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## Development of an Atomic Level Model for BiFeO<sub>3</sub> from First-Principles

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We develop a first-principles atomistic shell model for  $BiFeO_3$  to study its ferroelectric and structural properties at finite temperature. The parameters of the potential are adjusted to reproduce first-principles results in different relevant configurations. Molecular dynamics simulations show that the resulting model is able to describe the ground-state ferroelectric R3c structure which remains stable as the temperature increases. At about 1100 K, system displays a first-order phase transition to the paraelectric Pbnm phase. Our results indicate that the developed model captures the delicate structural behavior shown by the ab-initio calculations and is able to reproduce the temperature behavior observed in experiments.

Keywords Multiferroics; atomistic simulations; phase transitions; BiFeO<sub>3</sub>

#### Introduction

The perovskite oxide BiFeO<sub>3</sub> (BFO) is attracting much attention due to its unique properties and potential applications. BFO is, without doubt, the prototype compound for understanding multiferroic materials because it displays simultaneously ferroelectric (FE) and ferromagnetic properties at room temperature [1–3]. Even more, the interest in the BFO is not restricted to magnetoelectric properties. Its lead-free composition, high remnant polarization and high Curie temperature make it an attractive ferroelectric compound to environmentally friendly devices [4, 5]. Despite the efforts to understand its behavior, several aspects of are still controversial. For instance the nature of the phase above the Curie remains poorly undestood [6–8].

BFO can be considered as a highly distorted perovskite whose structure is usually described in terms of atomic displacements with respect to the ideal cubic configuration with Pm-3m symmetry [9]. The dominant distortions that present the high-symmetry reference structure correspond to the rotation of the oxygen octahedra and the off-center displacements of Bi cations. The ground state, for instance, has a ferroelectric rhombohedral symmetry with R3c space group and contains two formula units of the five-atom perovskite unit cell. In the structure, oxygen octahedra rotate around pseudocubic [111] direction with an antiferrodistortive pattern. In addition, Bi ions move with respect to O along the same

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direction, and their relative atomic displacements give raise the electric polarization. At  $T_{\rm C} = 1100$  K, the system transforms to an orthorhombic *Pbnm* phase that contains four formula units and is characterized by anti-phase oxygen rotations around [110] and in-phase rotations around [001] [10]. More complex combinations of both instabilities give rise to a wide variety of metastable phases that may become stable under strain, pressure, doping, and/or temperature [11].

First-principle calculations have contributed greatly to the understanding of the electronic structure and structural instabilities of BFO [12–16]. Nevertheless these methods are restricted to studying zero-temperature properties, and it is necessary to combine firstprinciple calculations with simple models to investigate finite temperature in large size systems. Recently, two different theoretical approaches were developed to investigate finitetemperatures properties in BFO [8, 17]. Although both methods were able to reproduce the observed low-temperature behavior, they display contradictory results for temperatures near and above  $T_{\rm C}$ . An alternative description that contributes to better understand the complex behavior of this system is highly desirable. In this work we present the development of an atomic level potential for BFO based on the shell-model description in order to simulate its behavior at finite temperature.

#### The Model

Atomic level simulations with the shell-model approach have been extensively used to study ferroelectric oxides [18, 19]. In the model, atoms are thought to consist of an ion core coupled to an "electronic" shell in order to include its electronic polarization (P). In this work, the core-shell coupling is described through an anharmonic spring described as  $V(\omega) = 1/2k_2\omega^2 + 1/24 k_4\omega^4$ , where  $\omega$  is the core-shell displacement. The model also includes electrostatic interactions among cores and shells of different atoms, and short-range interactions between shells described by a Rydberg potential,  $V(r) = (a+Br)exp(-r/\rho)$ . In addition, a Fe-O-Fe three-body bond bending term is included to improve the directional character of that interaction, represented by  $V_B(\theta) = \frac{1}{2} k_B (\cos(\theta) - \cos(\theta_0))^2$  where  $\theta_0$  is the equilibrium bond angle.

The input data to adjust the model parameters were obtained using the local-density approximation (LDA) to the density functional theory as implemented in the *ab-initio* VASP package [20], including the so-called LDA+U correction of Dudarev *et al.* [21] for a better treatment of iron's 3*d* electrons, and according to Ref. [13]. A G-type antiferromagnetic arrangement of Fe atom spins is assumed. Calculations were made considering a 40-atom cell, which allows the low-symmetry and low-energy structures that the compound presents [16]. The data correspond to values of total energies, forces on atoms and stresses at several volumes and different atomic distortions. We note that model results could depend on the choice of the exchange-correlation (XC) used to generate the required information. While the ground state of the compound is described correctly by various XC, energy differences between other possible stable or metastable phases are strongly dependent on the DFT functional [15, 16]. Since the information is translated to the model parameters in the fitting procedure, at the end it is expected that the temperature behavior described by the model will be affected by the XC. We choose LDA+U because it is often the preferred approach in the literature. The model parameters were adjusted using a least-square procedure.

Our first test is to employ the obtained model to relax different symmetry structures at zero temperature and compare them with the first-principles results used as reference data in the fitting procedure. The structural parameters for the R3c and Pbnm phases are

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Table 1
Optimized structures for BiFeO <sub>3</sub> in space groups R3c and Pbnm obtained with the model
and LDA calculations. Experimental values are included for comparison

			R3c		
Atom	Wyc.	Position	Model	LDA + U	Exp.
Bi	2a	х	0	0	0
Fe	2a	х	0.221	0.227	0.221
0	6b	х	0.531	0.54	0.538
		у	0.935	0.94	0.933
		Ζ	0.394	0.40	0.395
	a = b = c =		5.52 Å	5.52 Å	5.63Å
	$lpha=eta=\gamma=$		<b>59</b> .1°	<b>59.84</b> °	59.35°
			Pbnm		
Atom	Wyc.	Position	Model	PBEsol + U	Exp[10].
Bi	4c	х	-0.002	0.01	-0.001
		у	0.038	0.052	0.023
		Z	0.266	0.25	0.25
Fe	4b	х	0.5	0.5	0.5
		У	0	0	0
		Z	0	0	0
0	4c	Х	0.595	0.595	0.566
		У	0.972	0.972	0.979
		Z	0.25	0.25	0.25
0	8d	Х	0.304	0.304	0.212
		У	0.3	0.299	0.289
		Z	0.046	0.046	0.032
	а		5.42 Å	5.421Å	5.613Å
	b		5.54 Å	5.65 Å	5.647Å
	с		7.66 Å	7.77 Å	7.971Å

listed in Table 1. First, note that the model is able to reproduce correctly the ground state of BFO yielding as the lowest-energy configuration the rhombohedral *R3c* phase. Its lattice parameter coincides with the LDA+U result of a = 5.52 Å, although it is underestimated with respect to the experimental value of a = 5.63 Å [22]. The rhombohedral angle of 59.1° is also comparable to the LDA+U value of 59.78°, as well as the relative coordinates of the relaxed rhombohedral structure obtained by the model are in close agreement with LDA+U results. The model spontaneous polarization is  $P = 78 \,\mu\text{C/cm}^2$ , which is slightly underestimated with respect to the LDA+U value of 87.3  $\mu\text{C/cm}^2$ . Concerning the *Pbnm* structure, it is 17 meV/f.u above the *R3c* ground-state, in excellent agreement with the 14 meV/f.u. obtained with the LDA+U functional. The lattice parameters and relative atomic positions corresponding to the model relaxed structure are also in good agreement with the first-principles results, as seen in Table 1.

Figure 1 shows the energy pathway as a function of the atomic displacements that closely connects the two most-stable phases *Pbnm* and *R3c*, left and right panel, respectively.



**Figure 1.** Total energy as functions of atomic displacements from an *Imma* phase towards a *Pbnm* (left panel) and *R3c* (right panel). Atoms are moved following the pattern of the LDA relaxed structure, which is taken as the unit.

All calculations were done in a cubic cell with the same lattice parameter of the R3c structure, a = 3.90 Å. Note also that the energy curves are not referred to the prototype cubic Pm-3m phase which is 870 meV/f.u. above the R3c ground state, instead we use an *Imma* phase which is only 270 meV/f.u. above R3c. This phase is characterized by the anti-phase rotation of oxygen octahedron around the x and y axes ( $a^-a^-0$  in Glazer's notation), while Bi displacements are inhibited. Although this phase is not stable (the Bi ions tend to move from their ideal positions), one can reach the phases of interest by simple atomic displacements. The R3c structure is obtained by adding anti-phase  $O_6$  tilting along [001] ( $00a^-$ ), plus a polar atomic displacement along [111], whereas the *Pbnm* phase is reached with an additional in-phase tilting along [001] ( $00a^+$ ), and Bi displacements along [110]. The atomic-displacement pattern that defines each relaxed phase computed from first-principles (taken as the unity in the Fig.) is followed to move the atoms. As seen, the model reproduces the BFO instabilities with similar energetics and minimum locations to the LDA + U calculations. These results suggest that the model is able to capture the complex energy landscape that characterizes BFO.

#### **Molecular Dynamics Results**

We apply the potential to simulate the finite temperature behavior of compound. Molecular Dynamics (MD) simulations were carried out using the DL-POLY code [23] within a constant stress and temperature (N, $\sigma$ ,T) ensemble. A supercell size of 12 × 12 × 12 5-atom unit cells (8640 atoms) was used with periodic boundary conditions. The runs were made at temperature intervals of 50 K, and each MD run consists of 20000 time steps for thermalization and 40000 time steps for data collection, with a time step of 0.4 fs.

Figure 2 displays the temperature evolution of the relevant magnitudes that characterize the compound behavior: lattice parameters along pseudo-cubic directions are shown in (a), net polarization in (b), and oxygen octahedral tilting pattern in (c). The anti-phase tilting



**Figure 2.** Phase diagram of  $BiFeO_3$  at zero pressure resulting from the MD simulations. Thermal evolution of lattice parameters (a), net polarization (b) and oxygen octahedra tilting (c).

oxygen octahedra is described by  $\omega_R = 1/N \sum_i \omega_i (-1)^{n_x(i)+n_y(i)+n_z(i)}$ , where  $n_x$ ,  $n_y$  and  $n_z$  are integers that gives the position of the *i*-cell in the pseudo-cubic box. The in-phase oxygen octahedra tilting along z corresponds to  $\omega_M = 1/N \sum_i \omega_i (-1)^{n_x(i)+n_y(i)}$  [8].

At low-temperatures, the *R3c* phase is characterized by identical values of cell parameters (a = b = c), a macroscopic polarization pointing along the [111] direction ( $P_x = P_y = P_z$ ), and an anti-phase octahedral tilting pattern along the [111] direction ( $\omega_{Rx} = \omega_{Ry} = \omega_{Rz}$ ). The model results are in reasonable agreement with experimental values, although the fact that cell parameters are underestimated might be a result of the LDA input data used to fit the potential. At room-temperature, for instance, the model gives a spontaneous polarization  $P = 77 \ \mu \text{C/cm}^2$  which is comparable with the 60 – 100  $\mu \text{C/cm}^2$  reported for single crystals [24]. The obtained oxygen octahedral tilting around the polar axis of 13.8°, agrees well with 11° – 13° reported in the experiments [3].

The transition to a *Pbnm* phase with a strong first-order character is also correctly reproduced by our model description. The transition takes place at  $T_{\rm C} = 1100$  K in coincidence with the experiments. We note, however, that we would have expected a lower  $T_{\rm C}$  as a result of LDA data used in the model fitting. At  $T_{\rm C}$  sudden changes in the system properties are observed. Lattice parameters, that came growing with temperature in the *R3c* phase, display a marked reduction, being more pronounced the change along the *z* direction. The simulated volume contraction ~1.98% is close to the experimental one of 1.56% [10]. In addition, the net polarization P vanishes at  $T_{\rm C}$  ( $P_{\rm x} = Py = P_z = 0$ ), and oxygen octahedral tilting becomes in-phase along z ( $\omega_{\rm M} \neq 0$ ) while it remains unchanged along the [110] direction ( $\omega_{\rm Rx} = \omega_{\rm Ry} \neq 0$ ).

In the simulations, the *Pbnm* phase remains stable over a wide range of temperatures, and finally the system becomes cubic at about 2400 K. From this temperature, lattice constants are equivalents, and the order parameters related to polarization and the oxygen tilts are negligible. Experimentally, the *Pbnm* phase is stable over nearly 100 K above  $T_{\rm C}$ , and then transforms to a cubic metallic phase at 1204 K, before the melting point at 1240 K [11]. We note that the model description does not contemplate the high-temperature experimental situation where the compound becomes metallic. Instead, it describes a hypothetical situation where BFO remains in an insulator state.

#### Conclusions

Our results indicate that the developed model captures the delicate structural behavior showed by *ab-initio* calculations, and remarkably is able to reproduce satisfactorily the temperature behavior observed in experiments. In particular, the model correctly describes the main characteristics of the *R3c-Pbnm* transition, no/any stable intermediate phase of monoclinic symmetry between them is observed.

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