Multiferroic Bi$_2$NiMnO$_6$ Thin Films: A Computational Prediction

Oswaldo Diéguez$^{1,2}$ and Jorge Íñiguez$^3$

$^1$Department of Materials Science and Engineering, Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel

$^2$The Raymond and Beverly Sackler Center for Computational Molecular and Materials Science, Tel Aviv University, Tel Aviv 69978, Israel

$^3$Materials Research and Technology Department, Luxembourg Institute of Science and Technology, 5 avenue des Hauts-Fourneaux, L-4362 Esch/Alzette, Luxembourg

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We report first-principles calculations for one of the few materials that is believed to be a ferroelectric ferromagnet, Bi$_2$NiMnO$_6$. Our calculations show that, contrary to what it has been reported so far, bulk Bi$_2$NiMnO$_6$ does not have a polarization. Instead, like BiMnO$_3$, it crystallizes into a centrosymmetric structure with space group $C2/c$. We also predict that Bi$_2$NiMnO$_6$ will indeed be a ferroelectric ferromagnet if it is grown as an epitaxial film on a substrate with in-plane square symmetry and a lattice constant around 4 Å, such as BaTiO$_3$ or PbZr$_{1-x}$Ti$_x$O$_3$.

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I. INTRODUCTION

The possibility of manipulating the magnetization of a material by using an electric field is probably the most attractive envisioned application of magnetoelectric multiferroics—ferroelectrics with magnetic ordering. Even if the mechanisms responsible for ferroelectricity and magnetism are somehow exclusive of each other, in the last decade a large research effort has gone into searching for these materials. This effort has mainly focused on two groups of complex oxides: those where different species are responsible for the polarization and the magnetism, and those where the magnetic ordering breaks the inversion symmetry of the structure to create a small polarization. BiFeO$_3$ belongs to the first group and it is by far the most studied multiferroic mainly because it keeps both its ferroic orderings well above room temperature; it is also relatively easy to prepare in bulk and film form, and it has a simple crystal structure—a perovskite where inversion symmetry is broken to accommodate the lone pair of Bi in the A site, while the B site harbors the Fe ions whose $d$ electrons are responsible for magnetism. However, the ferromagnetic component in BiFeO$_3$ is tiny; instead, the spins of two neighboring Fe ions are almost perfectly antiparallel. In the difficult search for single-phase ferroelectric ferromagnets that would allow for a direct hysteresis loop of magnetization with electric field some candidate materials have been proposed. Examples include EuTiO$_3$ (although ferromagnetism only settles at around 4 K), LuFe$_2$O$_4$ (although whether this is a ferroelectric is still under debate), Fe$_3$O$_4$ (although the exact structure that arises below the Verwey transitions is not yet understood), CoCr$_2$O$_4$ (although both the magnetization and the polarization are very small), and, more recently, the metastable $c$-Fe$_2$O$_3$. Researchers have also explored perovskite oxides similar to BiFeO$_3$, but with other transition-metal ions instead of Fe. BiMnO$_3$ is the only member of this group that displays strong ferromagnetism. Initial reports attributed a polar $C2$ space group to bulk BiMnO$_3$, but more recent studies agree in that this is a paraelectric with $C2/c$ symmetry. It is possible to change the structure of this material by growing it as an epitaxial thin film, although the calculations of Spaldin and Hat showed that when the substrate-imposed distortion is small enough to keep the ferromagnetism in BiMnO$_3$, then a polarization does not develop, and our calculation showed that when the distortion is large enough to create a large polarization, then ferromagnetism turns into antiferromagnetism. Another way to try to modify the properties of these oxides is to add a second species in one of the sites of the perovskite. Azuma and coworkers reasoned that the Goodenough-Kanamori rules predict a ferromagnet if Mn and Ni shared the sites inside O$_6$ octahedra in a rock-salt pattern; when they prepared Bi$_2$NiMnO$_6$ by high-pressure synthesis, they indeed measured large parallel magnetic moments which persisted up to a Curie temperature of 140 K. After their synchrotron X-ray powder diffraction, they concluded that the material shows a heavily distorted double perovskite structure where the Ni$^{2+}$ and Mn$^{4+}$ ions are indeed ordered in a rock-salt configuration; they assigned the space group $C2$ to this crystal. Later, first-principles calculations characterized further
this structure and quoted a value of the polarization around 20 $\mu$C/cm$^2$.

Unlike those previous studies, our first-principles calculations show that bulk Bi$_2$NiMnO$_6$ is actually a paraelectric material with C2/c space group, the same situation as with BiMnO$_3$. However, we predict that when Bi$_2$NiMnO$_6$ films are grown under achievable tensile epitaxial strain, it will indeed become a ferroelectric ferromagnet with a large polarization (70 $\mu$C/cm$^2$) and a magnetization above 2 $\mu_B$ per transition metal cation, as in the bulk compound. We describe the methodology we have used for our calculations in Section II, present our results for the bulk material in Section III.A and for epitaxial films in Section III.B, and summarize the implications of our work in Section IV.

II. METHODS

Our first-principles calculations are based on density-functional theory (DFT). Following our previous study of BiMnO$_3$ we used two methods to treat the localized d orbitals of Ni$^{2+}$ and Mn$^{4+}$: (i) DFT with a “Hubbard $U$” using $U_{\text{Ni}} = 1$ eV, $J_{\text{Ni}} = 0$ eV, $U_{\text{Mn}} = 4$ eV, and $J_{\text{Mn}} = 1$ eV; and (ii) DFT with the HSE06 hybrid functional. For all our calculations we have used the VASP code; for this system, the second method demands two orders of magnitude more computer time than the first, but it predicts band gaps for solids that are much closer to experimental results, and in particular it performs well for perovskite oxides such as BiFeO$_3$.

We used the Perdew-Burke-Ernzerhof DFT exchange-correlation functional adapted to solids (PBEsol). To treat the ionic cores we resorted to the projector augmented-wave method solving for the following electrons: Ni’s and Mn’s 3p, 3d, and 4s; Bi’s 5d, 6s, and 6p; and O’s 2s and 2p. The plane-wave basis set kinetic-energy cutoff was 500 eV. We performed integrations in the Brillouin zone using k-point grids with densities similar to that of the 6 x 6 x 6 mesh for a 5-atom perovskite unit cell.

III. RESULTS

A. Bulk Phases

Our first set of calculations involves the optimization of Bi$_2$NiMnO$_6$ bulk structures that might be competitive in energy with the ground state. As mentioned in the Introduction, previous experimental and computational studies consider that this ground state belongs to the C2 space group; Refs. and 34 report the lattice parameters and Wickoff positions of the atoms in the crystal unit cell, and we have run optimizations starting from those configurations. In the future we call this structure GS—the structure that the bulk material displays at low temperature and low pressure. Another relevant phase is the one observed at high temperature with space group P2$_1$/n, fully described in Ref. 45; this phase is analogous to the Pnma phase that appears in many BiMnO$_3$ perovskites at high pressure and/or high temperature, but with reduced symmetry because of the superimposed rock-salt pattern of Ni$^{2+}$ and Mn$^{4+}$ cations. By analogy with our previous paper about BiMnO$_3$ we call this paraelectric phase P. Based on our previous experience in the search of new phases of BiFeO$_3$ BiCoO$_3$, and BiMnO$_3$ we also relaxed ferroelectric phases similar to the rhombohedral ground state of BiFeO$_3$ (so-called R phases) and to the supertetragonal ground state of BiCoO$_3$ (so-called T phases); we have enforced the same rock-salt cation pattern known to exist in both experimentally characterized phases of Bi$_2$NiMnO$_6$. We have optimized these structures using the DFT+U and the HSE06 methods, obtaining similar results with both approaches regarding their structural details. The atomic structure of the resulting optimized structures (with forces converged below 0.015 eV/Å and stress components below 0.1 GPa) is shown in Figure 1 while Table 1 contains the values of several magnitudes of interest for these phases.
TABLE I. Properties of Bi₂NiMnO₆ phases that are local energy minima according to our calculations (with DFT+U and HSE06), and comparison with experiment (from Refs. [33] and [35]). We report the space group, lattice parameters, lattice angles, Wickoff positions, polarization $P$, and energy difference with the GS phase $\Delta E$. GS, $p$, and $R$ label the ground-state phase, the high-temperature paraelectric phase, and the $R$ rhombohedral phase found in this study, respectively.

| Phase | Properties | DFT+U | HSE06 | Exp. |
|-------|------------|-------|-------|------|
| GS    | Space group | $C2/c$ | $C2/c$ | $C2$ |
|       | $a$ (Å)    | 9.3871| 9.3525| 9.4646|
|       | $b$ (Å)    | 5.3739| 5.3558| 5.4230|
|       | $c$ (Å)    | 9.5355| 9.4679| 9.5431|
|       | $\beta$ (°) | 107.64| 107.66| 107.82|
| Mn 1  | $(0.2500, 0.2500, 0.0000)$ | $(0.2500, 0.2500, 0.0000)$ | $(0.257, 0.250, 0.001)$ |
| Ni 1  | $(0.0000, 0.2648, 0.2500)$ | $(0.0000, 0.2609, 0.2500)$ | $(0.00, 0.252, 0.250)$ |
| Ni 2  | – | – | $(0.00, 0.737, 0.750)$ |
| Bi 1  | $(0.6308, 0.2323, 0.1235)$ | $(0.6314, 0.2250, 0.1248)$ | $(0.633, 0.214, 0.128)$ |
| Bi 2  | – | – | $(0.631, 0.772, 0.627)$ |
| O 1   | $(0.5897, 0.1970, 0.5833)$ | $(0.5914, 0.1949, 0.5823)$ | $(0.611, 0.176, 0.599)$ |
| O 2   | $(0.1582, 0.0385, 0.3860)$ | $(0.1602, 0.0344, 0.3860)$ | $(0.146, 0.013, 0.386)$ |
| O 3   | $(0.3498, 0.0350, 0.1577)$ | $(0.3493, 0.0374, 0.1565)$ | $(0.333, -0.021, 0.163)$ |
| O 4   | – | – | $(0.920, 0.279, 0.430)$ |
| O 5   | – | – | $(0.377, 0.941, 0.649)$ |
| O 6   | – | – | $(0.662, 0.453, 0.876)$ |
| $P$ ($\mu$C/cm²) | 0 | 0 | N/A |
| $\Delta E$ (meV/f.u.) | -30 | 24 | – |

$R$ phase properties:

| Phase | Properties | $R3$ | $R3$ | – |
|-------|------------|------|------|---|
|       | $a$ (Å)    | 5.4526| 5.4482| – |
|       | $\alpha$ (°) | 60.35| 60.02| – |
| Mn 1  | $(0.7250, 0.7250, 0.7250)$ | $(0.7208, 0.7208, 0.7208)$ | – |
| Ni 1  | $(0.2284, 0.2284, 0.2284)$ | $(0.2255, 0.2255, 0.2255)$ | – |
| Bi 1  | $(0.0000, 0.0000, 0.0000)$ | $(0.0000, 0.0000, 0.0000)$ | – |
| Bi 2  | $(0.4985, 0.4985, 0.4985)$ | $(0.4987, 0.4987, 0.4987)$ | – |
| O 1   | $(0.4114, -0.0566, 0.5483)$ | $(0.4122, -0.0646, 0.5450)$ | – |
| O 2   | $(0.0330, 0.4609, -0.0967)$ | $(0.0225, 0.4580, -0.1000)$ | – |
| $P$ ($\mu$C/cm²) | 70 | 79 | – |
| $\Delta E$ (meV/f.u.) | -4 | 17 | – |

The main results from Table I is that (i) our attempts to optimize the polar $C2$ phase always ended up in a non-polar structure with $C2/c$ space group; (ii) our PBSsol+U and HSE06 methods give different predictions regarding which phase is the ground state of bulk Bi₂NiMnO₆; (iii) there is a ferromagnetic $R$ phase with large polarization that is competitive with the phases known so far to exist, and (iv) no $T$ phase is obtained as a result of our optimizations. In the following, we provide more details about each of these points.

The original assignment of space group $C2$ to the GS phase[33] was done after obtaining synchrotron X-ray powder diffraction peaks that could be indexed as a monoclinic unit cell with the lattice parameters quoted in
Table I. Because the unit cell was similar to that of BiMnO$_3$, a Rietveld refinement was performed by assuming an initial model related to that of BiMnO$_3$ structure, and the validity of this model seemed satisfactory. At the time, the space group BiMnO$_3$ was being described as C2, but later it was shown\cite{26,27} that it is C2$/c$. While C2$/c$ is centrosymmetric, the C2 space group allows for a polarization along the monoclinic axis; calculations assuming a point-charge model or using the Berry-phase first-principles theory gave a value of around 20 $\mu$C/cm$^2$\cite{28,29,30}. As far as we know, no experimental measurement of the polarization has been done for bulk Bi$_2$NiMnO$_6$.

Our attempts to find a metastable C2 phase for Bi$_2$NiMnO$_6$ failed. Every structure we have set with that space group lowered its energy when their atoms were allowed to move, ending always in the C2$/c$ structure displayed in Fig. 1(a). This also happens for BiMnO$_3$: different C2 structures converge to the same lower-energy C2$/c$ structure\cite{26,27}. We must however mention that previous first-principles calculations\cite{31} did report that a C2 phase was found after optimization (albeit with quite different Wickoff positions than the experimental work).

We have tried to reproduce those calculations using a methodology similar to that of Ref. \cite{31} but by allowing enough relaxation steps the optimized structure slowly converged to the C2$/c$ one presented here. Other first-principles studies of Bi$_2$MnNiO$_6$ were done either fixing the structure to the experimental one\cite{32,33,34} or to the relaxed first-principles one of Ciuciuvara and coworkers.\cite{35}

Further support for the C2$/c$ space group is that the reported C2 structure contains two different environments for the Ni$^{2+}$ ions and one for the Mn$^{4+}$ ions, but there is no explanation so far for this—there are no signs of charge or orbital ordering, for example.

To add to the puzzle of the possible paraelectricity of bulk Bi$_2$NiMnO$_6$, a sizable polarization has indeed been measured in Bi$_2$NiMnO$_6$ films. The group that synthesized this double perovskite for the first time in bulk also grew it as a film on SrTiO$_3$ using pulsed laser deposition.\cite{36} They measured a polarization of 5 $\mu$C/cm$^2$ and a magnetic Curie temperature of 100 K. Their films displayed a pseudotetragonal structure with \(a = b = 3.91\) Å (matching the substrate) and \(c = 3.87\) Å, described as rather different from the bulk one, while keeping the same rock-salt pattern.\cite{36} Using a chemical solution deposition method, Lai et al.\cite{37} grew Bi$_2$NiMnO$_6$ films with and without SrTiO$_3$ buffer layers on a Pt(111)/Ti/SiO$_2$/Si(100) substrate, obtaining polarizations around 6 and 8 $\mu$C/cm$^2$. Again, the situation can be compared to that of BiMnO$_3$, where polarizations between 9 and 23 $\mu$C/cm$^2$ have been reported for films\cite{38,39} even if the bulk is nonpolar. For BiMnO$_3$ we proposed that those measurements might be related to the formation of film phases under strain that are polar.\cite{40}

We move on now to the issue of the predicted ground state by different methodologies. Table I shows that the three local minima of the energy surface of Bi$_2$NiMnO$_6$ lie within only 30 meV per formula unit (five-atom group of the standard perovskite unit cell; in our case, BiNi$_{1/2}$Mn$_{1/2}$O$_3$). Our DFT+U method predicts a higher energy for the GS phase than for the other two; this happened too for BiMnO$_3$\cite{41} where the situation is corrected by the HSE06 hybrid. We have shown in the past that different exchange-correlation functionals predict almost the same minima of the energy surface of BiMnO$_3$\cite{42} and BiFeO$_3$\cite{43} although how those minima are ordered in energy can vary from functional to functional. As for BiMnO$_3$, here we use the fast DFT+U method when we are interested in finding possible energy minima, or when we are interested in energy differences between very similar structures, while we will resort to the more accurate and slow HSE06 when it is important to evaluate energy differences between different phases.

Both DFT+U and HSE06 predict that there exists a metastable ferromagnetic rhombohedral structure with a polarization around 70 $\mu$C/cm$^2$ when computed using the Berry-phase formalism (we have checked that typical antiferromagnetic alignments are higher in energy; details are given later for similar films). This is a structure like that of bulk BiFeO$_3$, but where the superimposed rock-salt pattern of Mn$^{4+}$ and Ni$^{2+}$ causes a reduction from the $R3$ space group to the $R3$ symmetry; it is represented in Fig. 1(c). According to first principles calculations, a similar structure is also metastable for BiCoO$_3$\cite{44} and BiMnO$_3$\cite{45}.

Regarding the electronic structure, the GS, $p$, and $R$ phases display similar density of states profiles, as shown in Fig. 2 (this was also the case for different phases in BiFeO$_3$\cite{46}). The band gap in all cases is around 1 eV.

Unlike in BiCoO$_3$, BiFeO$_3$, and BiMnO$_3$, no $T$ structures appeared as local minima of the energy in our Bi$_2$NiMnO$_3$ search. We relaxed variations of the $T$ con-
figurations of those other materials with the added rock-salt pattern of Mn$^{4+}$ and Ni$^{2+}$, but the resulting structure was always one of the other three local minima.

B. Epitaxial Films

One possible way to stabilize a metastable phase of the bulk of a material is to grow it as a thin film on a substrate; in this way, the epitaxial misfit strain acts as a handle to vary the relative energies of the possible bulk phases. We have simulated coherent epitaxial (001) films of Bi$_3$NiMnO$_9$ by doing calculations of the bulk material where we impose mechanical boundary conditions determined by the lattice constant of the substrate, assumed to display in-plane square symmetry (this is indeed the case for many perovskite substrates cut perpendicularly to one of the principal axes).

As a starting point, we adapted the three bulk phases described in the previous section to the in-plane square symmetry. There are two inequivalent ways to do this for the GS and $p$ phases, and one way for the $R$ phase, as shown in Fig. 1. This causes small distortions to bring the in-plane lattice vectors to form a 90° angle and to be of the same magnitude (in the adapted $p$ and $R$ phases) or of a ratio of magnitudes equal to two (in the GS phase). In all cases, those distortions cost only a few meV per formula unit. Then, we do calculations in which we expand or contract the lattice vectors to mimic the effect of squared substrates with different lattice constants. We do this in intervals of 0.05 Å, and we use the Wickoff positions and out-of-plane lattice vector of the previous geometry as a starting point of the next geometry relaxation. In this way, we arrive at a graphic of the energy of the films as a function of in-plane lattice constant that we show in Fig. 3 (top). These calculations were done using the DFT+$U$ method.

For strains around the minimum of the energy curves the adopted configuration is paraelectric. However, for high enough tensile strains the $R$ phase has lower energy than the other phases. These strains correspond to in-plane lattice constants of the order of 4 Å, so this phase is expected to appear if the films are grown over perovskite oxides such as BaTiO$_3$ or PbZr$_{1-x}$Ti$_x$O$_3$ (PZT). Figure 3 (bottom) shows that the computed polarization of the films is similar to the 70 µC/cm$^2$ of the bulk phase. The electronic structure of the films is very similar to that of the bulk, as illustrated in Fig. 2 for the film with in-plane lattice parameter $a = 4$ Å.

All GS, $p$, and $R$ films at tensile epitaxial strains have magnetic cations with magnetic moments around 3$\mu_B$ for Mn$^{4+}$ and around 2$\mu_B$ for Ni$^{2+}$. Figure 2(a) shows that below in-plane lattice parameters around 4.05 Å ferromagnetism prevails over the alternative antiferromagnetic orderings typical of perovskites: G type (antiferromagnetism in-plane and out-of-plane), C type (ferromagnetism out-of-plane), and A type (ferromagnetism in-plane). This is not surprising, since the network of transition-metal ions and oxygens connecting them has angles and bond lengths similar to those of the bulk network, known to be ferromagnetic.

Following a prescription we have described in earlier articles, we have used the DFT+$U$ energy differences between magnetic arrangements to fit a simplified Heisenberg model. This model has as parameters two exchange constants $J_\parallel$ and $J_\perp$ that take into account the strength of the magnetic interaction between neighboring Ni–Mn pairs in plane and out of plane, respectively; their values are represented in Fig. 2(b). A Monte Carlo method on a lattice of $20 \times 20 \times 20$ spins was used with this Heisenberg model to study the behaviour of the magnetic ordering with temperature. Doing this, we found that the ferromagnetic order parameter takes values other than zero for temperatures below a Curie point of around 100 K, as shown in Fig. 2(c); this is in agreement with experimental measurements done in Bi$_2$NiMnO$_3$ films. The magnetic susceptibility computed from the Monte Carlo simulations with this Heisenberg model is plotted in Fig. 2(d).

The results for films presented so far were obtained using DFT+$U$ calculations. As for BiMnO$_3$, this methodology does not resolve the close energy differences between phases in agreement with experiment, but the HSE06 hybrid functional does. When we applied it to do computations for tensile films of Bi$_2$NiMnO$_6$ it also predicted that the $R$ phase is the most stable one for large enough strains, as shown in Fig. 3.

In order to further explore the energy surface of bulk
Bi$_2$NiMnO$_6$ in the search of minima that might be relevant in films, we did one more set of calculations. We took every film structure represented by a point in Fig. 3, removed the epitaxial constraints, performed a few steps of molecular dynamics to allow it to explore its surroundings, and relaxed this structure until the forces and stresses were almost zero. During this annealing process the atoms visited structures that were up to a few eV/fu higher in energy than the ground state. By the end of the search, most of the initial structures had converged to a higher in energy than the ground state. By the end of the search, most of the initial structures had converged to a higher in energy than the ground state. By the end of the search, most of the initial structures had converged to a higher in energy than the ground state.

Our first-principles calculations for bulk Bi$_2$NiMnO$_6$ are consistent with a non-polar crystal structure of space group $C2/c$. Previous reports pointed out to a (001)-oriented perovskite substrate of materials such as BaTiO$_3$ or PZT the epitaxial strain should favour a phase that is both ferroelectric and ferromagnetic. The polarization of these films is around $70 \mu$C/cm$^2$, similar to that of the most used ferroelectric materials. The films are predicted to be ferromagnetic with magnetic moments of $2.5 \mu_B$ per formula unit and a Curie temperature of around 100 K. Thus, our simulations predict that, in thin film form, Bi$_2$NiMnO$_6$ is one
of the very few known magnetoelectric multiferroics with
a strong ferromagnetic order.

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