

Structural phase diagram and electron-phonon interaction in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

A.I. Liechtenstein,* I.I. Mazin,[†] C.O. Rodriguez, O. Jepsen, and O.K. Andersen
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

M. Methfessel

Fritz-Haber-Institut, Faradayweg 4-6, D-1000 Berlin 33, Federal Republic of Germany

(Received 24 June 1991)

Using the local-density approximation and the full-potential linear muffin-tin-orbital method we have calculated the total energy of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for $x = 0$ and 0.5 as a function of tilting and breathing distortions. For $x = 0$ we find an instability for a combination of both distortions and we correctly reproduce the monoclinic structure. For $x = 0.5$ we correctly find the cubic phase to be stable. The frequencies of the tilting and breathinglike phonons are calculated for $x = 0$ and 0.5 . In the cubic structure we calculate the strength λ_b of the electron-phonon coupling for the breathing mode as a function of x using a rigid-band approximation. For $0.37 < x < 0.5$, $\lambda_b \approx 0.3$ and follows the trend of T_c . The superconductivity is conceivably mediated by the electron-phonon coupling.

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is distinct from other high-temperature superconductors:¹⁻³ Its bonding is three rather than two dimensional, CuO_2 planes are missing, and there are no indications of strong electronic correlations near $x = 0$. The mechanism for superconductivity ($T_c \approx 30$ K for $x \approx 0.4$) is presumably the electron-phonon coupling.⁴

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has a complicated structural phase diagram.^{5,6} For the semiconducting compositions ($0 \leq x < 0.12$) the structure is monoclinic ($I2/m$) and may be derived from the cubic perovskite structure by simultaneous tilting (t) and breathing (b) distortions of the BiO_6 octahedra. For $0.12 < x < 0.37$ the structure is orthorhombic ($Ibmm$) with a t , but no b , distortion and, for the superconducting compositions ($0.37 < x < 0.53$), the structure is simple cubic (sc) ($t = 0$, $b = 0$).

Several *ab initio* band-structure calculations using the local density-functional approximation (LDA) have been performed for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with the compositions $x=0$ (Refs. 7-10) and $x = 0.5$.¹⁰ More recently the stability of sc BaBiO_3 against t or b was studied by means of LDA total-energy calculations using, respectively, the pseudopotential and the linear augmented-plane-wave methods. The former calculation¹¹ found a t instability but was unable to find the energy minimum. The latter¹² found a b instability and a minimum of -6 mRy, but the experimental equilibrium structure could not be reproduced because no attempt was made to include t . In this paper we present LDA calculations for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x = 0$ and 0.5) with simultaneous t and b distortions and we quantitatively reproduce the phase diagram. Furthermore, we calculate the frequencies of the t - and b -like phonons for $x = 0$ and 0.5 . Finally, we evaluate the strength λ_b of the electron-phonon coupling in the sc phase for the breathing mode as a function of x using, for the electrons, the LDA bands.

The full-potential linear muffin-tin-orbital (FPLMTO) method¹³ which makes no shape approximation for the

potential or the charge density was used. In order to have sufficient variational freedom in the interstitial region between the nearly touching muffin-tin (MT) spheres, we included one or two basis functions per site and angular momentum ($2 \times s$, $2 \times p$, $2 \times d$, and $1 \times f$ for Ba, and $2 \times s$, $2 \times p$, and $1 \times d$ for Bi, K, and O. For the first radial function, $\kappa^2 = 0$ and, for the second, $\kappa^2 = -7$ eV). The MT radii were 2.9 (Ba, K), 2.0 (Bi), and 1.8 (O) Bohr radii. The semicore $\text{Ba}(5p)$, $\text{K}(3p)$, $\text{Bi}(5d)$, and $\text{O}(2s)$ states were treated as bands, while the other core states were treated as soft core. One energy panel was judged to suffice. Since the t , b , and combined tb distortions of the sc structure have $\mathbf{q} = (1, 1, 1)\pi/a = \mathbf{R}$, the total-energy and frozen-phonon calculations were performed with two $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ units per cell. The Brillouin-zone (BZ) integrations were done with the full-zone tetrahedron method with 47, 38, and 52 inequivalent \mathbf{k} points in the sc, orthorhombic, and monoclinic BZ's used for, respectively, b , t , and tb . For small b we used as many as 145 inequivalent \mathbf{k} points. The exchange-correlation potential of Ref. 14 and the scalar-relativistic Dirac equation were employed.

Energy-volume calculations for (hypothetical) sc BaBiO_3 yielded the bulk modulus: $B = 1.37$ Mbar and an equilibrium volume Ω_{sc} which is 3.6% smaller than the experimental one. Such an overbinding is expected for the LDA. The sc structure observed for $\text{Ba}_{0.5}\text{K}_{0.5}\text{BiO}_3$ has three possible simple superstructures with very similar energy bands and, choosing the structure with alternating Ba and K (111) planes, we calculated an equilibrium volume 5% smaller than the experimental one.⁵

Guided by the structural data for the orthorhombic phase,⁶ we took *tilting* to be rigid rotations of the BiO_6 octahedra around their [110] axes and with alternating sign ($\mathbf{q} = \mathbf{R}$). This means, that the orthorhombic lattice constants perpendicular to [110] vary with t according to $c(t) = 2l \cos t$ and $b'(t) = 2\sqrt{2}l \cos t$, whereas, along

[110], $a' = 2\sqrt{2}l = \sqrt{2}a$ is fixed. Here, l is the Bi-O distance and a the lattice constant in the sc phase ($t = 0$, $b = 0$). The double-cell volume therefore decreases with tilt: $\Omega(t) = 2\Omega_{sc} \cos^2 t$. If we now add *breathing*, the double-cell volume remains $\Omega(t)$ but alternate octahedra breathe out and in: $l_{\pm} \approx l \pm b$, $t_{\pm} \approx t(1 \mp b/l)$, and the structure becomes monoclinic. In order to obtain the phase diagram, we calculated the total energies for t , b , and tb distortions, starting from ($t = 0$, $b = 0$) and letting l be the value obtained from the *calculated* volume [$8l^3 = \Omega_{sc}$]. The results for $x = 0$ and $x = 0.5$ are shown in Fig. 1 and we now first discuss the case $x = 0$.

The breathing mode has caught attention because, for $x = 0$ and in the tight-binding nearest-neighbor *sp σ* model with Bi $6s$ orbitals (Cu $3d_{x^2-y^2}$ orbitals for the CuO₂ compounds) and O $2p$ orbitals, this mode opens a gap at the Fermi level throughout the BZ due to perfect nesting of the Fermi surface. In realistic calculations (Fig. 2), however, the nesting is far from perfect: O-O hopping increases the energy near $\mathbf{k} = \mathbf{W}$ ($\frac{1}{2}\mathbf{XM}$ in the sc BZ), and *pp σ* hopping between the O $2p$ and Bi $6p$ (Cu $3d_{3z^2-1}$) orbitals lowers the energy near \mathbf{L} ($\frac{1}{2}\mathbf{\Gamma X}$). To create a gap throughout the BZ requires

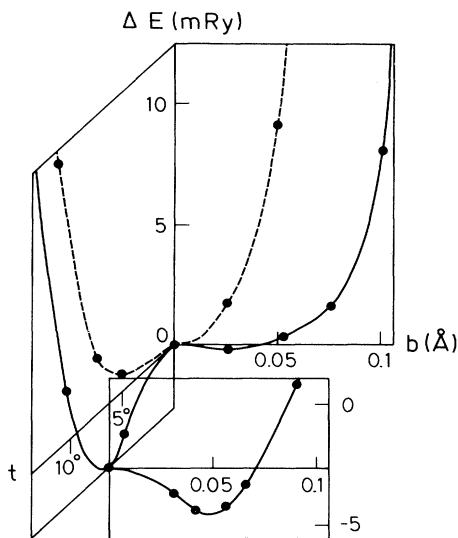


FIG. 1. Calculated total energy for $2\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ as a function of the breathing b of the BiO_6 octahedra and the angle t of their tilt around the [110] axis. Solid line: $x = 0$. Broken line: $x = 0.5$. As explained in the text the cell volume depends on tilt according to $\Omega(t, x) = 2\Omega_{sc}(x) \cos^2 t$, where $\Omega_{sc}(x)$ is the volume calculated for the sc structure. For simultaneous t and b , we displaced the O atom, which in the sc structure has its nearest-neighbor Bi atoms at $(0, 0, \pm l)$, by $d\mathbf{R} = l(\sin t/\sqrt{2}, -\sin t/\sqrt{2}, v)$. Hereby, the BiO_6 octahedra which breathe out (in) attain a Bi-O distance given by $l_{\pm} = l\sqrt{(\cos t \pm v)^2 + \sin^2 t} \approx l \pm b$, where $b \equiv vl \cos t$, and a tilt angle given by $\tan t_{\pm} = \sin t/(\cos t \pm v) \approx (1 \mp b/l)\tan t$. The octahedra stay cubic. For $x = 0$ the total energy (in Ry per 2BaBiO_3) is fitted by $E(u \equiv \sin t, v) = -0.358^2 u^2 - 1.463^2 v^2 - 2.043^4 u^4 - 3.294^4 u^2 v^2 + 7.155^4 v^4 + 3.024^6 u^6 + 3.428^6 u^4 v^2 + 5.164^6 u^2 v^4 - 7.130^6 v^6$.

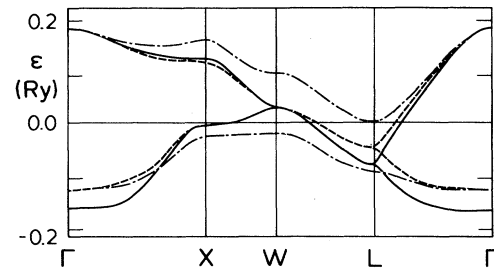


FIG. 2. The FPLMTO energy bands near the Fermi level for 2BaBiO_3 . Other bands are omitted from the figure. Solid line: $t = 0$, $b = 0$. Dashed line: $t = 10^\circ$, $b = 0$. Dot-dashed line: $t = 10^\circ$, $b = 0.09 \text{ \AA}$. The folding of the sc BZ is as follows: $\mathbf{R} \rightarrow \mathbf{\Gamma}$, $\mathbf{M} \rightarrow \mathbf{X}$, $\frac{1}{2}\mathbf{XM} \rightarrow \mathbf{W}$, and $\frac{1}{2}\mathbf{\Gamma R} \rightarrow \mathbf{L}$ (see Ref. 7).

$b > 0.08 \text{ \AA}$ (when $t = 0$). Breathing always lowers the sum of the one-electron energies, but this gain is nearly compensated by an increase of electrostatic energy and, as a result, there is only a tiny instability of the *pure b* type as seen from the full line in Fig. 1; the total-energy minimum is $\Delta E = -0.1 \text{ mRy}/2\text{BaBiO}_3$ and occurs for $b = 0.03 \text{ \AA}$. The shape of the curve at small b is mostly determined by the imperfectness of the nesting. It may be noted that, although the Bi $6s$ -charge transfer amounts to $\pm 0.15 e$ (between the Bi MT spheres for $b = 0.09 \text{ \AA}$), this charge is screened by the tails of O $2p$ orbitals to the extent that the total Bi MT-charge transfer is only $\pm 0.01 e$.

We find that sc BaBiO_3 is unstable against *pure* tilting too (Fig. 1); the total-energy minimum is $\Delta E = -3.5 \text{ mRy}/2\text{BaBiO}_3$ and occurs for $t = 8^\circ$. This tilt instability seems to be driven by the Madelung energy.

Now, in the tilted structure, the nesting becomes more perfect because the O $2p$ to Bi $6p$ hopping is reduced due to misalignment of the orbitals and, hence, the band is raised near \mathbf{L} (Fig. 2, dashed line). Consequently, *tilting helps breathing*. In order to find the equilibrium structure we performed total-energy calculations for about 20 (t, b) points and fitted to a sixth-order polynomial (Fig. 1). The resulting calculated equilibrium has $\Delta E = -4.6 \text{ mRy}/2\text{BaBiO}_3$, $t = 8.5^\circ$, and $b = 0.055 \text{ \AA}$, which is in quite good agreement with the experimental^{5,6} values: $t = 10.3^\circ$ and $b = 0.085 \text{ \AA}$. We finally checked the assumption of constant l by varying the cell volume away from $\Omega(t)$ at the (t, b) minimum.

Diagonalization of the dynamical matrix obtained from the second derivatives of the total energy at the global minimum, gave the normal-mode frequencies: 235 cm^{-1} (t -like) and 370 cm^{-1} (b -like). Taking the second derivatives under the constraint of constant volume, rather than constant pressure ($\approx \text{const } l$), made the phonon frequencies increase to 307 cm^{-1} (t -like) and 373 cm^{-1} (b -like). The total energy profile is extremely anharmonic, and this causes renormalization of the phonon frequencies. This we estimated perturbatively¹⁵ from the third and the fourth derivatives (neglecting interactions with all other phonons) and, for zero temperature and constant pressure, we found $\delta\omega/\omega = (\delta_3\omega/\omega) + (\delta_4\omega/\omega) =$

$-9\%+8\% = -1\%$ for the t -like, and $-23\%+9\% = -14\%$ for the b -like mode. The experimental phonon frequencies are controversial, which is hardly surprising in view of the strong anharmonicity and the line broadening due to strong electron-phonon interaction.

Considering now $x = 0.5$, we find that BaKBi_2O_6 is stable with respect to both t and b displacements (Fig. 1). The calculated phonon frequencies are, respectively, 105 and 530 cm^{-1} . (In this case, where the total-energy minimum is at $t = 0$, there is no difference between constant-volume and constant-pressure frequencies.) Since for $x = 0.5$ merely the lower quarter of the $sp\sigma$ band is full, the nesting effect which favors breathing is absent. Also, substitution of half the Ba by K weakens the tilt-favoring Madelung energy.

In the last part of this paper we evaluate the strength $\lambda_{\nu\mathbf{q}}$ of the electron-phonon (e -ph) coupling for the $\mathbf{q} = \mathbf{R}$ breathing mode in the sc structure (for tilting it vanishes by symmetry). This structure is the one which superconducts below a T_c which is shown in Fig. 3 as a function of x . We first describe the technique for calculating λ .

The linewidth of the $\nu\mathbf{q}$ phonon due to the e -ph coupling is given by Fermi's golden rule:¹⁶

$$\gamma_{\nu\mathbf{q}} = 2\pi \sum_{n,m,\mathbf{k}} [\theta(\epsilon_{m(\mathbf{k}+\mathbf{q})}) - \theta(\epsilon_{n\mathbf{k}})] \times \delta(\epsilon_{m(\mathbf{k}+\mathbf{q})} - \epsilon_{n\mathbf{k}} - \omega_{\nu\mathbf{q}}) |g_{\nu,n\mathbf{k},m(\mathbf{k}+\mathbf{q})}|^2. \quad (1)$$

Here, $|n\mathbf{k}\rangle$ are the electronic states in the undistorted crystal and $\epsilon_{n\mathbf{k}}$ are their energies relative to the Fermi

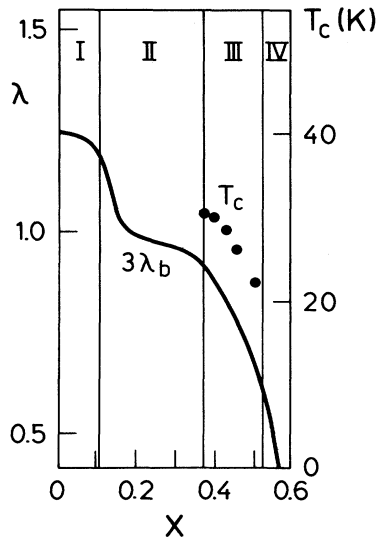


FIG. 3. Electron-phonon coupling constant for the oxygen breathing mode calculated for sc $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. We used the phonon frequency calculated for $x = 0.5$ ($\omega_b = 530 \text{ cm}^{-1}$), the self-consistent frozen-phonon potentials calculated for $x = 0$, and the rigid-band approximation for x values other than 0. Indicated by dots are the T_c values measured in Ref. 5. The vertical lines indicate the regions of stability of the monoclinic (I), orthorhombic (II), and sc (III) structures.

level. n and m run over the bands, the factor 2 is from the spin degeneracy, and the sum over \mathbf{k} is the average over the BZ [i.e., $\Sigma_{\mathbf{k}} \equiv (2\pi)^{-3} \Omega_{\text{sc}} \int d^3k$]. For the energy bands we shall use the LDA eigenvalues and, for sc $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in the virtual-crystal approximation, there is only one band ($n = m = 1$). In (1) the phonon energy is $\omega_{\nu\mathbf{q}}$ and the e -ph matrix element is

$$g_{\nu,n\mathbf{k},m(\mathbf{k}+\mathbf{q})} = \langle n\mathbf{k} | dV(\mathbf{r}) | m(\mathbf{k} + \mathbf{q}) \rangle / dQ_{\nu\mathbf{q}}. \quad (2)$$

Here, the perturbation of the self-consistent electronic potential due to the phonon is $dV(\mathbf{r}) = \Sigma_{ij} [\partial V(\mathbf{r}) / \partial R_{ij}] dR_{ij}$ with the displacement in the i direction of the j th atom given by $dR_{ij} = e_{ij,\nu\mathbf{q}} (2M_j \omega_{\nu\mathbf{q}})^{-1/2} dQ_{\nu\mathbf{q}}$. Here, $e_{\nu\mathbf{q}}$ is the phonon eigenvector normalized to unity in the primitive cell and M_j is the mass of the j th atom. For the b mode, only the three O atoms are involved and $e_{ij} = \delta_{ij} / \sqrt{3}$. Now, the Eliashberg function $\alpha^2 F(\omega)$ is essentially the phononic density of states weighted by the relative linewidth γ/ω . The strength λ of the e -ph coupling may therefore be expressed as¹⁶

$$\lambda \equiv 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega = \frac{1}{\pi N_{\uparrow}(0)} \sum_{\nu,\mathbf{q}} \frac{\gamma_{\nu\mathbf{q}}}{\omega_{\nu\mathbf{q}}^2} \equiv \sum_{\nu,\mathbf{q}} \lambda_{\nu\mathbf{q}}, \quad (3)$$

where $N_{\uparrow}(0) \equiv \Sigma_{n,\mathbf{k}} \delta(\epsilon_{n\mathbf{k}})$ is the electronic density of states per spin at the Fermi level.

If the energy bands are linear functions of \mathbf{k} within the energy range $\omega_{\nu\mathbf{q}}$ around the Fermi level and if $q \gg \omega_{\nu\mathbf{q}}/v_{n\mathbf{k}}$, where $v_{n\mathbf{k}} \equiv \partial \epsilon_{n\mathbf{k}} / \partial \mathbf{k}$ is the Fermi velocity, then (1) may be written as a line integral along the cut between the n th sheet of the Fermi surface, $\epsilon_{n\mathbf{k}} = 0$, and the m th sheet of the \mathbf{q} -displaced Fermi surface, $\epsilon_{m(\mathbf{k}+\mathbf{q})} = 0$:

$$\begin{aligned}
 \gamma_{\nu\mathbf{q}} / \omega_{\nu\mathbf{q}} &= 2\pi \sum_{n,m,\mathbf{k}} \delta(\epsilon_{m(\mathbf{k}+\mathbf{q})}) \delta(\epsilon_{n\mathbf{k}}) |g|^2 \\
 &= 2\pi \sum_{n,m} \int \frac{(2\pi)^{-3} \Omega_{\text{sc}} dk}{|v_{n\mathbf{k}} \times v_{m(\mathbf{k}+\mathbf{q})}|} |g|^2. \quad (4)
 \end{aligned}$$

For simplicity we have dropped the subscripts on g .

With muffin-tin orbitals and a frozen-phonon supercell technique, it is inconvenient to evaluate integrals like $\langle n\mathbf{k} | dV(\mathbf{r}) | m(\mathbf{k} + \mathbf{q}) \rangle$ which involve orbitals at the equilibrium positions and the potential for the displaced atoms. Instead, we obtain the e -ph matrix elements from the self-consistent energy bands with ($\tilde{\epsilon}$) and without (ϵ) the displacement, using that, for a point on the cut: $\epsilon_{n\mathbf{k}} = \epsilon_{m(\mathbf{k}+\mathbf{q})} = 0$, the degeneracy is split by $\Delta \tilde{\epsilon}_{\mathbf{k}} = 2 |\langle n\mathbf{k} | dV(\mathbf{r}) | m(\mathbf{k} + \mathbf{q}) \rangle|$. In practice, the nm cut is found by calculating the ϵ bands on a fine mesh in the sc BZ (145 irreducible points) and interpolating them linearly inside each tetrahedron. Using the supercell, where $\mathbf{k} + \mathbf{q}$ falls onto \mathbf{k} , the ϵ bands are then recalculated along the cut and, since this cut is merely interpolated, the n and m bands (those near the Fermi level) are split slightly, by $\Delta \epsilon_{\mathbf{k}}$. A self-consistent supercell calculation is now performed *with* the frozen phonon and, for the re-

sulting potential, the energy bands are traced along the interpolated cut. The splitting $\Delta\tilde{\epsilon}_k$ of the near-zero energies finally yields the e -ph matrix element according to $|\langle nk|dV(\mathbf{r})|m(\mathbf{k}+\mathbf{q})\rangle|^2 \approx [(\Delta\tilde{\epsilon}_k)^2 - (\Delta\epsilon_k)^2]/4$.

Using (4) we calculated the e -ph coupling strength $\lambda_b(x)$ for the breathing mode in the sc structure ($0.37 < x < 0.53$) using the phonon frequency ($\omega_b = 530 \text{ cm}^{-1}$) calculated for $x = 0.5$ plus the rigid-band approximation for the electrons. Specifically, we performed the self-consistent calculations with and without breathing ($b = 0.03 \text{ \AA}$ and 0) for sc BaBiO_3 and then moved the Fermi level within the resulting ϵ and $\tilde{\epsilon}$ bands according to the hole count x . Although this means that the screening of the frozen phonon corresponds to $x = 0$, rather than to $x \approx 0.5$, we believe that this procedure, which was dictated by its practicality, leads to a reasonable approximation.

The resulting $\lambda_b(x)$ is shown in Fig. 3, even for x outside the range of stability of the sc structure. The b mode presumably has the largest λ because this mode strongly modulates the $sp\sigma$ -hopping integral so that $|g|^2$ is large. Moreover, at least for small x , the phase space is large due to near Fermi-surface nesting [the Fermi velocities in (6) are nearly antiparallel]. From Fig. 3 two features are noticeable. Firstly, the sharp increase of λ_b as x decreases below 0.15. This is the nesting effect and, had we included the proper x dependence of the phonon frequency, λ_b would even have diverged for $x \approx 0.1$ because, here, the b phonon becomes unstable. Secondly, for the superconducting compositions, where the x dependence of ω_b is presumably negligible, $\lambda_b(x)$

follows the same trend as the experimental $T_c(x)$. This suggests that the pairing agents are, indeed, the breathinglike phonons. If we estimate the total λ to be about three times λ_b (roughly speaking, because of the 9 O modes 3 are stretching) we find $\lambda \approx 0.9$ at $x = 0.4$. This is close to the estimate found from model tight-binding calculations by Shirai, Suzuki, and Motzuki.⁴ By solving the Eliashberg equations using $\mu^* = 0.12$, these authors furthermore estimated that $T_c \approx 30 \text{ K}$, which is close to the experimental value. The McMillan formula¹⁷ yields about the same value. Hence, the superconductivity in sc $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ seems to be conventional and mediated by the e -ph coupling.

In summary, we have presented LDA calculations of the structural phase diagram of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for $x = 0$ and $x = 0.5$. We found equilibrium crystal structures in good agreement with experiments, namely, for $x = 0$ a simultaneous tilting and breathing distortion amounting to $t = 8.5^\circ$ and $b = 0.055 \text{ \AA}$ of the cubic structure and, for $x = 0.5$ the absence of both instabilities. The frequencies of the tilting and breathinglike phonons were calculated and for $x = 0$, the effect of anharmonicity was discussed. We calculated the e -ph coupling constant λ_b for the breathing mode as a function of x in the cubic structure. The result is in accord with the experimental values of $T_c(x)$ and this supports the view that the superconductivity is conventional.

Three of us (A.I.L., C.O.R., and I.I.M.) thank the Alexander von Humboldt Foundation for financial support.

*On leave from Institute of Chemistry, Sverdlovsk, U.S.S.R.

†On leave from Lebedev Physical Institute, Moscow, U.S.S.R.

¹L.F. Mattheiss, E.M. Gyorgy, and D.W. Johnson Jr., *Phys. Rev. B* **3**, 3745 (1988).

²R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp Jr., A.E. White, K. Short, W.F. Peck, and T.Y. Komemati, *Nature (London)* **332**, 814 (1988).

³D.G. Hinks, B. Dabrowski B.D. Jorgensen, A.W. Mitchell, D.R. Richards, S. Pei, and D. Shi, *Nature (London)* **333**, 836 (1988).

⁴M. Shirai, N. Suzuki, and K. Motzuki, *J. Phys. Condens. Matter* **2**, 3553 (1990).

⁵S. Pei, J.D. Jorgensen, B. Dabrowki, D.G. Hinks, D.R. Richards, A.W. Mitchel, J.M. Newsam, S.K. Sinha, D. Vaknin, and A.J. Jacobson, *Phys. Rev. B* **41**, 4126 (1990).

⁶D.E. Cox and A.W. Sleight, *Solid State Commun.* **19**, 969 (1976); *Acta Crystallogr. Sect. B* **35**, 1 (1979).

⁷L.F. Mattheiss and D.R. Hamann, *Phys. Rev. B* **28**, 4227 (1983).

⁸K. Takegahara and T. Kasuya, *J. Phys. Soc. Jpn.* **56**, 1478 (1987).

⁹N. Hamada, S. Massidda, A.J. Freeman, and J. Redinger, *Phys. Rev. B* **40**, 4442 (1989).

¹⁰L.F. Mattheiss and D.R. Hamann, *Phys. Rev. Lett.* **60**, 2681 (1988).

¹¹R. Zeyher and K. Kunc, *Solid State Commun.* **74**, 805 (1990).

¹²P. Blaha, K. Schwarz, G. Vielsack, and W. Weber, in *Electronic Properties of High- T_c Superconductors and Related Compounds*, edited by H. Kuzmany, M. Mehring, and J. Fink (Springer, Berlin, 1990).

¹³M. Methfessel, C.O. Rodriguez, and O.K. Andersen, *Phys. Rev. B* **40**, 2009 (1989).

¹⁴U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

¹⁵A.A. Maradudin and A.E. Fein, *Phys. Rev. B* **128**, 2589 (1962).

¹⁶P.B. Allen, *Phys. Rev. B* **6**, 2577 (1972).

¹⁷W.L. McMillan, *Phys. Rev.* **167**, 331 (1968).