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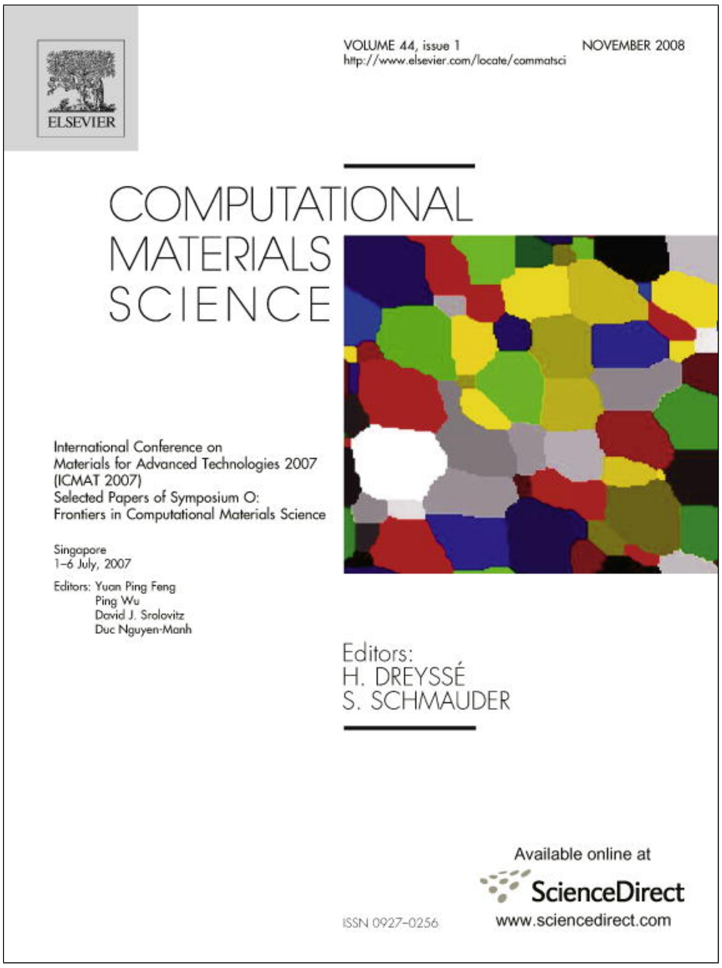

VOLUME 44, issue 1
http://www.elsevier.com/locate/commatsci
NOVEMBER 2008

COMPUTATIONAL MATERIALS SCIENCE

International Conference on
Materials for Advanced Technologies 2007
(ICMAT 2007)
Selected Papers of Symposium O:
Frontiers in Computational Materials Science

Singapore
1–6 July, 2007

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Available online at
ScienceDirect
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ISSN 0927-0256

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ScienceDirect
Computational Materials Science 44 (2008) 79–81
COMPUTATIONAL MATERIALS SCIENCE
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Ab-initio calculation of exchange interactions in $YMnO_3$

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Available online 4 March 2008

Abstract

The density functional based calculations of the electronic structure of $YMnO_3$ are performed for selected spin configurations and from the differences of the total energies the exchange integrals are determined. To improve the description of strongly correlated 3d electrons of Mn the LDA + U method is employed. The strongest exchange interaction is found between the nearest neighbor Mn spins, the interaction between the next nearest neighbors being more than order of magnitude weaker. Exchange integrals are inversely proportional to the parameter U, pointing to the dominance of the superexchange interaction. Due to the triangular arrangement of the nearest Mn the magnetism is geometrically frustrated so that biquadratic or/and anisotropic exchange may be important. The calculation of non-collinear spin structures indicates the presence of the biquadratic exchange interaction.

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PACS: 71.15.Mb; 71.70.Gm; 75.47.Lx

Keywords: Exchange interaction; Ab-initio calculation; Yttrium manganite

1. Introduction

Hexagonal $YMnO_3$ is a multiferroic compound with simultaneous presence of ferroelectric (below 900 K) and magnetic (below 86 K) order. $YMnO_3$ crystallizes in hexagonal symmetry and can be viewed as built of MnO_5 triangular corner-sharing bipyramids separated in c-direction by planar Y layers. In the high-temperature paraelectric phase it contains two formula units per elementary cell. The distortion of the crystal structure of $YMnO_3$ below the critical temperature of the ferroelectric transition consists essentially of a tilting of the oxygen bipyramids surrounding the Mn ion and a buckling of the Y layer [1]. The distortion results in a tripling of the elementary cell and a lowering of the symmetry from a centrosymmetrical $P6_3/mmc$ to a non-centrosymmetrical $P6_3cm$ space group.

The dominant magnetic interaction is expected to be an antiferromagnetic superexchange between the nearest Mn^{3+} ions. These ions form a 2D triangular network, which leads to a frustrated magnetism and results in rather low magnetic transition temperature. Neutron scattering measurements showed that a spin liquid state exists above T_N [2]. Below T_N the experimental results were interpreted in terms of a Heisenberg Hamiltonian with a small easy plane anisotropy. Besides the anisotropy of the exchange, the biquadratic exchange interaction may play an important role in the frustrated magnetic systems. In the present paper the exchange integrals of the isotropic Heisenberg model are calculated ab-initio. In order to assess the role of the biquadratic exchange non-collinear spin structures are considered.

The exchange energy per unit cell of the isotropic Heisenberg model is written as

$$E_{\mathrm{ex}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{N} n_i z_{ij} J_{ij} (\vec{S}_i \vec{S}_j), \qquad (1)$$

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doi:10.1016/j.commatsci.2008.01.028

where i, j numerate the sublattices, n_i is the number of i-th sublattice sites in the unit cell, z_{ij} is the number of sites belonging to the sublattice j that are neighbors of the site from sublattice i. $\vec{S}_i$ is the spin of atom on the i-th sublattice. The exchange integrals are evaluated from the differences of the total energies of spin configurations that have different directions of the sublattice spins [3].

The almost rigid tilting of the oxygen bipyramids in the ferroelectric phase of the compound is not likely to influence the superexchange interaction in the MnO layer. This is confirmed by the fact that the electronic structure of the compound in the high- and low-temperature phases is almost indistinguishable [4]. Therefore instead of rather complicated experimental low-temperature crystal structure ($P6_3cm$) a simpler one ($P6_3/mmc$) corresponding to the high-temperature paraelectric phase was considered as it simplifies the calculation and analysis of the results. The calculations were carried out using the experimental low-temperature lattice constants.

2. Collinear spins

There are two crystallographically equivalent Mn sites in the unit cell that lie in different c planes. For calculation of exchange interaction these two Mn sites must be made inequivalent. These two Mn sites are, however, the *next* nearest neighbors in the Mn lattice, as the nearest neighbors lie in the same c plane in corners of a regular hexagon. For calculation of the exchange interaction between the nearest Mn spins a different unit cell with orthorhombic symmetry has to be constructed. This contains four $YMnO_3$ formula units and has the *Pmma* space group. The magnetic structure of a MnO plane consists of linear ferromagnetic Mn chains running in the b direction, the chains with different spin being alternated along the a direction. The six nearest in-plane neighbors of a given $Mn_{\uparrow}^{(Pmma)}$ are divided in two $Mn_{\uparrow}^{(Pmma)}$ and four $Mn_{\downarrow}^{(Pmma)}$, the same holds for the next nearest neighbors.

The calculations were performed employing the WIEN2k program [5]. The number n_k of the k-points in the irreducible part of the Brillouin zone was 48 for the hexagonal and 8 for the *Pmma* crystal structure. The energy cutoff for the basis function is determined by the product $R_{MT}k_{max}$. We took $R_{MT}k_{max} = 6$ which corresponds to $\simeq 777$ (1720) augmented plane waves and 80 (160) local orbitals for hexagonal (*Pmma*) structure.

To improve the description of Mn 3d electrons we used the rotationally invariant version of the LDA + U method [6] with an effective value of the Hubbard parameter $U_{eff} = U - J$. In what follows the notation $U \equiv U_{eff}$ is used, but it should be kept in mind that we are dealing with the effective U which is somewhat smaller than the Hubbard parameter as $J/U \approx 0.1$–0.2. To see how the results depend on U, three values $U = 3$, 6, 9 and 12 eV were employed in addition to the LSDA calculation which corresponds to $U = 0$.

For the ferromagnetic spin configuration a metallic state, with the non-zero DOS at the Fermi energy, is predicted by the LSDA, while for LDA + U a gap opens when U is larger than ≈ 5 eV. The magnetic moments of individual atoms, the total moment and the gap magnitude are given in Table 1. The magnetic moments of Mn ions increase and moments on oxygens decrease as U is increased – this is a typical result of the LDA + U methods that tend to make the occupation of electron states integer. The electronic structure of the antiferromagnetic arrangement is very similar to the one of ferromagnet, the electrons are slightly more localized so that the gap is larger.

The dependence of the exchange integrals on U is displayed in Fig. 1. According to the theory of superexchange the exchange integrals should be inversely proportional to U, this is no longer true, however, for $U \to 0$. Full curves in Fig. 1 were calculated using

$$J = J_0 + |b|^2/U, \tag{2}$$

where $J_0 = -0.14$ meV, $|b|^2 = 3.75$ meV for J_{nn} and $J_0 = 0.0003$ meV, $|b|^2 = 0.04$ meV for J_{nnn}.

3. Non-collinear spins

The calculation were performed using the WIENNCM package [7]. To calculate the exchange interaction we

Table 1
LDA + U calculations for the ferromagnetic $YMnO_3$

U (eV)	0	3	6	9	12
m(Y)	0.02	0.02	0.01	0.01	0.01
m(Mn)	3.34	3.49	3.60	3.67	3.73
m(O_1)	0.08	0.39	0.03	0	−0.02
m(O_2)	0.04	0.01	0.0	−0.02	−0.03
gap (eV)	0	0	0.01	0.45	0.90

Magnetic moments in units of μ_B inside the atomic spheres of individual non-equivalent ions.

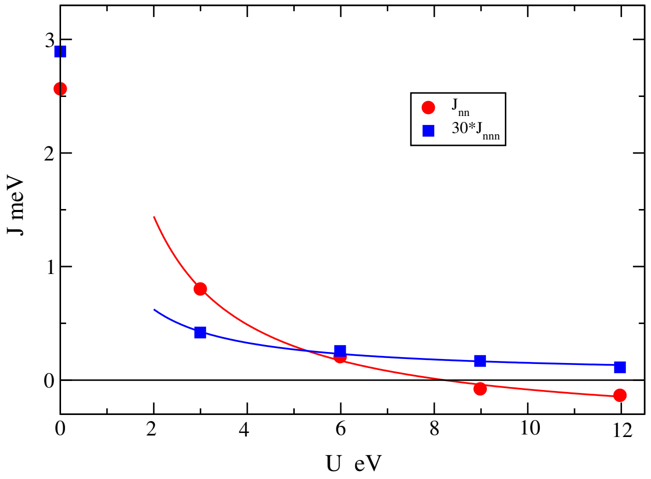

Fig. 1. Exchange integrals between the nearest and next nearest Mn spins as functions of U. Full curves correspond to Eq. (2).

Table 2
Position vectors expressed in fractions of unit cell parameters, polar and azimuthal angles of the spin of four Mn

	Mn1	Mn2	Mn3	Mn4
$\vec{r}$	$\frac{1}{4},\frac{1}{2},\frac{1}{6}$	$\frac{3}{4},\frac{1}{2},\frac{7}{6}$	$\frac{1}{4},0,\frac{2}{3}$	$\frac{3}{4},0,\frac{1}{3}$
ϕ, θ	0, 0	0, 0	$3\pi/2$, θ	$\pi/2$, θ

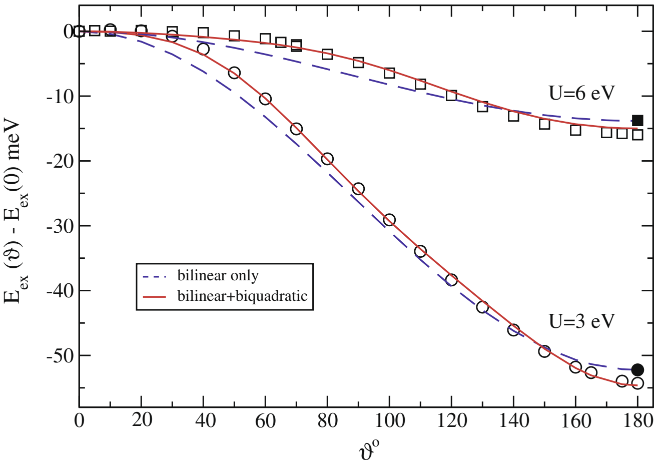

Fig. 2. Difference of total energy for canting angle θ and total energy of the ferromagnetic configuration. The curves are the least squares fits to bilinear + biquadratic exchange and to the bilinear exchange only. Full symbols correspond to the calculation with the collinear spins.

selected primitive unit cell that contains four $YMnO_3$ formula units. Original hexagonal axis in this structure is parallel to the [1 0 0] direction. Important is the subset of the four Mn sites in the unit cell. Corresponding position vectors, polar and azimuthal angles of their spins are given in Table 2.

The calculations were performed for $U = 3$ eV and $U = 6$ eV and for a number of θ values. The bilinear Heisenberg energy with the exchange parameters [3] obtained from the collinear spin calculation exhibits small, but systematic deviation from the calculated values (dashed lines in Fig. 2). No improvement results from variation of J_{nn}, J_{nnn} and we therefore added a biquadratic exchange interaction

$$E_{\mathrm{ex}}^{bq} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{N} n_i z_{ij} j_{ij} (\vec{S}_i\vec{S}_j)^2. \tag{3}$$

The least squares fit led to a good agreement between $E_{\mathrm{ex}}(\theta)$ calculated ab-initio and the one obtained with bilinear and biquadratic exchange. The full curves in Fig. 2 correspond to (j_{nn}, j_{nnn}) equal to (0.032 meV, −0.055 meV), (−0.035 meV, 0.011 meV) for $U = 3$ eV and 6 eV, respectively. Similar agreement can be obtained also for other j_{nn}, j_{nnn} combinations.

4. Discussion and conclusions

Our results are internally consistent and show that not only the Heisenberg exchange integrals, but also the information on other exchange mechanisms may be obtained from the ab-initio calculations. Note, however, that in order to obtain the anisotropy of exchange, spin-orbit coupling must be included in the Hamiltonian.

From the analysis of the inelastic scattering data J_{nn} was estimated to be ~6 meV, while $J_{nn} \approx 7.6$ meV was obtained from temperature dependence of the susceptibility [2]. These values are large comparing to our calculated values, even if the limit $U \to 0$ is taken (Fig. 1). The computational scheme used here was successfully applied to ferrites [3,8] so that this disagreement is rather surprising. It might be connected with the frustrated character of the $YMnO_3$ magnetism, but a first our attempt showed that the exchange in $YMnO_3$ is very sensitive to the crystal structure and the explanation is likely to be connected with this dependence.

Acknowledgement

The work was supported by the Project IAA100100627 of the Grant Agency of the ASCR. I.C., S.G. and G.S. acknowledge funding via a cooperation with the Leibniz Institute for Solid State and Materials Research Dresden e. V. within the "Pakt fuer Forschung und Innovation" of the BMBF and via Priority Programme SPP 1157 of the German Science Foundation.

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