PHYSICAL REVIEW B **84**, 020101(R) (2011)

Mechanism of exchange striction of ferroelectricity in multiferroic orthorhombic $HoMnO_3$ single crystals

N. Lee,[1] Y. J. Choi,[1] M. Ramazanoglu,[1] W. Ratcliff II,[2] V. Kiryukhin,[1] and S.-W. Cheong[1]

[1] *Rutgers Center for Emergent Materials and Department of Physics & Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*

[2] *NIST Center for Neutron Research, NIST, Gaithersburg, Maryland 20899, USA*

(Received 21 April 2011; published 1 July 2011)

E-type perovskite magnet $HoMnO_3$ is considered to be a prototype Mn-Mn exchange-striction driven multiferroic. We have grown orthorhombic $HoMnO_3$ single crystals and studied the directional dependence of their electric polarization $\boldsymbol{P}$. The direction of $\boldsymbol{P}$ is not along the crystallographic *a* axis, as predicted, but along the *c* axis. The magnetic state is incommensurate. The direction $\boldsymbol{P}$ along the *c* axis is primarily induced by Ho-Mn exchange striction, and Mn-Mn striction in the incommensurate spin state leads to an antiferroelectric order along the *a* axis. We predict the rotation of $\boldsymbol{P}$ with temperature in commensurate *E*-type $RMnO_3$ (*R* denotes magnetic rare earth).

DOI: 10.1103/PhysRevB.84.020101 PACS number(s): 77.80.−e, 75.30.Et, 75.80.+q

Multiferroics attract a significant amount of attention because of the cross coupling between magnetism and ferroelectricity (FE) and the related possibility of controlling magnetism with an electric field (and vice versa).[1,2] FE induced by magnetic order is especially interesting because of the strong effect of a magnetic field (*H*) on the ferroelectric order. Exchange striction is a major mechanism producing FE in magnetically ordered systems.[2] Both symmetric and antisymmetric parts of the exchange coupling can drive FE. The latter case is known to occur in spiral magnets, such as $TbMnO_3$.[2] These systems exhibit small electric polarizations ($\boldsymbol{P}$) of the order of 10^{-1} $\mu C/cm^2$ three orders of magnitude smaller than in proper ferroelectrics. Symmetric exchange is expected to produce much larger $\boldsymbol{P}$. However, the corresponding materials identified so far show similarly small values of $\boldsymbol{P}$.[3,4] Theoretical predictions[5,6] of a 100-times-larger $\boldsymbol{P}$ in the magnetic *E* phase of orthorhombic perovskite manganites *o*-$RMnO_3$ ($R =$ Ho-Lu and Y) induced by Mn-Mn exchange striction has, therefore, attracted a lot of interest.[7–10] Unfortunately, these compounds exhibit[9,10] maximum $\boldsymbol{P}$ values of only $\sim 10^{-1}$ $\mu C/cm^2$. In many cases (e.g., for $R =$ Ho), any significant $\boldsymbol{P}$ is achieved only below the rare-earth magnetic ordering temperature (*T*).[9] This indicates an essential role of the rare-earth magnetism, which is unaccounted for in the extant models. Importantly, all the *E*-type manganites studied so far have been synthesized only in the polycrystalline form, preventing characterization of many of their intrinsic properties.

In this paper, we report the studies on single crystals of orthorhombic $HoMnO_3$ (*o*-$HoMnO_3$). Unexpectedly, we find that $\boldsymbol{P}$ is pointing along the crystallographic *c* axis, contrary to the theoretical prediction[5,6] of $\boldsymbol{P} \| a$. We argue that Ho-Mn exchange striction plays a key role in this system, and we discuss possible outcomes of the Mn-Mn interaction in the orthorhombic manganites. Our model predicts that in magnetic rare-earth manganites, coexisting Mn-Mn and *R*-Mn interactions can give rise to a distinctive phenomenon—a temperature-dependent direction of $\boldsymbol{P}$.

o-$HoMnO_3$ crystallizes in a distorted perovskite structure (space group *Pbnm*), shown in Fig. 1(a). We have synthesized rodlike large single crystals with dimensions up to $2 \times 2 \times 7$ mm^3 [see Fig. 1(b)] utilizing the conventional Bi_2O_3 flux method. Previously, polycrystalline *o*-$HoMnO_3$ was obtained using high-pressure synthesis. We find that flux growth with Bi_2O_3, Ho_2O_3, and MnO_2 can stabilize both hexagonal *and* orthorhombic crystals at ambient pressure. A mixture of Bi_2O_3:Ho_2O_3:MnO_2 in a 6:0.5:1 ratio produces the hexagonal phase, whereas a 12:0.5:1 ratio leads to orthorhombic single crystals. The crystals exhibit an orthorhombic perovskite structure with $a = 5.2689(2)$, $b = 5.8450(2)$, and $c = 7.3698(2)$ Å at room temperature, and no twinning, as confirmed by refinement of single-crystal x-ray-diffraction data. This is consistent with the previously published structure of polycrystalline samples.[11,12] The absence of twinning was further confirmed by neutron-diffraction experiments, in which a careful search revealed no diffraction peaks due to possible twin domains. Magnetization (*M*) was measured with a SQUID magnetometer. $\boldsymbol{P}$ and the dielectric constant (ε) were obtained by integrating pyroelectric current measured with an electrometer and using an LCR meter at $f = 44$ kHz, respectively. Neutron-diffraction data were collected on a BT9 triple-axis spectrometer at the NIST Center for Neutron Research. In all figures, error bars (one standard deviation) are smaller than the symbol size.

Mn spins in *o*-$HoMnO_3$ order at $T_N \approx 40$ K, exhibiting ($0,A_y,0$)-type incommensurate structure with wave vector $Q = (h,k,l) = (0,\sim 0.4,0)$ and spins parallel to the *b* axis.[11] At a lower *T*, *some* polycrystalline samples[12] become commensurate with $k = 0.5$, exhibiting the *E*-type order discussed theoretically in Ref. 5 and shown in Fig. 1(a). For $T < 15$ K, Ho spins order in the ($a_x, f_y, 0$) pattern and the same *Q* as Mn.[11] Our data are consistent with these results. Magnetic-field (*H*) and *T* dependences of *M* are shown in Figs. 1(c) and 1(d). The anomalies corresponding to $T_N = 42$ K and $T_{Ho} = 15$ K are clearly observed in the *T* derivative of M_c shown in the inset in Fig. 1(d), as well as in the M_a and M_b derivatives (not shown). At low *T*, a substantial magnitude of M_b develops, possibly due to Ho contribution. Figure 2 shows the *T* dependence of various physical properties under zero *H*. The onset of tiny ferroelectric polarization along the *c* axis (P_c) occurs at $T =$ 30 K [Fig. 2(a)], and P_c exhibits an abrupt increase at $T_{Ho} =$ 15 K, reaching 1500 $\mu C/m^2$ at 2 K. The magnitudes of P_a and

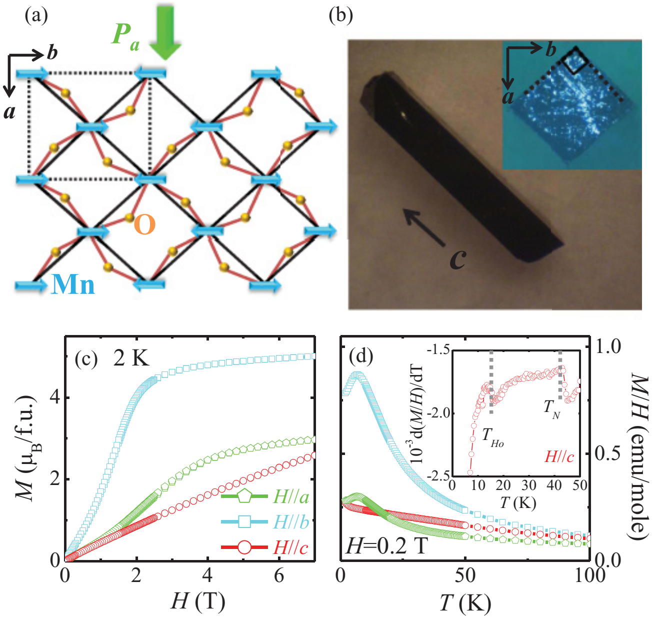

FIG. 1. (Color online) (a) Lattice and magnetic structure ($k = 0.5$) of *E*-type orthorhombic RMnO$_3$. *R* atoms are not shown. Oxygen displacements reflect the effect of Mn-Mn exchange striction. Dashed line shows structural unit cell. The magnetic unit cell is twice as large in the *y* direction. (b) Single crystal of *o*-HoMnO$_3$. (c) Magnetization vs magnetic field for $T = 2$ K. (d) Magnetic susceptibility vs temperature (1 emu $= 4\pi \times 10^{-6}$ m^3). The inset shows the temperature derivative of the susceptibility.

P_b are negligible at any *T*. The dielectric constant along the *c* axis (ε_c) displays a pronounced peak at T_{Ho}, in accordance with the appearance of FE, whereas ε_a increases broadly below T_N; see Fig. 2(b). The specific heat, shown in Fig. 2(d), exhibits a sharp peak at T_N, and a small (but discernable) anomaly at T_{Ho} is also visible.

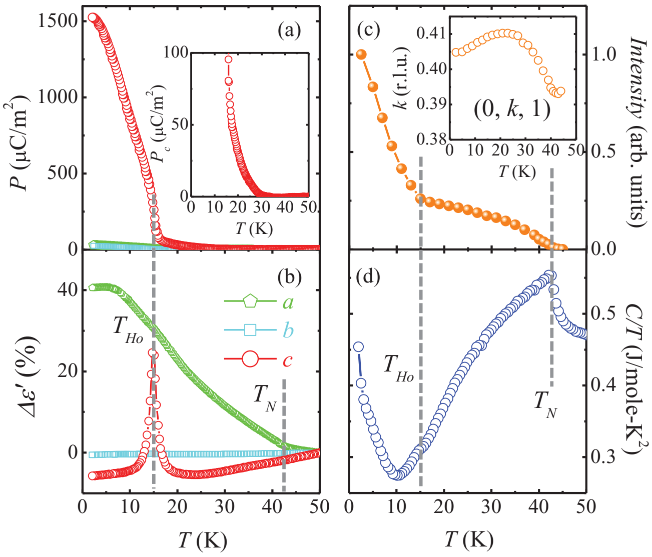

FIG. 2. (Color online) Temperature dependences of the electric polarization (a) and dielectric susceptibility (b) along the three crystallographic axes. (c) Integrated intensity of the (0, *k*, 1) magnetic peak vs temperature. The *k* component of the peak position is shown in the inset. (d) Temperature dependence of the specific heat.

Neutron-diffraction data show that our samples are incommensurate at all temperatures. Figure 2(c) shows the *T* dependence of the integrated intensity of the (0, *k*, 1) magnetic peak, $k \approx 0.4$. The magnetic order appears at $T_N = 42$ K, and the peak intensity increases significantly for $T < T_{\mathrm{Ho}}$, simultaneously with a large increase of P_c. The inset in Fig. 2(c) shows the *T*-dependent position *k* of the magnetic peak obtained from Gaussian fits. With decreasing *T*, *k* exhibits a slight variation but always stays close to $k = 0.4$. There appear to be changes in the slope of this dependence in the vicinity of the FE anomalies at ~30 K and at 15 K, reflecting the magnetoelectric coupling in this system.

The FE in the *E*-type manganites is currently believed[5,6] to be induced by Mn-Mn symmetric exchange striction, i.e., repulsion of coaligned Mn spins. This repulsion, together with the associated motion of the oxygen ions, leads to the appearance of P_a, as illustrated in Fig. 1(a) for the $k = 0.5$ commensurate state. The Mn spin is given by $S_y(y) = S \cos(ky - \varphi_i)$, where φ_0 and $\varphi_{1/2}$ are the phases for the two spin chains along the *b* axis in the unit cell, one at $x = 0$ and the other at $x = 0.5$ (*x*, *y* are in lattice units); see Fig. 3(a). In the *E*-type commensurate state, $k = 0.5$, $\Delta\varphi \equiv \varphi_{1/2} - \varphi_0 = \pi/2$, and the magnetic structure lacks the inversion symmetry, i.e., it is acentric. It is consistent with nonzero P_a when superimposed on the lattice structure. In the $k \neq 0.5$ state, the spin magnitude

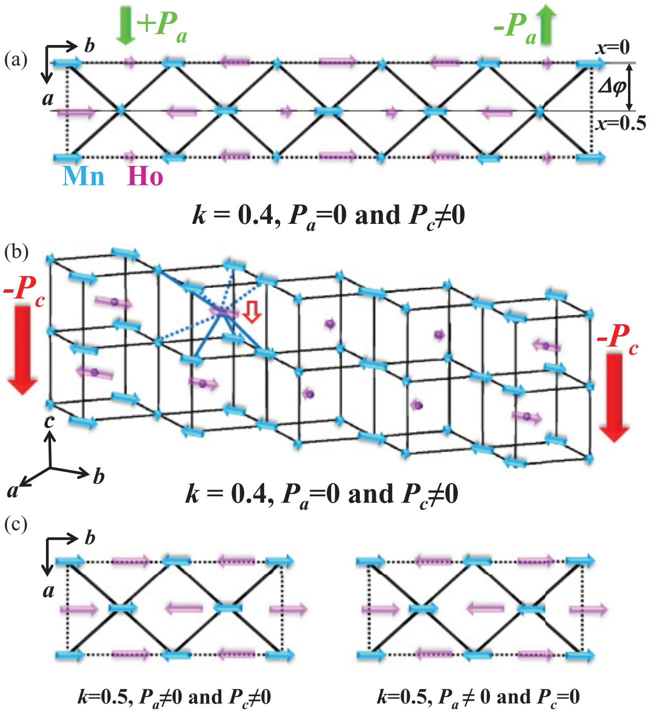

FIG. 3. (Color online) (a), (b) The magnetic order leading to $P_a = 0$ and $P_c < 0$ in the $k = 0.4$ state. Dashed line in (a) outlines the magnetic unit cell. In (b), thick solid and dashed lines designate attractive and repulsive Ho-Mn interactions, respectively. (c) Spin structures with zero and nonzero *c*-axis polarization in the $k = 0.5$ *E*-type state. In all figures, the *a*-axis components of the Ho spins are not shown.

is not constant, and other phase differences $\Delta\varphi$ are allowed, leading to both polar acentric (e.g., $\Delta\varphi = \pi/2$) and centric ($\Delta\varphi = 0$ and π) spin-density waves (SDW's).[13] In the latter case, $P_a = 0$ if the inversion centers of the SDW and the atomic structure coincide. In our samples, measured P_a is zero, and therefore the centric incommensurate SDW must be realized. One of the two possible Mn magnetic structures for the centric incommensurate SDW, corresponding to $\Delta\varphi = 0$, is shown in Fig. 3(a); the other with $\Delta\varphi = \pi$ simply has the opposite spin direction for $x = 0.5$. (For simplicity, the $k = 0.4$ state with a period of exactly five unit cells is shown.) These structures are antiferroelectric, with one-half of the unit cell having the opposite P_a to the other. The large increase of ε_a below T_N (Fig. 2) without the presence of P_a strongly supports this conclusion.

The primary result of our work is the unexpected direction of $\boldsymbol{P}$. Because of the clear association of FE with the Ho order, the natural candidate mechanism of multiferroicity is Ho-Mn interaction. In fact, rare-earth–3*d* element interaction was reported to be essential in multiferroic orthoferrites,[14,15] as well as to play a role in some spiral manganites.[16,17] We find that Ho-Mn exchange striction indeed provides a simple explanation for the observed phenomena. Disregarding the x component of the Ho spins, which does not contribute to the striction, the Ho SDW order essentially follows that of Mn, but with an experimentally undetermined phase shift between the two.[11] To maximize the energy gain from the Ho-Mn striction producing the c-axis displacement, the phase shift should be zero or π because it pairs large Ho and Mn spins adjacent in the x direction (the Mn spins adjacent in the y direction are antiparallel to each other for the same z, partially canceling the effect of the striction). As shown in Fig. 3(b) for one of these phase shifts, the Ho spin is then anti-aligned with the three Mn spins below, and aligned with the three Mn spins above, and moves down due to exchange striction. One can readily check that in this case, Mn-Ho exchange striction moves all the Ho spins of one chain (e.g., for $x = 0$) in the same direction along the c axis. The energy gain is the same for aligning with the Mn spins above or below the Ho atom, and therefore the $x = 0$ and 0.5 Ho chains in the magnetic unit cell can either have the same or the opposite directions of P_c. Experimentally, $P_c \neq 0$, and therefore the Ho order shown in Figs. 3(a) and 3(b), which produces the same P_c in every Ho chain, should be realized. Clearly, experimental confirmation of this phase relationship between the Ho and Mn SDW's, and whether it is affected by the poling used for P_c measurements, would be of significant interest. Finally, we note that the onset of the weak P_c at $T \approx 30$ K could be produced via the same mechanism due to the weak Ho moment induced by the Mn order, which was previously observed in polycrystalline samples.[12]

o-HoMnO$_3$ exhibits a strong magnetoelectric effect. Figure 4(a) shows the full suppression of P_c at $H = 2$ and 4 T for $H \| b$ and $H \| a$, respectively. For $H \| c$, only a small decrease of P_c is found. The suppression of P_c coincides with a drop in ε_c [Fig. 4(b)] and with an anomaly in dM/dH [inset in Fig. 4(a)]. The vanishing polarization is probably associated with field-induced reorientation of the Ho spins and the corresponding changes in the effects of Ho-Mn exchange striction. Our data show that the reorientation is easier to achieve in the *ab* plane, consistent with the magnetic anisotropy that tends to confine the Ho spins there.[11,12] Figures 4(c)–4(e) show T dependences of P_c and ε_c in various applied fields. Consistent with the data of Figs. 4(a) and 4(b), the magnetic field suppresses the ferroelectric state and decreases the ferroelectric transition temperature.

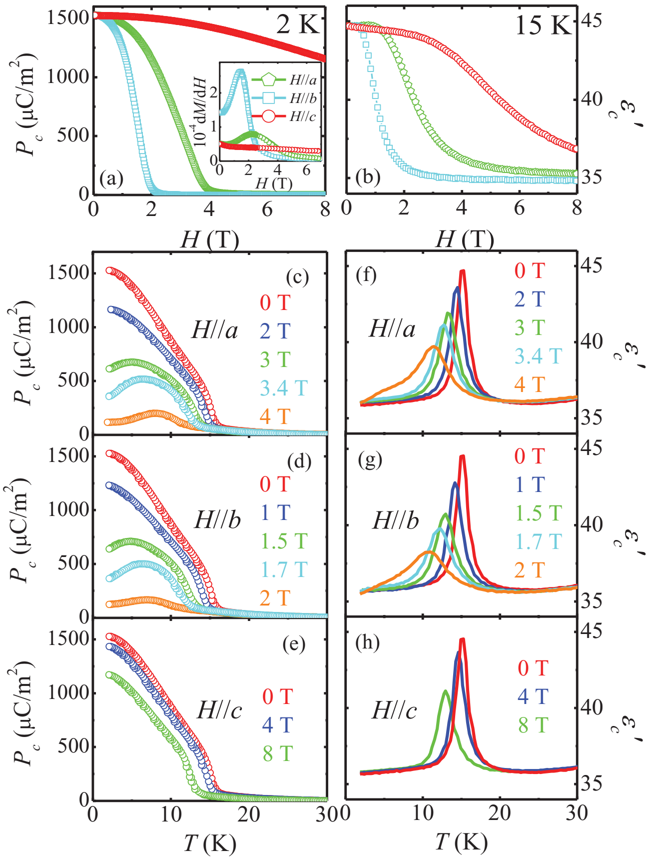

FIG. 4. (Color online) Magnetic-field dependences of the electric polarization P_c (a) and dielectric susceptibility ε_c (b) for different directions of H. Temperature dependences of the electric polarization (c)–(e) and the dielectric susceptibility (f)–(h) in various applied magnetic fields.

The presence of two coexisting exchange-striction mechanisms of multiferroicity in the *E*-type orthorhombic manganites is the key result of this work. Depending on the phase relationships within and between the Mn and Ho SDW's, both Mn-Mn and Ho-Mn interactions can produce zero or nonzero electric polarization along the a and c axis, respectively. The $k = 0.5$ state appears to be an exception for which the $P_a = 0$ state is absent, because centric SDW would imply zero Mn spin for half of the Mn ions. However, even for $k = 0.5$, states with both zero and nonzero P_c are possible, as illustrated in Fig. 3(c). The presence of two coexisting mechanisms producing different directions of $\boldsymbol{P}$ may open possibilities for distinctive magnetoelectric control, and should lead to previously unobserved phenomena. In our samples, only one mechanism (Ho-Mn) leads to FE. However, some of the previously studied polycrystalline *o*-HoMnO$_3$ samples[12] enter the $k = 0.5$ state at $T = T_L$, which is larger than T_{Ho}, and significant $\boldsymbol{P}$ is observed for $T_{\mathrm{Ho}} < T < T_L$. A large increase of $\boldsymbol{P}$ at T_{Ho} is also present in these samples. For these samples, our model predicts that the polarization is initially along the a axis, and that a large c-axis component develops in addition with decreasing T. Thus, we expect that the *direction* of $\boldsymbol{P}$ changes with T in the $k = 0.5$ crystals. The reason for the variation of the exact magnitude and T dependence of $\boldsymbol{P}$ and (in)commensurability among published results in polycrystalline specimens[11,12] and our crystal data is currently unclear, but the presence of defects or residual strains may play an important role. To verify the intriguing possibility of temperature-induced rotation of the $\boldsymbol{P}$, preparation of such $k = 0.5$ crystals is certainly desirable.

In summary, we report studies of single-crystalline o-HoMnO$_3$, which is currently considered to be a prototype E-type multiferroic with a symmetric exchange-striction mechanism. Contrary to the current belief, the ferroelectric polarization in our crystals is along the c axis. We argue that Mn-Mn and Ho-Mn exchange striction mechanisms coexist in this system. These mechanisms can lead to both ferroelectric and antiferroelectric orders along the a axis (Mn-Mn) and the c axis (Ho-Mn). In our samples, the Ho-Mn interaction produces the c-axis polarization, while the Mn-Mn exchange striction induces the a-axis antiferroelectric order. We also propose that under certain conditions, these coexisting mechanisms should lead to temperature-induced rotation of FE polarization in the E-type manganites.

We are grateful to T. Emge for experimental assistance. This work was supported by the NSF under Grants No. DMR-1004568 and No. DMR-0804109. Y.J.C. was supported partially by a subgrant with Seoul National University under Prime Agreement Award No. KRF-2008-220-C00012 from the Global Research Network Program of the National Research Foundation.

---

[1] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).

[2] S.-W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).

[3] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) **429**, 392 (2004).

[4] Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S.-W. Cheong, Phys. Rev. Lett. **100**, 047601 (2008).

[5] I. A. Sergienko, C. Sen, and E. Dagotto, Phys. Rev. Lett. **97**, 227204 (2006).

[6] S. Picozzi, K. Yamauchi, I. A. Sergienko, C. Sen, B. Sanyal, and E. Dagotto, J. Phys. Condens. Matter **20**, 434208 (2008).

[7] K. Yamauchi, F. Freimuth, S. Blugel, and S. Picozzi, Phys. Rev. B **78**, 014403 (2008).

[8] S. Ishiwata, Y. Kaneko, Y. Tokunaga, Y. Taguchi, T. Arima, and Y. Tokura, Phys. Rev. B **81**, 100411(R) (2010).

[9] B. Lorenz, Y.-Q. Wang, and C.-W. Chu, Phys. Rev. B **76**, 104405 (2007).

[10] S. M. Feng, Y. S. Chal, J. L. Zhu, N. Manivannan, Y. S. Oh, L. J. Wang, Y. S. Yang, C. Q. Jin, and K. H. Kim, New J. Phys. **12**, 073006 (2010).

[11] H. W. Brinks, J. Rodriguez-Carvajal, H. Vjellvag, A. Kjekshus, and B. C. Hauback, Phys. Rev. B **63**, 094411 (2001).

[12] A. Munoz, M. T. Casais, J. A. Alonso, M. J. Martinez-Lope, J. L. Martinez, and M. T. Fernandez-Diaz, Inorg. Chem. **40**, 1020 (2001).

[13] A related scenario is realized in YMn$_2$O$_5$; see L. C. Chapon, P. G. Radaelli, G. R. Blake, S. Park, and S.-W. Cheong, Phys. Rev. Lett. **96**, 097601 (2006).

[14] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. Arima, and Y. Tokura, Nat. Mater. **8**, 558 (2009).

[15] A. Stroppa, M. Marsman, G. Kresse, and S. Picozzi, New J. Phys. **12**, 093026 (2010).

[16] N. Aliouane, O. Prokhnenko, R. Feyerherm, M. Mostovoy, J. Strempher, K. Habicht, K. C. Rule, E. Dudzik, A. U. B. Wolter, A. Maljuk, and D. N. Argyriou, J. Phys. Condens. Matter **20**, 434215 (2008).

[17] M. Mochizuki, N. Furukawa, and N. Nagaosa, Phys. Rev. Lett. **105**, 037205 (2010).