Density functional study of a ferromagnetic ferroelectric LaMnO$_3$/BaTiO$_3$ superlattice

Adrian Ciucivara,[1] Bhagawan Sahu,[2] and Leonard Kleinman[1]

[1]*Department of Physics, University of Texas at Austin, Austin, Texas 78712-0264, USA*
[2]*Microelectronics Research Center, University of Texas at Austin, Austin, Texas 78758, USA*

Using the GGA+U density functional, we have calculated the lattice constants, atomic positions, magnetization, and ferroelectric polarization of a (LaMnO$_3$)$_{4.5}$(BaTiO$_3$)$_{4.5}$ superlattice containing five LaO and TiO$_2$ planes and four MnO$_2$ and BaO planes. Although LaMnO$_3$ is antiferromagnetic, it is ferromagnetic in the superlattice. An approximation to the ferroelectric polarization, obtained from a comparison of superlattice and bulk crystal atomic displacements and unit cell volumes, is found to agree reasonably well with that obtained from a Berry phase calculation. The electric polarization is polarized along the longer in-plane lattice vector, while the Mn spins, when the spin-orbit interaction and spin noncollinearity are included, have different magnitudes, but all point in essentially the same direction as the electric polarization.

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I. INTRODUCTION

Multiferroic materials form a class of compounds, which have recently received a lot of attention from the material physics community. In order for a compound to belong to this group, it requires at least two order parameters to coexist in the same phase. Considering elastic, electric, and magnetic properties, there are three distinct groups of multiferroics: piezoelectrics, which have elastic and electric properties, piezomagnets, which have elastic and magnetic properties, and magnetoelectrics, where ferroelectric (or antiferroelectric) and magnetic properties coexist. If the first two groups of multiferroics are relatively common, the magnetoelectric materials are much less so. A very important group of magnetoelectric multiferroics is formed by hexagonal rare-earth manganites, which have the overall formula RMnO$_3$ (R = Y, Ho, Er, Tm, Yb, Lu, Sc) and are ferroelectric, but all are antiferromagnetic.[1–4]

Ferroelectric ferromagnets are extremely rare. One compound, which has received a lot of attention recently, is BiMnO$_3$. It is well established that BiMnO$_3$ is a magnetic material with a magnetization of about 3.9 μ_B/f.u., a fact supported by a number of experimental and theoretical papers,[5–7] and it had also been believed to be ferroelectric with the noncentrosymmetric $C2$ space group, a conclusion based on powder neutron diffraction experiments.[8,9] Seshadri and Hill[10] attributed this structure to the stereochemical activity of the Bi $6s^2$ lone pair. However, very recently, Belik *et al.*,[11] having used selected area electron diffraction, convergent beam electron diffraction, and Rietveld analysis of neutron diffraction data on polycrystalline samples, concluded that BiMnO$_3$ crystallizes in the centrosymmetric $C2/c$ space group. Having first determined that the actual structure depends sensitively on the oxygen stoichiometry,[12] Montanari *et al.*[13] used neutron studies on polycrystalline BiMnO$_3$ as a function of temperature and magnetic field to conclude that the space group is $C2/c$. Baettig *et al.*[14] performed full computational structural optimizations of BiMnO$_3$ using the LDA+U method, finding that although the two proposed[8,9] polar $C2$ structures existed, they are higher in energy than an antiferroelectric centrosymmetric $C2/c$ structure.

As far as we know, there are only two ferromagnetic ferroelectrics thus far synthesized (or three if one counts

BiFeO$_3$, an antiferromagnetic ferroelectric with a small spin canting, resulting in a negligible ferromagnetic moment, and which in a 70 nm thick film was reported[15] to have a saturation magnetization of ∼1 μ_B). One of these is Bi$_2$NiMnO$_6$. This compound was recently synthesized by Azuma *et al.*[16] as a heavily distorted double perovskite with 4 f.u. in a monoclinic unit cell. We[17] recently reported the results of generalized gradient approximation (GGA) and GGA+U calculations of Bi$_2$NiMnO$_6$ in which the effects of spin orbit and spin noncollinearity were included. A magnetization of 4.94 μ_B/f.u. (4.99 with U) and a polarization of 18.41 μC/cm^2 (18.18 with U) were obtained. The other compound of which we are aware was synthesized by Gajek *et al.*[18] They reported that La$_{0.1}$Bi$_{0.9}$MnO$_3$ is a ferroelectromagnet, which retains its properties down to a 2 nm thick film, and have used it as a spin filtering tunnel barrier, the magnetization and electric polarization of which can be switched independently, giving rise to four different resistance states. The extraordinary challenge of creating these ferroelectromagnetic compounds suggests a superlattice approach. Murugavel *et al.*[19] have created a (PCMO)$_{10}$(BST)$_9$ superlattice, where PCMO is ferromagnetic Pr$_{0.85}$Ca$_{0.15}$MnO$_3$ and BST is ferroelectric Ba$_{0.6}$Sr$_{0.4}$TiO$_3$. The superlattice had ferromagnetic and ferroelectric transition temperatures, T_C=120 K and T_E=140 K, and showed a 40% magnetoresistance in a 7 T field at 80 K. Singh *et al.*[20] studied the structure of (La$_{0.7}$Ca$_{0.3}$MnO$_3$)$_n$/(BaTiO$_3$)$_m$ superlattices with various values of n and m and measured magnetizations, ferroelectric polarizations, and Curie temperatures. Interestingly, they found that a superlattice with n=m=4 was ferromagnetic up to 400 K, while thick films had a Curie temperature of only 145 K. The Curie temperature of bulk La$_{0.7}$Ca$_{0.3}$MnO$_3$ is about 250 K.

There are only two calculations of which we are aware that involve a ferroelectric interfacing with a ferromagnet. One involves a Fe/BaTiO$_3$ superlattice. The authors[21] fixed the transverse (i.e., in the interface plane) lattice constant of the superlattice[22] at the experimental BaTiO$_3$ lattice constant. Because this is smaller than their calculated BaTiO$_3$ lattice constant, ferroelectric polarization in the longitudinal direction was assured. They found a 0.37 μ_B difference between the sum of the Ti and Fe magnetic moments in the top and

bottom interfaces (where "top" is the direction of $BaTiO_3$ polarization) and suggested that if the magnetization of the surface of a few layers of iron on $BaTiO_3$ could be controlled by changing the sign of the ferroelectric polarization, useful applications might be found. The centered 2×2 Fe lattice constant is larger than the $BaTiO_3$ lattice constant to which it is nearly matched, so in actual fact, the transverse lattice constant of the superlattice will be slightly larger than that of $BaTiO_3$ and the ferroelectric polarization would be expected to lie in the plane in this case, but the concept is, nevertheless, interesting. The other calculation,[23] for a $Co_2MnSi/BaTiO_3$ superlattice, calculated lattice constants and found the Ti to be polarized at the Co_2/TiO_2 interface but probably not at the $MnSi/TiO_2$ interface.

In this paper, we present the results of completely relaxed electronic structure calculations for a $LaMnO_3/BaTiO_3$ superlattice, similar to that described in Ref. [20] except for the replacement of $La_{0.7}Ca_{0.3}MnO_3$ with $LaMnO_3$. The only reason for replacing $La_{0.7}Ca_{0.3}MnO_3$ with $LaMnO_3$ was to keep the calculation of feasible size, even if, by doing so, we expected to replace the ferromagnetism of Ca doped $LaMnO_3$ with the antiferromagnetism of pure $LaMnO_3$. In the following section, we describe our computational method, and in the last section, we present and discuss our results.

II. COMPUTATIONAL DETAILS

Our calculations were performed using the projected augmented wave[24] method, as implemented in the VASP code.[25] The generalized gradient approximation[26] plus Hubbard U approximation[27] $(GGA+U)$ was used for the exchange-correlation energy density functional. In order to properly describe $LaMnO_3$ as a semiconductor rather than a metal, we had to use the fairly large value of 7.5 eV for the Mn $U-J$ parameter,[28] equal to the value obtained from $2p$ core-level photoemission spectra[29] and less than the 9.22 eV obtained from "constrained" density functional calculations.[30] For Ti, we assumed that $U-J=0$. The Brillouin zone was sampled with a $7 \times 7 \times 3$ **k**-point grid. The basis set used contained all plane waves up to 20.79 Ry. The atomic positions were adjusted until all the forces on them were less than 10 meV/Å and the VASP code adjusted the lattice constants using a stress criterion based on the force criterion.

We originally constructed our superlattice to match that measured in Ref. [20], with four layers of $BaTiO_3$ alternating with four[31] of $LaMnO_3$. However, we were unable to get the forces to converge. Because the forces at the MnO_2/BaO interface were much larger than those at the LaO/TiO_2 interface, we constructed a superlattice with 4.5 layers of each compound, which contained only LaO/TiO_2 interfaces and had no further convergence problems. This seems to confirm what was found in Ref. [21] and assumed to be true in Ref. [23], namely, that the TiO_2 interface with a ferromagnet is much more stable than the BaO interface with the ferromagnet. The large electric fields which can occur between dissimilar interfaces may have played a role in the failure to converge. With the lattice constants and atomic positions thus obtained, the spin-orbit interaction and a continuously variable spin

TABLE I. Calculated lattice constants in Å and unit cell volumes in Å^3 of $BaTiO_3$ and a double $BaTiO_3$ unit cell for comparison with the $LaMnO_3$ unit cell and with the experiment. The last row lists the $(BaTiO_3)_{4.5}(LaMnO_3)_{4.5}$ lattice constants and unit cell volume.

	a	b	c	Vol.
$BaTiO_3$	3.9325	3.9325	3.9567	61.1886
	5.5614	5.5614	7.9134	244.7544
Expt.[a]	3.992	3.992	4.036	64.317954
$LaMnO_3$	5.5612	5.7607	7.8083	250.1240
Expt.[b]	5.532	5.742	7.669	243.569
Supercell	5.6498	5.7181	35.8470	1158.0591

[a]Reference [32].
[b]Reference [33].

quantization direction were included, and the calculation again brought to self-consistency.

III. RESULTS AND DISCUSSION

The calculated lattice constants of $BaTiO_3$ (Ref. [32]) and $LaMnO_3$ (Ref. [33]) are compared with the experiment in Table I. Also listed are lattice constants for four formula units of $BaTiO_3$ for comparison with the $LaMnO_3$ unit cell. The discrepancies between theory and experiment are typical for density functional calculations, although the sign of the discrepancy in $BaTiO_3$ is unexpected from a GGA density functional calculation. $LaMnO_3$ is triclinic but very close to being orthorhombic. This can be demonstrated by observing the ratio of the unit cell volume to the product of the lattice constants, 250.124/250.150 (calculated) and 243.569/243.592 (experiment). The antiferromagnetic $LaMnO_3$ magnetization was calculated to be 4.226 μ_B per Mn in fairly poor agreement with the experimental value[34] of 3.7 ± 0.1 μ_B. Better agreement could be obtained with smaller values of $U-J$. For example, 3.827 μ_B was obtained with $U-J=3.5$ eV. It is unfortunate that no single value of the $U-J$ parameter can yield both the correct energy gap and the correct magnetization. Using the Berry phase method,[35] the $BaTiO_3$ ferroelectric polarization was found to be 27.05 $\mu C/cm^2$, in good agreement with the experimental value[36] of 26.0 $\mu C/cm^2$. Berry phases exist only for filled bands, which caused us to choose the larger value of $U-J$.

The superlattice calculation (with no spin orbit or noncollinearity) was initiated with an antiferromagnetic Mn spin density similar to that of bulk $LaMnO_3$, but it converged to a ferromagnetic distribution. One might suspect that an antiferromagnetic local energy minimum exists, but if it does, VASP manages to avoid it. The last row of Table I lists the superlattice lattice constants. Note that the a and b constants are greater than the average of the $BaTiO_3$ and $LaMnO_3$ a and b. Similarly, c and the unit cell volume are larger than 2.25 times the sum of $BaTiO_3$ and $LaMnO_3$ $c's$ and volumes. There is at least one and perhaps two independent causes for the switch from bulk antiferromagnetism to superlattice ferromagnetism. The antiferromagnetic crystal has a unit cell

TABLE II. Components of the magnetization (in μ_B) projected on the outer and inner plane Mn in the $(BaTiO_3)_{4.5}(LaMnO_3)_{4.5}$ superlattice at two different energy minima. Discrepancies between the M_y of equivalent atoms in the two outer planes, of $0.002\mu_B$ or less, have been averaged out. Note that the magnitude of M on every atom is independent of energy minimum.

	M_x	M_y	M_z	M_x	M_y	M_z
Out1	0.014	4.301	0.012	0.618	4.255	0.111
Out2	0.007	4.675	0.009	0.818	4.601	0.116
In1	0.014	4.254	0.012	0.747	4.187	0.099
In2	0.010	4.258	0.012	0.616	4.212	0.102
	$E=-727.1502368$ eV			$E=-727.149665$ eV		

TABLE III. Comparison of the six nearest neighbor oxygen distances (in Å) to the Mn in $LaMnO_3$ and to the outer plane Mn in the $(BaTiO_3)_{4.5}(LaMnO_3)_{4.5}$ superlattice.

Bulk	Mn1	Mn2
1.938	2.006	2.146
1.938	2.009	2.147
2.041	2.028	2.153
2.041	2.021	2.155
2.078	2.115	2.078
2.078	2.186	2.155

twice as large as the ferromagnetic crystal, resulting in extra energy gaps and therefore a lowering of the band energy, but at a cost of reducing the magnitude of the exchange energy. Which of these contributions to the energy dominates depends on the lattice constants. We performed a bulk $LaMnO_3$ calculation using superlattice lattice parameters (a and b from Table I and $c=7.8928$ Å, the distance between the second and fourth LaO planes in the superlattice) and found it to be ferromagnetic. This alone explains why the superlattice is ferromagnetic. We found that the magnetization was larger on the interface planes than on the interior planes and, experimentally,[20] as previously mentioned, when the interfaces are dense, the Curie temperature is significantly higher that that of the bulk crystal, while when they are far apart, it is much lower than the bulk Curie temperature. Thus, interfaces increase the magnetization and may favor ferromagnetism over antiferromagnetism..

There are four Mn planes in the superlattice, each containing two inequivalent Mn atoms. The two inner planes are equivalent, as are the outer planes. Two sets of the components of the magnetization of these atoms are listed in Table II, which were obtained by including the spin-orbit interaction and allowing for possible noncollinearity. The ground state calculation was initiated with a ferromagnetic spin distribution. The metastable state[37] calculation was initiated with a random spin distribution [except for the identity of the inner (outer) plane spins]. As shown in Table II, all the ground state spins are polarized essentially along the **b** lattice vector,[38] whereas the metastable state Mn spins are not quite collinear and point in a direction of no particular symmetry. Because they are identical on the two outer (inner) planes, we believe that the small values of M_x and M_z in the ground state are real and not an artifact of the calculation. Note that the metastable and ground state spin *magnitudes* are identical. The two inner plane atom magnetizations are very slightly larger than those calculated for bulk $LaMnO_3$, whereas one of the outer two is slightly larger and one is significantly larger. This can be understood with an examination of the outer plane Mn bond lengths to their six neighboring oxygen atoms, which are listed in Table III. Since covalent bonds are not magnetic and longer bond lengths imply less covalency, the Mn with the longer bonds are more magnetic.

The calculated superlattice ferroelectric polarization is 13.079 $\mu C/cm^2$. It lies along the direction in which the $BaTiO_3$ is stretched by the $LaMnO_3$, i.e., along the same **b** lattice vector as the magnetization. It is about half as large as that calculated for bulk $BaTiO_3$, which was to be expected because the $BaTiO_3$ constitutes about half of the volume of the superlattice. It can be compared with the experimental value of 12 $\mu C/cm^2$ obtained for the $La_{0.7}Ca_{0.3}MnO_3/BaTiO_3$ superlattice.[20] The Berry phase polarization is uncertain to within some number of quanta,[35] $\Delta\mathbf{P}=e\mathbf{b}/\Omega=7.900$ $\mu C/cm^2$, where e is the electronic charge, **b** is the lattice vector, and Ω is the unit cell volume. To prove that no quanta should be added or subtracted from our result, we have calculated the polarization with the atoms displaced 75%, 50%, 25%, 10%, and 0% from their centrosymmetric positions and plotted the curve in Fig. 1. No other smooth curve can be drawn by subtracting any number of quanta from each point.[39]

It has been suggested[40] that in the case of a superlattice consisting of a ferroelectric and a metal where the Berry phase method is not applicable, one can estimate the polarization from the ratio of superlattice displacements away
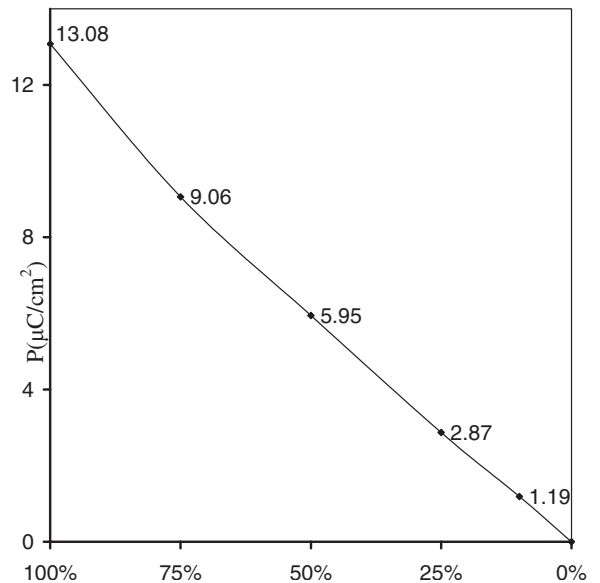

FIG. 1. Polarization as a function of the percentage of the atomic displacements from their centrosymmetric positions toward their equilibrium positions.

TABLE IV. Berry phase polarizations (in $\mu C/cm^2$), unit cell volumes, and the averaged displacements of the Ti and O atoms in the $(BaTiO_3)_{4.5}(LaMnO_3)_{4.5}$ superlattice compared with bulk $BaTiO_3$ and the superlattice polarizations P_{Ti} and P_O estimated therefrom.

	P	V (Å^3)	ΔTi (Å)	P_{Ti}	ΔO (Å)	P_O
Bulk	27.05	61.18861	0.024799		0.029807	
Supercell	13.088	1158.059	0.020692	11.925	0.033566	16.094

from centrosymmetry to those in the bulk crystal. It seemed that this would be a good opportunity to test that approximation. We have $P_{est}=(D/d)(v/V)P_{bulk}$, where D (d) is the sum of the superlattice (bulk crystal) displacements for either Ti or O and V (v) is the superlattice (bulk crystal) unit cell volume. In the first column of Table IV, P_{bulk} and $P_{supercell}$ are listed. The remaining columns list the average (for ease of comparison) Ti and O displacements and P_{Ti} and P_O, the polarizations estimated therefrom. We see that $P_{Ti}=0.911$ $P_{supercell}$ and $P_O=1.230$ $P_{supercell}$ and that their average, $P_{est}=1.070$ $P_{supercell}$ is a reasonable approximation. The outer plane Mn are displaced relative to the inner plane Mn by 0.33 and 0.28 Å in the opposite direction to the Ti displace-ment along the **b** lattice vector. This is not included in the approximate calculation and could account for its discrepancy with respect to the Berry phase calculation.

In summary, we have calculated the properties of antiferromagnetic $LaMnO_3$ and ferroelectric $BaTiO_3$ and of a $(LaMnO_3)_{4.5}(BaTiO_3)_{4.5}$ superlattice with LaO/TiO_2 interfaces. We found that the superlattice is ferromagnetic and showed that this was a consequence of the difference between bulk crystal and superlattice lattice constants, although interface effects, which strengthened the magnetization, might also favor ferromagnetism. The electric polarization density was calculated using the Berry phase method and found, as expected, to be about half that of $BaTiO_3$. Both the magnetic and electric polarizations were found to point along the in-plane **b** lattice vector. An approximate method, which must be used when the system is metallic, was found to be in fairly good agreement with the Berry phase result.

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[38] Because the superlattice is not quite orthorhombic, $\mathbf{b}=(5.59 \times 10^{-5}, 5.718\,07, 5.35 \times 10^{-5})$ Å.

[39] It is interesting to note that a very smooth curve can be drawn by subtracting 4, 3, 2, 1, and 0 quanta from the values with 100%, 75%, 50%, 25%, and 0% displacements, respectively, but there is no way to make the point at 10% displacement lie on that curve.

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