RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 5 1 AUGUST 1991-I

Correlation between axial-oxygen anharmonicity and T_c in $YBa_2Cu_3O_7$ and related compounds

J. Mustre de Leon, S. D. Conradson, I. Batistić, and A. R. Bishop
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 28 January 1991)

Cu-O radial distribution functions in $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.5}$, and $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$ at 10 K have been determined from Cu *K*-edge polarized extended x-ray-absorption fine structure of these materials, using model potentials to describe the effect of the Cu-O relative motion. The analysis shows that the axial oxygen atom moves in a double-well potential. A correlation between interwell tunneling and T_c is observed, and interpreted as a correlation between anharmonicity and T_c.

Changes in the ordering of oxygen in the Cu-O(1) basal planes of $YBa_2Cu_3O_{7-\delta}$ can be achieved by either oxygen removal or doping of $YBa_2Cu_3O_7$. A connection between the ordering of O(1) and the superconductivity in $YBa_2Cu_3O_{7-\delta}$ and related compounds was established early after its discovery.[1-3] However, a microscopic understanding of the effect of these structural changes in the Cu-O(2,3) plane electronic degrees of freedom, which are clearly involved in the superconductivity, is still lacking. The axial oxygen O(4) that serves as a bridge between the Cu(1)-O(1) chains and Cu(2)-O(2,3) planes provides a route by which these structural changes resulting from O(1) ordering or doping can influence the superconductivity taking place in the Cu(2)-O(2,3) planes. More specifically, the idea that the O(4) site is involved in structural changes that also affect the superconductivity, in $YBa_2Cu_3O_{7-\delta}$, has been demonstrated by several experiments.[4-6] Diffraction studies have indicated a correlation between changes of the Cu(1)-O(4) and Cu(2)-O(4) distances as a function of oxygen content δ and changes in T_c in $YBa_2Cu_3O_{7-\delta}$.[5] Also, Raman and infrared-absorption studies in Co-doped samples of $YBa_2Cu_{3-x}Co_xO_{7+\delta}$ find changes in peak amplitudes and frequencies of modes that involve Cu(1)-O(4) and Cu(2)-O(4) vibrations, and present anomalies around T_c, as the Co-doping concentration is varied, indicating that changes in the Cu-O bond lengths correlate with the observed changes in Raman and infrared frequencies.[7,8]

We have recently presented x-ray-absorption fine-structure (EXAFS) data from $YBa_2Cu_3O_7$ which indicate that the O(4) atom moves in a double-well potential.[9] Theoretical support for the existence of double-well potentials associated with Cu-O(4) bonds comes from charge-transfer models [based on descriptions of the highly polarizable O(4) ions],[10] and dynamical Jahn-Teller coupling models.[11] These models lead to anharmonic potentials[12] for the Cu-O(4) relative motion in $YBa_2Cu_3O_7$, predicting a more harmonic motion of the O(4) atom as the stoichiometry changes from $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_6$.[10] Also, infrared-absorption studies in $YBa_2Cu_{3-x}Co_xO_{7+\delta}$ have found that the 580-cm^{-1} mode, associated with the Cu(1)-O(4) vibration, exhibits a *decrease* in the anomalous frequency shift and change of the peak intensity across T_c, as the Co content is increased.[8] Our analysis of the EXAFS also showed that a lattice fluctuation involving the O(4) site accompanies the superconducting transition.[9] Consequently, this analysis provides evidence of a dynamical coupling between the O(4) vibrations and in-plane electronic degrees of freedom involved in the superconductivity. It is important to establish how such a coupling is affected by static structural changes due to changes in the oxygen content and doping. Here we present the analysis of Cu-O(4) and in-plane Cu-O contributions to the Cu *K*-edge polarized EXAFS of oriented samples of $YBa_2Cu_3O_7$ (T_c=92 K), $YBa_2Cu_3O_{6.5}$ (T_c=52 K), and $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$ (T_c=25 K) powders at T=10 K. From this analysis we have extracted the radial distribution function (RDF) of the Cu(1)-O(4) pair using a formalism for the analysis of EXAFS in anharmonic systems previously described.[9] The sample characteristics, experimental methods, and EXAFS data reduction have been discussed previously.[4] Here, we only note that as the listed temperature is that of the cold finger of the cryostat used in the experiment, the actual temperature may be as much as 5-10 K higher than the one quoted above and that x-ray pole figure analysis shows that the orientation of the powders is such that electric-field polarization vector $\hat{\epsilon}$ is aligned to better than 90% for the $\hat{\epsilon}\parallel c$ measurements.

The main local structural changes achieved by the removal of the O(1) atoms from the $YBa_2Cu_3O_{7-\delta}$ orthorhombic phase (for $\delta \leq 0.55$) are a decrease of the Cu(1)-O(4) bond length (~0.03 Å) and a large increase of the Cu(2)-O(4) bond length (~0.08 Å).[5,13] At low doping levels, Co substitutes specifically for Cu(1) and induces similar structural changes in the Cu-axial O bonds as those obtained by oxygen removal.[14] For the studied stoichiometries there is a small alteration of the Cu(2)-O(2,3) and Cu(1)-O(1) bond lengths.[5,15] This is shown in Fig. 1 (left panel), where it can be seen that the $\hat{\epsilon}\perp c$ Cu-O contributions in these three materials at 10 K are similar in both phase and amplitude. Figure 1 (right panel) also shows the combined EXAFS from Cu(1)-O(4) and Cu(2)-O(4) pairs, below $k=10$ Å^{-1} the total EXAFS signal suffers little change. However, doping does affect significantly the phase above $k=10$ Å^{-1}. The beat in the EXAFS in Fig. 1(b) around $10 \leq k \leq 12$ Å^{-1} is indicative of *two* Cu-O(4) positions separated by $0.12 \leq \Delta R \leq 0.15$ Å and thus a double-well potential.[9] Consequently in order to quantify the observed changes

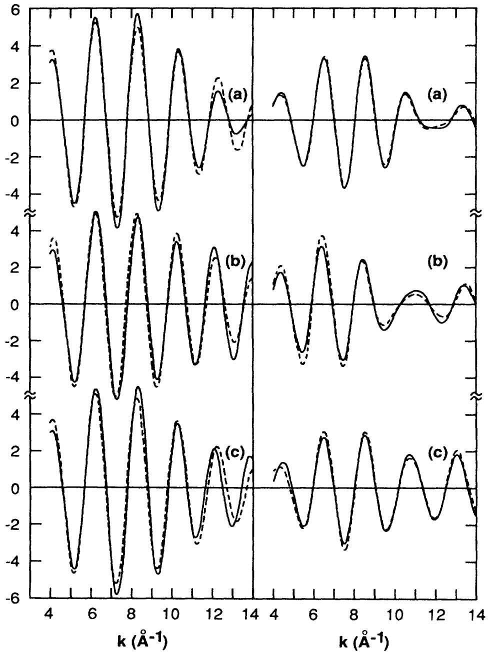

FIG. 1. Left panel: Experimental $\hat{\epsilon}\perp c$ EXAFS spectrum (solid line) and harmonic fit (dashed line), in (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{6.5}$, and (c) $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$. Right panel: Experimental $\hat{\epsilon}\parallel c$ EXAFS spectrum (solid line) and anharmonic fit (dashed line), in (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{6.5}$, and (c) $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$.

TABLE I. Cu-equatorial-O parameters resulting from harmonic fits to $\hat{\epsilon}\perp c$ EXAFS data.

Compound	r (Å)	N	σ (Å)	ΔE_0 (eV)
$YBa_2Cu_3O_7$	1.928	3.3	0.092	3.2
$YBa_2Cu_3O_{6.5}$	1.952	3.0	0.089	−0.2
$YBa_2Cu_{2.8}Co_{0.2}O_{7-\delta}$	1.942	3.3	0.092	1.3

we make use of the formalism we have developed earlier to fit EXAFS using a general form for the pair potential.[9]

The EXAFS signal fit to the data is modeled by

$$\langle\chi\rangle=\int dz g(z)\chi(k,r)\,, \qquad (1)$$

where $\chi(k,r)$ denotes the single-scattering polarized EXAFS contribution arising from O atoms located at a distance r from a Cu absorbing atom, and the photoelectron momentum $k=[(2m/\hbar^2)(E-E_0)]^{1/2}$ is referenced to the arbitrary energy origin $E_0=9000$ eV. The RDF $g(z)$ is expressed in terms of single-particle wave functions $\{\psi_i(z)\}$ and single-particle energy levels $\{\varepsilon_i\}$;

$$g(z)=\frac{\sum_i|\psi_i(z)|^2e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}\,. \qquad (2)$$

The temperature of the system T is introduced through $\beta=1/k_BT$ and z denotes the relative displacement from the bond equilibrium position along the bond, i.e., $\mathbf{r}=\mathbf{R}+z\hat{\mathbf{R}}$. The wave functions $\{\psi_i(z)\}$ are determined by solving the Schrödinger equation using the reduced mass for an isolated Cu-O pair and a model potential $V(z)$.

The Cu-O contributions to the EXAFS with $\hat{\epsilon}\perp c$ could be fit to the data accurately using a harmonic formulation. The experimental signal was obtained by Fourier filtering the total EXAFS signal (with $\hat{\epsilon}\perp c$) within the ranges $3\le k\le 15$ Å^{-1} and $1.0\le r\le 2.0$ Å. In order to avoid distortions introduced by the filtering process, the fits were performed in the range $4\le k\le 14$ Å^{-1}. No attempt was made to fit the individual Cu(2)-O(2), Cu(2)-O(3), and Cu(1)-O(1) contributions. Thus the average Cu-O distance R and a harmonic Debye-Waller factor σ were used as fitting parameters. EXAFS amplitudes and phase functions, entering in the definition of $\chi(k,r)$ [cf. Eq. (1)], were extracted from EXAFS in $LaCu_2O_4$,[9] and the energy reference E_0 was also allowed to vary to account for the lack of chemical transferability. The average coordination number was fixed at crystallographically determined values.[5,15] As shown in Table I there is a small change in the average bond length R, the good correspondence between the experimental and calculated EXAFS is shown in Fig. 1 (left panel). The average bond length is in good agreement with previously reported values.[5,15] These results do *not* preclude *out-of plane anharmonic* motion of these atoms (see below).

For the fits to the EXAFS signal when $\hat{\epsilon}\parallel c$ the Cu-O signal was isolated by Fourier filtering within the ranges $3\le k\le 15$ Å^{-1} and $1.0\le r\le 2.0$ Å. Anharmonic fits including both the Cu(1)-O(4) and Cu(2)-O(4) were performed in the range $4\le k\le 14$ Å^{-1}, using the model potential,

$$V(z)=\frac{a}{2}(z-z_1)^2,\ z\le z_0;\ \ \frac{b}{2}(z-z_2)^2,\ z\ge z_0\,, \qquad (3)$$

where z_0 is determined by the continuity condition $V(z_0^+)=V(z_0^-)$. In this case a, b, z_1, and z_2 were used as fitting parameters.[9] The EXAFS phase and amplitude functions derived from the Cu-O signal from the $\hat{\epsilon}\perp c$ data were used in these fits and it was not found necessary to vary the energy reference E_0. The coordination number for the Cu-O pairs was fixed at $N=2$. The values of the parameters for the Cu(1)-O(4) bond are given in Table

TABLE II. Cu(1)-O(4) parameters resulting from the fit to $\hat{\epsilon}\parallel c$ EXAFS data.

Compound	Short R_1 (Å)	Long R_1 (Å)	a_1 (10^6K/Å^2)	b_1 (10^6K/Å^2)	$\hbar\omega_T$ (K)
$YBa_2Cu_3O_7$	1.822	1.954	1.85	1.85	153
$YBa_2Cu_3O_{6.5}$	1.815	1.953	1.86	1.87	123
$YBa_2Cu_{2.8}Co_{0.2}O_{7-\delta}$	1.851	1.996	1.83	1.91	89

II,[16] and the fits are shown in Fig. 1(b). The Cu-O(4) bond lengths, obtained by a weighted average of the two O(4) positions, and the Cu(1)-Cu(2) distance are in good agreement with crystallographically determined values.[5,15]

The potential, $V(z)$ and RDF $g(z)$, obtained from the $\hat{\epsilon}\|c$ fits are shown in Fig. 2. The RDF is determined only from the first two eigenstates of the Hamiltonian, since higher energy levels are separated from these first two levels by >1200 K. In going from $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$, we observe the following changes: (a) the minima of the double-well potentials move further apart—from $\Delta R=0.013$ Å in $YBa_2Cu_3O_7$, $\Delta R=0.014$ Å in $YBa_2Cu_3O_{6.5}$ to $\Delta R=0.0145$ Å in $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$; (b) the RDF $g(z)$ becomes more asymmetric in the same progression, going from near equal populations for both sites in $YBa_2Cu_3O_7$ to a ratio 2:1 for the population of the shorter site compared to the longer site in $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$. These structural changes produce an increase of the height and the width of the potential barrier between the two wells leading to a decreased tunneling between the two sites. This change is quantified by the tunneling frequency $\hbar\omega_T=\varepsilon_1-\varepsilon_0$ (see Fig. 3), where ε_0 is the energy of the (symmetric) ground state and ε_1 is the energy of the (antisymmetric) first excited state.

Although there are not enough cases to establish quantitative trends, we can conclude that the tunneling frequency systematically decreases as the critical temperature decreases.[17] We interpret these changes as an indication that the motion of the O(4) atom becomes more *harmonic* with decreasing T_c, i.e., the motion of the O(4) in each well becomes *decoupled*, and the occupation of only *one site* is favored. Indeed in the case of $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$ ($T_c=25$ K) it was possible to fit the $\hat{\epsilon}\|c$ data using a purely harmonic treatment, with physically reasonable values for the fitting parameters and a quality of fit similar to that obtained in anharmonic fits. The correlation between anharmonicity and T_c is consistent with correlations between global structural phase-transition temperatures, anharmonicity, and T_c in high-temperature superconductors.[18]

In an attempt to understand the observed correlation between the tunneling frequency and T_c, we calculated T_c using the Eliashberg equation modified to include the *specific* anharmonic phonon derived from the Cu(1)-O(4) potential obtained from the EXAFS fit. Other parameters, i.e., the density of electronic states at the Fermi level $N(0)$ and the (bare) electron-phonon interaction parameter α, were kept fixed (as a function of oxygen content or doping) in this calculation. We found that the predicted changes in T_c were much smaller than the actual variations for reasonable ranges of $N(0)$ and α. This may suggest that the coupling of electrons to the specific nonlinear phonon [derived from the Cu(1)-O(4) double well] taken in isolation is not the sole factor determining T_c.[19] Indeed in Refs. 11, 20, and 21 it has been proposed that c-axis anharmonicity of the CuO_2 planes is also important for determining superconducting properties. Experimental evidence for such in-plane anharmonicity comes from optical spectroscopy.[22] Although it is not possible to study this effect in the Cu(2)-O $\hat{\epsilon}\perp c$ EXAFS, preliminary results indicate that the $\hat{\epsilon}\perp c$ Cu(2)-Cu(2) contribution (which is sensitive to the c-axis O motion through multiple scattering) shows a similar temperature dependence as the Cu(1)-O(4) EXAFS, suggesting c-axis in-plane anharmonicity.[23] We also note that a correlation between the tunneling frequency and changes in T_c had been anticipated in Ref. 20.

We are presently developing a more specific nonlinear electron-phonon coupling model which naturally models polarizable oxygen ions in perovskitelike structures.[21] This model leads to *both* double-well onsite anharmonicity *and* multiphonon–electron-density coupling terms, in ad-

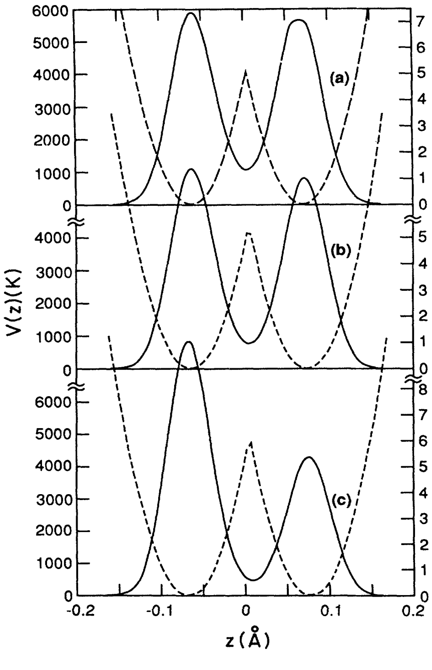

FIG. 2. Radial distribution function $g(z)$ and potential $V(z)$ for (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{6.5}$, (c) $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$.

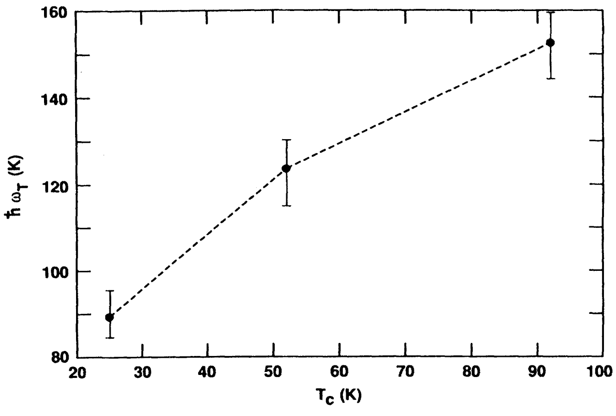

FIG. 3. Tunneling frequency ω_T as a function of T_c in $YBa_2Cu_3O_7$ ($T_c=92$ K), $YBa_2Cu_3O_{6.5}$ ($T_c=52$ K), and $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$ ($T_c=25$ K) (Ref. 19).

dition, it is proposed that the Cu-O(4) anharmonicity drives anharmonic modes in the plane.

In our earlier analysis of $YBa_2Cu_3O_7$ we observed a significant variation in the tunneling frequency ω_T across T_c as a result of the coupling of a two-level system, derived from the deep double well, and fluctuations of the superconducting order parameter.[9] In the case of more harmonic motion, a decrease in this elastic-electronic coupling is expected.[9,10] Consequently, a smaller effect, i.e., a smaller change in the tunneling frequency across T_c, should be observed in $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_{2.8}$-$Co_{0.2}O_{7+\delta}$. This trend has been observed in the anomalous frequency shift and intensity peak of the 580-cm^{-1} infrared-active mode in $YBa_2Cu_{3-x}Co_xO_{7+\delta}$.[8] As the Co content is increased and T_c decreases, the observed anomalies decrease in magnitude,[8] the same trend has been reported for the anomalous contribution to the specific heat across T_c.[24]

In summary, we have observed that the motion of the Cu-O(4) pairs is well described by a double-well potential, with an RDF that becomes more *harmonic* as the T_c of the system decreases, leading to a correlation between the interwell tunneling frequency and T_c. The more harmonic motion of O(4) in materials with lower T_c, implies that lattice fluctuations, involving O(4), associated with the superconductivity should be smaller for materials with lower T_c. This is consistent with results obtained from specific heat and infrared measurements.[8,24]

We would like to thank Ian Raistrick for stimulating discussions, and critical comments. This work was supported by the U.S. Department of Energy.

---

[1] R. J. Cava *et al.*, Physica **153–155C**, 560 (1988).

[2] R. J. Cava *et al.*, Physica **156C**, 523 (1988).

[3] C. H. Chen *et al.*, Phys. Rev. B **38**, 2888 (1988).

[4] S. D. Conradson *et al.*, Science **248**, 1394 (1990).

[5] R. J. Cava *et al.*, Physica **165C**, 419 (1990).

[6] R. P. Sharma *et al.*, Phys. Rev. Lett. **62**, 2869 (1989).

[7] M. Kakihana *et al.*, Phys. Rev. B **40**, 6787 (1989).

[8] H. S. Obhi and E. K. Salje, Physica **171C**, 547 (1990).

[9] J. Mustre de Leon *et al.*, Phys. Rev. Lett. **65**, 1678 (1990).

[10] I. Batistić *et al.*, Phys. Rev. B **40**, 6869 (1989).

[11] K. H. Johnson *et al.*, Mod. Phys. Lett. B **3**, 1367 (1989).

[12] It is interesting to note that electron-phonon coupling in *A*15 compounds was also suggested to lead to double-well potentials: see C. C. Yu and P. W. Anderson, Phys. Rev. B **29**, 2165 (1984).

[13] S. Katano *et al.*, Jpn. J. Appl. Phys. **26**, L1049 (1987).

[14] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 7458 (1988); T. J. Kistenmacher, *ibid.* **38**, 8862 (1988).

[15] P. F. Micelli *et al.*, Phys. Rev. B **37**, 5932 (1988); F. Bridges *et al.*, *ibid.* **39**, 11 603 (1989).

[16] The Cu(2)-O(4) contribution is only ~10% compared to the Cu(1)-O(4) contribution, and thus it has a small effect in the quality of the fits in the beat region (Ref. 9).

[17] The error bars correspond to changes in ω_T that result from changing the potential parameters in such a way that the quality of the fit to experiment change by 15%. This estimate results in very similar error bars to those presented in Ref. 9.

[18] A. Bussmann-Holder *et al.* (unpublished).

[19] N. M. Plakida *et al.*, Europhys. Lett. **4**, 1309 (1987); J. R. Hardy and J. W. Flocken, Phys. Rev. Lett. **60**, 2191 (1988).

[20] D. P. Clougherty, K. H. Johnson, and M. E. McHenry, Physica **162–164C**, 1475 (1989).

[21] A. Bussmann-Holder, A. R. Bishop, and I. Batistić, Phys. Rev. B **43**, 13 728 (1991).

[22] R. Li *et al.*, Physica **175C**, 89 (1991).

[23] S. D. Conradson *et al.* (unpublished).

[24] J. W. Loram *et al.*, Physica **171C**, 243 (1990).