Spin-spiral states in undoped manganites

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The experimental observation of multiferroic behavior in perovskite manganites with a spiral spin structure demands to clarify the origin of these magnetic states and their relation to ferroelectricity. We show that spin-spiral phases with diagonal wavevector and also the E-type phase exist for intermediate values of the Hund’s rule and the Jahn-Teller coupling in the orbitally ordered and insulating state of the standard two-band model Hamiltonian for manganites. Our results support the spin-current mechanism for ferroelectricity and present an alternative view to earlier conclusions where frustrating superexchange couplings were crucial to obtain spin-spiral states.

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The coexistence of long-range magnetic order with spontaneous electric polarization is commonly referred to as multiferroic behavior [1]. In recent years multiferroic materials have attracted special attention from the condensed matter community because of their potential for applications in memory and data storage devices [2, 3]. Despite the initial observation that materials with coexisting ferroelectric and magnetic orders are rare in nature [4], an increasing number of multiferroic materials with interesting properties has been discovered [5–8]. Different mechanisms for the origin of multiferroic behavior have been proposed and partially identified [2, 4, 14]. In a selected class of multiferroics ferroelectricity is driven by the existence of a non-trivial magnetic order, e.g., with a spiral spin structure [15, 16]. It has therefore become a key issue to clarify the conditions under which non-trivial spin states can occur in different models and materials.

Hole-doped perovskite manganites are known for their rich phase diagrams and complex transport phenomena [13]. The recent observations of ferroelectricity in TbMnO3 and DyMnO3 stimulated further research also on the undoped materials. The magnetic groundstate of RMnO3 with R = La, Pr, Nd and Sm is an A-type antiferromagnet (AFM), with ferromagnetic (FM) order in the a-b plane and a staggered spin pattern along the c-axis. It changes to a spiral magnet for R = Tb and Dy, and finally to an E-type AFM for R = Ho, where zigzag FM chains alternate in their preferred spin direction [17, 21]. Although the A-type order of the prototype compound LaMnO3 is well understood in terms of Goodenough-Kanamori rules and orbital ordering [19], the magnetic structure of the materials with smaller ionic radii are much less understood. It was proposed that due to GdFeO3-type structural distortions longer range interactions become relevant and thereby may lead to complex magnetic groundstates with spiral or E-type spin patterns [17, 21]. The existence of an E-type pattern in these models with longer range interactions has been put into question recently [22].

In this letter we explore the magnetic groundstates in a two-band model for RMnO3 without invoking the next-nearest neighbor or even longer range interactions. The model consists of itinerant electrons coupled locally to core spins via the Hund’s rule coupling $J_H$, and a nearest neighbor antiferromagnetic interaction between the spins. Importantly, we refrain from taking the commonly adopted double-exchange limit $J_H \to \infty$. The two-orbital nature of the model allows for the inclusion of the Jahn-Teller (JT) distortions as a source for orbital order and hence the insulating character of the undoped manganites. We find that both the spiral spin states and the E-type states are stable in the parameter regime relevant for manganites. The experimentally observed transitions between different magnetic states are obtained only for finite JT couplings and intermediate values of $J_H$.

Specifically, we consider a two-dimensional two-band model with the Hamiltonian [23]:

$$H = - \sum_{ij} J_{ij} (c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + H.c.) - J_H \sum_{i\alpha} \mathbf{S}_i \cdot \mathbf{\sigma}_{i\alpha} + J_s \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

(1)

at quarter filling to describe the undoped manganites RMnO3. Here, $c_{i\alpha\sigma}$ and $c_{i\alpha\sigma}^\dagger$ are annihilation and creation operators for electrons with spin $\sigma$ in the $e_g$ orbital $\alpha \in \{x^2 - y^2, 3z^2 - r^2\}$, which from here onwards is labeled as 1 and 2, respectively. $t^{ij}_{\alpha\beta}$ denote the hop-
ping amplitudes between the two $e_g$ orbitals on nearest-neighbor sites and have the cubic perovskite specific form:

$$t_{11}^{y} = t, \quad t_{22}^{y} = t, \quad t_{12}^{y} = -t/\sqrt{3},$$

where $x$ and $y$ mark the spatial directions. In a commonly used approximation for manganites, the core spins are treated as classical vectors with $|S| = 1$; the justification of this approximation was quantitatively verified.

\[ \sigma_{\alpha} \] denotes the electronic spin operator defined as $\sigma_{\alpha} = \sum_{\sigma} c_{\alpha \sigma} \Gamma_{\sigma \alpha} c_{\alpha \sigma}$, where $\Gamma_{\sigma}$ are the Pauli matrices. The one-band version of the above model and the Kondo lattice model with $J_s = 0$ have been previously analyzed in one- and two-dimensions in search for non-trivial magnetic groundstates. Although spin-spiral states were found for selected combinations of band fillings and Hund’s rule coupling, the connection to the spin spirals observed in the RMnO$_3$ is unclear since the insulating character of orbitally ordered RMnO$_3$ is not captured by the one-band models.

By applying a canonical transformation we rewrite the Hamiltonian in a basis where the spin-quantization axis is site-dependent and points in the direction of the local core spin. Introducing polar and azimuthal angles $\theta$ and $\phi$, respectively, the transformation is defined as:

$$\begin{bmatrix} c_{i \alpha \uparrow} \\ c_{i \alpha \downarrow} \end{bmatrix} = \begin{bmatrix} \cos(\phi/2) & e^{i\phi_i/2} \\ \sin(\phi/2) & e^{-i\phi_i/2} \end{bmatrix} \begin{bmatrix} d_{i \alpha \uparrow} \\ d_{i \alpha \downarrow} \end{bmatrix} \equiv U(\theta_i, \phi_i) \begin{bmatrix} d_{i \alpha \uparrow} \\ d_{i \alpha \downarrow} \end{bmatrix}$$

Here $d_{i \alpha \uparrow}$ annihilates an electron at site $i$ in orbital $\alpha$ with spin parallel (antiparallel) to the core spin. In terms of $d$ operators the Hamiltonian reads:

$$H = -\sum_{ij} t_{ij}^\alpha (f_{s s'} d_{i \alpha \uparrow}^\dagger d_{j \beta \downarrow} + H.c.) - J_s \sum_{i \alpha} (n_{i \alpha \uparrow} - n_{i \alpha \downarrow}) + J_s \sum_{i} S_i \cdot S_j ,$$

with $n_{i \alpha \sigma} = d_{i \alpha \sigma}^\dagger d_{i \alpha \sigma}$. The coefficients $f_{s s'}$, are explicitly given by,

$$\begin{bmatrix} f_{pp} & f_{pa} \\ f_{ap} & f_{aa} \end{bmatrix} = U^\dagger(\theta_i, \phi_i) U(\theta_j, \phi_j),$$

The advantage of this transformation is that the Hund’s rule term now becomes diagonal. For a fixed configuration of classical spins the Hamiltonian is bilinear in the fermion operators. However the one-particle Schrödinger equation can not be solved in closed form for an arbitrary spin configuration. We therefore selectively analyze the core spin configurations described by the polar and azimuthal angles $\theta_i = \Theta$ and $\phi_i = q \cdot r_i$. We refer to $\Theta$ as the cone angle and $q$ as the spiral wavevector. Despite this restriction most of the well known spin patterns as observed in various magnetic materials are included, e.g., ferromagnetic, antiferromagnetic, canted-ferromagnetic, and spin-spiral patterns.

For this choice of variational spin states the Hamiltonian matrix reduces to a $4 \times 4$ matrix after Fourier transformation with, $d_{i \alpha s} = N^{-1/2} \sum_k d_{k \alpha s}$, and the kinetic energy term in Eq. (3) is then written as, $H_{kin} = \sum_k D_k^\dagger H(k) D_k$, where, $D_k^\dagger = \begin{bmatrix} d_{k1p}^\dagger & d_{k1a}^\dagger & d_{k2p}^\dagger & d_{k2a}^\dagger \end{bmatrix}$, and the $4 \times 4$ matrix $H$ is given by

$$H(k) \equiv \begin{bmatrix} h_{pp}^{pp} & h_{pp}^{pa} & h_{pp}^{pp} & h_{pp}^{pa} \\ h_{pa}^{pp} & h_{pa}^{pa} & h_{pa}^{pp} & h_{pa}^{pa} \\ h_{pp}^{pp} & h_{pp}^{pa} & h_{pp}^{pp} & h_{pp}^{pa} \\ h_{pa}^{pp} & h_{pa}^{pa} & h_{pa}^{pp} & h_{pa}^{pa} \end{bmatrix},$$

with the matrix elements,

$$h_{\alpha \beta}^{pp} = 2 \sum_{\mu=x,y} \frac{\mu^\alpha \beta}{2} \cos^2 \left( \frac{\Theta}{2} \right) \cos k_{\mu}^+ + \sin^2 \left( \frac{\Theta}{2} \right) \cos k_{\mu}^-$$

$$h_{\alpha \beta}^{pa} = 2 \sum_{\mu=x,y} \frac{\mu^\alpha \beta}{2} \cos^2 \left( \frac{\Theta}{2} \right) \cos k_{\mu}^- + \sin^2 \left( \frac{\Theta}{2} \right) \cos k_{\mu}^+$$

$$h_{\alpha \beta}^{pp} = 2 \sum_{\mu=x,y} \frac{\mu^\alpha \beta}{2} \sin(\Theta) \sin \left( \frac{\Theta}{2} \right) \sin k_{\mu} = h_{\alpha \beta}^{pa} \equiv h_{\alpha \beta}^{pa},$$

with $k_{\mu}^\pm = k_\mu \pm q_{\mu} / 2$. For a single band $H_{kin}$ reduces to a $2 \times 2$ matrix structure and therefore the eigenspectrum is straightforwardly obtained in a closed form expression.

For the two-band case considered here the closed form result for the dispersion is rather involved and we therefore diagonalize the above $4 \times 4$ matrix numerically for each momentum $k$ on finite lattices of up to $256 \times 256$ sites.

In Fig. 1 we plot the values of the cone angle $\Theta$ and the wavevector $(q_x, q_y)$ of the lowest-energy spiral state as a function of $J_H$ for, (a) $J_s = 0$ and (b) $J_s = 0.04 t$. The inset in (a) shows the $J_s$ dependence of the critical value of $J_H$ required to obtain the FM state.
from $\pi/2$. The ground state jumps discontinuously from an antiferromagnet with $q = \pi$ to a spiral with $q < \pi$. Inset in Fig. 1(a) shows the variation with $J_s$ of the critical value of Hund’s rule coupling $J_H^c$ for the transition to a ferromagnet.

Before arriving at the magnetic phase diagram of the Hamiltonian, it is essential to consider other states which are not captured by the ansatz $(\theta_i, \phi_i) = (\Theta, q, \tau_i)$ [21, 22]. The energies of the earlier suggested candidate states, including the E-type states, for the magnetic order in manganites are obtained by exact numerical diagonalization and compared with those of the spiral states.

The ground state phase diagram for the quarter filled system is shown in Fig. 2(a). The E-type phase is stable in a wide region of parameter space. Spiral states are favored for larger values of $J_s$, and also in a narrow window between the FM and the E-type states. Here, the FM state in a two-dimensional model is representative of a single plane of the A-type AFM state. In the experiments on RMnO$_3$ two transitions are observed, first from the A-type AFM to the spiral state and subsequently to the E-type phase, upon reducing the ionic radius of the rare-earth element [17]. Therefore the existence of a direct FM to E-type transition appears to contradict the experimental observation. Moreover, the phase diagram of Fig. 2(a) corresponds to a metallic state with a finite bandwidth due to the Mn-O-Mn bond angle moving further away from 180°. For the model calculations, it is simpler to vary $J_s$ and $\lambda$ rather than changing the hopping parameters which control the bandwidth. In Fig. 3 we therefore show the phase diagrams in the parameter space of $J_s$ and $\lambda$ for two representative values of $J_H$. For $J_H = 5t$, the small $J_s$ regime is ferromagnetic, which describes a single plane of the A-type AFM observed in RMnO$_3$ with $R = $ La, Pr, Nd and Sm. A two-step transition occurs from FM via the spiral to the E-type state by increasing both $\lambda$ and $J_s$ (indicated by the arrow in Fig. 3(a)), which effectively translates to reducing the bandwidth. In the (1,1) spiral state the pitch $q$ increases along the direction of the arrow (see Fig. 3(a)). The values of $q$ at the two end-points of the planar spiral phase

$$H_{JT} = \lambda \sum_i [Q_{zi}\tau_{zi} + Q_{zi}\tau_{zi}] + \frac{K}{2} \sum_i |Q_i|^2.$$

In Eq. (7), $Q_{zi}$ and $Q_{zi}$ are lattice distortions corresponding to two different JT modes. $\tau_{zi} = \sum_{\sigma} (c_{1z\sigma}^\dagger c_{2z\sigma} + c_{2z\sigma}^\dagger c_{1z\sigma})$ and $\tau_{zi} = \sum_{\sigma} (c_{1z\sigma}^\dagger c_{1z\sigma} - c_{2z\sigma}^\dagger c_{2z\sigma})$ are orbital pseudospin operators [19]. In the undoped manganites staggered JT distortions are accompanied by orbital ordering with transition temperatures much higher than the temperatures scale for magnetic ordering [17]. Therefore the pattern for the JT distortions is expected to be robust upon cooling even though the magnitude of the distortions may depend on the magnetic structure. A real-space Monte Carlo study verified the staggered ordering of the $Q_z$ components when $H_{JT}$ is included in the Hamiltonian [30]. Therefore we adopt this pattern for the lattice distortions and set $Q_{zi} = Q_{zi}^0 e^{i(\pi,\pi,\tau_i)}$ and $Q_{zi} = 0$. The second term in Eq. (7) is the energy cost associated with the distortion of the lattice with $|Q_i|^2 = Q_{zi}^2 + Q_{zi}^2$. We set the stiffness constant $K = t$ as in previous theoretical model analyses of manganites [19, 20]. We treat $Q_{zi}^0$ as a variational parameter in the calculations and optimize it by minimizing the total energy. Therefore $Q_{zi}^0$ is allowed to vary in the different magnetic states.
For a review see: D. Khomskii, Physics of Ferromagnets by S. Picozzi, T. Kimura, T. Kaplan and S. Mahanti, J. Betouras, G. Giovannetti, and J. van den Brink, Phys. Rev. B 73, 024422 (2006).

The presence of a spiral structure in an insulator has been identified as one possible source for a spontaneous electric polarization \( P \) by generating spin currents \[ 11 \]. The direction of \( P \) is perpendicular to both the direction of the spiral pitch vector \( q \) and the cone axis of the spiral \[ 12 \]. Our model of choice is isotropic in spin space and thus cannot determine the orientation of the cone axis relative to the crystallographic directions. Using the input from the experiments regarding the direction of the cone axis for the spiral state we indeed obtain the direction of \( P \) consistent with the experiments \[ 20, 31 \]. Within the spin-current mechanism the magnitude of \( P \) is controlled by the length of the pitch vector \( q \), which we obtained in the experimentally relevant range.

Therefore our results verify that already the standard two-band model for manganites has all the necessary ingredients to sustain the magnetic spiral and the E-type phases as observed in the undoped perovskite manganites. A finite Hund’s rule coupling of the order of the bandwidth leads to a spiral pattern and a wavelength which both compare well with the observed magnetic structure in TbMnO\(_3\) and DyMnO\(_3\). These results support the applicability of the spin current mechanism as the source for ferroelectricity in RMnO\(_3\). Lattice distortions of the GdFeO\(_3\)-type are likely to give rise to additional longer-range couplings, which may further stabilize the spiral and the E-type states. The essential physics of these non-trivial spin states is already contained in the simpler short-range two-orbital model with finite \( J_H \).

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