LA-UR- 08-5744

Title:

Inhomogeneous Field Induced Magnetoelectric Effect in Mott Insulators.

Author(s):

L. N. Boulaevskii, Z # 113479, T-11
C. D. Batista, Z # 167590, T-11

Intended for:

Journal: Physics Review Letters

Los Alamos
NATIONAL LABORATORY
EST.1943

Inhomogeneous Field Induced Magnetoelectric Effect in Mott Insulators

L.N. Bulaevskii and C.D. Batista[1]

[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

(Dated: September 2, 2008)

We consider a Mott insulator like HoMnO$_3$ whose magnetic lattice is geometrically frustrated and comprises a 3D array of triangular layers with magnetic moments ordered in a 120° structure. We show that the effect of a *uniform magnetic field gradient*, ∇H , is to redistribute the electronic charge of the magnetically ordered phase leading to a *uniform electric field gradient*. The resulting voltage difference between the crystal edges is proportional to the square of the crystal thickness, or inter-edge distance, L. It can reach values of several volts for $|\nabla H| \approx 0.01$ T/cm and $L \simeq$ 1mm, as long as the crystal is free of antiferromagnetic domain walls.

PACS numbers:

The magnetoelectric properties of Mott insulators became recently the focus of numerous studies due to their potential for new technological applications [1]. The most interesting cases are crystals that exhibit simultaneous charge and magnetic orderings (multiferroics). Antiferromagnetic (AFM) Mott insulators can exhibit magnetoelectric effects driven by magnetic ordering [3]. The low-energy charge response is entirely determined by the spin degrees of freedom and thus sensitive to external magnetic fields. Similarly, the magnetic ordering becomes sensitive to an applied electric field.

The minimal Hamiltonian for describing Mott insulators is the Hubbard model which accounts for a strong on-site Coulomb repulsion U and hopping terms of amplitude t between nearest-neighbor sites $\langle i,j\rangle$:

$$\mathcal{H} = t\sum_{\langle i,j\rangle,\sigma} a^{+}_{i\sigma}a_{j\sigma} + \frac{U}{2}\sum_{j}(n_i-1)^2, \quad n_i = \sum_{\sigma} a^{+}_{i\sigma}a_{i\sigma}. \tag{1}$$

The operator $a^{+}_{i\sigma}$ creates an electron with spin σ on site i while n_i is the number of electrons on site i. The Mott insulating phase only appears at half-filling and for large enough U/t. In particular, each electron becomes localized on a given site for $t=0$ and the ground state subspace generated by the wave functions $|\tilde{\psi}_\nu\rangle$ is 2^{N_s} fold degenerate with respect to spin orientations (N_s is the total number of sites). The excited or polar states described by wave functions $|\phi_\nu\rangle$ contain $m \geq 1$ doubly occupied and empty sites so their energy is mU.

The ground state degeneracy is lifted by any nonzero t that mixes the wave functions $|\tilde{\psi}_\nu\rangle$ with the polar states $|\phi_\nu\rangle$. The new set of 2^N_s low-energy eigenvectors $|\psi_\nu\rangle$ generates the subspace $\mathcal{S}$ of magnetic states that are related to the wave-functions $|\tilde{\psi}_\nu\rangle$ by a unitary transformation: $|\psi_\nu\rangle = e^{-S}|\tilde{\psi}_\nu\rangle$. The projection of $\mathcal{H}$ into $\mathcal{S}$ leads to an effective Heisenberg spin Hamiltonian $\tilde{\mathcal{H}} = Pe^{S}\mathcal{H}e^{-S}P$, where P is the projector on the subspace $\mathcal{S}$. The magnetic states are responsible for the low-energy response of the crystal. The non-magnetic states (states in $\mathcal{S}^{\perp}$) are separated by a gap of order U. Single electron transport is only possible if the system is in one of such high-energy states. Therefore, the system is an insulator due to the strong on-site Coulomb repulsion. When the insulating character is driven by this mechanism, the corresponding material is called Mott insulator.

This classification of the eigenvectors of $\mathcal{H}$ into "magnetic" states, that are responsible for the magnetic properties, and high-energy states responsible for the electric response is not absolute. For small but nonzero values of the transfer integral t, the magnetic states of Mott insulators are linear combinations of non-polar and polar states, $|\psi_\nu\rangle = b|\tilde{\psi}_\nu\rangle + \sum_\alpha a_\alpha|\phi_\alpha\rangle$, and can exhibit low energy electrical properties due the polar contribution. The coefficients a_α are a function of t/U (they vanish for $t/U \to 0$) and the spin structure of the non-polar state $|\tilde{\psi}_\nu\rangle$. In particular, this polar state contribution can modify the local charge on each site leading to non-uniform charge distributions that depend on the magnetic ordering. This phenomenon can lead to magnetoelectric effects without involving the spin-orbit relativistic coupling [2]. Namely, the electronic charge redistribution can be induced by a magnetic field and while a spin rearrangement can be induced by an electric field. As it was demonstrated in Ref. [3], Mott insulators comprising magnetic lattices with odd hopping loops (odd number of spins in the loop) exhibit this magnetoelectric behavior.

Here we show that a small uniform magnetic field gradient leads to an electronic charge redistribution in Mott insulators that comprise equilateral triangular lattices of magnetic ions such as HoMnO$_3$. This phenomenon only occurs in Mott insulators. The lattice unit cells become uniformly charged in the bulk of the crystal, while the compensating opposite charge is accumulated in the crystal edge. The uniform *electric field* gradient produced by this charge distribution leads to a voltage difference between the crystal edges that is quadratic in crystal length (see Fig. 1). This phenomenon is driven by the Zeeman energy as electrons try to minimize their energy by reorienting their spins and moving to sites with stronger magnetic field. However, such electronic redistribution is not a single-particle effect but a collective phenomenon, as it originates from the dependence of the coefficients a_α on the global spin structure of the ground state.

We consider the half-filled Hubbard model, Eq.(1), on a triangular lattice. The perturbative calculation of $\tilde{\mathcal{H}}$ up to second order in t leads to the Heisenberg Hamiltonian:

$$\tilde{\mathcal{H}} = \sum_{\langle i,j\rangle} J(\mathbf{S}_i\cdot\mathbf{S}_j - 1/4) - \mu\sum_{i}\mathbf{H}_i\cdot\mathbf{S}_i, \tag{2}$$

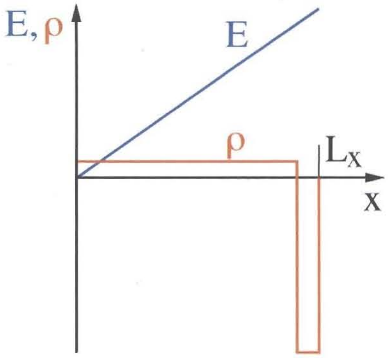

FIG. 1: (color online) Charge density and the electric field inside the crystal in presence of a uniform magnetic field gradient. The charge is positive inside the crystal and the negative compensating charge is accumulated at the crystal edge. For such charge configuration, the electric field increases linearly with x inside the crystal.

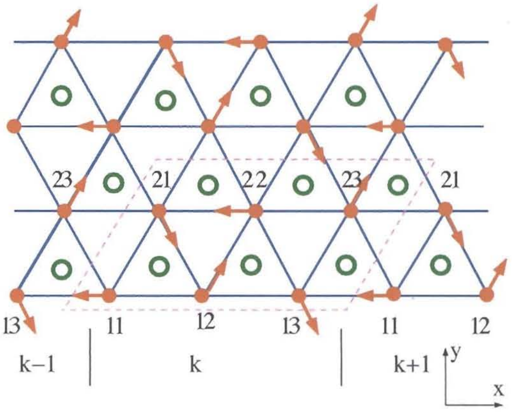

FIG. 2: (color online) Positions of oxygen ions O^{2-} (open circles) and Mn^{3+} ions (full circles) in the basal plane. The arrows indicate the ordering of the Mn spins. The labels inside the dashed line denote the different Mn spins inside the magnetic unit cell k.

where $J = 4t^2/U$ is the exchange interaction between nearest-neighbor sites $\langle i,j\rangle$, μ is the magnetic moment of each S=1/2 spin, $\mathbf{S}_i$, and $\mathbf{H}_i$ is the magnetic field on the site i. In general, the projection of any observable $\mathcal{O}$ into the low-energy subspace of magnetic states leads to an effective operator $\tilde{\mathcal{O}} = Pe^S\mathcal{O}e^{-S}P$ that only depends on the spin operators $\mathbf{S}_i$. In particular, as it was shown in Ref. [3], the effective operator for the local electron number operator n_i deviates from one to third order in t/U:

$$\tilde{n}_i - 1 = 8\frac{t^3}{U^3}\sum_{\langle j,k;i\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j + \mathbf{S}_i\cdot\mathbf{S}_k - 2\mathbf{S}_j\cdot\mathbf{S}_k). \qquad (3)$$

$\langle j,k;i\rangle$ indicates that the sum runs over the sites j,k that share a triangle with the site i. The effective operators $\tilde{n}_j$ and $\tilde{n}_k$ for a triangle (i,j,k) are obtained by cyclic permutations of the indices i,j,k. The operator $\tilde{n}_i - 1$ vanishes to second order in t/U because $\tilde{n}_i$ is a scalar under a spin-rotation and the only bilinear spin scalar is $\mathbf{S}_i\cdot\mathbf{S}_j$. From charge conservation we have $\tilde{n}_i + \tilde{n}_j = 2$, while the spatial symmetry $i \leftrightarrow j$ implies that $\tilde{n}_i = 1$. The scalar combination of three spins presented in Eq. (3) becomes nonero to third order t/U due to a three-hopping process on a triangular loop. We note that $\tilde{n}_i = 1$ on a bipartite lattice to any order in t/U [4].

The expression for the effective operator $\tilde{n}_i$ remains the same for any spin S due to the following symmetry considerations: it must be a scalar, it must vanish when the three spins are ferromagnetically aligned, and it must be symmetric under the permutation $j \leftrightarrow k$. Only the numerical prefactor (8 for $S = 1/2$) depends on the spin S. In addition, the constant 1/4 of Eq. (2) must be replaced by S^2.

Eq. (3) leads to an increase of the electron density on the two sites of a single triangle whose spins have a stronger singlet character ($t < 0$). This simple notion shows that spin bond-orerings that make the sites inequivalent (in addition to the bonds) are accompanied by an electronic charge redistribution (the ions also move due to magnetostriction) or charge density wave (CDW) that may have a net electric polarization if allowed by the broken symmetry. We will see that while a uniform magnetic field induces a CDW without net electric polarization in a C_3 symmetric crystal, a *uniform magnetic field gradient* induces a uniform electric field gradient.

We consider $HoMnO_3$ as an example of a layered crystal of magnetic ions Mn^{3+} ($S = 2$). These ions are located inside oxygen pyramids, while the small magnetic moment Ho ions lie between layers and order at temperatures well below the Neel temperature T_N of the Mn ions. The positions of the Mn and the most important oxygen ions in the basal plane are depicted in Fig. 2. This figure also shows the spin ordering for the phase below below $T_N = 72$ K and above the transition temperature $T_{SR} \approx 40$ K to a different magnetic structure. From now on we will label the spin sites and unit cells as it is shown in Fig. 3. We assume a strong easy-plane anisotropy and treat the spins as 2D classical vectors of magnitude S and phase φ_{nk}, where k labels magnetic unit cell along the x axis, and n labels the six sites inside each unit cell ($n = 11, 12, 13, 21, 22, 23$). The zero field magnetic ordering comprises a three sublattice structure with angles $\varphi_{0,12} = -\varphi_{0,13} = \pi/3$ and $\varphi_{0,11} = \pi$ relative to the x-axis of the basal plane. The spin ordering of the next layer is obtained by changing the signs of $\varphi_{0,12}$ and $\varphi_{0,13}$. The magnetic sites of the next layer are shifted by $a/\sqrt{3}$ along the y-axis, where a is the distance between neigboring sites along the x-axis.

From now on we will only consider the intra-layer exchange and assume that there is a C_3-invariant single-ion anisotropy term of amplitude D that leads to three easy-axes in the x,y plane. The electron number on each site is equal to one ($\langle\tilde{n}_{nk}\rangle = 1$) at zero field because all the bonds are equivalent. A nonzero magnetic field induces small deviations, α_{nk}, relative to the zero field angles φ_{0n}. We assume that the field values H_i are small enough to have a local Zeeman energy much smaller than the anisotropy energy: $\mu H_i \ll DS$. We first consider that the magnetic field is applied along the x-axis. By expressing the Hamiltonian in terms of the deviations α_{nk} and minimizing with respect to these variables, we obtain linearized equations for $\alpha_{nk} \ll 1$:

$$\begin{aligned}
&(6+d)\alpha_{11,k} - \alpha_{12,k} - \alpha_{13,k} - 2\alpha_{21k} - 2\alpha_{23,k-1} = h_{1k},\\
&(6+d)\alpha_{12,k} - \alpha_{11,k} - \alpha_{13,k} - 2\alpha_{21,k} - 2\alpha_{22,k} = h_{2k},\\
&(6+d)\alpha_{13,k} - \alpha_{11,k+1} - \alpha_{12,k} - 2\alpha_{22,k} - 2\alpha_{23,k+1} = h_{3k},\\
&(6+d)\alpha_{21,k} - 2\alpha_{11,k} - \alpha_{12,k} - \alpha_{22,k} - 2\alpha_{23,k-1} = h'_{1k},\\
&(6+d)\alpha_{22,k} - 2\alpha_{12,k} - 2\alpha_{13,k} - \alpha_{21,k} - \alpha_{23,k} = h'_{2k},\\
&(6+d)\alpha_{23,k} - 2\alpha_{11,k+1} - 2\alpha_{13,k-1} - \alpha_{11,k} - \alpha_{22,k} = h'_{3k}.
\end{aligned} \tag{4}$$

Here $d = D/J$ is a dimensionless anysotropy parameter, while $h_{nk} = (k+n-1)h_g$ and $h'_{nk} = (k+n-1/2)h_g$, with $h_g = \mu a \nabla H_i/JS$ being a dimensionless magnetic field gradient. The angle deviation α_{nk} leads to a spin change $\delta \mathbf{S}_{nk} = \tilde{\mathbf{S}}_{0n}\alpha_{nk}$, where $\tilde{\mathbf{S}}_{0n} = \pm S(-\sin\varphi_{0n}, \cos\varphi_{0n})$ is perpendicular to the zero-field spin orientation $\mathbf{S}_{0n}$. The local charges on each magnetic site are obtained by expressing Eq. (3) as a function of the deviations α_{nk} that result from Eq. (4). Finally, the electric field inside the crystal is determined by the Maxwell equation $\partial E_x/\partial x = 4\pi e n(x)$.

A uniform magnetic field $\mathbf{H}$ only redistributes the electronic charge inside the magnetic unit cell. For $\mathbf{H} \parallel \hat{\mathbf{x}}$, we obtain $\langle \tilde{n}_{12,k}\rangle - 1 = -(\langle \tilde{n}_{13,k}\rangle - 1) = -6\sqrt{3}A\mu H/(JS)$. There is no net polarization due to the C_3 symmetry of the angle deviations with respect to any spin site. Thus, the induced CDW follows the symmetry of the zero field magnetic structure. The effect of an inhomogeneous magnetic field is drastically different because its spatial variation eliminates the symmetries of the spin ordering that exclude an electric polarization vector. If a uniform magnetic field gradient is applied along the x-axis, the angles α_{nk} increase linearly with k. For a big enough number N of magnetic unit cells along the x-axis, the bulk solution (deep inside the crystal) is $\alpha_{nk} = f_n k + g_n$, with $f_{11} = f_{22} = 0$ and $f_{12} = f_{23} = -f_{13} = -f_{21} = h_g/\sqrt{3}$. The coefficients g_n are of order unity and the net charge of each magnetic unit cell does not depend on them. The corresponding change of the electronic charge of the magnetic unit cell k is

$$Q_k = 3\sqrt{3}Ae(\alpha_{11,k} - \alpha_{11,k+1}/3 - 2\alpha_{11,k-1}/3 + \alpha_{13,k} - \alpha_{13,k-1} - \alpha_{21,k} + \alpha_{21,k+1} - \alpha_{23,k-1} + \alpha_{23,k}) = -3Aeh_g.$$

The charge that compensates this variations and keeps the system neutral is accumulated on the right edge (near Nth unit cell) where the magnetic field is strongest ($t < 0$). The same result holds for the second layer in the 3D magnetic unit cell. Hence, the contributions to the electric polarization of the two different layers do not compensate each other.

The electric field inside the crystal induced by such a charge distribution has a constant gradient:

$$E_x(k) = (12\pi\epsilon_0 A h_g e/ab)k, \tag{5}$$

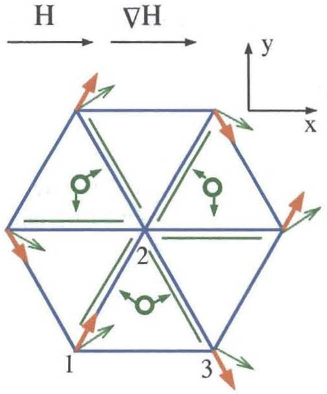

FIG. 3: (color online) Tilting of spins relative to their zero field orientations (full big arrows) induced by the applied magnetic field gradient (open big arrows). The double-line bonds become stronger and the electron density is consequently bigger. The oxygen ions are shifted towards these bonds as shown by the small arrows.

where b is the interlayer distance. This field generates a voltage difference between the crystal edges

$$eV = 6\pi A e^2 h_g N^2 = 6\pi\epsilon_0 A N e^2 \mu \Delta H/(bJS), \tag{6}$$

where $\Delta H = aN\nabla_x H_x$ is the the magnetic field difference between the crystal edges. In the right hand side of Eqs. (5) and (6), we introduced the dielectric constant ϵ_0 (of order 10) to account for the electric polarization due to ions and other electrons. This result corresponds to a charge shift $\delta n \approx 12e(\mu a \nabla H/U)(t/U)k$ from the magnetic cell k to the neighboring cell in the gradient direction. For the case of HoMnO$_3$, a charge of $\simeq 0.05e$ would be accumulated on the right edge of the crystal for $\Delta H = 10$ G. This corresponds to a voltage $V \simeq 1$ V between the edges of a mm-size crystal free of AFM domain walls. Similar results are obtained for a uniform magnetic field gradient along the y-direction. In this case, the numerical coefficient of Eq. (5) is $20/\sqrt{3}$ instead of 12 and the induced electric field is parallel to the y-axis.

These results where obtained in the linear response approximation, i.e., for $h_g N \ll D/J$. Under this condition, the energy of the induced electric field, $\epsilon_0(E_x N)^2/8\pi$, can be neglected because it is much smaller than the anisotropy energy ND. The sign of the induced electric polarization depends on the sign of the average spins. Hence, opposite AFM domains have opposite polarizations leading to a cancellation of the net electric field.

We will discuss now the magnetostrictive effect, i.e., the ion displacements produced by the applied magnetic field. A uniform magnetic field results in ionic shifts consistent with the CDW that we found for the electronic charge redistribution. However, a unifrom magnetic field gradient induces a uniform electric field inside the crystal that corresponds to a voltage difference $eV_{\text{str}} \approx \mu\Delta H$.

We use the label m for the oxygen ions shown in Fig. 3 to expand the exchange integrals J_{ij} in the ion displacements $\mathbf{u}_m$ and account for the corresponding elastic energy. The additional contribution to the Hamiltonian of Eq. (2) is

$$\mathcal{H}_{\rm str} = \sum_{m}[K\mathbf{u}_m^2/2+\sum_{ij}(\mathbf{u}_m\cdot\nabla_{\mathbf{u}_m}J_{ij})(\mathbf{S}_i\cdot\mathbf{S}_j-S^2)], \quad (7)$$

where K is the elastic module that we assume isotropic for simplicity. The dependence of the ionic displacements $\mathbf{u}_m$ on the spin structure is determined by minimizing the total energy. We split $\mathbf{u}_m$ into three components that are perpendicular to the sides of triangle (1,2,3) as shown in Fig. 3: $\mathbf{u}_m(123) = \mathbf{u}_m(12) + \mathbf{u}_m(13) + \mathbf{u}_m(23)$, i.e., $\mathbf{u}_m(ij)$ is perpendicular to the side (ij). The final result is:

$$\mathbf{u}_m(23) = C\langle\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_1\mathbf{S}_3 - 2\mathbf{S}_2\mathbf{S}_3\rangle, \quad (8)$$

with $C = K^{-1}\nabla_{\mathbf{u}_m(23)}J_{ij}$, and similar expressions hold for $\mathbf{u}_m(12)$ and $\mathbf{u}_m(13)$ with the same coefficient $C \approx aJ/U \approx 10^{-3}a$ due to the C_3 symmetry of our system. The oxygen ions are displaced toward the side with lowest exchange energy, i.e., where the angle between spins is closer to π. The ion displacements along the x and y-axis, $2u_{mx} = u_x(23) - u_x(12)$ and $u_{my} = -u_y(13)$, are shown in Fig. 3. The contribution of the oxygen ion to the polarization of the unit cell k is

$$P_x(k) = (\sqrt{3}eC/2)[7(\alpha_{1k} - \alpha_{1,k+1}) + 3(\alpha_{21,k+1} - \alpha_{21,k})].$$

Finally, we obtain that the net polarization of the crystal due to magnetostriction is:

$$\mathcal{P}_x = (3\sqrt{3}Ceh_gN/(2a^2b) = 3\sqrt{3}Ce(\mu\Delta H/2abJ), \quad (9)$$

where the boundary effect has been neglected. Thus, the net ionic polarization (as well as the voltage difference between the crystal edges) is proportional to the crystal length along the magnetic field gradient. Though C is bigger than A by a large factor (U/t), the even larger factor $N/2$ does not appear in the ionic polarization. Hence, the ionic contribution to the electric polarization is negligible in comparison with the electronic contribution for a long enough crystal size. This remmarkable result is simply a consequence of the fact that the same effective spin operator determines the change of the electronic charge density [Eq.(3)] and the shift of the oxigen ions [Eq.(8)]. While a uniform ionic displacement produces a uniform polarization or electric field, a uniform charge density incudes a *uniform electric field gradient*.

Although our results for the induced electric field were obtained for a static magnetic field, they hold for time dependent magnetic fields as long as the characteristic frequency is much smaller than the gap $\Delta \approx (JD)^{1/2}$ in the spectrum of magnetic excitations. It is also instructive to compare the response of a Mott insulator to a uniform magnetic field gradient with that of a fully polarized metal (itinerant ferromagnet). In the latter case, the electrons also move to the edge with highest magnetic field due to the Zeeman energy gradient. However, the induced electric field compensates the Zeeman force and the net result is a uniform electric field induced inside the sample. This different behavior results from the the fact that quasiparticles are free to move in a metal. Although this free motion does not exist in a Mott insulator, there is still a partial electronic delocalization that depends on the spin degrees of freedom. The charge distribution that results from this partial delocalization minimizes the sum of the exchange, Zeeman and electrostatic energies.

In conclusion, we have shown that a uniform magnetic field gradient induces a uniform electric field gradient in Mott insulators on a triangular lattice. This is the result of an electronic charge redistribution that only occurs on lattices containing odd numbers of sites in the hopping loops (geometric frustration) and for non-collinear zero field magnetic orderings. We note that weak next-nearest-neighbor exchange interactions on a square lattice result in a nonzero $\tilde{n}_i - 1$, but still $\langle\tilde{n}_i\rangle = 1$ because the spin ordering is collinear for $H = 0$. The voltage difference between the crystal edges that results from the magnetolectric effect described in this letter is proportional to the square of the crystal length. This novel effect can be used for measuring magnetic field gradients.

The authors thank S.-W. Cheong for stimulating this work and D. Khomskii for useful discussions. This research was supported by the US DOE under the contracts # W-7405-Eng-36 (LANL).

[1] M. Fiebig, J. Phys. D **38**, R123 (2005): D.I. Khomskii, JMMM **306**, 1 (2006): S.-W. Cheong and M.V. Mostovoy, Nature Materials **6**, 13 (2007).

[2] H.Katsura, N.Nagaosa and A.V.Balatsky, Phys. Rev. Lett. **95**, 057205 (2005); I.A. Sergienko and E.Dagotto, Phys. Rev. B **73**, 094434) (2006).

[3] L.N. Bulaevskii, C.D. Batista, M. Mostovoy, D.I. Khomskii, Phys. Rev. B **78**, 024402 (2008).

[4] L.N. Bulaevskii, Sov. Phys. JETP **24**, 154 (1967).

[5] O.P. Vajk, M. Kenzelmann, J.W. Lynn, S.B. Kim, S.-W. Cheong, Phys. Rev. Lett. **94**, 087601 (2006).