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Dependence of the critical temperature on atomic structure in orthorhombic $YBa_2Cu_3O_x$

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The method of parent compounds has been used to establish an approximate correlation between the variation of the critical temperature, T_c, and the variation of the potential difference, ΔV_A, of a hole at the apex and planar oxygen sites within the superconducting phase region of $YBa_2Cu_3O_x$. The resulting model was used to predict the pressure derivative of T_c under hydrostatic pressure, giving derivatives and standard uncertainties of $dT_c/dP=6.1\pm0.5$ K/GPa for $x=6.6$ and $dT_c/dP=-0.6\pm0.3$ K/GPa for $x=6.93$. [S0163-1829(96)05518-X]

I. INTRODUCTION

Almost since the very beginning of the massive effort to understand the phenomenon of high-temperature superconductivity, it has been known that the superconducting characteristics of $YBa_2Cu_3O_x$ vary significantly with the oxygen content of the material.[1,2] The critical temperature, T_c, provides the most dramatic illustration of this dependence. The value of T_c appears to approach a maximum value in the range 91 to 93 K as x approaches a value of 7, and the value of T_c falls to 0 K as x decreases to 6.4.

According to the charge transfer model,[1] the superconducting characteristics of $YBa_2Cu_3O_x$ are varied by the transfer of charge between the CuO_2 planes and the CuO chains in the orthorhombic crystalline structure. Conceptually, the model appears to be appropriate whether the charge transfer is produced chemically, by changing the composition, or mechanically, by applying an external stress to a specimen of fixed composition.

Significantly, the crystallographic symmetry and unit cell dimensions also vary measurably with changes in the oxygen content.[3] In the composition range in which superconductivity is observed, $6.4\leqslant x\leqslant7.0$, the crystal structure has an orthorhombic symmetry, while for $x<6.4$ the crystal has a tetragonal structure. In these ranges, the dimensions of the crystallograhic unit cell vary approximately linearly with x. As the distances between the ions change, the potential energy at each site changes, and those changes may be expected to affect quantitative aspects of superconductivity, such as the magnitude of T_c. This influence has been confirmed to some extent by studies of the pressure dependence of T_c for which a relation of the form

$$T_c(n,P)=T_{c,\max}(P)-A[n(P)-n_{\rm op}]^2$$

can be used, where n is the number of carriers per CuO_2, $n_{\rm op}$ is the optimal carrier density, P is the pressure, and $T_{c,\max}$ and A are adjustable parameters.[4] In that work, both the carrier density and the maximum T_c were found to vary with the pressure, reflecting the changes in the site potentials resulting from the compression of the structure.

These observations suggest that there is a correlation between the quantitative variation of T_c and the variation of the structure and the associated apical and planar oxygen site potential energies. Some insight into this correlation may be provided by considering the Madelung site potentials or, more specifically, the difference of potential between the apical and planar oxygen sites.

For an ionic crystal, the electrostatic potential energy $V(\mathbf{r}_i)$ of charge q_i at the ith ionic position, $\mathbf{r}_i$, is given by

$$V(\mathbf{r}_i)=\sum_j{}' q_iq_j/|\mathbf{r}_j-\mathbf{r}_i|, \tag{1}$$

where the sum is taken over all sites in the crystal except $j=i$. Given the ionic valence states and the coordinates of all the ions in a unit cell of the material, the sum in Eq. (1) can be evaluated readily by well established methods.[5]

For $YBa_2Cu_3O_x$, the positions of the ions in the unit cell may be obtained from studies of the crystallography of the material. There is a problem, however, in the assignment of the charge q_i at site i because of the nonstoichiometry of the oxygen content. In the structure of $YBa_2Cu_3O_x$ for $x=7$, Fig. 1 and Table I, the atomic sites are fully occupied. For $YBa_2Cu_3O_x$ with $6.4<x<7.0$, the average occupancy at the O[4] site is less than one; i.e., the O[4] site is occupied in some unit cells of the bulk sample, but unoccupied in other unit cells. Ordering of the oxygens to produce well defined superstructures is not clear experimentally except, perhaps, in the case with $x=6.5$. Consequently, the evaluation of Eq. (1) is hindered by both the lack of charge assignments at the oxygen sites and the lack of a well defined superstructure which is essential to the evaluation of the lattice summation in Eq. (1).

A further difficulty occurs regarding the valence states of the Cu ions in $YBa_2Cu_3O_7$. Given the valence states of -2 for each oxygen, $+3$ for Y, and $+2$ for each Ba, charge neutrality requires that the Cu ions have an average valence of $+2.33$. This average valence implies that the one Cu(1) ion is in the $+3$ state while the two Cu(2) ions are in $+2$ states. Calculations by Iguchi *et al.*[6] confirm that these valence assignments are reasonable. Experimentally, however, there does not appear to be any evidence to support the occurrence of a $+3$ Cu valence in $YBa_2Cu_3O_7$.

The only case for which these difficulties do not occur is the case of $YBa_2Cu_3O_{6.5}$. For this material, electron diffraction data indicate that half of the O[4] sites are unoccupied such that if the site (0,1/2,0) is assumed to be occupied, then

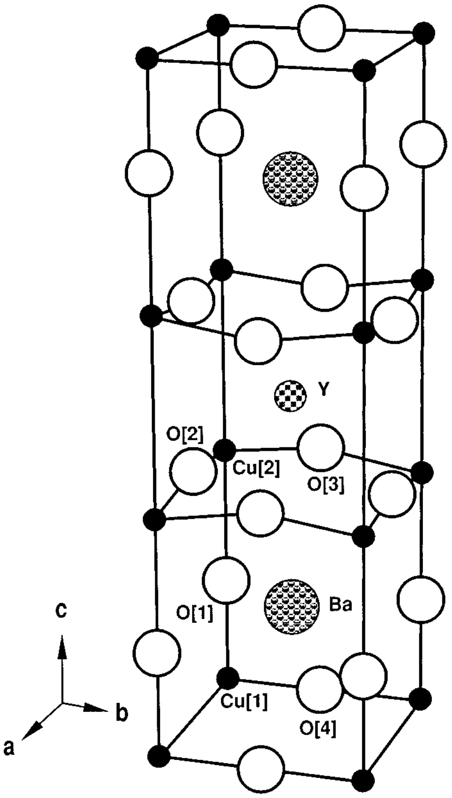

FIG. 1. The structure of $YBa_2Cu_3O_x$ for $x=7$.

the site (1,1/2,0) is unoccupied.[7,8] In this way, a well defined supercell of dimensions $2a,b,c$ is obtained. Futhermore, the normal valence states of the ions provide the required charge neutrality: Y(+3), Ba(+2), Cu(+2), and O(−2). Consequently, the evaluation of Eq. (1) for this case is unambiguous.

Since $YBa_2Cu_3O_{6.5}$ is a superconducting material, Ohta *et al.*[9] observed that the essential electronic energy level structure required for superconductivity must already be present in the energy level structure for this particular case. Hence they concluded that energy levels for $YBa_2Cu_3O_{6.5}$ should be representative of the entire superconducting phase region, $6.4<x<7$. They further noted that such well defined cases, which they called parent compounds, can be constructed for most of the superconducting cuprates. Based on the valence states of the parent compounds and the appropriate atomic coordinates, they proceeded to calculate the Madelung site potentials for selected cases of numerous cuprates and to relate those results to the critical temperatures. In particular, they related the critical temperature that occurred in a superconducting phase region to the difference, ΔV_A, between the potential of a hole at the apex (O[1]) and the in-plane (O[2] and O[3]) oxygen sites. They found that T_c varied approximately monotonically with ΔV_A when the results for all the cuprates were viewed jointly.

TABLE I. Site notation and atomic coordinates (x,y,z) of the ions of $YBa_2Cu_3O_x$ (Fig. 1) with respect to the orthorhombic (space group *Pmmm*) unit cell parameters (a,b,c).

Ion	x	y	z
Y	0.5	0.5	0.5
Ba	0.5	0.5	z_{Ba}
Cu[1]	0	0	0
Cu[2]	0	0	$z_{\mathrm{Cu[2]}}$
O[1]	0	0	$z_{\mathrm{O[1]}}$
O[2]	0.5	0	$z_{\mathrm{O[2]}}$
O[3]	0	0.5	$z_{\mathrm{O[3]}}$
O[4]	0	0.5	0

In the present work, we study the variation of T_c within the superconducting phase region of a single cuprate, namely $YBa_2Cu_3O_x$, and apply the method of Ohta *et al.* to obtain an estimate of the correlation between the variation of T_c and the variation of ΔV_A. In proceeding in this manner, there is an implicit assumption that changes in the charge carrier density are strongly correlated to dimensional changes and that the resulting empirical correlation of T_c and ΔV_A absorbs the absolute differences resulting from using the parent compound to calculate ΔV_A. While this approach is somewhat heuristic, the utility of the method is shown by using the relation between ΔV_A and T_c to calculate the variation of T_c (for $x=6.6$ and $x=6.93$) under the isotropic conditions of hydrostatic pressure. The model is applied further to discuss the variation of T_c under the anisotropic strain conditions of uniaxial stress.

II. METHOD

The ideal orthorhombic $YBa_2Cu_3O_{6.5}$ is taken as the parent compound for the superconducting orthorhombic phase $YBa_2Cu_3O_x$. Figure 2(a) illustrates the oxygen ordering in the basal plane that results in the computational supercell with cell edge lengths of $2a$, b, and c. This parent compound with all ions in their normal valence states is used to calculate the Madelung potentials for selected sites. Special attention is focused on the difference in the potential of a hole at the apex oxygen sites and the planar oxygen sites. In the parent compound, there are two inequivalent Cu[1] ions because alternate rows of O[4] ions are vacant. Correspondingly, there are two inequivalent O[1] ions, denoted O[1] and O′[1], in each supercell. Further, the potentials of the O[2] and O[3] sites are slightly different in keeping with the orthorhombic symmetry of the material, and in the supercell, the sites O[2], O′[2], O[3], and O′[3] should be distinguished. In practice, however, it appears that the values obtained from these nearly equivalent sites are highly correlated. Consequently, it is more convenient to consider only the average potential difference defined as

$$\Delta V_A=(\Delta V_{A1}+\Delta V_{A2})/2, \tag{2a}$$

where

$$\Delta V_{A1}=V_{\mathrm{O[1]}}-(V_{\mathrm{O[2]}}+V_{\mathrm{O[3]}})/2, \tag{2b}$$

$$\Delta V_{A2}=V_{\mathrm{O'[1]}}-(V_{\mathrm{O'[2]}}+V_{\mathrm{O'[3]}})/2 \tag{2c}$$

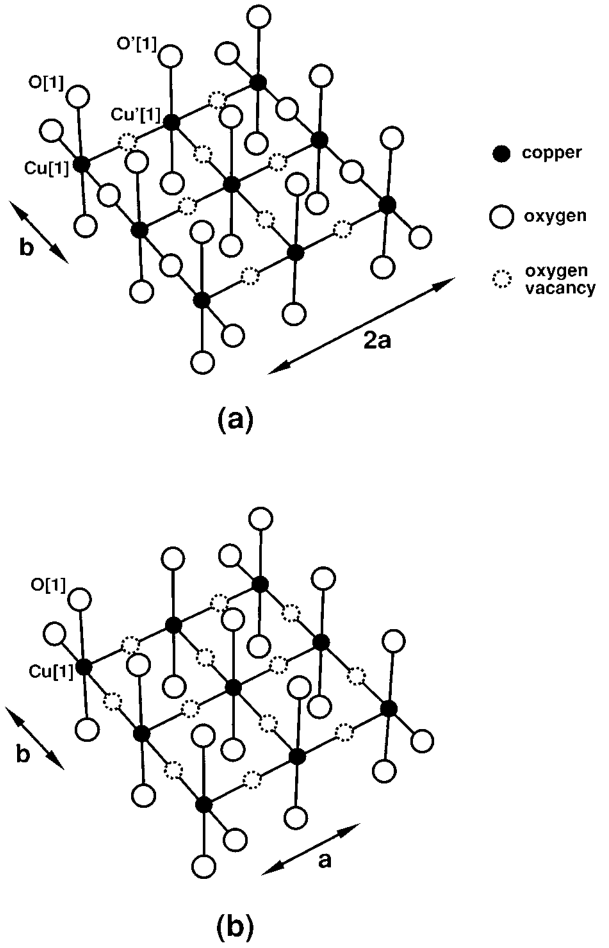

FIG. 2. Oxygen ordering in the basal plane (a) $YBa_2Cu_3O_{6.5}$ and (b) $YBa_2Cu_3O_6$.

and where V_i is the Madelung potential to introduce a hole at site i. It is shown in the following section that the quantity ΔV_A is a sensitive function of the changes in the atomic coordinates.

For completeness, the calculations are extended into the tetragonal phase region, $6<x<6.4$, by using $YBa_2Cu_3O_6$ as the parent compound for that phase region. For $YBa_2Cu_3O_6$, the O[4] site is vacant, and the computational cell, Fig. 2(b), has dimensions (a,a,c). Charge neutrality requires the average valence of the Cu ions to be 5/3 which can be achieved by assuming that the valence of Cu[1] is $+1$ while the two Cu[2] ions have valences of $+2$.

III. RESULTS

Calculations were performed for various oxygen contents using atomic coordinates selected in accordance with the structural refinements reported in the literature.[3,10] These calculations determined an effective relation between ΔV_A and oxygen content. Then, given the empirical relation between T_c and oxygen content,[3,10–24] the effective relation between T_c and ΔV_A was deduced. This relation was then used to calculate the variation of T_c with hydrostatic and uniaxial stresses.

The results for ΔV_A are given in Figs. 3–5. The variation of ΔV_A with oxygen content, Fig. 3, is monotonic but changes rapidly across the phase boundary near $x=6.4$. The influence of various dimensional changes on the value of ΔV_A is suggested by Fig. 4 in which the ΔV_A is plotted against the individual lattice parameters and the z coordinates of the Ba, O[1], and Cu[2] ions. Using the empirical relation between T_c and oxygen content allows the effective relation between T_c and ΔV_A to be obtained as in Fig. 5.

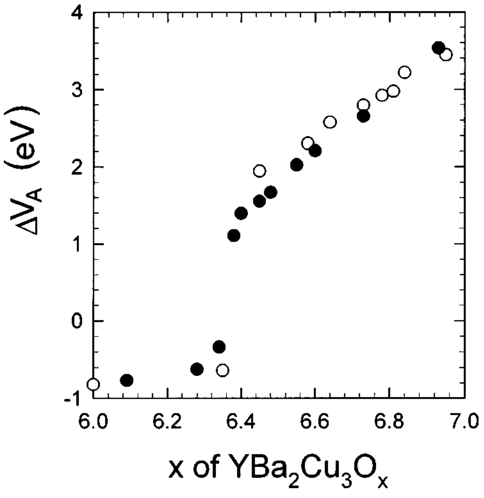

FIG. 3. The variation of ΔV_A with oxygen content (x).

The results of Fig. 5 provide a basis for calculating the rate of change, dT_c/dP, of T_c with pressure (P). The primary result of applying hydrostatic pressure to a specimen of fixed composition is the compression of the material structure. Thus, from the known pressure dependence of the lattice parameters and the atomic coordinates, ΔV_A vs P can be calculated and used to evaluate the rate of change, $d(\Delta V_A)/dP$. Then, the results of Fig. 5 can be used to evaluate $dT_c/d(\Delta V_A)$, and the two rates can be combined to yield $dT_c/dP=[dT_c/d(\Delta V_A)][d(\Delta V_A)/dP]$.

The pressure dependence of T_c and the structural parameters for two compositions, $x=6.6$ and $x=6.93$, are given in the paper by Jorgensen *et al.*[20] Using these data, ΔV_A was determined as a function of pressure, Fig. 6, for both compositions, and the rates of change, $d(\Delta V_A)/dP$, were determined to be

$$d(\Delta V_A)/dP=0.16\pm 0.01 \ \text{eV/GPa} \quad \text{for } x=6.6, \tag{3a}$$

$$d(\Delta V_A)/dP=-0.06\pm 0.02 \ \text{eV/GPa} \quad \text{for } x=6.93, \tag{3b}$$

where the standard uncertainties were estimated from the least squares fits. From Fig. 5,

$$dT_c/d(\Delta V_A)=38\pm 1 \ \text{K/eV} \quad \text{at } T_c=58 \ \text{K} \quad \text{for } x=6.6, \tag{4a}$$

$$dT_c/d(\Delta V_A)=10\pm 1 \ \text{K/eV} \quad \text{at } T_c=91 \ \text{K} \quad \text{for } x=6.93. \tag{4b}$$

Combining these results, we estimate

$$dT_c/dP=6.1\pm 0.5 \ \text{K/GPa} \quad \text{for } x=6.6, \tag{5a}$$

$$dT_c/dP=-0.6\pm 0.3 \ \text{K/GPa} \quad \text{for } x=6.93. \tag{5b}$$

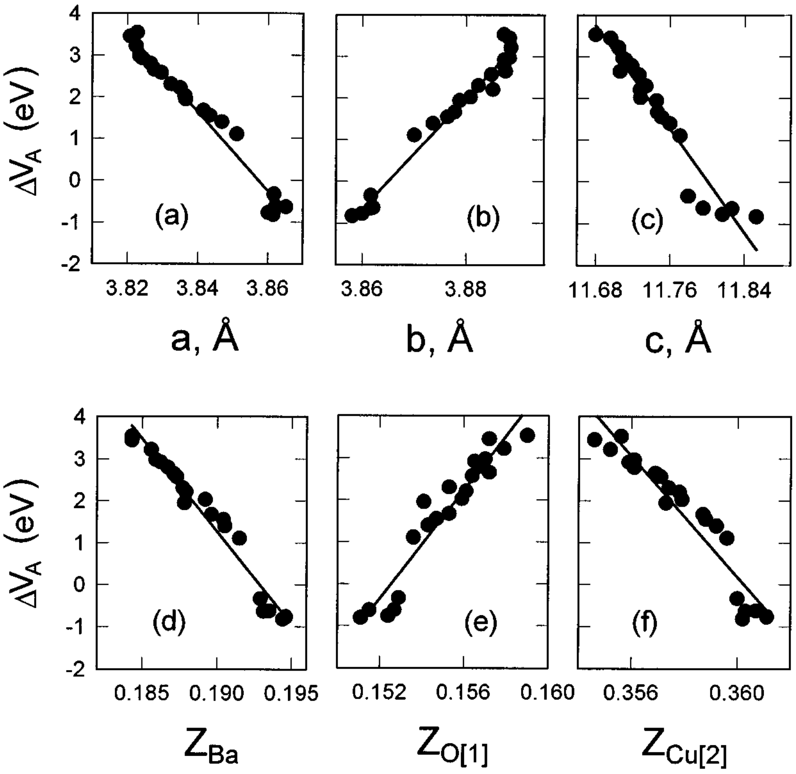

FIG. 4. The variation of ΔV_A with lattice parameters (a) a, (b) b, (c) c, and relative atomic coordinates (d) z_{Ba}, (e) $z_{\mathrm{O}[1]}$, and (f) $z_{\mathrm{Cu}[2]}$.

While the results for these two cases are strikingly different from each other, they compare very favorably with the experimental results:[25–31]

$$4 \text{ K/GPa} \leqslant dT_c/dP \leqslant 7 \text{ K/GPa} \quad \text{for } x=6.6, \tag{6a}$$

$$-0.8 \text{ K/GPa} \leqslant dT_c/dP \leqslant 1 \text{ K/GPa} \quad \text{for } x=6.93. \tag{6b}$$

A more sensitive application of the current model is provided by the variation of T_c under uniaxial stress. Experimentally, the stress derivatives of the critical temperature, dT_c/ds_i for $i=a$, b, and c, are found to be -2 K/GPa along the a axis, 1.9 K/GPa along the b axis, and -0.3 K/GPa along the c axis for a composition having $T_c=91.2$ K which corresponds approximately to $x=6.95$.[32] It is shown here that the strains in the lattice parameters and the relative atomic coordinates can account for these values in the context of the present approximation. It will be seen that the results are especially sensitive to the values of the relative coordinates.

The strains in the lattice parameters can be estimated by using the elasticity tensor[33] and the observed conditions of uniaxial stress. However, there does not appear to be any experimental data on the strains of the relative coordinates under uniaxial stress. Based on the results from the study under hydrostatic pressure, Fig. 7, the strains in the relative coordinates can be expected to be nonuniform under uniaxial stress. Attention, therefore, is focused on (1) estimating the relative influence of the contributing strain factors and (2)

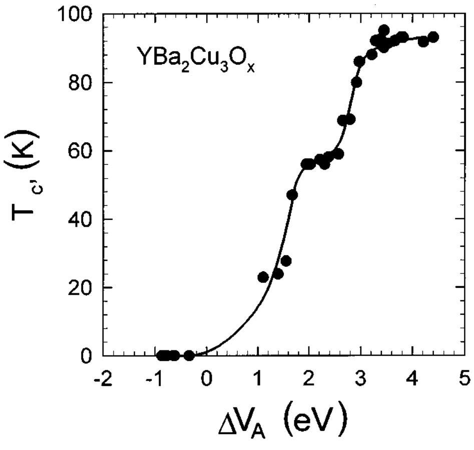

FIG. 5. The variation of T_c with ΔV_A.

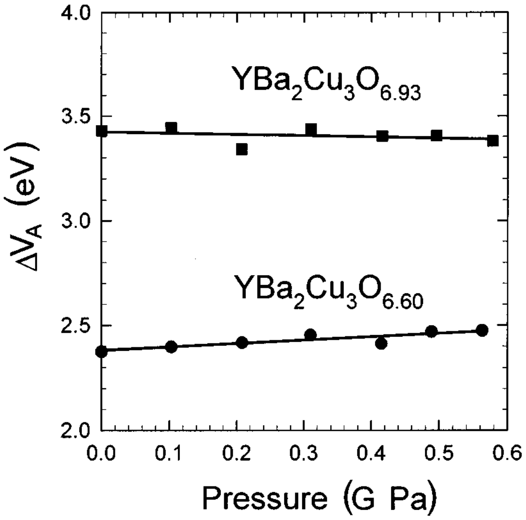

FIG. 6. The variation of ΔV_A with hydrostatic pressure.

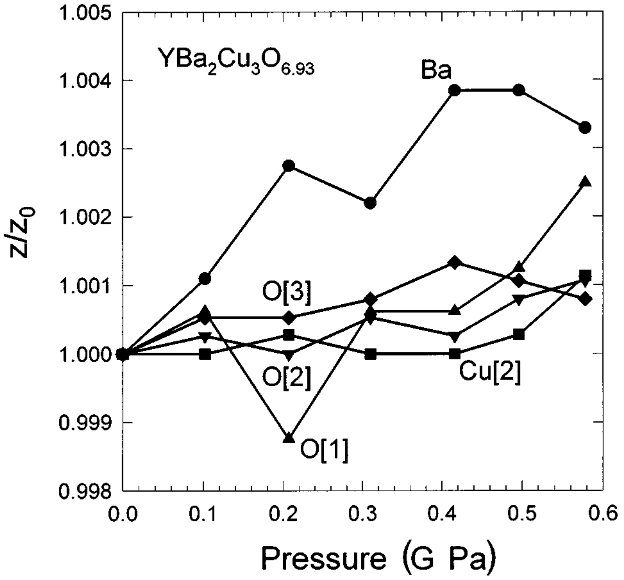

FIG. 7. The change in the relative atomic coordinates, z, under hydrostatic pressure [based on the data of Jorgensen *et al.* (Ref. 20)].

TABLE II. The parameters of Eq. (8) for $YBa_2Cu_3O_{6.93}$. (The values were computed to an uncertainty of one unit in the last displayed digit.)

Parameter [unit]	Value
f_0 [eV]	3.4217
γ_1 [eV/Å]	0.904
γ_2 [eV/Å]	−0.467
γ_3 [eV/Å]	0.221
$(\partial f/\partial z_{\mathrm{Ba}})_0$ [eV]	−163.6
$(\partial f/\partial z_{\mathrm{Cu[2]}})_0$ [eV]	−193.9
$(\partial f/\partial z_{\mathrm{O[1]}})_0$ [eV]	76.4
$(\partial f/\partial z_{\mathrm{O[2]}})_0$ [eV]	135.8
$(\partial f/\partial z_{\mathrm{O[3]}})_0$ [eV]	132.0

demonstrating that suitable estimates of the strain values can be made yielding stress derivatives in agreement with the experimental results.

The relative contributions of the contributing strains can be obtained by noting that the change in the magnitude of ΔV_A with strain is relatively small. Consequently, ΔV_A may be considered as a function, $f(\xi)$, of the atomic coordinates, ξ, and may be expressed as an expansion series about its zero strain value

$$\Delta V_A = f(\xi) = f_0 + \sum_i (\partial f/\partial \xi_i)_0 \delta\xi_i + \cdots , \tag{7}$$

where the summation is over all the spacial coordinates of all the ions in the unit cell. The Y, Cu[1], and O[4] ions occupy special sites whose relative coordinates are constrained by symmetry. Thus, for example, the Y ion contributes to the sum in Eq. (7) only the quantity

$$\begin{aligned}&(\partial f/\partial[x_Y a])_0 \delta[x_Y a] + (\partial f/\partial[y_Y b])_0 \delta[y_Y b]\\&\quad + (\partial f/\partial[z_Y c])_0 \delta[z_Y c]\\&\quad = (\partial f/\partial a)_0 \delta a + (\partial f/\partial b)_0 \delta b + (\partial f/\partial c)_0 \delta c,\end{aligned}$$

and likewise for Cu[1] and O[4]. The remaining ions occupy sites with symmetry constraints on the relative coordinates along the a axis and the b axis, but not along the c axis. Thus, the relative coordinates of the Ba, Cu[2], O[1], O[2], and O[3] ions along the c axis can change with uniaxial stress. Thus, for example, the Ba ion contributes the quantity

$$\begin{aligned}&(\partial f/\partial[x_{\mathrm{Ba}} a])_0 \delta[x_{\mathrm{Ba}} a] + (\partial f/\partial[y_{\mathrm{Ba}} b])_0 \delta[y_{\mathrm{Ba}} b]\\&\quad + (\partial f/\partial[z_{\mathrm{Ba}} c])_0 \delta[z_{\mathrm{Ba}} c]\\&\quad = (\partial f/\partial a)_0 \delta a + (\partial f/\partial b)_0 \delta b + (\partial f/\partial c)_0 \delta c\\&\quad + (\partial f/\partial z_{\mathrm{Ba}})_0 \delta z_{\mathrm{Ba}},\end{aligned}$$

and similar contributions occur for the Cu[2], O[1], O[2], and O[3] ions. Consequently, Eq. (7) can be written as

$$\begin{aligned}\Delta V_A = {}& f_0 + \gamma_1 \delta a + \gamma_2 \delta b + \gamma_3 \delta c + (\partial f/\partial z_{\mathrm{Ba}})_0 \delta z_{\mathrm{Ba}},\\& + (\partial f/\partial z_{\mathrm{Cu[2]}})_0 \delta z_{\mathrm{Cu[2]}}, + \Sigma_{k=1,2,3} (\partial f/\partial z_{\mathrm{O}[k]})_0 \delta z_{\mathrm{O}[k]}.\end{aligned} \tag{8}$$

Equation (8) provides an explicit representation of the individual contributions to ΔV_A that result from the strain in the lattice parameters and the relative atomic coordinates. The coefficients in Eq. (8) may be evaluated readily using the parent compound model calculations. The coefficients evaluated in this manner are given in Table II. It is evident from these results that small changes in the relative coordinates can have significant effects on the value of ΔV_A. While the currently available experimental data are not sufficient to determine the strains in the relative coordinates uniquely, Table III shows one possible set of strains that result in stress derivatives in agreement with the experimental values.

TABLE III. One possible set of the lattice parameters and relative atomic coordinates for the indicated conditions of uniaxial stress, s, yielding $dT_c/ds = -2$ K/GPa along the a axis, 1.9 K/GPa along the b axis, and −0.3 K/GPa along the c axis. (The numbers of digits given in these values were selected to yield a computational accuracy of 1% in the computed value of dT_c/ds.)

s, GPa	a, Å	b, Å	c, Å	z_{Ba}	$z_{\mathrm{Cu[2]}}$	$z_{\mathrm{O[1]}}$	$z_{\mathrm{O[2]}}$	$z_{\mathrm{O[3]}}$
0	3.8181	3.8840	11.6832	0.18230	0.35435	0.1608	0.37447	0.37629
0.1, a axis	3.8157	3.8837	11.6882	0.18260	0.35453	0.1609	0.37467	0.37649
0.1, b axis	3.8177	3.8818	11.6880	0.18235	0.35440	0.1609	0.37457	0.37639
0.1, c axis	3.8197	3.8857	11.6678	0.18245	0.35445	0.1609	0.37462	0.37643

IV. CONCLUSION

The method of parent compounds has been used to establish an empirical correlation between the variation of T_c and the variation of the difference in potential energy, ΔV_A, of a hole at the apex and planar oxygen sites. The model successfully predicted the pressure derivative of T_c under hydrostatic pressure, giving derivatives and standard uncertainties of $dT_c/dP=6.1\pm0.5$ K/GPa for $x=6.6$ and $dT_c/dP=-0.6\pm0.3$ K/GPa for $x=6.93$. It was shown further that the values of the stress derivatives are sensitive functions of the strains in the relative atomic coordinates. The model, the elasticity tensor, and the experimental uniaxial stress derivatives of T_c were used to show that strains in the relative atomic coordinates of only a few parts in 10^4 were significant in accounting for the values of the stress derivatives of T_c under uniaxial stress.

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