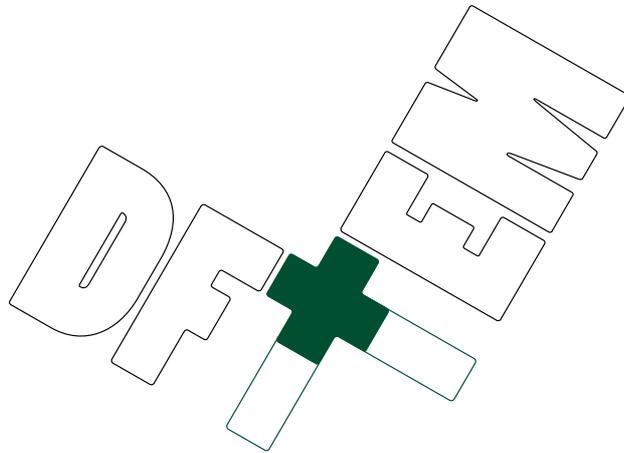Joachim Luitz et al. (Eds.)

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Complex structural instabilities in ferroelectics: soft modes and beyond

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The study and design of ferroelectric materials has experienced a renovated activity in the last years through the application of DFT methods. Numerous DFT calculations have shown that for simple perovskites such as $BaTiO_3$ or $PbTiO_3$, the ferroelectric transition mechanism has the features of a "soft-mode" model: 1) Instability of the calculated high-symmetry paraelectric phase at 0 K with respect to a single polar optical mode at the Brillouin zone centre. 2) Absence of any other comparably unstable (imaginary) phonon branches (if any unstable branches do exist, they exhibit much smaller imaginary frequencies). 3) Agreement of the experimental ferroelectric structural distortion with the calculated unstable mode and its associated "off-center" minima. 4) Approximately constant (quartic) anharmonicity of all the modes along the phonon branch, so that it can be considered local. Within this model the system can be approximated considering as active degrees of freedom only those corresponding to the unstable soft-mode phonon branch, the rest being subsumed in the heat bath. The resulting effective Hamiltonian has then a single vector-like local degree of freedom per unit cell, and the anharmonic terms are Einstein-like, i.e. a quartic crystal field for the local variable. This approach has been very successful in reproducing the essential properties of these simple perovskites, (see [1] for a review).

More complex situations can happen when several modes corresponding to quite different local degrees of freedom are unstable. This is the case of the compound $SrBi_2Ta_2O_9$ (SBT) belonging to the Aurivillius family, which are layered bismuth oxides formed by the regular stacking of Bi_2O_2 slabs and perovskite-like blocks. In SBT we showed [2] that a complex interplay of different structural instabilities, present in this type of compounds, is at the origin of the sequence of phase transitions observed in this compound. Each transition corresponds to the freezing of one of the unstable symmetry-breaking modes. In general, it is not expected that more than one of these instabilities are active at a single transition. However, a sequence of transitions of such type is apparently absent in other compounds of the family such as $SrBi_2Nb_2O_9$ (SBN) and $Bi_4Ti_3O_{12}$ (BTO), although they also have a similar ground state with several analogous symmetry-breaking modes. Hence, we have continued our investigation of this family of compounds performing total-energy and phonon calculations for BTO, which we have analysed within a rigorous group theoretical framework that allows a thorough quantitative comparison with experimental results.

Both SBT and BTO exhibit a high-temperature high-symmetry phase with $I4/mmm$ space group. SBT has perovskite slabs with an equivalent thickness of two TaO_6 octahedra, while those in BTO are three octahedra thick (see Figure 1). Several X-ray and neutron powder diffraction studies, including very recent ones [3] report for room-temperature BTO a $B2cb$ (N. 41) structure (keeping the axis setting of the tetragonal phase), while a single-crystal X-ray analysis [4] claimed an additional monoclinic distortion, with $B1a1$ as space group. To elucidate this problem we relaxed BTO (keeping the experimental lattice parameters) under $B1a1$ symmetry, which includes the orthorhombic space group $B2cb$ as a supergroup. Before making any comparison to experiment, in this complex case where several modes of different symmetries may be frozen, it is essential to describe the structure in terms of symmetry-adapted

distortions. The space of distortions of $B1a1$ symmetry has seven subspaces that can be distinguished by different irreducible representations (irreps) of $I4/mmm$ or by the different space groups that they keep invariant [4], and can be listed as [X_3^+ ($Bmab$), E_u ($F2mm$), X_1^- ($Bbab$), X_2^+ ($Bbam$), E_g ($I12/m1$), A_{2u} ($I4mm$), X_4^- ($Bmam$)].
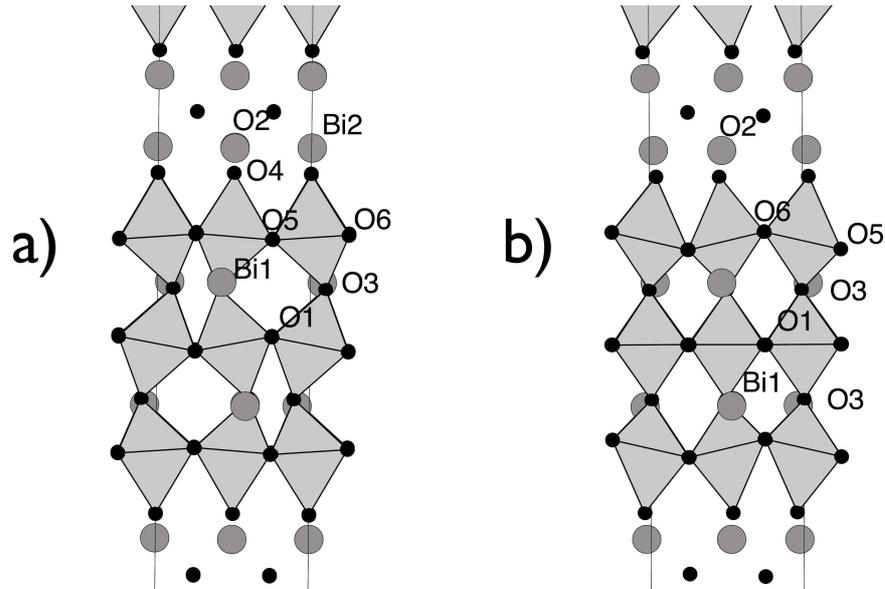

Fig. 1 a) Sketch of the distortion produced by the most unstable normal mode of X_3^+ symmetry (projection along the x-axis b) the same for second unstable mode of X_3^+ symmetry.

The polar E_u distortion is responsible for the spontaneous polarization along the x-axis, while the polar A_{2u} mode should induce a polarization component along the z-axis. The presence of any two of the first three modes is sufficient for reducing the system to the $B2cb$ symmetry, while any of the remaining four modes further reduce the symmetry to $B1a1$. A general $B1a1$ distortion has 51 additional degrees of freedom with respect to the $I4/mmm$ configuration, which are distributed into the seven subspaces above in the form $(8, 11, 3, 5, 8, 9, 7)$. This means, for instance, that a distortion of symmetry X_3^+ can be described by a normalized eight-dimensional "eigenvector" plus a global amplitude $Q_{X_3^+}$ which has dimensions of length. Decomposing the experimental $B1a1$ structure [4] in this form, the seven amplitudes (in bohrs) turn out to be $(1.60, 1.43, 0.96, 0.62, 0.08, 0.22, 0.13)$. It is important to note that the amplitudes are expressed in a common absolute scale and can be compared, indicating the relative weight of each of the distortions. The above decomposition shows the importance of the first two distortions in the $B2cb$ configuration, and the dominant role of the X_2^+ mode in the further symmetry break into $B1a1$. The amplitudes for the relaxed structure are $(-1.77, -1.33, 1.07, 0.96, 0.82, -0.10, 0.25, -0.11)$, in excellent agreement with the experimental values. The agreement for the corresponding eigenvectors is even better, practically coinciding except for the weakest modes. The opposite signs of some of the amplitudes indicate that the relaxation has arrived to a structure different but physically equivalent to the experimental one. A direct comparison of atomic coordinates between the two structures would have been meaningless. The above analysis supports $B1a1$ as the symmetry of this phase. The X_2^+ mode only involves rotations

around the z-axis of the central octahedra within the perovskite-type blocks, with the participation of a small number of oxygen atoms. This distortion would produce minor changes in the diffraction diagram, thus explaining the difficulty to resolve it with powder diffraction techniques.
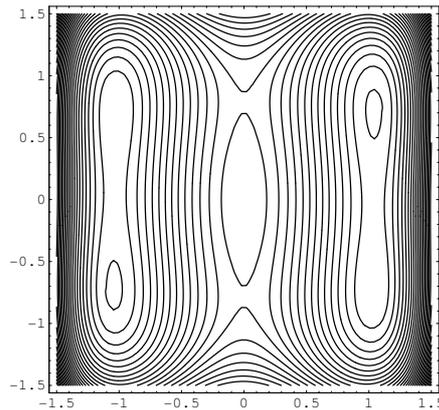

Fig. 2 Contour map of the total energy of BTO within the subspace spanned by the unstable polar normal modes of E_u symmetry. The x and y axis correspond to the amplitude of modes 1 and 2 (see text).

Following the "soft-mode" picture mentioned above, one would expect that the experimental distortion should be the result of the freezing of three unstable normal modes with the relevant symmetries: X_3^+ and E_u modes producing a $B2cb$ configuration (with the E_u mode being responsible of the spontaneous polarization), and a third X_2^+ soft mode responsible for the final $B1a1$ symmetry (the rest of the distortions are marginal). However, the actual relation of the static structure of BTO with the harmonic normal modes of the prototype structure is much more complex. The two most unstable normal modes of the system do have indeed E_u and X_3^+ symmetries (the polar one being more unstable). However, for each of those symmetries the system has an additional unstable mode. This situation had already been pointed out for the polar modes by a previous ab-initio study [5]. The action of the two unstable X_3^+ modes, for an arbitrary amplitude, is depicted in Fig. 1. The most unstable mode (mode 1) is concentrated in the center of the perovskite-like slabs, tilting the central octahedral around the x-axis, but keeping essentially unmoved the Bi_2O_2 layers and the apical oxygens of the neighboring octahedra. Reversely, mode 2 involves mainly displacements of the bismuth atoms in the Bi_2O_2 layers and of the neighboring apical oxygens. Both these two normal "soft" modes strongly distort the BiO_6 octahedra, clearly distinguishing the energy landscape of BTO from the one we observed in SBT. A similar localization of the two eigenvectors within the perovskite blocks and at the Bi_2O_2 layers happens for the two E_u unstable modes. The corresponding phonon branches are thus very flat along the z-direction, showing the very weak coupling of the modes along this direction. One can then infer a strong relaxational character for these modes and an order-disorder behaviour for the resulting transition(s), in agreement with recent experimental reports. The two additional unstable modes of X_3^+ and E_u symmetries are present in the experimental static distortion with a weight comparable to that of the most unstable mode of the same symmetry. In fact, the approximate rigidity of the BiO_6 octahedra observed in the experimental distortion is achieved through this important linear combination of two normal modes that by themselves would strongly distort the octahedra. In other words, in contrast with what it is usually assumed, the octahedra are only rigid through anharmonic

coupling and not in the harmonic approximation. For the E_u modes the coupling is so small that the energy cost of changing the relative signs of the two modes is only about 0.5 mRy (per formula unit) compared with the depth of 31 mRy of the absolute minimum for the "right" combination of the two E_u modes (see Figure 2)). One can then speculate about the possibility of a two-step process for the bulk polarization switching in these materials, as follows. The total spontaneous polarization of the system in the ferroelectric phase is necessarily the result of adding the contributions of the two modes (of similar magnitude), but a minimal opposite field could be enough to favour the antiparallel configuration of the two modes, reducing drastically the polarization. In a second step and at higher field, the dominant most unstable mode would then change sign overcoming a much higher barrier. This peculiar interplay of the polar modes might explain the early characterization of BTO as a "ferrielectric" [6].

A final point to discuss is how the symmetry break $I4/mmm \to B1a1$ takes place in BTO between the phase above 675 C and the room-temperature phase. Although there have been claims of some interme-diate phase [4], up to now there is only clear evidence for a single phase transition at about 675 C. This single transition is connected with a strong peak in the dielectric constant, suggesting the condensation at this point of the ferroelectric distortion associated with the E_u modes. This is also in agreement with our characterization of the polar instability as the strongest one. Hence, if there were indeed a sequence of phase transitions associated to the different active irreps, the expected symmetry changes as temper-ature is decreased would be $I4/mmm \to F2mm \to B2cb \to B1a1$, with two intermediate (ferroelectric) phases and the successive spontaneous freezing of distortions of symmetry E_u, X_3^+ and X_2^+. Although not impossible, the simultaneous condensation of these three different order parameters in a single phase transition would be an extraordinary phenomenon even for a discontinuous transition. There are only a few cases reported in the literature for the simultaneous condensation of two modes. This requires in general a negative quadratic coupling of the order parameters (OPs) in the Landau potential governing the phenomenology around the transition. We have therefore explored the energy landscape and the rel-evant couplings for the active modes mentioned above, obtaining positive couplings in all cases, i.e. the modes do not cooperate in the energy minimization. The freezing of one of them renormalizes positively the stiffness coefficients of the others. We cannot discard that thermal effects may be so strong as to change the sign of these couplings, but what is clear is that there is no feature in the energy map that would favour the simultaneous condensation of the three primary symmetry-breaking modes present in the ground state of the system. Therefore, the apparent absence of intermediate phases in BTO remains a puzzle.

References
[1] D. Vanderbilt, Curr. Opin. Solid State and Mat. Science **2**, 701, (1997); R. Resta, Modelling Simul. Mater. Sci. Eng. **11**, R69 (2003)
[2] J.M. Perez-Mato, M. Aroyo, A. Garcia, P. Blaha, K. Schwarz, J. Schweifer, K. Parlinski, Phys. Rev. B**70**, 214111 (2004).
[3] Q. Zhou, B.J. Kennedy, C.J. Howard, Chem. Mater. 2003, 50025 (2003).
[4] A.D. Rae, J.G. Thompson,R.L. Withers, A.C. Willis, Acta Cryst. B **46**, 474 (1990).
[5] R. Machado, M.G. Stachiotti and R.L. Migoni, Phys. Rev. B **70**, 214112 (2004)
[6] D.L. Hamilton, J. Appl. Phys. **38**, 10 (1967).