



First principles study of the spontaneous electric polarization in $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$

Daniel Stoeffler*

Institut de Physique et de Chimie des Matériaux de Strasbourg UMR 7504 CNRS-UDS, 23 rue du Loess BP43, 67034 Strasbourg cedex 2, France

ARTICLE INFO

Available online 23 December 2012

Keywords:

Electronic structure calculations
Electric polarization
Multiferroic

ABSTRACT

The spontaneous electric polarization (SEP) in the multiferroic $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ ($x = 1/2, 1, 3/2$) systems is determined from their electronic structure using a first principles method and the modern theory of polarization. This is done by following carefully the SEP on a path connecting the polar and centrosymmetric structures. For the antiferromagnetic GaFeO_3 system, the SEP is found to be $-25.0 \mu\text{C}/\text{cm}^2$ which is 10 times larger than previous estimation given into the literature a few years ago. Similar SEP values are obtained for $x = 1/2$ and $3/2$ where the system is highly magnetized. The homogeneous switching of this SEP through a centrosymmetric structure is discussed in terms of the total energy barrier and it is exhibited that such a process is particularly difficult to achieve in relation with the tetrahedral environment of half of the Ga atoms into the polar structure.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Magnetoelectric materials presenting coupled ferroelectricity and ferromagnetism are particularly interesting because of their potential use into storage devices but also from a fundamental point of view [1–3]. The intensively investigated GaFeO_3 (GFO) is one of these systems: it is antiferromagnetically ordered at room temperature [4] and a large spontaneous electric polarization (SEP) has been recently theoretically predicted [5,6]. GFO presents easily Ga–Fe chemical disorder so that it presents a net magnetization even for $x = 1$; this net magnetization as well as its critical temperature increases with x [7]. However, the SEP remains difficult to establish experimentally in such kind of systems.

From a fundamental viewpoint, the electric polarization corresponds to a rearrangement of the bound electrons in the material, which creates an additional charge density at the surface [8]. However, such an approach would require surface calculations which are much more computer time consuming than considering the SEP as a bulk property which limits the study to a unit cell. The polarization switching mechanism into such systems represents also a challenge from a theoretical viewpoint: for example, ferroelectric domain wall motion investigations involving large atomic movements require to build very large cells containing a few hundred of atoms. A recent theoretical analysis [6] has shown that, like in most ferroelectric systems, a homogeneous reversal of the SEP corresponds to a very high energy barrier and cannot be achieved experimentally mainly because the switching of the SEP seems to be difficult to get. This very high energy barrier finds its origin into the large atomic displacements required to transit via a centrosymmetric structure during the homogeneous reversal of the SEP. In the present work, the same approach is used in order to investigate the

role of the Ga versus Fe occupation onto the SEP and the energy barrier of $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ for $x = 1/2, 1$ and $3/2$. Even if it is not expected that the energy barrier drops dramatically when x is varied – the polar structure remains the same whatever x is – it is particularly interesting to investigate its role because x varies between 0.8 and 1.4 in experimental samples. Note that the Ga–Fe chemical disorder is not taken into account here.

2. Method of calculation

The relaxed structures, the electronic structure, the magnetic properties and the SEP are calculated using the Vienna Ab initio Simulation Package (VASP5.2) [9]. The Projected Augmented Wave (PAW) [10] method is used with ultrasoft pseudopotentials and the Perdew–Burke–Ernzerhof formulation of the Generalized Gradient Approximation (GGA) [11] with the Hubbard correction (GGA + U) [12] taking $U_{\text{Fe}} = 4$ eV and $J_{\text{Fe}} = 0.89$ eV. These values have been chosen according to the literature where, depending on the system and the used method, various values can be found: (i) for magnetite, where Fe is surrounded by an O octahedron like in GFO, $U_{\text{Fe}} = 4$ eV [13] or 4.5 eV [14] and (ii) for FeO, $U_{\text{Fe}} = 4.6$ eV has been used [15]. Moreover, Roy et al. [5] use $U_{\text{Fe}} = 5$ eV and $J_{\text{Fe}} = 1$ eV because the structural properties are weakly affected by small variations of U. Finally, by fitting the bandgap, Ibrahim and Alouani [16] adopt a larger value of 8 eV for U_{Fe} but the structure is found very similar to the one obtained with $U_{\text{Fe}} = 4$ eV. The Ga valence states consist in $4s^2 3d^{10} 4p^1$, the Fe ones consist in $3d^7 4p^1$ and the O ones consist in $2s^2 2p^4$. All calculations are done with a plane wave cutoff energy of 650 eV.

The relaxation is done in a standard way, i.e., by determining the energy minimum as a function of the volume of the cell on the equation of state curve where each point corresponds to a full relaxation calculation at constant cell volume with a k-points sampling of $7 \times 4 \times 4$. Finally, the densities of states (DOS) and the SEP are calculated with a larger

* Tel.: +33 3 88 10 70 65; fax: +33 3 88 10 72 49.

E-mail address: daniel.stoeffler@ipcms.unistra.fr.

number of k-points corresponding respectively to a $(10 \times 6 \times 5)$ and a $(11 \times 6 \times 6)$ mesh for the $Pna2_1$ and the centrosymmetric structures.

3. Structure, magnetism and electronic structure

In order to determine the SEP in Section 4, we will have to connect the polar structure to a centrosymmetric one through a continuous deformation path as previously discussed [17,6]. The two extreme structures on the path are determined using the same approach as in reference [6]: (i) the polar structure is fully relaxed in terms of internal position and cell parameters into the $Pna2_1$ space group, (ii) the PSEUDO code [18] is used to search for pseudosymmetry and to get the corresponding nearest centrosymmetric structure (the pseudosymmetric structure being obtained by a slight distortion of the centrosymmetric one) and, (iii) a fully relaxed centrosymmetric one is obtained by starting the relaxation calculation from the one given by the PSEUDO code. Tables 1, 2 and 3 give the structural data of the structures obtained for $Ga_{2-x}Fe_xO-3$ for $x = 1, 1/2$ and $3/2$ respectively.

For $x = 1$ (perfect GFO) the comparison with the results obtained with the ABINIT [19] code in reference [6] shows small differences for the $Pna2_1$ polar structure and more pronounced differences for the $Pnna$ centrosymmetric one as a consequence of the use of standard pseudopotential with the ABINIT code. However, the presently obtained $Pna2_1$ structure shows a better agreement with the experimental ones [4,7] with a cell volume slightly overestimated which is a usual problem in density functional theory calculations [5]. This solution has zero total magnetic moment: even if the two Fe sites do not carry strictly opposite magnetic moments, it has to be considered as antiferromagnetic AFM-A (the ferromagnetic solution being higher in energy by 200 meV/f.u.) in agreement with experiment. Concerning the $Pnna$ structure, which is found to be the most stable between all candidates given by the PSEUDO code, it is worth noting that if the displacements relative to the $Pna2_1$ structure remain small in the z direction (which is the direction of the SEP [6]), they are large in the y direction for the Fe atoms and large in the x direction for nearly all kind of atoms. These large displacements are a direct consequence of the tetrahedral environment of the Ga1 atom which has to become octahedral into the $Pnna$ structure where all Fe and all Ga sites are equivalent. Consequently, this solution is strictly antiferromagnetic AFM-A and 2/3 of the O atoms carry not magnetic moment.

For $x = 1/2$, the excess Ga atoms (Ga^*), located preferentially on the Fe2 site of the $Pna2_1$ structure (the configuration with Ga^* located on the Fe1 site being 11 meV/f.u. less stable), do nearly not affect the internal atomic positions but the cell volume is reduced by 3.5%. The most stable corresponding centrosymmetric structure is this time a $Pbcn$ structure where the Ga2 and Ga^* sites are equivalent. Contrary

Table 1

Structural data and local magnetic spin moments of the $Pna2_1$ (left) and $Pnna$ (right) full relaxed structures for $GaFeO_3$: cell parameters and reduced coordinate for the inequivalent atoms (the positions are also given into the $Pna2_1$ representation for the $Pnna$ structure).

	$Pna2_1$ a = 5.133 Å, b = 8.831 Å, c = 9.505 Å	m (μ_B)	$Pnna$ a = 5.051 Å, b = 8.6109 Å, c = 9.7717 Å	m (μ_B)
Ga1	(0.1733, 0.1530, 0.0001)	-0.021	(0.3054, 0.1544, 0.0282)	-0.025
Ga2	(0.8166, 0.1605, 0.3080)	0.016	(0.6946, 0.1544, 0.3051)	0.025
Fe1	(0.1853, 0.1529, 0.5830)	4.103	(0.2004, 0.0607, 0.5527)	4.059
Fe2	(0.6717, 0.0326, 0.7957)	-4.097	(0.7996, 0.0607, 0.7806)	-4.059
O1	(0.9803, 0.3214, 0.4254)	0.077	(0.8492, 0.3382, 0.3918)	0.080
O2	(0.5162, 0.4887, 0.4323)	-0.001	(0.3808, 0.5000, 0.4166)	0.000
O3	(0.6585, 0.9979, 0.2021)	0.018	(0.5000, 0.0160, 0.1666)	0.000
O4	(0.1556, 0.1616, 0.1979)	-0.068	(0.0000, 0.1616, 0.1666)	0.000
O5	(0.8408, 0.1686, 0.6725)	0.075	(1.0000, 0.1755, 0.6666)	0.000
O6	(0.5129, 0.1688, 0.9396)	-0.098	(0.6508, 0.1618, 0.9415)	-0.080

Table 2

Structural data and local magnetic spin moments of the $Pna2_1$ (left) and $Pbcn$ (right) full relaxed structures for $Ga_{1.5}Fe_{0.5}O_3$: cell parameters and reduced coordinate for the inequivalent atoms (the positions are also given into the $Pna2_1$ representation for the $Pbcn$ structure).

	$Pna2_1$ a = 5.077 Å, b = 8.743 Å, c = 9.370 Å	m (μ_B)	$Pbcn$ a = 5.065 Å, b = 9.005 Å, c = 9.524 Å	m (μ_B)
Ga1	(0.1763, 0.1525, -0.0028)	0.005	(0.2500, 0.0306, 0.0000)	0.014
Ga2	(0.8141, 0.1615, 0.3075)	0.024	(0.7340, 0.1516, 0.1997)	0.028
Fe1	(0.1915, 0.1525, 0.5867)	4.193	(0.2500, 0.1589, 0.5000)	4.211
Ga*	(0.6774, 0.0299, 0.7981)	0.036	(0.7660, 0.1516, 0.8003)	0.028
O1	(0.9763, 0.3228, 0.4240)	0.126	(1.0967, 0.3386, 0.3862)	0.192
O2	(0.5202, 0.4897, 0.4303)	0.070	(0.5623, 0.4944, 0.3878)	0.134
O3	(0.6517, 0.0005, 0.2046)	0.178	(0.5623, 0.9944, 0.1122)	0.134
O4	(0.1549, 0.1592, 0.1963)	0.018	(0.0800, 0.1693, 0.1330)	0.015
O5	(0.8457, 0.1680, 0.6730)	0.308	(0.9033, 0.1617, 0.6138)	0.192
O6	(0.5184, 0.1671, 0.9388)	0.009	(0.4200, 0.1693, 0.8670)	0.015

to the previous case, the displacements of all atoms between both structures are large in x, y and z directions.

For $x = 3/2$, the excess Fe atoms (Fe^*), located preferentially on the octahedral Ga2 site of the $Pna2_1$ structure (the configuration with Fe^* located on the Ga2 site being 124 meV/f.u. less stable), do again nearly not affect the internal atomic positions with nearly no variation of the cell volume. The Fe^* site carries a negative magnetic moment like the Fe2 one (the solution with a positive magnetic moment on the Fe^* located on the Ga2 site being 70 meV/f.u. less stable) so that the total magnetic moment is equal to $-5\mu_B$ per Fe^* atom.

These results agree with a similar study previously done by Ibrahim and Alouani [16]. The most stable corresponding centrosymmetric structure is a $Pbcn$ structure, which is surprisingly similar to the one obtained for $x = 1/2$, where the Fe2 and Fe^* sites are equivalent. Because the magnetic configuration for $x = 1/2$ and $x = 3/2$ is no more antiferromagnetic, some oxygen atoms carry a magnetic moment up to $0.3\mu_B$ contrary to the case for $x = 1$ where they remain smaller than $0.1\mu_B$.

The densities of states (DOS) for these six structures are given into Figs. 1 to 3. For $x = 1$ (Fig. 1), the comparison with the DOS obtained with the Full Potential Linearized Augmented Plane Wave (FLAPW) method [6,20] shows a very nice agreement; the bandgap obtained here is a little bit larger due certainly to the small differences between the relaxed structures (for the FLAPW calculation, the structures have been relaxed using the ABINIT code). These figures show clearly that, because the Fe atoms remain in an octahedral site, the DOS obtained for the polar and the centrosymmetric structures are very similar. This explains why the magnetic moments of the various Fe sites do not vary significantly (considering the 6 structures, its magnitude varies between 4.04 and 4.21 μ_B). It is of particular importance for

Table 3

Structural data and local magnetic spin moments of the $Pna2_1$ (left) and $Pbcn$ (right) full relaxed structures for $Ga_{0.5}Fe_{1.5}O_3$: cell parameters and reduced coordinate for the inequivalent atoms (the positions are also given into the $Pna2_1$ representation for the $Pbcn$ structure).

	$Pna2_1$ a = 5.123 Å, b = 8.868 Å, c = 9.551 Å	m (μ_B)	$Pbcn$ a = 5.085 Å, b = 8.8913 Å, c = 9.6805 Å	m (μ_B)
Ga1	(0.1746, 0.1525, 0.0002)	-0.041	(0.2500, 0.0342, 0.0000)	-0.054
Fe^*	(0.8041, 0.1592, 0.3080)	-4.148	(0.7428, 0.1479, 0.2068)	-4.109
Fe1	(0.1946, 0.1521, 0.5829)	4.038	(0.2500, 0.1590, 0.5000)	4.085
Fe2	(0.6811, 0.0344, 0.7955)	-4.110	(0.7572, 0.1479, 0.7932)	-4.109
O1	(0.9776, 0.3246, 0.4277)	-0.147	(1.0896, 0.3377, 0.3883)	0.023
O2	(0.5157, 0.4882, 0.4334)	-0.108	(0.5627, 0.4933, 0.3870)	-0.090
O3	(0.6539, 0.9958, 0.2009)	-0.112	(0.5627, 0.9933, 0.1130)	-0.090
O4	(0.1537, 0.1594, 0.1967)	-0.251	(0.0912, 0.1702, 0.1325)	-0.314
O5	(0.8466, 0.1690, 0.6724)	0.033	(0.9103, 0.1622, 0.6117)	0.023
O6	(0.5152, 0.1693, 0.9389)	-0.106	(0.4086, 0.1702, 0.8675)	-0.314

Download English Version:

<https://daneshyari.com/en/article/1666426>

Download Persian Version:

<https://daneshyari.com/article/1666426>

[Daneshyari.com](https://daneshyari.com)