

Effect of the Magnetic Configurations on the Polarization Strength in the Hexagonal YMnO₃

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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 YMnO₃. 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 YMnO₃ would cause the polarization variation and may shed light on the potential for applications.

INTRODUCTION

As an important multiferroic material, YMnO₃ 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 YMnO₃ 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 YMnO₃ 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 YMnO₃ 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 YMnO₃ 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 YMnO₃, the positions of the Mn atoms have the close relationship with the antiferromagnetism. The Mn positions not only affect the intraplane exchange

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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 *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 YMnO₃ 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 5×5×3 *k*-grid sampling of the 30-atom hexagonal unit cell to perform the Brillouin-zone integrals. After full relaxation of hexagonal YMnO₃, 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 YMnO₃.

RESULTS AND DISCUSSION

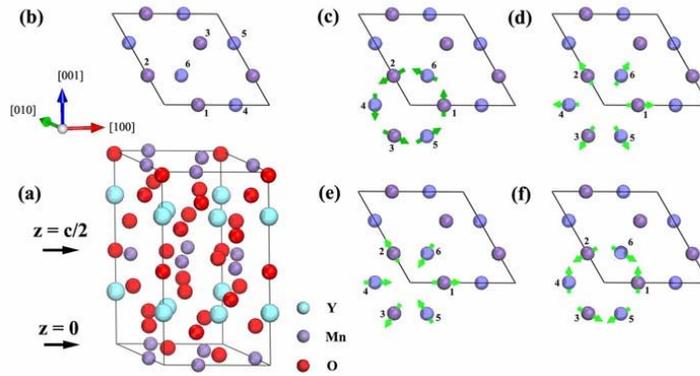


Figure 1. Hexagonal YMnO_3 unit cell (a), its projection (b) along the $[001]$ direction, and four possible magnetic structures: $\Gamma 1$ (c), $\Gamma 2$ (d), $\Gamma 3$ (e) and $\Gamma 4$ (f). The oxygen (yttrium) atoms are indicated by the red (light green) spheres, the manganese atoms located in 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_{tot}) per formula unit, lattice constants (a and c) and local magnetic moments (m_{Mn}) of different magnetic configurations for bulk hexagonal ymno_3 .

Configuration	a (Å)	c (Å)	E_{Tot} (eV)	M_{Mn} (μB)
Experiments	6.130	11.400 [19]		3.30 [20]
	6.155	11.403 [16]		2.90 [16]
				3.09 [21]
FM	6.266	11.447	-39.245	
Collinear AFM	6.465	11.638	-39.663	
$\Gamma 1$	6.180	11.428	-40.250	2.963
$\Gamma 2$	6.127	11.327	-40.280	3.252
$\Gamma 3$	6.159	11.434	-40.370	3.261
$\Gamma 4$	6.189	11.429	-40.346	2.970

After full relaxations of hexagonal YMnO_3 with different magnetic configurations, the polarization strength $\mathbf{P}^{(i)}$ of unit cell i can be calculated by Born effective charge method [15] as following:

$$\mathbf{P}^{(i)} = \frac{e}{\Omega_c} \sum_{\alpha} w_{\alpha} Z_{\alpha}^* \cdot \mathbf{u}_{\alpha}^{(i)} \quad (1)$$

where e is the electron charge, Ω_c is the volume of the unitcell, index α runs over all atoms of unitcell i , w_{α} is the weight factor and Z_{α}^* is Born effective charge, $\mathbf{u}_{\alpha}^{(i)}$ is the displacement of atom α 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 $\mu\text{C}/\text{cm}^2$, all of which are obviously different but comparable with the measured value (5.5 $\mu\text{C}/\text{cm}^2$ [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.

Atoms	$\Gamma 1$	$\Gamma 2$	$\Gamma 3$	$\Gamma 4$		
Y1	0.207	0.243		0.212	0.216	
Y2	0.004	0.091		0.013	0.017	
Y3	-0.292		-0.253	-0.287	-0.277	
Y4	-0.495		-0.405		-0.488	-0.483
Y5	-0.495	-0.406		-0.487	-0.482	
Y6	-0.291	-0.255		-0.287	-0.278	

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 transitioned 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 $\Gamma 1$ and $\Gamma 2$ 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 $\Gamma 3$ and $\Gamma 4$ 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 $\Gamma 3$ 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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