

Fcc breathing instability in BaBiO<sub>3</sub> from first principles

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(Received 23 March 2006; published 28 June 2006)

We present first-principles density-functional calculations using the local density approximation to investigate the structural instability of cubic perovskite BaBiO<sub>3</sub>. This material might exhibit charge disproportionation and some evidence thereof has been linked to the appearance of an additional fourth peak in the experimental IR spectrum. However, our results suggest that the origin of this additional peak can be understood within the picture of a simple structural instability. While the true instability consists of an oxygen-octahedra breathing distortion and a small octahedra rotation, we find that the breathing alone in a fcc-type cell doubling is sufficient to explain the fourth peak in the IR spectrum. Our results show that the oscillator strength of this particular mode is of the same order of magnitude as the other three modes, in agreement with experiment.

DOI: [10.1103/PhysRevB.73.212106](https://doi.org/10.1103/PhysRevB.73.212106)

PACS number(s): 77.80.-e, 71.20.-b, 78.30.-j, 63.20.-e

Over the last few decades, BaBiO<sub>3</sub> has been a subject of continuing interest for several reasons. First, this material is an end member of the series (Ba,K)(Pb,Bi)O<sub>3</sub>, which includes one of the few high-temperature superconductors that do not contain copper. Second, the formal valence of Bi for the cubic perovskite BaBiO<sub>3</sub> is 4+, suggesting that the Bi should exhibit charge disproportionation  $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$  leading to a charge-ordered state. A better understanding of such ordered states could lead to the design of new charge-ordered ferroelectrics, a class of materials that has recently attracted considerable attention.<sup>1</sup> Experimental evidence for static charge disproportionation in BaBiO<sub>3</sub> has been linked to the interpretation of an additional, fourth strong peak in its IR spectrum,<sup>2-5</sup> while group theory predicts only three peaks for the cubic perovskite structure.

Our goal in this paper is to show that not only charge disproportionation, but also a much simpler mechanism—i.e., a structural breathing instability—can account for all four peaks in the experimental IR spectrum of BaBiO<sub>3</sub>. To this end, we first perform density-functional theory (DFT) calculations to investigate the structural instability of cubic perovskite BaBiO<sub>3</sub>. Thereafter, we calculate the IR active phonons and the Born effective charges, which in turn allows us to determine the IR oscillator strength of all four modes mentioned previously. We would also like to point out that for our calculations we assumed a simple fcc cell-doubling breathing distortion, which is sufficient to warrant nonzero oscillator strengths for all four modes. The full structural instability, however, consists not only of a breathing of the oxygen octahedra, but also of a small nearly rigid rotation thereof.<sup>6-8</sup>

Our first-principles density-functional-theory calculations were performed using the VASP package<sup>9</sup> and PAW potentials<sup>10</sup> with a 520 eV kinetic-energy cutoff. Note that we included the Ba  $5s^2$  and Bi  $5d^{10}$  states as valence states. The exchange-correlation energy functional was evaluated within the local density approximation (LDA), as parametrized by Perdew and Zunger.<sup>11</sup> Brillouin-zone integrals were approximated with the Monkhorst-Pack scheme on a  $14 \times 14 \times 14$  mesh of special k points.<sup>12</sup> Spin-orbit effects were not taken into account, since previous calculations showed that their effect on the band structure around the Fermi energy is small.<sup>13</sup>

The high-temperature phase of BaBiO<sub>3</sub> above 750 K has the simple cubic perovskite structure with five atoms per unit cell.<sup>6</sup> The simple cubic lattice constant of 4.328 Å for our calculations was derived from reported experimental values. In this structure, BaBiO<sub>3</sub> has an odd number of electrons per unit cell and therefore is metallic. However, lower-temperature experiments and calculations show that the unit cell for the low temperature phase is monoclinic,<sup>6-8</sup> and that the material is a semiconductor with an estimated gap of 0.2 eV.<sup>14</sup> The monoclinic phase results from a distortion of the cubic cell consisting mainly of a breathing of the oxygen octahedra and a small nearly rigid rotation thereof. As mentioned previously, for our investigation we limit ourselves to the pure breathing of the octahedra, which is enough to explain the appearance of all four peaks in the IR spectrum. In the breathing distortion, the oxygen atoms can move along the Bi-O bond to produce two inequivalent Bi sites with different Bi-O bond lengths, without breaking any point symmetries. This results in a doubling of the unit cell to ten atoms, following the three dimensional checkerboard pattern sketched in Fig. 1. The resulting fcc lattice has a conventional lattice constant of 8.655 Å. This distortion has previously been proposed by Uchida and coworkers.<sup>2</sup>

Figure 2 depicts the resulting double-well potential when the oxygen atoms are moved along the Bi-O bonds in the vicinity of the high symmetry oxygen position of 1/4, marked as A. The different curves correspond to different dense k meshes. Our results show that a  $8 \times 8 \times 8$  mesh, i.e., 60 k points in the irreducible part of the Brillouin zone (IBZ), which is usually sufficient for calculations on similar perovskites, does not provide converged results. A very dense mesh of  $14 \times 14 \times 14$  k points (i.e., 280 k points in IBZ) is necessary to describe this sensitive breathing distortion correctly. This is partly due to the fact that—as we will see later—the system is close to the metal/semiconductor transition. The double well has minima of depth 6.7 meV per 10-atom unit-cell at a displacement of  $\pm 0.00507$  (B), corresponding to the symmetry-equivalent choices of breathing a given octahedron either in or out. The shape of our double-well potential agrees well with LMTO calculations for breathing where a rotation of 13° has been frozen in.<sup>15</sup> Other calculations find for the double well without rotation a depth

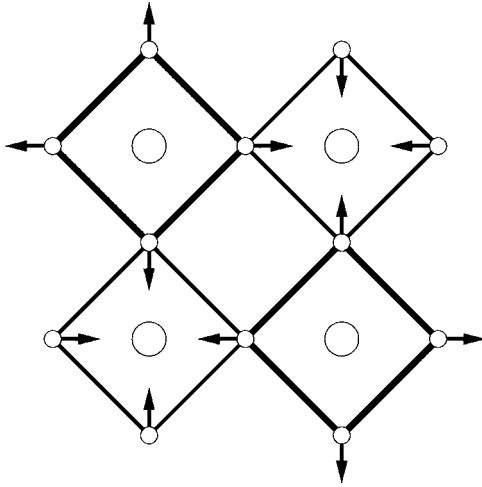


FIG. 1. Distortion of the oxygen octahedra. Small circles denote oxygen atoms and big circles denote bismuth atoms, respectively. In three dimensions, this breathing distortion produces a checkerboard pattern of adjacent smaller and larger octahedra, doubling the primitive simple cubic unit cell to fcc.

of 20 meV at a larger displacement of 0.07 Å (LMTO)<sup>8</sup> and a depth of 50 meV at 0.06 Å (LAPW).<sup>16</sup> Lichtenstein and co-workers, including combined tilting and breathing, find a minimum of 14 meV at 0.055 Å with 8.5° rotation.<sup>7</sup> Note that the experimental values at 150 K are a rotation of 11.2° and a displacement of 0.085 Å.

Henceforth, we will abbreviate in this paper our calculated optimal oxygen displacement as  $\pm 0.005$   $\text{Å} \approx \pm 0.005$ , keeping in mind that all calculations were actually done at the exact minimum position. At the minima, the oxygen atoms are displaced 0.04 Å. As a result, the simple cubic Bi-O bond length of 2.164 Å splits into 2.120 Å and 2.208 Å for Bi(1)-O and Bi(2)-O. We also studied the shape of the double-well potential as a function of pressure. It turns out that pressure decreases the depth of the double well and moves its minimum closer to the high-symmetry position, thereby stabilizing the structure.

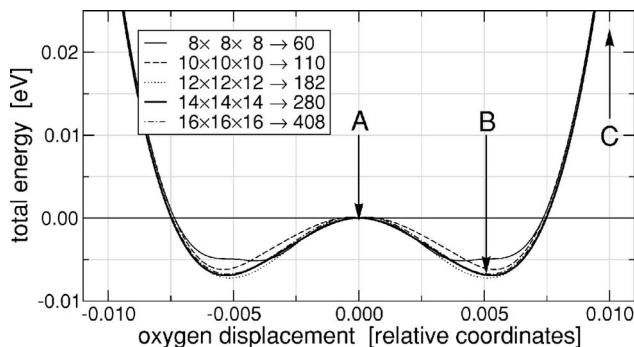


FIG. 2. K-mesh dependence of the total energy of fcc BaBiO<sub>3</sub> as a function of oxygen displacement from the high symmetry position of 1/4 (point A) given in relative Cartesian coordinates. Results are plotted for meshes from  $8 \times 8 \times 8$  (i.e., 60 k points in the IBZ) up to  $16 \times 16 \times 16$  (i.e., 408 k points in the IBZ). Convergence is reached with a  $14 \times 14 \times 14$  mesh, which produces results indistinguishable from any denser mesh. The minima of the double-well potential are at  $\pm 0.005$  (B), resulting in octahedra of two different sizes.

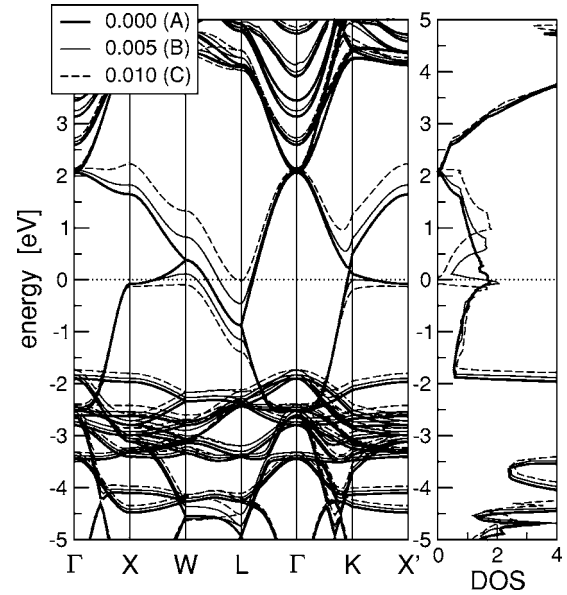


FIG. 3. Band structure and DOS of BaBiO<sub>3</sub> for the oxygen displacements A, B, and C of Fig. 2. Calculation A corresponds to the simple cubic perovskite cell and reflects the metallic character expected. The oxygen displacement of 0.005 (B) splits the degenerate band along  $W-L$  and decreases the DOS around the Fermi energy. The results are plotted with respect to the Fermi energy and the DOS is given in states/eV.

In order to investigate the effect of the breathing upon the gap, we calculated the band structure and DOS for different oxygen displacements as depicted in Fig. 3. It can be seen that at the minima of the double well (B), a small band overlap along  $W-L$  is present, rather than a gap. This finding is in agreement with previous calculations<sup>13</sup> and the discrepancy is consistent with the well-known tendency of LDA to underestimate the gap. For the larger displacement according to point C, the gap is clearly open. It can also be seen that the degenerate band along  $W-L$  in the simple cubic structure splits as the oxygens move. The splitting is almost constant along the band and of the order of 1 eV. Calculations by Mattheiss and Hamann, including the breathing and tilting of the octahedra, show that this splitting is primarily due to the breathing,<sup>13</sup> and is therefore captured correctly within our approach. In addition, the bands at  $K$  repel each other. Both effects together provide a mechanism to open the gap in agreement with the observed semiconducting character of BaBiO<sub>3</sub>.<sup>14</sup>

We next used a frozen-phonon approach to calculate the zone-center phonon frequencies and eigenvectors for the minimum-energy fcc structure with oxygen displacements of  $\pm 0.005$ , corresponding to point B in Fig. 2. The optical modes in this case are

$$\Gamma^{\text{opt}} = A_{1g} + E_g + T_{2u} + 2T_{2g} + 4T_{1u} + T_{1g}, \quad (1)$$

four of which are IR active ( $T_{1u}$ ). The symmetry adapted calculation gives for these four modes the frequencies  $\omega_1 = 444$  (438),  $\omega_2 = 198$  (231),  $\omega_3 = 157$  (136), and  $\omega_4$

TABLE I. Born effective charges  $Z_{k,\alpha\beta}^*$  for atom  $k$  in units of  $|e|$  for fcc BaBiO<sub>3</sub>. All  $Z_{k,\alpha\beta}^*$  are diagonal. Bi(1) and Bi(2) are located in the center of a larger and smaller octahedra, respectively. For the O atoms we refer to  $Z_{\parallel}^*$  and  $Z_{\perp}^*$ , denoting the components parallel and perpendicular to the Bi-O bond.

Atom	$Z_{k,11}^*, Z_{k,22}^*, Z_{k,33}^*$	Atom	$Z_{\parallel}^*$	$Z_{\perp}^*$
Bi(1)	+4.78	O(1-6)	-4.55	-1.85
Bi(2)	+6.22			
Ba(1), Ba(2)	+2.75			

=32 (98) cm<sup>-1</sup>, where the experimental values in parenthesis are taken from Ref. 4. Considering that we neglected the rotational distortion, the agreement of the high-frequency modes is reasonable, while the low-frequency mode at 31 cm<sup>-1</sup> differs considerably from the experimental value.

Next, we calculated the Born effective charge tensors  $Z_{k,\alpha\beta}^*$  using a Berry-phase scheme.<sup>17,18</sup> This calculation could not be carried out directly for the minimum-energy fcc structure, as it is metallic due to a small band overlap, as described previously. We computed the Born effective charges for the semiconducting structure obtained by displacing the oxygens by an additional 0.03 Å to the experimental displacement of 0.08 Å, since at this point the gap has just opened. This procedure is justified by the fact that the phonon corresponding to the oxygen displacement is nonpolar and the Born effective charges are expected to be smooth near the metal/semiconductor transition. Indeed, we investigated the dependence of the effective charges upon the oxygen displacement by performing calculations for a larger displacement corresponding to 0.010 (point C in Fig. 2). Our results show that the effective charges for the displacement 0.009 and 0.010 differ only by approximately 1%. All  $Z_{k,\alpha\beta}^*$  are found to be diagonal and the results are collected in Table I. The values for the effective charges are reminiscent of similar perovskites, such as BaTiO<sub>3</sub>.<sup>19</sup> The splitting of  $Z^*$  for Bi(1) and Bi(2) is quite striking, however, note that this “Born effective charge disproportionation” is not necessarily the result of static charge transfer.

For the simple cubic perovskite structure group theory predicts three three-fold degenerate IR active phonons.<sup>2</sup> When the unit cell is doubled as described above, the zone-boundary  $R$ -point phonons are folded back to the zone center. This leads to a mixing of one of the folded-back phonons (with alternating Bi displacements relative to their surrounding oxygen octahedra) and the IR active zone-center phonons. In the five-atom cell this phonon has no oscillator strength since the contributions of neighboring Bi cancel. In the doubled cell, the octahedra of different sizes create different environments for the bismuth atoms sitting in their centers and the contributions no longer cancel. As a result, the oscillator strength of this particular mode becomes non-zero, which explains the additional, fourth peak in the experimental IR spectrum. Note that materials such as BaTiO<sub>3</sub> or SrTiO<sub>4</sub>, that have a single valence for the Ti ion (4+), only show three strong peaks in the IR spectrum—as expected from group theory.

As the last step, we calculate the oscillator strengths of

the IR active modes. The oscillator strength  $S_i$  of mode  $i$  can be calculated as

$$S_i = \sum_{\alpha} \left( \sum_{\beta,k} \frac{Z_{k,\alpha\beta}^* \xi_{\beta}(k,i)}{\sqrt{m_k}} \right)^2, \quad (2)$$

where  $\xi(k,i)$  is the displacement of atom  $k$  according to the eigenvector of the  $i$ th phonon mode,  $m_k$  is the mass of atom  $k$ , and  $Z_{k,\alpha\beta}^*$  are the Born effective charges. Our results for the oscillator strengths are  $S_1=2.097$ ,  $S_2=0.457$ ,  $S_3=0.661$ , and  $S_4=0.617$ . The three modes  $S_i$  ( $i=1,2,4$ ) have been associated with the simple cubic perovskite structure and can be identified in the experimental spectrum.<sup>2-5</sup> The oscillator strength of the fourth mode  $S_3=0.661$  is of the same order of magnitude as the ones associated with the simple cubic perovskite structure. Indeed, as a result, a fourth peak is clearly visible in experiments. The fact that our calculations predict an oscillator strength for this mode comparable to the other modes goes beyond pure group theory, which cannot make any predictions about the oscillator strength. As our main result, we conclude that DFT calculations for a pure fcc-type breathing can explain the existence of all four peaks in the IR spectrum of BaBiO<sub>3</sub>.

Further analysis of  $S_3$  reveals that its value is almost independent of the Born-effective-charge splitting between the two inequivalent Bi atoms. If we remove the splitting between  $Z_{\text{Bi(1)}}^*=4.78$  and  $Z_{\text{Bi(2)}}^*=6.22$  by hand and replace these values with the average of 5.5, the oscillator strength changes only by a few percent. It follows that the oscillator strength is mainly determined by the eigenvector of the corresponding phonon mode. Furthermore, we find that about half of the oscillator strength is a result of the asymmetry in displacement of the Bi(1) and Bi(2) atoms. The rest is mostly due to the displacement of the four oxygen atoms in the plane perpendicular to the Bi movement.

To conclude, we have performed first-principles DFT calculations to investigate the electronic structure and structural instability of cubic perovskite BaBiO<sub>3</sub>. We investigate the effect of a fcc-like unit-cell doubling produced by a breathing distortion of the oxygen octahedra. The oxygen atoms are thereby displaced 0.04 Å along the Bi-O bond, which generates smaller and larger octahedra throughout the crystal. The distortion is very small, and yet we find that properties such as the bandgap or the Born effective charges are very sensitive to it. This cell-doubling distortion turns on the oscillator strength of an additional fourth mode, observed as an additional strong peak in the experiment. In particular, our calculations show that the oscillator strength of this certain mode is of the same order of magnitude as the strengths of the remaining three modes. In future work, we would like to improve our results by including not only the breathing distortion, but also the rotation of the octahedra. Furthermore, although BaBiO<sub>3</sub> is not considered a strongly correlated system, it might be interesting to investigate the effect of LDA+U in conjunction with the structural instability.

The authors acknowledge fruitful discussions with D. Vanderbilt, D. R. Hamann, P. Sun, and C. J. Fennie. This work was supported by ONR project No. N00014-00-01-0261.

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