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BiFeO₃ films under tensile epitaxial strain from first-principles

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Density-functional calculations are performed to predict structural and magnetic properties of (001) BiFeO₃ films under tensile epitaxial strain. These films remain monoclinic (*Cc* space group) for misfit strains between 0% and $\approx 8\%$, with the polarization, tilt axis and magnetization all rotating when varying the strain. At a tensile strain $\approx 8\%$, these films undergo a first-order phase transition towards an orthorhombic phase (*Ima2* space group). In this novel phase, the polarization and tilt axis lie in the epitaxial plane, while the magnetization is along the out-of-plane direction and the direction of the antiferromagnetic vector is unchanged by the phase transition. An unexpected additional degree of freedom, namely an antiphase arrangement of Bi atoms, is also found for all tensile strains.

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Multiferroic compounds are very challenging and fascinating systems in which several order parameters (polarization, strain, magnetism, tilting of oxygen octahedra, etc...) coexist and exhibit subtle interplays [1]. Understanding the properties of such materials is not only a fundamental challenge of modern condensed matter physics but also a strong requirement in view of future applications. Among multiferroic materials, BiFeO₃ (BFO) is unique because it exhibits both ferroelectricity (polar order) and antiferromagnetism (magnetic order) at room temperature, making it a potential candidate for various applications in spintronics [2].

In its bulk rhombohedral *R3c* ground state, BFO possesses a large polarization $\approx 90 \mu\text{C}/\text{cm}^2$ along the pseudo-cubic [111] direction, coupled to strong antiferrodistortive (AFD) motions about the same axis [3]. The magnetic structure of BFO systems is rather complex. As a matter of fact, the long-period cycloidal spin modulation existing in the bulk [4, 5] disappears in epitaxial films [6–8] in favor of a canted spin-configuration in which a strong G-type antiferromagnetism coexists with a weak ferromagnetism. In most potential devices, BFO would be epitaxially grown as a *thin film*, therefore experiencing a compressive or tensile strain arising from the substrate. Interestingly, theoretical and experimental studies have recently evidenced many unexpected features in *compressively*-strained (001) BFO films. Remarkable examples include (i) a decrease of the Curie temperature with the magnitude of the compressive strain [9] that contrasts with the case of "classical" ferroelectrics such as BaTiO₃ [10–12]. This decrease was attributed to a strain-induced competition between the polarization and the oxygen octahedra tilts; and (ii) a phase transition for misfit strains $\approx -5\%$ showing that BFO can sustain rather large misfit strain, leading to the appearance of a novel phase having high-tetragonality ($c/a \approx 1.23$ or more) [13–16] (note also that magnetoelectric coefficients are dra-

matically enhanced just before this transition [17, 18]).

While the last years efforts were concentrated on the compressive strain effects, surprisingly, the tensile part of the phase diagram of BFO films remains mostly unexplored [9, 19] despite the possibility of discovering new phenomena. The aim of this Letter is therefore to explore the tensile part of the phase diagram of (001) BFO films by using first-principles calculations. In particular, a novel strain-induced orthorhombic phase accompanied by the occurrence of a giant polarization and a spin-flip of the magnetization is found at high misfit strain. Another order parameter is also discovered for all non zero tensile misfit strains, in addition to polarization, oxygen octahedra tiltings, antiferromagnetic vector and magnetization. Such order parameter is associated with peculiar in-plane antiphase displacement of Bi atoms.

We have performed density-functional calculations within the Local Spin Density Approximation (LSDA), using the SIESTA [20, 21] (with Troullier-Martins pseudopotentials) and VASP [22–25] (in the Projector Augmented Wave formalism) codes. Moreover and as done in Refs. [15–17], the only difference we assume compared to the simulation of a BFO bulk is that in epitaxial (001) BFO films, some components of the strain tensor, $\{\eta\}$, are frozen, while the others are relaxed. More precisely, mechanical boundary conditions of this film are mimicked by imposing that (in the basis for which the x -, y - and z -axis lie along the pseudo-cubic [100], [010] and [001] directions, respectively) $\eta_{xy} = \eta_{yx} = 0$ and $\eta_{xx} = \eta_{yy} = \delta$, with δ being the value forcing the film to adopt the in-plane lattice constant of the (cubic) substrate [10–12]. The various configurations are optimized by making the σ_{zz} , σ_{xz} , σ_{zx} , σ_{yz} and σ_{zy} components of the stress tensor as well as the atomic forces vanish. σ_{xx} , σ_{yy} , σ_{xy} and σ_{yx} are thus non zero and obtained from the DFT calculation as the epitaxial stress. The reference for the calculation of the diagonal components of the strain tensor η_{xx} and

η_{yy} is the lattice constant of bulk rhombohedral BFO in the LSDA approximation.

Technically, we employ a 20-atom supercell with a unit cell being doubled along the z direction and rotated by 45° in-plane (in terms of the pseudocubic cell of BFO), in which a G-type antiferromagnetism is enforced. Different configurations, corresponding to different epitaxial strains ranging between 0% and +11.5%, are first optimized using the SIESTA code using a *collinear magnetism* scheme. These calculations allow us to extract many physical quantities such as the total energy profile, the polarization, the antiferrodistortive angles and the stress, as a function of epitaxial strain [26]. For each simulated δ strain, the ground state structure predicted with the SIESTA code is then used as an input of additional calculations, that are performed with the VASP code and that include *non-collinear magnetism* and spin-orbit coupling. These latter simulations allow to predict, for a given direction of the antiferromagnetic vector, the magnitude and direction of the magnetization (if any).

At this point we emphasize that, above misfit strains of a few percent, BFO films can exhibit strain relaxation through interface dislocations or microcracks and thus cannot be achieved. However, such relaxation occurs above a given thickness. It is also important to realize that, in the compressive part of the phase diagram, BFO films have been grown without strain relaxation (at least for films of several tens of nanometers) up to large compressive strains of $\approx -4.5/5\%$ on LaAlO_3 substrates [16], and even of the order of -7% in the case of YAlO_3 substrates [14]. BFO is thus, from this point of view, very unusual. This is probably due to the complex interplay between ferroelectric and AFD degrees of freedom, that coexist in BFO, and that dramatically vary with strain, allowing the appearance of new local minima with different equilibrium lattice constants. Moreover, new phases predicted at high tensile strain at $T = 0$ K can usually be observed at lower strain but for finite temperature [10, 12]. Such considerations justify our study of BFO films up to large misfit strain.

Figure 1 gathers the structural, polar and magnetic properties of BFO films under tensile strain up to 11.5%. A clear phase transition occurs around $\delta \approx 8\%$, that we will discuss later. Let us first focus on the misfit strain region for which $\delta \leq 8\%$. Figure 1 indicates that, in this region, the optimized structure is monoclinic and belongs to the Cc space group that is naturally expected from the epitaxy of the bulk rhombohedral $R3c$ structure on a cubic substrate. Interestingly, the same space group is found in the compressive part between 0% and $\approx -5\%$ [9, 13–17]. However, for δ ranging between 0% and $\approx 8\%$, the out-of-plane component of the polarization decreases continuously with the strain magnitude whereas its in-plane component increases, while opposite behaviors were found for the compressive region of the Cc space group. As a consequence, the polarization \mathbf{P} globally in-

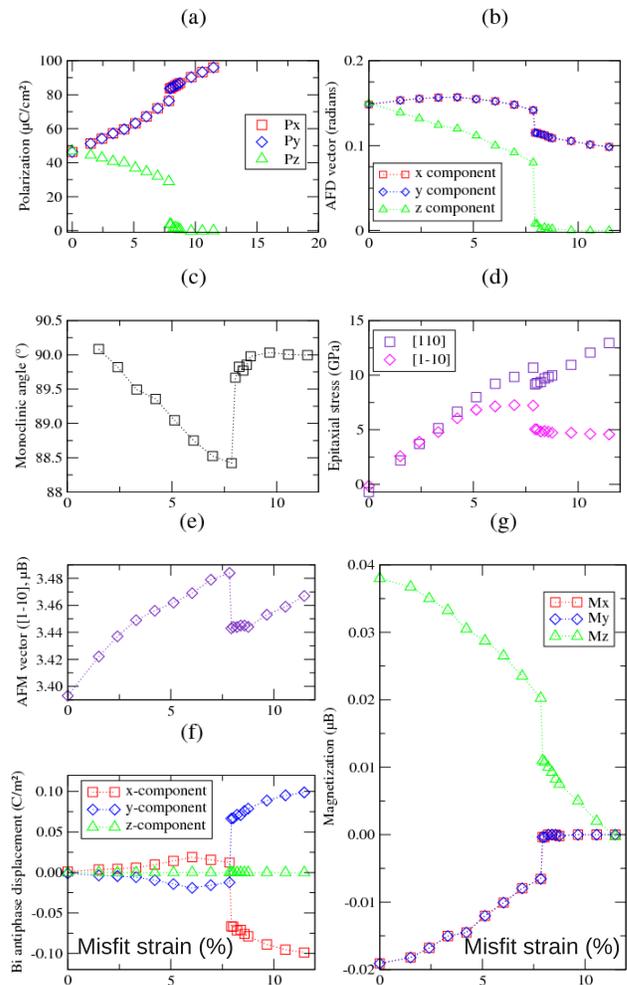


FIG. 1: Physical properties of (001) BFO films as a function of tensile misfit strain. Panel (a) shows the polarization in $\mu\text{C}/\text{cm}^2$, while Panel (b) displays the Cartesian components of the AFD vector in radians. Panels (c) and (d) represent the monoclinic angle and epitaxial stress, respectively. Panel (e) shows the magnitude of the antiferromagnetic vector, while Panel (g) displays the Cartesian components of the magnetization (for the most stable direction of the antiferromagnetic vector, *i.e.*, $[1 \bar{1} 0]$). These magnetic moments are expressed in Bohr magneton per Fe atom. Panel (f) displays the x, y and z-components of the order parameter quantifying the Bi antiphase displacements. The lines are guides for the eyes.

creases in magnitude and continuously rotates by bending towards the epitaxial plane (from $\approx 35^\circ$ to 15°), as the tensile strain increases from 0% to $\approx 8\%$ (Fig. 1-(a)). Let us now take a look at the AFD vector, defined such as its direction characterizes the axis about which the oxygen octahedra tilt, while its magnitude corresponds to the angle of such tilt. Figure 1-b shows that the in-plane x- and y-components of the AFD vector remain quasi-constant ≈ 0.15 radians (8.6°) whereas its z-component is linearly reduced with strain by up to $\approx 50\%$ in the

tensile part of the Cc phase. The axis about which the oxygen octahedra tilt thus also rotates when varying the tensile strain. Furthermore, the monoclinic angle that is a characteristic of this Cc state decreases from $\approx 90.5^\circ$ to 88.5° (Fig. 1-(c)). Interestingly, a peculiar additional displacement pattern – that is absent at 0 % misfit strain – is further observed in this Cc phase. It corresponds to nearest-neighbor Bi atoms moving in opposite directions, parallel or antiparallel to the $[1 \bar{1} 0]$ pseudo-cubic direction. Such Bi antiphase displacements, that are denoted as BAD in the following, therefore occur within the epitaxial plane and are orthogonal to both the polarization and the AFD vector [27]. We quantify them by computing the order parameter \mathbf{gp} having the following α Cartesian components: $gp_\alpha = \frac{1}{V} \sum_j Z_{Bi,\alpha\alpha}^* \delta r_{j,\alpha}^{Bi} e^{i\vec{k}_{\bar{R}} \cdot \vec{R}_j}$,

where \vec{R}_j locates the center of the j^{th} 5-atom cell, $\vec{k}_{\bar{R}}$ is the R point of the Brillouin zone associated with 5-atom cells, and $\delta r_{j,\alpha}^{Bi}$ is the α -component of the displacement of the Bi atom in the j^{th} 5-atom cell (with respect to a centrosymmetric configuration). Finally, Z_{Bi}^* is the effective charge tensor of Bi atoms and V is the supercell volume. The sum runs over all the 5-atom cells j belonging to the supercell. The evolution of the \mathbf{gp} vector with respect to misfit strain is shown in Fig. 1-(f). One can see that the BAD first increase in magnitude between 0 % and ≈ 6 % and decreases for higher strain in the Cc phase, thus exhibiting a maximum (0.02 C/m^2) at ≈ 6 %.

In this monoclinic phase, the aforementioned calculations using the VASP code allow us to get insight into magnetism. Practically, for each considered epitaxial tensile strain, the electronic structure was recomputed for three different choices for the direction of the antiferromagnetic vector, \mathbf{L} : along the $[110]$ pseudo-cubic direction (that precisely coincides with the in-plane component of the polarization \mathbf{P}), along the $[1\bar{1}0]$ pseudocubic direction (that is still an in-plane direction but that is now perpendicular to the in-plane component of the polarization) and along the (out-of-plane) $[001]$ pseudocubic direction. For any considered tensile strain, the lowest energy is provided when \mathbf{L} lies along the $[1\bar{1}0]$ easy axis, which is in excellent agreement with the recent measurements of Ref. [19] in (001) BFO films under tensile strain. Based on this experimental evidence, we did not try to set \mathbf{L} along other directions.

The magnitude of the antiferromagnetic vector and components of the magnetization resulting from the spin canting are shown in Figs. 1 (e) and (g), respectively (when \mathbf{L} lies along $[1\bar{1}0]$). The magnitude of \mathbf{L} only slightly (relatively) increases with the tensile strain in the Cc phase. On the other hand, the weak magnetization arising from the canted spin-arrangement significantly (relatively) decreases its magnitude at the same time (Fig. 1 (g)), as a result of the fact that this weak

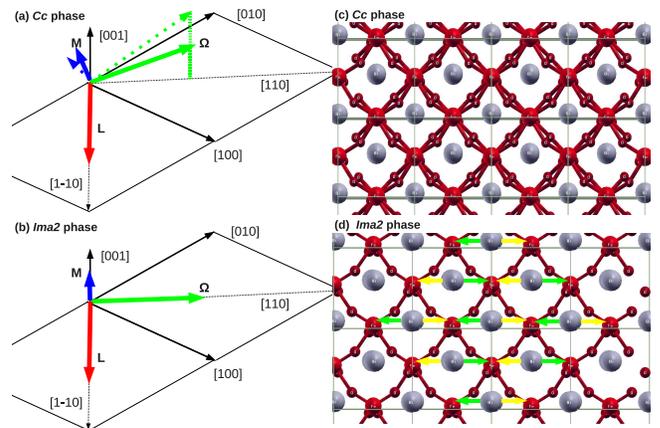


FIG. 2: Left panel: schematic view of the antiferrodistortive vector Ω , antiferromagnetic vector \mathbf{L} and magnetization \mathbf{M} in the two phases found in the present work: (a) Cc phase; (b) $Ima2$ phase. In panel (a), the solid and dashed arrows are related to two different tensile epitaxial strain (low strain in the dashed case, higher strain in the solid case). Right Panel: top view ($[001]$ axis perpendicular to the picture) of the two phases observed under tensile epitaxial strain. (c): Cc monoclinic phase (tensile strain smaller than $\approx 8\%$), with the oxygen octahedra tilting around $[001]$, as well as, the ferroelectric distortions (in-plane component of the polarization *i.e.* along the pseudocubic $[110]$ direction) being clearly visible. (d): $Ima2$ orthorhombic phase (tensile strain larger than $\approx 8\%$), with the very strong ferroelectric distortions being clearly visible, as well as the Bi antiphase displacements (that also exist in the Cc phase). The yellow and green arrows feature these Bi motions in two consecutive planes perpendicular to the out-of-plane direction, illustrating the antiphase character of this displacement pattern.

magnetization is driven by the coupling between magnetism and oxygen octahedra tiltings [7, 8], and that these tilts are decreasing in magnitude when increasing the strength of the tensile strain, see Fig. 1-(b). More importantly, Fig. 1-(g) reveals that the magnetization *rotates* from a $[\bar{1}\bar{1}2]$ to a $\approx [\bar{1}\bar{1}3]$ pseudo-cubic direction (Fig. 2), when the tensile strain increases from 0% to $\approx 8\%$. Such rotation occurs in order to allow the magnetization to remain perpendicular to the axis about which the oxygen octahedra tilt for any tensile strain in the Cc state.

One additional and important information revealed by Figs. 1 is that (001) BFO films undergo a first-order strain-driven phase transition from the monoclinic Cc phase to an orthorhombic $Ima2$ phase for $\delta \approx 8\%$. In this novel latter phase, both the polarization and the AFD vector lie in the epitaxial plane along the same $[110]$ direction. We are not aware of any previous finding reporting the existence of a $Ima2$ state in BFO films [28]. In this newly discovered orthorhombic phase, the polarization reaches very high values $\approx 120\text{-}130 \mu\text{C/cm}^2$ that further increase with the tensile strain. On the

other hand, the oxygen octahedra tiltings become weaker (Fig. 1 -(b)), which therefore results in the reduction of the magnitude of the magnetization (Fig. 1-(g)). Note that the most stable direction for the antiferromagnetic vector in the *Ima2* phase is still the easy $[1\bar{1}0]$ -axis, as in the *Cc* state. Interestingly, the magnetization arising from the spin canting has now suddenly moved to be along the out-of-plane $[001]$ direction at the *Cc*-to-*Ima2* transition as shown schematically in Fig. 2, in order to remain perpendicular to the AFD vector. The spin-flip of the magnetization towards the $[001]$ pseudocubic direction, in addition to the structural and polar softness during this phase transition, may result in huge magnetoelectric effects [17, 18]. This phase transition is also numerically found (see Fig. 1d) to induce a strong relaxation of the epitaxial stress $([\sigma_{[110]} + \sigma_{[1\bar{1}0]}])/2$ discontinuously jumps from ≈ 9 GPa to ≈ 7 GPa – both components are strongly relaxed. This discontinuity confirms the first-order character of this transition (note that a strong first-order phase transition also occurs at the ferroelectric-to-paraelectric phase transition in bulk BFO with a strong variation of the volume of the order of 1.4% [30]). Interestingly, the BAD are also significant in the *Ima2* phase (see Fig. 2d), with each component of **gp** changing its sign at the phase transition (see Fig. 1f).

Among substrates favourable to the appearance of this orthorhombic phase, one might think of alkaline-earth oxides with rocksalt structure. Also, this new phase is likely to occur at smaller misfit strain at *finite* temperature, since novel phases usually appear at smaller strain when the temperature is increased, as can be inferred for instance from the temperature-misfit strain diagram of standard ferroelectrics such as barium titanate [10, 12]. This novel orthorhombic phase possesses similarities with the high-tetragonality phase that has been found in the highly compressive part of the phase diagram of (001) BFO film [13–17]: indeed, the oxygen octahedra are strongly distorted as shown in Fig. 2 with four Fe-O bonds being similar and relatively short while two Fe-O bonds being strongly stretched in-plane (in the compressive part, only one Fe-O bond is strongly elongated out-of-plane). For instance, at 9.66 % misfit strain, the short Fe-O distances are 1.94 (in-plane), 1.94 (in-plane), 1.89 (out-of-plane) and 1.89 Å (out-of-plane) while the two other Fe-O distances (that are in-plane) are 2.44 Å. These strong ferroelectric distortions are responsible for the large value of the (in-plane) polarization in this orthorhombic phase.

In this work, we have studied, from first-principles, structural, polar and magnetic properties of (001) BFO films under tensile epitaxial strain. We have found that these important materials (i) remain in a monoclinic *Cc* phase exhibiting oxygen octahedra tilts and non-zero components of the polarization along x , y and z between 0 and $\approx 8\%$, with both the axis about which the oxygen octahedra tilt and the polarization rotating with

the magnitude of the strain; (ii) undergo a first-order strain-driven phase transition, at $\delta=8\%$, towards a novel orthorhombic phase of *Ima2* space group in which the tilts and the polarization have no out-of-plane components; and (iii) exhibit an antiphase displacement pattern (involving mainly Bi atoms) in both the *Cc* and *Ima2* phases. For all investigated tensile strains, the antiferromagnetic vector is found to be the most stable along an in-plane $[1\bar{1}0]$ direction, among three directions tested ($[1\bar{1}0]$, $[110]$ and $[001]$). This allows **L** to remain perpendicular to both the polarization and AFD vector for any strain. Moreover, the *Cc* and *Ima2* phases both exhibit a weak ferromagnetic vector (coming from a spin canting), with this vector rotating and decreasing in magnitude with strain in the *Cc* state while it flips along the out-of-plane direction in the *Ima2* phase. In other words, tensile strain not only controls the direction and magnitude of several structural order parameters (namely, the polarization, AFD vector and Bi antiphase displacements), but also affects the direction and magnitude of magnetization. Some magnetoelectric coefficients may thus be dramatically modified by tensile strains in (001) BFO films. We hope that our study is of large benefits to the active research fields of multiferroics and nanoscience, by, e.g., opening a new route for further investigations in BFO phase diagrams.

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