \cdot K^{-1} \cdot Z^{\text{m}} \,, \tag{2}$$

i.e., as a matrix product of the dynamical Born electric charge  $Z^{\text{e}}$ , the inverse force-constant matrix  $K^{-1}$ , and the dynamical magnetic charge  $Z^{\text{m}}$ ,

$$Z_{m\nu}^{\rm m} = \Omega_0 \frac{\partial M_{\nu}}{\partial u_m} \Big|_{\mathcal{E},\mathbf{H},\eta} = \mu_0^{-1} \frac{\partial F_m}{\partial H_{\nu}} \Big|_{\mathcal{E},\eta}, \qquad (3)$$

which is the magnetic analog of the Born charge. Here m is a composite labels for atom and displacement direction,  $u_m$  is the internal displacement,  $F_m$  is the atomic force,  $\Omega_0$  is the unit cell volume and  $\eta$  is a homogeneous strain. Our previous first-principles study has shown that exchange striction acting on noncollinear spin structures induces much larger magnetic charges than when  $Z^m$  is driven by spin-orbit coupling (SOC), providing a promising mechanism for large MECs [7].

The hexagonal manganites  $RMnO_3$  and ferrites  $RFeO_3$ (R=Sc, Y, In, Ho-Lu) shown in Fig. 1 exhibit strong couplings between electric, magnetic and structural degrees of freedom. The transition-metal ions in the basal plane are antiferromagnetically coupled through superexchange so as to form a 120° spin arrangement. There are two types of magnetic orders in  $Mn^{3+}$  that allow a linear MEC to be present, the A<sub>1</sub> phase (P6<sub>3</sub>cm) and the



FIG. 1. Structure of ferroelectric hexagonal  $RMnO_3$  and  $RFeO_3$ .



FIG. 2. The magnetic phases of hexagonal  $RMnO_3$  and  $RFeO_3$ . (a) The  $A_2$  phase has spins on the two  $Mn^{3+}$  layers pointing outward (inward) as a magnetic monopole. (b) The  $A_1$  phase has the  $Mn^{3+}$  spins pointing in the tangential direction, forming a magnetic vortex pattern. The  $A_1$  and  $A_2$  phases only differ by a 90° global rotation of the spins.

 $A_2$  phase (P6<sub>3</sub>c'm'), shown in Fig. 2. In this work, we use first-principles density functional methods to study the transverse magnetic charges, and the spin-lattice and spin-electronic MECs, in hexagonal HoMnO<sub>3</sub>, ErMnO<sub>3</sub>, YbMnO<sub>3</sub>, LuMnO<sub>3</sub> and LuFeO<sub>3</sub>, in the A<sub>1</sub> and A<sub>2</sub> phases, clarifying the conditions under which exchange striction leads to enhanced magnetic charges and anomalously large in-plane spin-lattice ME effects.

As the spins are non-collinearly aligned in the basal plane, the transverse magnetic charges are driven by both SOC and exchange striction. As the exchange-striction strength can exceed the SOC by orders of magnitude in some materials, it is worthwhile to understand the effect of SOC, compared with exchange striction, in  $RMnO_3$ and  $RFeO_3$ . In Table I, we present a selection of our results on the transverse magnetic charges induced with

TABLE I. Transverse magnetic charge components  $Z^{\rm m}$   $(10^{-2}\mu_{\rm B}/{\rm \AA})$ , without SOC and total including SOC, for ErMnO<sub>3</sub> in the A<sub>2</sub> phase and HoMnO<sub>3</sub> in the A<sub>1</sub> phase.

	A <sub>2</sub> phase ErMnO <sub>2</sub>			A <sub>1</sub> phase HoMnO <sub>2</sub>	
	No SOC	Total		No SOC	Total
$Z_{xx}^{\mathrm{m}}(\mathrm{R}_1)$	-21.74	-21.02	$Z_{yx}^{m} Ho_1$	-27.83	-24.45
$Z_{xx}^{\mathrm{m}}(\mathrm{R}_2)$	2.98	5.85	$Z_{xx}^{m}$ Ho <sub>2</sub>	-18.14	-14.70
$Z_{yx}^{\mathrm{m}}(\mathrm{R}_2)$	11.96	11.27	$Z_{yx}^{\mathrm{m}}\mathrm{Ho}_2$	2.87	-0.81
$Z_{xx}^{\mathrm{m}}(\mathrm{Mn})$	-9.79	-6.92	$Z_{yx}^{m}$ Mn	53.47	92.07
$Z_{zx}^{m}(Mn)$	-21.79	-38.43	$Z_{xy}^{m}$ Mn	1.80	-9.79
$Z_{yy}^{\rm m}({\rm Mn})$	32.36	-7.35	$Z_{zy}^{m}$ Mn	47.72	41.08
$Z_{xx}^{\tilde{\mathrm{m}}}(\mathrm{O}_{\mathrm{T}1})$	6.07	5.84	$Z_{ux}^{m}O_{T1}$	27.64	22.46
$Z_{zx}^{\mathrm{m}}(\mathrm{O}_{\mathrm{T}1})$	154.04	149.71	$Z_{xy}^{m}O_{T1}$	-6.86	-7.34
$Z_{yy}^{\mathrm{m}}(\mathrm{O}_{\mathrm{T}1})$	21.72	21.49	$Z_{zy}^{m}O_{T1}$	-229.85	-187.73
$Z_{xx}^{\mathrm{m}}(\mathrm{O}_{\mathrm{T}2})$	18.45	15.80	$Z_{yx}^{m}O_{T2}$	-66.85	-57.11
$Z_{zx}^{\mathrm{m}}(\mathrm{O_{T2}})$	160.49	139.70	$Z_{xy}^{m}O_{T2}$	-25.70	-19.56
$Z_{yy}^{\mathrm{m}}(\mathrm{O}_{\mathrm{T2}})$	-46.09	-47.67	$Z_{zy}^{\tilde{m}}O_{T2}$	-231.43	-192.11
$Z_{xx}^{\mathrm{m}}(\mathrm{O}_{\mathrm{P1}})$	-421.57	-391.56	$Z_{yx}^{m}O_{P1}$	-551.22	-483.14
$Z_{xx}^{\mathrm{m}}(\mathrm{O}_{\mathrm{P2}})$	201.65	214.54	$Z_{xx}^{m}O_{P2}$	461.15	394.63
$Z_{yx}^{\mathrm{m}}(\mathrm{O}_{\mathrm{P2}})$	-354.57	-334.71	$Z_{yx}^{\mathrm{m}}\mathrm{O}_{\mathrm{P2}}$	252.87	183.98

and without SOC, focusing on  $ErMnO_3$  in the  $A_2$  phase and  $HoMnO_3$  in the  $A_1$  phase. It is obvious that the SOC contributions are an order of magnitude smaller for many transverse components.

We then calculate the spin-lattice MEC from Eq. (2) using our computed Born charges, force-constant matrices and magnetic charges. The spin-electronic MECs are calculated using the definition in Eq. (1) with the lattice degrees of freedom frozen. In Fig. 3, we show the transverse MECs  $\alpha_{xx}$  for RMnO<sub>3</sub> and LuFeO<sub>3</sub> in the A<sub>2</sub> phase. In Fig. 3(a), the spin-lattice ME response is one order of magnitude stronger than the SOC induced ME



FIG. 3. The spin-lattice, spin-electronic and the total spin ME constants  $\alpha_{xx}$  of RMnO<sub>3</sub> and LuFeO<sub>3</sub> in the A<sub>2</sub> phase.

TABLE II. Transverse ME constants  $\alpha_{xy}$  (in ps/m) without SOC, and total including SOC, for the A<sub>1</sub> phase HoMnO<sub>3</sub>.

	No SOC	Total
Spin-lattice	-4.88	-9.55
Spin-electronic	-5.35	-5.24
Total spin	-10.23	-14.79

in  $Cr_2O_3$  [8], as a result of the exchange-striction mechanism. Surprisingly, the effect of SOC on the spin-lattice MECs is comparable to the effect of exchange striction, although the SOC acts only as a perturbation to most of the  $Z^{\mathrm{m}}$ . The underlying reason is that the spin-lattice MEC is smaller than expected as a result of a large degree of cancellation between the contributions from different infrared-active modes. Thus, small perturbations to the magnetic charges can lead to large relative changes in the MEC result. From Fig. 3(b) it can be seen that the spin-electronic contribution is not negligible, and it counteracts the ME effect from the spin-lattice channel in  $RMnO_3$ . The total transverse ME effect is summarized in Fig. 3(c). Because of the large SOC effect and the cancellation between the lattice and electronic contributions, the total spin MEC  $\alpha_{xx}$  is ~ 1.2 ps/m in the A<sub>2</sub> phase. In LuFeO<sub>3</sub>, the spin-lattice and the spin-electronic terms are all smaller than in  $RMnO_3$ . However, as the exchangestriction induced spin-lattice MEC term has the opposite sign compared to  $RMnO_3$ , the cancellation induced by the SOC perturbation and the spin-electronic contribution is avoided, so that  $LuFeO_3$  has the largest total spin MEC of  $\sim -3 \,\mathrm{ps/m}$  in the A<sub>2</sub> phase.

For the A<sub>1</sub> phase, we present the MECs for HoMnO<sub>3</sub> in Table II. Unlike the MECs in the A<sub>2</sub> phase RMnO<sub>3</sub>, the spin-lattice, spin-electronic and SOC contributions all have the same sign. As each term contributes  $\sim -5 \text{ ps/m}$ , the spin-total MEC  $\alpha_{xy}$  reaches to  $\sim -15 \text{ ps/m}$ , which is the largest in all of the RMnO<sub>3</sub> and LuMnO<sub>3</sub> materials we studied.

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