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Temperature dependency of polar modes in hybrid improper ferroelectrics

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Abstract

An atomistic effective Hamiltonian, along with a presently-developed analytical model, are employed to investigate and analyze low-frequency polar, antipolar and antiferrodistortive phonons at finite temperature in a prototypical hybrid improper ferroelectric, that is $(BiFeO_3)/(NdFeO_3)$ (abbreviated as $(BFO)_1/(NFO)_1$) 1:1 superlattice. In the high-temperature paraelectric phase, phonons having both polar and antipolar characters are found to exist, as a result of a bilinear coupling between different cation motions, with these phonons having frequencies that are basically independent of temperature. In contrast, phonons having fluctuations of either in-phase or anti-phase octahedral tiltings are soft in this high-temperature phase (with these two fluctuations being uncoupled), which results in their condensation below some critical temperature and the emergence of a low-temperature phase. In this latter low-temperature phase, trilinear energetic couplings between these two types of octahedral tiltings and Bi and Nd cations' motions lead to the appearance of a spontaneous polarization, as consistent with the nature of hybrid improper ferroelectricity. These trilinear energetic couplings also yield an increase of the number of phonons possessing both polar and antipolar characters in the low-temperature phase, with most of these phonons softening when approaching the ferroelectric-to-paraelectric transition from below, as a result of the fact that they also exhibit antiferrodistortive features. The different temperature behaviors of polar modes at high versus low temperatures emphasize the uniqueness of hybrid improper ferroelectrics.

I. INTRODUCTION

Ferroelectric materials have wide applications, including piezoelectric transducers, tunable capacitors, high capacity computer memory cells, etc.^{1–3}. This partly explains why the recent discovery of a new class of ferroelectrics, namely the so-called hybrid-improper ferroelectrics (HIF)^{4–8}, has attracted a lot of attention, especially since some of these HIFs also hold promise to realize high-temperature magnetoelectric devices⁹. Practically, HIF systems can be realized by, e.g., creating superlattices (SL) made of two perovskite compounds, each adopting the Pnma space group – which possesses in-phase and anti-phase oxygen octahedral tiltings as well as antipolar motions. It is known that ferroelectricity in such HIF stacking arises from a trilinear coupling between polarization and these two oxygen octahedralt ilting modes (see, e.g., Ref.¹⁰ and references therein). Many works based on density functional calculations have been done to reveal and characterize HIF materials^{5,6,8,11,12}, and an atomistic theory has been even proposed to further understand them^{10,13}.

Interestingly, all these aforementioned works have focused on *static* properties on HIF, especially at 0K. Consequently, finite-temperature *dynamical* properties of HIF remain mostly unexplored. For instance, one may wonder how the ferroelectric (polar), antiferroelectric (antipolar), and octahedral tilting modes evolve with temperature. In particular, do the polar (and antipolar) modes soften when the material undergoes the phase transition into a ferroelectric phase¹, as in proper ferroelectrics, or are they rather hard at any temperature as in improper ferroelectrics^{14,15}? Do these polar and antipolar phonon modes mix with phonons associated with fluctuations of oxygen octahedral tiltings in the paraelectric and ferroelectric phases because of the trilinear energetic coupling, or rather does this hypothetical mixing only occur when in-phase and/or anti-phase tiltings have condensed?

The goal of the article is to answer all these questions, by performing atomistic simulations on a specific HIF material, namely $(BiFeO_3)/(NdFeO_3)$ 1:1 superlattice. In particular, we will demonstrate that, and explain why, most polar and antipolar modes are hard in the high-temperature paraelectric phase while they soften on approaching the ferroelectric-toparaelectric phase transition from below. In other words, due to their "hard" behavior in the paraelectric phase *versus* their "soft" behavior in the ferroelectric phase near the Curie temperature, polar phonons of HIF, in overall, neither follow the behavior of polar phonons of proper ferroelectrics nor the behavior of polar phonons of improper ferroelectrics. The structure of the article is as follows. In section II we describe the method used here. In section III, the results of our calculations are reported and analyzed. In section IV, we further discuss our results in the frame of an analytically derived model. Finally, section V provides the conclusions of our study.

II. METHOD

Here, the effective Hamiltonian (H_{eff}) scheme of Refs.^{16,17} is employed to investigate finite-temperature properties of $(BFO)_1/(NFO)_1$ superlattice. Such effective Hamiltonian considers the following degrees of freedom: (i) the local soft modes $\{u_i\}$ centered on the A sites (i.e., on Bi or Nd ions), which are directly related to the local electric dipoles on site $i^{18,19}$; (2) the homogeneous $\{\eta_H\}$ and inhomogeneous $\{\eta_I\}$ strain tensors^{18,19}; (3) the pseudo vector $\{\omega_i\}$ that characterizes the oxygen octahedral tilting about the Fe site i^{20} and (4) the magnetic moment $\{m_i\}$ centered on Fe ions at site *i*. The total energy of this H_{eff} has two main terms:

$$E_{total} = E_{BFO}(\{u_i\}, \{\eta_H\}, \{\eta_I\}, \{\omega_i\}, \{m_i\}) + E_{alloy}(\{u_i\}, \{\omega_i\}, \{m_i\}, \{\eta_{loc}\}), \qquad (1)$$

where E_{BFO} is the effective Hamiltonian of pure BFO, while E_{alloy} characterizes the effect of substituting Bi ions by Nd ions. The analytical expression of E_{BFO} is provided in Ref.²¹ while that of E_{alloy} is given in Refs^{16,17}. In particular, E_{total} contains trilinear couplings between local modes and two octahedral tiltings [13]

$$\Delta E_1 = \sum_i \sum_{\substack{l,m,m=0,1 \\ \alpha \neq \beta}} \sum_{\substack{\alpha,\beta=x,y,z \\ \alpha \neq \beta}} K_{1i} (-1)^{(lx+my+nz)_{\alpha}} \omega_{ilmn,\alpha} u_{i,\beta} \omega_{ilmn,\beta} , \qquad (2)$$

where the summation over *i* runs over all the A sites and where the *x*, *y* and *z* axes are chosen to lie along the pseudocubic [100], [010], and [001] directions, respectively. $\omega_{ilmn,\alpha}$ denotes the octahedral tilting that is centered around the Fe site that can be reached from the Fe site *i* by a translation of the lattice vector $a_{lat}(l\mathbf{x} + m\mathbf{y} + n\mathbf{z})$ with l,m,n=0 or 1, and a_{lat} is the 5-atom lattice parameter (note that the Fe site *i* can be reached from the A site *i* through a translation by $\frac{-a_{lat}}{2}(\mathbf{x} + \mathbf{y} + \mathbf{z})$). As shown in Ref.¹⁶, the net HIF polarization arising in the (BFO)₁/(NFO)₁ superlattice below a certain temperature originates from the difference in the K_{1i} coefficient for the sites containing Bi versus Nd ions. More details about the energy terms E_{BFO} and E_{alloy} are provided in Ref. [22] (see Supplemental Material [22] and references therein [16-20]).

The total energy of Eq. (1) is first used in Monte-Carlo (MC) simulations to investigate *static* finite-temperature properties of $(BFO)_1/(NFO)_1$ superlattice. This SL is constructed within a 12x12x12 supercell with BFO and NFO layers alternating along the [001] pseudocubic direction (this supercell therefore contains six BFO/NFO units along the z-axis). 20,000 MC sweeps are used for equilibration and another 20,000 MC sweeps are employed to calculate thermal averages.

We also performed Molecular Dynamics (MD) simulations using this effective Hamiltonian method and the aforementioned 12x12x12 supercell to investigate *dynamical* properties of $(BFO)_1/(NFO)_1$. Technically, the MD simulations run over 4×10^5 steps with a time step of 0.5 fs. In particular, different frequency-dependent responses related to different order parameters are computed from the MD data, as described by the following formula:

$$\chi_{\alpha\beta}^{AA'}(\nu) = \left\langle A_{\alpha}(t)A_{\beta}'(t) \right\rangle + i2\pi\nu \int_{0}^{\infty} dt e^{i2\pi\nu t} \left\langle A_{\alpha}(t)A_{\beta}'(0) \right\rangle, \qquad (3)$$

where ν is frequency, α and β denote Cartesian components, A(t) and A'(t) are order parameters at time t, and " $\langle ... \rangle$ " indicates thermal averages. Practically, we focused on the following physical A quantities: (i) the \mathbf{u}_{Nd} and \mathbf{u}_{Bi} vectors that characterize the vectorial sum of the local modes at the Nd and Bi sites averaged over all these sites, respectively; (ii) the \mathbf{u}_{Γ} and \mathbf{u}_X vectors that are directly proportional to the overall electrical polarization and antiferroelectric (AFE) vector associated with the X point of the 5-atom cubic Brillouin zone, respectively. Note that the \mathbf{u}_{Γ} and \mathbf{u}_X vectors are related to \mathbf{u}_{Nd} and \mathbf{u}_{Bi} , by being equal to $\frac{1}{2}(\mathbf{u}_{Nd} + \mathbf{u}_{Bi})$ and $\frac{1}{2}(\mathbf{u}_{Nd} - \mathbf{u}_{Bi})$, respectively; and (iii) the anti-phase and in-phase rotations of the oxygen octahedral tiltings (also known as antiferrodistortive or AFD motions), that are quantified by the $\boldsymbol{\omega}_R$ and $\boldsymbol{\omega}_M$ pseudovectors, respectively. Note that some of these quantities are energetically coupled to each other via the different local trilinear couplings involved in Eq. (2). For instance, the z-component of $\boldsymbol{\omega}_M$ is involved in a term that can be written (in a macroscopic form) as^{10,13}

$$E_{trilinear,\omega_{M,z}} = C\{\sum_{\alpha=x,y} \kappa_{Nd} u_{Nd,\alpha} \omega_{R,\alpha} \omega_{M,z} + \kappa_{Bi} u_{Bi,\alpha} \omega_{R,\alpha} \omega_{M,z}\}$$

$$= C\{\sum_{\alpha=x,y} D_{\Gamma} u_{\Gamma,\alpha} \omega_{R,\alpha} \omega_{M,z} + D_{X} u_{X,\alpha} \omega_{R,\alpha} \omega_{M,z}\}$$
(4)

where C is a coefficient, the sums over α run over the x and y Cartesian components, and κ_{Nd} and κ_{Bi} are the K_{1i} parameters of Eq. (2) with i=Nd and i=Bi, respectively. Moreover, $D_{\Gamma} = \frac{1}{2}(\kappa_{Nd} + \kappa_{Bi})$, and $D_X = \frac{1}{2}(\kappa_{Nd} - \kappa_{Bi})$.

Furthermore, the imaginary part of the complex susceptibilities computed by Eq. (3) for any studied order parameter A is fitted by a sum of Damped Harmonic Oscillators (DHO) models of the form:

$$\chi = \frac{S^2}{\nu_r^2 - \nu^2 - i\nu\gamma} , \qquad (5)$$

where ν_r , γ , and S are the resonant frequency, damping constant, and oscillator strength, respectively. The fitting of the imaginary part of the complex susceptibilities arising from the MD data therefore yields, in particular, the natural frequencies, ν_r , of the phonon modes associated with the chosen physical quantities.

III. NUMERICAL RESULTS

Figure 1a displays the supercell average of the \mathbf{u}_{Γ} and \mathbf{u}_X vectors as a function of temperature, while Fig. 1c reports the temperature evolution of the ω_R and ω_M pseudovectors. All these quantities are obtained from Monte-Carlo simulations, and vanish above 1520K. Such vanishing corresponds to the occurrence of the P4/mmm space group at high enough temperature¹⁶. On the other hand, below 1520K, the x and y components of \mathbf{u}_{Γ} become finite and equal to each other, as do the x and y components of both \mathbf{u}_X and ω_R , along with the z-component of ω_M becoming non-null (all the other Cartesian components of \mathbf{u}_{Γ} , \mathbf{u}_X , ω_R and ω_M can be assumed to be statistically null, except the z-component of ω_R that is finite but rather small). In other words, below 1520K, an electrical polarization and an antipolar vector both develop along the pseudo-cubic [110] direction, which is accompanied by oxygen octahedra titling in anti-phase fashion about this same [110] direction and inphase tiltings about the out-of-plane [001] direction of the superlattice. Such features are indicative of ordered Bi_{0.5}Nd_{0.5}FeO₃ (BNFO) basically acquiring the $Pmc2_1$ space group below a critical temperature of 1520K¹⁶.

Moreover, Fig. 1b also reveals that, below 1520K, the average displacement of Nd ions along the [110] direction is positive and larger in magnitude than that of the Bi ions which move in opposite direction (that is along the $[\bar{1}\bar{1}0]$ direction). This difference in magnitude explains why \mathbf{u}_{Γ} is non-null while the opposite motions between Nd and Bi ions naturally result in \mathbf{u}_X having larger strength than \mathbf{u}_{Γ} below 1520K, since $\mathbf{u}_{\Gamma} = \frac{1}{2}(\mathbf{u}_{Nd} + \mathbf{u}_{Bi})$ and $\mathbf{u}_X = \frac{1}{2}(\mathbf{u}_{Nd} - \mathbf{u}_{Bi})$. Note that the results shown in Figure 1 are essentially the same as the ones obtained in Ref¹⁶ but with a difference in the size of a supercell. We needed to show those results again here in order to introduce the the overall system behavior. Note also that Fig. 2 of Ref.¹⁷ demonstrates that transition temperatures predicted by the presently used effective Hamiltonian can be accurate in (Bi,Nd)FeO₃ systems.

Furthermore, Fig. 2 (b) displays the imaginary part of the susceptibility $\chi^{AA'}_{\alpha\alpha}(\nu)$ for the order parameter $A=A'=\mathbf{u}_X$ and for $\alpha\alpha = x'x'$ (where x' is along the pseudo-cubic [110] direction) at the temperature of 1780K- that is within the P4/mmm state. Two narrow peaks can be clearly seen: one peak occurring at around 116 cm^{-1} and the other at 134cm⁻¹. Two peaks also happen at the same frequencies for the order parameter $A=A'=\mathbf{u}_{\Gamma}$ and for $\alpha \alpha = x'x'$, but the second one appease as a weak shoulder (*cf* Fig. 2a and its inset). These peaks in Figs 2b and 2a therefore indicate that the lowest two frequencies of the AFE phonon mode are identical to those of the ferroelectric (FE) mode, and are thus associated with the *coupled* oscillations of the \mathbf{u}_X and \mathbf{u}_{Γ} vectors along the x' direction. Such coupled oscillations originate from the facts that (1) both \mathbf{u}_X and \mathbf{u}_{Γ} are related to \mathbf{u}_{Nd} and \mathbf{u}_{Bi} ; and that (2) two peaks can also be clearly seen in Fig. 2c at, once again, 116 cm^{-1} and 134 cm^{-1} for the the oscillations of the \mathbf{u}_{Nd} vector along the x' direction, and to a less extent in Fig. 2d for the oscillations of \mathbf{u}_{Bi} mode along such direction too. As a matter of fact and as we will discuss later on (see Section IV), \mathbf{u}_{Nd} and \mathbf{u}_{Bi} are coupled to each other via a short-range bilinear energetic interaction of the form $Ju_{Nd,\alpha}u_{Bi,\alpha}$, where J is a coefficient and $\alpha = x$ or y. We will thus call these two frequencies as $\nu_{cation,1}^{P4/mmm}$ and $\nu_{cation,2}^{P4/mmm}$, in order to emphasize that they involve cation displacements and occur in the high-temperature P_4/mmm phase.

In addition to the FE and AFE modes let us also look at the modes having AFD character at high temperatures. For that, Fig. 2 (e) displays the imaginary part of the susceptibility corresponding to the oscillation of the (anti-phase tilting) ω_R order parameter along the x' direction at the same temperature of 1780K, while Fig. 2(f) shows similar information but for the zz component of the susceptibility of the (in-phase tilting) order parameter $A = A' = \omega_M$. Both of these susceptibilities possess a unique peak, that is located at 42 cm⁻¹ in Fig. 2(e) versus 37 cm⁻¹ in Fig. 2f, and that corresponds to frequencies we denote as $\nu_{\omega_R}^{P4/mmm}$ and $\nu_{\omega_M}^{P4/mmm}$, respectively. Since these two latter frequencies are different from each other, and also differ from $\nu_{cation,1}^{P4/mmm}$ and $\nu_{cation,2}^{P4/mmm}$, one can deduce that anti-phase and in-phase tiltings are neither dynamically coupled to each other nor to the FE and AFE motions in the high-temperature P4/mmm state.

Let us now focus on results at 750K, that is for a representative temperature within the $Pmc2_1$ state. For that, the imaginary part of the susceptibilities of the order parameters $A = A' = \mathbf{u}_{\Gamma}, \mathbf{u}_X, \mathbf{u}_{Nd}, \mathbf{u}_{Bi}, \boldsymbol{\omega}_R$ and $\boldsymbol{\omega}_M$ are shown in Figure 3 for the same $\alpha\alpha$ components than in Fig. 2. Seven peaks are seen around 83 cm⁻¹, 121cm⁻¹, 134 cm⁻¹, 162 cm⁻¹, 174 cm⁻¹, 211cm⁻¹ and 228 cm⁻¹ in *all* these susceptibilities, therefore revealing an increase of the number of peaks with respect to the high-temperature phase for all these dynamical responses and suggesting a specific dynamical coupling *mixing* cation motions (ferroelectric degrees of freedom and antipolar motions), and in-phase and anti-phase tiltings in the low-temperature $Pmc2_1$ state. As we will see later, this specific coupling is the trilinear energetic coupling of Eq. (4) between the x and y components of \mathbf{u}_{Nd} and \mathbf{u}_{Bi} (or equivalently, of the FE mode, \mathbf{u}_{Γ} , and AFE mode, \mathbf{u}_X) with the x and y components of the anti-phase AFD mode, $\boldsymbol{\omega}_M$. The frequencies associated with these seven peaks seen in Fig. 3 are denoted as $\nu_i^{Pmc2_1}$, with *i* being an integer ranging from 1 to 7.

Moreover, Figure 4 displays the temperature evolution of $\nu_{cation,1}^{P4/mmm}$, $\nu_{cation,2}^{P4/mmm}$, $\nu_{\omega_R}^{P4/mmm}$ and $\nu_{\omega_M}^{P4/mmm}$ in the P4/mmm phase, as well as that of the $\nu_i^{Pmc2_1}$'s in the $Pmc2_1$ state. Several important results can be inferred from this figure. First of all, $\nu_{cation,1}^{P4/mmm}$ and $\nu_{cation,2}^{P4/mmm}$ frequencies remain more-or-less constant in the entire range of investigated temperature within the P4/mmm state and, in particular, do not have any tendency of softening when approaching the P4/mmm—to— $Pmc2_1$ phase transition under cooling. In fact, this latter phase transition is driven by the condensation of the z-component of the ω_M in-phase oxygen octahedral tiltings and of the x and y components of the ω_R anti-phase oxygen octahedral tiltings below the temperature of 1520K (see Fig. 1c), as also evidenced by the facts that $\nu_{\omega_R}^{P4/mmm}$ and $\nu_{\omega_M}^{P4/mmm}$ both soften dramatically upon approaching the phase transition from above (i.e, within the P4/mmm state). When decreasing the temperature further (i.e., below 1520K), the x and y-components of \mathbf{u}_{Nd} and \mathbf{u}_{Bi} (or, equivalently, of \mathbf{u}_{Γ} and \mathbf{u}_{X}) become finite (see Figs 1a and 1b) because of their trilinear couplings given in Eq. (4) with the now-condensed ω_R and ω_M modes¹⁶. Such couplings also further lead to the emergence of the seven peaks seen in Figure 3 for any displayed response, as we will demonstrate later on. Figure 4 further shows that most of the seven $\nu_i^{Pmc2_1}$ frequencies soften when increasing the temperature within the $Pmc2_1$ state close to the critical temperature of $\simeq 1520$ K, as a result of them containing AFD characters. One exception to this softening concerns $\nu_2^{Pmc2_1}$, that is basically independent of temperature and rather hard within the stability region of $Pmc2_1$. Such exception resides in the fact that the mode associated with $\nu_2^{Pmc2_1}$ mostly involves motions of Bi ions, and consequently has also large FE and AFE characters, along the x' direction, as evidenced by the strong peaks seen in Figs. 3(a), (b) and (d) at this frequency. Such characters also explain why $\nu_2^{Pmc2_1}$ is rather close in value to $\nu_{cation,1}^{P4/mmm}$.

Let us now try to further understand the numerical results depicted in Figs 2 and 3, that is to indeed demonstrate that \mathbf{u}_{Nd} and \mathbf{u}_{Bi} modes are dynamically bilinearly coupled in the P4/mmm state while the fluctuations of \mathbf{u}_{Nd} , \mathbf{u}_{Bi} , $\boldsymbol{\omega}_R$, and $\boldsymbol{\omega}_M$ are all coupled in the $Pmc2_1$ state due to trilinear energetic couplings. For that, we develop, and describe below, an analytical model for the high and low-temperature states.

IV. MODEL

Let us start with the equation of motion associated with our considered degrees of freedom:

$$M_A \frac{d^2 q_{A,l\alpha}}{dt^2} = F_{A,l\alpha} \tag{6}$$

where A is one of the structural modes in the system, $q_{A,l\alpha}$ is the α Cartesian component of the corresponding displacement in the *l*'s primitive cell, *t* is time, and M_A is the mass of mode A. Furthermore, the right part of Equation (6) is the force given by:

$$F_{A,l\alpha} = -\frac{dE_{total}}{dq_{A,l\alpha}} \tag{7}$$

where E_{total} is the total energy of the system and the derivative is taken in the ground state.

Let us now define the reduced force as:

$$f_{A,l\alpha} = \frac{F_{A,l\alpha}}{\sqrt{M_A}} \tag{8}$$

Correspondingly, one can introduce the reduced displacement associated with mode A as

$$S_{A,l\alpha} = \sqrt{M_A} q_{A,l\alpha} \tag{9}$$

Then Eq. (6) can be rewritten in a symmetric form which does not contain mass in equation of motion explicitly:

$$\frac{d^2 S_{A,l\alpha}}{dt^2} = f_{A,l\alpha} \tag{10}$$

To simplify this differential equation, we now express the reduced displacements in a harmonic way:

$$S_{A,j\alpha} = e^{-i[\omega t + \mathbf{k}_A \cdot \mathbf{R}(j)]} S_{A,\mathbf{k}_A,\alpha}$$
(11)

where \mathbf{k}_A is a wave vector associated with mode A, $\mathbf{R}(j)$ is the vector locating the position of the *j*-th primitive cell, and $S_{A,\mathbf{k}_A,\alpha}$ is the Fourier transform of $S_{A,j\alpha}$. Now Equation (10) transforms to the following form:

$$-\omega^2 \Delta S_{A,\boldsymbol{k}_A,\alpha} = f_{A,\boldsymbol{k}_A,\alpha} \tag{12}$$

where $\Delta S_{A,\mathbf{k}_A,\alpha}$ is the fluctuation of mode A and the right part is the Fourier transform of the reduced force:

$$f_{A,\boldsymbol{k}_A,\alpha} = \frac{1}{N} \sum_{j} e^{i[\omega t + \boldsymbol{k}_A \cdot \boldsymbol{R}(j)]} f_{A,j\alpha}$$
(13)

with N being the number of sites.

Now the equilibrium condition for mode A takes the form:

$$\langle f_{A,\boldsymbol{k}_A,\alpha} \rangle = 0 \tag{14}$$

where the angle brackets present time averaging.

To simplify Equation (12) further on, we can linearize it. For that, we present the reduced force in the form of the expansion with respect to different structural displacements. This can be done because the force at equilibrium is zero and gets finite only due to the displacements from the ground state. In the linear approximation, we neglect all higher order terms in this expansion and thus get:

$$f_{A,\boldsymbol{k}_{A},\alpha} = -\sum_{B} \sum_{\beta} D_{A,\boldsymbol{k}_{A},\alpha;B,\boldsymbol{k}_{B},\beta} \Delta S_{B,\boldsymbol{k}_{B},\beta}$$
(15)

where $D_{A,\mathbf{k}_{A},\alpha;B,\mathbf{k}_{B},\beta}$ is the dynamical matrix defined via:

$$D_{A,\boldsymbol{k}_{A},\alpha;B,\boldsymbol{k}_{B},\beta} = -\left\langle \frac{\partial f_{A,\boldsymbol{k}_{A},\alpha}}{\partial S_{B,\boldsymbol{k}_{B},\beta}} \right\rangle$$
(16)

Here the angle brackets represent averaging over time as done in the self-consistent approximation developed for strongly anharmonic crystals²³. Note also that the dependence of this derivative on time can arise only because of terms in energy higher than bilinear. For example, trilinear coupling terms can be responsible for the time dependency of this quantity.

By plugging Equation (15) to Equation (12), we now get the final form of our equation:

$$\omega^2 \Delta S_{A,\boldsymbol{k}_A,\alpha} = \sum_B \sum_{\beta} D_{A,\boldsymbol{k}_A,\alpha;B,\boldsymbol{k}_B,\beta} \Delta S_{B,\boldsymbol{k}_B,\beta}$$
(17)

Finally, the frequencies in this new equilibrium state are the roots of the following equation:

$$|\hat{D} - \omega^2 \hat{I}| = 0 \tag{18}$$

where \hat{I} is the unity matrix.

Thus the central role in the model is played by the dynamical matrix. First, we should select our basic structural modes. In line with the results of our aforementioned calculations, we take seven modes, $q_{A,\mathbf{k}\alpha}$, that are: $u_{Bi,x}$, $u_{Bi,y}$, $u_{Nd,x}$, $u_{Nd,y}$, $\omega_{M,z}$, $\omega_{R,x}$ and $\omega_{R,y}$. Their associated wave vectors, in $2\pi/a$ units, are (i) the zone-center for $u_{Bi,x}$, $u_{Bi,y}$, $u_{Nd,x}$, $u_{Nd,y}$; (iii) $[\frac{1}{2}, \frac{1}{2}, 0]$ for $\omega_{M,z}$; and (iii) $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ for $\omega_{R,x}$ and $\omega_{R,y}$.

Correspondingly, we obtain, within our model, the form of the dynamical matrix given in Table I. There are seven diagonal elements denoted as $\Omega_{q_{A,\alpha}}^2$, since Nd and Bi have different masses as well as different quadratic energy terms for the local modes centered on them. Note that some of these seven elements can be equal to each other, such as $\Omega_{R,x}^2$ and $\Omega_{R,y}^2$ (for the anti-phase tiltings). Regarding nondiagonal terms, we include (i) bilinear coupling constants d_{xx} and d_{yy} that are related to the microscopic effective Hamiltonian short-range bilinear energetic $J_{ij,\alpha\beta}$ coefficients (see the energy term E^{short} of Eq. (4) in Ref. [22]); and (ii) trilinear terms between local modes and tiltings, which yield elements that are made of a product between a quantity we denote as d_{xx}^{Bi} , d_{yy}^{Bi} , d_{xx}^{Nd} or d_{yy}^{Nd} , and a corresponding time-average of the appropriate tilting mode. Note that d_{xx}^{Bi} , d_{yy}^{Bi} , d_{xx}^{Nd} or d_{yy}^{Nd} are related to the effective Hamiltonian trilinear coupling coefficients between local modes and AFD motions (which are denoted by $K_{ij,\alpha\beta}$ in Eq. (6) of Ref. [22])

Let us now study the solutions of Equation (18), once choosing the dynamical matrix of Table I, in the cases of the high-temperature and low-temperature phases of our investigated HIF system.

Case I: The P4/mmm phase

In this case, the average of the $\omega_{M,z}$, $\omega_{R,x}$ and $\omega_{R,y}$ all vanish and they are all decoupled from each other as well as from the local modes centered on Bi and Nd ions. The average of the modes on Bi and Nd is also zero. However, these latter local modes are coupled to each other via the $d_{\alpha\alpha}$ terms of Table I. Correspondingly, the equation of motions become:

$$(\Omega_{Nd,\alpha}^2 - \omega^2) S_{Nd,\alpha} = -d_{\alpha\alpha} S_{Bi,\alpha}$$
⁽¹⁹⁾

$$(\Omega_{Bi,\alpha}^2 - \omega^2) S_{Bi,\alpha} = -d_{\alpha\alpha} S_{Nd,\alpha}$$
⁽²⁰⁾

As we have only two modes (both for the x and y directions) that are bilinearly coupled, we only have 2 peaks located at the same frequencies in the responses shown in Figs 2c and 2d for the Nd and Bi ions, respectively. Indeed, the eigenvalues of Equations (19) and (20) can be found from Equation (18):

$$\omega_{\alpha}^{2} = \frac{\Omega_{Nd,\alpha}^{2} + \Omega_{Bi,\alpha}^{2}}{2} \pm \sqrt{\left(\frac{\Omega_{Nd,\alpha}^{2} - \Omega_{Bi,\alpha}^{2}}{2}\right)^{2} + d_{\alpha\alpha}^{2}}$$
(21)

One can see that these two solutions for $\alpha = x', y'$ are indeed close to the bare frequencies of the Nd and Bi modes, but are shifted from them because of the coupling constant $d_{\alpha\alpha}$.

Case II: The $Pmc2_1$ phase

This case is more complex. It definitely provides seven lines in each of the responses depicted in Fig. 3, because all the aforementioned seven modes are coupled via all the terms reported in Table I. Indeed, now, the trilinear terms are finite because the average of $\omega_{R,x}$, $\omega_{R,y}$ and $\omega_{M,z}$ are all now finite.

Moreover, by employing Equation (14), we can determine the polarization. Indeed, Equation (14) takes for the Nd and Bi modes in $Pmc2_1$ phase the following form:

$$\Omega_{Nd,\alpha}^2 \left\langle S_{Nd,\alpha} \right\rangle + d_{\alpha\alpha} \left\langle S_{Bi,\alpha} \right\rangle + d_{\alpha\alpha}^{Nd} \left\langle S_{M,z} \right\rangle \left\langle S_{R,\alpha} \right\rangle = 0 \tag{22}$$

$$\Omega_{Bi,\alpha}^2 \left\langle S_{Bi,\alpha} \right\rangle + d_{\alpha\alpha} \left\langle S_{Nd,\alpha} \right\rangle + d_{\alpha\alpha}^{Bi} \left\langle S_{M,z} \right\rangle \left\langle S_{R,\alpha} \right\rangle = 0 \tag{23}$$

The solutions of these equations are:

$$< S_{Nd,\alpha} >= \frac{-d^{Nd}_{\alpha\alpha}\Omega^{2}_{Bi,\alpha} + d^{Bi}_{\alpha\alpha}d_{\alpha\alpha}}{\Omega^{2}_{Nd,\alpha}\Omega^{2}_{Bi,\alpha} - d^{2}_{\alpha\alpha}} \langle S_{M,z} \rangle \langle S_{R,\alpha} \rangle$$

$$< S_{Bi,\alpha} >= \frac{-d^{Bi}_{\alpha\alpha}\Omega^{2}_{Nd,\alpha} + d^{Nd}_{\alpha\alpha}d_{\alpha\alpha}}{\Omega^{2}_{Bi,\alpha}\Omega^{2}_{Nd,\alpha} - d^{2}_{\alpha\alpha}} \langle S_{M,z} \rangle \langle S_{R,\alpha} \rangle$$
(24)

These formulas show that $\langle S_{Nd,\alpha} \rangle$ and $\langle S_{Bi,\alpha} \rangle$ are finite only if $\langle S_{M,z} \rangle$ and $\langle S_{R,\alpha} \rangle$ are finite, implying that it is the condensation of the tilting modes that gives rise to finite cation displacements below 1520K. Moreover, not only $d_{\alpha\alpha}^{Nd}$ and $d_{\alpha\alpha}^{Bi}$ have different magnitudes, they are also of opposite signs. Consequently, and since $\Omega_{Nd,\alpha}^2$ is also different from $\Omega_{Bi,\alpha}^2$, $\langle S_{Nd,\alpha} \rangle$ and $\langle S_{Bi,\alpha} \rangle$ have different magnitude and have different signs. As a result, one can get a finite electrical polarization, which is simply related to $\langle \frac{S_{Nd,\alpha}}{\sqrt{M_{Nd}}} \rangle + \langle \frac{S_{Bi,\alpha}}{\sqrt{M_{Bi}}} \rangle$ in our superlattice, which is the essence of HIF. Note also that their difference will contribute to the antiferroelectric displacement, that is proportional to $\langle \frac{S_{Nd,\alpha}}{\sqrt{M_{Nd}}} \rangle - \langle \frac{S_{Bi,\alpha}}{\sqrt{M_{Bi}}} \rangle$.

Moreover, when approaching the transition temperature of 1520K from below (i.e., within the Pmc2₁ phase), the *bare* ω_R and ω_M tilting modes should soften as similar to their behavior when approaching this transition from above (i.e., within the P4/mmm state, as shown in Fig. 4). The couplings of these tilting modes with the FE and AFE modes within the Pmc2₁ state (these couplings are evidenced in Eqs (22) and (23)) naturally result in the softening of modes having FE and AFE characters when approaching this transition from below – as indeed seen in Fig. 4.

V. CONCLUSION

In summary, we studied here phonon frequencies in $(BFO)_1/(NFO)_1$ superlattice when cooled from high temperatures. This system possesses a tetragonal paraelectric P4/mmmstate at high temperatures, and a polar $Pmc2_1$ phase at low temperature, as in line with its HIF character. Our results reveal that the resonant frequencies of all polar and antipolar modes are rather hard and nearly independent of temperature within the P4/mmm state. On the other hand, most of them abruptly become soft in the low-temperature $Pmc2_1$ phase near the ferroelectric-to-paraelectric transition, because of the very specific trilinear couplings mixing polar and antipolar distortions with the soft oxygen octahedral tilting modes. Such mixing increases the number of peaks of polar and antipolar phonons, which then each possesses polar, antipolar but also antiferrodistortive characters when passing through the phase transition from the P4/mmm to $Pmc2_1$ phase. Note that the different behaviors of polar modes at high versus low temperature render hybrid improper ferroelectrics dramatically different from proper ferroelectrics (where polar modes soften both in the high and low-temperature phases when approaching the transition¹) and from improper ferroelectrics (where polar modes are hard in both the high and low-temperature phases^{14,15}). We developed a simple analytical model that naturally explains all these features. We hope that the present study deepens the understanding of ferroelectrics, in general, and their dynamics, in particular.

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VI. REFERENCES

- M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Clarendon Press, Oxford, 1977).
- [2] K. Abe and S. Komatsu, J. Appl. Phys. 77, 6461 (1995).
- [3] K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors*, (Kluwer Academic Publishers, Boston, 1996).
- [4] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J. -M. Triscone, and P. Ghosez, Nature 452, 732 (2008).
- [5] N. A Benedek and C. J. Fennie, Phys. Rev. Lett. **106**, 107204 (2011).
- [6] J. M. Rondinelli and C. J. Fennie, Adv. Mater. 24, 1961 (2012).
- [7] J. Young and J. M. Rondinelli, Chem. Mater. 25, 4545 (2013).
- [8] A. T. Mulder, N. A. Benedek, J. M. Rondinelli, and C. J. Fennie, Adv. Funct. Mater. 23,

4810 (2013).

- [9] H. J. Zhao, W. Ren, Y. Yang, J. Iiguez, X. M. Chen, and L. Bellaiche, Nat. Commun. 5, 4021 (2014).
- [10] H. J. Zhao, J. Íñiguez, W. Ren, X. M. Chen, and L. Bellaiche, Phys. Rev. B 89, 174101 (2014).
- [11] M. Stengel, C. J. Fennie, and P. Ghosez, Phys. Rev. B 86, 094112 (2012).
- [12] Z. Zanolli, J. C. Wojdel, J. Iñiguez, and P. Ghosez, Phys. Rev. B 88, 060102(R) (2013).
- [13] L. Bellaiche and J. Íñiguez, Phys. Rev. B 88, 014104 (2013).
- [14] A. P. Levanyuk and D. G. Sannikov, Uspekhi Fiz. Nauk 112, 561 (1974).
- [15] W. Kaczmarek and F. Gervaid, Ferroelectrics 80, 197 (1988).
- [16] B. Xu, D. Wang , H. J. Zhao, J. Iñiguez, X. M. Chen, and L. Bellaiche, Adv. Funct. Mater. 25, 3626 (2015).
- [17] B. Xu, D. Wang, J. Íñiguez, and L. Bellaiche, Adv. Funct. Mater. 25, 552 (2015).
- [18] W. Zhong, D. Vanderbilt, and K. Rabe, Phys. Rev. Lett. 73, 1816 (1994).
- [19] W. Zhong, D. Vanderbilt, and K. Rabe, Phys. Rev. B 52, 6301 (1995).
- [20] I. A. Kornev, L. Bellaiche, P. E. Janolin, B. Dkhil, and E. Suard, Phys. Rev. Lett. 97, 157601 (2006).
- [21] S. Prosandeev, D. Wang, W. Ren, J. Iñiguez, and L. Bellaiche, Adv. Funct. Mater. 23, 234 (2013).
- [22] See Supplemental Material at [URL will be inserted by publisher] for details about the energy terms in our effective Hamiltonian and for the dependence of the magnitude of the antiferromagnetic vector on temperature.
- [23] H. Böttger, Principles of the Theory of Lattice Dynamics (Berlin: Akademie-Verlag, 1983).

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	Bi_x	Bi_y	Nd_x	Nd_y	M_z	\mathbf{R}_x	\mathbf{R}_y
Bi_x	$\Omega^2_{Bi,x}$		d_{xx}		$\mathrm{d}_{xx}^{Bi}\langle S_{R,x}\rangle$	$\mathrm{d}_{xx}^{Bi}\langle S_{M,z}\rangle$	
Bi_y		$\Omega^2_{Bi,y}$		d_{yy}	$\mathrm{d}_{yy}^{Bi}\left\langle S_{R,y}\right\rangle$		$\mathrm{d}_{yy}^{Bi} \langle S_{M,z} \rangle$
Nd_x	d_{xx}		$\Omega^2_{Nd,x}$		$\mathrm{d}_{xx}^{Nd}\left\langle S_{R,x}\right\rangle$	$d_{xx}^{Nd} \langle S_{M,z} \rangle$	
Nd_y		d_{yy}		$\Omega^2_{Nd,y}$	$\mathrm{d}_{yy}^{Nd} \langle S_{R,y} \rangle$		$\mathrm{d}_{yy}^{Nd} \langle S_{M,z} \rangle$
M_z	$\mathrm{d}_{xx}^{Bi} \langle S_{R,x} \rangle$	$\mathrm{d}_{yy}^{Bi} \langle S_{R,y} \rangle$	$\mathrm{d}_{xx}^{Nd} \langle S_{R,x} \rangle$	$\mathrm{d}_{yy}^{Nd} \langle S_{R,y} \rangle$	$\Omega^2_{M,z}$	$\mathrm{d}_{xx}^{Bi}\langle S_{Bi,x}\rangle + \mathrm{d}_{xx}^{Nd}\langle S_{Nd,x}\rangle$	$\mathrm{d}_{yy}^{Bi}\langle S_{Bi,y}\rangle + \mathrm{d}_{yy}^{Nd}\langle S_{Nd,y}\rangle$
\mathbf{R}_x	$\mathrm{d}_{xx}^{Bi} \langle S_{M,z} \rangle$		$\mathrm{d}_{xx}^{Nd} \langle \overline{S_{M,z}} \rangle$		$\mathrm{d}_{xx}^{Bi}\langle S_{Bi,x}\rangle + \mathrm{d}_{xx}^{Nd}\langle S_{Nd,x}\rangle$	$\Omega^2_{R,x}$	
\mathbf{R}_y		$\mathrm{d}_{yy}^{Bi} \langle S_{M,z} \rangle$		$\mathrm{d}_{yy}^{Nd} \langle S_{M,z} \rangle$	$\mathrm{d}_{yy}^{Bi}\langle S_{Bi,y}\rangle + \mathrm{d}_{yy}^{Nd}\langle S_{Nd,y}\rangle$		$\Omega^2_{R,y}$

TABLE I. Form of the dynamical matrix in our model. For simplification of notations, $u_{Bi,x}$, $u_{Bi,y}$, $u_{Nd,x}$, $u_{Nd,y}$, $\omega_{M,z}$, $\omega_{R,x}$ and $\omega_{R,y}$ are simply denoted as Bi_x , Bi_y , Nd_x , Nd_y , M_z , R_x and R_y , respectively, here.

Figure Captions:

Figure 1 (Color online). Temperature dependence of the (a) the supercell averaged \mathbf{u}_{Γ} and \mathbf{u}_X vectors characterizing the electrical polarization and antiferroelectric vector at the X-point of the cubic first-Brilloun zone, respectively; (b) the local mode centered on Nd and Bi cations (\mathbf{u}_{Nd} and \mathbf{u}_{Bi} , respectively); (c) $\boldsymbol{\omega}_R$ and $\boldsymbol{\omega}_M$ pseudo vectors quantifying antiphase and in-phase tiltings, respectively, of the oxygen octahedra in the (BFO)₁/(NFO)₁ superlattice.

Figure 2 (Color online). Frequency dependence of the imaginary part of the $\chi_{\alpha\alpha}^{AA'}(\nu)$ susceptibilities in our (BFO)₁/(NFO)₁ superlattice, for the following order parameters (a) \mathbf{u}_{Γ} , (b) \mathbf{u}_{X} , (c) \mathbf{u}_{Nd} , (d) \mathbf{u}_{Bi} , (e) $\boldsymbol{\omega}_{R}$, and (f) $\boldsymbol{\omega}_{M}$ at a temperature of 1780K – that is, for the P4/mmm state. For Panels (a-e), $\alpha = x'$ where x' is along the pseudo-cubic [110] direction, while $\alpha = z$ (that is along [001]) for Panel f .The black line displays the MD data while the red line represents their fit by DHOs. Insets zoom over particular peaks that are more difficult to see.

Figure 3 (Color online). Same as Fig. 2 but for the temperature of 750K – that is, for the Pmc2₁ state.

Figure 4 (Color online). Temperature dependence of natural frequencies of phonon modes having ferroelectric, antiferroelectric and antiferrodistortive characters. See text for the notations of these resonant frequencies. The vertical dashed line delimits the two different phases obtained in our calculations. Error bars for $\nu_6^{Pmc2_1}$ arise from the slight difference in frequency that different responses (see Fig. 3) can have around this frequency.









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