Effect of the Magnetic Configurations on the Polarization Strength in the Hexagonal YMnO$_3$

Dong Chen, Yinlian Zhu and Xiuliang Ma

ABSTRACT

Using the first-principles method, we calculate the total energies per formula unit, lattice constants and local magnetic moments of different magnetic configurations for the hexagonal YMnO$_3$. By analysis of atomic relative displacements and magnetic configurations, we study the effect of the magnetic configurations on the polarization strength and find that different magnetic configurations have different polarization strengths, which suggests that changing the magnetic structure of YMnO$_3$ would cause the polarization variation and may shed light on the potential for applications.

INTRODUCTION

As an important multiferroic material, YMnO$_3$ has attracted a great deal of attention both theoretically and experimentally because it exhibits intriguing coexistence of ferroelectricity and magnetism with many promising technological applications, such as magnetoelectric transducers, multiple state memory elements, smart sensing and actuating devices [1-3]. It is well known that the hexagonal YMnO$_3$ compound has a ferroelectric transition at very high temperature (~900K) and an antiferromagnetic transition at a much lower temperature (~70K) [4]. That is to say, the hexagonal YMnO$_3$ is a multiferroic material which simultaneously shows ferroelectric and magnetic ordering at low temperatures. Hexagonal manganites are improper ferroelectrics, which are also called geometric ferroelectrics. By first-principles calculations, Van Aken et al. [5] revealed that the hexagonal YMnO$_3$ ferroelectric properties are determined by the Y atoms along the c-axis, and its antiferromagnetic properties by the Mn atoms whose non-collinear spins are ordered in a triangular arrangement. To coexist with magnetism, the ferroelectricity in hexagonal YMnO$_3$ is driven by electrostatic and size effects, which is different from that in perovskite ferroelectrics because the transition metal $d$ electrons are responsible for magnetism suppress the off-center ferroelectric distortion [6]. In hexagonal YMnO$_3$, the positions of the Mn atoms have the close relationship with the antiferromagnetism. The Mn positions not only affect the intraplane exchange
interactions but also tune the signs of interplane super-exchange interactions. Due to
the nearest neighbor antiferromagnetic exchange interaction and hexagonal lattice in
the $ab$ plane, they are magnetically frustrated and have a high degeneracy of the
magnetic ground states [7]. A specific magnetic configuration is determined by the
positions taken up by the Mn atoms in order to release spin frustration [8]. Magnetic
frustration releases through coupling of spins with lattice degrees of freedom,
facilitating the stabilization of a specific magnetic ground state [9].

First-principles density functional theoretical calculations have been very
effective in quantitatively understanding spin-orbit coupling (SOC) which is a
natural coupling between lattice and spin, and stabilizes a noncollinear magnetic
ordering. In this work, different antiferromagnetic orderings of the Mn magnetic
moments are taken into account, and the effects of magnetic structures on the
polarization strength are comprehensively studied by using the first-principles
method.

**COMPUTATIONAL METHODOLOGY**

First-principles calculations have been performed using spin polarized density
functional theory (DFT) as implemented in the Vienna \emph{ab initio} Simulation Package
(VASP) [10-11]. All calculations are carried out within the local spin-density
approximation (LSDA) and the projector augmented wave (PAW) [12] method in
which semi-core electrons have been included. The plane-wave basis energy cutoff
is chosen as 500 eV. The Y 4$s$, 4$p$, 4$d$ and 5$s$, Mn 3$s$, 3$p$, 4$s$ and 3$d$, O 2$s$ and 2$p$, Mg
2$p$ and 3$s$, La 5$s$, 5$p$, 5$d$ and 6$s$ orbitals are chosen as valence states. The atomic
positions are fully relaxed until atomic forces are less than 10 meV/Å and the total
energy is obtained when it converges to 0.1 meV in the electronic self-consistent
loop. The Monkhorst-Pack [13] (MP) scheme is used for the $k$-point sampling and
the Brillouin zone integration is performed with the Gaussian smearing method.
During the calculations of electronic structures, the exchange correlation effects are
treated within the rotational invariant LSDA + U approach. For the YMnO$_3$
compound, the values of $U = 8.0$ eV and $J = 0.88$ eV are applied for the Mn 3$d$
states [14]. We use a $5\times5\times3$ $k$-grid sampling of the 30-atom hexagonal unit cell to perform
the Brillouin-zone integrals. After full relaxation of hexagonal YMnO$_3$, the
ferroelectric polarization strength of the unit cell can also be calculated by Born
effective charge method [15] in which the Born effective charges are took from Ref
5. Then we successively calculate the ground-state properties of the perfect bulk
YMnO$_3$. 

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RESULTS AND DISCUSSION

Figure 1. Hexagonal YMnO$_3$ unit cell (a), its projection (b) along the [001] direction, and four possible magnetic structures: $\Gamma_1$ (c), $\Gamma_2$ (d), $\Gamma_3$ (e) and $\Gamma_4$ (f). The oxygen (yttrium) atoms are indicated by the red (light green) spheres, the manganese atoms located in the $z = 0$ plane are shown by the purple color and the ones in the $z = c/2$ plane are the light blue color.

The magnetic structures in the hexagonal manganites are the complicated non-collinear AFM state. According to the neutron-diffraction experiments [16-17], there may be four possible magnetic structures of the hexagonal YMnO$_3$ oxides (space group $P6_3cm$). Figure 1 shows the hexagonal (ferroelectric) YMnO$_3$ unit cell (30 atoms/cell) (a), its projection (b) along the [001] direction, and four possible magnetic structures: $\Gamma_1$ (c), $\Gamma_2$ (d), $\Gamma_3$ (e) and $\Gamma_4$ (f). In the hexagonal YMnO$_3$, there are six formula units per unit cell. The six Mn atoms are distributed in the $z = 0$ and $z = 1/2$ planes. Each Mn atom occupies the center of a triangular bipyramid whose vertices are oxygen atoms. In the projections, only Mn atoms are shown. For $\Gamma_1$ and $\Gamma_4$, the magnetic moments are in a plane perpendicular to the $z$ axis. In both cases the Mn magnetic moments are also perpendicular to the [100] axes. For $\Gamma_1$ the magnetic coupling between the two layers $\{z = 0 \text{ and } z = 1/2\}$ is antiferromagnetic whereas for $\Gamma_4$ the coupling is ferromagnetic. For $\Gamma_2$ and $\Gamma_3$, the component in the basal plane is parallel to the [100] axes. For $\Gamma_2$ the coupling between the two $\{z\}$ layers is antiferromagnetic but for $\Gamma_3$ the coupling is ferromagnetic.

Then, the first-principles calculations have been performed for these magnetic structures. Table 1 lists the total energies per formula unit, lattice constants, local magnetic moments of different magnetic configurations for bulk hexagonal YMnO$_3$. Although the collinear antiferromagnetic (AFM) state is not natural for hexagonal YMnO$_3$, the energy of collinear AFM ordering is obviously lower than that of ferromagnetic (FM) state. This is the reason why the previous researchers used the collinear AFM state to simulate the complicated noncollinear AFM state of hexagonal YMnO$_3$ for the magnetic properties [18]. For the noncollinear AFM states, the lattice constants and magnetic moments are both in reasonable agreement with the experimental values [16, 19-21]. In the table, it can be seen that the ground state of YMnO$_3$ is the $\Gamma_3$ structure because its energy is of relative stability. However, it should be paid attention to that all the noncollinear AFM states are located in a narrow energy range lower than the collinear AFM state, which is expected for the frustrated magnetic systems.
Table 1. Total energies ($E_{\text{tot}}$) per formula unit, lattice constants ($a$ and $c$) and local magnetic moments ($M_{\text{Ms}}$) of different magnetic configurations for bulk hexagonal YMnO$_3$.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$E_{\text{tot}}$ (eV)</th>
<th>$M_{\text{Ms}}$ ($\mu$B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments</td>
<td>6.130</td>
<td>11.400</td>
<td>3.30 [19]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.155</td>
<td>11.403</td>
<td>2.90 [16]</td>
<td>3.09 [21]</td>
</tr>
<tr>
<td>FM</td>
<td>6.266</td>
<td>11.447</td>
<td>-39.245</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>6.180</td>
<td>11.428</td>
<td>-40.250</td>
<td>2.963</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>6.127</td>
<td>11.327</td>
<td>-40.280</td>
<td>3.252</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>6.159</td>
<td>11.434</td>
<td>-40.370</td>
<td>3.261</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>6.189</td>
<td>11.429</td>
<td>-40.346</td>
<td>2.970</td>
</tr>
</tbody>
</table>

After full relaxations of hexagonal YMnO$_3$ with different magnetic configurations, the polarization strength $P^{(i)}$ of unit cell $i$ can be calculated by the Born effective charge method [15] as following:

$$P^{(i)} = \frac{e}{\Omega_c} \sum_{\alpha} w_{\alpha} Z_{\alpha}^* \cdot \mathbf{u}_{\alpha}^{(i)}$$

where $e$ is the electron charge, $\Omega_c$ is the volume of the unit cell, index $\alpha$ runs over all atoms of unit cell $i$, $w_{\alpha}$ is the weight factor and $Z_{\alpha}^*$ is Born effective charge, $\mathbf{u}_{\alpha}^{(i)}$ is the displacement of atom $\alpha$ from its centrosymmetric position. Table 2 lists the calculated relative displacements from the centrosymmetric positions of Y atoms in the hexagonal YMnO$_3$ unit cell with different magnetic configurations. It shows that the Y atoms can be moved along the [001] direction according to the basis vectors of $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ and $\Gamma_4$ below Néel temperature. For example, Y1 and Y6 atoms are allowed to move in opposite directions referring to the centrosymmetric positions, but their displacements are different for each magnetic configuration. Then using equation (1) together with the atomic displacements including Table 2 we can get the polarization strength of the magnetic configuration. The obtained polarization values for $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ and $\Gamma_4$ are respectively 6.3, 7.1, 6.9 and 7.5 $\mu$C/cm$^2$, all of which are obviously different but comparable with the measured value (5.5 $\mu$C/cm$^2$ [22-23]). It can be found that there exists a different magnetic contribution to the ferroelectric polarization among all the magnetic configurations, which suggests that changing the magnetic structure of YMnO$_3$ would cause the polarization variation.

Table 2. Calculated relative displacements from the centrosymmetric positions of Y atoms in the hexagonal YMnO$_3$ unit cell with different magnetic configurations.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$\Gamma_1$</th>
<th>$\Gamma_2$</th>
<th>$\Gamma_3$</th>
<th>$\Gamma_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>0.207</td>
<td>0.243</td>
<td>0.212</td>
<td>0.216</td>
</tr>
<tr>
<td>Y2</td>
<td>0.004</td>
<td>0.091</td>
<td>0.013</td>
<td>0.017</td>
</tr>
<tr>
<td>Y3</td>
<td>-0.292</td>
<td>-0.253</td>
<td>-0.287</td>
<td>-0.277</td>
</tr>
<tr>
<td>Y4</td>
<td>-0.495</td>
<td>-0.405</td>
<td>-0.488</td>
<td>-0.483</td>
</tr>
<tr>
<td>Y5</td>
<td>-0.495</td>
<td>-0.406</td>
<td>-0.487</td>
<td>-0.482</td>
</tr>
<tr>
<td>Y6</td>
<td>-0.291</td>
<td>-0.255</td>
<td>-0.287</td>
<td>-0.278</td>
</tr>
</tbody>
</table>

In the work, we predict that the magnitude of polarization strength would be determined by the magnetic configuration, and there would be a fluctuant
polarization if the magnetic configuration could be transited from one state to another. In the Reference 24, all the magnetic configurations in the hexagonal YMnO₃ were divided into two groups: The first group includes Γ₁ and Γ₂ where the magnetic moments in the planes z = 0 and c/2 can be transformed to each other by the simple rotations. The second group includes Γ₃ and Γ₄ where these rotations should be additionally combined with the time inversion. Therefore, it might be relatively easy to realize the change of electronic polarization if the inter-transform magnetic configurations belong to the same group. Anyway, the value of the ferroelectric polarization could be controlled by changing the magnetic state in the hexagonal YMnO₃.

SUMMARY

In this work, we use the first-principles method to identify the magnetic structures in the hexagonal YMnO₃ and study the effects of different antiferromagnetic orderings on the polarization strength. Although the Γ₃ structure is the ground state of YMnO₃, it is notable that all the noncollinear AFM states are located in a narrow energy range. By analysis of atomic relative displacements and magnetic configurations, the estimated polarization strengths indicate that the ferroelectric property might depend on the magnetic structure in the hexagonal of YMnO₃.

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REFERENCES