ATOM SPECIES ENERGY DEPENDENCE ON MAGNETIC CONFIGURATIONS IN THE PEROVSKITE YTTRIUM ORTHOFERRITE

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Abstract. The article represents the results of studying of the influence of atom species in the perovskite multiferroic yttrium orthoferrite $YFeO_3$ on magnetic configurations by ab-initio methods. Four magnetic configurations possible in magnetic sublattice that were formed by iron atoms were analyzed. It is shown that different magnetic orderings change the lattice parameters and the ions occupied positions while preserving symmetry of the unit cell, the lowest state responds G-AFM type magnetic ordering. The lattice parameters are in good relevant published experimental data. The atom species energy dependence shows that the main role in magnetic properties goes to iron and oxygen. In the ground state, magnetic properties relate with Dzyaloshinskii – Moriya interaction, while in other configurations, these relate with superexchange through Fe-O-Fe chains. Obtained results are useful for analyzing and designing straintronics devices. Also, the results can be interesting for interpretation and predicting magnetic properties of partially or fully substituted orthoferrites including substitution on rare-earth elements.

Keywords: multiferroic, perovskite, orthoferrite, ab-initio, antiferromagnetic, magnetic ordering.

Conflict of interests. The authors declare no conflict of interests.

Introduction

Multiferroics are materials which combine (ferro)magnetic and ferroelectric ordering. These materials are very interesting both radioelectronic applications and new scientific directions, such as straintronics, which use effects and phenomena created by deformations for new devices creation. Early we described different magnetic orderings in the perovskite $YFeO_3$ and the dependence of the structural properties on them with ab-initio methods were established [1].

The difference in total energy and structural parameters of the various magnetic configurations of the $YFeO_3$ appears due to the interaction of iron d-shell electrons in magnetic sublattice, formed by iron ions, and interaction between iron ions neighboring yttrium, and oxygen ions which change electron density distribution and total energy in the material. Unfortunately, the contribution of each atom species to the total energy in various magnetic configurations of the $YFeO_3$ is unknown.

Dependence of Fe ions d-shell electron energy for these states in the $YFeO_3$ is also unknown. This information can be useful for engineering magnetic properties of a multiferroics with perovskite structure for physical and technical applications. Thereby in this work we study energy contribution for each atom species and changing spin-resolved energy in iron d-shell electrons in the dependence of the $YFeO_3$ magnetic configurations by ab-initio methods. Also, we study the evolution of Fe ions magnetic moments and a state of the d-shell through Mulliken populations analysis.

Methods of calculation

We performed our ab-initio calculations within the density functional theory and pseudopotential theory as implemented in the OpenMX code [2–4]. We chose generalized gradient approximation (GGA) and the Perdew – Burke – Ernzerhof exchange-correlation functional while taking into account of spin polarization [5]. We used pseudopotentials with the following valence state configurations: Y – 4s, 4p, 4d, and 5s states; Fe – 3p, 3d, and 4s states; O – 2s and 2p states. We selected the basis sets with 2 primitive pseudoatomic orbital (PAO) functions for each electronic state and 1 adding primitive PAO function as polarized for better description of chemical bonding. For the numerical integrations and the solution of the Poisson's equation, we chose $60 \times 80 \times 56$ real-space grid, which approximately equals the cutoff energy 4200 eV [4].

The integration over Brillouine zone the $4 \times 3 \times 5$ regular Γ-centered k-points mesh was performed. Self-consistent field calculation was stopped when the difference between two consecutive iterations is less than 10^{-6} eV/atom. The total and orbitally decomposed energies were obtained for equilibrium lattices for each magnetic configuration after structure relaxation, which stopped, when the forces acting on each atom and each component of stress-tensor became less than 0.01 eV/Å.

Results and discussion

The perovskite multiferroic $YFeO_3$ with orthorhombic primitive Bravais lattice has a centrosymmetric primitive cell that includes 4 formulae units (Fig. 1, *a*). In the process of structural relaxation, it was found that while the lattice parameters and the positions occupied by the ions change, the initial symmetry of the unit cell is preserved. Thus, in this crystal four magnetic orderings are allowed: one ferromagnetic (FM) and three antiferromagnetic (AFM), also called as A-AFM, C-AFM and G-AFM. Although all orderings formed by the Fe magnetic sublattice, they are not equivalent in energy sense, what causes differences lattice parameters and atom positions. Our earlier calculations and the experiments of the other researchers showed that the G-AFM ordering in $YFeO_3$ is the main ordering [1, 6].

Following [1], the total energy of the $YFeO_3$ is monotonously decreasing from ferromagnetic (FM) to antiferromagnetic (AFM) state with close energy distances per formulae unit between neighboring magnetic configurations in set FM → A-AFM → C-AFM → G-AFM (Tab. 1). Differences in a spin configuration in an iron sublattice changes energy for each atomic species in different ways (Fig. 1, *b*). In all cases, the zero energy is a relative value.
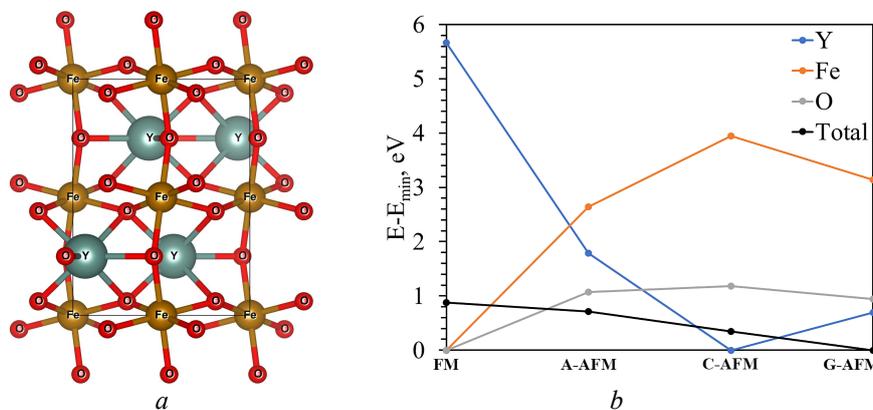
Fig. 1. $YFeO_3$ perovskite structure: *a* – primitive cell; *b* – atom species contribution dependence on magnetic configuration

Table 1. Structural properties of $YFeO_3$ with different magnetic ordering

Magnetic ordering	Lattice parameter, Å			Volume, Å^3	ΔE (per formulae unit), meV
FM	5.67438	7.55454	5.27973	226.328	228
A-AFM	5.65376	7.60403	5.30612	228.117	179
C-AFM	5.62010	7.70463	5.30326	229.635	87
G-AFM	5.63788	7.65396	5.30518	228.930	0
Experiment (G-AFM) [7]	5.58770	7.59510	5.27430	223.837	–

Decomposition of the total energy on atom species show that yttrium energy states decreasing in the order FM → A-AFM → C-AFM, with increasing in G-AFM ordering a case. The behavior of iron and oxygen atoms is opposite, and deviation of energy is less than for yttrium. It says about the primary role of the interaction between iron and oxygen atoms on magnetic properties of the $YFeO_3$. For better understanding processes behind the interaction between all atom species in the $YFeO_3$ we appreciated their magnetic moments in different magnetic configurations through Mulliken populations analysis. In this case magnetic moments can be roughly estimated as a difference between populations with up spin and down spin states.

Following symmetry of the crystal all yttrium and iron atoms are equivalent, and oxygen atoms divided in 2 groups of equivalent atoms – 4 atoms in the first group and 8 atoms in the second, which we will designate as O(1) and O(2) respectively. All information is presented in Tab. 2, the zero energy is a relative value. In all cases magnetic moment of yttrium atoms is either small or zero. It says about a weak role of this element in the magnetic properties of the $YFeO_3$.

The magnetic and energetic behavior of iron and oxygen atoms correlated for 3 out of 4 magnetic configurations, but the absolute magnetization of oxygen in the G-AFM phase is either very small or zero. It says about the primary role of antisymmetric exchange, or the so-called Dzyaloshinskii – Moriya interaction (DMI), not the superexchange mechanism as for other magnetic configurations, what is consistent with the experimental data. For FM, A-AFM, and C-AFM the main mechanism of magnetization is superexchange between two next-to-nearest neighbor iron atoms through an oxygen atom.

Table 2. The magnetic moments per atom for each atom species group
in the $YFeO_3$ with different magnetic ordering

Atom species group	Magnetic moment, μ_B			
	FM	A-AFM	C-AFM	G-AFM
Y	0.04	0.00	0.01	0.00
Fe	3.39	3.77	3.92	3.90
O(1)	0.11	0.00	0.19	0.00
O(2)	0.13	0.17	0.02	0.02

For better understanding of Fe-Fe and Fe-O interaction energy dependence of iron t_{2g}- and e_g-orbitals as well as Mulliken populations of its d-states from magnetic configurations were studied (Fig. 2, zero energy is a relative value). The lowest energy state of iron d-electrons corresponds to ferromagnetic ordering, but does not for t_{2g}-orbitals spin up states, which has the lowest energy in G-AFM ordering. Opposite behavior of t_{2g}-orbitals, which interacts with oxygen p-orbitals can relate to the angle change in Fe-O-Fe chains and distance between iron and oxygen atoms.
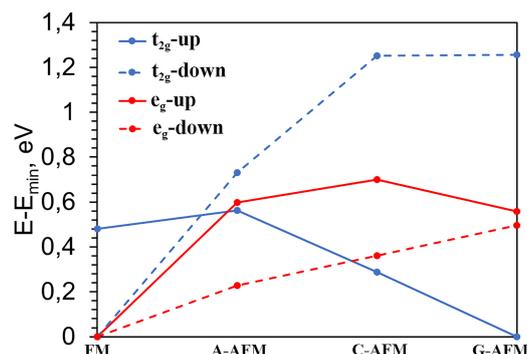
Fig. 2. Spin-resolved energy dependence in different magnetic configurations of $YFeO_3$
Fe t_{2g}- and e_g-orbitals contribution

Conclusion

Thus, in this work we studied the energy contribution dependence for each atom species for various magnetic states in $YFeO_3$ perovskite multiferroic and energy contribution dependence for iron d-shell electrons from the magnetic configuration, by ab-initio methods. It was shown, that the main role in the magnetic properties of configurations, excluding the ground state G-AFM, performs superexchange through Fe-O-Fe chains, which is being replaced by the antisymmetric exchange, or the Dzyaloshinskii – Moriya interaction responsible for the experimentally observed weak magnetism in this material. Changes in magnetic moments of iron atoms are underestimated compared to the experiments, but slightly, about 10 %. Configuration transition to G-AFM showed strong changes in the energetic behavior of t_{2g}-orbitals, related to the rearrangement of crystal lattice and changes in angles of Fe-O-Fe chains and distances between iron and oxygen atoms. The distance between the nearest two magnetic orderings C-AFM – G-AFM is about 90 meV per formulae unit, what allows to save this ordering at room temperatures. It was shown, that density functional theory with localized basis set allows to accurately describe both structural and magnetic properties in perovskite multiferroic $YFeO_3$. A small energetic distance between magnetic configurations and its monotonic changes allows recommend perovskite multiferroics for straintronic memory devices as well as for other applications. We think that describing more complicated materials, such as $NdFeO_3$, (Y,Nd)(Al,Fe)O_3 with varying substitution degrees of both yttrium and iron also possible without significant changes in the chosen methods, that is very useful and it inspires to receive new fundamental and practical knowledge in condensed matter physics.

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Authors' contribution

All authors have equally contributed to the development of the concept and planning provided by research, data acquisition, analysis and interpretation.

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