

The Breathing Mode of BaBiO₃: Electric Field Gradient and Total Energy Calculations*

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We present *ab initio* full-potential linearized augmented plane wave (LAPW) band structure calculations for BaBiO₃. We focus on total energies and electric field gradients at the oxygen site and present results for the breathing mode in the experimentally observed cubic and monoclinic structures of doped and undoped Ba_{1-x}K_xBiO₃.

Key words: BaBiO₃; Total energy; Electric field gradient; Energy band structure; Breathing mode

1. Introduction

BaBiO₃ is the parent compound of the new class of high T_c superconductors that contain no copper. By partially replacing Ba with K (or Bi with Pb) Ba_{1-x}K_xBiO₃ becomes superconducting in a small range of x . The undoped material is a semiconductor in which the perovskite structure is unstable with respect to a breathing-like distortion (Fig. 1) of the oxygen octahedron (Bi disproportionates into two inequivalent Bi valences) and a rotation of these octahedra leads to a monoclinic structure [1]. Substitution removes these distortions and leads to an ideal perovskite (simple cubic) structure and to superconductivity. Several *ab initio* band structure calculations are available, [2–5] but the stability of the simple cubic (sc) BaBiO₃ with respect to the breathing distortion differs, although the band structures are very similar. The results depend on the method used and the computational details how the Bi and Ba semicore states are treated. The following results were found i) no breathing instability at all [3], ii) a small instability [5] of 0.1 mRy, iii) one of 3 mRy [4] or iv) a relative large instability [2] of about 6 mRy. In the present paper we investigate the total energy as a function of this

breathing distortion using the LAPW+LO method [6], in which the energy dependence of the radial wave function is not just linearized (as in standard LAPW), but local orbitals are added to make the basis functions more flexible. We also focus on the electric field gradient (EFG) at the oxygen position as a function of doping, structure, and the breathing distortion and compare the results with experimental data [7, 8].

2. Computational Details

We use a modified version of the full-potential linearized-augmented-plane-wave (LAPW) method as embodied in the WIEN93 code [9] based on the local density approximation (LDA). In this method the basis set of augmented plane waves is extended with

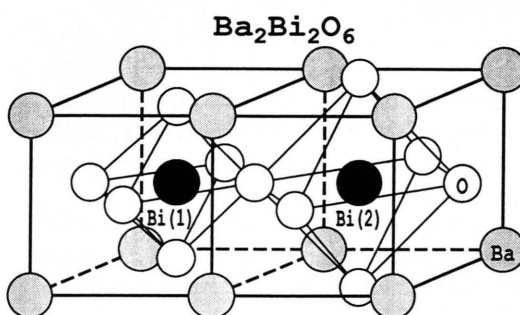


Fig. 1. Structure of BaBiO₃ with an inward breathing of the oxygens around Bi(1) (left cube) and the corresponding outward breathing around Bi(2) (right cube).

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local orbitals (LO) as introduced by Singh [6]. With such a method the Bi-5p, 5d, 6s, 6p, Ba-5s, 5p, 6s, 6p and O-2s, 2p states can be treated simultaneously as (formally) valence states (using a single energy window). Analysing the discrepancies between our previous results [2] and the various published total energy calculations [3–5], we find that the treatment of the so-called semi-core states (Bi-5p, 5d; Ba-5s, 5p) has a crucial influence of the results. Generally, a one window calculation, which neglects the polarization of these states, gives no (or small) stabilization of the breathing distortion, while a two window calculation yields a large stabilization but suffers from nonorthogonality problems between semi-core and valence states. Using the LAPW + LO method, this ambiguity is removed. All other lower lying states are included as thawed (\mathbf{k} -independent, but self-consistently calculated) atomic core states. These core states are treated fully relativistically, whereas for the valence states a scalar-relativistic version without spin-orbit coupling is used. Tight-binding calculations [10] including the spin-orbit coupling found only minor changes in the position of the valence bands. In particular, the Fermi surface nesting properties are affected very little by relativistic effects. We choose a cutoff parameter $R_{\text{MT}}|\mathbf{k} + \mathbf{K}_{\text{max}}| = 7.5$, where R_{MT} corresponds to the smallest muffin-tin radius, resulting in about 1500 plane waves for unit cells containing two formula units. Inside each atomic sphere both, the charge density and the potential, are expanded into lattice harmonics up to $L = 6$. We use 35, 75, and 100 \mathbf{k} -points in the irreducible wedge of the Brillouin zone for the sc, fcc and monoclinic structure, respectively.

3. Total energy

We first compute the total energy of sc BaBiO₃ as a function of the lattice parameter (Fig. 2) and obtain the equilibrium volume and the bulk modulus ($B = 1.38$ Mbar) in close agreement with previous calculations [4, 5] and experiment [1].

Next we investigate the breathing mode of BaBiO₃ (Fig. 1) taking a lattice constant $a_0 = 8.15$ a.u. at about the theoretical equilibrium. The corresponding unit cell contains two formula units and has the fcc structure. The total energy of this fcc Ba₂Bi₂O₆ as a function of oxygen displacement u (open circles in Fig. 3) shows a minimum at $u = 0.006$ corresponding to an O-displacement of 0.095 a.u. It can be approximately

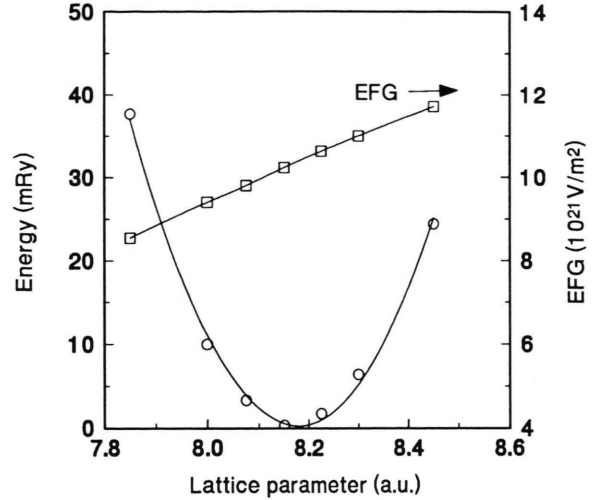


Fig. 2. Total energy (circles) and EFG (squares) of simple cubic BaBiO₃ (perovskite structure) as function of lattice spacing.

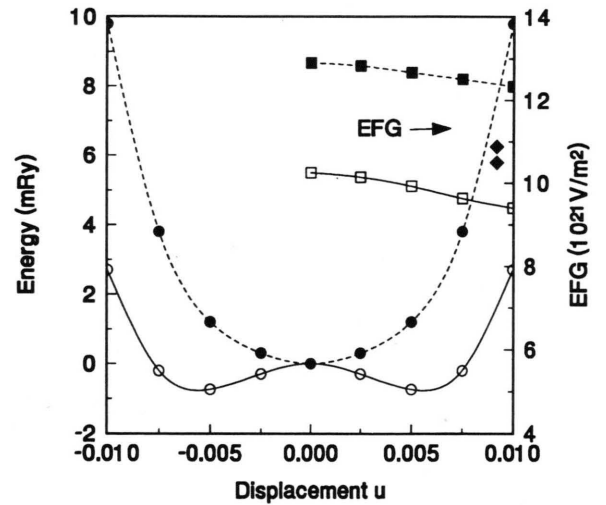


Fig. 3. Total energy (circles) taken with respect to the undistorted case and EFG (squares) of fcc BaBiO₃ as a function of the oxygen breathing distortion u (in units of $a_0 = 16.3$ a.u.). Undoped BaBiO₃: empty symbols; doped Ba_{0.8}K_{0.2}BiO₃: filled symbols. The full diamonds correspond to the theoretical EFGs using the experimental monoclinic structure.

compared with the experimental value [1] of about 0.16 a.u., but the latter corresponds to a structure that contains, besides the breathing, a tilting of the octahedron that is neglected in the present calculation. We found that the equilibrium value of u is very sensitive to the computational details, especially to the treatment of Bi-5s and Bi-5d semi-core states. The same

sensitivity is found for the energy stabilization caused by the breathing distortion which is slightly smaller than 1 mRy according to our present calculation. This energy is much smaller than the one obtained either in our previous study [2] or in a recent LMTO calculation [4], both of which used a two-window calculation, but it is distinctly higher than those of a one window LMTO calculation [5].

Ba is not involved in covalent bonding as to be expected, but is mostly ionic and thus donates its electrons. Therefore we can use an extremely simple model (a kind of virtual crystal approximation) to estimate the effect of substituting K for Ba. Namely we artificially reduce the atomic number of Ba and thus simulate the situation that K donates less electrons than Ba. The breathing distortion of doped BaBiO₃ studied by this model is shown in Fig. 3 (full circles) and corresponds to a composition of Ba_{0.8}K_{0.2}BiO₃. This total energy curve has its minimum at $u=0$ and shows no instability with respect to breathing in agreement with experiment [1], according to which this breathing distortion disappears already at low doping ($x=0.1$), while the additional tilting remains up to $x=0.4$.

In the present study we have not investigated how the total energy varies as function of the additional rotation of the oxygen octahedron (tilting), but it was shown by other groups [4, 5] that this tilting mode lowers the energy and a combination of both, tilting and breathing, leads to the lowest total energy, in agreement with experiment. Since such results are already available, we performed calculations just for the experimentally observed monoclinic structure [1] and obtained a total energy for the undoped BaBiO₃ (and the doped Ba_{0.8}K_{0.2}BiO₃) which is about 14 mRy lower (10 mRy higher) than that of the respective perovskite structure. From these calculations we conclude that undoped BaBiO₃ is non-cubic, while the cubic structure becomes the most stable upon small K doping, in accord with experiment.

4. Electric Field Gradient

The EFG is a ground state property of a system and is defined as the second derivative of the Coulomb potential with respect to the coordinates at the nuclear positions, written as a traceless tensor. The EFG can be accurately measured by various experimental techniques such as NMR or NQR. It can be computed

by a first principle's scheme and is obtained directly from the calculated total charge density of the crystal [11, 12]. In a multipole expansion of the Coulomb potential only the $L=2$ terms contribute to the EFG and the Cartesian components can be obtained from

$$V_{zz} = \sqrt{\frac{5}{4\pi}} (2V_{20}).$$

The expansion coefficients V_{20} are related to the charge density $\varrho(\mathbf{r})$ via the spherical harmonics Y_{20} by

$$V_{20} \propto \int \varrho(\mathbf{r}) Y_{20}(\hat{\mathbf{r}}) / r^3 d\mathbf{r}.$$

From this equation and our experience with previous calculations [12] we know that the EFG is mainly determined by the nonspherical charge density distribution near the origin (due to the factor $1/r^3$) and this asymmetry in the charge distribution is directly related to chemical bonding.

The extremely difficult ¹⁷O NMR measurements [7, 8] on undoped BaBiO₃ lead to a value of 11.9, and later experiments to $10.2 \cdot 10^{21}$ V/m² for the oxygen EFG (using $Q = -0.026 b$ for the ¹⁷O nuclear quadrupole moment). In the monoclinic structure there are two inequivalent oxygen positions, but this experimental group was unable to resolve these two frequencies. In our present calculation, however, we can resolve them and obtain EFG values for both oxygen positions of 10.9 and $10.5 \cdot 10^{21}$ V/m², respectively, with asymmetry parameters η smaller than 0.04, well within the range of both experiments.

In order to study the sensitivity of the EFG we have examined how the EFG tensor varies with volume, K substitution or O displacement connected with the breathing distortion. The volume dependence of the EFG is shown in Fig. 2, where (for BaBiO₃ in the sc structure) the O-EFG increases with volume. Figure 3 shows that the EFG decreases slightly (by about 10%) as function of the breathing distortion in the range of u studied. We note that the difference in the theoretical EFGs calculated for the experimental monoclinic (full diamonds in Fig. 3) and the ideal perovskite structure (open square at $u=0$) is fairly small, thus the tilting of the oxygen octahedron must have the opposite effect on the EFG than the breathing.

The EFG increases much more (at least within the present version of the virtual crystal approximation) by K doping than by structural changes due to breathing or tilting. For Ba_{0.8}K_{0.2}BiO₃ the EFG

increases by about 30% (full squares in Fig. 3), while for Ba_{0.6}K_{0.4}BiO₃ (the composition of the superconducting phase) we find an O-EFG as large as $15.3 \cdot 10^{21}$ V/m². The O-EFG is directly related to the difference in occupation of p_z with respect to p_x , p_y orbitals. In a purely ionic model all oxygen p orbitals would be fully occupied corresponding to an O²⁻ ion. However, covalent interactions between Bi and O lead to bonding and antibonding Bi-6s O-2 p_z states, where the latter σ bonds are only partly occupied. Therefore, the O-2 p_z charge is smaller than that of p_x or p_y leading to the large EFG. Upon doping, the number of electrons is reduced and thus the p_z orbitals (which form antibonding Bi-O σ -bonds close to E_F) are further depleted, resulting in an increase of the EFG.

In the present case we found that the use of local orbitals is very important for the total energy, but the oxygen EFG is less sensitive. This is in contrast to the recent results [13] on TiO₂ in the rutile structure, where the use of LOs was essential and even changed the sign of the EFGs, and it was only with this improvement that reliable EFG values could be obtained.

5. Summary

We have performed band structure and total energy calculations in the Ba_{1-x}K_xBiO₃ system and showed the importance of the Bi semi-core states and their proper treatment concerning orthogonality. In agreement with experiment we find the cubic (perovskite) structure to be stable only upon doping, while the undoped compound displays both, a breathing and a tilting distortion. The theoretical O-EFG values fall between the two available experimental data, and we predict an increase of this EFG upon doping.

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