Theoretical investigation of NMR spectra in rare-earth manganites

L E Gonchar$^{1,2}$, J V Leskova$^2$ and A E Nikiforov$^2$

$^1$ Ural State Railway Transport University, 620034, 66 Kolmogorov St., Ekaterinburg, Russia
$^2$ Ural Federal University, 620000, 51 Lenin Av., Ekaterinburg, Russia

lyudmila.gonchar@usu.ru

Abstract. The work is aimed to theoretical investigation of orbital and magnetic structure of manganites. The orbitally-dependent exchange interaction model was used in order to describe the superexchange interaction in all range of RMnO$_3$ (R=La, Pr, Nd, Tb, Dy, Ho) orthorhombic compounds. The model of nearest-neighbour and next-nearest neighbour exchange was used to describe the magnetic structures of manganites with small rare-earth ion sublattice (R=Dy, Tb, Ho). We investigate different types – A, E, non-collinear – of magnetic structures. The models of NMR spectra calculation of Mn$^{3+}$ ion in RMnO$_3$ compounds are proposed. The theoretical study of the magnetic structure could distinguish The NMR-spectra of antiferromagnetic (A or E) or strongly non-collinear ordering type.

1. Introduction
The investigation of manganite crystals with general formula RMnO$_3$ (R is a trivalent rare-earth ion) and orthorhombic crystal structure (denoted as Pbnm or Pnma space symmetry group) was very intensive last two decades because of colossal magnetoresistance effect taking place in alkaline-earth doped crystals. These compounds are the striking examples of a strong correlation between crystal, charge, orbital, and magnetic subsystems. The modern studies pay now their attention to one’s more intriguing feature of orthorhombic manganites, i.e. multiferroicity [1, 2].

The reason of the multiferroical behavior of orthorhombic manganites with small rare-earth ions sublattice is proposed to be strongly canted magnetic structure [2]. The type of magnetic structure could be non-commensurate sinusoidal, bc-cycloidal and ac-cycloidal (in Pbnm-notation) with different angles between magnetic moments [3].

Thus, the observed types of magnetic structures in orthorhombic rare-earth manganites are antiferromagnetic A-type (R=La, Pr, Nd) [4] non-commensurate or cycloidal (R=Dy, Tb)[2, 3] and E-type (R=Ho, Er) [1]. The mechanism of forming A-type magnetic structure is the orbital structure [5]. The causes of cycloidal, sinusoidal and E-type structures are named to be the Dzyaloshinsky-Moria antisymmetric exchange interaction and second-neighbor [3] or third neighbor superexchange interaction [6] in addition to orbitally-dependent nearest-neighbor superexchange.

This paper is devoted to the theoretical investigation of the microscopic origin of interrelation between crystal, orbital and magnetic structures over all the rare-earth ions range in manganite compounds. We predict the nuclear magnetic resonance spectra of different magnetic structures.
2. Crystal structure and superexchange interaction model of orthorhombic rare-earth manganites

The crystal structure of orthorhombic manganites is described by a space group with two denominations – \( Pnma \) or \( Pbnm \).

The distortions are of two kinds: the rotational distortions of oxygen octahedral and lanthanum ions shift like in orthoferrite crystal and the Jahn-Teller distortions of oxygen octahedra of \( e \)-type [7]. The strong electron-lattice interaction causes the presence of \( e \)-type distortions due to degenerated trivalent manganese ion ground state and helps the orbital structure to be established.

![Figure 1. Crystal and orbital structures. Lanthanum ions are omitted. Manganese ions are drawn as \( e \)-orbitals. Numbers enumerate orbital and magnetic (A-type) sublattices. Axes are given in \( Pnma \) orientation.]

The wave function of the ground state of each manganese ion in distorted perovskite crystal is [7]:

\[
\psi_n = \sin\left(\frac{\phi_n}{2}\right)\varphi_{\epsilon}\theta + \cos\left(\frac{\phi_n}{2}\right)\varphi_{\epsilon}\theta \varepsilon,
\]

where \( \varphi_{\epsilon}\theta \) and \( \varphi_{\epsilon}\theta \varepsilon \) are the eigenfunctions of degenerated \( 5E \) term. The values of \( \phi_n \) could be derived from experimental data, using parameters of lattice distortions [8] within the framework of strong electron-lattice coupling. The orbital structure is described by correlation of orbital angles:

\[
\phi_1 = \phi_2 = \phi_3 = \phi_4 = \phi_5 = \phi_6 = \phi_7 = \phi_8 = \phi_9 = \phi_10,
\]

where \( \phi \) characterize the orbital state of \( Mn^{3+} \) sublattice according to equation (2).

Within the framework of the strong electron-lattice correlation [7], the parameter of orbital function’s mixing could be calculated as function of symmetrized crystal lattice distortion:

\[
\cos \phi_n = -\frac{Q_{\epsilon 0}}{\sqrt{Q_{\epsilon 0}^2 + Q_{\epsilon c}^2}}; \cos \phi_n = -\frac{Q_{\epsilon c}}{\sqrt{Q_{\epsilon 0}^2 + Q_{\epsilon c}^2}}
\]

2.1. Orbitally dependent superexchange interaction

In order to predict the magnetic structure, we use following spin-Hamiltonian:

\[
\hat{\mathcal{H}} = J_b \sum_{n \neq m} (\mathbf{S}_n \cdot \mathbf{S}_m) + J_{ac} \sum_{n \neq m} (\mathbf{S}_n \cdot \mathbf{S}_m) + J_2 \sum_{n \neq m} (\mathbf{S}_n \cdot \mathbf{S}_m) + \hat{\mathcal{H}}_{anis}^{\text{ax}}
\]

where

\[
J_b = J_0 \frac{\cos^2 \varphi_{\epsilon}}{r_{10}^6} \left[ 1 + 2 \alpha \cos \phi + \beta \cos^2 \phi \right],
\]
\[ J_{ac} = J_0 \frac{\cos^2 \phi_{ac}}{r_{10}^2} \left[ 1 - \alpha \cos \phi + \beta \left( \cos^2 \phi - \frac{3}{4} \right) \right], \]  

(5)

the parameters of dependencies are \[ J_0 = 1.69 \times 10^4 \text{ K} \cdot \text{Å}^{-10}, \alpha = 1.0, \beta = 4.5, \] and the experimental structural parameters are \( \phi_{bn}, \phi_{ac} \) (Mn–O–Mn bond angles), \( r_{bn} = 1.97 \text{ Å}, r_{ac} = 2.05 \text{ Å} \) (mean Mn–O distances), \( \phi \) (angle of orbital mixing). These parameters one could find in the table 1. \( J_2 \) is included into Hamiltonian by authors of papers [2, 3] second neighbour superexchange interaction.

The single-ion anisotropy of manganese ions in octahedral oxygen environment [5]:

\[ H_{n}^{\text{anis}} = D_n \cdot S_{nz}^2 + E_n \cdot \left( S_{nx}^2 - S_{ny}^2 \right), \]

(6)

where \( P = -1.15 \text{ K} \) [5], \( n \) enumerate manganese ions, 1 denote local axes of octahedra, nearly corresponding to cubic axes. In order to take into account the rotational distortions, we have to transform the Hamiltonian (6) into \( P_{nma} \) axes.

**Table 1.** Lattice parameters of rare-earth manganites. The parameters of the crystal structure are calculated using experimental data of paper [8]

| R   | \( \phi \), deg | \( \varphi_{bn} \), deg | \( \psi \), deg | \( \phi_{ac} \), deg | \( \psi_{ac} \), deg | \( r_{bn} \), Å | \( r_{ac} \), Å |
|-----|-----------------|------------------------|----------------|-----------------|-----------------|----------------|----------------|
| La  | 107.1           | 12.1                   | 9.9            | 155.5           | 155.1           | 1.97           | 2.04           |
| Pr  | 110.9           | 13.5                   | 12.6           | 152.4           | 150.5           | 1.95           | 2.06           |
| Nd  | 111.5           | 14.1                   | 12.9           | 150.9           | 149.6           | 1.95           | 2.06           |
| Tb  | 115.5           | 16.5                   | 14.9           | 145.0           | 145.4           | 1.94           | 2.06           |
| Dy  | 115.7           | 17.3                   | 15.2           | 143.2           | 144.7           | 1.94           | 2.06           |
| Ho  | 116.3           | 17.6                   | 15.5           | 142.5           | 144.1           | 1.94           | 2.06           |
| Er  | 116.2           | 17.6                   | 15.3           | 142.9           | 143.9           | 1.94           | 2.05           |
| Y   | 116.3           | 17.3                   | 15.3           | 143.5           | 144.6           | 1.94           | 2.05           |

The nearest-neighbor superexchange parameters and Neel temperatures of the manganite compounds are placed in the table 2. This table is a result of our calculation taking into account only orbitally-dependent nearest-neighbor exchange interaction.

**Table 2.** Calculated exchange parameters and Neel temperature of the rare-earth manganites

| R  | \( J_b \), K | \( J_{ac} \), K | \( T_{N_b} \) K theory | \( T_{N_b} \) K exper. [2] | \( T_{N_b} \) K – | \( T_{N_b} \) K – |
|----|--------------|----------------|------------------------|--------------------------|-----------------|----------------|
| La | 13,1         | -18,9          | 135                    | 140                      | 100             | 85             |
| Pr | 14,0         | -13,7          | 112                    | 100                      | 100             | 85             |
| Nd | 13,9         | -12,9          | 107                    | 85                       | 85              | 85             |
| Tb | 14,5         | -9,2           | 89                     | ~40*                      | ~40*            | ~40*           |
| Dy | 13,7         | -9,0           | 86                     | ~40*                      | ~40*            | ~40*           |
| Ho | 13,7         | -8,5           | 83                     | ~40*                      | ~40*            | ~40*           |
| Er | 14,2         | -9,0           | 87                     | ~40*                      | ~40*            | ~40*           |
| Y  | 14,4         | -9,0           | 88                     | ~40* [1]                 | ~40*            | ~40*           |

* The temperature of transition from incommensurate to paramagnetic phase. The temperature of transition from \( E \)-type to incommensurate phase is lower [2].

As it was proposed in the papers [2, 3], the second-neighbor exchange interaction is acting in the manganites with a small rare-earth radii. That type of exchange as the paper [2] proposes arises due to
interaction of orbital structure with strong rotational distortion. Not considering the microscopic reasons of the exchange interaction, we try to describe the magnetic structure and resonance spectra.

3. Possible magnetic structures of manganite

The magnetic structure of manganite is determined by exchange interaction and single ion anisotropy. Within the framework of the model of paper [2], the magnetic structure is a result of competing exchange interaction between nearest neighbour magnetic ions and second-neighbour magnetic ions. We have studied 8-sublattice commensurate model. (see figure 2).

**Figure 2a.** One $ac$-plane of $A$-type magnetic structure (magnetic sublattices 1,2). Orbital structure of manganese ions is shown. The directions of magnetic moments of the neighbouring $ac$-plane (sublattices 3,4) are opposite. The orbitals directions are the same.

**Figure 2b.** One $ac$-plane of non-collinear magnetic structure (magnetic sublattices 1–4). Orbital structure of manganese ions is shown. The directions of magnetic moments of the neighbouring $ac$-plane (sublattices 5–8) are opposite. The orbitals directions are the same.

**Figure 2c.** One $ac$-plane of $E$-type magnetic structure (magnetic sublattices 1–4). Orbital structure of manganese ions is shown. The directions of magnetic moments of the neighbouring $ac$-plane (sublattices 5–8) are opposite. The orbitals directions are the same.
This model results two cases.

I. $J_2 \ll J_{ac}$: $A$-type magnetic structure. Large rare-earth ion leads to small rotation of MnO$_6$ octahedra. The second-neighbour exchange interaction is small $[2, 3]$. The type of magnetic structure is $\{A X FY GZ\}$. This case takes place if $R=$La, Pr, Nd. The single-ion anisotropy described by Hamiltonian (6) is sufficient to mark out an easy magnetic axis of the crystal (see figure 2a).

II. $J_2 \sim J_{ac}$: strongly non-collinear structure. Small rare-earth ion leads to large rotation of MnO$_6$ octahedra. The second-neighbour exchange interaction is of the same order as ferromagnetic exchange in $ac$-plane. $[2, 3]$. This case take place if $R=$Dy, Tb, Er, Ho. The single-ion anisotropy described by Hamiltonian (6) causes strongly canted structure (see figure 2b). For description of $E$-type structure neither the single-ion anisotropy (6) nor antisymmetric exchange interaction $[3]$ are not sufficient using commensurate model. The single-ion anisotropy like $DS_{x^2}$ helps to establish collinear $E$-type magnetic structure (see figure 2c).

4. Nuclear magnetic resonance model

In order to investigate the magnetic subsystem, we propose the model of NMR on $^{55}$Mn ion. The spin-Hamiltonian of the model is

$$\hat{H} = \hat{H}_Q - \gamma_N h (\hat{H}_{dip} + \hat{H}_{hf}) \cdot \hat{I},$$

(7)

where hyperfine interaction

$$\hat{H}_{hf} = H_{hf}(\phi) = A_s (\hat{S} \cdot \hat{I}) + A_{II} \left[3S_z I_z - (\hat{S} \cdot \hat{I})\right] \cos \phi + \sqrt{3} I_x S_x - S_x I_x \sin \phi$$

(8)

is dependent upon orbital mixing angle $\phi$ and could be divided into two parts – anisotropic (with $A_s$ constant) and anisotropic (with $A_{II}$ constant);

$$\hat{H}_Q = \nu Q \left[3 I_z^2 - I(I-1)\right] + \eta \left(I_x^2 - I_z^2\right)$$

(9)

is nuclear quadrupole interaction; and the values of the fields are approximately equal to $H_{dip} \approx 0.1$ T, $H_{hf} \approx 30$ T. The nuclear spin of $^{55}$Mn ion is $I=5/2$, and $\gamma_N=10.46$ MHz/T – is nuclear hystromagnetic factor. Considering the magnetic ion, the magnetic hyperfine interaction is much stronger than quadrupole interaction, thus, it determines the NMR spectra completely.

The ab initio calculation of hyperfine interaction (HFI) was carried out within the framework of unlimited MO LCAO SCF Hartree-Fock-Ruthaan method using GAMESS programs $[9]$.

![Figure 3. Dependency of magnetic isotropic HFI (solid circles) of Mn$^{3+}$ and Neel temperature (open circles) in manganites (considered $A$-type magnetic structure)](image)
We calculate the line position of NMR spectra of trivalent manganese ion of RMnO$_3$ compounds (R=La, Pr, Nd, Tb, Dy, Ho).

The changes of rare-earth sublattice lead to changes of Mn-O bond configuration. The rotational and shift distortion change their magnitude. The magnetic structure changes its parameters and even the type. In our work, the hyperfine parameters are calculated for different rare-earth ions sublattice. The results of calculation are presented on figure 3.

The isotropic term of HFI (7) is dependent upon the Mn-O bond length. If the ionic radius of rare-earth element becomes smaller, the bond length decreases and the covalence effect become stronger. The anisotropic part of HFI (7) is dependent on orbital and magnetic structure. After taking into account the anisotropic term of HFI, the direction of HF field on the nucleus changes and depends upon the orbital structure. In the dependence of figure 3, only A-type of magnetic structure is used. For small rare-earth ions, the other types of magnetic structures could be used. The results of prediction of the NMR line position are presented in the table 3.

The changes of the magnetic structure type cause the shift of the NMR line. In this work, the NMR spectrum of HoMnO$_3$ was taken as an example.

| Table 3 NMR line position, MHz |
|-----------------------------|
| La  | Pr  | Nd  | Tb  | Ho  |
| 360 | 336 | 333 | 314 | 312 (A) |
|     |     |     |     | 324 (E) |
|     |     |     |     | 442  |
|     |     |     |     | (non-collinear) |

The results of model for HoMnO$_3$ show that one could not reliably distinguish A or E magnetic structure using NMR method. Nevertheless, the non-collinear structure is appreciably different. The cycloidal magnetic structure, proposed in paper [3] gives three lines instead one as in presented model.

5. Summary

Thus, we have carried out the theoretical study of different rare-earth manganites. The type of rare-earth sublattice effects not only on the crystal structure but also upon orbital and magnetic orderings. The orbital dependence of superexchange interaction is very important microscopic mechanism of interplay between crystal, orbital, and magnetic structures. Nevertheless, for the small-size rare-earth ion in R$^{3+}$ sublattice, the rotational distortions have much stronger effect on exchange interaction comparing with lanthanum manganite. These two mechanisms form A, E, or non-collinear magnetic structure of manganites. We propose the NMR method as a local probe of magnetic structure.

References

[1] Zhou J-S et al. 2006 Phys. Rev. B 74 014422
[2] Kimura T et al. 2003 Phys. Rev. B 68 060403(R)
[3] Mochizuki M and Furukawa N 2009 Phys. Rev. B 80 134416
[4] Jirak Z et al. 1985 J. Magn. Magn. Mater. 53 153
[5] Gontchar L E and Nikiforov A E 2002 Phys. Rev. B 66 014437
[6] Soloviev I V 2011 Phys. Rev. B 83 054404
[7] Nikiforov A E, Popov S E and Shashkin S Yu 1999 Phys. Met. Met. 87 16
[8] Alonso J A et al. 2000 Inorg. Chem. 39 917
[9] Schmidt M W et al. 1993 Comput. Chem. 14 1347.