

# Lattice dynamics of Ti-based pnictide superconductors $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$

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The lattice dynamics of layered  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  pnictides ( $0 \leq x \leq 0.3$ ) is studied experimentally by means of Raman scattering and theoretically within the density functional theory. Both symmetry allowed Raman-active modes are observed in the spectra and assigned to the lattice eigenmodes:  $z$ -axis motion of Sb ions ( $A_{1g}$ -symmetry mode) and in- $xy$ -plane displacement of Sb ( $E_g$ -symmetry vibration). Calculated and experimental frequencies of these modes are found to be in good agreement. The  $E_g$  mode exhibits a nonmonotonous dependence of its frequency upon doping, which is found to correlate with the variation of Sb-Ti distances and strength of the interaction between  $\text{Ti}_2\text{Sb}_2\text{O}$  slabs.

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The discovery of Fe-based pnictide superconductors ( $\text{LaFeAsO}_{1-x}\text{F}_x$ ) several years ago<sup>1-3</sup> was followed by an intense wave of developments in a search of novel materials with superconducting properties. Over the years several related classes of superconducting materials were identified, such as doped  $A_{1-x}(\text{Sr/Ba})_x\text{Fe}_2\text{As}_2$ <sup>4,5</sup> and intrinsic  $\text{LiFeAs}$ <sup>6</sup>, for example. Even though the highest critical superconducting temperature  $T_c$  of these materials does not exceed 55 K, considerable progress has been made over the years in understanding their properties. The unconventional nature of the superconductivity was clearly established both theoretically and experimentally with magnetic excitations (spin-density waves) being at the heart of the pairing mechanism.<sup>7,8</sup> Thus, a strong competition between magnetism and superconductivity has been established (see, e.g., Refs. 9 and 10 and references therein). As far as optical spectroscopy results, phonon and electronic Raman scattering and infrared reflection experiments on various classes of iron pnictides were detrimental in monitoring specific lattice dynamical features due to nonvanishing electron-phonon interaction<sup>11-14</sup> and structural phase transitions,<sup>15,16</sup> establishing the gap symmetry and a multigap behavior,<sup>17,18</sup> as well as a pseudogap regime.<sup>19</sup>

Recently, a new class of transition-element pnictide oxide was shown to exhibit superconducting properties upon proper doping:  $\text{BaTi}_2\text{Sb}_2\text{O}$ .<sup>20</sup> The  $\text{Na}^+$  for  $\text{Ba}^{2+}$  substitution leads to a suppression of the spin-density waves phase and material exhibits bulk superconductivity within the doping range  $0.05 < x < 0.33$ , with the critical temperature reaching its maximum  $T_c = 5.5$  K at  $x \approx 0.15$ .

We will further focus on the dynamical properties of the lattice of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$ . The group-theoretical analysis of lattice vibrations is performed and the activity of the vibrational mode is determined. Further, performed density functional calculations yield mode frequencies and the displacement pattern for all optical modes. These results are compared with the experimental Raman-scattering data.

Single crystals of  $\text{BaTi}_2\text{Sb}_2\text{O}$  were synthesized by high-temperature reactions of the appropriate starting materials in welded Nb containers, as described earlier in Ref. 20. The

crystallographic structure of  $\text{BaTi}_2\text{Sb}_2\text{O}$ , shown in Fig. 1, features the antiperovskite-type  $\text{Ti}_2\text{O}$  layers (similar, but “inverse” to the  $\text{CuO}_2$  layers in cuprates), that are capped by Sb atoms on both sides.

All Raman scattering spectra were measured in the backscattering geometry at room temperature on a Horiba Jobin Yvon T-64000 triple spectrometer equipped with an optical microscope and a liquid-nitrogen-cooled charge-coupled device (CCD) detector. The spectral resolution did not exceed  $1.0 \text{ cm}^{-1}$ . An  $\text{Ar}^+$  laser ( $\lambda_{\text{las}} = 514.5 \text{ nm}$ ) for used for the excitation excitation. The incident laser power was kept below 1.0 mW in order to minimize heating of the sample.

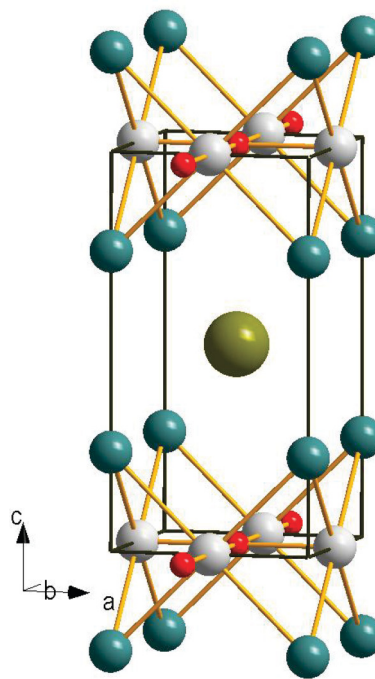


FIG. 1. (Color online) The crystallographic structure of  $\text{BaTi}_2\text{Sb}_2\text{O}$ , featuring  $\text{Sb}_2\text{Ti}_2\text{O}$  slabs (blue, grey, and small red spheres, respectively). Ba atoms are shown in green.

TABLE I. Wyckoff position, cite symmetry, and irreducible representations of the nonequivalent atomic sites in the  $P4/mmm$  structure of  $\text{BaTi}_2\text{Sb}_2\text{O}$  (Refs. 20 and 21).

Atom	Wyckoff notation	Cite symmetry	Irreducible representations
Ba	1d	4/mmm	$A_{2u} + E_u$
Ti	2f	mmm	$A_{2u} + B_{2u} + 2E_u$
Sb	2g	4mm	$A_{1g} + A_{2u} + E_g + E_u$
O	1c	4/mmm	$A_{2u} + E_u$
Modes classification			
$\Gamma_{\text{acoustic}} = A_{2u} + E_u$			
$\Gamma_{\text{Raman}} = A_{1g} + E_g$			
$\Gamma_{\text{IR}} = 3A_{2u} + 4E_u$			

The results of the group theoretical analysis of lattice vibrations of  $\text{BaTi}_2\text{Sb}_2\text{O}$  (space group  $P4/mmm$ ) are summarized in Table I. Ba, Ti, and O ions occupy centrosymmetric lattice sites and consequently none of them contributes to the even-parity Raman active vibrations. Thus, only two Sb-related modes are expected to be observed in Raman spectra:  $A_{1g}$  due to the  $z$ -axis displacement, and the doubly degenerate  $E_g$  due to motion within the  $xy$  plane.

The first-principles calculations of the electronic ground state of Na-doped  $\text{BaTi}_2\text{Sb}_2\text{O}$  were performed within the generalized-gradient approximation with Perdew-Burke-

TABLE II. Calculated and experimental frequencies (in  $\text{cm}^{-1}$ ) of optical vibrations  $\text{BaTi}_2\text{Sb}_2\text{O}$  and their assignment.  $A_{2u}$  and  $E_u$  modes are infrared active.

Mode	Frequency calculated	Frequency experimental	Assignment
$A_{1g}$	158	152	Sb, $z$ axis
$E_g$	110	126	Sb, $xy$ plane
$A_{2u}(1)$	82		Ba, $z$ axis
$A_{2u}(2)$	226		O + Ti, $z$ axis
$A_{2u}(3)$	290		O - Ti, $z$ axis
$E_u(1)$	72		Ba-(Ti + O), $xy$ plane
$E_u(2)$	146		(Ti + O)-Sb, $xy$ plane
$E_u(3)$	263		Ti, $xy$ plane
$E_u(4)$	446		O, $xy$ plane
$B_{2u}$	221	silent	Ti, $z$ axis

Ernzerhof<sup>22</sup> local functional, using the CASTEP code.<sup>23</sup> The norm-conserving pseudopotentials and experimental lattice parameters of the crystal<sup>20</sup> were used. For self-consistent calculations of the electronic structure and other relevant electronic properties the integration over the Brillouin zone was performed over the  $25 \times 25 \times 13$  Monkhorst-Pack grid<sup>24</sup> in the reciprocal space. These results are found to be in good agreement with those reported recently by Singh.<sup>25</sup> In particular, the Fermi surface clearly shows the existence of nearly parallel sheets, a fact which points towards magnetic instability of the parent compound.<sup>26,27</sup>

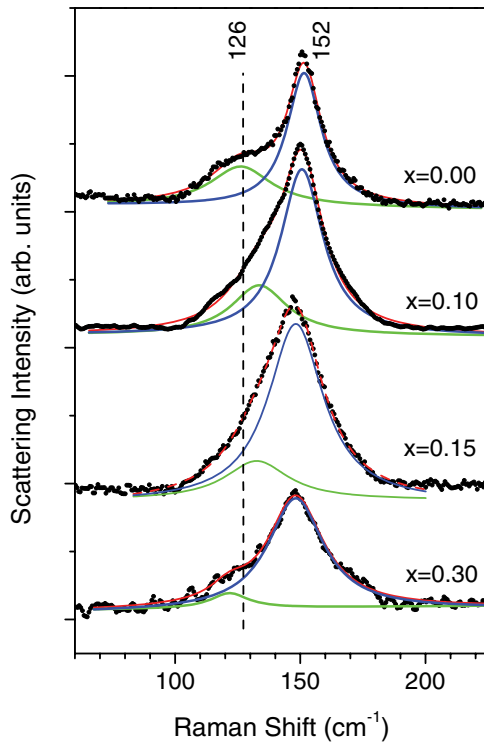


FIG. 2. (Color online) Raman-scattering spectra of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  as obtained at room temperature with  $\lambda_{\text{exc}} = 514.5\text{-nm}$  excitation (solid point) and their decomposition into two Lorentzian lines. Spectra are shifted vertically for clarity. The vertical dotted line marks the position of the low-energy phonon mode for the parent compound  $x = 0$ . Note a nonmonotonous shift of this mode upon doping.

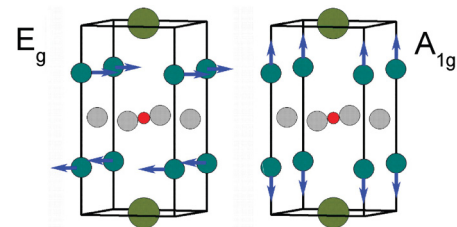
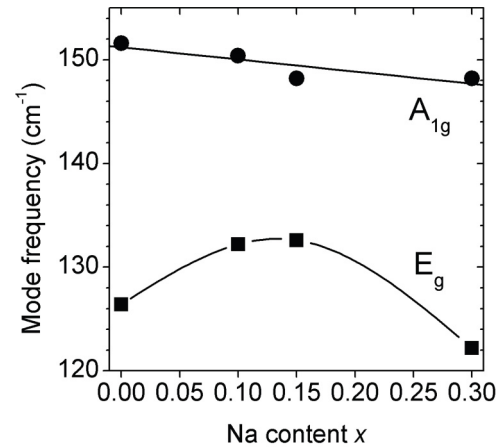


FIG. 3. (Color online) The position of modes in the Raman-scattering spectra of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  as a function of doping  $x$  (lines are a guide to the eye). Calculated displacement patterns for both modes are shown in the lower part of the figure (lower frequency  $E_g$  mode on the left and higher frequency  $A_{1g}$  mode on the right).

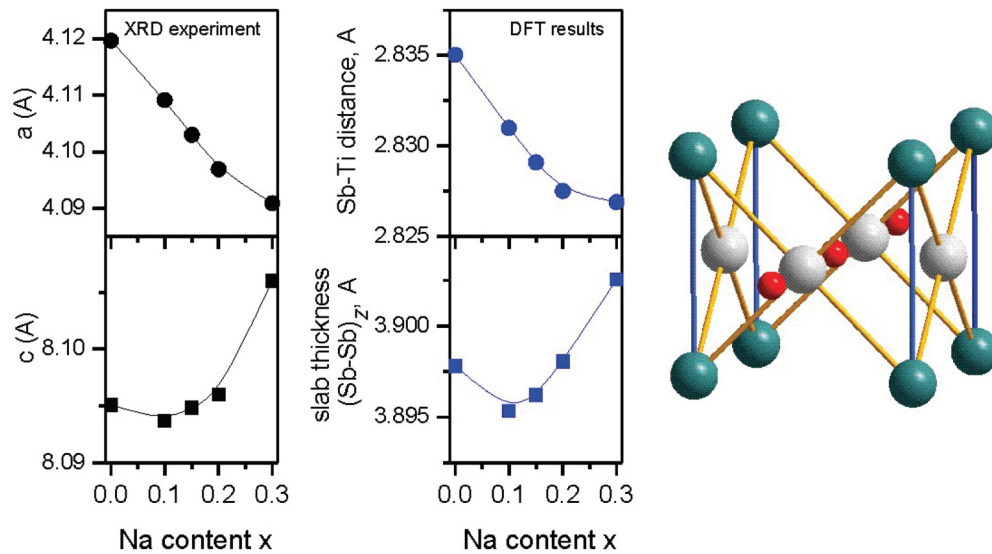


FIG. 4. (Color online) Experimental crystal lattice parameters  $a$  and  $c$  (x-ray-diffraction data) of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  as a function of doping are shown in the left panel. The DFT-calculated  $\text{Sb}_2\text{Ti}_2\text{O}$  “slab thickness”  $(\text{Sb-Sb})_z$  (blue vertical lines in the picture on the right) and the Sb-Ti distance of a relaxed unit cell (yellow lines) are presented in the middle panel. Lines are a guide to the eye. Note a nonmonotonous behavior upon doping of the  $c$ -axis parameter and the slab thickness  $(\text{Sb-Sb})_z$ .

The lattice dynamics of  $\text{BaTi}_2\text{Sb}_2\text{O}$  was calculated within the local-density approximation with Perdew-Wang local functional<sup>28</sup>, using DMOL<sup>3</sup> code<sup>29,30</sup> by means of finite displacements method. The frequencies of all optical Brillouin-zone center modes are listed in Table II. Two of them, the even-parity  $A_{1g}$  and  $E_g$ , are Raman active, seven odd-parity vibrations ( $A_{2u}$  and  $E_u$ ) are infrared active, and there is also one silent mode ( $B_{2u}$ ).

In Fig. 2 Raman spectra of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  crystals are shown for several compositions  $x$ . In the parent compound two lines are clearly distinguished in the spectra which, according the DFT calculations, correspond to the in- $xy$ -plane  $E_g$  ( $126\text{ cm}^{-1}$ ) and  $z$ -axis  $A_{1g}$  ( $152\text{ cm}^{-1}$ ) modes; their displacement pattern is shown in the lower part of Fig. 3. This latter mode shift slightly and monotonously towards smaller wave numbers upon doping in the whole concentration range. The lower frequency  $E_g$  vibration exhibits much larger shifts and, more importantly, a nonlinear behavior: upon doping its frequency first increases, reaches the maximum around  $x \approx 0.15$ , and further decreases, as shown in the upper part of Fig. 3.

In Fig. 4 the variation of the lattice parameters of the crystallographic unit cell of  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  is presented, which shows monotonous compression upon doping of the unit cell within the  $xy$  plane due to smaller  $\text{Na}^+$  ionic radius in comparison to  $\text{Ba}^{2+}$ . The  $c$ -axis lattice parameter exhibits, however, a nonmonotonous behavior: the unit cell initially slightly contracts upon doping, and further (for  $x \geq 0.15$ ) starts to expand. The DFT calculation results, presented in the two lowest panels of Fig. 4, show that this behavior is also valid for the interatomic  $(\text{Sb-Sb})_z$  distance along the  $c$  axis within the  $\text{Sb}_2\text{Ti}_2\text{O}$  slab.

In relation to the doping dependence of the vibrational modes, the  $A_{1g}$  involves both stretching and bending of Sb-Ti bonds and for a fixed cation-anion interaction strength its frequency is expected to increase as a result of a shortening of corresponding bonds. Experimentally, however, the  $A_{1g}$  mode frequency decreases slightly upon doping, which signals some weakening of the Sb-Ti interaction due to charge redistribution. More interesting is that the slab thickness, which is characterized by the Sb-Sb distance along the  $c$  axis, shows a nonmonotonous change upon doping: it initially shrinks, but starts to expand for  $x > 0.15$ . And this is directly reflected in a pronounced softening of the  $E_g$  mode in the same concentration range  $x > 0.15$ . It is important to note that the superconducting critical temperature  $T_c$  also reaches its maximum around  $x \approx 0.15$ ,<sup>20</sup> and its drop upon further doping could be related to a weakening of Sb-Ti and interslab interactions.

In summary, Raman-scattering spectra of superconducting layered  $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$  single crystals have been measured and both allowed by symmetry modes were observed experimentally and assigned to the  $z$  axis ( $A_{1g}$  symmetry) and  $xy$  plane ( $E_g$  symmetry) vibrations of Sb ions. Their frequencies are in good agreement with those calculated within the density functional theory. A nonmonotonous dependence of the position of the  $E_g$  mode is found upon doping, which is shown to correlate with the Sb-Ti spacing and interaction between  $\text{Sb}_2\text{Ti}_2\text{O}$  slabs.

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