

Uniaxial Strain Dependence of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_7$: Internal Strain Induced Intralayer Charge Transfer

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Results of *ab initio* calculations on uniaxially strained $\text{YBa}_2\text{Cu}_3\text{O}_7$ are correlated with known values of the uniaxial strain dependencies $dT_c/d\epsilon_\alpha$ ($\alpha = x, y, z$) of the superconducting critical temperature T_c . Internal strains are found to dominate the strain dependence, with the strong nontetragonality correlating directly with the measured nontetragonality of $dT_c/d\epsilon_\alpha$. Charge rearrangements within the CuO_2 layers overwhelm any chain-to-layer charge transfer and strongly suggest that the relative amount of Cu and O character within the layers determines the strain dependence of T_c . [S0031-9007(97)02615-X]

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Although there is still no consensus on the microscopic pairing mechanism in the high temperature superconductors (HTS), the extensive research of the past ten years has led to some understanding of several of their general properties. A widely noted example is the relation between the transition temperature T_c of a given system relative to the maximum T_c^{max} in that system, and the “hole concentration” n per layer Cu [1]

$$\frac{T_c(n)}{T_c^{\text{max}}} = 1 - \left(\frac{n - n_{\text{opt}}}{\Delta n} \right)^2. \quad (1)$$

This relation has been obtained for several cuprate materials for most of the range of n that is accessible and for which the result is positive. Values of the half range $\Delta n \approx 0.10$ – 0.13 and the optimal concentration $n_{\text{opt}} \approx 0.16$ – 0.20 are common to many compounds. Equation (1) emphasizes the similarity of the cuprates, the fact that some of the essential physics is common to all members. The “essential physics” in this context encompasses the behavior within the CuO_2 layers: the doping that transforms the antiferromagnetic insulating phase into a paramagnetic metal with a superconducting ground state.

On the other hand, there is little understanding of the single most exciting feature of the HTS: the very high value of T_c^{max} (but only in some members), and what distinguishes a member with very high T_c such as $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ($T_c^{\text{max}} = 135$ K) [2] from one with a modest one such as $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{4+\delta}$ ($T_c^{\text{max}} = 20$ K) [3]. If the essential physics of the cuprates within the layers is common to all members, then the origin of their widely differing values of T_c^{max} must originate outside of the CuO_2 layers. Another remarkable, unexplained feature is the pressure induced rise in $T_c^{\text{max}}(P)$ in $\text{Hg}1223$ from 135 to above 160 K (more than half room temperature) upon application of pressure [4]. Since the 135 K material is already optimally doped, the pressure-enhanced rise in T_c , that is, the increase of the coupling constant, is due to something other than change in doping level.

In this Letter we confront this question, using $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) as the paradigm. Since we make no pretense that we understand the pairing mechanism or know how the coupling constant depends on material parameters, we are limited to comparing *calculated* properties with *measured* shifts in T_c and establishing correlations. Previous studies have looked for correlations with Cu-O bond lengths (both planar and axial), electronegativities, Madelung potentials, and valence bond sums [5]. Early on, Torrance and Metzger [5] noted correlations with the difference between Cu and O Madelung potentials in the CuO_2 layer. An extensive study of this ionic picture by Ohta *et al.* [5] uncovered correlations of several energy differences across a variety of classes of cuprates, and they emphasized the difference in Madelung potentials between apical O and planar O. The manner in which any of these differences can couple strongly to the strength of the pairing interaction remains unclear.

Correlating the pressure dependence of calculated materials properties with the measured $T_c(P)$ is a promising way to get at the microscopic origin of T_c^{max} , and there is substantial experimental data and phenomenological analysis on $T_c(P)$ for several systems [6]. However, the fact that nonstoichiometry (either on oxygen or on cation sublattices) is essential in maximizing T_c in many systems is a great complication when attempting to treat the full atomic and electronic structure of the unit cell. Moreover, the net pressure dependence is the sum of uniaxial pressure dependencies within the plane and perpendicular to the plane, and as we describe below, these dependencies may not be at all as expected on the basis of simple models.

Here we use strong orthorhombicity to advantage, and for the first time establish that consideration of internal strains is crucial for any understanding of the (uniaxial and total) pressure dependence of T_c . We address YBCO, the most highly studied HTS, for which the uniaxial strain dependence of T_c is known. Meingast *et al.* [7] and Welp *et al.* [8] have made independent determinations. Their

values of the uniaxial pressure dependencies agree well, and to within 0.1 K/GPa agreement their mean values are

$$dT_c/dp_a = -2.0 \text{ K/GPa},$$

$$dT_c/dp_b = +2.0 \text{ K/GPa},$$

$$dT_c/dp_c = +0.2 \text{ K/GPa}.$$

Kund and Andres [9] reported values that have identical trends but are $\approx 30\%$ smaller. Lei *et al.* [10] have determined the full elastic moduli c_{ij} , and from the relation connecting stresses and strains

$$dT_c/d\epsilon_i = - \sum_j c_{ij} dT_c/dp_j \quad (2)$$

the above values translate to uniaxial strain dependencies of

$$dT_c/d\epsilon_a = +212 \text{ K},$$

$$dT_c/d\epsilon_b = -244 \text{ K},$$

$$dT_c/d\epsilon_c = -8 \text{ K}.$$

Two features of these results are remarkable. Many models of HTS emphasize interlayer coupling, which would suggest that \hat{c} axis strain should be the crucial variable that dominates the pressure dependence [11]. Clearly that is *not* the case in $\text{YBa}_2\text{Cu}_3\text{O}_7$. Also, the CuO_2 layer is roughly square planar, but the remarkably large nontetragonality, i.e., the large and opposing coefficients for \hat{a} and \hat{b} axis strains, reflects strong influence from the nontetragonal part of the cell, i.e., the CuO chains. The measured shifts in T_c indicate, as do the values of T_c^{max} throughout the cuprates, that occurrences *outside* the CuO_2 planes are dominating the strain dependencies, as they dominate the value of T_c^{max} itself.

Here we analyze results of local density approximation (LDA) calculations on uniaxially strained YBCO, and concentrate on properties that LDA predicts reliably. We use the full potential linearized augmented plane wave (FLAPW) method [12,13] used in previous studies of cuprates [14,15]. A very extensive set of 1650 basis functions was used. Self-consistency was obtained on a regular $4 \times 4 \times 2 = 32$ k point mesh in the irreducible Brillouin zone. We have adopted the experimental \hat{a} , \hat{b} , and \hat{c} axis lattice constants of 3.821, 3.884, and 11.676 Å, respectively, to allow the most direct comparison with experimental data.

We use the usual notation where the chain (layer) Cu atom is Cu1 (Cu2), the chain (apical) oxygen atom is O1 (O4), and the layer oxygens are O2 and O3, with O3 lying below/above the chain O1 atom. The equilibrium atomic positions obtained by minimizing the energy are similar to those obtained previously [16] by relaxing atoms only individually, and to those reported recently by Kouba *et al.* [17]. In this Letter we focus on changes with \hat{a} and \hat{b} axis strains only, since these results are of primary

importance. A full report of all calculated changes (including \hat{c} axis strain) will be presented elsewhere.

We have applied 2% uniaxial compression in each direction, which corresponds roughly to pressures of 5 GPa for planar strains, or half that amount for \hat{c} axis strain. These strains are small enough to be within the range of linearity of dT_c/dP [18] but large enough to allow differences to be obtained without overly stringent convergence criteria. The atoms with z coordinates that are not restricted by symmetry (Ba, Cu2, O2, O3, O4) relax under uniaxial stress, and these internal strains have been calculated by energy minimization.

Internal strains.—The internal displacements induced by the 2% strains are pictured in Fig. 1. For \hat{a} axis compression, all internal strains are negative, i.e., all atoms relax toward the nearest chain; hence the two CuO_2 layers are squeezed apart. For \hat{b} axis compression, all internal strains except for O2 are positive: compressing the chain pushes the O4 and Ba ions away, and on average pushes the two CuO_2 layers closer together. The O2 ion, with no chain O1 ion above it, relaxes toward the chain in either case. The net effect is that the \hat{b} axis strain, which increases T_c , makes the CuO_2 layer geometry more tetragonal; in fact, at the 2% compression the O2 and O3 heights become equal and the planar lattice constants differ by only 0.5%, so the CuO_2 layer is almost exactly tetragonal. The a uniaxial compression, on the contrary, increases the orthorhombicity of the layers.

van Hove critical points.—There is great interest in the van Hove singularities (vHs) that lie near the Fermi level E_F . Present interpretation of angle-resolved photoelectron emission data places an extended vHs at both X and Y points of the Brillouin zone [19]. LDA calculations place one vHs on each side of these symmetry points, and not as near E_F . Each of the planar uniaxial strains results in the movement of one of the vHs toward E_F , consistent with an increase in hopping amplitude due to decreased bond length in that direction [20]. However,

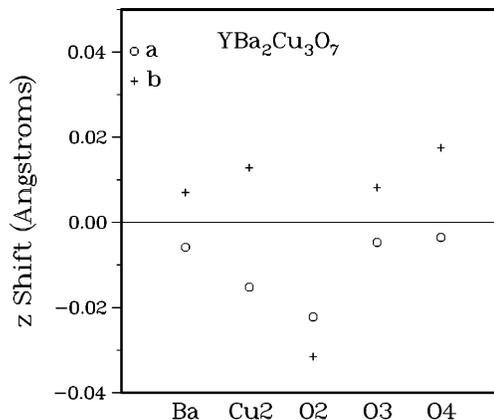


FIG. 1. Calculated internal shifts (in the z direction) for 2% compressive \hat{a} and \hat{b} axis strains for the five atoms that are allowed by symmetry to relax.

\hat{c} axis strain results in both vHs moving through and above E_F , in agreement with their known sensitivity to layer-layer coupling [20]. Since \hat{c} axis strain has virtually no effect on T_c , we must conclude that there is no correlation of the position of the vHs in the LDA band structure and the magnitude of T_c . However, the possibility that tetragonality promotes a more well defined vHs that enhances T_c [21] is consistent with our findings.

Charge rearrangements.—Now we consider rearrangements of the charge density due to uniaxial strain. We have analyzed several features: charges in the FLAPW spheres, shifts in core eigenvalues, and planar-averaged densities. We consider here the latter quantities, which are the most revealing. Because of the widespread discussion of charge transfer between the chain region and layer region, we average the density parallel to the \hat{a} - \hat{b} plane and look at its response to strain. The differences (strained minus unstrained) of this averaged electron density are plotted versus z/c in Fig. 2 for both uniaxial strains in the layer.

The density shifts are large only in the CuO_2 layer region, and are opposite for \hat{a} and \hat{b} axis strains, mirroring the uniaxial strain shift in T_c . Our results indicate negligible chain-to-layer transfer of charge, unlike the parametrized tight-binding calculations of Gupta and Gupta [22] that did not include internal strains and were not charge self-consistent. For these 2% strains, the charge rearrangement amounts roughly to planar “surface” charge densities $\sigma^\pm = \pm 0.2 e/ab$ obtained by integrating the curves shown in Fig. 2 (ab is the unit cell cross-sectional area) displaced from another one of opposite sign by $d = 0.05c \approx 1$ bohr, corresponding to a surface dipole moment density $D = (\sigma^+ - \sigma^-)d \approx 4 \times 10^{-3} e/\text{bohr}$. This surface dipole translates into a shift in (planar-averaged) potential between the two CuO_2 layers (i.e., within the yttrium layer) with respect to elsewhere in the cell by $\Delta\phi = 4\pi eD = 1.2$ eV (0.6 eV/% strain). For the \hat{b}

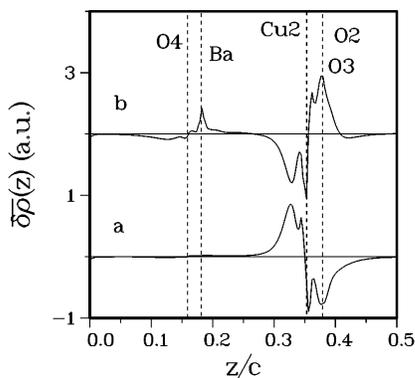


FIG. 2. Plots of the change due to the 2% uniaxial strains of the planar-integrated charge density. The units are electrons/bohr, with the curve for \hat{b} axis strain results displaced upward by two units for clarity. The vertical dashed lines indicate the positions of planes of atoms, as labeled.

axis compression the sign of the dipole is such that it adds to the strong ionic dipole that is already present in the $\text{Cu}^{2+\delta}\text{O}_2^{-(2-\epsilon)}$ planes due to the relative displacement of the Cu2 and O2, O3 layers.

Shifts in potential.—We relate this change to strain induced changes ΔV_α in site Madelung potentials V (as seen by a negatively charged electron) that arise from the internal strain. We assign the nominal charges to Y^{3+} , Ba^{2+} , Cu^{2+} , and $\text{O}4^{2-}$, but to obtain charge neutrality in this metallic system we suppose other oxygen charges of $\text{O}1^{1.8-}$, $\text{O}2^{1.8-}$, and $\text{O}3^{1.8-}$. These values are reasonable for semiquantitative purposes, which is all that is intended here. The resulting shifts are given in Table I. The magnitudes may not be physical, due to screening that is neglected when calculating the Madelung potentials, but the trends should be meaningful.

We concentrate again on the differences between \hat{b} axis and \hat{a} axis strains. The largest differences are -0.39 eV for Y and $+0.31$ eV for Cu1. These atoms lie on opposite sides of the CuO_2 layer, and the changes are consistent with the aforementioned picture of strain induced surface dipoles (see Fig. 2) in the CuO_2 layer. The O2/O3 shifts are opposite in sign to the Cu2 shifts, and of a direction that favors O2/O3 site occupation by electrons at the expense of Cu2 occupation. Moreover, the O2 and O3 Madelung shifts approach each other for \hat{b} axis strain, while for \hat{a} axis strain they tend to diverge. This result confirms the earlier indication that in YBCO increased tetragonality of the CuO_2 layer correlates with increased T_c . The behavior of the difference in Madelung potential $V^{\text{O}4} - V^{\text{O}2,\text{O}3}$ between the apical O4 and the planar O2, O3 ions is consistent (qualitatively) with the viewpoint of Ohta *et al.* [5], who emphasize that larger values of this quantity correlate with larger values of T_c . This value increases by 0.14 eV for \hat{b} axis strain but only by 0.04 eV for \hat{a} axis strain.

Physical interpretation.—The picture that arises then is that increasing T_c is connected to increasing tetragonality [23], both structural and electronic, and to increasing charge on the layer oxygen ions driven by internal strain,

TABLE I. Shifts in the site Madelung potentials (eV) due to the internal strains that result from the given compressive uniaxial strains. The choices of ionic charges are given in the text. The atoms are listed in decreasing value of z/c so the trend $\Delta V_b - \Delta V_a$ with position in the cell can be seen.

	V_o	ΔV_a	ΔV_b	$\Delta V_b - \Delta V_a$
Cu1	28.31	-0.02	0.29	0.31
O1	-15.96	-0.10	-0.08	0.02
O4	-18.64	-0.13	-0.23	-0.10
Ba	19.37	0.25	0.36	0.11
Cu2	23.88	0.26	0.13	-0.13
O2	-22.22	-0.19	-0.32	-0.13
O3	-22.06	-0.15	-0.42	-0.27
Y	26.69	-0.05	-0.44	-0.39

and that it is essential to determine the internal strains self-consistently with the charge rearrangement. In a local picture, the charge transfer (CT) energy scale $\Delta_{CT} = \epsilon_p - \epsilon_d > 0$, in terms of the layer oxygen $2p\sigma$ level and the layer Cu $3d_{x^2-y^2}$ level, has long been considered an important quantity. For decreasing Δ_{CT} , i.e., softer charge transfer excitations, the Zhang-Rice singlet [24] becomes less strongly bound. Also, tetragonality of the CuO_2 plane promotes a larger intrinsic O2/O3 bandwidth (via direct O-O hopping t_{pp} along coplanar bonds). Both changes should reduce correlation effects due to Cu site Coulomb repulsion.

Relation to mechanisms.—A change in Δ_{CT} will affect the coupling strength due to spin fluctuations (SF), charge fluctuations (CF), and lattice fluctuations, and no doubt also hybrid mechanisms. Monthoux and Pines [25] find that T_c in their SF model depends comparably on the SF energy scale, the SF coherence length, and on the coupling constant, and due to its phenomenological nature it is unclear which of these properties might be most dependent on Δ_{CT} and on tetragonality. The CFs in the model of Varma and co-workers, which includes current fluctuations on the planar O ions surrounding Cu ions [26], may be anticipated to strengthen with increased tetragonality. Evaluation of the conventional electron-phonon coupling strength in $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ [27] and in YBCO [28] suggests that Fermi surface shifts with strain could lead to enhanced coupling due to stronger nesting. Of course, unusual hardening of important phonons could enhance T_c . Our calculated zone center A_g phonons show normal variation with strain (mild hardening), with one remarkable exception. The highest frequency mode, under \hat{b} axis compression only, increases by 30% (by 140 cm^{-1}). This mode involves out-of-phase O3 and (apical) O4 motion, whereas the highest mode for \hat{a} (and \hat{c}) strain is essentially an O4 local mode. Tachiki and Takahashi [29] have outlined an unconventional phonon mechanism in which CFs couple to longitudinal optic (LO) phonons. Although not couched in terms of the parameters of a tight-binding model, one can surmise that the coupling will become stronger as the CT excitation energy softens (as suggested by our Madelung potential shifts) and thereby approaches the LO phonon energy.

In summary, we have carried out self-consistent studies of YBCO under uniaxial strain, and found that internal strain dominates the changes in the electronic structure. The measured strong increase (decrease) in T_c with \hat{b} (\hat{a}) axis strain correlates with increasing (decreasing) tetragonality of both the CuO_2 layer structure, with the electronic structure, and with closer (more separated) CuO_2 layers. These results provide strong constraints that should help in identifying the microscopic pairing mechanism.

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