Research articles

Orbital state dependence of insulating manganites' magnetic ordering

L.E. Gonchar

Ural State University of Railway Transport, 66, Kolmogorov St., Ekaterinburg 620034, Russia
Ural Federal University, 19, Mira St., Ekaterinburg 620002, Russia

ARTICLE INFO

ABSTRACT

In insulating manganites, a semi-empirical model of orbital structure is proposed. The model allows us to account for the non-linear and non-local effects of a crystal structure on the orbital ordering of a trivalent manganese sublattice. This allows the variation of only two parameters for each degenerated manganese ion. They include the main part – the linear vibronic interaction – and additional parts (as long-range Coulomb fields or non-linear vibronic interactions). This is why one can define the orbital structure with respect of the magnetic structure without explicit microscopic definition of the non-linear and non-local terms. The continuous changes to the orbital mixing parameters are important for magnetic structure description. Within the framework of orbitally-dependent superexchange interaction, magnetic structures dependent on orbital orderings are considered. For manganite crystals $LaMnO_3$, $BiMnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, $La_{0.333}Ca_{0.667}MnO_3$, phase diagrams of the orbital and magnetic structures with an unchanged crystal structure are drawn. The role of orbital ordering in frustrated magnetic structures is emphasized. The insufficiency of the linear vibronic approach is shown.

1. Introduction

Jahn-Teller magnetic oxides are currently of interest in theoretical and applied physics [1] because of the effects of the strong correlation between crystalline, charge, orbital and magnetic subsystems. Rare-earth manganite crystals with alkaline-earth doping $R_{1-x}A_xMnO_3$ (R^{3+} is the rare-earth metal ion, Bi^{3+} or Y^{3+}, A^{2+} is the alkaline-earth element, and $0 \leq x < 1$ is the doping rate) are vivid examples of this class of compounds. They belong to the pseudocubic distorted structure and the nearly octahedral oxygen neighborhood of Mn^{3+} ions. Thus, the Mn^{3+} ion is a Jahn-Teller (JT) ion [2] with the orbital degenerated state ^5E in an undistorted octahedron of O^{2-} ions. Because of the regular trivalent manganese sublattice, these crystals are distorted due to a cooperative JT effect [2]. Thus, the ground state multiplet ^5E of the Mn^{3+} sublattice is split. The orbital states of insulating manganese ions form a regular structure, which is called an orbital ordering (OO) [3]. In the case of non-isovalent doping, the charge carriers can be localized on manganese ions [3,4]. This effect of charge localization leads to charge ordering (CO). CO means a regular structure of Mn^{3+}/Mn^{4+} ions. The magnetic structures (MS) of manganites are various. There are: *A*-type ordering in lanthanum, praseodymium, neodymium manganites [3,5], low doped manganites [6], *E*-type dysprosium, holmium, terbium, ytterbium manganites [5,7,8], *CE*-type in half-doped CO manganites, *C*-type in strongly doped manganites [9,10], and *F*-type in $x \sim 0.3$ doped CMR manganites [3,9] and in bismuth manganite [11]. The bismuth manganite is also considered to be a multiferroic crystal because of the

lone-pair s-electrons of Bi^{3+} ions [11,12]. Its crystal and orbital structures are quite different to those of rare-earth manganites. The multiferroic character of E-manganite is also investigated [8]. Some manganites have a frustrated magnetic structure [11,13]. The especial features of MS in JT compounds are mostly explained by OO. The problem of manganites' orbital structure was mentioned long ago [2,3]. It is dependent upon crystal structure and charge distribution [12,14–20]. The interrelation between orbital and magnetic subsystems was discussed [14–20]. The orbital state of insulating manganites is well described in the scientific literature. However, there are some problems.

The experimental investigation of orbital structure is difficult because of the absence of direct observation of the electronic densities distribution. The methods of experimental OO detection are: neutron scattering [3,10,13,21], resonant X-ray scattering (RXS) [22,23], nuclear magnetic resonance (NMR) [24], electronic microscopy methods (scanning tunneling microscopy (STM), and transmission electron microscopy (TEM)) [25]. Nevertheless, these methods do not allow us to determine orbital mixing coefficients exactly. The neutron scattering method estimates OO and CO using Mn–O distances due to cooperative JT distortions [7,10,11,13,21]. However, this can only find the approximate orbital states of JT ions. Shifts in the oxygen neighborhood of manganese ions can point to JT-type distortions around the trivalent manganese ion sublattice. Approximately equal Mn–O distances indicate a tetravalent manganese ion sublattice without any orbital degeneration. However, the local neighborhood distortion is not an

exhaustive description of the orbital state of an ion. There are non-local and non-linear terms in the vibronic interactions, which affect the orbital structure [18]. The approximation of RXS takes into account some discrete values of coefficients [22]. However, lots of interaction influencing the orbital state lead to deviation from these values [17,18]. Changes in the orbital mixing coefficients could drastically affect the magnetic structure in cases of magnetic frustration [18] or if the orbitally dependent superexchange interaction has a low value [17]. The NMR method is local but far too indirect for OO [24]. The TEM method is also a local method, but it indicates only the presence, absence or breaking of the superstructure [25]. The authors of the experimental investigations in [25] admit the importance of continuous orbital states' range of Mn^{3+}.

The theoretical problem of OO description is choosing the driving mechanism of cooperative ordering. The *ab initio* calculations used for manganite description are very sensitive to correlations in manganese and oxygen ions [4,12,19,23,26,27]. To describe the orbital part, the authors mainly use the Kugel-Khomskii model. The most popular Kugel-Khomskii model [14,16] normally is used within the approximation of comparable vibronic and superexchange interaction. Nevertheless, some papers [4,16,19] point out the role of electron-phonon (or vibronic) interaction and the JT effect in the formation of orbital structure. The other reason for orbital ordering is vibronic interaction [2,17–19,24,28]. This model is the choice of the current paper as a basis for generalization.

Models of exchange interaction in insulating manganites are also under discussion. The rich set of MS makes it difficult to create a general model. The main rules for the estimation of the signs and relative values of the nearest-neighbor superexchange parameters are the Goodenough-Kanamory rules [3]. These rules use OO to MS explanation. The absence of precise values leads to difficulties in the MS description for magnetically frustrated compounds such as $La_{1/3}Ca_{2/3}MnO_3$, $BiMnO_3$. For the description of superexchange parameters, *ab initio* calculations [4,19,20,29,30], the Kugel-Khomskii model [14,16], the orbitally-dependent phenomenological model [8,17,18], the next-nearest neighbor model [8,12,31], and double-exchange model [12,19,23,26] are applied. *Ab initio* calculations need a preliminary assumption of the magnetic and crystal structure. In the case of charge-ordered and frustrated MS, it is difficult to assume the whole set of possible structures. This method does not allow us to draw any dependency of MS upon OO parameters. The double-exchange model is not applicable to charge localization. We use the previously proposed orbitally-dependent superexchange model [17,18] to find the possible MS for different orbital mixing within the framework of crystal symmetry.

The aim of the current investigation is to present a uniform phenomenological model of JT manganites' orbital structure with only a few parameters. The application of this model uses the magnetic structures prediction within the framework of the orbitally-dependent superexchange model. This approach gives a possibility to describe or predict most magnetic structures even with magnetic frustration.

2. Methods

2.1. Orbital state of Mn^{3+} sublattice

The ground state of the Mn^{3+} ion's orbital subsystem with a total spin S = 2 in an octahedral ligand neighborhood is the ^5E multiplet. This state is twofold degenerated: thus some distortions of the neighborhood lead to the removal of degeneration [2]. Other multiplets ($^3T_1$ and $^5T_2$) have a noticeable gap with the ground state and are not taken into account.

We use the electron-phonon (or vibronic) model for OO description. The main part of the interaction is the linear coupling of the orbital subsystem with the local ligand's neighborhood distortions. However, it is necessary to take into account the long-range crystal field [32], non-

linear terms [18], and far-neighbor interaction [18]. In order to account for all of them, the phenomenological approach is needed. We use symmetry consideration for the description.

The symmetry of the interaction operator causing the degeneration removal is $\{E \times E\}^s = A_1 + E$. We can use *e*-type orbital operators X acting on the many-electron eigenfunctions of the ground state ($\theta\rangle$, $|\varepsilon\rangle$) in a linear combination as follows

$$\widehat{H}_{eff} = \alpha_1 X_\theta + \alpha_2 X_\varepsilon, \tag{1}$$

where the operators in matrix form are

$$X_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{matrix}\theta \\ \varepsilon\end{matrix}; \quad X_\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{matrix}\theta \\ \varepsilon\end{matrix}. \tag{2}$$

The α_1 and α_2 coefficients are model parameters and account for all interactions with the linear dependence upon the X-operators. The interactions included in the effective Hamiltonian (1) are considered to be dependent upon crystal structure. The crystal lattice is considered to be hard and unchanged by orbital and magnetic interactions.

Taking into account the effective interaction (1), one can consider the new non-degenerated ground state function as a linear combination of ^5E eigenfunctions:

$$\Psi = C_1 |\theta> + C_2 |\varepsilon>, \tag{3}$$

where the normalization condition is $C_1^2 + C_2^2 = 1$.

Now the ground state of the manganese ion is

$$E = -\sqrt{\alpha_1^2 + \alpha_2^2} \tag{4}$$

and the energy gap is

$$\Delta E = 2\sqrt{\alpha_1^2 + \alpha_2^2}. \tag{5}$$

More convenient are the polar coordinates:

$$\alpha_1 = \rho \cos \Theta, \quad \alpha_2 = \rho \sin \Theta, \quad \Theta \in [0; \ 2\pi). \tag{6}$$

Thus,

$$E = -\rho, \Delta E = 2\rho; \tag{7}$$

$$C_1 = \pm|\cos(\Theta/2)| \ \mathrm{sgn}(\alpha_2), \quad C_2 = \mp|\sin(\Theta/2)| \tag{8}$$

and

$$\Psi = \begin{cases} \left|\cos \dfrac{\Theta}{2}\right| |\theta\rangle - \left|\sin \dfrac{\Theta}{2}\right| |\varepsilon\rangle, \ \alpha_2 > 0, \\ \left|\cos \dfrac{\Theta}{2}\right| |\theta\rangle + \left|\sin \dfrac{\Theta}{2}\right| |\varepsilon\rangle, \ \alpha_2 < 0. \end{cases} \tag{9}$$

The problem of wave function has an ambiguous solution. For the prediction of magnetic properties, the mean values of the X-operators are needed. The sign of the wave function coefficients (8) – plus or minus – does not play any role in the mean values of the operators:

$$<X_\theta> = -\cos \Theta; \quad <X_e> = -\sin \Theta. \tag{10}$$

There is a sublattice of manganese ions in the crystal,. The orbital wave functions and orbital operators must be indexed by the manganese ion number. Thus, there are two sets of orbital interaction characteristics for *n*th Mn^{3+} ion: 1) $\alpha_{1,n}$ and $\alpha_{2,n}$; 2) ρ_n, Θ_n. For orbital state function (9), only one of the characteristics is needed. We shall use the Θ_n angle in all consequent considerations as a mixing parameter of the orbital eigenfunction.

Traditionally, an elastic energy is added to the vibronic Hamiltonian to find the adiabatic potential minimum [2,14,16,19,28]. This helps to propose the mechanism of JT ions' local neighborhood distortions. The elastic term leads to an exchange-like orbital Hamiltonian of the Kugel-Khomskii model [14,15,19]. Nevertheless, this approach excludes other interactions in the crystal lattice, which make it stable at a wide temperature range [28].

For our work, it is sufficient to use the crystal structure described by experimental papers. This is why the distortions mechanisms are not taken into account.