Long-Range Magnetic Interactions Induced by the Lattice Distortions and the Origin of the E-type Antiferromagnetic Phase in the Undoped Orthorhombic Manganites

Igor SOLOVYEV

Computational Materials Science Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

With the increase of the lattice distortion, the orthorhombic manganites $R$MnO$_3$ ($R=$ La, Pr, Nd, Tb, and Ho) are known to undergo the phase transition from the layered A-type antiferromagnetic (AFM) state to the zigzag E-type AFM state. We consider the microscopic origin of this transition. Our approach consists of the two parts. First, we construct an effective lattice fermion model for the manganese 3$d$-bands and derive parameters of this model from the first-principles electronic structure calculations. Then, we solve this model in the Hartree-Fock approximation (HFA) and analyze the behavior of interatomic magnetic interactions. We argue that the nearest-neighbor interactions decrease with the distortion and at certain stage start to compete with the longer range (particularly, second- and third-neighbor) AFM interactions in the orthorhombic ab-plane, which lead to the formation of the E-phase. The origin of these interactions is closely related to the orbital ordering, which takes place in the distorted orthorhombic structure. The model is able to capture the experimental trend and explain why LaMnO$_3$ develops the A-type AFM order and why it tends to transform to the E-type AFM order in the more distorted compounds. Nevertheless, the quantitative agreement with the experimental data crucially depends on other factors, such as the magnetic polarization of the oxygen sites and the correlation interactions beyond HFA.

KEYWORDS: undoped manganites, phase diagram, magnetic interactions, first-principles calculations, effective model

1. Introduction

For the long time LaMnO$_3$ was regarded as a prototypical example of parent (or undoped) manganites, where the strong Jahn-Teller distortion was believed to coexist with the (layered) A-type antiferromagnetic (AFM) state.$^{1-5}$ The origin of this AFM state was one of the most disputed points about one decade ago, right after the new wave of interest to the phenomenon of the colossal magnetoresistance in the manganite compounds has just emerged.$^{6-11}$ Despite many differences in details, all theories of that period of time seemed to agree that the Jahn-Teller effect plays an important role in the alternating population of the $3x^2-r^2$ and $3y^2-r^2$ orbitals (Fig. 1), which is primary responsible for the directional anisotropy of interatomic
magnetic interactions underlying the A-type AFM phase. Indeed, simple considerations for

![Diagram](image)

Fig. 1. (Color online) (a): experimental phase diagram of $RMnO_3$ versus temperature and ionic radius of rare-earth elements (from ref. 14). Magnetic phases are denoted as paramagnetic (P), A-type AFM (A), spiral AFM (S), incommensurate (IC), and E-type AFM (E). (b) and (c): spin arrangement in the orthorhombic $ab$-plane, which takes place in the AFM phases of the A- and E-type, respectively. (d): alternating $3x^2-r^2$ and $3y^2-r^2$ orbitals and main magnetic interactions in the $ab$-plane, which are responsible for the relative stability of the A- and E-states.

the superexchange (SE) interactions suggest that the alternating (antiferro) ordering of the $3x^2-r^2$ and $3y^2-r^2$ orbitals in the orthorhombic $ab$-plane leads to the ferromagnetic (FM or F) coupling, while stacking (ferro) orbital ordering in the $c$-direction is responsible for the weak AFM coupling.\(^5\)\(^,\)\(^12\)\(^,\)\(^13\)

The main surprise came later when it was found that after replacing La by smaller rare-earth elements ($R$), which \textit{systematically increases} all kinds of the lattice distortions (including the Jahn-Teller one), the orthorhombic $RMnO_3$ compounds undergo the change of the magnetic ground state (Fig. 1).\(^14\) Briefly, the least distorted LaMnO$_3$ forms the A-type AFM structure. The opposite-end compounds (starting from HoMnO$_3$) form the so-called E-type (zigzag) AFM structure. In the intermediate region, the magnetic structure is incommensurate and keeps some features of the both A- and E-type AFM phases. The appearance of the E-type AFM structure, which \textit{breaks the inversion symmetry} in otherwise centrosymmetric crystal environment, is particularly interesting. It can be hardly understood in terms of the
nearest-neighbor (NN) SE interactions alone, because such a mechanism would inevitably imply the change of the orbital state and operate against the large energy gain associated with the Jahn-Teller distortion. Therefore, it seems that the more realistic scenario should involve some longer range interactions.

At the purely phenomenological level, the competition between the A- and E-type AFM phases in the ab-plane can be rationalized in terms of the following interaction parameters and trends (Fig. 1):

- the NN interaction $J_1^\parallel$, which, depending on its sign, favors either FM or bipartite AFM arrangement;

- the 3rd-neighbor AFM interaction $J_3$ which couples all 3rd-neighbor spins antiferromagnetically, as required for the E-type AFM structure. Therefore, $J_3$ should be an indispensable ingredient of the model analysis. As we will see below, the main details of the magnetic phase diagram of RMnO$_3$ depend on the competition between $J_1^\parallel$ and $J_3$. If considered alone, the 3rd-neighbor AFM interactions would favor the formation of an infinitely degenerate group of states, including two zigzag AFM structures propagating along the orthorhombic a- and b-axes. The experimentally observed E-type AFM structure is the one of them, which propagates along the a-axis and where the spins are antiferromagnetically coupled along the b-axis;

- the 2nd-neighbor AFM interactions $J_2^b$, which lifts the degeneracy and together with $J_3$ determines the direction of propagation and the periodicity of the E-type AFM phase. The combination of $J_2^b$ and $J_3$ appears to be sufficient to bind the directions of spins in each of the orbital sublattices, which are denoted as $3x^2-r^2$ or $3y^2-r^2$ in Fig. 1.

Loosely speaking, if ferromagnetic $J_1^\parallel$ dominates over $J_2^b$ and $J_3$, the magnetic ground state will be of the A-type. On the other hand, if the longer range interactions dominates, the magnetic ground state will tend to be of the E-type. The last ingredient, which stabilizes the E-type AFM phase is the small difference between the parameters $J_1^\parallel$ acting in the FM and AFM bonds, which can be caused by either the exchange stiction or the orbital ordering effects. This difference is necessary in order to stabilize the directions of spins in two orbital sublattices relative to each other.

The purpose of this work is to show that all these features are in fact closely related to the crystal distortion and the type of the orbital ordering realized in the orthorhombic RMnO$_3$ compounds. We use the same strategy as in the previous work devoted to BiMnO$_3$. First, we derive an effective low-energy model for the Mn(3d) bands and extract parameters of this model from the first-principles electronic structure calculations based on the linear-muffin-tin-orbital (LMTO) method. Then, we solve this model in the Hartree-Fock approximation and analyze behavior of interatomic magnetic interactions and the total energies.
Table I. Crystal structure parameters of $R$MnO$_3$ compounds. $a$, $b$, and $c$ are the orthorhombic lattice constants, Mn-O are the interatomic distances, and $\angle$Mn-O-Mn are the bond angles (the first line is the angle in the $c$-direction and the second line is the angle in the $ab$-plane). All data are taken at room temperature except for LaMnO$_3$, corresponding to 4.2 K.

|                | LaMnO$_3$ | PrMnO$_3$ | NdMnO$_3$ | TbMnO$_3$ | HoMnO$_3$ |
|----------------|-----------|-----------|-----------|-----------|-----------|
| $a$ (Å)       | 5.532     | 5.449     | 5.416     | 5.302     | 5.257     |
| $b$            | 5.742     | 5.813     | 5.849     | 5.856     | 5.835     |
| $c$            | 7.668     | 7.586     | 7.543     | 7.401     | 7.361     |
| Mn-O (Å)     | 1.906     | 1.909     | 1.905     | 1.889     | 1.905     |
|               | 1.959     | 1.953     | 1.951     | 1.946     | 1.943     |
|               | 2.188     | 2.210     | 2.227     | 2.243     | 2.222     |
| $\angle$Mn-O-Mn ($^\circ$) | 157       | 152       | 150       | 144       | 142       |
|               | 154       | 151       | 149       | 146       | 144       |

The existence of the long-range magnetic interactions in LaMnO$_3$ was previously considered in ref. 17, in the context of the local stability of the A-type AFM state with respect to other magnetic states. In the present work, we will further consolidate this idea and argue that it constitutes the basis for understanding the magnetic properties of all undoped manganites.

The paper is organized as follows. In the next two sections we briefly discuss the main details of the experimental crystal structure (Sec. 2) and the electronic structure in the local-density approximation (LDA, Sec. 3). The construction of the model Hamiltonian for the Mn(3$d$) bands is considered in Sec. 4 and the strategy employed for the analysis of this Hamiltonian is briefly reviewed in Sec. 5. The behavior of interatomic magnetic interactions are discussed in Sec. 6. Sec. 7 is devoted to comparison with the experimental data. Particularly, we will consider the behavior of the correlation energies and the magnetic polarization of the oxygen sites, which is typically missing in the low-energy model. Finally, the brief summary will be given in Sec. 8.

2. Crystal Structure

All considered compounds crystallize in the highly distorted orthorhombic structure. The space group is $D^{16}_{2h}$ in Schönflies notations (No. 62 in International Tables). The primitive cell has four formula units. The crystal structure itself and its implications to the magnetic properties of LaMnO$_3$ have been discussed in many details in previous publications.\textsuperscript{6–8} Some crystal structure parameters are summarized in Table I. It also includes the references to the experimental lattice parameters, which have been used in the calculations. Generally, the crystal distortion in $R$MnO$_3$ tends to increase in the direction La$\rightarrow$Pr$\rightarrow$Nd$\rightarrow$Tb$\rightarrow$Ho. For example, such a tendency is clearly seen for the $b/a$ and $b/c$ ratios as well as for the Mn-O-
Mn angles. On the other hand, the Jahn-Teller distortion is not monotonous and takes the maximum in TbMnO$_3$. For example, the ratio of the maximal and minimal Mn-O bond lengths is 1.187 in TbMnO$_3$ (in comparison with 1.148 in the least distorted LaMnO$_3$), and only 1.166 in the following it HoMnO$_3$. This structural anomaly is directly related to the anomaly of the crystal-field (CF) splitting, which will be discussed in Sec. 4.

3. Electronic Structure in the Local-Density Approximation

An example of the LDA band structure as obtained in the LMTO calculations for LaMnO$_3$ and HoMnO$_3$ is shown in Fig. 2. The LMTO bases, which was used in the valence part of the spectrum, typically included the Mn(3$d^{4}$sp), $R$(5$d^{6}$sp), and O(2$sp$) states. The $R$(4$f$) states were treated as the (non-spin-polarized) core states. The atomic spheres radii were determined in two steps. First, we perform the LMTO calculations for the nominal composition, which includes 4 Mn, 4 $R$, and 12 O atoms, and find the atomic radii from the charge neutrality condition inside the spheres. Then, in order to better fill the unit cell volume and reduce the overlap between the atomic spheres, we add 12 to 16 empty spheres with the 1$s^{2}$2$p$-basis. Typically, such a procedure guarantee a good agreement with the more accurate full-potential calculations.

The electronic structure near the Fermi level is mainly formed by the Mn(3$d$) states. There is also a considerable weight of the Mn(3$d$) states in the oxygen band. Due to the strong crystal-field (CF) effects in the MnO$_6$ octahedra, the electronic structure near the Fermi level splits into the “pseudocubic” Mn($e_g$) and Mn($t_{2g}$) bands. The Jahn-Teller distortion further splits the Mn($e_g$) band in two subbands lying at around 1 and 3 eV (Fig. 3). In NdMnO$_3$, TbMnO$_3$, and HoMnO$_3$, these subbands are separated by an energy gap, whereas in the least...
Fig. 3. (Color online) LDA energy bands for LaMnO$_3$ (left) and HoMnO$_3$ (right) as obtained in the original electronic structure calculations using the LMTO method and after the tight-binding (TB) parametrization using the downfolding method. Twelve low-lying bands spreading from around -1.0 till 0.4 eV are the “$t_{2g}$ bands” and the next eight bands are the “$e_g$” bands. Notations of the high-symmetry points of the Brillouin zone are taken from ref. 26.

In distorted LaMnO$_3$ and PrMnO$_3$, there is a small overlap between them. In the majority of the considered compounds, there is also a small overlap between upper Mn($e_g$) and R(5$d$) bands. An exception is HoMnO$_3$, where these bands are separated by a small energy gap.

4. Construction and Parameters of the Model Hamiltonian

Our next goal is the construction of an effective model Hamiltonian for the Mn(3$d$) bands located near the Fermi level. For these purposes we use the method proposed in ref. 23. Many details can be found in the review article. The model itself is specified as follows:

$$\hat{H} = \sum_{RR'} \sum_{\alpha_1 \alpha_2} t_{\alpha_1 \alpha_2}^{RR'} \hat{c}_{R \alpha_1}^{\dagger} \hat{c}_{R' \alpha_2} + \frac{1}{2} \sum_{\{\alpha\}} U_{\alpha_1 \alpha_2 \alpha_3 \alpha_4} \hat{c}_{R_{\alpha_1}}^{\dagger} \hat{c}_{R_{\alpha_3}} \hat{c}_{R_{\alpha_2}} \hat{c}_{R_{\alpha_4}},$$

where $\hat{c}_{R \alpha}^{\dagger}$ creates (annihilates) an electron in the Wannier orbital $\tilde{W}_{R \alpha}^R$ centered at the Mn-site $R$, and $\alpha$ is a joint index, incorporating the spin ($s=\uparrow$ or $\downarrow$) and orbital ($m=xy, yz, z^2, zx, or x^2-y^2$) degrees of freedom.

The one-electron Hamiltonian $t_{RR'}=|t_{\alpha_1 \alpha_2}^{RR'}|$ consists of the two parts: the site-diagonal elements ($R=R'$) describe the crystal-field effects, whereas the off-diagonal elements ($R \neq R'$) stand for the transfer integrals, describing the kinetic energy of electrons. They are derived from the LDA band structure by using the formal downfolding method, which is totally equivalent to the use of the Wannier-basis in the projector-operator method. The comparison between the original LDA bands and the ones obtained in the downfolding method is shown in Fig. 3. In LaMnO$_3$, the agreement is nearly perfect for the Mn($t_{2g}$) and the most of the Mn($e_g$) bands located in the low-energy part of the spectrum. In this region, the original electronic structure of the LMTO method is well reproduced after the downfolding. Since upper Mn($e_g$) bands overlap with the La(5$d$) bands, it is virtually impossible to reproduce all de-
tails of the electronic structure in the minimal model (1) limited to the five Wannier-orbitals centered at each Mn-site. In this sense, the electronic structure obtained in the downfolding method is only an approximation to the original LDA band structure. Similar situation occurs in PrMnO$_3$, NdMnO$_3$, and TbMnO$_3$. In HoMnO$_3$, all Mn(3$d$) bands are separated from the Ho(5$d$) ones and well reproduced by the downfolding method.

The one-electron parameters in the real space are obtained after the Fourier transformation. Since we do not consider here the relativistic spin-orbit interaction, the matrix elements $t_{RR'}^{\alpha_1\alpha_2}$ are diagonal with respect to the spin indices: i.e., $t_{RR'}^{\alpha_1\alpha_2}=t_{RR'}^{m_1m_2}\delta_{s_1s_2}$. Then, the site-diagonal part of $\hat{t}_{RR'}=||t_{RR'}^{m_1m_2}||$ describes the CF effects. For example, the CF splitting is obtained after the diagonalization of $\hat{t}_{RR}$. It is particularly strong for the $e_g$ levels, being of the order of 1.5 eV (Fig. 4), and increases with the increase of the crystal distortion. As was pointed out in Sec. 2, some decrease of the $e_g$-level splitting in HoMnO$_3$ in comparison with TbMnO$_3$ is related to the decrease of the Jahn-Teller distortion. For all considered compounds,

![Crystal-field splitting](image)

Fig. 4. Crystal-field splitting. Three low-lying levels are of the “$t_{2g}$”-type and the next two levels are of the “$e_g$”-type.

the CF splitting is caused by the difference in the Mn(3$d$)-O(2$p$) hybridization in different Mn-O bonds, which after the elimination of the O(2$p$)-states gives rise to the site-diagonal elements in the model Hamiltonian. The effect of nonsphericity of the Madelung potential, which plays a crucial role in the $t_{2g}$ compounds,\textsuperscript{27,28} is relatively small for the $e_g$-systems. For example in HoMnO$_3$, it changes the $e_g$-levels splitting by less than 3%.

The directions of the CF splitting alternate on the perovskite lattice according to the $D_{2h}^{16}$ space group. The corresponding distribution of the $e_g$-electron densities (or the orbital ordering) is shown in Fig. 5.\textsuperscript{29} As will be discussed in Sec. 5, this orbital ordering is directly responsible for the behavior of not only the NN but also the longer range magnetic interactions.
Fig. 5. Orbital ordering in LaMnO$_3$ derived from crystal-field $e_g$ orbitals of downfolded Hamiltonian (more specifically, the distribution of the electron density corresponding to the lowest $e_g$ level in Fig. 4).\textsuperscript{29} Oxygen atoms are shown by small spheres. The vectors a, b, and c show the directions of orthorhombic axes. Other symbols show interatomic magnetic interactions in and between the planes, which are related to the given orbital ordering.

Because of complexity of the transfer integrals, it is rather difficult to discuss the behavior of individual matrix elements of $|t_{RR'}^{m_1m_2}|$. Nevertheless, some useful information can be obtained from the analysis of averaged parameters

$$
\bar{t}_{RR'}(d) = \left( \sum_{m_1m_2} t_{RR'}^{m_1m_2} t_{RR'}^{m_2m_1} \right)^{1/2},
$$

where $d$ is the distance between the Mn-sites $\mathbf{R}$ and $\mathbf{R}'$. All transfer integrals are well localized and practically restricted by the nearest neighbors at around 4Å (Fig. 6). Already between the next nearest neighbors, the transfer integrals are considerably smaller. Generally, $\bar{t}_{RR'}$ are larger for the least distorted LaMnO$_3$ and smaller for the more distorted HoMnO$_3$.

The screened Coulomb interactions $U_{RR'}^{R}$ have usual dependence on the spin indices:

$$
U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{R} = U_{m_1m_2m_3m_4}^{R} \delta_{s_1s_2} \delta_{s_3s_4}.
$$

Generally, the matrix $\hat{U}^{R} = \|U_{m_1m_2m_3m_4}^{R}\|$ can depend on the site-index $\mathbf{R}$. The intersite matrix elements of $\hat{U}$ are considerably smaller.\textsuperscript{23}

The matrix $\hat{U}^{R}$ itself has been computed in two steps.\textsuperscript{23,24} First, we perform the conventional constrained LDA (cLDA) calculations, and derive parameters of on-site Coulomb and exchange interactions between pseudoatomic Mn(3$d$) orbitals. These parameters are typically rather large because the do not include the so-called self-screening effects caused by the same 3$d$ electrons, which participate in the formation of other bands due to the hybridization.\textsuperscript{24} The major contribution comes from the O(2$p$) band, which has a large weight of the
Fig. 6. (Color online) Distance-dependence of averaged transfer integrals, $t_{RR'}(d) = \left( \sum_{m_1m_2} t_{R'\neq R}^{m_1m_2} \right)^{1/2}$.

Mn(3$d$) states (Fig. 2). This channel of screening can be efficiently taken into account in the random-phase approximation (RPA) by starting from the interaction parameters obtained in cLDA and assuming that the latter already include all other channels of screening. All RPA calculations have been performed by starting from the LDA band structure. Nevertheless, in order to simulate the electronic structure close to the saturated (ferromagnetic) state, we used different Fermi levels for the majority ($\uparrow$-) and minority ($\downarrow$-) spin states. Namely, it was assumed that the Mn(3$d$) band is empty for the $\downarrow$-spin channel and accommodates all 16 electrons (per one primitive unit) for the $\uparrow$-spin channel. Meanwhile, we get rid of the unphysical metallic screening by switching off all contributions to the RPA polarization function, which are associated with the transitions within the Mn(3$d$) band.

Then, at each Mn site we obtain the $5 \times 5 \times 5 \times 5$ matrix $\hat{U}_R$ of the screened Coulomb interactions. Since the RPA screening incorporates some effects of the local environment in solid, the symmetry of such matrices differs from the spherical one. Nevertheless, just for the explanatory purposes, we fit each matrix in terms of three parameters, which specify interactions between the 3$d$-electrons in the spherical environment: the Coulomb repulsion $U = F^0$, the intraatomic exchange coupling $J = (F^2 + F^4)/14$, and the “nonsphericity” $B = (9F^2 - 5F^4)/441$, where $F^0$, $F^2$, and $F^4$ are the radial Slater’s integrals. These parameters have the following meaning: $U$ is responsible for the charge stability of certain atomic configuration, while $J$ and $B$ are responsible for the first and second Hund rule, respectively. The results of such a fitting are shown in Table II. One can clearly see that the Coulomb repulsion $U$ appears to be relatively small due to the self-screening effects, while $J$ and $B$ are much closer to the atomic limit.

The model (1) does not explicitly include the oxygen states. This could be a serious prob-
Table II. Results of fitting of the effective Coulomb interactions in terms of three atomic parameters: the Coulomb repulsion $U$, the exchange coupling $J$ and the nonsphericity $B$. All energies are measured in eV.

| compound    | $U$  | $J$  | $B$  |
|-------------|------|------|------|
| LaMnO$_3$   | 2.15 | 0.85 | 0.09 |
| PrMnO$_3$   | 2.07 | 0.85 | 0.09 |
| NdMnO$_3$   | 2.11 | 0.85 | 0.09 |
| TbMnO$_3$   | 2.24 | 0.86 | 0.09 |
| HoMnO$_3$   | 2.16 | 0.85 | 0.09 |

In the case of manganites, which are known to be close to the charge-transfer regime.$^{30}$ On the other hand, it is well known that in many cases a good semi-quantitative description of the magnetic properties of manganites can be achieved already in a minimal model comprising only of the Mn($e_g$) bands.$^{17}$ We will pursue the same point of view and concentrate on the behavior of the Mn(3$d$) bands. The magnetic polarization of the oxygen states will be considered in Sec. 7, where it will be also argued that this effect is partially compensated by correlation interactions in the Mn(3$d$) band beyond the Hartree-Fock approximation.

5. Solution and Analysis of the Model

The model Hamiltonian (1) was solved in the Hartree-Fock (HF) approximation.$^{15,24,28}$ After the solution for each magnetic state, the total energy changes corresponding to infinitesimal rotations of the spins magnetic moments near this state were mapped onto the Heisenberg model:$^{31,32}$

$$E_{\text{Heis}} = -\frac{1}{2} \sum_{RR'} J_{RR'} e_R \cdot e_{R'},$$

where $e_R$ is the direction of the magnetic moment at the site $R$. The parameters \{\$J_{RR'}$\} can be expressed through the one-electron (retarded) Green function, $\hat{G}_{RR'}(\omega)$, and the spin-dependent part of the one-electron potential, $\Delta \hat{V}_R$, obtained from the self-consistent solution of the HF equations. For some applications, it is convenient to consider $J_{RR'}$ as the function of the band filling:

$$J_{RR'}(\omega) = \int_{-\infty}^{\omega} d\omega' J_{RR'}(\omega'),$$

where

$$J_{RR'}(\omega') = \frac{1}{2\pi} \text{Im} \text{Tr}_L \left\{ \hat{G}_{RR'}^{\uparrow}(\omega') \Delta \hat{V}_R \hat{G}_{RR'}^{\downarrow}(\omega') \Delta \hat{V}_R \right\}$$

and $\text{Tr}_L$ is the trace over the orbital indices. In order to obtain the observable parameters, $J_{RR'}(\omega)$ should be taken at the Fermi energy $\varepsilon_F$: $J_{RR'} \equiv J_{RR'}(\varepsilon_F)$. Some details of this procedure can be found in the review article$^{24}$ as well as in the recent publication devoted to
6. Electronic Structure and Behavior of Interatomic Magnetic Interactions

A typical example of the densities of states obtained in the HF calculations for the FM and several AFM phases of LaMnO$_3$ is shown in Fig. 7. Even in LaMnO$_3$, which is the least distorted compound, the small value of $U$, obtained in the combined cLDA+RPA approach, appears to be sufficient to open the gap in the $e_g$ band, so that all magnetic phases, including the FM one, become insulating. As expected, the increase of the number of the AFM bonds associated with the change of the magnetic state in the direction FM→A-type AFM→E-type AFM results in the narrowing of all bands. Thus, the opening of the band gap is considerably facilitated by the interplay of the crystal distortion with the AFM arrangement of spins. For example, even small Jahn-Teller distorted appears to be sufficient to open the gap in the quasi-two-dimensional FM planes of the A-phase.$^{33,34}$ A similar situation is expected for the quasi-one-dimensional spin chains in the case of the E-phase.$^{35}$ In other compounds, with the increase of the crystal distortion the bandwidths will additionally decrease. In other respects, the position of the main bands is similar to the one displayed in Fig. 7.

The distance-dependence of interatomic magnetic interactions $J_{RR'}$ is shown in Fig. 8. One can clearly distinguish four types of interactions, which mainly contribute to the magnetic properties of $RMnO_3$: the NN interaction in the orthorhombic $ab$-plane, $J_{1}^{||}$, which strongly

Fig. 7. (Color online) Densities of states obtained in the Hartree-Fock calculations for the ferromagnetic (F), A- and E-type antiferromagnetic phases of LaMnO$_3$. The Fermi level is at zero energy (shown by dash-dotted line). Other symbols show the positions of the main bands. Different spin states are indicated by the arrows.
Fig. 8. (Color online) Distance-dependence of interatomic magnetic interactions, as obtained in the Hartree-Fock calculations for the ferromagnetic state. The interactions, which mainly contribute to the stability of the A- and E-type AFM phases, are shown in groups. The notations of these interactions are explained in Fig. 5.

depends on the crystal distortion; the NN AFM interaction along the c-axis, $J^\perp_1$; the 2nd-neighbor interaction in the ab-plane, $J^b_2$, which operates along the orthorhombic b-axis; and the 3rd-neighbor AFM interaction in the ab-plane, $J_3$, which operates only between those Mn-sites whose occupied e_g orbitals are pointed towards each other (see Fig. 5). Other interactions are considerably weaker. Particularly, the 2nd-neighbor interactions along the a-axis as well as the 3rd-neighbor interactions in the direction perpendicular to the occupied e_g orbitals are small and can be neglected.

The details of the behavior of the main magnetic interactions are shown in Fig. 9. The interaction $J^\parallel_1$ appears to be the most affected by the crystal distortion. When the crystal distortion increases in the direction La→Pr→Nd→Tb→Ho, $J^\parallel_1$ gradually decreases and changes the sign at around Pr-Nd. Thus, the NN coupling in the ab-plane is FM at the beginning of the series and becomes AFM at the end of it. At the phenomenological level, such a behavior can be related to the change of the orbital ordering in the Mn-O-Mn bond (Fig. 10). In LaMnO_3, the Mn-O-Mn angle is closer to 180° (Table I). Therefore, the arrangement of the occupied e_g-orbitals at the neighboring Mn-sites is nearly “antiferromagnetic”, which according to the Goodenough-Kanamori rules should correspond to the FM coupling between the spins. In HoMnO_3, the deviation of the Mn-O-Mn angle from 180° is substantially larger. Therefore, the “antiferromagnetic orbital ordering” is strongly distorted so that the spin coupling can become AFM. Nevertheless, as we will see below, although such a phenomenological interpretation is strongly affected by other details of the electronic structure and particularly – by the hybridization between the t_{2g} and e_g states, which is caused by
Fig. 9. (Color online) The behavior of the main interatomic magnetic interactions for the $RMnO_3$ compounds, as obtained in the Hartree-Fock calculations for the FM state: the nearest-neighbor interaction in the $ab$-plane, $J^\parallel_1$ (a); the nearest-neighbor interaction between the planes, $J^\perp_1$ (b); and the longer range interactions in the $ab$-plane, $J^b_2$ and $J_3$ (correspondingly, b and c). The notations of the magnetic interactions are explained in figure 5.

Fig. 10. (Color online) Fragment of the orbital ordering in the plane formed by the single Mn-O-Mn bond in the case of LaMnO$_3$ (left) and HoMnO$_3$ (right).

the crystal distortion.

Other magnetic interactions also depend on the crystal distortion. However, the distortion does not change the character of these interactions, and $J^\perp_1$, $J^b_2$ and $J_3$ are AFM for all considered compounds.

The most striking result of the present calculations is the existence of relatively strong longer range AFM interactions $J^b_2$ and $J_3$. The appearance of $J_3$ is expected for the given type of the orbital ordering (Figs. 1 and 5). It operates between such 3rd neighbor sites $\mathbf{R}$ and $\mathbf{R}'$ in the $ab$-plane, whose occupied $e_g$ orbitals are directed towards each other, and is mediated by the intermediate site, whose occupied $e_g$ orbital is nearly orthogonal to the bond $\langle \mathbf{R}\mathbf{R}' \rangle$. Although the direct transfer integrals between such sites $\mathbf{R}$ and $\mathbf{R}'$ are small (Fig. 6, note that the distance between 3rd neighbors in the $ab$-plane is about 8 Å), the on-site Coulomb repulsion $U$ is also relatively small (Table II). Therefore, the longer range AFM interactions, which are mediated by unoccupied $e_g$ orbitals of intermediate Mn-sites, have the same origin.
as the SE interactions, operating in the charge-transfer insulators via the oxygen states,\(^{37-39}\) and the mechanism itself can be called the “super-superexchange”. Another 3rd-neighbor interaction, operating between Mn-sites in the \(ab\)-plane whose occupied \(e_g\) orbital are nearly orthogonal to the bond connecting these sites, is negligibly small. A similar situation occurs in the low-temperature monoclinic phase of BiMnO\(_3\).\(^{15}\) The main difference is that the orbital ordering realized in BiMnO\(_3\) is different from the one which takes place in the orthorhombic compounds. Therefore, the long-range AFM interactions in BiMnO\(_3\) will tend to stabilize another magnetic state, which is also different from the E-state.

The mechanism responsible for the appearance of the relatively strong interaction \(J_{b}^{2}\) is not so straightforward. Nevertheless, as we will show below, some useful information can be gained from the analysis of the band-filling dependence of the 2nd-neighbor interactions in the \(ab\)-plane.

Fig. 11 shows the behavior of the NN magnetic interactions as a function of the band filling. Somewhat unexpectedly, the NN interactions in LaMnO\(_3\) are mainly formed by the

![Diagram](image)

**Fig. 11.** (Color online) Band-filling dependence of the nearest-neighbor magnetic interactions in the \(ab\)-plane \((J_{1}^{||})\) and between the planes \((J_{1}^{\perp})\). The magnetic interactions were calculated in the FM state for LaMnO\(_3\) (left) and HoMnO\(_3\) (right). Upper panel shows the behavior of the integrant (3), while the lower panel shows the exchange coupling (2). The Fermi level is at zero energy (shown by dash-dotted line). The positions of the \(t_{2g}\) and \(e_g\)-bands are indicated by symbols.
t_{2g}-band. Particularly, the values of both $J^\parallel_1$ and $J^\perp_1$ are well reproduced already after integration over the $t_{2g}$-band spreading from -3.5 eV till -2.0 eV. The distribution of $J_{RR'}^{\text{RR'}}$ in the region of the occupied $e_g$-band is antisymmetric. Therefore, there is a strong cancelation of contributions to $J_{RR'}^{\text{RR'}}$ coming from the bottom and the top of the occupied $e_g$-band, so that the total integral (2) over the $e_g$-band practically vanishes. In this sense, our explanation for the A-type AFM order in LaMnO$_3$ is rather different from the one adopted in the model calculations,$^8,10,11$ which typically do not consider the rotations of the MnO$_6$ octahedra. According to the present calculations, the behavior of the NN magnetic interactions in LaMnO$_3$ is mainly related to the hybridization between the atomic $t_{2g}$- and $e_g$-orbitals, which is induced by these rotations. Without the hybridization, all contribution of the half-filled $t_{2g}$-band to the NN magnetic interactions are expected to be antiferromagnetic.$^{10,11}$ Our analysis shows that the hybridization can easily change the character of these interactions.

The $t_{2g}$-$e_g$ hybridization becomes even stronger in the more distorted HoMnO$_3$, so that the contributions of the $t_{2g}$-band become ferromagnetic both for $J^\parallel_1$ and $J^\perp_1$. On the contrary, all contributions of the $e_g$-band to the NN interactions are antiferromagnetic. Therefore, the $e_g$-band is totally responsible for the AFM character of NN magnetic interactions in the case HoMnO$_3$.

The behavior of 2nd-neighbor interactions in the ab-plane as a function of the band filling is shown in Fig. 12. Generally, the integrant $J_{RR'}^{\text{RR'}}(\omega)$ oscillates in sign. Moreover, as the distance between the lattice centers $R$ and $R'$ increases, the number of such oscillations also increases. This property can be rigorously proven for the tight-binding bands, assuming that all transfer integrals (or “hoppings”) are restricted by the nearest neighbors. Then, the number of nodes of $J_{RR'}^{\text{RR'}}(\omega)$ becomes proportional to the minimal number of hopes, which are required in order to reach the center $R'$ starting from the center $R$.$^{40,41}$ Thus, $J_{RR'}^{\text{RR'}}(\omega)$ is expected to have more nodes for the 2nd-neighbor interactions in comparison with the NN ones, as it is clearly seen from the comparison of Figs. 11 and 12. Nevertheless, the lattice distortion and orbital ordering effects can cause some violation of these simple tight-binding rules. Let us consider the behavior of $J_{RR'}^{\text{RR'}}(\omega)$ in the region of the $e_g$-band, where $J^\parallel_1(\omega)$ has only one node, which is qualitatively consistent with the tight-binding rules. Then, $J^\perp_2(\omega)$ has two nodes, which is again consistent with the tight-binding rules. Such a behavior is responsible for the strong cancelation of positive and negative contributions to $J^\perp_2$ in the process of integration over $\omega$ and readily explains the fact that the final values of $J^\perp_2$ are relatively small for all considered compounds. However, the $\omega$-dependence of $J^\parallel_2(\omega)$ appears to be strongly deformed. In the region of the $e_g$-band it has only one node. Therefore, the strong cancelation, which took place for $J^\parallel_2$, does not occur for $J^\perp_2$. This leads to the strong anisotropy of the 2nd-neighbor interactions in the ab-plane, $|J^\parallel_2| \gg |J^\perp_2|$, which plays a vital role in the formation of the E-type AFM structure. Particularly, it readily explains the fact why the FM
Fig. 12. (Color online) Band-filling dependance of the second-neighbor magnetic interactions in the \textit{ab}-plane. The magnetic interactions were calculated in the FM state for LaMnO$_3$ (left) and HoMnO$_3$ (right). Upper panel shows the behavior of the integrant (3), while the lower panel shows the exchange coupling (2). The notations of the magnetic interactions are explained in Fig. 5. The Fermi level is at zero energy (shown by dash-dotted line). The positions of the $t_{2g}$- and $e_g$-bands are indicated by symbols.

zigzag chains in the observed E-type AFM structure propagate along the \textit{a}-direction and are antiferromagnetically coupled along the \textit{b}-axis (and not vice versa).

Thus, the behavior of the main magnetic interactions replicates the gradual change of the crystal distortion. The form of both NN and long-range magnetic interactions is closely related to the orbital ordering realized in the distorted orthorhombic structure. Particularly, the crystal distortion explains

- the gradual change of $J_{\parallel}^1$ from FM in the case of LaMnO$_3$ to AFM at the end of the series. Near the point of the FM-AFM crossover, $J_{\parallel}^1$ is small and the magnetic ground state is mainly controlled by the longer range interactions.

- the existence of the longer range AFM interactions $J_{\parallel}^2$ and $J_3$, which bind the spin magnetic moments within each orbital sublattice, and determine both the direction of propagation and the periodicity of the E-phase.

Nevertheless, there should be an additional mechanism responsible for the relative orien-
tation of spin magnetic moments in two orbital sublattices, which are marked as $3x^2-r^2$ and $3y^2-r^2$ in Fig. 1. Since each spin in the E-type AFM structure participates in the formation of two FM and two AFM bonds with the nearest neighbors in the $ab$-plane, some difference between parameters $J_1^\parallel$ acting in the FM and AFM bonds is required in order to fix the directions of spins in the two orbitals sublattices relative to each other.\(^{42}\) Such a modulation of the parameters $J_1^\parallel$ can be caused by several mechanisms. Generally, once the symmetry is broken by the AFM spin order, orbital and lattice degrees of freedom will tend to adjust this symmetry change.

One mechanism is purely electronic and related to the small deformation of the orbital ordering in the AFM phase. For example, in BiMnO$_3$ such a mechanism facilitates the formation of the $\uparrow\downarrow\downarrow\uparrow$ AFM structure, which breaks the inversion symmetry.\(^{15}\) Nevertheless, in $R$MnO$_3$ the situation appears to be different. For all considered compounds, the NN interactions calculated in the E-phase satisfy the following condition: $J_1^\parallel(\uparrow\uparrow) < J_1^\parallel(\uparrow\downarrow)$, where the notations $\uparrow\uparrow$ and $\uparrow\downarrow$ are referred to the FM and AFM bonds, respectively (Fig. 13). Thus, as far as the NN interactions are concerned, the E-phase appears to be unstable with respect to the spin rotations of two orbital sublattices relative to each other.\(^{43}\) Apparently, such a situation is realized in the intermediate region, corresponding to the IC- and S-states in Fig. 1. Nevertheless, in order to stabilize the E-phase, we need another mechanism, which enforces the inequality $J_1^\parallel(\uparrow\uparrow) > J_1^\parallel(\uparrow\downarrow)$. Such a mechanism does exist and is related to the atomic displacements, which further minimize the total energy of the system via magneto-elastic interactions.\(^{44,45}\) Although we do not consider it in the present work, from rather general

---

**Fig. 13.** (Color online) Nearest-neighbor magnetic interactions in the $ab$-plane of E-type antiferromagnetic phase. The magnetic coupling in the FM and AFM bonds is denoted as $\uparrow\uparrow$ and $\uparrow\downarrow$, respectively.
properties of the double exchange and SE interactions,\(^{46}\) it is reasonable to expect that the AFM character of \(J_{\parallel}(\uparrow\downarrow)\) can be enforced by the conditions, which further enhance of the transfer integrals in the AFM bond.\(^{47}\) This can be achieved by either shrinking the Mn-Mn bond or increasing the Mn-O-Mn angle. The opposite distortions will favor the FM coupling, which are relevant to \(J_{1}(\uparrow\uparrow)\).

7. Total Energies and Comparison with the Experimental Data

In this section we consider the quantitative aspects of the problem. Particularly, we investigate whether the experimental phase shown in Fig. 1 can be reproduced by the low-energy model (1) for the Mn(3\(d\)) bands and, if not, which ingredients are missing in the model.

We begin with the total energy calculations for the model (1) in the HF approximation (14). In LaMnO\(_3\), the lowest energy corresponds to the A-type AFM state, in agreement with the experiment. However, the next E-type AFM state is separated from the A-state by only 1.1 meV per one formula unit. In PrMnO\(_3\) and NdMnO\(_3\), the energy of the E-type AFM state appears to be lower than the one of the A-state, although experimentally both of these compounds are the A-type antiferromagnets (Fig. 1). Finally, for TbMnO\(_3\) and HoMnO\(_3\), the model (1) yields the G-type AFM ground state, where all NN spins are coupled antiferromagnetically. Thus, although the model (1) predicts the change of the magnetic ground state, it clearly overestimates the tendencies towards the antiferromagnetism, so that the transition from the A- to E-type AFM state is expected in the wrong place (around PrMnO\(_3\) and NdMnO\(_3\) instead of HoMnO\(_3\)). The correlation interactions beyond the HF approximation, will additionally stabilize the AFM states,\(^{28}\) and only worsen the agreement with the experimental data. Therefore, before considering the correlation effects, one should find some
mechanism, which works in the opposite direction and additionally stabilizes the FM interactions.

Such a mechanism can be related to the magnetic polarization of the oxygen sites.\textsuperscript{48,49} Although the model (1) is designed for the Mn(3d) bands, the Wannier functions, which constitute the basis of the low-energy model (1), may have some tails spreading to the oxygen and other atomic sites. The weight of these tails in the Wannier functions is proportional to the weight of the O(2p)-states in the total density of states for the Mn(3d) bands (Fig. 2). In the case of the FM alignment of the Mn-spins, these tails will lead to some finite polarization at the intermediate oxygen sites (Fig. 15). Since the intraatomic exchange coupling $J_O$ associated

![Diagram](image)

Fig. 15. (Color online) Polarization of the oxygen sites caused by the tails of the Wannier functions centered at the manganese sites. In the perovskite structure, each oxygen site is located near the midpoint between two manganese sites. Then, in the case of the FM alignment, the tails from the Mn-sites have the same direction of spins, yielding the net magnetic moment also at the oxygen sites. In the case of the AFM arrangement, these tails cancel each other and the oxygen atoms remain nonmagnetic.

with the oxygen atoms is exceptionally large,\textsuperscript{49–51} even small polarization can lead to the substantial energy gain. This contribution is missing in the model (1), where the form of the Coulomb and exchange interactions is assumed to be the same as in the limit of isolated Mn-atoms. In the case of the AFM alignment, the tails of the Wannier functions cancel each other and the net magnetic polarization at the oxygen sites is zero.
Table III. Magnetic polarization of the oxygen sites in different magnetic states of HoMnO$_3$ (namely, the absolute values of the magnetic moments at the oxygen sites in $\mu_B$). The first value was derived from the model analysis for the isolated Mn(3$d$) bands, while the second value (shown in the parentheses) was obtained in the LSDA calculations, which also take into account the polarization of the O(2$p$) band. O$_{ab}$ and O$_c$ denote the oxygen sites located in the ab-plane and between the planes, respectively. Two lines in the case of the E-phase stand for the polarization in the FM (first line) and AFM (second line) Mn-O-Mn bonds. The finite polarization in some AFM Mn-O-Mn bonds is related to the oxygen displacements from the midpoint positions in the $D_{2h}^{16}$ structure.

| phase | O$_{ab}$  | O$_c$   |
|-------|-----------|---------|
| F     | 0.26 (0.11) | 0.23 (0.04) |
| A     | 0.25 (0.09) | 0 (0)   |
| C     | 0.08 (0.02) | 0.20 (0.03) |
| G     | 0.07 (0.03) | 0 (0)   |
| E     | 0.24 (0.07) | 0 (0)   |
|       | 0.09 (0.01) | 0 (0)   |

Below we present quantitative estimates of this effect for HoMnO$_3$. By expanding the Wannier functions over the original LMTO basis functions,$^{23,28}$ one can find the distribution of the magnetic moments over all sites of the perovskite lattice in different magnetic structures. The obtained values of the magnetic moments at the oxygen sites, $M_O$, are given in Table III. The parameters $J_O$ can be derived from the LMTO calculations in the local-spin-density approximation (LSDA).$^{52}$ It yields $J_O = 2.1$ and 2.2 eV for the oxygen sites located in the ab-plane and between the planes, respectively. Then, the energy gain, caused by the polarization of the oxygen sites, can be estimated from the formula $\Delta E_O = -\frac{1}{4}M_O^2$ (with subsequent summation over all oxygen sites in the formula unit), which yields $\Delta E_O = -102$, $-63$, $-29$, $-5$, and $-33$ meV for the states F, A, C, G, and E, respectively. The effect is clearly too big. For example, by combining these values with the total energies shown in Fig. 14, we would arrive to the FM ground state, which again contradicts to the experimental data. Then, what is missing?

One effect is related to the polarization of the O(2$p$)-band, which is not explicitly included in the model (1). It is true that since the O(2$p$)-band is filled, it does not contribute to the total magnetic moment. However, it can contribute to the local moments, which cancel each other after the summation over the unit cell. Particularly, the polarization of the oxygen states in the O(2$p$)-band appears to be the opposite to the one in the Mn(3$d$)-band, as it follows from the form of the Mn(3$d$)-O(2$p$) hybridization.$^{53}$ This effect is clearly seen by comparing the moments obtained for the isolated Mn(3$d$)-bands with results of the all-electron calculations.
Table IV. Correlation energies for several AFM states of HoMnO$_3$ measured in meV per one formula unit relative to the FM state. The correlation energies have been computed in the random-phase approximation (RPA), the second-order perturbation theory, and the $T$-matrix method starting from the Hartree-Fock approximation for each magnetic state.

| method  | A    | C    | G    | E    |
|---------|------|------|------|------|
| RPA     | −4.9 | −19.5| −24.7| −14.1|
| 2nd order | −6.7 | −14.9| −17.9| −10.3|
| $T$-matrix | −4.6 | −9.8 | −11.7| −7.6 |

which take into account the contributions of the O(2$p$)-band (Table III). Indeed, the O(2$p$)-band substantially reduces the values of the magnetic moments associated with the oxygen sites (by factor two and more). Therefore, $\Delta E_O$ will be also reduced. For example, by using the LSDA values for $M_O$ (Table III), we find that $\Delta E_O$ is reduced till $-13$, $-9$, $-1$, $-4$, and $-11$ meV per one formula unit for the states F, A, C, G, and E, respectively. By combining these $\Delta E_O$ with the total energies shown in Fig. 14, we readily obtain the E-type AFM structure is realized as the ground state, in agreement with the experiment. The new values of the total energies, measured relative to the FM state, are $-15$, $-15$, $-27$, and $-33$ meV per one formula unit for the states A, C, G, and E, respectively.

Another factor, which strongly affects the relative stability of different magnetic states, is the correlation interactions beyond the HF approximation. In order to estimate the energies of these correlation interactions, we tried three perturbative techniques starting from the HF solutions for each magnetic state. One is the random-phase approximation (RPA), which takes into account the lowest-order polarization processes, involving the excitation and subsequent deexcitation of an electron-hole pair.$^{54–56)$ For these purposes, the RPA expression for the correlation energy has been adopted for the model calculations.$^{57)$ Another method is the second order perturbation theory for the correlation interactions,$^{24,28,58,59)$ and the third one is the $T$-matrix method,$^{58,60)$ which takes into account higher-order effects. Results of these calculations for HoMnO$_3$ are shown in Table IV. Since the on-site Coulomb repulsion $U$ is relatively small, all three methods provide rather consistent explanation for the behavior of the correlation energies, which tend to stabilize the AFM states relative to the FM one. The energy gain increases with the number of the AFM bonds in the direction $F \rightarrow A \rightarrow E \rightarrow C \rightarrow G$. Thus, the correlation interactions act against the magnetic polarization of the oxygen sites and again tend to destabilize the E-state relative to the G-state. The situation is rather fragile and whether the E-state is realized as the ground state of HoMnO$_3$ depends on the delicate balance of these two effects and also on the approximations employed for the correlation energy. For example, RPA and the second-order perturbation theory seem to overestimate the correlation energy of the G-state and make the E-state unstable. On the other hand, the E-state, which
breaks the orthorhombic $D_{2h}^{16}$ symmetry, should be additionally stabilized through the lattice relaxation.

8. Summary and Conclusions

On the basis of first-principles electronic structure calculations, we propose a microscopic model for the behavior of interatomic magnetic interactions in the series of orthorhombic manganites $RMnO_3$ ($R$ = La, Pr, Nd, Tb, and Ho), which explains the phase transition from the A-type AFM state to the E-state with the increase of the lattice distortion. Our picture is clearly different from the ones proposed in the previous studies. In fact, several authors emphasized the importance of the 2nd-neighbor interactions $J_b^2$ and $J_b^2$ in the orthorhombic $ab$-plane. For example, Kimura et al.\textsuperscript{61} considered the superexchange processes mediated by the O(2p) orbitals in the distorted perovskite structure and argues that they can be responsible for the AFM interaction $J_b^2$ and weakly FM interaction $J_b^2$. Other authors\textsuperscript{62,63} performed the mapping of the total energies derived from the first-principles electronic structure calculations onto the Heisenberg model and argued that under certain conditions $J_a^2$ and $J_b^2$ become comparable with $J_1^1$. However, such a mapping crucially depend on the form of the \textit{a priori} postulated model, where the lack of some interactions (such as $J_3$) can lead to an incomplete picture. In this sense, our approach to the problem is more consistent.

- It does not make any \textit{a priori} assumptions about the form of the Heisenberg model.
- It goes beyond the conventional superexchange processes and takes into account other contributions to interatomic magnetic interactions.\textsuperscript{32}

Particularly, the contributions associated with the “super-superexchange” processes in the regime of relatively small on-site Coulomb interactions, give rise to the 3rd-neighbor coupling $J_3$, which was overlooked in the previous studies.\textsuperscript{64} According to our point of view, $J_3$ is one of the key players, which triggers the transition to the E-type AFM state in orthorhombic manganites.

- The existence of $J_3$ is directly related to the form of the orbital ordering.
- $J_3$ is responsible for the AFM coupling between 3rd-neighbor spins in the $ab$-plane, which is realized in the E-phase (Fig. 1).

Since the longer range AFM interactions seem to be the intrinsic property of all undoped manganites, these interactions should be seen in the experiment, for example, on the inelastic neutron scattering. We expect the longer range interactions to take place even in $LaMnO_3$. Although it has A-type AFM ground state, the longer range interactions participate as the precursors of the E-phase, which is finally realized in the more distorted compounds. The neutron-scattering measurements on $LaMnO_3$ are available today. Nevertheless, the experimental data are typically interpreted only in terms of the NN interactions.\textsuperscript{65,66} Definitely, the problem deserves further analysis. Particularly, it would be interesting to reinterpret the
experimental data by permitting the longer range interactions, particularly $J_2^b$ and $J_3$. This point was already emphasized in ref. 17. It is possible that the longer range interactions are not particularly strong in LaMnO$_3$, which has the highest Néel temperature ($T_N$, Fig. 1) and where the NN interactions clearly dominate. From this point of view, it would be more interesting to consider two other A-type AFM systems, PrMnO$_3$ and NdMnO$_3$, which have smaller $T_N$ and where the relative contribution of the longer range interactions to the magnon spectra is expected to be stronger.

Although the proposed model is able to unveil the microscopic origin of the magnetic phase transition, the quantitative agreement with the experimental data crucially depends on the combination of the following three factors:

- the correlation effects beyond the HF approximation;
- the magnetic polarization of the oxygen sites;
- the lattice relaxation in the E-phase, which breaks the inversion symmetry and gives rise to the multiferroic behavior.

The detailed analysis of these effects presents and interesting and important problem for the future investigations.

Acknowledgment

I am grateful to Zlata Pchelkina for valuable discussions and the help with preparation of Figs. 5 and 10. The work is partly supported by Grant-in-Aid for Scientific Research in Priority Area “Anomalous Quantum Materials” and Grant-in-Aid for Scientific Research (C) No. 20540337 from the Ministry of Education, Culture, Sport, Science and Technology of Japan.
References

1) E. O. Wollan and W. C. Koehler: Phys. Rev. 100 (1955) 545.
2) J. B. Goodenough: Phys. Rev. 100 (1955) 564.
3) J. Kanamori: J. Appl. Phys. Suppl. 31 (1960) 14S.
4) G. Matsumoto: J. Phys. Soc. Jpn. 29 (1970) 606.
5) K. I. Kugel and D. I. Khomskii: Sov. Phys. Usp. 25 (1982) 231.
6) N. Hamada, H. Sawada, and K. Terakura: in Spectroscopy of Mott Insulators and Correlated Metals, ed. A. Fujimori and Y. Tokura (Springer Series in Solid-State Sciences), Vol. 119, p. 95.
7) W. E. Pickett and D. J. Singh: Phys. Rev. B 53 (1996) 1146.
8) I. Solovyev, N. Hamada, and K. Terakura: Phys. Rev. Lett. 76 (1996) 4825.
9) H. Sawada, Y. Morikawa, K. Terakura, and N. Hamada: Phys. Rev. B 56 (1997) 12154.
10) R. Shiina, T. Nishitani, and H. Shiba: J. Phys. Soc. Jpn. 66 (1997) 3159.
11) R. Maezono, S. Ishihara, and N. Nagaosa: Phys. Rev. B 58 (1998) 11583.
12) J. B. Goodenough: Magnetism and the Chemical Bond (Interscience, New York, 1963).
13) J. Kanamori: J. Phys. Chem. Solids 10 (1959) 87.
14) M. Tachibana, T. Shimoyama, H. Kawaji, T. Take, and E. Takayama-Muromachi: Phys. Rev. B 75 (2007) 114425.
15) I. V. Solovyev and Z. V. Pchelkina: New. J. Phys. 10 (2008) 073021.
16) O. K. Andersen: Phys. Rev. B 12 (1975) 3060.
17) I. V. Solovyev and K. Terakura, in Electronic Structure and Magnetism of Complex Materials, ed. D. J. Singh and D. A. Papaconstantopoulos (Springer, Berlin, 2003), p. 253.
18) J. B. A. A. Elemans, B. van Laar, K. R. van der Veen, and B. O. Loopstra: J. Sol. State Chem. 3 (1971) 238.
19) J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, and M. T. Fernández-Díaz: Inorg. Chem. 39 (2000) 917.
20) T. Mori, N. Kamegashira, K. Aoki, T. Shishido, and T. Fukuda: Materials Letters 54 (2002) 238.
21) J. Blasco, C. Ritter, J. García, J. D. de Teresa, J. Pérez-Cacho, and M. R. Ibarra: Phys. Rev. B 62 (2000) 5609.
22) A. Muñoz, M. T. Casáis, J. A. Alonso, M. J. Martínez-Lope, J. L. Martínez, and M. T. Fernández-Díaz: Inorg. Chem. 40 (2001) 1020.
23) I. V. Solovyev: Phys. Rev. B 73 (2006) 155117.
24) I. V. Solovyev: J. Phys.: Condens. Matter 20 (2008) 293201.
25) I. V. Solovyev, Z. V. Pchelkina, and V. I. Anisimov: Phys. Rev. B 75 (2007) 045110.
26) C. J. Bradley and A. P. Cracknell: The Mathematical Theory of Symmetry in Solids (Clarendon Press, Oxford, 1972).
27) M. Mochizuki and M. Imada: Phys. Rev. Lett. 91 (2003) 167203.
28) I. V. Solovyev: Phys. Rev. B 74 (2006) 054412.
29) Note that according to the formal valence arguments, four 3d electrons will reside on the three $t_{2g}$ levels and the lowest $e_g$ level for the majority-spin states, while all minority-spin states will be unoccupied.
30) T. Mizokawa and A. Fujimori: Phys. Rev. B 54 (1996) 5368.
31) A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Guanov: J. Magn. Magn. Matter.
67 (1987) 65.
32) I. V. Solovyev: in Recent Research Developments in Magnetism and Magnetic Materials (Transworld Research Network, India, 2003) Vol. 1, p. 253.
33) I. V. Solovyev and K. Terakura: J. Korean Phys. Soc. 33 (1998) 375.
34) L. P. Gor’kov and V. Z. Kresin: JETP Lett. 67 (1998) 985.
35) T. Hotta, M. Moraghebi, A. Feiguin, A. Moreo, S. Yunoki, and E. Dagotto: Phys. Rev. Lett. 90 (2003) 247203.
36) In the present context, the “antiferromagnetic orbital arrangement” corresponds to the maximal overlap between occupied and empty states.
37) T. Oguchi, K. Terakura, and A. R. Williams: Phys. Rev. B 28 (1983) 6443.
38) J. Zaanen and G. A. Sawatzky: Can. J. Phys. 65 (1987) 1262.
39) I. V. Solovyev and K. Terakura: Phys. Rev. B 58 (1998) 15496.
40) V. Heine and J. H. Samson: J. Phys. F: Metal Phys. 10 (1980) 2609.
41) V. Heine and J. H. Samson: J. Phys. F: Metal Phys. 13 (1983) 2155.
42) Otherwise, the FM and AFM contributions to the exchange energy will cancel each other and the directions of spins can be arbitrary.
43) More precisely, such a configuration corresponds to the local maximum of the total energy rather that to a minimum.
44) C. Wang, G.-C. Guo, and L. He: Phys. Rev. Lett. 99 (2007) 177202.
45) S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko, and E. Dagotto: Phys. Rev. Lett. 99 (2007) 227201.
46) Note that some aspects of the double exchange physics can be applied to the band insulators. The situation was discussed in ref. 15.
47) I. V. Solovyev and K. Terakura: Phys. Rev. Lett. 82 (1999) 2959.
48) Wei Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar: Phys. Rev. Lett. 89 (2002) 167204.
49) V. V. Mazurenko, S. L. Skornyakov, A. V. Kozhevnikov, F. Mila, and V. I. Anisimov: Phys. Rev. B 75 (2007) 224408.
50) I. I. Mazin and D. J. Singh: Phys. Rev. B 56 (1997) 2556.
51) I. V. Solovyev: New. J. Phys. 10 (2008) 013035.
52) The intraatomic exchange coupling $J_O$ at the oxygen sites was obtained from the formula $\Delta^{ex}_O = J_O M_O$, where $\Delta^{ex}_O$ is the intraatomic exchange splitting and $M_O$ is the local magnetic moment. The values of $\Delta^{ex}_O$ and $M_O$ were taken from the LSDA calculations for the FM state. Particularly, $\Delta^{ex}_O = C^\uparrow - C^\downarrow$ can be related to the centers of gravity for the minority- and majority-spin 2p-states (the so-called $C$-parameters of the LMTO method – ref. 16).
53) Since the $\uparrow$-spin Mn(3d)-states are closer in energy to the O(2p)-states, the former will be strongly admixed into the $\uparrow$-spin O(2p)-band in comparison with the similar weight of the Mn(3d)-states in the $\downarrow$-spin O(2p)-band. Since the total number of electrons in the $\uparrow$- and $\downarrow$-spin O(2p)-bands is conserved, the increase/increase of the weight of the Mn(3d)-states is compensated by the O(2p)-states. Therefore, the O(2p)-states in the O(2p)-band will be polarized opposite to the Mn(3d)-band.
54) D. Pines: Elementary Excitations in Solids (Westview Press, Oxford, 1999) p. 138.
55) U. von Barth and L. Hedin: J. Phys. C 5 (1972) 1629.
56) F. Aryasetiawan, T. Miyake, and K. Terakura: Phys. Rev. Lett. 88 (2002) 166401.
57) Details will be published elsewhere.
58) I. V. Solovyev: J. Exp. Theor. Phys. 105 (2007) 46.
59) Here, the correlation interaction is defined as the difference between the true many-body Hamiltonian (1) and its one-electron counterpart, obtained at the level of the HF approximation.
60) J. Kanamori: Prog. Theor. Phys. 30 (1963) 275.
61) T. Kimura, S. Ishihara, H. Shintani, T. Arima, K. T. Takahashi, K. Ishizaka, and Y. Tokura: Phys. Rev. B 68 (2003) 060403(R).
62) S. Picozzi, K. Yamauchi, G. Bihlmayer, and S. Blügel: Phys. Rev. B 74 (2006) 094402.
63) H. J. Xiang, S.-H. Wei, M.-H. Whangbo, and J. L. F. Da Silva: Phys. Rev. Lett. 101 (2008) 037209.
64) In fact, the interaction $J_3$ was considered in ref. 17. However, because of the additional approximations employed in ref. 17, it was impossible to separate the contributions of two inequivalent bonds connecting the 3rd neighbors in the ab-plane. Thus, ref. 17 reported only an averaged value over these two bonds.
65) K. Hirota, N. Kaneko, A. Nishizawa, and Y. Endoh: J. Phys. Soc. Jpn. 65 (1996) 3736.
66) F. Moussa, M. Hennion, J. Rodriguez-Carvajal, H. Moudden, L. Pinsard, and A. Revcolevschi: Phys. Rev. B 54 (1996) 15149.