# Theory of the ferroelastic transition in barium sodium niobate

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The tetragonal-orthorhombic phase transition of barium sodium niobate is theoretically investigated. Available structural data are examined and it is concluded that the change in space symmetry is from $P4bm$ ($C_{4v}^2$) to $Ccm2_1$ ($C_{2v}^{12}$), thus differing from previous assignments. The order parameter of the transition is shown to be distinct from the spontaneous shear strain characterizing the ferroelasticity of the orthorhombic phase. The symmetry properties of the order parameter are found to be described by a two-dimensional irreducible representation of $P4bm$ corresponding to the $Z$ point $[\vec{k} = (0,0,\pi/c)]$ of the first Brillouin zone. The free-energy expansion is constructed on this basis and the behavior of elastic constants is examined. Comparison is made to experimental data.

## I. INTRODUCTION

Barium sodium niobate, $Ba_2NaNb_5O_{15}$ (BSN), belongs to a large family of crystalline compounds with a structure of the tungsten-bronze type.[1] It undergoes a ferroelectric phase transition, situated at 585 °C for the stoichiometric composition. The change in point symmetry associated with the onset of the spontaneous polarization can be described by the symbolic notation $4/mmmF4mm$ of Aizu's classification.[2]

In contrast to most similar ferroelectric niobates, BSN does not keep a tetragonal symmetry down to room temperature. Another transition occurs at 300 °C into an orthorhombic symmetry, giving rise to ferroelastic properties.[3] The symmetry change corresponds to Aizu's species $4mmFmm2$.

Ferroelectric and ferroelastic properties coexist at room temperature. However they are not coupled: A BSN crystal possesses four stable orientation states[4] corresponding to two antiparallel polarization directions along [001] and two opposite values of the spontaneous strain tensor.[5] Referred to the conventional axes of the tetragonal phase (Fig. 1) the spontaneous strain is a pure shear in the (001) plane.

Many studies have been carried out on the physical properties of BSN mainly aimed at investigating and optimizing the outstanding nonlinear optical, electro-optical, and piezoelectric properties of this material. Less attention has been given to the understanding of the mechanisms of the two structural phase transitions. In particular, the origin of the ferroelastic transition is not clear. The order parameter of this transition has been difficult to identify because the space symmetry of the tetragonal phase is not yet experimentally established. Moreover, some ambiguity remains on the nature of the room-temperature orthorhombic space group.

In this paper we investigate the symmetry properties of the order parameter (OP) and elaborate a phenomenological theory of the considered transition.

In Sec. II it will be demonstrated, on the basis of recent elasticity measurements,[6] that the spontaneous strain can be ruled out as a possible OP of the transition, in contradiction with a previous theory by Yamada *et al.*[7] A careful examination of the available structural data will then be carried out, and the symmetry properties of the OP will be investigated by group theory. In Sec. III the form of the free-energy expansion will be determined, the behavior of elastic constants will be deduced and compared with experimental results.

## II. SYMMETRY PROPERTIES OF THE ORDER PARAMETER

According to Landau's theory of phase transitions,[8] the order parameter (OP) of a transition transforms according to an irreducible representation (IR) of the space group of the more symmetric phase. In BSN, this phase is tetragonal and stable above 300 °C.

Let us first discuss the previous assumption[7] of an OP coinciding with a shear strain in the (001) plane.

The shear strain in the (001) plane transforms according to the $\Gamma_4$ representation of the $4mm$ point group (Table I), and is translationally invariant ($\vec{k}=0$). The free-energy expansion corresponding to this particular OP can be constructed in the usual way.[9] We obtain

$$\begin{aligned} F = {} & \tfrac{1}{2}\tilde{C}_{66}e_6^2+\tfrac{1}{4}\beta e_6^4+\tfrac{1}{6}\gamma e_6^6+\tfrac{1}{2}\tilde{C}_{11}(e_1^2+e_2^2) \\ & +\tilde{C}_{12}e_1e_2+\tilde{C}_{13}(e_1+e_2)e_3+\tfrac{1}{2}\tilde{C}_{33}e_3^2 \\ & +\delta_1(e_1+e_2)e_6^2+\delta_2e_3e_6^2+\theta(e_i,P_j)\;. \end{aligned} \qquad (1)$$

In this expression, the frame of reference is set parallel to the tetragonal axes and the Voigt contracted notation[10] is used for strain $e_i$ and elastic components $\tilde{C}_{ij}$. Tilded elastic constants are referred to the tetragonal axes, while untilded ones correspond to the orthorhombic axes (Fig. 1). The

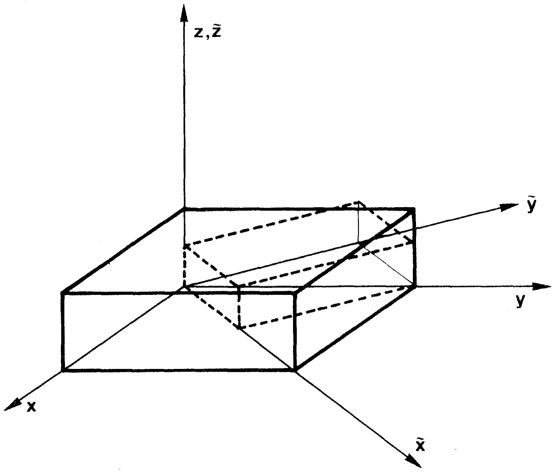

FIG. 1. Reference axes used in barium sodium niobate. ($\tilde{x}\tilde{y}\tilde{z}$): conventional axes of the tetragonal phase (Ref. 10). ($xyz$): Conventional axes of the orthorhombic phase. The two frames correspond to each other by a rotation of 45° around the common $z$ axis.

function $\theta(e_i, P_j)$ contains linear invariants of $e_1$, $e_2$, $e_3$ as well as polarization $P_j$ and piezoelectric terms.

Below the transition, the orthorhombic elastic constants $C_{11}$ and $C_{22}$ have different values. Their difference can be expressed in the tetragonal axes as[11]

$$|C_{22} - C_{11}| = 4|\tilde{C}_{16}| \ .$$

The component $\tilde{C}_{16}$, which vanishes in the tetragonal phase, can be calculated, below the transition, from the free-energy expansion. We have

$$\tilde{C}_{16} = \frac{\partial^2 F}{\partial e_1 \partial e_6} = 2\delta_1 e_6 \ .$$

The difference $C_{22} - C_{11}$ is seen to be proportional to the spontaneous strain $e_6$. Consequently, it is predicted to decrease when the phase transition is approached from below. This conclusion holds for both a second- and first-order transition. A similar behavior will also occur if the OP, though distinct from the spontaneous strain, transforms according to the same $\Gamma_4$ representation.[12]

We have shown recently[6] that an opposite behavior was actually observed. The difference $C_{22} - C_{11}$ was measured by Brillouin scattering and was found to increase markedly between 20° and 300 °C, before vanishing above the transition. The assumption of an OP transforming according to $\Gamma_4$ can thus be ruled out.

The other translationally invariant IR can also be discarded. It is seen on Table I that the $\Gamma_2$ and $\Gamma_5$ representations are associated with incorrect changes of point symmetry. On the other hand, the $\Gamma_3$ representation, though inducing the $mm2$ symmetry, leads to an orthorhombic cell rotated by 45° in respect to the observed one.[1]

The translational symmetry of the OP must therefore correspond to another point of the Brillouin zone than its center ($\vec{k} \neq 0$). Consequently it will not be invariant under the primitive translations of the tetragonal phase and will determine a breakdown of translational symmetry at the transition. A superstructure is then likely to be detected in the orthorhombic phase by x-ray measurements. To identify this expected feature, we now examine the available structural data for BSN.

### A. Space symmetry of BSN

The room-temperature crystal structure of BSN has been studied by Jamieson, Abrahams, and Bernstein (JAB).[13] It is constituted by a framework of oxygen octahedra sharing corners and forming three types of tunnels (Fig. 2) of different shape and size. The four triangular tunnels can only accommodate small ions such as $Li^+$. They remain empty in BSN. The cubic and pentagonal tunnels, respectively, contain the $Na^+$ and $Ba^{++}$ ions.

The space group inferred by JAB from x-ray systematic extinctions is $Cmm2$ ($C_{2v}^{11}$) for a crystal cell whose constants are[14]

$$a \approx 17.592 \text{ Å}, \quad b \approx 17.625 \text{ Å}, \quad c \approx 3.995 \text{ Å} \ .$$

TABLE I. Character table of the point group $4mm$ of the tetragonal phase of barium sodium niobate. The lowering of symmetry associated with each irreducible representation has been indicated.

| $4mm$ | $E$ | $2C_4$ | $C_2$ | $2\sigma_v$ | $2\sigma_d$ | Symmetry induced | Polarization and strain components |
|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | $4mm$ | $P_3$; $e_3$; $e_1 + e_2$ |
| $\Gamma_2$ | 1 | 1 | 1 | −1 | −1 | 4 | |
| $\Gamma_3$ | 1 | −1 | 1 | 1 | −1 | $mm2$[a] | $e_1 - e_2$ |
| $\Gamma_4$ | 1 | −1 | 1 | −1 | 1 | $mm2$[b] | $e_6$ |
| $\Gamma_5$ | 2 | 0 | −2 | 0 | 0 | $m$; 1 | $(P_1, P_2)(e_4, e_5)$ |

[a] Mirror planes of $mm2$ parallel to the tetragonal cell of the initial phase.

[b] Mirror planes of $mm2$ rotated by 45° in respect to the tetragonal cell.

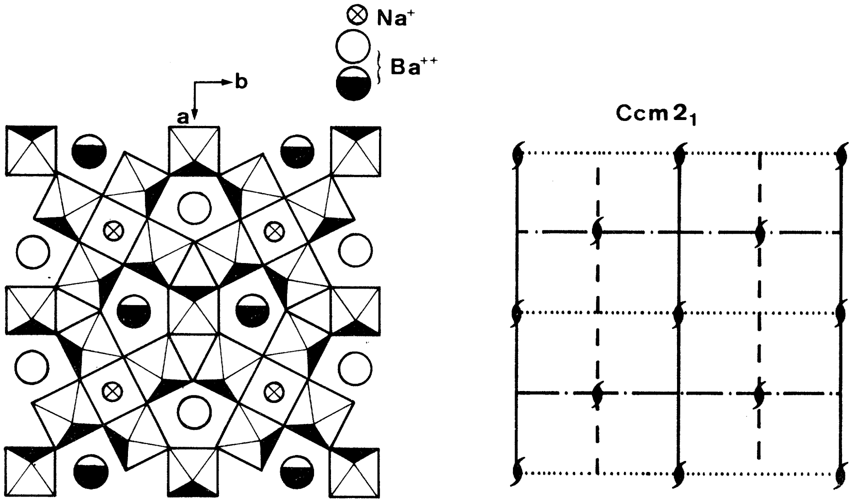

FIG. 2. Schematic representation of the distorted tungsten-bronze structure of barium sodium niobate (after Ref. 16). Barium atoms of two categories are distinguished: half-shaded atoms lie outside symmetry planes. Unshaded ones are in special positions on mirror planes. The tilt of the axes of oxygen octahedra with respect to the $z$ axis has been exagerated. Half of the unit cell is represented. In the consecutive half-cell along [001], the tilts of octahedra and the positions of shaded barium atoms are inverted. This structure corresponds to the space group $Ccm2_1$ reproduced on the right.

However, it has been stressed by these authors and experimentally confirmed by Bobb *et al.*[15] and Giess *et al.*[1] that the true orthorhombic unit cell is two times larger, with a $c$ spacing of 7.99 Å. Further checking by other investigators[16] on crystals of different laboratories assert that this double $c$ spacing is a well-established characteristics of BSN.

The possible structural origin of this superstructure has been mentioned by JAB. Their x-ray investigation has shown that barium and oxygen atoms with $z \approx 0.5$ (in the smaller unit cell) are found to occupy one of two alternate positions, whose distances projected on the (001) plane, range from 0.283 to 0.556 Å. Two situations were then considered by JAB. In the first place, a disordered occupation could occur with the atoms randomly distributed throughout the crystal, among the two positions. On the other hand, an ordered arrangement would be set if the considered atoms occupy alternate positions in consecutive cells along the [001] direction. The experimental evidence of a double $c$ parameter is clearly consistent with the ordered pattern.

It was also emphasized by JAB that the orthorhombicity of the BSN structure is mainly related to the location of the same barium and oxygen atoms which induce the double $c$ spacing. It appears from the data of JAB that if we fix these atoms at a middle point between their two positions, the structure becomes compatible with a tetragonal symmetry.

The preceding argument suggests that the doubling in the [001] direction and the orthorhombic distortion of BSN will set in simultaneously at the tetragonal-orthorhombic transition. Structural data thus support the group-theoretical prediction of a breakdown of translational symmetry at 300 °C.

To work out more precisely the symmetry of the OP, the knowledge of the space groups of BSN is needed. Let us first discuss the nature of the orthorhombic space group.

As mentioned before, the $Cmm2$ ($C_{2v}^{11}$) group was assigned by JAB to a subcell with 4-Å $c$ spacing. This group does not constitute the required space group since it does not take into account the actual lattice constant along the [001] direction.

A careful analysis of the cell structure has consequently been carried out, with the relevant barium and oxygen atoms blocked in ordered positions along the $c$ axis. It is found (Fig. 2) that the only space group compatible with the ordered structure is $Ccm2_1$ ($C_{2v}^{12}$).

Assignment to $Ccc2$ ($C_{2v}^{13}$) had been previously suggested by Bobb *et al.*[15] This group is not consistent with the structure of the subcell. It would require, in particular, some oxygen atoms with $z \approx 0.5$ ($c \approx 4$ Å) to be located at special positions on the binary axes of the space group $Ccc2$. They actually lie outside these axes. In contrast, $Ccm2_1$ only contains screw axes and allows an asymmetric position for these atoms.

The x-ray reflection conditions have been listed in Table II for the three considered space groups: $Cmm2$, $Ccc2$, and $Ccm2_1$. It appears that $Cmm2$, referred to the subcell gives rise to identical systematic extinctions as $Ccc2$ referred to the true unit cell. An additional series of ($h0l$) reflections defines $Ccm2_1$, with $h$ even and $l$ odd. They have not yet been observed.

It can, however, be noted that the missing re-

TABLE II. Reflections conditions relative to three space groups considered for the room-temperature phase of barium sodium niobate. In column 2 are listed the conditions checked for the observed reflections with Miller indices referred to a reduced $c$ parameter (4 Å). These are relabeled in column 3 by use of the actual $c$ parameter (8 Å). The three columns differ, for group $Ccm2_1$, by the $(h0l)$ reflections.

| | $Cmm2$ $(C_{2v}^{11})$ | | | |
|---|---|---|---|---|
| Miller indices | subcell $C \approx 4$ Å | relabeling $C \approx 8$ Å | $Ccc2$ $(C_{2v}^{13})$ $C \approx 8$ Å | $Ccm2_1$ $(C_{2v}^{12})$ $C \approx 8$ Å |
| $hkl$ | $h+k=2n$ | $h+k=2n$ | $h+k=2n$ | $h+k=2n$ |
| $0kl$ | $(k=2n)$ | $l=2n$; $(k=2n)$ | $l=2n$; $(k=2n)$ | $l=2n$; $(k=2n)$ |
| $h0l$ | $(h=2n)$ | $l=2n$; $(h=2n)$ | $l=2n$; $(h=2n)$ | $(h=2n)$ |
| $kk0$ | $(h+k=2n)$ | $(h+k=2n)$ | $(h+k=2n)$ | $(h+k=2n)$ |
| $h00$ | $(h=2n)$ | $(h=2n)$ | $(h=2n)$ | $(h=2n)$ |
| $0k0$ | $(k=2n)$ | $(k=2n)$ | $(k=2n)$ | $(k=2n)$ |
| $00l$ | no conditions | $(l=2n)$ | $(l=2n)$ | $(l=2n)$ |

flections have their origin in the doubling of the $c$ axis, which has been difficult to detect experimentally.[15,16] Their intensity is likely to be weak and they might have been overlooked during previous investigations.

We now discuss the space symmetry of the tetragonal phase. Only powder x-ray data are presently published for this phase.[17] Its point group, $4mm$, is safely deduced from optical, pyroelectric, dielectric, electro-optic, elastic, and dilatometric measurements.[7,18,19]

We note that this crystal class is identical to that of other similar tungsten-bronze ferroelectrics which keep a tetragonal symmetry down to room temperature. For three of these materials, namely, barium strontium niobate,[20] potassium lithium niobate,[21] and mixed barium niobate titanate,[22] the structures and space groups of the tetragonal phase are known. They possess a common space symmetry described by the $P4bm$ $(C_{4v}^2)$ group. Unit-cell constants are $a \approx 12$ Å and $c \approx 4$ Å.

On the other hand, as mentioned above, it is possible to induce a tetragonal symmetry in BSN by slightly displacing the barium and oxygen atoms with $z \approx 0.5$ into a more symmetrical position. It is then easily checked that the resulting structure also has $P4bm$ space symmetry.

On the basis of these arguments and of an inferred doubling of the $c$ parameter we therefore assume that, above 300 °C, BSN acquires the $P4bm$ space group and a unit cell with constants $a \approx 12$ Å and $c \approx 4$ Å. These constants allow a satisfactory indexing of x-ray powder spectra.[17]

The symmetry change at the ferroelastic transition appears to be from $P4bm$ to $Ccm2_1$. It occurs with a doubling of the cell constant in the [001] direction. However, no breakdown of translational symmetry is expected in the (001) plane.

We had considered the possibility of such a breakdown in a previous work,[23] by noting that the orthorhombic cell ($\approx 17 \times 17 \times 8$ Å$^3$) is four times larger than the tetragonal one ($\approx 12 \times 12 \times 4$ Å$^3$). In fact, the Bravais lattice of the lower phase is of the $C$ type (one face centered). Thus, its true primitive cell, which has monoclinic symmetry, is two times smaller ($\approx 12 \times 12 \times 8$ Å$^3$) than the orthrhombic cell. Moreover, it has been experimentally checked[15] that no superstructure was observed along the $a$ and $b$ axes. A recently published theoretical work[24] was, nevertheless, based on the assumption that a doubling does occur in the $ab$ plane at the ferroelastic transition of BSN. The arguments stated above show that this theory cannot account for the actual symmetry change at the phase transition.

### B. Determination of the irreducible representation

It is well known[9] that the IR of a given space group, $\Gamma_n(\vec{k})$ can be labeled with the help of two indices. The $\vec{k}$ vector, corresponding to a point of the first Brillouin zone, describes its translational symmetry properties. The $n$ index defines a small IR, noted $\tau_n$ of the little group $G(\vec{k})$. The dimension of $\Gamma_n(\vec{k})$ is a product of the dimension of $\tau_n$ and of the number of arms in the star of the $\vec{k}$ vector.

Lavrencic *et al.*[25] have summarized the conditions which define the $\vec{k}$ vector associated with the OP of a phase transition. These are

$$e^{-i\vec{k}\cdot\vec{T}_0} = 1, \quad e^{-i\vec{k}\cdot\vec{T}} \neq 1\ .$$

The vector $\vec{T}_0$ is any primitive translation of the distorted phase and $\vec{T}$ is a primitive translation of the high-symmetry phase which is no longer present below the transition. For a doubling of $c$ parameter in space group $P4bm$, the only compatible $\vec{k}$ vector is

$$\vec{k}_0 = (0, 0, \pi/c)\ .$$

It corresponds to the $Z$ point of the Brillouin-zone

TABLE III. Character table for the little group corresponding to the $Z$ point of the Brillouin zone of space group $P4bm$. Rotational and translational parts have been indicated for each element of the group. $\vec{T}_a, \vec{T}_b, \vec{T}_c$: primitive translations of the tetragonal lattice. $\vec{t}_1$: nonprimitive translation $(\frac{1}{2}a, \frac{1}{2}a, 0)$. The standard origin for $Ccm2_1$ is displaced in respect to that of $P4bm$ by translation $(0, \frac{1}{2}a, 0)$.

| Origin at center | $\{E \mid 0\}$ | $\{C_4 \mid 0\}$ | $\{C_2 \mid 0\}$ | $\{C_4^3 \mid 0\}$ | $2\{\sigma_v \mid \vec{t}_1\}$ | $2\{\sigma_d \mid \vec{t}_1\}$ | $\vec{T}_a$ | $\vec{T}_b$ | $\vec{T}_c$ | Symmetry induced |
|---|---|---|---|---|---|---|---|---|---|---|
| Origin displaced by $(0, \frac{1}{2}a, 0)$ | $\{E \mid 0\}$ | $\{C_4 \mid \vec{t}_1\}$ | $\{C_2 \mid 0\}$ | $\{C_4^3 \mid \vec{t}_1\}$ | $2\{\sigma_v \mid \vec{t}_1\}$ | $2\{\sigma_d \mid 0\}$ | $\vec{T}_a$ | $\vec{T}_b$ | $\vec{T}_c$ | |
| $\tau_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $-1$ | $P4bm$ |
| $\tau_2$ | 1 | 1 | 1 | 1 | $-1$ | $-1$ | 1 | 1 | $-1$ | $P4nc$ |
| $\tau_3$ | 1 | $-1$ | 1 | $-1$ | 1 | $-1$ | 1 | 1 | $-1$ | $P4_2bc$ |
| $\tau_4$ | 1 | $-1$ | 1 | $-1$ | $-1$ | 1 | 1 | 1 | $-1$ | $P4_2nm$ |
| $\tau_5$ | 2 | 0 | $-2$ | 0 | 0 | 0 | 2 | 2 | $-2$ | $Ccm2_1$<br>$Pna2_1$ |

boundary of the simple tetragonal lattice.[26]

The star of $\vec{k}_0$ has one arm. The dimensions of the various IR of the $\Gamma_n(\vec{k}_0)$ type, are therefore the same as the dimensions of the respective small representations $\tau_n$.

The character table of $G(\vec{k}_0)$ is reproduced on Table III. Its factor group is isomorphous to the point group $4mm$.[26] There are five real IR, four of which are one dimensional. The last one, labeled $\tau_5$, is two dimensional.

All five IR are acceptable to describe the symmetry change at a phase transition, as they fulfill the two conditions stated by Landau[8]:

(i) The symmetric cube $[\tau^3]$ does not contain the totally symmetric IR of the $P4bm$ group. This result is a consequence of the fact that the $[\tau^3]$ corresponds to the $\vec{k}$ vector $3\vec{k}_0 \neq 0$, while the totally symmetric IR is translationally invariant ($\vec{k} = 0$).

(ii) The antisymmetric square $\{\tau^2\}$ has no IR in common with the vector representation. This condition is obviously obeyed by each one-dimensional IR as its square $\tau^2$ is totally symmetric. On the other hand, $\{\tau_5^2\}$ coincides with the $\Gamma_2$ representation of the $4mm$ point group (Table I) while the vector representation reduces to $\Gamma_1 + \Gamma_5$.

The space groups determined by each IR for the lower-symmetry phase are listed on Table III. They have been obtained by the shortened procedure described by Birman[27] and Lavrencic[25]: It has been checked that a given IR of $P4bm$ contains the totally symmetric IR of the low-symmetry group.

It will be noted that each one-dimensional IR keeps unchanged the point symmetry of the crystal. Thus, none of the four one-dimensional IR can describe the observed symmetry change of BSN. In contrast, the $\tau_5$ small representation induces the correct point symmetry $mm2$. Moreover, it is compatible with the space group $Ccm2_1$ assigned to the orthorhombic phase.

However, as pointed out by Landau,[8] a multidimensional IR such as $\tau_5$, does not determine unambiguously the symmetry of the distorted phase. It is shown on Table III that another orthorhombic space group $Pna2_1$ is also associated with $\tau_5$. Lower point symmetries can be obtained, as well, which have not been indicated. The actual symmetry onseting below the transition is defined by stability criteria which will be recalled in Sec. III.

The preceding group-theoretical analysis thus establishes that the OP of the ferroelastic transition in BSN transforms, under the space symmetry $P4bm$, according to the two-dimensional IR, $\Gamma_5(\vec{k}_0)$. We can note that the space group $Ccc2$ considered by Bobb *et al.*,[15] though being a subgroup of $P4bm$, cannot be related to an IR of the $\Gamma_n(\vec{k}_0)$ type.

## III. PHENOMENOLOGICAL THEORY OF BSN

To account for the temperature dependence of physical quantities in the vicinity of a phase transition it is well known[8] that a free-energy expansion compatible with the high-symmetry space group may be used. The expansion is restricted to quantities which vary rapidly in the considered temperature range. These are the OP and the relevant macroscopic quantities (strain, polarization) which can couple to it.

The OP adopted for BSN has been shown to transform according to $\Gamma_5(\vec{k}_0)$. Consequently, it possesses two independent components. It was pointed out that the IR of the factor group of $G(\vec{k}_0)$ are isomorphous to those of the point group $4mm$ (Table I). Accordingly we choose a basis $(\eta, \zeta)$ in the two-dimensional space of the OP which corresponds to the $(x, y)$ components of the vector representation. Besides, we refer macroscopic quantities to the tetragonal axes (Fig. 1).

The free energy is then constructed from invariants of $P4bm$ by the usual projector technique.[9] We can write

$$F = \Phi(\eta, \zeta) + \Phi_1(e_i, P_j) + \Phi_2(e_i, P_j) + \Phi_3(e_i, P_j, \eta, \zeta) + \Phi_4(e_i, P_j, \eta, \zeta) \ . \qquad (2)$$

Various contributions to $F$ have been distinguished. The function $\Phi$ contains the invariants built from the OP. We obtain for it

$$\Phi = \tfrac{1}{2}\alpha(\eta^2 + \zeta^2) + \tfrac{1}{4}\beta_1(\eta^4 + \zeta^4) + \tfrac{1}{2}\beta_2\eta^2\zeta^2 + \tfrac{1}{6}\gamma_1(\eta^6 + \zeta^6) + \tfrac{1}{2}\gamma_2\eta^2\zeta^2(\eta^2 + \zeta^2) \ . \qquad (3)$$

Sixth-order invariants have been introduced in agreement with the first thermodynamic order which is experimentally found for the transition.[23,28]

The function $\Phi_1$ contains the linear invariants of strain and polarization components (Table I). It accounts for the thermal expansion and pyroelectricity of the tetragonal phase of BSN. The $\Phi_2$ contribution is related to the elastic, dielectric, and piezoelectric energies of the crystal. It has been restricted to quadratic terms. Besides, we have not included polarization and strain components which do not couple simply to the OP. We get

$$\Phi_1 = \lambda P_3 + \mu_1(e_1 + e_2) + \mu_2 e_3 \ , \qquad (4)$$

$$\Phi_2 = \tfrac{1}{2}\tilde{C}_{11}(e_1^2 + e_2^2) + \tilde{C}_{12}e_1e_2 + \tilde{C}_{13}(e_1 + e_2)e_3 + \tfrac{1}{2}\tilde{C}_{33}e_3^2 + \tfrac{1}{2}\tilde{C}_{66}e_6^2 + \tfrac{1}{2}\tilde{\chi}_3^0 P_3^2 + \tilde{a}_{33}P_3e_3 + \tilde{a}_{31}(e_1 + e_2)P_3 . \qquad (5)$$

$\tilde{\chi}_3^0$ is an inverse susceptibility component and $\tilde{a}_{ij}$, a piezoelectric coefficient. Other notations have been defined for Eq. (1).

The functions $\Phi_3$ and $\Phi_4$ express the coupling between the OP and the strain and polarization components. They are limited to terms which are linear in the macroscopic quantities. We obtain

$$\Phi_3 = \tfrac{1}{2}[\delta_1(e_1 + e_2) + \delta_2 e_3 + \delta_3 P_3](\eta^2 + \zeta^2) \ , \qquad (6)$$

$$\Phi_4 = \tfrac{1}{2}\nu_1(e_1 - e_2)(\eta^2 - \zeta^2) + \nu_2 e_6 \eta\zeta \ . \qquad (7)$$

Only the last contribution $\Phi_4$ will induce a lowering of macroscopic symmetry at the transition.

At a given temperature, the stable or metastable states of a BSN crystal are defined by the following set of conditions:

$$\frac{\partial F}{\partial \eta} = \frac{\partial F}{\partial \zeta} = 0 \ , \qquad \frac{\partial^2 F}{\partial \eta^2} \geq 0, \quad \frac{\partial^2 F}{\partial \zeta^2} \geq 0, \quad \frac{\partial^2 F}{\partial \eta^2}\frac{\partial^2 F}{\partial \zeta^2} \geq \left(\frac{\partial^2 F}{\partial \eta \partial \zeta}\right)^2 \ . \qquad (8)$$

Besides, in the absence of external stress and electric field, we can write

$$\frac{\partial F}{\partial e_i} = \frac{\partial F}{\partial P_j} = 0 \ . \qquad (9)$$

These conditions are fulfilled for any minimum of $F$. The experimentally observed equilibrium state will correspond to the absolute minimum of the free energy. For an arbitrary set of numerical values for the coefficients appearing in the function $F$, this stable state will not necessarily possess the desired space symmetry. To single out the correct linear combination of $(\eta, \zeta)$ let us therefore examine, with help of conditions (9), the symmetry of the strain which onsets below the transition temperature $T_c$. Thus

$$\frac{\partial F}{\partial e_1} - \frac{\partial F}{\partial e_2} = (\tilde{C}_{11} - \tilde{C}_{12})(e_1 - e_2) + \nu_1(\eta^2 - \zeta^2) = 0 \qquad (10)$$

and

$$\frac{\partial F}{\partial e_6} = \tilde{C}_{66}e_6 + \nu_2\eta\zeta = 0 \ . \qquad (11)$$

It appears that if $|\eta| \neq |\zeta|$, both the $e_1 - e_2$ and $e_6$ strain components will in general acquire spontaneous values below $T_c$. The resulting symmetry will be monoclinic if $\eta$ and $\zeta$ are nonzero. It will be orthorhombic with space group $Pna2_1$ if $\eta = 0$ or $\zeta = 0$ (orthorhombic and tetragonal axes parallel to each other).

To obtain a pure shear strain $e_6$ and the correct space group $Ccm2_1$, one must have

$$\eta = \pm\zeta \ . \qquad (12)$$

The two signs define the ferroelastic domains of the orthorhombic phase.

By introducing the linear combination (12) into the stability conditions (8) and (9), one is able to find the temperature dependences of $\eta$ and of the macroscopic quantities $e_1$, $e_2$, $e_3$, $P_3$, and $e_6$.

Since we are dealing with a first-order transition, calculations lead to complicated algebraic expressions. It will be shown in Sec. IV that experimental data are not accurate enough, at present, to allow an useful quantitative comparison. We therefore restrict to a qualitative analysis of the predicted behaviors.

We first note that the effect of the linear function $\Phi_1$ is essentially to shift the transition temperature. It also superimposes on the critical behavior in the vicinity of $T_c$, the normal variations of the relevant quantities due to the thermal expansion or the pyroelectricity. If we neglect these slowly varying quantities, we get, from conditions (9),

$$\Delta(e_1 + e_2) = -k_1\eta^2, \quad \Delta e_3 = -k_2\eta^2, \quad \Delta P_3 = -k_3\eta^2, \quad e_1 - e_2 = 0, \quad e_6 = \pm(\nu_2/\tilde{C}_{66})\eta^2 \ , \qquad (13)$$

where $k_1$, $k_2$, and $k_3$ are functions of the elastic, dielectric, and piezoelectric coefficients as well as of the coupling coefficients $\delta_1$, $\delta_2$, and $\delta_3$. They can be taken, in the first approximation, as temperature independent.

The stability condition (8) then becomes

$$\frac{\partial F}{\partial \eta} = \eta[\alpha + (\beta_1 + \beta_2 - \delta_1 k_1 - \delta_2 k_2 - \delta_3 k_3 - \nu_2^2/\tilde{C}_{66})\eta^2$$

$$+(\gamma_1+3\gamma_2)\eta^4]=0 \quad . \qquad (14)$$

The occurrence of a phase transition requires

$$\alpha=\alpha_0(T-T_0) \quad .$$

In addition, to account for the first order of the transition, the coefficient of $\eta^2$ must be negative while that of $\eta^4$ is positive.

The variations of $\eta$ are qualitatively known. The OP vanishes above $T_c$. In the orthorhombic phase, its modulus decreases on heating the crystal and goes to zero discontinuously at the transition. A similar behavior is predicted from relations (13) to the strain and polarization components.

The developed theory can also be useful to infer the variations of elastic constants. The procedure has been described by Dvorak[29] in his study of the ferroelectric-ferroelastic transition of gadolium molybdate. It involves calculation of the second derivatives of the free energy with respect to strain components.

The results are reproduced on Table IV. An important feature deduced from the theory is that all elastic constants are expected to be temperature independent in the tetragonal phase. This result is well known to hold for any improper transition.[12]

According to the present theory the ferroelastic transition of BSN is of the improper type: The occurrence of a spontaneous strain is a secondary effect resulting from the quadratic coupling of the OP to the shear strain component in the (001) plane. Let us now compare these predictions with the available experimental data.

It is important to show, first, that the anomalous increase of the elastic anisotropy $C_{22}-C_{11}$, pointed out in Sec. II, can be accounted for by the present theory.

On Table IV, the $\tilde{C}_{16}$ component, proportional to $C_{22}-C_{11}$, is expressed as

$$\tilde{C}_{16}=\pm\nu_2\delta_1[(\beta_1+\beta_2)+2(\gamma_1+3\gamma_2)\eta^2]^{-1} \quad .$$

TABLE IV. Temperature dependence of the elastic constants below the transition. $\Delta C_{ij}=C_{ij}^P-C_{ij}$ ($C_{ij}^P$ is the elastic constant at constant polarization; $C_{ij}$ is the temperature-independent elastic constant above the transition). $\rho=(\beta_1+\beta_2)+2(\gamma_1+3\gamma_2)\eta^2$. $\beta_1$, $\beta_2$, $\gamma_1$, $\gamma_2$, $\delta_1$, $\delta_2$, and $\nu_2$ are coefficients of the free-energy expansion; $\eta$ is the order parameter.

| Tetragonal axes | Expression below $T_c$ | Orthorhombic axes | Expression below $T_c$ |
|---|---|---|---|
| $\Delta\tilde{C}_{11}$ | $-\delta_1^2/\rho$ | $\Delta C_{11}$ | $-(\delta_1\pm\nu_2)^2/\rho$ |
| $\Delta\tilde{C}_{12}$ | $-\delta_1^2/\rho$ | $\Delta C_{22}$ | $-(\delta_1\mp\nu_2)^2/\rho$ |
| $\Delta\tilde{C}_{66}$ | $-\nu_2^2/\rho$ | $\Delta C_{66}$ | 0 |
| $\Delta\tilde{C}_{33}$ | $-\delta_2^2/\rho$ | $\Delta C_{12}$ | $(\nu_2^2-\delta_1^2)/\rho$ |
| $\Delta\tilde{C}_{13}$ | $-\delta_1\delta_2/\rho$ | $\Delta C_{33}$ | $-\delta_2^2/\rho$ |
| $\lvert\tilde{C}_{16}\rvert$ | $\lvert\nu_2\delta_1/\rho\rvert$ | $\Delta C_{13}$ | $-\delta_2(\delta_1\pm\nu_2)/\rho$ |
| $\lvert\tilde{C}_{36}\rvert$ | $\lvert\nu_2\delta_2/\rho\rvert$ | $\Delta C_{23}$ | $-\delta_2(\delta_1\mp\nu_2)/\rho$ |

It can be deduced from Eq. (14) that the denominator in the expression of $\tilde{C}_{16}$ keeps a positive sign below $T_c$. Thus, on heating the crystal, as $\eta^2$ decreases, $\lvert\tilde{C}_{16}\rvert$ will increase in agreement with the experimentally observed variations of $C_{22}-C_{11}$. Let us now examine the anomalies predicted by the theory for polarization and strain components.

We note first that experimental investigations[18] have detected no discontinuity at $T_c$ in the variation of the polarization. No anomaly was observed either in the dielectric constant. These results can be due to the incidentally small numerical values of the $\delta_3$ and $k_3$ coefficients. A dielectric anomaly has been detected, for instance, in lithium-substituted BSN compositions.[30]

An anomalous behavior of the strain components can be looked for on thermal expansion curves of BSN. Thus, it can be deduced from the work of Abell *et al.*[19] that $e_1+e_2$, $e_3$, and $e_6$ vary rapidly in the vicinity of $T_c$, in qualitative agreement with Eqs. (13) of the preceding section. These results seem to be composition dependent. Besides, their accuracy is not sufficient to make a quantitative comparison with theory. In particular the temperature dependence of the spontaneous strain $e_6$ cannot be accurately plotted near the transition.

One important pecularity of improper ferroelastic transitions, such as that established for BSN by the present theory, is that elastic constants are expected to remain temperature independent in the high-symmetry phase. From Table IV these quantities are found to undergo a downward jump at $T_c$, then to increase when the temperature is lowered.

Elasticity measurements near $T_c$ have been performed by Yamada[7] through piezoelectric resonances of plates. In this work, experimental results were obtained for the elastic compliances $S_{11}$, $S_{22}$, and $S_{33}$ across the transition. No abrupt step variation was seen on the high-temperature side of the plotted curves. The compliances peak at about 280 °C. They decrease with similar slopes on both sides of the peak.

This deviation from the predicted behavior is not unusual. It has been noted, in particular, for the elastic constants of gadolinium molybdate.[11] These should remain temperature independent. They actually vary in a large temperature interval above the transition, probably due to fluctuations, which are not considered by Landau-type theories. In this material, however, a discontinuous jump, consistent with the theory, was clearly detected while no similar effect is observed in BSN.

We can point out that recent measurements[28] have shown that the transition of BSN is slightly diffused.[31] The birefringence in the (001) plane does not go to zero discontinuously at $T_c$. Its vanishing is spread over a temperature interval of about 30 °C, ranging from 275 to 305 °C. This behavior has been related to a departure from stoichiometry in the investigated samples. Compositional disorder, known to occur for this material, is assumed to induce local variations of the transition temperature.

This feature can clearly account for a blurring of the possible discontinuities of elastic constants. The observed continuous variations could result from the combined effects of fluctuations in the tetragonal phase and of the diffuseness of the transition.

In conclusion, a consistent phenomenological theory of the phase transition of BSN has been given. First, it has been shown, from examination of the behavior of the elastic anisotropy $C_{22}-C_{11}$ that the phase transition of BSN necessarily involves a change in the number of atoms in the unit cell of the crystal. From a comparison of the elementary cell constants in the orthorhombic phase ($12\times 12\times 8$ Å$^3$) and of the cell constants of the tetragonal tungsten-bronze structure ($12\times 12\times 4$ Å$^3$), it has been inferred that the change in unit-cell volume is achieved by a doubling of the $c$ parameter. This conclusion is consistent with the structural data which show that the double $c$ axis and the orthorhombicity of BSN are related to the asymmetric position of the same particular barium and oxygen atoms in the structure. The change in space group at $T_c$ was accordingly deduced to be from $P4bm$ to $Ccm2_1$. A group-theoretical analysis has then demonstrated that this symmetry change agrees with Landau's criteria, while transitions to other considered space groups are not allowed. In addition, the free-energy expansion constructed on this basis accounts for the anomalous behavior observed for $C_{22}-C_{11}$. It does not disagree with other experimental data, if the proven diffuseness of the transition is taken into account.

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