

## Symmetry of Multiferroicity in a Frustrated Magnet $\text{TbMn}_2\text{O}_5$

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(Received 21 April 2006; published 10 April 2007)

Based on measurements of soft-x-ray magnetic scattering and symmetry considerations, we demonstrate that the magnetoelectric effect in  $\text{TbMn}_2\text{O}_5$  arises from an internal field determined by  $\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}$  with  $\vec{S}_{\vec{q}}$  being the magnetization at modulation vector  $\vec{q}$ , whereas the magnetoelastic effect in the exchange energy governs the response to external electric fields. Our results set fundamental symmetry constraints on the microscopic mechanism of multiferroicity in frustrated magnets.

DOI: 10.1103/PhysRevLett.98.157202

PACS numbers: 75.25.+z, 77.80.-e, 78.70.Ck

Materials which exhibit coexistence of magnetism and ferroelectricity with cross coupling, termed multiferroicity, are attractive because they offer the possibility for realizing mutual control of electric and magnetic properties. The key phenomenon behind such mutual control lies in the capability for the induction of magnetization by an electric field or of electric polarization by a magnetic field, known as the magnetoelectric effect [1,2]. The magnetoelectric effect is an important characterization of multiferroicity but has been poorly understood. The effect could be largely enhanced by the presence of internal fields. However, such enhancement requires the coexistence and strong coupling of magnetism and ferroelectricity, which rarely happen in real materials. Recent discoveries of giant magnetoelectric couplings in frustrated magnets [3,4] thus offer new opportunities for a thorough scientific understanding of multiferroicity as well as multiferroic applications.

In frustrated magnets, such as  $\text{RMnO}_3$  and  $\text{RMn}_2\text{O}_5$  ( $R = \text{Tb}, \text{Dy}, \text{and Ho}$ ) [3–13], the spontaneous electric polarization ( $\vec{P}$ ) appears in certain antiferromagnetic (AFM) phases. Unlike old examples of multiferroics, the magnetoelectric couplings exhibited by these materials are gigantic, and the magnetic phases involved are complicated and commonly incommensurate with lattice. The magnetic transition temperature is higher than the ferroelectric one, suggesting that the ferroelectricity is induced by magnetic order. Furthermore, the inversion symmetry in the magnetic phases with ferroelectricity is broken [11,12], implying that the magnetic order couples to odd orders of  $\vec{P}$ . In addition, these magnets show anomalies in the temperature dependence of dielectric constant  $\epsilon$ . For  $\text{RMnO}_3$ , the ferroelectric transition is accompanied by a magnetic transition from incommensurate sinusoidal to spiral AFM order [11,12]. Kenzelmann *et al.* have applied the Ginzburg-Landau theory to understand the multiferroic behavior [11]. In contrast, although Chapon *et al.* [13] found that the ferroelectricity in  $\text{YMn}_2\text{O}_5$  results from acentric spin-density waves, little is known about the

underlying mechanism of multiferroicity in  $\text{RMn}_2\text{O}_5$  because of their structural complexity. The exact relation and interplay between AFM order and ferroelectricity in frustrated magnets are unknown and remain controversial [12–16].

The presence of internal fields is the simplest origin of the cross coupling between magnetism and ferroelectricity. Microscopically, however, it is difficult to identify them due to their weak effect. Historically, scattering has been shown to be powerful for measuring accumulated microscopic changes and for revealing orderings and their relations directly. Neutron scattering [17], for example, first convincingly proved the existence of the antiferromagnetic phase of MnO. Here, by resorting to soft-x-ray magnetic scattering [18] and an analysis based on the phenomenological Ginzburg-Landau approach, we demonstrate that the magnetically induced ferroelectricity in  $\text{TbMn}_2\text{O}_5$  arises from an internal field determined by  $\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}$  with  $\vec{S}_{\vec{q}}$  being the magnetization at modulation vector  $\vec{q}$ . The results indicate that the noncollinearity of spins is essential for the existence of induced  $\vec{P}$ , independent of commensurability and chirality. In contrast, the external electric fields alter the exchange coupling, yielding anomalies in the temperature dependence of the dielectric constant.

We present measurements of soft-x-ray magnetic scattering around the  $L_3$  ( $2p_{3/2} \rightarrow 3d$ ) absorption edge of Mn to reveal the detailed coupling of ferroelectricity and AFM order in  $\text{TbMn}_2\text{O}_5$ . Soft-x-ray magnetic scattering is a newly developed technique which is sensitive to the magnetic moment of transition-metal  $d$  electrons [18–21], allowing us to probe magnetic order with high sensitivity. The scattering amplitude is proportional to the magnetization  $\vec{S}_{\vec{q}}$ , which is  $\sum_j \vec{S}_j e^{i\vec{q}\cdot\vec{r}_j}$  with  $\vec{S}_j$  and  $\vec{r}_j$  being spin moments and position vectors, respectively. We performed scattering measurements with the elliptically polarized-undulator beam line at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The inset

of Fig. 1 illustrates a schematic view of scattering geometry. A single crystal of  $\text{TbMn}_2\text{O}_5(100)$  with dimensions of  $(2 \times 1 \times 1) \text{ mm}^3$  was cut and polished to achieve a mirror-like surface, followed by a high-temperature annealing to remove built-up strain during polishing. The modulation vector  $\vec{q}$  is the momentum transferred from the materials and lies in the scattering plane defined by the  $a$  and  $c$  axes, i.e.,  $\vec{q} = (q_a, 0, q_c)$ . For photons of 639 eV, the intrinsic  $q$  resolution in terms of half width at half maxima (HWHM) is estimated to be of  $0.001 \text{ \AA}^{-1}$ , including the effect of photon penetration depth. The scattering results reveal that  $\text{TbMn}_2\text{O}_5$  exhibits an AFM order below 42 K. Figure 1 shows the energy dependence of HWHM and scattering intensity with  $\vec{q} = (\frac{1}{2}, 0, \frac{1}{4})$  in the reciprocal lattice units, which reflects the absorption of x rays. To reduce self-absorption, we used photons with an energy just below the Mn  $L_3$  edge in the following discussion on the temperature and polarization dependence; for example, the penetration depth ( $\sim 1800 \text{ \AA}$ ) of 639 eV photons is much larger than the correlation length of AFM order ( $\sim 800 \text{ \AA}$  defined as the inverse of HWHM).

Temperature-dependent measurements indicate that the AFM order of  $\text{TbMn}_2\text{O}_5$  occurs with modulation vectors  $(\frac{1}{2} \pm \delta_a, 0, \frac{1}{4} + \delta_c)$ , in which  $\delta_a$  and  $\delta_c$  characterize the incommensurability. The temperature dependence of  $q_a$  is plotted in Figs. 2(a) and 2(b) for  $\pi$  and  $\sigma$  polarizations, respectively. As the temperature decreases, the incommen-

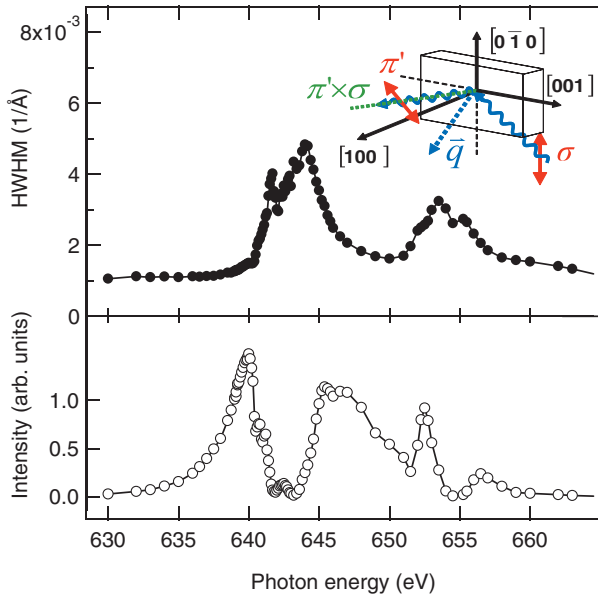


FIG. 1 (color). Photon-energy dependence of HWHM and scattering intensity of  $\text{TbMn}_2\text{O}_5$  with  $\vec{q} = (\frac{1}{2}, 0, \frac{1}{4})$  and  $\sigma$  polarization at 30 K. The intensity was obtained by fitting the  $q$  scan at each photon energy with a Lorentzian function and a linear background. Inset: Scattering geometry with  $\sigma$  and  $\pi'$  polarizations for incident and scattered photons, respectively. With  $\vec{q}$  near  $(\frac{1}{2}, 0, \frac{1}{4})$ , the angle between the scattered x ray and the  $a$  axis is  $\sim 6^\circ$  and that between the incident x ray and the  $c$  axis is  $\sim 19^\circ$ .

surate AFM order of  $\text{TbMn}_2\text{O}_5$  begins to develop at 42 K, in agreement with neutron results [7]. For the temperature between 37 and 30 K, the incommensurate scattering intensity decreases monotonically; the  $q_a$  of the incommensurate ordering moves toward 0.5. In contrast, the commensurate ordering appears between 37 and 24 K, coexisting with the incommensurate ordering. The scattering intensities plotted in the insets of Figs. 2(a) and 2(c) demonstrate the coexistence of commensurate and incommensurate AFM orderings, similar to the coexistence of commensurate and incommensurate AFM phases observed in  $\text{YMn}_2\text{O}_5$  [13]. As shown in Fig. 3(a), the onset of spontaneous electric polarization is accompanied by the

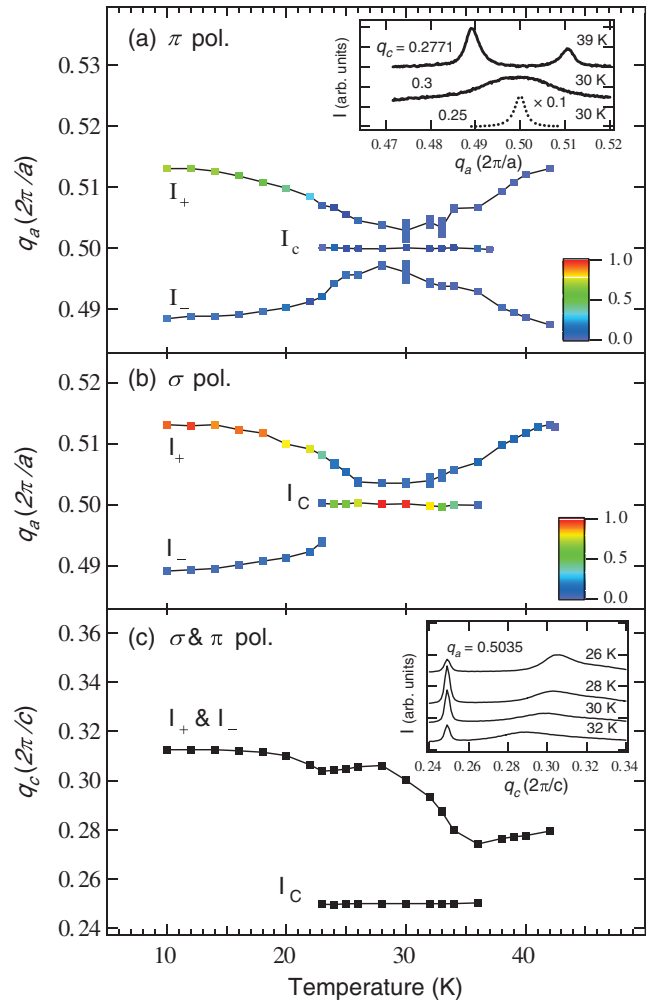


FIG. 2 (color). Temperature-dependent  $\vec{q}$  of AFM order of  $\text{TbMn}_2\text{O}_5$ : (a),(b)  $q_a$  component measured with  $\pi$  and  $\sigma$  polarizations; (c)  $q_c$  component. The vertical size of rectangular symbols indicates the uncertainties of  $q_a$  and  $q_c$ . Intensities normalized to that of the commensurate AFM order at 30 K with  $\sigma$  polarization are expressed by means of color. The temperature dependence of  $q_c$  is without showing relative intensities. Intensities of incommensurate AFM order with  $\vec{q} = (\frac{1}{2} \pm \delta_a, 0, \frac{1}{4} + \delta_c)$  are denoted as  $I_{\pm}$ , and of the commensurate ordering as  $I_C$ . The insets of (a) and (c) are, respectively, scattering intensities of  $q_a$  and  $q_c$  scans at selected temperatures.

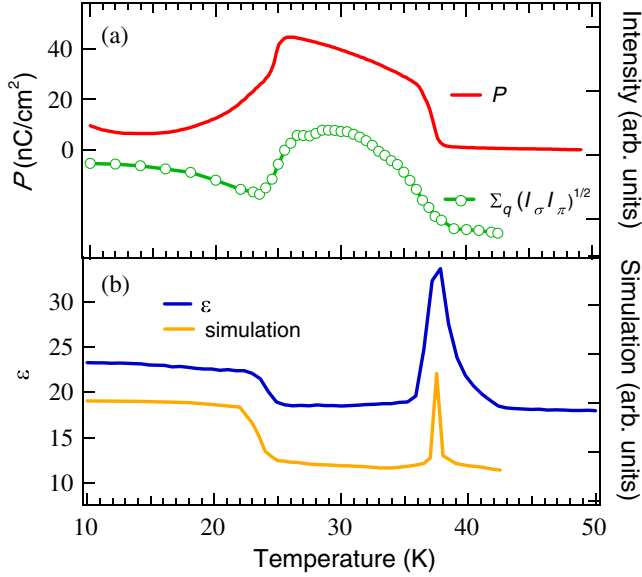


FIG. 3 (color online). Temperature dependence of AFM order and ferroelectric properties of  $\text{TbMn}_2\text{O}_5$ : (a) Comparison of  $P$  and intensities  $\Sigma_{\vec{q}}(I_\sigma I_\pi)^{1/2}$ ; (b) comparison of 1 kHz  $\epsilon$  along the  $b$  axis and simulation of  $\chi_b$  with  $|S_q|^2 = (I_\sigma + I_\pi)$ . Here  $\chi_0 g_2(q_{1C}) = 0.01$ ,  $\chi_0 g_2(q_C) = -0.01$ ,  $g_1(q_{1C}) = 10$ , and  $g_1(q_C) = 0$ .  $|\delta \vec{S}_{\vec{q}}|^2$  is simulated with a Lorentzian distribution centered at 37.5 K with a HWHM of 0.5 K. Note that  $I_\sigma$  and  $I_\pi$  are the average intensities for  $\sigma$  and  $\pi$  polarizations, respectively, i.e.,  $I_{\sigma/\pi} \equiv (I_+ + I_-)/2$  for incommensurate ordering and  $I_{\sigma/\pi} \equiv I_C$  for commensurate ordering.  $P$  and  $\epsilon$  are reproduced data of zero magnetic field from Ref. [4].

incommensurate-commensurate AFM transition at 37 K, contrary to  $\text{RMnO}_3$  [3,11,12]. On further lowering the temperature, a commensurate-incommensurate transition occurs at 23 K; the commensurate ordering disappears.

The polarization dependence of x-ray scattering provides the information about the direction of magnetic moments. Hannon *et al.* [18] have shown that the magnetic moment along a direction  $\hat{\mathbf{Z}}$  probed in x-ray scattering is proportional to  $(\mathbf{e}^{*} \times \mathbf{e}) \cdot \hat{\mathbf{Z}}$ , where  $\mathbf{e}^*$  is the electric field of the scattered light. For an incident x ray of  $\sigma$  polarization, the scattered x ray from  $\text{TbMn}_2\text{O}_5$  with  $\mathbf{e}^* \parallel b$  (denoted as  $\sigma'$  polarization) makes no contribution to the magnetic scattering, and the scattered x ray with  $\mathbf{e}^* \perp b$  ( $\pi'$  polarization) is predominantly sensitive to the magnetic moment along the  $a$  axis, i.e.,  $|S_q^a|$ , because  $\pi'^* \times \sigma$  is  $\sim 6^\circ$  away from the  $a$  axis. Conversely, if the incident x ray has  $\pi$  polarization, the scattered x ray has either  $\pi'$  or  $\sigma'$  polarization;  $\pi'^* \times \pi$  is parallel to the  $b$  axis, whereas  $\sigma'^* \times \pi$  is predominantly along the  $c$  direction. As neutron measurements indicate that the magnetic moments are in the  $ab$  plane [7,8], the scattering with  $\pi$  polarization is predominantly sensitive to the magnetic moment along the  $b$  axis, i.e.,  $|S_q^b|$ .

The knowledge of  $|S_q^a|$  and  $|S_q^b|$  enables one to investigate how  $\vec{P}$  is induced by magnetization based on the Ginzburg-Landau approach [11,22–24]. As hinted from

the broken inversion symmetry, there must be odd orders of  $\vec{P}$  coupling to  $\vec{S}_{\vec{q}}$ . Clearly, the lowest order coupling is that an internal field  $\vec{E}_{\text{in}}$  couples to  $\vec{P}$ , and the free energy  $F$  can be written as  $F = P^2/2\chi_0 - \vec{E}_{\text{in}} \cdot \vec{P}$  with  $\chi_0$  being the electric susceptibility. The minimization of  $F$  thus leads to  $\vec{P} = \chi_0 \vec{E}_{\text{in}}$ . From symmetry point of view, because  $\vec{S}_{\vec{q}}$  changes sign under time reversal,  $\vec{E}_{\text{in}}$  must be quadratic in magnetization and contains at least two components in  $\vec{S}_{\vec{q}}$ . Since both  $\vec{q}$  and  $-\vec{q}$  must be paired to make  $\vec{P}$  uniform in real space,  $\vec{E}_{\text{in}}$  must contain both  $\vec{S}_{\vec{q}}$  and  $\vec{S}_{-\vec{q}}$ . Under the inversion operation  $\vec{r}_j \rightarrow -\vec{r}_j$ ,  $\vec{S}_{\vec{q}}$  becomes  $\vec{S}_{-\vec{q}}$ . Since  $\vec{P}$  changes sign,  $\vec{E}_{\text{in}}$  must change sign to fulfill  $F$  being invariant. Out of the quantities that characterize the magnetic order and the underlying lattice, there are two possible combinations for  $\vec{E}_{\text{in}}$ :  $\hat{u} \times (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}})$  or  $(\vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}})\hat{q}$ , where  $\hat{u}$  is  $\hat{a}$ ,  $\hat{b}$ ,  $\hat{c}$ , or their combinations [25], representing the most important anisotropic direction in the spin-spin interaction. Since  $(\vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}}) = |\vec{S}_{\vec{q}}|^2$  is finite for any magnetic phase occurring below the Néel temperature  $T_N$ , an internal field of the form  $(\vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}})\hat{q}$  implies that transition temperature for nonvanishing  $\vec{P}$  is identical to  $T_N$ , which disagrees with experimental observation of  $\text{TbMn}_2\text{O}_5$ . On the other hand,  $\hat{u} \times (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}})$  does discern different magnetic phases. In particular, it vanishes for collinear or inversion-invariant magnetic phases. Therefore, we conclude that  $\vec{E}_{\text{in}} = \sum_{\vec{q}} i\gamma_{\vec{q}} \hat{u} \times (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}})$  is the only candidate that is consistent with symmetry considerations for  $\text{TbMn}_2\text{O}_5$ . Here  $\gamma_{\vec{q}}$  is some unknown function to be determined by microscopic models. Then the induced polarization  $\vec{P}$  is  $\chi_0 \sum_{\vec{q}} i\gamma_{\vec{q}} \hat{u} \times (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}})$  [24].

For  $\text{TbMn}_2\text{O}_5$ , because  $S_q^c$  vanishes,  $\vec{P}$  is along the  $b$  axis if one takes  $\hat{u} = \hat{q}$ , consistent with experimental observations. The choice of  $\hat{u} = \hat{q}$  is also consistent with the work by Mostovoy [24], where the proposed expression, after being averaged over space, also shows that  $\vec{P}$  is determined by  $\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}$ . In addition, checking the magnitude of  $\vec{P}$  provides another justification. Since  $P \propto \sum_{\vec{q}} \gamma_{\vec{q}} |S_q^a| |S_q^b| \sin(\phi_a - \phi_b)$  [26] with  $\phi_{a/b}$  being phases of  $S_q^{a/b}$ , the appearance of  $\vec{P}$  requires nonvanishing  $\phi_a - \phi_b$ , reflecting the requirement of noncollinear spin structure for inducing polarization. Since the change of  $\vec{q}$  is small,  $\gamma_{\vec{q}}$  is almost temperature independent. With further assumption of  $\phi_a - \phi_b$  being roughly independent of temperature, we have  $P \propto \sum_{\vec{q}} (I_\pi I_\sigma)^{1/2}$ . Figure 3(a) shows the comparison of  $P$  with the sum of the intensities  $(I_\pi I_\sigma)^{1/2}$  over commensurate and incommensurate magnetic orderings. Clearly, they follow each other closely, indicating the validity of the proposed  $\vec{E}_{\text{in}}$  and the assumption on the temperature independence of  $\phi_a - \phi_b$ . These observations also indicate that the coexisting incommensurate and commensurate orderings break the inversion symmetry. Furthermore, since  $\vec{P}$  is an odd function in

any component of  $\vec{S}_{\vec{q}}$ , strong magnetic fields can simply change the sign of just one component in  $\vec{S}_{\vec{q}}$  and result in the observed reversal of  $\vec{P}$  in direction [4].

For a complete understanding of the ferroelectricity, we further discuss dielectric responses of  $\text{TbMn}_2\text{O}_5$ , as summarized in Fig. 3(b). Two anomalies are observed:  $\epsilon$  exhibits a sharp maximum at the incommensurate-commensurate transition (37 K) and a steplike structure at the commensurate-incommensurate transition (23 K). As shown below, both anomalies reflect the magnetoelasticity of the exchange energy. Specifically, because the exchange energy  $J$  is sensitive to positions of atoms [16], applying  $\vec{E}$  induces  $\delta J$  that depends on the change of polarization  $\delta\vec{P}$ . Experimental data indicate that only the component  $E_b$  along the  $b$  axis couples to the magnetic order [4] so that  $\delta J$  only depends on  $\delta P_b$  and can be expressed as  $\delta J = -g_1(q)E_b\delta P_b + g_2(q)(\delta P_b)^2/2$  with  $g_1$  and  $g_2$  being positive numbers that characterize the corresponding couplings. Here the first term contributes the potential energy of the electric dipole, and when combined with  $-\vec{E} \cdot \delta\vec{P}$ , it corrects  $E_b$ . The second term is the elastic energy that contributes a correction to the original elastic energy  $P^2/2\chi_0$  and changes  $\chi_0$ . Including these corrections, the electric susceptibility becomes  $\chi_b = \chi_0(1 + \sum_q g_1(q)\langle|\vec{S}_q|^2\rangle)/(1 + \chi_0\sum_q g_2(q)\langle|\vec{S}_q|^2\rangle)$  [27].

The expression of  $\chi_b$  enables one to explain the behavior of  $\epsilon$  phenomenologically. We first note that, for the commensurate ordering at  $\vec{q}_C$ , the magnitude of  $\vec{S}_{\vec{q}_C}$  saturates. It is then plausible to assume that the exchange energy reaches maximum at commensurate ordering, i.e.,  $\partial\delta J/\partial\delta P_b = 0$ , which enables one to eliminate  $E_b$  and obtains  $\delta J = -g_2(q)(\delta P_b)^2/2$ . This is equivalent to set  $g_1(q_C) = 0$  and  $g_2(q_C) < 0$  from the beginning. Since  $\langle|\vec{S}_q|^2\rangle$  can be written as the sum of spin fluctuations,  $\langle|\delta\vec{S}_q|^2\rangle$ , and square of moments,  $|\vec{S}_q|^2$ , the enhancement of spin fluctuations near the incommensurate-commensurate transition explains the observed sharp maximum [22] of  $\epsilon$  at 37 K. In contrast, for the incommensurate ordering below 37 K, the magnitude of  $\vec{S}_{\vec{q}}$  is not saturated. In this case, since  $g_1(q_{IC}) > 0$  and  $g_2(q_{IC}) > 0$ ,  $\chi_b$  is thus more sensitive to the numerator. Figure 3(b) shows the comparison of the measured  $\epsilon$  along the  $b$  axis and our phenomenological simulation of  $\chi_b$  with  $|S_{\vec{q}}|^2 = (I_\sigma + I_\pi)$ . Note that  $\chi_b$  differs from  $\epsilon$  by a constant. The resemblance of these two curves shows that the response to  $\vec{E}$  indeed arises from magnetoelasticity of the exchange energy.

We thank C.-H. Hsu, C. H. Chen, S. Ishihara, Y. Tokura, G. Y. Guo, and T. K. Lee for fruitful discussions and comments, and L. L. Lee and H. W. Fu for their technical

support. This work was supported in part by the National Science Council of Taiwan. Work at Rutgers was supported by Contract No. NSF-MDR-052471.

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- [25] Note that the possibility  $\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}$  is not considered because it does not couple to the lattice; furthermore, its direction is also not consistent with experiments.
- [26] Because  $\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}$  changes sign when  $\vec{q}$  is changed to  $-\vec{q}$  in the summation,  $\gamma_{\vec{q}}$  must be odd in  $\vec{q}$  with the lowest possible term being  $\sin q_a$  or  $\sin q_c$ . Thus, for  $\gamma_{\vec{q}} = \sin q_a$ ,  $P \propto \sum_q |S_q^a| |S_q^b| \sin q_a \sin(\phi_a - \phi_b)$ , which is in agreement with microscopic considerations [15,16].
- [27] The lowest-order terms for the change of  $F$  can be written as  $\delta F = [\vec{P}/\chi_0 - i\sum_q \gamma_q \hat{u} \times (\vec{S}_q \times \vec{S}_{-q})] \cdot \delta\vec{P} + (\delta\vec{P})^2/2\chi_0 - \vec{E} \cdot \delta\vec{P} + \sum_q \delta J \langle \vec{S}_q \cdot \vec{S}_{-q} \rangle$ . Here the first term vanishes upon using the proposed relation between  $\vec{P}$  and  $\vec{S}_q \times \vec{S}_{-q}$ .