Ferromagnetic zigzag chains and properties of the charge ordered perovskite manganites

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Abstract

The low-temperature properties of the so-called "charge ordered" state in 50% doped perovskite manganites are described from the viewpoint of the magnetic spin ordering. In these systems, the zigzag antiferromagnetic ordering, combined with the double-exchange physics, effectively divides the whole sample into the one-dimensional ferromagnetic zigzag chains and results in the anisotropy of electronic properties. The electronic structure of one such chain is described by an effective $3\times3$ Hamiltonian in the basis of Mn$(3de_g)$ orbitals. We treat this problem analytically and consider the following properties: (i) the nearest-neighbor magnetic interactions; (ii) the distribution of the Mn$(3de_g)$ and Mn$(4p)$ states near the Fermi level, and their contribution to the optical conductivity and the resonant x-ray scattering near the Mn $K$-absorption edge. We argue that the anisotropy of magnetic interactions in the double-exchange limit, combined with the isotropic superexchange interactions, readily explains both the local and the global stability of the zigzag antiferromagnetic state. The two-fold degeneracy of $e_g$ levels plays a very important role in the problem and explains the insulating behavior of the zigzag chain, as well as the appearance of the orbital ordering in the double-exchange model. Importantly, however, the charge ordering itself is expected to play only a minor role and is incompatible with the ferromagnetic coupling within the chain. We also discuss possible effects of the Jahn-Teller distortion and compare the tight-binding picture with results of band structure calculations in the local-spin-density approximation.

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I. INTRODUCTION

It appears that many perovskite manganites, when doped by holes up to the level corresponding to the formal valence of Mn $^{+3.5}$, exhibit very specific properties, inherent to only this particular hole concentration and different from other doping regimes. The compounds are insulating and at certain temperature range (typically at low temperatures) form rather peculiar magnetic ordering consisting of ferromagnetic (FM) zigzag chains, coupled antiferromagnetically – see Fig. 1. In the case of three-dimensional manganites, this is the well known CE-type antiferromagnetic (AFM) ordering, which was proposed long ago by Goodenough and first observed by Wollan and Koehler in La$_{1-x}$Ca$_x$MnO$_3$ near $x=0.5$. The zigzag AFM ordering appeared to be a more generic and was observed recently in a number of systems, including the layered manganite La$_{1/2}$Sr$_{3/2}$MnO$_4$ (Refs. 3,4) and the double-layer manganite LaSr$_2$Mn$_2$O$_7$ (Ref. 5). The magnetic ordering is accompanied by the orbital ordering, which is also shown in Fig. 1. The insulating zigzag AFM state can be transformed into the metallic FM state by applying an external magnetic field. Other examples of such compounds and detailed description of their properties can be found in the review articles.

The systems are usually referred to as the ”charge ordered” manganites, implying that the homogeneous state of Mn$^{3.5+}$ ions in the lattice is unstable towards the charge disproportionation amongst two alternately aligned types of sites: $2\text{Mn}^{3.5+}\rightarrow\text{Mn}^{4+}+\text{Mn}^{3+}$. The electronic configurations of the Mn$^{4+}$ and Mn$^{3+}$ ions are $t_{2g}^3$ and $t_{2g}^3e_g^1$, respectively. Thus, the $t_{2g}$ orbitals are half-filled in both cases, giving rise to the AFM superexchange interaction between nearest neighbors. Due to the strong Hund’s rule coupling, the $e_g$ electron and three $t_{2g}$ electrons at the Mn$^{3+}$ site are aligned ferromagnetically. It is assumed that the $e_g$ electron is mobile and can hop to the neighboring Mn$^{4+}$ by forming the FM double-exchange (DE) coupling in a certain number of Mn$^{3+}$-Mn$^{4+}$ bonds. The occupied $e_g$ orbitals are ordered in the direction of these bonds so to maximize the DE coupling. This is the basic physical idea underlying Goodenough’s conjecture for the CE-type AFM ordering. The picture had no solid justification and for many years remained to be on the level of a hypothesis.

Only very recently it was realized by several authors that, at least at very low temperatures, the basic properties of the ”charge ordered” manganites can be understood exclusively
from the viewpoint of the DE physics.\textsuperscript{9,10,11} Due to the strong Hund’s rule coupling, the Mn ions form a high-spin state in manganites. Therefore, the intraatomic exchange splitting is large. If it is much larger than the kinetic hoppings between nearest-neighbor $e_g$ orbitals, the minority-spin $e_g$ states can be projected out of the problem. In the case of AFM ordering, this will suppress all kinetic hoppings between Mn-sites with opposite directions of the spin magnetic moments. In the following we will refer to this picture as the DE limit. Thus, the CE phase in the DE limit will be effectively divided into the one-dimensional zigzag chains. This will create two geometrically different types of Mn-sites: the so-called bridge sites $A$ and $A'$, and the corner sites $B$ and $B'$ – see Fig. \textsuperscript{1} However, the difference is not necessarily related with the integer change of atomic charges when going from one type of Mn-sites to another. In the other words, the bridge sites are not necessarily occupied by the Mn$^{3+}$ ions and the corner sites - by the Mn$^{4+}$ ions. The two-fold degeneracy of $e_g$ levels plays a very important role in the problem. The isolated chain behaves as a band insulator. The only occupied $e_g$ orbitals at the sites $A$ and $A'$ are $3x^2-r^2$ and $3y^2-r^2$, respectively, that is exactly the orbital ordering shown in Fig. \textsuperscript{1} In our recent Letter (Ref. \textsuperscript{10}) we argued that the local stability of the zigzag AFM state can be explained by the anisotropy of the interatomic magnetic interactions in the DE limit, whereas the charge ordering itself may be irrelevant to the problem.

In the present paper we will further elaborate this DE picture. In Sec. \textsuperscript{II} we will derive the tight-binding (TB) Hamiltonian for the zigzag chain, discuss basic features of the electronic structure, and obtain several useful expressions for matrix elements of the Green function and for the wavefunctions. In Sec. \textsuperscript{III} we will derive analytical expressions for magnetic interactions in the DE limit and address the problem of local and global stability of the zigzag AFM ordering. These two sections will also clarify the main results published in Ref. \textsuperscript{10}. In Sec. \textsuperscript{IV} we will turn to the optical properties of the zigzag chain and discuss possible implications for the resonant x-ray scattering near Mn $K$-absorption edge.\textsuperscript{4} In Sec. \textsuperscript{V} we will discuss validity of the TB picture by comparing it with results of first-principles band structure calculations in the local-spin-density approximation (LSDA). A brief summary will be given in Sec. \textsuperscript{VI}.

We would like to emphasize from the very beginning that we treat the minimal model which can be proposed for perovskite manganites. The model is based on the DE physics and takes into account the two-fold degeneracy of the $e_g$ levels. The combination of these two
ingredients represents a necessary basis for the analysis of manganite compounds. The main purpose of this paper is to argue that such a simple degenerate DE model provides a very consistent description for the low-temperature properties of the CE state in manganites. At present it is not clear whether the same DE model will be sufficient in the high-temperature regime. In Sec. VI, we will collect some remarks on this matter.

We are planning this paper as the first part in the series of two publications dealing with the electronic structure and properties of the charge ordered manganites. The present work contains mainly the model analysis. Results of the first-principles band structure calculations and the structure optimization will be presented in Ref. 12. The first reports about this activity can be found in Refs. 13, 14, 15. In fact, the basic idea of the DE picture discussed in Ref. 10 was inspired by LSDA calculations of the zigzag AFM phase in layered manganites (Ref. 13).

II. ELECTRONIC STRUCTURE OF THE SINGLE ZIGZAG CHAIN

A. Tight-binding Hamiltonian

The basic translation properties of the single zigzag chain are given by the symmetry operation \( \hat{S}_1 = \{ \hat{C}(\pi) | R_0 \} \), which combines the 180° rotation around the axis \([1, 1, 0]\), \( \hat{C}(\pi) \), with the translation \( R_0 = [a_0, a_0, 0] \) connecting the sites \( A \) and \( A' \). Therefore, it is convenient to choose the atomic bases at different sites in such a form that they can be transformed to each other by the operation \( \hat{S}_n = \{ \hat{C}(n\pi) | nR_0 \} \), where \( n \) is the integer number of translations separating two sites. For the \( e_g \) states this can be achieved by adopting the following basis orbitals:

\[
|1\rangle_A = -\frac{1}{2}|3z^2 - r^2\rangle_A + \frac{\sqrt{3}}{2}|x^2 - y^2\rangle_A \equiv |3x^2 - r^2\rangle_A
\]

\[
|2\rangle_A = -\frac{\sqrt{3}}{2}|3z^2 - r^2\rangle_A - \frac{1}{2}|x^2 - y^2\rangle_A \equiv |y^2 - z^2\rangle_A
\]

at the site \( A \),

\[
|1\rangle_B = |3z^2 - r^2\rangle_B
\]

\[
|2\rangle_B = |x^2 - y^2\rangle_B
\]

at the site \( B \),

\[
|1\rangle_{A'} = -\frac{1}{2}|3z^2 - r^2\rangle_{A'} - \frac{\sqrt{3}}{2}|x^2 - y^2\rangle_{A'} \equiv |3y^2 - r^2\rangle_{A'}
\]

\[
|2\rangle_{A'} = -\frac{\sqrt{3}}{2}|3z^2 - r^2\rangle_{A'} + \frac{1}{2}|x^2 - y^2\rangle_{A'} \equiv |x^2 - z^2\rangle_{A'}
\]
at the site $A'$, and
\[
|1\rangle_{B'} = |3z^2 - r^2\rangle_{B'} \\
|2\rangle_{B'} = -|x^2 - y^2\rangle_{B'}
\] (4)
at the site $B'$, which are periodically repeated to the whole chain.

We assume that the kinetic hoppings between nearest-neighbor $e_g$ orbitals are of the $dd\sigma$ type and can be parameterized in accordance with the Slater-Koster rules. In the above basis, this yields the following nonvanishing matrix elements between sites $A$, $B$ and $A'$ of the chain 1 in Fig. 1:
\[
\begin{align*}
t_{11}^{BA} = t_{11}^{BA'} & = -\frac{1}{2} \\
t_{21}^{BA} = -t_{21}^{BA'} & = \frac{\sqrt{3}}{2}
\end{align*}
\] (5)

In the notation $t_{nn'}^{LL'}$, $n$ and $n'$ stand for the site indices, $L$ and $L'$ - for the orbital (basis) indices. The absolute value of the $dd\sigma$ two-center integral is used as the energy unit. The atomic orbitals $|2\rangle$ of the sites $A$ and $A'$ are inert and do not participate in the hoppings. In the local representation given by Eqs. (1)-(4), any translation $n\mathbf{R}_0$ in the real space will transform the matrix of kinetic hoppings to itself. Therefore, we can apply the generalized Bloch transformation $\sum_n \hat{C}(n\pi)e^{ink}, -\pi \leq k \leq \pi$, to the DE Hamiltonian in the real space $\hat{H} = \| -t_{nn'}^{LL'} \|$. This leads to the following $3\times3$ Hamiltonian in the reciprocal space, in the basis of generalized Bloch orbitals of $|1\rangle_{A(A')}$, $|1\rangle_{B(B')}$ and $|2\rangle_{B(B')}$ type:
\[
\hat{H}(k) = \begin{pmatrix}
0 & \frac{1}{2}(1 + e^{-ik}) - \frac{\sqrt{3}}{2}(1 - e^{-ik}) & \\
\frac{1}{2}(1 + e^{ik}) & \Delta C & 0 \\
-\frac{\sqrt{3}}{2}(1 - e^{ik}) & 0 & \Delta C
\end{pmatrix}.
\] (6)
The parameter $\Delta C > 0$ was added in order to simulate the charge disproportionation between the sites $A(A')$ and $B(B')$. The Hamiltonian has the following eigenvalues:
\[
\varepsilon_k^\pm = \frac{1}{2}(\Delta C \pm \sqrt{\Delta C^2 + 8 - 4\cos k}),
\]
the bonding ($-$) and antibonding ($+$) bands, and
\[
\varepsilon^0 = \Delta C,
\]
a nonbonding band, which has nonvanishing weight only at the sites $B$ and $B'$.

All three bands are separated by energy gaps. Thus, if there is exactly one electron per two sites $A$ and $B$, the low-lying bonding band is fully occupied and the system behaves as an one-dimensional band insulator. Therefore, the insulating behavior of the so-called "charge ordered" manganites may not be related with the charge ordering. Rather, it may be a consequence of the peculiar zigzag AFM ordering, combined with the DE physics. Corresponding densities of states are shown in Fig. 2 (Details of calculations are given in
Appendix A) As expected for the one-dimensional system, the densities of states diverge at the band edges. Since only \(3x^2-r^2\) \((3y^2-r^2)\) state are occupied at the sites \(A(A')\), the zigzag AFM ordering in the degenerate DE model automatically leads to the orbital ordering shown in Fig. 11.

B. Elements of the Green function

In the reciprocal space, the Green function for the Hamiltonian \(\hat{H}\) is given by \(\hat{G}(k, \varepsilon)=[\varepsilon-\hat{H}(k)+i\eta]^{-1}\), where \(\eta\) is a positive infinitesimal. It has the following matrix elements:

\[
G_{AA}^{11}(k, \varepsilon) = \frac{1}{\varepsilon_k^+ - \varepsilon_k^-} \left\{ \frac{\varepsilon_k^+}{\varepsilon - \varepsilon_k^+ + i\eta} - \frac{\varepsilon_k^-}{\varepsilon - \varepsilon_k^- + i\eta} \right\},
\]

\[
G_{BB}^{11}(k, \varepsilon) = \frac{1 + \cos k}{2(\varepsilon_k^+ - \varepsilon_k^-)} \left\{ \frac{1}{\varepsilon_k^+(\varepsilon - \varepsilon_k^+ + i\eta)} - \frac{1}{\varepsilon_k^-(\varepsilon - \varepsilon_k^- + i\eta)} \right\} + \frac{3(1 - \cos k)}{2(2 - \cos k)} \frac{1}{\varepsilon - \Delta_C + i\eta},
\]

\[
G_{BB}^{22}(k, \varepsilon) = \frac{3(1 - \cos k)}{2(\varepsilon_k^+ - \varepsilon_k^-)} \left\{ \frac{1}{\varepsilon_k^+(\varepsilon - \varepsilon_k^+ + i\eta)} - \frac{1}{\varepsilon_k^-(\varepsilon - \varepsilon_k^- + i\eta)} \right\} + \frac{1 + \cos k}{2(2 - \cos k)} \frac{1}{\varepsilon - \Delta_C + i\eta},
\]

\[
G_{AB}^{11}(k, \varepsilon) = -\frac{1 + e^{-ik}}{2(\varepsilon_k^+ - \varepsilon_k^-)} \left\{ \frac{1}{\varepsilon - \varepsilon_k^+ + i\eta} - \frac{1}{\varepsilon - \varepsilon_k^- + i\eta} \right\},
\]

\[
G_{AB}^{12}(k, \varepsilon) = \sqrt{3} \frac{(1 - e^{-ik})}{2(\varepsilon_k^+ - \varepsilon_k^-)} \left\{ \frac{1}{\varepsilon - \varepsilon_k^+ + i\eta} - \frac{1}{\varepsilon - \varepsilon_k^- + i\eta} \right\},
\]

\[
G_{BB}^{12}(k, \varepsilon) = -\frac{\sqrt{3i}}{2(\varepsilon_k^+ - \varepsilon_k^-)} \left\{ \frac{1}{\varepsilon_k^+(\varepsilon - \varepsilon_k^+ + i\eta)} - \frac{1}{\varepsilon_k^-(\varepsilon - \varepsilon_k^- + i\eta)} + \left( \frac{1}{\varepsilon_k^-} - \frac{1}{\varepsilon_k^+} \right) \frac{1}{\varepsilon - \Delta_C + i\eta} \right\}.
\]

The Green function elements in the real space are obtained by the Fourier transformation:

\[
G_{\tau\tau'+n}(\varepsilon) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dk e^{in\varepsilon} G_{\tau\tau'}^{LL'}(k, \varepsilon),
\]

where \(\tau\) and \(\tau'\) correspond to either A or B in Eqs. (7)-(12). This is the local representation for the Green function, meaning that the form of the basis orbitals \(L\) and \(L'\) varies from site to site as prescribed by Eqs. (11)-(14).
C. Wave-functions

We search the wave-functions of the Hamiltonian (6) in the form:

\[ |\Psi\rangle = \begin{pmatrix}
\cos \theta \\
\pm \frac{1+e^{ik}}{\sqrt{2(1+\cos k)}} \sin \theta \sin \phi \\
\pm \frac{1-e^{ik}}{\sqrt{2(1-\cos k)}} \sin \theta \cos \phi
\end{pmatrix}. \quad (13)\]

By substituting this expression into the secular equation \((\hat{H} - \varepsilon)|\Psi\rangle = 0\), the wavefunctions can be found as follows.

For the bonding and antibonding states \(\varepsilon_{\pm} \) we obtain: \(\cot \phi_{\pm} = -\sqrt{3} \tan \frac{k}{2}\) and \(\tan \theta_{\pm} = \frac{\varepsilon_{\pm} k}{\sqrt{2 - \cos k}}\). Corresponding wave-functions are given by

\[ |\Psi_{\pm}\rangle_A = \cos \theta_{\pm} |3x^2 - r^2\rangle_A \] at the site \(A\), and

\[ |\Psi_{\pm}\rangle_B = \frac{\sin \theta_{\pm}}{\sqrt{2 - \cos k}} \left\{ \frac{1}{2} (1 + e^{ik}) |3z^2 - r^2\rangle_B - \frac{\sqrt{3}}{2} (1 - e^{ik}) |x^2 - y^2\rangle_B \right\} \] at the site \(B\).

For the nonbonding states \(\varepsilon^0 = \Delta_C\) we have: \(\tan \phi_0 = \sqrt{3} \tan \frac{k}{2}\) and \(\theta_0 = \pi/2\). Then, the wave-functions will have nonvanishing elements only at the corner sites. They are given by

\[ |\Psi_0\rangle_B = \frac{1}{\sqrt{2 - \cos k}} \left\{ \frac{\sqrt{3}}{2} (1 + e^{ik}) \tan \frac{k}{2} |3z^2 - r^2\rangle_B + \frac{1}{2} (1 - e^{ik}) \tan^{-1} \frac{k}{2} |x^2 - y^2\rangle_B \right\}. \quad (15)\]

The wave-functions at the sites \(A'(B')\) are related with the ones at the site \(A(B)\) by the transformation:

\[ |\Psi\rangle_{A'(B')} = e^{ik\hat{C}(\pi)} |\Psi\rangle_{A(B)}. \quad (17)\]

III. MAGNETIC INTERACTIONS AND STABILITY OF THE CE STATE

We consider small nonuniform rotations of the spin magnetic moments on a discrete lattice, characterized by the angles \(\{\delta \varphi_i\}\). If \(\mathbf{e}^0_i\) is the direction of the spin magnetic moment at the site \(i\) corresponding to an equilibrium, the new direction is given by \(\mathbf{e}_i = \mathbf{e}^0_i + \delta \mathbf{e}_i\), where

\[ \delta \mathbf{e}_i = \delta^{(1)} \mathbf{e}_i + \delta^{(2)} \mathbf{e}_i = [\delta \mathbf{e}_i \times \mathbf{e}^0_i] - \frac{1}{2} (\delta \mathbf{e}_i)^2 \mathbf{e}^0_i. \quad (18)\]
In the second order of \{δϕ_i\}, the total energy change takes isotropic Heisenberg form (Ref. 17, see also Appendix B):
\[
\Delta E_t = -\frac{1}{2} \sum_{ij} J_{ij} \left\{ (δ^{(2)} e_i \cdot e_j^0) + (δ^{(1)} e_i \cdot δ^{(1)} e_j) + (e_i^0 \cdot δ^{(2)} e_j) \right\},
\]
and the parameters \{J_{ij}\} can be expressed through the second derivatives of the total energy with respect to the angles \{δϕ_i\}. In the AFM state we have \(e_i^0 = e_j^0\) if the sites \(i\) and \(j\) belong the same (different) sublattices.

Following the work by de Gennes (Ref. 18) we assume that the total energy consists of two contributions: \(E_t[\{e_i\}] = E_D[\{e_i\}] + E_S[\{e_i\}]\), where \(E_D[\{e_i\}]\) is the kinetic (double-exchange) energy of the \(e_g\) electrons, and \(E_S[\{e_i\}] = -\frac{1}{2} J^S \sum_{\langle ij \rangle} e_i \cdot e_j\) is the energy of AFM superexchange interactions between nearest neighbors \(\langle ij \rangle\). In practice, the coupling \(J^S < 0\) is associated with the localized \(t_{2g}\) spins, and may also account for some interactions amongst \(e_g\) electrons beyond the DE limit. In this model, the nearest-neighbor magnetic interaction is the sum of generally anisotropic DE coupling \(J^D_{ij}\) (the second derivative of the kinetic energy of the \(e_g\) electrons) and the isotropic superexchange coupling: \(J_{ij} = J^D_{ij} + J^S\).

Parameters \{\(J^D_{ij}\)\} depend on the magnetic state in which they are calculated and define conditions of the local stability of this magnetic state. The magnetic ordering is stabilized globally if it has the lowest energy amongst all possible locally stable magnetic states. In other words, this is the magnetic ground state of the system. Although the total energy change near \(\{e_i^0\}\) has the form of the Heisenberg model – Eq. (19), it does not necessary mean that the same expression is applicable for the absolute value of the total energy in the point \(\{e_i^0\}\), i.e. generally it does not hold \(E_t[\{e_i^0\}] = -\frac{1}{2} \sum_j J_{0j}(e_i^0 \cdot e_j^0)\). One example illustrating such a violation is the DE model, where only interatomic DE interactions in the FM bonds contribute to the kinetic energy. The total energy in the DE model can still be expressed in terms of \{\(J_{ij}\)\}, but the form of this expression will be different from the Heisenberg model.

A. Intra-chain magnetic interactions

In the DE limit, magnetic interactions between nearest neighbors located in the same chain, \(J^D_{A_1B_1}\) (see Fig. 1 for notations), can be calculated as:
\[
J^D_{A_1B_1} = -\frac{1}{2\pi} \text{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \left\{ G_{A_1B_1}^{11}(\varepsilon) t_{B_1A_1}^{11} + G_{A_1B_1}^{12}(\varepsilon) t_{B_1A_1}^{12} \right\}.
\]
Using matrix elements of the Green function, Eqs. (10) and (11), and the kinetic hoppings, Eq. (5), we obtain:

\[ J_{A_1B_1}^D = \frac{1}{4\pi} \int_0^\pi dk \frac{2 - \cos k}{\sqrt{\Delta_C^2 + 8 - 4\cos k}}. \]  

(21)

The interaction \( J_{A_1B_1}^D \) is always positive and responsible for the FM coupling within the chain. The numerical value for \( \Delta_C=0 \) is \( J_{A_1B_1}^D(0) \approx 0.174 \).

The charge disproportionation will reduce \( J_{A_1B_1}^D \). Indeed, the former is defined as the difference of atomic populations at the sites \( A \) and \( B \), \( \Delta n=n_A-n_B \), which yields:

\[ \Delta n = \frac{1}{\pi} \int_0^\pi dk \frac{\Delta_C}{\sqrt{\Delta_C^2 + 8 - 4\cos k}}. \]

The dependence \( J_{A_1B_1}^D \) versus \( \Delta n \) is shown in Fig. 3. As \( \Delta n \) increases, \( J_{A_1B_1}^D \) decreases. Therefore, the charge ordering suppresses the FM DE coupling within the chain and plays a destructive role in the magnetic stability of the CE-type AFM ordering.

B. Inter-chain magnetic interactions in the \( x-y \) plane

In the DE limit, magnetic interactions between antiferromagnetically coupled atoms are given by the following expression:

\[ J_{ij}^D = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{\epsilon_F} d\varepsilon \sum_{kl} \text{Tr}_L \left\{ \hat{G}_{ik}(\varepsilon)\hat{t}_{kj} \hat{G}_{jm}(\varepsilon)\hat{t}_{mi} \right\}, \]  

(22)

where \( \text{Tr}_L \) is the trace over the orbital indices. In Eq. (22), the sites \( i \) and \( k \) belong to one zigzag chain, and the sites \( j \) and \( m \) belong to another zigzag chain, different from the first one.

If \( i=A_1 \) and \( j=B_2 \) for the geometry shown in Fig. 1 we will have the following six nonvanishing contributions to the exchange coupling (22):

\[ G_{A_1A_1}^{11}(\varepsilon) t_{A_1B_2}^{11} G_{B_2B_2}^{11}(\varepsilon) t_{B_2A_1}^{11}, \]

\[ G_{A_1A_1}^{11}(\varepsilon) t_{A_1B_2}^{12} G_{B_2B_2}^{22}(\varepsilon) t_{B_2A_1}^{21}, \]

\[ G_{A_1A_1}^{22}(\varepsilon) t_{A_1B_2}^{21} G_{B_2B_2}^{11}(\varepsilon) t_{B_2A_1}^{12}, \]

\[ G_{A_1A_1}^{22}(\varepsilon) t_{A_1B_2}^{22} G_{B_2B_2}^{22}(\varepsilon) t_{B_2A_1}^{22}, \]

\[ G_{A_1A_1'}^{11}(\varepsilon) t_{A_1'B_2}^{11} G_{B_2B_2}^{11}(\varepsilon) t_{B_2A_1'}^{11}. \]
\[ G_{A_1 A_1'}^{11}(\varepsilon) t_{A_1' B_2}^{12} G_{B_2 B_2}^{22}(\varepsilon) t_{B_2 A_1}^{21}. \]

The nonbonding \( x^2-z^2 \) (\( y^2-z^2 \)) orbitals of \( A (A') \) sites are unoccupied and can be dropped in the analysis of magnetic interactions of the single zigzag chain. However, they contribute to the inter-chain interactions. The corresponding element of the Green function is \( G_{A_1 A_1'}^{22}(\varepsilon)=(-\Delta+\Delta_O+i\eta)^{-1} \), where \( \Delta_O \) is the energy position of the atomic \( x^2-z^2 \) (\( y^2-z^2 \)) levels. The remaining elements of the Green function listed above are given by Eqs. (7)-(9). Corresponding hopping matrix elements in the local coordinate frame are \( t_{A_1 B_2}^{11}=t_{A_1' B_2}^{11}={\sqrt{3} \over 4} \), \( t_{A_1 B_2}^{12}=-t_{A_1' B_2}^{12}={\sqrt{3} \over 4} \), and \( t_{A_1 B_2}^{22}=-{3 \over 4} \). Then, noting that \( \hat{G}_{B_2 B_2}(\varepsilon)\hat{G}_{B_1 A_1}(\varepsilon) \), we obtain the following expression:

\[ J_{A_1 B_2}^D = \frac{1}{32\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon \left\{ (G_{B_2 B_2}^{11}(\varepsilon) + 3G_{B_2 B_2}^{22}(\varepsilon)) (G_{A_1 A_1'}^{11}(\varepsilon) + 3G_{A_1 A_1'}^{22}(\varepsilon)) + (G_{B_1 B_1}(\varepsilon) - 3G_{B_1 B_1}(\varepsilon)) \right\} G_{A_1 A_1'}^{11}(\varepsilon) \]

The numerical value of this integral for \( \Delta_O=\Delta_C=0 \) is \( J_{A_1 B_2}^D(0)\approx0.106 \), which is significantly smaller than the value of the intra-chain integral \( J_{A_1 B_1}^D(0) \). Such an anisotropy of magnetic interactions in the DE limit readily explain the local stability of the CE-type AFM ordering. In the three-dimensional case, the inequality (24) shall be combined with remaining two conditions of the local stability in the bonds \( A_1-A_3 \) and \( B_1-B_3 \) connecting neighboring \( x-y \) planes – see Fig. [11]

\[ J_{A_1 B_2}^D < |J_S^D| < J_{A_1 B_1}^D, \]

i.e., we require the total coupling \( J_{ij}^D+J_S^D \) to be FM within the chain and AFM between the chains. Since \( J_{A_1 B_2}^D(0)<J_{A_1 B_1}^D(0) \), this condition can be easily satisfied.

In the two-dimensional case, this is the only condition of the local stability of the zigzag AFM ordering. In the three-dimensional case, the inequality (24) shall be combined with remaining two conditions of the local stability in the bonds \( A_1-A_3 \) and \( B_1-B_3 \) connecting neighboring \( x-y \) planes – see Fig. [11]

**C. Inter-chain magnetic interactions between neighboring \( x-y \) planes**

In the local basis of atomic orbitals [11]-[11], the kinetic hoppings between sites \( A_1 \) and \( A_3 \), along the \( z \) direction, are \( t_{A_1 A_3}^{11}={\sqrt{3} \over 2} \), \( t_{A_1 A_3}^{12}={\sqrt{3} \over 2} \), and \( t_{A_1 A_3}^{22}={3 \over 4} \). Then, applying Eq. (22) for \( i=A_1 \) and \( j=A_3 \), and noting that \( \hat{G}_{A_1 A_1}(\varepsilon)\hat{G}_{A_3 A_3}(\varepsilon) \), we obtain

\[ J_{A_1 A_3}^D = \frac{1}{32\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon \left( G_{A_1 A_1'}^{11}(\varepsilon) + 6G_{A_1 A_1'}^{22}(\varepsilon) \right) G_{A_1 A_1'}^{11}(\varepsilon). \]
The numerical value of this integral for $\Delta_O=\Delta_C=0$ is $J_{A_1A_3}^D(0)\approx 0.076$.

For the $B$-sites, the only nonvanishing hopping along the $z$-direction is $t_{B_1B_3}^{11}=1$. Then, applying Eq. (22) for $i=B_1$ and $j=B_3$, and noting that $\hat{G}_{B_1B_1}(\varepsilon)=\hat{G}_{B_3B_3}(\varepsilon)$, we obtain:

$$J_{B_1B_3}^D = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \left( G_{B_1B_1}^{11}(\varepsilon) \right)^2.$$  \hspace{1cm} (26)$$

For $\Delta_O=\Delta_C=0$, $J_{B_1B_3}^D$ can be estimated as $J_{B_1B_3}^D(0)\approx 0.117$, which is different from the value reported in Ref. 10. The reason is the following. In Ref. 10, we employed a different basis of atomic orbitals at the sites $B$ and $B'$. In that basis, the Green function $\hat{G}_{B_1B_1}(\varepsilon)$ has off-diagonal elements with respect to the orbital indices, which have been neglected in the analysis of magnetic interactions in Ref. 10. The new values of the exchange integrals take into account these terms. The correction appears to be small for the in-plane exchange interaction $J_{A_1B_2}^D(0)$ and modifies it only in the fourth digit after the comma. However, the change of the inter-plane exchange interaction $J_{B_1B_3}^D(0)$ appears to be more significant. With this new value of $J_{B_1B_3}^D(0)$, the main statement of Ref. 10 appears to be even stronger.

If $J^S$ satisfies the condition

$$\max \{ J_{A_1B_2}^D, J_{A_1A_3}^D, J_{B_1B_3}^D \} < |J^S| < J_{A_1B_1}^D,$$  \hspace{1cm} (27)$$

the FM coupling is stabilized in the bond $A_1-B_1$, and the AFM coupling is stabilized in the bonds $A_1-B_2$, $A_1-A_3$ and $B_1-B_3$. Since $J_{B_1B_3}^D(0)\equiv \max \{ J_{A_1B_2}^D(0), J_{A_1A_3}^D(0), J_{B_1B_3}^D(0) \}< J_{A_1B_1}^D(0)$, appearance of the three-dimensional CE-type AFM ordering can be fully explained by the anisotropy of magnetic interactions in the DE limit. We will call Eq. (27) the "hard" condition of the local stability. Similar to Ref. 10, we can also consider the CE-type AFM ordering in the regime:

$$J_{A_1B_2}^D < |J^S| < J_{B_1B_3}^D,$$  \hspace{1cm} (28)$$

when the total coupling in the bond $B_1-B_3$ is ferromagnetic. Even in this case, the CE-type AFM ordering may remain stable due to the joint effect of magnetic interactions in the bonds $A_1-A_3$, $A_1-B_1$ and $A_1-B_2$. We will call Eq. (28) the "soft" condition of the local stability.
D. Local and global stability of the zigzag antiferromagnetic ordering

In Ref. 20 we argued that in the DE limit the kinetic energy for a collinear magnetic state \( M \) is related with the interatomic DE coupling parameter in the FM bonds, \( J_{↓↑}(M) \), as \( E_D(M) = -2z_{↑↑}J_{↓↑}(M) \), where \( z_{↑↑} \) is the number of FM bonds. The superexchange energy is given by \( E_S(M) = -\frac{1}{2}J_S(z_{↑↑} - z_{↑↓}) \), where \( z_{↑↓} \) is the number of AFM bonds. This represents the connection between the parameters \( \{ J_{↓↑}, J_S \} \) and the total energy of the DE model.

Let us consider the three-dimensional case. For the hole concentration \( x = 0.5 \) we can expect three possibilities: the FM ordering (\( M = F, z_{↑↑} = 6, \) and \( z_{↑↓} = 0 \)), the A-type AFM ordering (\( M = A, z_{↑↑} = 4, \) and \( z_{↑↓} = 2 \)), and the CE-type AFM ordering (\( M = CE, z_{↑↑} = 2, \) and \( z_{↑↓} = 4 \)). The chain-like C-type AFM ordering is unstable for \( x = 0.5 \) and can be excluded from the analysis. Corresponding total energies are given by: \( E_t(F) = -12J_{↓↑}(F) - 3J_S \), \( E_t(A) = -8J_{↑↑}(A) - J_S \), and \( E_t(CE) = -4J_{↑↑} + J_S \).

Conditions of the local stability of the FM and A-type AFM states are \( |J_S| < J_{↑↑}(F) \) and \( J_{↑↑}(A) < |J_S| < J_{↑↑}(A) \), respectively, where \( J_{↑↑}(A) \) is the nearest-neighbor exchange interaction between antiferromagnetically coupled atoms in the DE limit. "Hard" and "soft" conditions of the local stability of the CE-type AFM ordering are given by Eqs. (27) and (28), respectively.

Numerical values of the exchange integrals for \( x = 0.5 \) and \( \Delta_C = \Delta_O = 0 \) are \( J_{↑↑}(F) \approx 0.093, J_{↑↑}(A) \approx 0.115 \) and \( J_{↑↓}(A) \approx 0.089 \)\(^{19,20,23} \). Corresponding phase diagram is shown in Fig. 4, where we plot the total energies for each magnetic state on the interval inside of which this magnetic state is locally stable. We also added the data for two canted spin states which may exist for \( x = 0.5 \). These solutions of the DE model can be regarded as intermediate states between:

1. the FM and A-type AFM ordering (the canted spin state of the FA type);
2. the A- and G-type AFM ordering (the canted spin state of the AG type).\(^{24} \)

From Fig. 4 we can conclude that the CE-type AFM ordering may coexist only with the A-type AFM ordering and the canted spin ordering of the AG type. The FM ordering and the canted spin ordering of the FA type may develop only for smaller \( |J_S| \), when the CE-type AFM ordering is already unstable. If \( |J_S| > 0.112 \) (the crossing point of CE and A total energy curves), the CE-type AFM state has the lowest energy amongst the states CE, A and AG, and is the magnetic ground state of the system.
In the two-dimensional case, the phase diagram is very simple: the total energy of the zigzag AFM state \((z_{↑↑}=2, z_{↑↓}=2)\), \(E_t(\text{zigzag})=-4J_{A_1B_1}^D\), shall be compared with the total energy of the two-dimensional FM state \((z_{↑↑}=4, z_{↑↓}=0)\), \(E_t(\text{ferro})=-8J_{A_1B_1}^D(\text{ferro})-2J^S\), where \(J_{A_1B_1}^D(\text{ferro})\approx0.115\). Conditions of the local stability are: \(|J^S|<J_{A_1B_1}^D(\text{ferro})\) for the two-dimensional FM ordering, and Eq. (24) for the zigzag AFM ordering. Two states coexist in the interval \(J_{A_1B_2}^D<|J^S|<J_{A_1B_1}^D(\text{ferro})\). If \(|J^S|>0.112\), the zigzag AFM state has lower energy than the FM state and vice versa.

E. Simple model for the Jahn-Teller distortion around the bridge sites

We assume that the Jahn-Teller distortion (JTD) results in the shifting of atomic \(y^2-z^2/3x^2-r^2\) levels of the \(A (A')\) sites by \(\pm\frac{1}{2}\Delta_{JT}\). This is equivalent to the following choice of the parameters of our original Hamiltonian: \(\Delta_O=\Delta_{JT}\) and \(\Delta_C=\frac{1}{2}\Delta_{JT}\), i.e. in addition to the local splitting at the \(A (A')\) sites, we shift all the states upwards by \(\frac{1}{2}\Delta_{JT}\). Obviously, the constant shift does not affect the magnetic interactions.

Thus, the JTD in such a picture will be accompanied by a charge disproportionation, and suppress the FM DE coupling within the chain (see Fig. 3). This is, in principle, a negative consequence which lowers the upper boundary of the local stability of the zigzag AFM ordering. Nevertheless, for relatively small distortions, the change of \(J_{A_1B_1}^D\) is also expected to be small. The effect of \(\Delta_{JT}\) on the interatomic interactions in the AFM bonds \(A_1-B_2\), \(A_1-A_3\) and \(B_1-B_3\) is more dramatic. The results are summarized in Fig. 5.

In order to evaluate the magnitude of the oxygen displacement which results in the splitting \(\Delta_{JT}\), we consider the following procedure: \(\Delta_{JT}\) (i) we start with a general TB Hamiltonian on an undistorted cubic lattice, in the basis of Mn(3de) and O(2p) orbitals interacting via nearest-neighbor \(pd\sigma\) hoppings, the distance-dependence of which is simulated by the Harrison low: \((pd\sigma)\propto d^{-7/2}\); (ii) we switch on the JTD of the MnO\(_6\) octahedra around the bridge sites, the \(Q_3\) mode\(^{20}\) (it is assumed that the total volume of the MnO\(_6\) octahedron remains to be constant); (iii) we project out the O(2p) states. This results in the on-site splitting of \(e_g\) orbitals, \(\Delta_{JT}\approx28\delta\) (in units of the effective \(dd\sigma\) two-center integral for the undistorted cubic lattice), where the oxygen displacement is described by the parameter \(\delta=(d_L-d_S)/(d_L+d_S)\), with \(d_L\) (\(d_S\)) being the long (short) Mn-O bond length in the distorted MnO\(_6\) octahedron.

Then, the behavior of magnetic interactions shown in Fig. 3 suggests that even a modest
distortion $\delta = 0.02$ (\(\Delta_{JT} \approx 0.56\), see also Ref. 27) may reduce the FM contribution to the AFM bonds $A_1-B_2$ and $B_1-B_3$ by up to 20%, whereas the coupling in the FM bond $A_1-B_1$ remains practically unchanged. Therefore, the JTD significantly lowers the low boundary of the local stability for the zigzag AFM ordering. As the result, the range of parameters $|J^S|$ which stabilize the zigzag AFM ordering significantly widens.

IV. OPTICAL PROPERTIES OF THE ZIGZAG CHAIN

In order to evaluate the optical conductivity tensor $\hat{\sigma}(\omega)$ for the single zigzag chain we take the following steps. First, we include the Mn(4$p$) states in our model and evaluate their admixture into the eigenfunctions of Hamiltonian (6) using the simplest perturbation theory. We assume that the main perturbation is caused by the kinetic hoppings between nearest-neighbor Mn(4$p$) and Mn(3$de_g$) orbitals. The hoppings are of the $pd\sigma$ type and can be parameterized in accordance with Slater-Koster rules. It is further assumed that the energy splitting between the atomic 4$p$ and 3$de_g$ levels, $\Delta_{4p-e_g}$, is much larger than the corresponding bandwidths, so that the band dispersion can be neglected in the perturbation theory expansion (this is certainly a very crude approximation, especially for the 4$p$ band, the validity of which will be discussed in Sec. V). Thus, the mixture of the Mn(4$p$) and Mn(3$de_g$) states will be controlled by the parameter $\alpha = (pd\sigma)_{4p-e_g}/\Delta_{4p-e_g}$, where $(pd\sigma)_{4p-e_g}$ is the 4$p$-3$de_g$ two-center integral. Then, by knowing distribution of the Mn(4$p$) and Mn(3$de_g$) states we can find matrix elements of the interband optical transitions $\varepsilon_k^- \rightarrow \varepsilon^0$ and $\varepsilon_k^- \rightarrow \varepsilon_k^+$, and express them through the intra-atomic dipole 4$p$-3$de_g$ matrix elements. Finally, the optical conductivity can be calculated using the Kubo formula. Due to the one-dimensional character of the problem, the solution along this line can be carried out analytically. For simplicity we will consider only the case of homogeneous charge distribution ($\Delta_C = 0$).

The simple TB picture considered in this section is of course very oversimplified and cannot provide a good quantitative description. However, it appears to be very useful in the analysis of symmetry properties and the structure of the conductivity tensor in terms of partial contributions from different sites of the system.
A. Distribution of Mn(4p) states

First, we consider the admixture of the 4p-orbitals $|x\rangle$ and $|y\rangle$ into the bonding and antibonding states of the Hamiltonian (4). Taking into account the explicit form of the wavefunctions at the sites $A$ and $A'$ given by Eqs. (14) and (17), and considering the nearest-neighbor $pd\sigma$ hoppings from the sites $A$ and $A'$ to the site $B$ of the chain 1 in Fig. 1, we obtain the following corrections to the wavefunctions at the site $B$, in the first order of $\alpha$:

$$|\delta\Psi_{\pm}\rangle_{B} = -\alpha \cos \theta_{\pm} \left\{ |x\rangle_{B} + e^{ik}|y\rangle_{B} \right\}. \quad (29)$$

Starting with the sites $B$ and $B'$ and considering the hoppings onto the site $A$, we obtain:

$$|\delta\Psi_{\pm}\rangle_{A} = \frac{i\alpha \sin \theta_{\pm} \sin k}{\sqrt{2 - \cos k}} |x\rangle_{A}. \quad (30)$$

Similar analysis applied to the nonbonding state $|\Psi_{0}\rangle$ yields:

$$|\delta\Psi_{0}\rangle_{A} = \sqrt{3i\alpha} \frac{\cos k}{\sqrt{2 - \cos k}} |x\rangle_{A}. \quad (31)$$

Since $|\Psi_{0}\rangle$ has nonvanishing elements only at the sites of $B$ and $B'$ type and the kinetic $3de_{g}-4p$ hoppings are restricted by the nearest neighbors, the correction $|\delta\Psi_{0}\rangle$ may exist only at the (neighboring) sites of $A$ type.

Corresponding corrections at the sites $A'$ and $B'$ can be found using Eq. (17).

B. Matrix elements of the optical transitions

The nonvanishing intra-atomic dipole matrix elements obey the following rules:

$$\langle 3x^2-r^2|x\rangle = \langle 3y^2-r^2|y\rangle = \beta, \quad \langle 3z^2-r^2|x\rangle = \langle 3z^2-r^2|y\rangle = -\frac{1}{2}\beta, \quad \text{and} \quad \langle x^2-y^2|x\rangle = -\langle x^2-y^2|y\rangle = \frac{\sqrt{3}}{2}\beta.$$ 

Then, using results of Secs. II C and IV A for $\Delta_{C}=0$, we obtain the following matrix elements:

$$\langle \Psi_{-}|\tilde{x}\delta\Psi_{0}\rangle_{A} = \langle \Psi_{-}|\tilde{y}\delta\Psi_{0}\rangle_{A'} = -\sqrt{\frac{3}{2}}i\alpha\beta \frac{\cos k}{\sqrt{2 - \cos k}} \quad (32)$$

for the bonding-nonbonding transitions at the sites $A$ and $A'$;

$$\langle \delta\Psi_{-}|\tilde{x}|\Psi_{0}\rangle_{B} = \langle \delta\Psi_{-}|\tilde{y}|\delta\Psi_{0}\rangle_{B'} = \langle \delta\Psi_{-}|\tilde{x}|\delta\Psi_{0}\rangle_{B'} = \langle \delta\Psi_{-}|\tilde{y}|\delta\Psi_{0}\rangle_{B'} = -\sqrt{\frac{3}{8}}i\alpha\beta \frac{1}{\sqrt{2 - \cos k}} \quad (33)$$
for the bonding-nonbonding transitions at the sites \(B\) and \(B'\):

\[
\langle \delta \Psi_- | \hat{x} | \Psi_+ \rangle_A + \langle \Psi_- | \hat{x} | \delta \Psi_+ \rangle_A = \langle \delta \Psi_- | \hat{y} | \Psi_+ \rangle_A' + \langle \Psi_- | \hat{y} | \delta \Psi_+ \rangle_A' = -i \alpha \beta \frac{\sin k}{\sqrt{2 - \cos k}}
\]

(34)

for the bonding-antibonding transitions at the sites \(A\) and \(A'\); and

\[
\langle \delta \Psi_- | \hat{x} | \Psi_+ \rangle_B + \langle \Psi_- | \hat{x} | \delta \Psi_+ \rangle_B = \langle \delta \Psi_- | \hat{y} | \Psi_+ \rangle_B' + \langle \Psi_- | \hat{y} | \delta \Psi_+ \rangle_B' = \langle \delta \Psi_- | \hat{y} | \Psi_+ \rangle_B + \langle \Psi_- | \hat{y} | \delta \Psi_+ \rangle_B = \langle \delta \Psi_- | \hat{y} | \Psi_+ \rangle_B' + \langle \Psi_- | \hat{y} | \delta \Psi_+ \rangle_B' = 1
\]

(35)

for the bonding-antibonding transitions at the sites \(B\) and \(B'\).

C. Optical conductivity

The inter-band optical conductivity tensor can be obtained using the Kubo formula:

\[
\sigma_{\gamma \gamma'}(\omega) \propto \frac{1}{\omega} \int_0^{\pi} dk \langle \Psi_i | \hat{\gamma} | \Psi_f \rangle \langle \Psi_f | \hat{\gamma}' | \Psi_i \rangle \delta(\omega - \epsilon_{f}^i + \epsilon_{k}^i),
\]

(36)

where \(\gamma(\gamma') = x, y\); \(\Psi_i\) and \(\epsilon_{k}^i\) stand for the initial state \(i = "-"\); \(\Psi_f\) and \(\epsilon_{k}^f\) stand for the final state \(f = "0"\) or \("+"\). We consider only site-diagonal contributions in Eq. (36). The integral can be evaluated along the same line as for the local densities of states in Appendix A. Then, we obtain the following nonvanishing contributions to the conductivity tensor:

\[
\sigma_{xx}^A(\omega) = \sigma_{yy}^{A'}(\omega)
\]

(37)

at the sites \(A\) and \(A'\), where

\[
\sigma_{xx}^A(\omega) \propto \frac{3}{\omega^2} \frac{(2 - \omega^2)^2}{\sqrt{(3 - \omega^2)(\omega^2 - 1)}}
\]

(38)

for the bonding-nonbonding transitions (we drop the common multiplier \(\alpha^2 \beta^2\)), and

\[
\sigma_{xx}^{A'}(\omega) \propto \frac{1}{2\omega^2} \sqrt{(12 - \omega^2)(\omega^2 - 4)}
\]

(39)

for the bonding-antibonding transitions;

\[
\sigma_{xx}^B(\omega) = -\sigma_{xy}^B(\omega) = -\sigma_{yx}^B(\omega) = \sigma_{yy}^B(\omega)
\]

(40)

and

\[
\tilde{\sigma}^B(\omega) = \tilde{\sigma}^B(\omega),
\]

(41)
at the sites $B$ and $B'$, where
\[ \sigma_{xx}^B(\omega) \propto \frac{3}{4\omega^2} \frac{1}{\sqrt{3-\omega^2}(\omega^2-1)} \] (42)
for the bonding-nonbonding transitions, and
\[ \sigma_{xx}^B(\omega) \propto \frac{1}{8\omega^2} \sqrt{12-\omega^2}(\omega^2-4) \] (43)
for the bonding-antibonding transitions.

The results are shown in Fig. 6. The conductivity spectrum consists of two parts originating from the bonding-nonbonding and bonding-antibonding transitions, and spreading within the intervals $1 \leq \omega \leq \sqrt{3}$ and $2 \leq \omega \leq 2\sqrt{3}$, respectively. Taking into account that a realistic estimate for the effective $dd\sigma$ two-center integral is about 0.7 eV (for the undistorted lattice, without buckling of Mn-O-Mn bonds),\textsuperscript{19} they roughly correspond to the energy ranges $0.7 \leq \omega \leq 1.2$ eV and $1.4 \leq \omega \leq 2.4$ eV. We note that the components of the conductivity tensor associated with the bridge ($A,A'$) and the corner ($B,B'$) sites are characterized by different optical axes. The tensors $\hat{\sigma}^A(\omega)$ and $\hat{\sigma}^{A'}(\omega)$ are diagonal in the basis of cubic axes $x=[1,0,0]$ and $y=[0,1,0]$ shown in Fig. 1. In this basis, each of the tensors has only one nonvanishing diagonal element, correspondingly $\sigma_{xx}^A(\omega)$ and $\sigma_{yy}^{A'}(\omega)$, connected by the symmetry transformation (37). Therefore, the total conductivity $\hat{\sigma}^A(\omega)+\hat{\sigma}^{A'}(\omega)$ behaves as an isotropic object in the plane $x-y$. Conversely, the tensors $\hat{\sigma}^B(\omega)=\hat{\sigma}^{B'}(\omega)$ are diagonal in the basis of orthorhombic axes $a=[1,1,0]$ and $b=[\bar{1},1,0]$, which are rotated with respect to cubic ones by $45^\circ$. In the orthorhombic frame, they have only one nonvanishing diagonal element $\sigma_{bb}^B(\omega)=\sigma_{bb}^{B'}(\omega)=2\sigma_{xx}^B(\omega)$ in the direction of propagation of the zigzag chain (the $b$-direction). This gives rise to an anisotropy of the optical conductivity, which has been observed experimentally in La$_{1/2}$Sr$_{3/2}$MnO$_4$ by using a birefringence technique.\textsuperscript{20}

The energy range corresponding to the bonding-nonbonding transitions roughly agrees with the position of the mid-infrared peak observed in La$_{1/2}$Sr$_{3/2}$MnO$_4$ around 1.0-1.3 eV.\textsuperscript{15,30} High intensity of experimental peak may be partly attributed to the (quasi-) one-dimensional character of the problem and divergence of the optical conductivity at the band edges. Another possibility is the lack of the inversion symmetry at the corner sites $B$ and $B'$. In this case, the atomic $3de_g$ and $4p$ orbitals may belong to the same representation of the local symmetry group. This is an additional channel of mixing of the $3de_g$ and $4p$ states at the corner atoms, which contributes to probabilities of the optical transitions.
The JTD around the bridge sites can affect the conductivity spectrum indirectly, through the induced charge disproportionation, in a way similar to the intra-chain DE interaction considered in Sec. 1111. Since the charge disproportionation $\Delta C > 0$ increases the energy gap between the bonding and nonbonding bands and decrease the width of the former, we expect the upward shift of the optical absorption center and narrowing of the spectrum in the region of the bonding-nonbonding transitions.

If the charge disproportionation does not take place ($\Delta C = 0$), the optical conductivity is expected to be the smooth function in the region of bonding-antibonding transitions and reveals the same symmetry properties as for the bonding-nonbonding ones.

D. Resonant x-ray scattering near the Mn $K$-absorption edge

The resonant x-ray scattering near the Mn $K$-absorption edge is considered as a powerful experimental tool, which allows to probe the charge and orbital distribution in the perovskite manganites.4,31 The interpretation of experimental data is, however, hampered by the fact that the direct dipole transitions are allowed to the 4$p$ states but not directly to the 3$d$ states in the case of $K$-absorption. Therefore, the understanding of how the 4$p$ states interact with polarized 3$de_g$ orbitals represents a special interest.32,33 Here we would like to show how the geometry of the zigzag chain imposes some constraints on the distribution of the Mn(4$p$) states, which should be reflected in the lowest energy part of the $K$-absorption spectrum of manganites with the zigzag AFM ordering.

In accordance with the TB picture (Fig. 2), the first unoccupied band which is involved in the transitions is the nonbonding band composed of the 3$de_g$ orbitals of the corner atoms $B$ and $B'$. If the hoppings between 3$de_g$ and 4$p$ orbitals are restricted by nearest neighbors, the 4$p$ states will have nonvanishing weight only at the bridge sites $A$ and $A'$ in the nonbonding part of the spectrum. This interaction, given by Eqs. 31 and 17, results in the ordering of $|x\rangle_A$ and $|y\rangle_{A'}$ orbitals. Since the $e_g$ orbitals of the bridge atoms do not contribute to the nonbonding band, there is nothing to re-expand over the 4$p$ orbitals of the neighboring (corner) atoms, and the corresponding weight of the 4$p$ states at the corner atoms will be zero.

Thus, in accordance with our TB picture, the lowest energy part of the $K$-absorption spectrum probes the $|x\rangle_A$ and $|y\rangle_{A'}$ states of the bridge atoms, which carry the information
about the distribution of the $e_g$ states at the corner atoms.

V. COMPARISON WITH LSDA BAND STRUCTURE CALCULATIONS

The purpose of this section is to discuss validity of the TB model for the zigzag AFM state by comparing it with results of first-principles band structure calculations in the local-spin-density approximation (LSDA). LSDA and its extension in the form of the generalized gradient approximation (GGA) work reasonably well in manganites.\textsuperscript{19,34,35,36,37,38} There are several unresolved problems, such as the relative stability of the Jahn-Teller distorted insulating A-type AFM state and the metallic FM state in LaMnO$_3$; the standard band calculations account well for various magnetic properties of LaMnO$_3$ with the experimental crystal structure,\textsuperscript{34,35} however the full optimization of the crystal structure substantially reduces the JTD and makes the A-type AFM state energetically less favorable than the FM state.\textsuperscript{36} To say the truth, similar problem was encountered also in La$_{1/2}$Sr$_{3/2}$MnO$_4$, where after the structure optimization in GGA the FM state had lower energy than the zigzag AFM state.\textsuperscript{12} However, it is also true that at present the problem has no feasible solution. For example, the LDA+$U$ (or GGA+$U$) approach only worsen the picture of magnetic interactions in LaMnO$_3$.\textsuperscript{39} This may be related with the fact that the relative position of the oxygen 2$p$ and Mn(3$d$) states (the so-called charge-transfer energy) is incorrect in LDA+$U$, that leads to a large error in the calculated parameters of magnetic interactions.\textsuperscript{40} Thus, we believe that the LSDA provides the most reliable reference point for the analysis of magnetic properties of manganites.

The quasi-one-dimensional TB model is a substantial simplification for realistic material, in several respect. (i) The DE limit is not realized in perovskite manganites.\textsuperscript{19} So, in the zigzag AFM state the chains are not fully isolated from each other, and the system is not strictly one-dimensional. (ii) The distribution of Mn(3$d_{e_g}$) states is affected by other factors, which are not included explicitely in the TB model, particularly by the oxygen 2$p$ and Mn(3$d_{t_{2g}}$) states.\textsuperscript{41} (iii) The Mn(4$p$) states generally form a very broad band. In this respect, our attempt to simulate the optical properties by starting with atomic 4$p$-levels and considering their interactions with the $e_g$ bands in a perturbative manner was a crude approximation. It allows to catch the basic symmetry properties of the optical conductivity tensor, but certainly not all the details and the absolute values of the conductivity itself.
We use the ASA-LMTO method in the nearly orthogonal representation. The Wigner-Seitz sphere radii for nonequivalent sites were chosen from the charge neutrality condition inside the spheres. The calculations have been performed for the phenomenological virtual-crystal alloy $Y_{1/2}Sr_{3/2}MnO_4$ using the lattice parameters of the real two-dimensional perovskite $La_{1/2}Sr_{3/2}MnO_4$. In addition, we also investigated the effect of the JTD around the bridge sites. The latter is characterized by the parameter $\delta$ introduced in Sec. III E.

The partial densities of Mn($3d_{eg}$) and Mn($4p$) states are shown in Fig. 7. They reveal many similarities to the TB picture. There are also some differences. We note the following. First, there is the clear splitting of the majority-spin $3d_{eg}$ states into the bonding band located around $-0.5$ eV (the case of $\delta=0$), the nonbonding bands around 0.7 eV, and the antibonding band around 1.7 eV. Two nonbonding bands are composed of the $e_g$ states of the corner ($B$ and $B'$) atoms and the $y^2-z^2$ ($x^2-z^2$) states of the bridge $A$ ($A'$) atoms. Even without the JTD, the system is insulating and the band gap is 0.3 eV. This value is however smaller than the estimate 0.7 eV expected from the tight-bonding analysis (the value of effective two-center $dd\sigma$ integral). The difference is caused by the additional broadening of the bonding and nonbonding bands in the LSDA. The JTD increases the band-gap (for example, for $\delta=0.03$ the band-gap is 0.7 eV). Second, the partial densities of states in the bonding part of the spectrum clearly shows the characteristic peaks at the band edges, which is the signature of (quasi-) one-dimensional behavior. The bandwidth is however larger than $(\sqrt{3}-1)\times0.7\simeq0.5$ eV, expected from the TB analysis. The density of nonbonding and antibonding state is modified more significantly. Particularly, the nonbonding and antibonding parts of the spectrum overlap with the minority-spin $t_{2g}$ band (not shown in Fig. 7). The minority-spin $t_{2g}$ states may interact with the majority-spin $e_g$ states of the neighboring zigzag chains either directly, via next nearest-neighbor hoppings (note, that the nearest-neighbor hoppings between the $t_{2g}$ and $e_g$ orbitals are forbidden in the cubic lattice – Ref. 16), or indirectly, via the oxygen $2p$ band. As the result, the ”nonbonding” states associated with the corner atoms $B$ and $B'$ are significantly broadened (to be compared with the $\delta$-peak expected from the TB analysis - Fig. 2). Conversely, the $y^2-z^2$ and $x^2-z^2$ states of the bridge sites $A$ and $A'$ are only weakly bonded, resulting in the high peak of the density of states around 0.5 eV.

Due to the hybridization, the distribution of the majority-spin Mn($4p$) states around the Fermi level repeat the characteristic bonding-nonbonding-antibonding splitting of the
Mn(3d_{eg}) states. The nonbonding part of the spectrum is composed mainly of the \( x \) (\( y \)) orbitals of the bridge atoms \( A \) (\( A' \)). The contribution of the 4\( p \) orbitals of the corner atoms into this region is significantly smaller.

The corresponding optical conductivity is shown in Fig. 8. Some details of calculations can be found in Refs. 37, 39. Here we only would like to mention that in order to speed up rather heavy calculations (note that taking into consideration the zigzag AFM ordering, the unit cell of \( Y_{1/2}Sr_{3/2}MnO_4 \) consists of 56 atoms), the Brillouin zone integration in the calculations of optical conductivity was replaced by a summation with the phenomenological Lorentzian broadening of 0.136 eV. This causes some artificial broadening of the spectrum. Nevertheless, we believe that all important features are preserved in it, and were not washed out by the broadening. As the test, one can consider the off-diagonal element \( \sigma_{xy}(\omega) \) in the low-energy part of the spectrum. It clearly shows two peak around 0.4 eV and 0.8 eV (the case of \( \delta=0 \)), corresponding to two peaks of the (quasi-) one-dimensional density of states in the bonding region (Fig. 7), in a close analogy with the TB picture (Fig. 6).

Surprisingly however that the shape of diagonal conductivity in the \( xy \)-plane is very different, contrary to our expectations based on the TB model. In the low-energy part of the spectrum it has only one large peak at 0.7 eV. The difference cannot be simply attributed to the broadening effects, because otherwise similar broadening would be expected also for the off-diagonal component of the conductivity tensor. Unfortunately, on the level of first-principles band structure calculations, it is rather difficult to decompose the optical conductivity unambiguously into partial contributions and to elucidate the origin of the spectral shape. Most probably, the difference between the LSDA calculations and the TB analysis is caused at once by several factors outlined in the beginning of this section.

In the TB model, two contributions to the conductivity spectrum in the region of bonding-nonbonding transitions, \( \sigma^A_{xx}(\omega) \) and \( \sigma^B_{xx}(\omega) \), are comparable (see Fig. 6). The off-diagonal element of the conductivity tensor, which is responsible for the anisotropy of optical properties, is related with the diagonal one by Eq. (40). Therefore, \( \sigma_{xy}(\omega) \) is expected to be of the same order of magnitude as the total diagonal conductivity \( \sigma^A_{xx}(\omega)+\sigma^B_{xx}(\omega) \). However, in a more realistic situation, when the system is not strictly one-dimensional, the optical anisotropy is significantly reduced. For example, in the LSDA we have only 0.1\( \sigma_{xx}(\omega) \) in the region of bonding-nonbonding transitions.

The JTD around the bridge sites results in the upward shift of the low-energy peak and
the simultaneous decrease of its intensity. Two experimental groups reported somewhat different results for the peak position at the low temperature: 1.0 eV (Ref. 15) and 1.3 eV (Ref. 30). Both are larger than 0.7 eV obtained in the LSDA calculations without the JTD. The JTD $\delta = 0.03$ yields the new peak position 1.0 eV, in agreement with one of the experimental reports. However, the obtained intensity $700 \, \Omega^{-1}\text{cm}^{-1}$ at the peak maximum appears to be smaller than the experimental one, which is about $1100 \, \Omega^{-1}\text{cm}^{-1}$. Another effect of the JTD is the redistribution of the in-plane conductivity around 2.0 eV, in the region of bonding-antibonding transition.

As expected for the layered perovskite compound, the in-plane ($\sigma_{xx}$) and out-of-plane ($\sigma_{zz}$) components of the optical conductivity reveal a strong anisotropy, in a good agreement with the experimental finding for La$_{1/2}$Sr$_{3/2}$MnO$_4$.\textsuperscript{15}

Finally, we calculate nearest-neighbor magnetic interactions in Y$_{1/2}$Sr$_{3/2}$MnO$_4$ as the function of the Jahn-Teller distortion $\delta$, using the same approach as in Ref. 35. For small $\delta$ we obtain $J_{A_1B_1}(\delta) \approx 43 + 313\delta$ meV and $J_{A_1B_2}(\delta) \approx 12 - 680\delta$ meV. Therefore, even without the JTD, the magnetic interactions in the zigzag AFM state show a very strong anisotropy $J_{A_1B_1}(0) > J_{A_1B_2}(0)$, in a good agreement with the TB analysis. In the LSDA, a small JTD $\delta \geq 0.02$ becomes indispensable to stabilize the AFM coupling $J_{A_1B_2}(\delta) < 0$ between neighboring zigzag chains.

VI. SUMMARY

Properties of the so-called ”charge-ordered” manganites are typically regarded as one of the most striking examples of the strong coupling amongst the spin, charge and orbital degrees of freedom. The coupling, which is reflected in the number of transport, structural and magnetic phenomena, is also believed to be responsible for the peculiar form of the ordered state realized at low temperatures.

In the present work we tried to elucidate the cause of such an unusual behavior and to understand it from the viewpoint of the magnetic spin ordering. We found that the zigzag form of the antiferromagnetic spin ordering, combined with the DE physics, already provides a very consistent description for various low-temperature properties of the ”charge-ordered” manganites. In the DE limit, the one-dimensional FM zigzag chains become effectively separated from each other. The one-dimensional character of the chains leads to the anisotropy
of electronic properties. The anisotropy of nearest-neighbor magnetic interactions in the DE limit, combined with the isotropic superexchange interaction $J^S$, readily explains the local stability of the zigzag AFM state. Formally, the basic DE picture is sufficient to understand the local stability. The JTD significantly reduces the FM DE contribution to the AFM bonds, and in this way widens the region of local stability of the zigzag AFM ordering. It appears that in the wide range of parameters $J^S$, the zigzag AFM ordering is stable not only locally, but also globally, meaning that this is indeed the magnetic ground state of the system. We also expect the anisotropy of optical properties, which is related with the distribution of the $e_g$ states at the corner atoms of the zigzag chain. The two-fold degeneracy of the $e_g$ levels plays a very important role in the problem, and is responsible for the insulating behavior and the orbital ordering developed at the bridge sites of the zigzag chain.

Thus, we believe that the nature of the low-temperature CE state in manganites is magnetic. The charge ordering reduces mobility of the $e_g$ electrons and tends to destroy the ferromagnetic coupling within the chain. Therefore, it is expected to be small and play only minor role in the problem.

Applicability of this picture to the high-temperature regime is still in question. Particularly, many charge ordered manganites are characterized by the existence of two transition temperatures: the long-range AFM ordering occurs below the Néel temperature $T_N$, whereas the charge and orbital ordering orderings occur simultaneously below another critical temperature $T_{CO}$. In accordance with neutron scattering measurements, it holds $T_N<T_{CO}$ (see, e.g., Ref. 3). This fact is typically considered as the strong experimental evidence that the charge and orbital degrees of freedom play a decisive role in the interval $T_N<T<T_{CO}$ and drive the AFM CE ordering at $T_N,44,45$ However, other experimental data suggest that the exact nature of the state realized between $T_N$ and $T_{CO}$ is much more complicated, and still far from the complete understanding.

1) Some magnetic experiments simply ”do no see” the existence of the transition point $T_N$. For example, the behavior of spin magnetization in the external magnetic field shows the characteristic metamagnetic transition both below and above $T_N$, which disappears only at $T_{CO}$.46,47 The magnetic susceptibility shows a pronounced peak at $T_{CO}$ and no anomaly at $T_N$.47 These data suggest that, although there is no long-range magnetic order, the magnetic fluctuations and the effects of short-range order continue to play a very important role in the interval $T_N<T<T_{CO}$.

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2) The high-resolution electron microscopy clearly reveals the existence of the one-dimensional chains (stripes) even above $T_N$, though the exact form of the stripes is not quite clear yet. It is also not clear whether these stripes have a magnetic origin or not. If they do, it would be a strong argument in the favor of the magnetic scenario considered in the present work, although the perfect geometry of the FM zigzag chain may be destroyed at elevated temperatures. In this respect, an interesting theoretical result has been obtained by Hotta et al. They argued that the class of one-dimensional zigzag objects, which preserves the insulating behavior at $x=0.5$ is actually much wider and is not limited by the zigzag chain shown in Fig. 1. All these new zigzag configuration have higher energies, and therefore are not realized as the ground state at low temperatures. However, they may carry a considerable weight in the thermodynamics averages and therefore contribute to the high-temperature behavior of the charge ordered manganites.

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**APPENDIX A: LOCAL DENSITIES OF STATES FOR THE ZIGZAG CHAIN**

The local density of states at the site $\tau$ is given by

$$N_L^\tau(\epsilon) = -\frac{1}{\pi} \text{Im} G_{\tau\tau}^{LL}(\epsilon). \quad (A1)$$

Using the explicit expressions for the matrix elements of the Green function, Eqs. (4)-(9), noting that $-\frac{1}{\pi} \lim_{\eta \to 0^+} \text{Im}[\epsilon - \epsilon' + i\eta]^{-1} = \delta(\epsilon - \epsilon')$, and taking into account that

$$\int dk \delta(\epsilon - \epsilon_k^\pm) = \frac{1}{|d\epsilon_k^\pm/d\epsilon|}, \quad (A2)$$

where the derivative is evaluated at the point $\epsilon_k^\pm = \epsilon$, one can find the following expressions for the partial densities of states:

$$N_A^1(\epsilon) = \frac{1}{\pi} \frac{|\epsilon - \Delta_C|}{\sqrt{3 + \epsilon(\Delta_C - \epsilon)[\epsilon(\epsilon - \Delta_C) - 1]}}, \quad (A3)$$

$$N_B^1(\epsilon) = \frac{1}{2\pi|\epsilon - \Delta_C|} \sqrt{\frac{3 + \epsilon(\Delta_C - \epsilon)}{\epsilon(\epsilon - \Delta_C) - 1} + \frac{3 - \sqrt{3}}{2} \delta(\epsilon - \Delta_C)}, \quad (A4)$$
The total density of states, \( N(\varepsilon) = N_A(\varepsilon) + N_B^1(\varepsilon) + N_B^2(\varepsilon) \), is given by

\[
N(\varepsilon) = \frac{1}{\pi} \frac{|2\varepsilon - \Delta C|}{\sqrt{[3 + \varepsilon(\Delta C - \varepsilon)][\varepsilon(\varepsilon - \Delta C) - 1]}} + \delta(\varepsilon - \Delta C). \tag{A6}
\]

**APPENDIX B: THE TOTAL ENERGY CHANGE DUE TO SMALL ROTATIONS OF THE SPIN MAGNETIC MOMENTS**

Here we argue that the invariance of the total energy with respect to uniform rotations of all spin magnetic moments by the same angle automatically leads to the isotropic Heisenberg form for the total energy change associated with small rotations of an arbitrary type – Eq. \( \text{(19)} \). For simplicity we consider the FM ordering for which \( e_0^i \equiv e^0 \) does not depend on the site \( i \). By expanding \( E_t\{e_0^i + \delta e_i\} \) in the Taylor series we obtain in the second order:

\[
E_t\{e_0^i + \delta e_i\} \simeq E_t[e^0] - \sum_i f_i (\delta^{(2)}e_i \cdot e^0) - \frac{1}{2} \sum_{ij} J_{ij}(\delta^{(1)}e_i \cdot \delta^{(1)}e_j). \tag{B1}
\]

In Eq. \( \text{(B1)} \) we employed the requirement of rotational invariance for the perturbed system: if all spins are rotated the same angle, the total energy does not change. Therefore, \( e^0 \) and \( \delta e_i \) may enter the expression for the total energy change only through the scalar products. Noting that \( \delta^{(1)}e_i \) and \( \delta^{(2)}e_i \) are given by Eq. \( \text{(18)} \) and employing again the requirement of rotational invariance for the unperturbed system (that is the total energy does not change if all spins \( \{e_0^i\} \) are rotated by the same angle \( \delta \varphi_i \equiv \delta \varphi \)) we find the following condition:

\[
f_i = \sum_j J_{ij}.
\]

This proves validity of Eq. \( \text{(19)} \) for the FM ordering. The generalization to the AFM ordering is straightforward, because similar arguments can be applied both for the intra- and inter-spin-sublattice interactions in the AFM state.

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Note that in the "charge ordering" regime \( n_B=1-n_A \), \( n_A=-\frac{1}{\pi} \int_{-\infty}^{\infty} d\varepsilon G^{11}_{AA}(\varepsilon) \), and \( G^{11}_{AA}(\varepsilon) \) is given by Eq. (7).

Since the pole of \( G^{22}_{AA}(\varepsilon) \) is located in the unoccupied part of the spectrum, the term propor-
tional to \( (G_{A_1A_1}(\varepsilon))^2 \) does not contribute to the exchange coupling and can be dropped.

Here we consider only the "hard" condition of the local stability of the A-type AFM ordering and require the sign of the nearest-neighbor magnetic coupling to correspond directly the type of the magnetic ordering. For example, due to existance of the longer-range interactions between the antiferromagnetically coupled layers, the stability of the A-type AFM ordering with respect to the spin canting is given by a "softer" condition, where the lower boundary for \( |J^S| \) is only 0.063 when \( x=0.5 \).

The canted spin states of the FA type have been considered in our previous work (Ref. 20). The canted spin states of the AG type can be generated along the same line and corresponds to the combination of angles \((\theta_{xy}, \pi)\), in the notations of Ref. 20. If stable, the AG states have the lowest energy amongst the collinear FM, A-, C-, and G-type AFM states and all possible intermediate canted states for \( x=0.5 \).

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FIG. 1: Spin, orbital and "charge" ordering in two neighboring planes of the CE-type antiferromagnetic structure: symbols $A$ and $A'$ stand for the bridge sites, symbols $B$ and $B'$ stand for the corner sites. $a_0 = |A_1B_1|$ is the cubic lattice parameter.
FIG. 2: Total and partial densities of states of the tight-binding model for $\Delta_C=0$ (no charge disproportionation).

FIG. 3: Effect of the charge disproportionation on the ferromagnetic double-exchange coupling within the chain.
FIG. 4: Total energies (bottom) and the regions of local stability (top) for various magnetic states in the three-dimensional (3D) and two-dimensional (2D) perovskite lattices for $x=0.5$. The data for the CE-type antiferromagnetic ordering are divided in two parts corresponding to the hard (h) and soft (s) regimes of the local stability.
FIG. 5: Nearest-neighbor interactions in the double-exchange limit as the function of the Jahn-Teller distortion at the bridge sites.

FIG. 6: Partial contributions to the conductivity tensor of the tight-binding model.
FIG. 7: Partial densities of Mn(3de_g) (top) and Mn(4p) (bottom) states for $Y_{1/2}Sr_{3/2}MnO_4$ in the zigzag antiferromagnetic state. Two panels show results of calculations with (right) and without (left) the Jahn-Teller distortion. The Fermi level (the top of occupied band) is at zero. The arrows $↑$ and $↓$ stand for the majority- and minority-spin states.
FIG. 8: Elements of the conductivity tensor for $\text{Y}_{1/2}\text{Sr}_{3/2}\text{MnO}_4$ in the zigzag antiferromagnetic state. Different lines correspond to different values of the Jahn-Teller distortion $\delta$. 