Evidence for an Axial Oxygen-Centered Lattice Fluctuation Associated with the Superconducting Transition in $YBa_2Cu_3O_7$

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The axial oxygen contributions to the Cu K-edge, polarized, extended x-ray-absorption fine structure of $YBa_2Cu_3O_7$ are analyzed for $10 \leq T \leq 105$ K, using a novel approach in which the radial distribution function is directly calculated from model potentials. The best fit is obtained with a double-well potential with two nearly equally populated O(4) sites 0.13 Å apart. The site separation decreases 0.02 Å in a region near T_c. This perturbation of the structure is accompanied by a large increase of the tunneling frequency of ~80 K between the two wells, suggesting a coupling between superconducting fluctuations and nonlinear phonons.

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Although no consensus has been reached on the microscopic mechanism of superconductivity in copper-oxide materials, experimental evidence supports the idea that the axial oxygen [O(4)] is important in the superconductivity in $YBa_2Cu_3O_7$ and related materials.[1-3] Charge-transfer instabilities may couple directly with phonon modes in the plane, but they are certainly expected to couple with O(4) vibrations involved in charge transfer between chains and planes.[4] A special role for the O(4) atom is suggested by infrared reflectivity studies[5] that indicate an anomalously large strength for a phonon mode associated with a Cu(1)-O(4) charge transfer, and Raman profiles which suggest that a structural instability related to the A_g Cu(1)-O(4) stretching vibration could be coupled to charge transfer.[6] Batistić *et al.*[7] have interpreted these measurements using a charge-transfer electron-phonon model that leads to anharmonic potentials[7] for the O(4) relative displacement (RD) that, when coupled to in-plane electronic degrees of freedom, could enhance Jahn-Teller or buckling modes.

Cu-O(4) elastic anomalies have been found across T_c in $ErBa_2Cu_3O_7$ by ion-channeling experiments,[8] and also in extended x-ray-absorption fine structure (EXAFS) studies of unoriented $YBa_2Cu_3O_7$.[3,9] We have recently presented polarized EXAFS results which indicate that the RD of the axial oxygen atom in $YBa_2Cu_3O_7$ and other high-T_c materials is not harmonic and is altered within a fluctuation region around T_c.[10] Here we present the Cu(1)-O(4) radial distribution function (RDF) calculated from Cu K-edge polarized EXAFS data in a thin slice of $YBa_2Cu_3O_7$ oriented powder, with c parallel to the radiation polarization vector and parallel to the surface of the slice, for temperatures $T = 10$–105 K. We examine the behavior of ion dynamics associated with the potential used to fit the EXAFS. We have incorporated the effect of ionic motion, in an arbitrary potential, on EXAFS by calculating the RDF directly from model potentials. The samples, experimental methods, and EXAFS data reduction have been described elsewhere.[10] As the listed temperatures T_{nom} are those of the cold finger of the cryostat used in the experiment,[10] the actual temperature of the sample may be as much as 5–10 K higher.

The presence of two Cu-O(4) distances, indicative of a double well, is signaled by the beat in the EXAFS (Fig. 1) around $k = 12$ Å^{-1}, where $k = [(2m_e/\hbar^2)(E - E_0)]^{1/2}$ denotes the photoelectron momentum defined

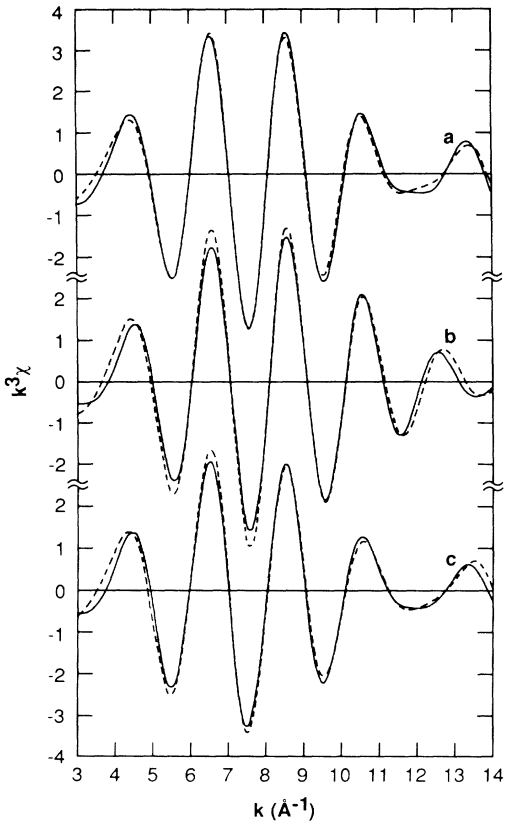

FIG. 1. Comparison between experimental EXAFS spectrum (solid line) and fit $\langle\chi\rangle$ (dashed line) [Eq. (1)] calculated using the potential $V(z)$ [Eq. (3)], at (a) $T_{nom} = 10$ K, (b) $T_{nom} = 86$ K, and (c) $T_{nom} = 105$ K.

with respect to an arbitrary energy origin E_0 ($\equiv$9000 eV). The error in the EXAFS phase for the beat was obtained by averaging spectra measured at temperatures outside the fluctuation region around T_c and calculating the standard deviation between this average and the individual spectra. We find that the probability that the absence of the beat in the spectra at $T_{\text{nom}}=83$ and 86 K results from noise and other types of errors in the data and its reduction is less than 0.5%.

The effect of the RDs of the Cu-O(4) pairs on the EXAFS signal was calculated by performing a statistical average of the single-scattering EXAFS formula for polarized x rays incident on an oriented sample for a static bond.[11] The usual EXAFS analysis of the atomic motion in terms of the harmonic approximation[12] or cumulant expansions[13,14] for the Debye-Waller factor are inadequate when the atomic RDs are highly anharmonic, such as the double-well potential we consider.[10,15] Therefore, this average was calculated using the density matrix associated with a single-particle Hamiltonian describing the O(4) motion. This average can be expressed in terms of an RDF, $g(z)$;

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

where $\chi(k,r)$ denotes the single-scattering polarized EXAFS contribution arising from O(4) atoms located at a distance r from a Cu absorbing atom, and z denotes the O(4) displacement relative to the average Cu-O(4) distance R, i.e., $\mathbf{r}=\mathbf{R}+\hat{\mathbf{k}}z$, where we consider only motion along the c axis. The RDF, $g(z)$, is given in terms of single-particle wave functions $\{\psi_i(z)\}$ and single-particle energy levels $\{E_i\}$;

$$g(z)=\frac{\sum_i|\psi_i(z)|^2e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}\,, \tag{2}$$

and the temperature of the system T is introduced through $\beta=1/k_BT$. The wave functions $\{\psi_i(z)\}$ are determined by solving the Schrödinger equation using the reduced mass for an isolated Cu-O(4) pair, and the model potential $V(z)$;

$$V(z)=\begin{cases}\frac{1}{2}a(z-z_1)^2, & z\le z_0,\\ \frac{1}{2}b(z-z_2)^2, & z\ge z_0\,,\end{cases} \tag{3}$$

where z_0 is determined by the continuity condition $V(z_0^+)=V(z_0^-)$. Harmonic and single- and double-well-modified ϕ^4 potentials $[V(z)=az^2+bz^4+cz^3]$ yielded significantly worst fits than those obtained using Eq. (3). Since correlation between different O(4) atoms is neglected, this treatment is analogous the Einstein approximation.[11]

A nonlinear-squares fit including *both* the Cu(1)-O(4) and Cu(2)-O(4) contributions was performed over $k=3$-14 Å^{-1} on Fourier-filtered data (filtered over the range $k=2$-15 Å^{-1} and backtransformed over the range $1.0\le R\le 2.0$ Å) measured at $T_{\text{nom}}=10$, 83, 86, 88, 95, and 105 K, using as parameters to be determined R, E_0, and the potential parameters a,b,z_1,z_2, for each bond. The temperature-independent EXAFS amplitude and phase functions in $\chi(k,r)$ were obtained from the EXAFS of Cu-O bonds in the a-b plane, and the number of O(4) atoms at a distance R from Cu(1) was fixed at 2. The comparison between experiment and the achieved fits is presented in Fig. 1, and Table I lists the Cu(1)-O(4) parameters. The values of the Cu(1)-O(4) parameters indicate that the motion of the O(4) atom must be described quantum mechanically, since only the ground and first excited states are appreciably occupied even at $T_{\text{nom}}=105$ K (Table I). The Cu(2)-O(4) parameters are $a_2=358$, 335, 348, 435, 416, and 388 (10^4 K)/Å^2; $b_2=358$, 335, 348, 375, 362, and 388 (10^4 K)/Å^2; short Cu(2)-O(4) distances of 2.179, 2.176, 2.181, 2.179, 2.183, and 2.189 Å; long Cu(2)-O(4) distances of 2.312, 2.299, 2.303, 2.313, 2.319, and 2.322 Å, at $T_{\text{nom}}=10$, 83, 86, 88, 95, and 105 K, respectively. These values indicate a rapid damping of the Cu(2)-O(4) EXAFS, such that its contribution is less than 10% of the observed EXAFS amplitude at $k\sim 11$ Å^{-1}.[16] We note that, although residuals from other shells (estimated to be $\le 10\%$) introduce uncertainties in the fitting parameters, changes in the parameters do not depend on these residuals and can be ascribed to fluctuations near T_c.

TABLE I. Cu(1)-O(4) (short R_1, long R_1, a_1, b_1, ω_T) parameters resulting from the fit to EXAFS data; Cu(2)-O(4) parameters are given in the text.

T_{nom} (K)	Short R_1 (Å)	Long R_1 (Å)	a_1 [(10^6 K)/Å^2]	b_1 [(10^6 K)/Å^2]	$\hbar\omega_T$ (K)
10	1.820	1.955	1.85	1.85	153
83	1.821	1.941	1.64	1.64	205
86	1.823	1.945	1.51	1.51	274
88	1.820	1.955	1.85	1.95	157
95	1.821	1.955	1.91	1.98	137
105	1.821	1.954	1.89	1.89	155

The beat disappears in a fluctuation region around T_c because the separation between the minima of the potential $V(z)$ decreases by $\sim$0.02 Å. This small change in distance is well within the sensitivity of these data because it moves the beat from $k=12$ Å^{-1} to beyond $k=14$ Å^{-1}; the structural change lowers the potential barrier between the two wells (Fig. 2). As shown in Fig. 2, $g(z)$ exhibits two maxima located 0.13 Å apart for $T_{\text{nom}}\sim 10$ K and $T_{\text{nom}}>86$ K. Within the fluctuation region, $T_{\text{nom}}=83$ and 86 K, the separation between maxima decreases by $\sim$0.02 Å, leading to a decrease in the root-mean-square deviations of the Cu(1)-O(4) bond length, consistent with ion-channeling results.[8] We do not yet have data to establish the lower limit of the fluc-

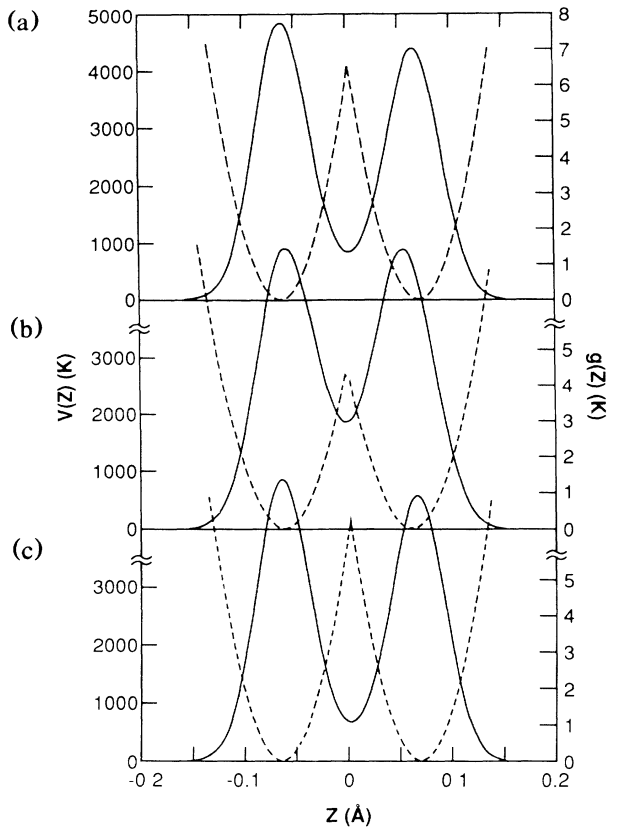

FIG. 2. Radial distribution function $g(z)$ [Eq. (2)] (solid line) and potential $V(z)$ [Eq. (3)] (dashed line) for (a) $T_{\rm nom}=10$ K, (b) $T_{\rm nom}=86$ K, and (c) $T_{\rm nom}=105$ K.

tuation region. The changes in the RDF can be described as a result of an increased tunneling of the wave function through the potential barrier between the two wells (Fig. 2) [effective polarization of the O(4) may also contribute]. The average of the two Cu(1)-O(4) distances ($\sim$1.875 Å) is in good agreement with previously reported crystallographic and EXAFS values,[8,17] and does not show appreciable variations as a function of temperature.[13] The sum of the Cu(1)-O(4) and Cu(2)-O(4) bond lengths [obtained using the average O(4) position] deviates by less than 0.005 Å from the crystallographically determined Cu(1)-Cu(2) distance.[17,18]

The motion of the O(4) atom in the deep, double-well potential $V(z)$ can be described by a two-level Hamiltonian $H=(\omega_T/2)\sigma_z$, such that $H|A\rangle=+(\omega_T/2)|A\rangle$, and $H|S\rangle=-(\omega_T/2)|S\rangle$, where σ_z is a Pauli spin matrix, and $|S\rangle,|A\rangle$ denote the (symmetric) ground state and (antisymmetric) first excited state, respectively, separated by an energy $\hbar\omega_T=\hbar\omega_1-\hbar\omega_0$. In a ferroelectric system at the order-disorder limit a double well with two (nearly degenerate) levels also occurs, but intrawell interactions favor the occupancy of one of the sites at low temperatures, and both sites at high temperatures.[19] For the fluctuation we observe, although both

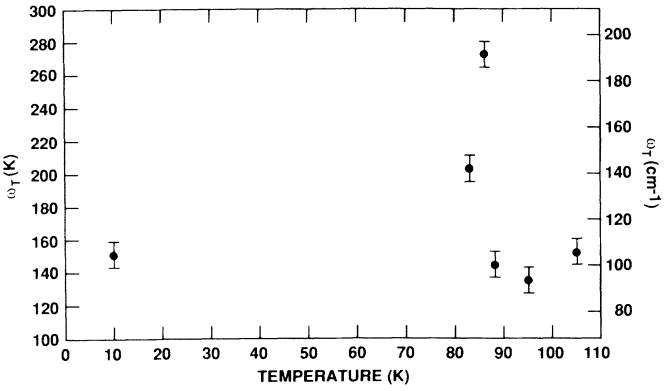

FIG. 3. Tunneling frequency ω_T between the two O(4) sites, as a function of temperature, obtained from the solution of the Schrödinger equation using the potential $V(z)$ [Eq. (3), with parameters obtained obtained from fit to experiment]. The error bars result from the error analysis described in the text.

sides of the well are nearly equally occupied over the entire temperature range, the splitting between levels increases within the fluctuation region. Figure 3 shows the tunneling frequency ω_T as a function of temperature. An increase of $\sim$80 K in ω_T is observed for $T_{\rm nom}=83$ and 86 K. The values of ω_T are in fair agreement with the frequency of the O(4) motion obtained in harmonic lattice-dynamics calculations.[20]

The observed fluctuation is *not* directly driven by temperature, but rather is a result of the coupling of the electronic degrees of freedom involved in the superconducting transition and the elastic degrees of freedom leading to the potential describing the ionic motion. Such a coupling has been discussed phenomenologically,[21] by describing the coupling between a Ginzburg-Landau free energy for a superconductor and a strain field. We assume a similar coupling between the proposed two-level system and the superconducting order parameter Ψ, leading to a free energy F of the form

$$F=\tfrac{1}{2}\omega_T^0\langle\phi|\sigma_z|\phi\rangle-A|\Psi|^2+\tfrac{1}{2}B|\Psi|^4 +C|\Psi|^2\langle\phi|\sigma_x|\phi\rangle\,, \quad (4)$$

where $|\phi\rangle$ is a spinor denoting the state of the two-level system, the Pauli matrix σ_x introduces hopping between $|S\rangle$ and $|A\rangle$, and ω_T^0 is the tunneling frequency in the absence of any coupling. We analyze the case in which the effect of the coupling [cf. Eq. (4)] on the order parameter is small. Taking into account the effect of fluctuations $\langle(\Delta\Psi)^2\rangle$ (that diverge at T_c) about the mean-field value of Ψ_0, we find a change in the tunneling frequency:

$$\omega_T/2=[(\omega_T^0/2)^2+C^2|\Psi_0|^4+C^2\langle(\Delta\Psi)^2\rangle^2]^{1/2}. \quad (5)$$

This result agrees qualitatively with Fig. 3, however, a detailed quantitative comparison will require more ex-

perimental data in the fluctuation region. While in normal superconductors this fluctuation region is very small, in the high-temperature materials it is expected to extend several K around T_c.[21] If the coupling between the superconducting order parameter and the nonlinear phonons is strong, it is insufficient to consider the effect of this coupling in the phonon system and one has to solve self-consistently the two equations that result from the minimization of the free energy F [cf. Eq. (4)].

In summary, we have obtained the temperature dependence of the Cu-O(4) RDFs. Above or away from T_c, we find two sites for the O(4) atom with a separation of 0.13 Å. For temperatures near T_c this separation decreases leading to an increased tunneling. We note that similar effects have been observed in Tl-based and -doped 1-2-3 samples.[10] This lattice fluctuation should also be reflected in changes in pressure dependence and other thermodynamically related properties, including the speed of sound, ultrasonic attenuation, and changes in specific heat. Our results are consistent with a coupling between a Ginzburg-Landau free energy and a two-level system describing the O(4) RD in a double-well potential. The microscopic connection between the observed changes and superconductivity is deferred for future study.[22] However, we note that (i) changes in the electronic properties of the Cu(2) planes are suggested by fluctuations in the x-ray-absorption near-edge structure,[10] which may support dynamic Jahn-Teller coupling; and (ii) we may conclude O(4) coupling to the *gradient* of the superconducting order parameter, which could also affect flux pinning.

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[16]The rapid damping of the Cu(2)-O(4) EXAFS and the position of the beat implies that the beat at $k \sim 11$ Å^{-1} cannot be explained as interference between Cu(1)-O(4) and Cu(2)-O(4) EXAFS. Although z_1 and z_2 are the same for the Cu(1)-O(4) and Cu(2)-O(4) bonds since both Cu(1) and Cu(2) "see" the same O(4) atom, a and b differ, reflecting the stronger nature of the Cu(1)-O(4) bond compared to the Cu(2)-O(4) interaction (Ref. 13).

[17]Compare, e.g., J. J. Caponi *et al.*, Europhys. Lett. **3**, 1301 (1987); M. A. Beno *et al.*, Appl. Phys. Lett. **51**, 57 (1987); A. Williams *et al.*, Phys. Rev. B **37**, 7960 (1988).

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