



STRUCTURAL PHASE DIAGRAM OF BaBiO_3 IN THE POTENTIAL INDUCED BREATHING MODEL

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Structural stability of BaBiO_3 and of BaKBi_2O_6 is studied using an ionic density-functional-based model. The experimental structure is reasonably reproduced. It is shown that there is no instability against charge disproportionation and against breathing distortion *separately*, but there is an instability against them both *simultaneously*. This proves that at least partially the breathing instability is not due to the "nesting" effect. BaKBi_2O_6 is stable in the cubic structure, as in the experiment.

1. Introduction

In last years BaBiO_3 (BBO) compound has been a subject of numerous experimental and theoretical studies. It is mainly due to the discovery of the 30K superconductivity in the K -doped BBO¹. In the moment BBO shows the highest T_c among those superconductors for which the electron-phonon mechanism may be considered as proven. In the same time it shares some features with the copper-based layered superconductors with yet unclear mechanism of superconductivity. They all have perovskite-like crystal structures, relatively low density of states at the Fermi level, considerable contribution of the oxygen p -states in the conductivity band. There are also some differences. The most important one is the lack of transition metal ions and hence of the magnetism and strong electronic correlations.

As mentioned above, there is convincing evidence that BBO is a conventional superconductor, first of all we mean the large isotope effect², quite usual tunneling spectra², and the estimates of the electron-phonon coupling of the order of 0.8-1.0^{3,4} (which together with the characteristic phonon frequencies of 300-500 cm^{-1} provides the needed T_c). However, somewhat earlier the situation was less clear. This stimulated searches for an unconventional superconductivity. These works⁵⁻⁷, as well as those due to the conventional mechanism^{4,8}, connected the superconductivity with the structural phase transitions that characterize BBO. Namely, at high temperatures ($T \geq 700\text{K}$) BBO has the simple cubic perovskite structure. At lower temperatures it becomes orthorhombic, since BiO_6 octahedra tilt around the crystallographic (110) axis (Bi-O distances do not change). At $T \approx 400\text{K}$ an

additional distortion appears, crystallographically described as alternating along (111) axis breathing of the oxygen octahedra towards and out from the Bi ions. Now two Bi ions are not any more crystallographically equivalent, which led to speculations about charge disproportionation between two Bi ions^{5,6,8}.

The first kind of the instability, it is, the tilting one, is common among perovskites. The first high- T_c superconductor La_2CuO_4 has it too. For the latter compound it has been shown¹⁰ that this instability is driven chiefly by electrostatic ionic forces. To the same conclusion about BBO came the authors of⁴ by analyzing their band-structure calculations of the total energies of the BBO system. In this paper we prove that more directly in the same manner as it has been done in¹⁰ for La_2CuO_4 .

The situation with the breathing instability in the BBO is less clear. Initially it was explained as a consequence of the static charge disproportionation $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$ (which was claimed to be an internal property of Bi ion)^{5,6,10}. The idea is that the negative oxygen ions tend to come closer to the Bi^{5+} , thus causing the observed breathing. Moreover, the cubic structure of BBO existing at high temperatures or in the K -doped compound was considered as dynamically disordered system, again consisting of the Bi^{3+} and Bi^{5+} ions. After that the Bi^{3+} and Bi^{5+} ions considered as the source of electrons or holes bipolarons, hence leading to a bipolaron-type superconductivity. However, neither the photoemission spectroscopy¹¹ nor density-functional calculations^{4,12} reveal any reasonable charge transfer between two Bi sites.

Several researches emphasized the fact that a cubic perovskite in the tight-binding nearest-neighbor

model has a particular band structure⁸. Namely, at half-filling the Fermi surface has nesting pieces in all (111) directions, which might cause a phase transition with doubling the unit cell along (111) axis. However, this idea is also not very convincing, since actual band structure calculations^{4, 12} render the "nesting" band (the one which is flat in the nearest-neighbor model) as wide as ~ 1 eV. Surely an effect due to the splitting of the band in question does exist. Electronic contribution to the total energy connected with a sum over the one-particle energies is always diminishing due to this splitting, but it is not clear how large the effect is and whether it is sufficient to produce the corresponding instability. Incidentally, a breathing instability has not been found in La_2CuO_4 where the same logic is valid and where Weber had predicted the instability of the same "nesting" origin¹³. To distinguish the situation from the perfect nesting of the nearest-neighbor model, we shall avoid the term "nesting" in this regard, using instead the word "quasineesting" or referring simply to band-structure energy effect.

Recently a few attempts have been made to study the phase diagram of BBO in the frameworks of the density functional method, using ab initio pseudopotential technique with respect to the tilting distortion¹⁴, full-potential LAPW method with respect to the breathing distortion¹⁵ and finally in Ref.4 both kinds of distortions were considered by means of the full-potential LMTO method. In the last work, particularly, the equilibrium crystal structure was accurately reproduced, thus proving the validities of the conventional local-density functional approach.

In this relation one can mention also calculations of the electron-phonon coupling^{3, 4}, where it has been found that the coupling is especially strong for the breathing mode. This, together with the high energy of this mode in $(Ba,K)BiO_3$, provides high T_c . However, in a full-potential method it is difficult to separate different distorting mechanism so to make a choice between the models above.

In this paper, in order to get more insight in the energetics of BBO, we used of the so-called potential induced breathing model¹⁶, which is also based on the density-functional theory. The crystal is represented as the superposition of ions sitting in potential wells imitating the Madelung potential, and the kinetic energy of electrons is calculated by the Thomas-Fermi functional. This model does not take into account any peculiarity of the band structure, like quasineesting, so it can serve as a probe for the role played by such effects. It may provide

also a valuable information concerning the stability of different ions in a given crystal lattice, thus giving a tool for investigating the chemical mechanism for *Bi* disproportionation.

The structure of the paper is as follows. In the second section we describe in somewhat more details the PIB model and other calculational moments. In the following section we present numerical results which are discussed and summarized in section IV.

2. Calculational procedure

In this work we used the so-called Potential-induced breathing (PIB) model, proposed about ten years ago¹⁶. The main idea of the model is that the electronic density of a crystal can be reasonably approximated by the superposition of ionic densities. Then the total energy can be calculated by means of the density-functional theory, with a suitable approximation for the density functional. Such an approach had been successfully used by Kim and Gordon¹⁷ for rare gases crystals; a principal improvement introduced in the PIB model is that the superposed densities are not the free ions densities, but the densities of ions in external potentials, imitating the crystal potential. More precisely, ions are supposed to be surrounded by neutralizing spheres, and the radii are so chosen that the constant potential inside be equal to the Madelung potential on corresponding sites. In particular the radius changes with the crystal structure changes, so that the ions are "breathing", hence the name of method. The PIB method has been shown to work surprisingly well for a wide class of materials, among them different oxides, nitrides¹⁶, and copper-based perovskites¹⁰. The method yields correct lattice parameters, atomic position, phonon frequencies, shear moduli etc. We refer to the original papers¹⁶ for further details. The calculations in this work follow these papers closely, except for some technical amendments¹⁸. An important question in the PIB model is the choice of the ionic charges. While it is obvious for simple oxides, for such compounds as high- T_c superconductors it might be problematic. In Ref.19 it was suggested to choose the charges so that the resulting charge distribution be most close to that calculated by the full-potential LAPW method. In this work we have chosen another prescription, namely to treat ionic charges as free parameters to minimize the total energy.

To facilitate the further discussion let us set up here the terminology concerning the crystal structures. As already mentioned in the introduction BBO has three modifications: the high-temperature cubic, the middle-

temperature orthorhombic and the low-temperature monoclinic. The later two is derived from the former one by tilting the BiO octahedra around (110) axe and by applying a breathing distortion. The final monoclinic structure can be characterized by the tilting angle θ and by the breathing coordinate b . In this work we use as b the difference between two Bi-O bond lengths over their sum. Experimental structure at T=0 is described by the Bi-O bond lengths $l=2.29\text{\AA}$ and $l=2.12\text{\AA}$ ($b=0.038$) and by $\theta=9-10^\circ$

3. Numerical results

First of all let us show the results for the cubic undoped BBO. Here by symmetry two Bi ions are equivalent, so the formal valence of each Bi is +4. The calculated equilibrium volume is about 1.61% less than the experimental (in the monoclinic structure)⁹. The Bi-O bond length is 0.54% less than in the experiment. An overbinding of this order is quite common in LDA. Full-potential LMTO calculations give the numbers 3.6% and 1.7%, respectively.

The next question is whether the Bi ions in the cubic BBO are indeed unstable against disproportionation, as suggested in^{5 6 9}. To check this we calculated the total energy as a function of the ionic charge transfer δ by taking alternating Bi ions $\text{Bi}^{+4\pm\delta}$, $\delta \leq 1$ (see Fig.1). This figure shows, that the total energy increases with δ . It means, opposite to the claim of Ref.5-7, that Bi^{4+} ion is stable when sitting in cubic perovskite lattice. The same is true also for expanded or contracted lattice, so the statement is quite general. On the other hand, the energy loss due to the disproportionation for Bi^{4+} ion is much smaller than, say, for Pb^{4+} , thus making full or partial disproportionation easier.

Fig.2 displays the dependence of the total energy on the breathing displacement of the O^{2-} ions, keeping Bi valence equal to +4. The symmetric configuration turns out to be stable. The analysis show that in this case the real charge in the atomic spheres of Bi ions changes considerably, because of the additional penetration of the "tails" from the surrounding oxygens to one sphere and the corresponding outflow from the other. This correspond in PIB the gain energy due to Madelung contribution from the point ion, but the loss energy due to the repulsive two-particle potential between Bi and O ions. The latter surpasses the gain energy leading to the stability the symmetric configuration.

Thus, both these processes, that is a charge transfer and a breathing distortion are energetically unfavor-

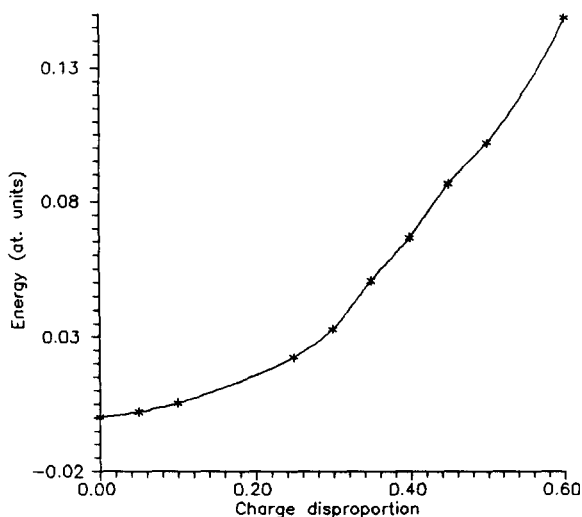


Fig.1. Total energy of cubic BaBiO_3 as function of the PIB charge transfer. The line is a guide to eye.

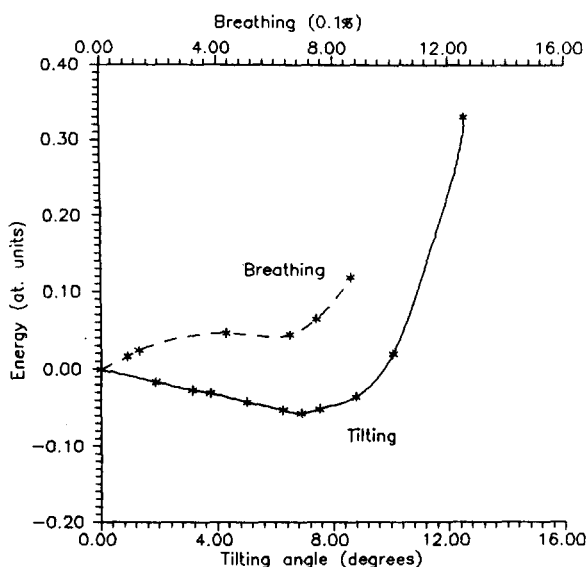


Fig.2. Total energy of BaBiO_3 as function of the breathing and tilting distortions, keeping the charge transfer optimal. The lines are guides to eye.

able when taken separately. However, this situation will be changed if we consider the combined process of a breathing distortion together with a charge transfer. We investigated that by looking for the optimal Bi valence that yields the minimal total energy for a given breathing distortion. This is a very tedious and numerically delicate procedure, especially for small breathing distortion b (b is the displacement of an O ion relative to the Bi-Bi distan-

ce). Nevertheless we were able to find that the optimal valence change δ increases rapidly with b and reaches about 0.4 for $b \approx 0.026-0.04$. Let us remember that experimentally b is slightly less than 0.04. We found minimal total energy at $b=0.030$ and $\delta=0.38$ to be about 2.5 mRy/formula lower than for the undistorted crystal ($b=\delta=0$).

What is the connection between our result obtained in framework of an ionic crystal approach and the "chemical" model for the breathing instability? First of all, we do not see any special "chemical" instability of the Bi^{4+} ion with respect to the disproportionation into Bi^{3+} and Bi^{5+} . Instead we found (at least for large distortion b) the instability only in respect to the breathing together with the disproportionation. Moreover, the optimal δ found as described above corresponds to nearly full screening of the charge change due to the penetration or the outflow of the oxygen ions "tails". In other words, when we take two Bi 's to be Bi^{3+} and Bi^{4+} , and then displace O 's toward Bi^{4+} by $b \approx 0.0075$, the total charge transfer between two Bi 's is rather small. Numerically, charge transfer between the Bi MT-spheres is 0.066, 0.086 or 0.13, for the MT-radius equal to 1.00 Å, 1.13 Å or 1.21 Å, respectively. This is illustrated by the map of the difference between electronic densities for $b=\delta=0$ and $b=0.030$, $\delta=0.4$ (Fig.3). The fact that the charge transfer between Bi MT-spheres is very small has been noted also in LMTO calculations⁴, so it is not an artifact of PIB model.

However, there is an important differences between our results and those of full-potential band structure calculating. For small values of b our calculations show that up to $b \approx 0.01$ the total energy is larger than for $b=0$. The undistorted structure is therefore metastable. This is to be compared with the full-potential LDA calculations of Schwarz et al¹⁵ and Liechtenstein et al⁴. In both these calculations the structure was found to be *unstable* (not *metastable*) against breathing with different values of the energy gain (a few mRy in Ref.15 and a few tenth of mRy in Ref.4). It most probably this discrepancy is due to the absence of the band-structure (quasineesting) effects in the PIB model. We speculate that their role is to make the structure unstable (from metastable).

Now we turn to the second type of distortions found in BBO. Fig.2 shows the dependence of the total energy from the tilting coordinate t , when tilting is performed keeping $Bi-O$ bond length constant. The curve looks quite like that obtained in⁴, thus confirming that

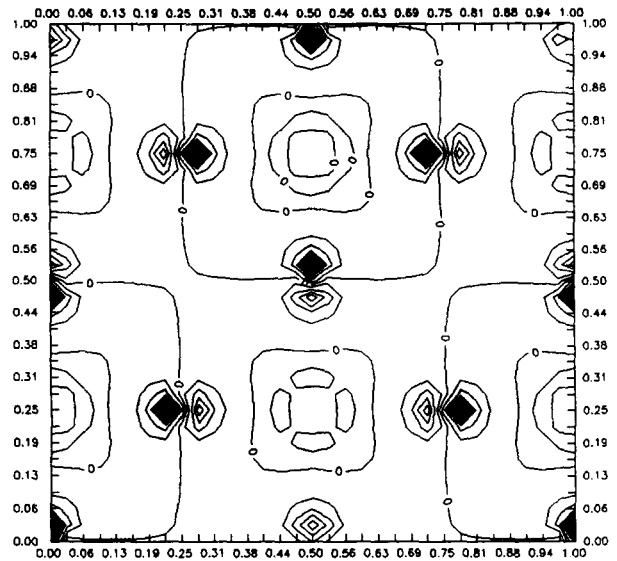


Fig.3. The map of the difference of the electronic densities for the cubic $BaBiO_3$ ($\delta=0$) and for the structure with the equilibrium breathing and the optimal charge transfer ($b=0.03$, $\delta=0.4$). Contour lines by 0.005 $e/a.u.^3$.

the band-structure effects do not play any important role in the tilting instability. Actually, the most important reason for this instability is simply the possibility to pack ions closer in tilted structure. It manifests itself through the ionic Madelung energy.

An intriguing question is due to the interrelations between the breathing and the tilting instabilities. Liechtenstein et al⁴ have shown that in the full-potential LMTO the energy gained by breathing increases a lot when the starting lattice includes tilting in other words, the breathing is much more favorable energetically when introduced on top of tilting. The proposed explanation was that the "quasineesting" effect is enhanced in the tilted structure, due to the narrowing of the conductivity band. We did not find any positive influence of the tilting on the depth of the breathing-induced potential well. On the contrary, in our calculations this depth was slightly less in the structure with the optimal tilting than for the untilted BBO. It supports the idea that the enhancement found in Ref.4 is due to the quasineesting effect.

We were not able to calculate the total energy as a function of two variables, breathing and tilting magnitudes, keeping the valence parameter δ always optimal. However, we were able to study the total energy around the experimental crystal structure, which corresponds to

$b \approx 0.038$ and $t \approx 9^\circ$. We found the equilibrium crystal structure in PIB model to have $b=0.03$ and $t=7^\circ$, not far from the experiment. In this connection we can mention also $BaKBi_2O_6$, which is stable in simple perovskite structure. Our PIB calculations for this compound with Ba and K forming $NaCl$ lattice also do not show any instability.

4. Discussion and summary

The first result of this work is the fact that the PIB model correctly describes the crystal structure of the semiconducting BBO, as well as of the metallic $BaKBi_2O_6$, this is not surprising and proves again that to large extent the energies of such materials can be reasonably described in terms of an ionic crystal, independently of whether it is metallic or not. The same conclusion was made about La_2CuO_4 in the work¹⁰. The reason that most of valent electrons are sitting in fully occupied bands, thus being essentially ionic.

Less trivial result concerns the "chemical model" of the breathing instability^{5 6 9}. Our calculation shows that the simple disproportionation like $2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$ causes a strong charge transfer in the real space and is energetically unfavorable. However, Coulomb energy of the whole system decreases when O ions are displaced accordingly to the breathing pattern together with a moderate charge disproportionation ($\delta \approx 0.4$). In this case charge disproportionation does not mean real charge transfer, to the contrary, it compensates the charge transfer due to oxygen displacement. It is clear that the picture emerged from our calculations is more closer to the results of LMTO considerations than to the "chemical model". An intriguing question appears why the approaches, which have so different driving forces for the breathing instability, lead really to very similar results. In our case the driving force connects with the Madelung contributions from point ions, but in LMTO calculations that arises from the sum of the one-electron energies. The simple answer on this question is that the lattice stability are governed by the total energy depending on

the charge redistribution, but the PIB model gives in our case near the same charge redistribution as the LMTO calculations. As a result it gives near the same lattice structure. That concerns the driving forces they have very relative meaning. They appear as a result of our representation the whole energy as a sum of the partial contribution, that is, a Madelung term, a sum of the one-particle energies, exchange and correlation energy etc. The actual energy difference between two crystal structures is a result of compensation of these different contribution, and a meaningful separation of the single driving force is not always possible. The moral is that the lattice stability as a quantitative problem and should be studied numerically using appropriate quantitative approaches.

To summarize, we present calculations of the total energy of $BaBiO_3$ in different crystal structure, using an ionic model, namely the potential induced breathing model. The model reproduces adequately the complicated crystal structure of this system, and allows to analyze its physical origin. Due to the lack in this model of band-structure effects it can not reproduce the right behavior of the system at low amplitudes of the breathing and tilting distortions the interrelations between the breathing and tilting distortions.

In the end we would like to make one general remark: speculations about how different parts (one-electron energy, Madelung energy etc.) of total energy must be have, are useful on the stage of interpretation of numerical, quantitative results. However, their predictive force is doubtful. Indeed, the final changes of the total energy result from a nearly full compensations of different contributions, and the very separation of the total energy in these contributions depends of the calculational method and even of the tastes of a researcher. One should keep in mind that the lattice stability is, after all, a quantitative problem and should be studied by quantitative means. However, using different numerical approach one can get more insight in the physics of the problem.

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