Structural instabilities and sequence of phase transitions in SrBi$_2$Nb$_2$O$_9$ and SrBi$_2$Ta$_2$O$_9$ from first principles and Monte Carlo simulations

Urko Petralanda and I. Etxebarria

Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, P.K. 644, 48080 Bilbao, Spain.

Despite their structural similarities, SrBi$_2$Ta$_2$O$_9$ (SBT) and SrBi$_2$Nb$_2$O$_9$ (SBN) undergo a different sequence of phase transitions. The phase diagram of SBT as a function of the temperature includes an intermediate phase between the high-temperature phase and the ferroelectric ground state, while in the Niobium compound the intermediate phase is suppressed and a single transition between the high- and low temperature structures is observed. We present ab initio calculations that reveal the relevance of a trilinear coupling between three symmetry-adapted modes to stabilize the ground state in both compounds, being this coupling much stronger in SBN. Within the framework of the phenomenological Landau theory, it is shown that by solely increasing the strength of the trilinear coupling the topology of the phase diagram of SBT can change up to suppress the intermediate phase. Monte Carlo simulations on an idealized $\phi^4$ Hamiltonian confirm that the trilinear coupling is the key parameter that determines the sequence of phase transitions and that for higher dimensionality of the order parameters the stability region of the intermediate phase is narrower.

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I. INTRODUCTION

The Aurivillius phases are layered bismuth compounds that obey the general formula Bi$_{2m}$A$_{n-m}$B$_n$O$_{3n+m}$. The family includes many members that present ferroelectricity at room temperature, and they have been widely studied for potential technological applications mainly in thin film nonvolatile memories. SrBi$_2$Ta$_2$O$_9$ (SBT) and SrBi$_2$Nb$_2$O$_9$ (SBN) are members of the family, with $n = 2$ and $m = 1$ and their structure is formed by alternating two SrMO$_3$ (M=Ta, Nb) perovskite blocks and one Bi$_2$O$_2$ slab (Fig. 1).

Tantalum and Niobium present very similar physical and chemical properties, including the valence and atomic radii. As a result, SBT and SBN present isomorphous polar structures at room temperature and analogous mechanical and electrical characteristics. However, their phase diagrams are qualitatively different: on increasing the temperature SBT undergoes a phase transition to a non-polar orthorhombic phase that does not arise in SBN.

Previous first-principles calculations by Perez-Mato et al revealed that the trilinear coupling of two primary unstable modes and a secondary hard mode is critical to stabilize the ground state of SBT. This work provided a simple and plausible scheme in contrast with others alternatives where the eventual existence of negative bi-quadratic coupling triggers the simultaneous condensation of several modes. Later, the key role of the trilinear coupling has been found in several other compounds and its influence has been proposed as the origen of the so-called avalanche phase transitions and the hybrid improper ferroelectricity.

In this work we revisit the SBT and extend the ab initio study to SBN in order to investigate the role of the trilinear coupling in the stabilization of the ferroelectric structure and its influence in the sequences of phase dia-

II. SYMMETRY CONSIDERATIONS, DISTORTIONS AND PHASE TRANSITIONS

The high- and low-temperatures structures of SBT and SBN are isomorphous: tetragonal with space group $I4/mmm$ (No. 139) at high enough temperatures and orthorhombic $A2am$ (No. 36) at low temperatures. In the case of SBN there is a direct phase transition from the tetragonal to the ferroelectric structure at 800K whereas SBT presents an intermediate non-
polar orthorhombic \textit{Am} \textit{am} phase (No. 63) between 500-600K and 770K. The cell parameters of the two orthorhombic phases are related to the tetragonal ones according to \( a_T = b_T = 3.917 \text{Å} \) and \( c_T = 25.114 \text{Å} \) for the tetragonal structure and \( a_O = 5.531 \text{Å} \), \( b_O = 5.534 \text{Å} \) and \( c_O = 24.984 \text{Å} \) for the ferroelectric phase. The deformation of the cell is very small with respect to the parent tetragonal structure. According to the isotropy subgroup, the origin does not change the arithmetic center of the parent structure and can be considered as the primary order parameter.

The tetragonal space group (\( I4/mmm \)) is a supergroup of the two orthorhombic space groups, the intermediate phase of SBT (\textit{Am} \textit{am}) and the ground state of both compounds (\textit{A}2\textit{om}). In consequence, the low temperature structures can be described in terms of symmetry-adapted distortions with respect to the parent tetragonal structure.\footnote{Table I shows this decomposition in terms of the symmetry-adapted modes that break the tetragonal symmetry for the experimental structures of SBT and SBN obtained with the aid of the tool AMPLIMODES (www.cryst.ehu.es).} The hierarchy of the modes is similar in both compounds: the amplitude of \( X_{3}^{−} \) is dominant and can be considered as the primary order parameter and the \( X_{2}^{+} \) distortion seems to play a secondary role. The analysis of the \( \Gamma_{5} \) polar distortion is more delicate because due to the polar character of the ground state its amplitude depends on the origin. In Table I the chosen origin does not change the arithmetic center of the parent structure. According to the isotropy subgroups the intermediate phase of SBT is naturally explained as a condensation of the \( X_{3}^{−} \) mode, and in terms of the Landau theory of phase transitions the \( I4/mmm \rightarrow Amam \) transition can be continuous. The second transition to the ferroelectric structure should then consist of the condensation of the polar mode. In the case of SBN a direct transition between the tetragonal and the ferroelectric phase can be solely described by the simultaneous condensation of at least any pair of the three modes, and according to Landau theory, it should be first order: the three relevant modes condense simultaneously in an \textit{avalanche} phase transition.\footnote{A complete description of the atomic displacements associated with the three modes can be found in Ref. [12]. In summary, among the 18 degrees of freedom that constitute a generic distortion that links the tetragonal and ferroelectric structure, seven correspond to \( X_{3}^{−} \), and they mainly account for tiltings of the oxygen octahedra around the \((1,1,0)_{T}\) direction of the tetragonal cell and displacements of the Bi cations along the \((1,−1,0)_{T}\) direction. The octahedra behave as rigid units and, in consequence, neighboring octahedra show antiphase tiltings. The polar \( \Gamma_{5} \) distortion involves essentially an antiphase displacement of the Bi atoms and the perovskite blocks, along the \((1,1,0)_{T}\) direction. Among the eight independent displacements associated with the \( X_{2}^{+} \) distortion the main amplitudes correspond to tiltings of the oxygen octahedra around the \( z \) axis and antiphase displacements of the oxygens in the \( Bi_{2}O_{2} \) slabs along the \((1,1,0)_{T}\) direction.}

### III. COMPUTATIONAL DETAILS

The WIEN2k code, based on the full potential LAPW+lo method, was employed for the \textit{ab initio} calculations. Exchange and correlation effects were treated within the GGA approximation with the Perdew-Burke-Ernizohf parameterization. The \( R_{K}^{\text{max}} \) parameter, which is related to the number of radial basis functions used to describe the the inside spheres, was chosen to be 7.5 for both compounds. Calculations in the tetragonal symmetry were performed using a Monkhorst-Pack \( k \) point mesh of \( 8 \times 8 \times 8 \), which is equivalent to 56 independent \( k \) points in the irreducible Brillouin wedge. For calculations in the orthorhombic symmetry a \( k \)-mesh of \( 5 \times 5 \times 5 \), representing 27 independent \( k \) points in the IBZ, was chosen in order to keep the \( k \) point density as constant as possible. In the case of SBT the radii of the atomic spheres chosen for the calculations were 2.0(Sr), 2.26(Bi), 1.8(Ta), 1.6(O) bohrs in the tetragonal structure and 2.25(Sr), 2.3(Bi), 1.8(Ta), 1.6(O) bohrs in the orthorhombic \( A_{2}om \) phase. For SBN, the radii were 2.26(Sr), 2.26(Bi), 1.8(Nb), 1.66(O) bohrs for both the tetragonal and the orthorhombic basis. The choice of the parameters was preceded by energy difference convergence tests which confirmed their validity. The con-

\begin{table}[h]
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Irrep & Direction & subgen & Isotropy & \multicolumn{3}{c|}{Amplitude (Å)} \\
\hline
& & & & SBT & SBN & SBN \\
\hline
\hline
\hline
X_{3}^{−} & (a,−a) & & Amam(63) & 0.90 & 0.86 & 1.12 & 0.81 & 1.14 \\
& & & & (0.99) & (0.99) & (0.99) & (0.99) & (0.99) \\
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\end{tabular}
\end{table}
The primary character of the three relevant distortion modes is manifest in both compounds. However, the role of the other two distortions seems to be different in both compounds. In SBT, $\Gamma_5^-$ presents a well defined energy minimum, while the $X_2^+$ mode is slightly soft at low amplitudes and rapidly hardens for medium amplitudes (Fig. 2) reinforcing its secondary character. In SBN, the energy wells for the $\Gamma_5^-$ and $X_2^+$ modes are very similar and a clear hierarchy between both distortions cannot be established (Fig. [2]).

The energy variations around the tetragonal configuration in terms of the amplitudes of the three relevant modes can be described by a polynomial composed of symmetry invariant terms. The knowledge of the coefficients in the energy expansion allows the quantification of the energy for a general distortion and the strength of the couplings between modes. The energetic contribution of a general combination of $X_3^-$, $\Gamma_5^-$ and $X_2^+$ can be expressed up to fourth order by:

$$\Delta E = E_{X_3^-} + E_{\Gamma_5^-} + E_{X_2^+} + E_{X_3^- \Gamma_5^-} + E_{X_3^- X_2^+} + E_{X_3^- \Gamma_5^- X_2^+}$$

The energy due to the pure modes is given by:

$$E_{X_3^-} = \frac{1}{2} \kappa_{X_3^-} Q_{X_3^-}^2 + \beta_{X_3^-} Q_{X_3^-}^4$$
$$E_{\Gamma_5^-} = \frac{1}{2} \kappa_{\Gamma_5^-} Q_{\Gamma_5^-}^2 + \beta_{\Gamma_5^-} Q_{\Gamma_5^-}^4$$
$$E_{X_2^+} = \frac{1}{2} \kappa_{X_2^+} Q_{X_2^+}^2 + \beta_{X_2^+} Q_{X_2^+}^4$$

The biquadratic couplings read:

$$E_{X_3^- \Gamma_5^-} = \delta_{X_3^- \Gamma_5^-} Q_{X_3^-} Q_{\Gamma_5^-}^2$$
$$E_{X_3^- X_2^+} = \delta_{X_3^- X_2^+} Q_{X_3^-} Q_{X_2^+}^2$$
$$E_{X_3^- \Gamma_5^- X_2^+} = \delta_{X_3^- \Gamma_5^- X_2^+} Q_{X_3^-} Q_{\Gamma_5^-} Q_{X_2^+}$$

and the trilinear coupling is:

$$E_{X_3^- \Gamma_5^- X_2^+} = \gamma_{X_3^- \Gamma_5^- X_2^+} Q_{X_3^-} Q_{\Gamma_5^-} Q_{X_2^+}$$

The coefficients of the polynomials for both compounds were determined by fitting the ab initio energies calculated in more than 60 points of the configuration space for each compound (Table [III]). The most remarkable difference between both compounds is the magnitude of the trilinear coupling, its value in SBN being much larger than in SBT. The magnitudes of the rest of coefficients are quite similar although the stiffness constants of $\Gamma_5^-$ and $X_2^+$ modes approximately exchange their values and, in consequence, their role as the least unstable distortion.

The condensation of two of the three relevant symmetry modes is enough to lower the tetragonal symmetry down to the ferroelectric space group. However, in both compounds the simultaneous freezing of any pair of modes is penalized by the strong and positive biquadratic couplings $\delta$. Fig. [3](a) shows the renormalization of the energies due to the biquadratic coupling for SBT: the presence of a nonzero $\Gamma_5^-$ distortion stabilizes the soft $X_3^-$ mode and a simultaneous condensation of both modes becomes energetically unfavourable. The inclusion of the $X_2^+$ mode is essential to explain the polar ground state of SBT. In fig. [3](b) is shown the energy of SBT as a function of the amplitude of the pure $X_2^+$ mode and when a mixed distortion with $Q_{X_3^-}=0.90 \ \text{\AA}$ and $Q_{\Gamma_5^-}=0.84 \ \text{\AA}$
The stability regions of Fig. 4 correspond to the parent phase of symmetry $I 4/m m m$ (no modes are frozen), the $A_21 a m$ ground state (the three modes are frozen), and three phases associated with the condensation of a single mode: $A m a m$ for $X_3^-$, $F 2 m m m$ for $\Gamma_5^-$ and $A b a m$ for $X_1^+$. The phase diagram of SBN presents a finite gate that joins the stability regions of the tetragonal and ferroelectric phases. Thus, an appropriate renormalization of the order parameters could drive the system directly from the ferroelectric state to the parent structure without an intermediate phase. However, the topology of the phase diagram for SBT forbids this possibility and the intermediate phase must be present in a finite range of temperatures. This result could explain the existence of an avalanche phase transition only in the case of SBN.

The fundamental influence of the strength of the trilinear coupling in the features of the phase diagrams is shown in Fig 4(c). It corresponds to SBT but with the trilinear coupling constant changed to that of SBN, that is, $\kappa_{X^+_3}$ and $\kappa_{X^+_2}$ for SBT, and $\kappa_{X^-_3}$ and $\kappa_{X^-_2}$ for SBN. The diagrams correspond to a particular section where the difference between the stiffness constants $\kappa_{X^+_5}$ and $\kappa_{X^-_5}$ remains constant, which implies a similar temperature renormalization in both order parameters. The stability regions of Fig. 4 correspond to the parent phase of symmetry $I 4/m m m$ (no modes are frozen), the $A_21 a m$ ground state (the three modes are frozen), and three phases associated with the condensation of a single mode: $A m a m$ for $X_3^-$, $F 2 m m m$ for $\Gamma_5^-$ and $A b a m$ for $X_1^+$. The phase diagram of SBN presents a finite gate that joins the stability regions of the tetragonal and ferroelectric phases. Thus, an appropriate renormalization of the order parameters could drive the system directly from the ferroelectric state to the parent structure without an intermediate phase. However, the topology of the phase diagram for SBT forbids this possibility and the intermediate phase must be present in a finite range of temperatures. This result could explain the existence of an avalanche phase transition only in the case of SBN.

The fundamental influence of the strength of the trilinear coupling in the features of the phase diagrams is shown in Fig 4(c). It corresponds to SBT but with the trilinear coupling constant changed to that of SBN, that is, $\gamma = -22.55$ mRy/bohr$^3$ instead of $\gamma = -13.81$ mRy/bohr$^3$. The higher value of the coupling induces a wide direct passage that allows an avalanche phase transition. This suggests that the trilinear coupling does not only stabilize the ground states of the two compounds, but it also governs their sequence of phase transitions.

### V. APPROXIMATE PHASE DIAGRAM

The expansion of the energy in the previous section can be considered as the zero temperature free energy of the system, and a phenomenological free energy can be approximated under the assumptions of the Landau theory of phase transitions. Then, the temperature renormalization is solely contained in the quadratic terms and the stiffness constants present a linear dependence on temperature, such that $\kappa_i = a_i (T - T_{0,i})$ for a given $i$ mode, where $a_I$ and $T_{0,i}$ are constants. Thus, the $ab$ initio stiffness constants are related to the transition temperatures and renormalization constants of the modes by $\kappa_i = -a_i T_{0,i}$. In a first approximation the temperature dependence of higher order terms can be neglected and the free energy reads:

$$F = \sum_{i}^3 \left( \frac{a_i}{2} (T - T_{0,i}) Q_i^2 + \beta_i Q_i^4 \right) + E_{X_3^{-} \Gamma_5^{-}} + E_{X_3^{-} X_3^{+}} + E_{\Gamma_5^{-} X_3^{+}} + E_{X_3^{-} \Gamma_5^{-} X_3^{+}}$$

Fig. 4(a) and (b) show the phase diagrams of the two compounds in the space of the two more negative stiffness constants, $\kappa_{X^-_3}$ and $\kappa_{X^-_2}$ for SBT, and $\kappa_{X^-_3}$ and $\kappa_{X^-_2}$ for SBN. The diagrams correspond to a particular section where the difference between the stiffness constants $\kappa_{X^-_5}$ and $\kappa_{X^-_2}$ remains constant, which implies a similar temperature renormalization in both order parameters. The stability regions of Fig. 4 correspond to the parent phase of symmetry $I 4/m m m$ (no modes are frozen), the $A_21 a m$ ground state (the three modes are frozen), and three phases associated with the condensation of a single mode: $A m a m$ for $X_3^-$, $F 2 m m m$ for $\Gamma_5^-$ and $A b a m$ for $X_1^+$. The phase diagram of SBN presents a finite gate that joins the stability regions of the tetragonal and ferroelectric phases. Thus, an appropriate renormalization of the order parameters could drive the system directly from the ferroelectric state to the parent structure without an intermediate phase. However, the topology of the phase diagram for SBT forbids this possibility and the intermediate phase must be present in a finite range of temperatures. This result could explain the existence of an avalanche phase transition only in the case of SBN.

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### VI. DIMENSIONALITY OF THE ORDER PARAMETERS AND TRILINEAR COUPLING

The expressions of the previous section are not completely general since they do not take into account the correct dimensionality of the the order parameters. As usual in such calculations, the expansion of the energy in terms of distortions from the high-symmetry configuration has been done by fixing the orientation of the multi-dimensional order parameters along a specific direction, the direction that corresponds to one of the observed domains of the low-temperature structure. In the case of SBT and SBN the three order parameters, $X_3^-$, $\Gamma_5^-$ and $X_2^+$, are two-dimensional and the experimental distortion...
FIG. 2: Energy per formula unit relative to the tetragonal structure of SBT (left) and SBN (right) in terms of the amplitudes of the $X_3^-$, $\Gamma_5^-$ and $X_2^+$ distortions.

FIG. 3: Energy per formula unit of SBT along selected lines of the configuration space: (a) in terms of the amplitudes of the the pure polar mode (squares), and the same mode after the $X_3^-$ distortion has been frozen to 1 Å (circles). b) in terms of the amplitude of the pure $X_2^+$ mode (squares) and the same mode after the amplitudes of $X_3^-$ and $\Gamma_5^-$ distortions have been fixed to 0.90 Å and 0.84 Å respectively (circles). The plots have been shifted vertically to fix a common origin.

corresponds to the specific direction indicated in Table I and the symmetry-equivalent ones.

A general distortions must be expressed as two-dimensional vectors and, in order to simplify the notation, we will use the following correspondences in cartesian and polar coordinates:

$$Q_{X_3^-} = \varphi \equiv (\varphi_1, \varphi_2) = (\rho_{\varphi} \cos \theta_\varphi, \rho_{\varphi} \sin \theta_\varphi)$$

$$Q_{\Gamma_5^=} = \psi \equiv (\psi_1, \psi_2) = (\rho_\psi \cos \theta_\psi, \rho_\psi \sin \theta_\psi)$$

$$Q_{X_2^=} = \eta \equiv (\eta_1, \eta_2) = (\rho_\eta \cos \theta_\eta, \rho_\eta \sin \theta_\eta)$$
The invariant polynomials for general directions of the order parameters obtained with the aid of the INVARIANTS utility are given in Table IV in cartesian and polar coordinates. The lowest order term that includes anisotropy is the third order invariant related to the trilinear coupling; moreover, the presence of this term is enough to explain the observed ground state. For a negative trilinear coupling the absolute minimum corresponds to the ground state to the parent phase. The right panel corresponds to SBT but with the value of the trilinear coupling switched to that of SBN and it presents a wide passage that opens the possibility of a direct transition. The arrows show the same hypothetical paths along the three phase diagrams.

FIG. 4: Phase diagrams for SBT (left) and SBN (center). The variables of the abscises correspond to the second more unstable mode, $\Gamma_5^-$ for SBT and $X_4^+$ for SBN. The diagram for SBN presents a narrow gate that allows a direct transition from the ground state to the parent phase. The right panel corresponds to SBT but with the value of the trilinear coupling switched to that of SBN and it presents a wide passage that opens the possibility of a direct transition. The arrows show the same hypothetical paths along the three phase diagrams.

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TABLE IV: Invariant polynomials up to fourth order of the components of the order parameters in cartesian and polar coordinates. $\varphi$, $\psi$ and $\eta$ correspond to $X_3^-$, $\Gamma_5^-$ and $X_4^+$ respectively.

| Cart. coor. | 2nd order | $|\varphi|^2, |\psi|^2, |\eta|^2$ |
|-------------|-----------|---------------------------------|
| 3rd order   | $\varphi_1 \psi_1 \eta_1 + \varphi_2 \psi_2 \eta_2 - \varphi_2 \psi_2 \eta_1 - \varphi_1 \psi_2 \eta_1$ |
| 4th order   | $|\varphi|^4, |\psi|^4, |\eta|^4$, $\varphi_1^4 + \varphi_2^4, \psi_1^4 + \psi_2^4, \eta_1^4 + \eta_2^4$, $|\varphi|^2|\psi|^2|\eta|^2$, $\varphi_1^2 \psi_1^2 \eta_1^2 + \varphi_2^2 \psi_2^2 \eta_2^2$, $\varphi_1 \psi_1 \eta_1 \psi_2 \eta_2$ |

| Polar coor. | 2nd order | $\rho_\varphi^2, \rho_\psi^2, \rho_\eta^2$ |
|-------------|-----------|---------------------------------|
| 3rd order   | $\rho_\varphi \rho_\psi \rho_\eta [\cos \theta_\varphi \cos (\theta_\psi + \theta_\eta) - \sin \theta_\varphi \sin (\theta_\psi - \theta_\eta)]$ |
| 4th order   | $\rho_\varphi^4, \rho_\psi^4, \rho_\eta^4$, $\rho_\varphi^4 (3 + 4 \cos 4 \theta_\varphi), \rho_\psi^4 (3 + 4 \cos 4 \theta_\psi), \rho_\eta^4 (3 + 4 \cos 4 \eta)$, $\rho_\varphi^2 \rho_\psi^2 \rho_\eta, \rho_\varphi^2 \rho_\psi^2 \rho_\eta, \rho_\varphi^2 \rho_\psi^2 \rho_\eta$, $\rho_\varphi^2 \rho_\psi^2 \rho_\eta, \rho_\psi^2 \rho_\eta \sin 2 \theta_\psi \sin 2 \theta_\eta, \rho_\varphi^2 \rho_\psi^2 \rho_\eta \sin 2 \theta_\psi \sin 2 \theta_\eta$, $\rho_\varphi^2 \rho_\psi^2 \rho_\eta \sin 2 \theta_\psi \sin 2 \theta_\eta$ |

focus on the effect of the trilinear coupling term and to maintain the analogy with the one-dimensional case of Ref. 22, we have not included in the Hamiltonian the rest of the fourth order terms that are allowed by symmetry. The complete Hamiltonian reads:

$$H = H_\varphi + H_\psi + H_\eta + H_{\varphi, \psi, \eta}$$

The analysis of all the possible combinations of the parameters of the Hamiltonian is beyond the scope of this work and we have limited the study to some particular cases. First, we have considered the same
units of the trilinear coupling. Temperature is given in a narrow range of temperatures and the low temperature transition is first-order, and finally, for stronger couplings \( E/C = 0 \) and statistics were collected during at least \( 10^6 \) Monte Carlo steps after a proper equilibration. Fig. 5 shows the equilibrium amplitudes of the order parameters for the order-disorder case \( E/C = 10 \) and three different values of the trilinear coupling. Temperature is given in units of \( C_\varphi \). Three different regimes can be observed, for low values of \( \gamma \) [Fig. 5(a)] both transitions are continuous and the range of stability of the intermediate phase is quite wide; for intermediate values of the trilinear coupling [Fig. 5(b)] the intermediate phase is stable in a narrow range of temperatures and the low temperature transition is first-order, and finally, for stronger couplings [Fig. 5(c)] the intermediate phase disappears and a direct discontinuous \textit{avalanche} phase transition between the tetragonal and ferroelectric phase occurs with the simultaneous condensation of the three distortions.

Although results are qualitatively similar to those of previous works with one-dimensional order parameters, the different calculation methods, mean field approximations and Monte Carlo simulations, prevent a quantitative evaluation of the role of the dimensionality in the stability of the phases. Therefore, we have also performed Monte Carlo simulations of the one-dimensional model and the comparison between the phase diagrams for both cases are shown in Fig. 6. An accurate estimation of the transition temperatures was obtained by inspecting the probability distributions of the amplitudes of the distortions with simulations close to the critical regions. In the displacive regime the intermediate phase is suppressed for \( \gamma \sim 2.5E_\varphi \) and \( \gamma \sim 2.0E_\varphi \) for one and two-dimensional order parameters respectively [Fig. 6(a)]. The influence of the dimensionality is more remarkable in the order-disorder regime where the \textit{avalanche} phase transition appears for \( \gamma \sim 0.45E_\varphi \) in the 1d case, and \( \gamma \sim 0.3E_\varphi \) when the multidimensionality of the order parameters is considered. It can be concluded that for higher dimensionalities of the irreducible representations associated to the order parameters the trilinear coupling is more efficient to favour a direct phase transition between the high and low-temperature phases.

Multidimensional order parameters are ubiquitous in structural phase transitions. For instance, in completely different compounds as the ferroelectric \( \text{Ca}_3\text{Mn}_2\text{O}_7 \), antiferroelectric \( \text{PbZrO}_3 \) (PZO) and the double perovskites \( \text{Sr}_2\text{MWO}_6 \) \( M = \text{Zn}, \text{Ca} \) and Mg, that do not present any dielectric anomaly, the trilinear coupling is critical to stabilize the ground state as in SBT and SBN. Table V shows the relevant irreducible representations and their dimensions. Whereas the case of \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) is similar to the SBT/SBN compounds, the high dimensionality of the irreps in the case of PZO could favour the observed strongly-discontinuous transition observed upon cooling from the cubic phase.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Compound} & \textbf{X}_3^+ (2) & \textbf{X}_3^- (2) & \textbf{X}_2^+ (2) \\
\hline
\text{Ca}_3\text{Mn}_2\text{O}_7 & \text{X}_3^+ (2) & \text{X}_3^- (2) & \text{X}_2^+ (2) \\
\text{PbZrO}_3 & \text{R}_5 (3) & \Sigma_2(12) & \Sigma_3(12) \\
\text{Sr}_2\text{MWO}_6 & \Gamma_5^+ (3) & \Gamma_5^- (3) & \Gamma_2^+ (6) \\
\text{SBT/SBN} & \text{X}_3^- (2) & \Gamma_5^- (2) & \text{X}_2^+ (2) \\
\hline
\end{tabular}
\caption{Three examples of the multidimensionality of order parameters that couple trilinearly (the labels of the irreducible representations and their dimensions are listed). The \( M \) cation in \( \text{Sr}_2\text{MWO}_6 \) corresponds to \( \text{Zn}, \text{Ca} \) and Mg.}
\end{table}

\section{VII. CONCLUSIONS}

Despite the different sequence of phase transitions that SBT and SBN go through, first principles calculations shows that the nature and main features of the instabilities in both compounds are qualitatively very similar, and that most of the conclusions about SBT obtained in Ref. 12 can be extended to SBN. Among the three symmetry adapted distortions \( (X_3^-, \Gamma_5^- \text{ and } X_2^+) \) that take
part to drive the tetragonal $I4/mmm$ parent phase to the polar $A2_{1}am$ structure, $X_{3}^{-}$ is dominant with the highest amplitude and the deepest energy well ($\sim 11$ mRy per formula unit). The depths of the secondary distortions $\Gamma_{5}^{-}$ and $X_{2}^{+}$ are similar in SBN ($\sim 3.5$ mRy p.f.u.), while in SBT $X_{2}^{+}$ is hardly unstable and $\Gamma_{5}^{-}$ slightly deeper (5.2 mRy p.f.u.).

In both compounds, the simultaneous condensation of the primary instability $X_{3}^{-}$ with any of the other two distortions is penalized energetically by positive strong biquadratic couplings. Thus, the trilinear coupling is the key ingredient that allows the simultaneous condensation of the three modes and its role is essential to stabilize the observed ground state.

The most noticeable difference between SBT and SBN is associated with the magnitude of the trilinear term. The polynomial expansion of the energy of both compounds shows that the trilinear coupling is much stronger in SBN than in SBT, suggesting that its magnitude could be crucial to suppress the intermediate phase in SBN. Moreover, the analysis of phenomenological phase diagrams for SBT and SBN shows that a higher value of this constant is enough to change the topology of the phase diagram, allowing a direct phase transition from the parent phase to the ground state.

Finally, a simplified $\phi^{4}$ Hamiltonian that retains the symmetry requirements and the correct dimensionality of the order parameters has been developed for the SBT/SBN system. Monte Carlo simulations do not show qualitatively differences in comparison with the one-dimensional case: the different sequence of phase transitions observed in both compounds can be reproduced by changing the strength of the trilinear coupling. However, according to the present calculations, the increment of the fluctuations associated with the higher dimensionality of the order parameters tends to favour the suppression of the intermediate phase and to reinforce the first order character of the direct transition between the high- and low-temperature structures.

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**References**

1. B. Aurivillius, Ark. Kemi 1, 463 (1949); 1, 499 (1949).
2. C.A. Paz de Araujo, J.E. Cuchiaro, L.D. McMillan, M.C. Scott and J.F. Scott, Nature (London) 374, 627 (1995).
3. J.F. Scott, Phys. World 8, 46 (1995)
4. K. Amanuma, T. Hase, and Y. Miyasaka, Appl. Phys. Lett. 66, 221 (1995)
5. A.D. Rae, J.G. Thompson and R.L. Withers, Acta Crystallogr. Sect. B: Struct. Sci. 48, 418 (1992).
6. Y. Shimakawa, Y. Kubo, Y. Nakagawa, S. Goto, T. Kamiyama, H. Asano and F. Izumi, Phys. Rev. B 61, 6559 (2000).
7. R.E. Newham, R.W. Wolfe, and J.F. Dorrian, Mater. Res. Bull. 6, 1029 (1971); R.E. Newham, R.W. Wolfe, R.S. Horsey, and F.A. Diaz-Colon, ibid. 8, 1183 (1973)
8. Ismunandar, B.J. Kennedy, Gunawan and Marsongkohadi,
