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X-ray absorption fine structure of systems in the anharmonic limit

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ABSTRACT

A new approach to the analysis of x-ray absorption fine structure (XAFS) data is presented. It is based on the use of radial distribution functions directly calculated from a single-particle ion hamiltonian containing model potentials. The starting point of this approach is the statistical average of the XAFS for an atomic pair. This average can be computed using a radial distribution function (RDF), which can be expressed in terms of the eigenvalues and wavefunctions associated with the model potential. The pair potential describing the ionic motion is then expressed in terms of parameters that are determined by fitting this statistical average to the experimental XAFS spectrum. This approach allows the use of XAFS as a tool for mapping near-neighbor interatomic potentials, and allows the treatment of systems which exhibit strongly anharmonic potentials which can not be treated by perturbative methods. Using this method we have analyzed the high temperature behavior of the oxygen contributions to the Fe K-edge XAFS in the ferrosilicate minerals andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) and magnesiowustite ($\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$). Using a temperature dependent anharmonic correction derived from these model compounds, we have found evidence for a local structural change in the Fe-O coordination environment upon melting of the geologically important mineral fayalite (Fe_2SiO_4). We have also employed this method to the study of the axial oxygen contributions to the polarized Cu K-edge XAFS on oriented samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and related compounds. From this study we find evidence for an axial oxygen-centered lattice distortion accompanying the superconducting phase transition and a correlation between this distortion and T_c . The relation of the observed lattice distortion to mechanisms of superconductivity is discussed.

1. INTRODUCTION

X-ray absorption fine structure spectroscopy (XAFS), has been commonly used to obtain quantitative information about the local structure around an absorbing atom, i.e., bond lengths, coordination numbers, and vibrational and static disorder.¹ The precision in the determination of structural parameters is often limited by the approximate treatment of the effect of lattice vibrations in XAFS.

The relevant vibrational modes for XAFS involve the *relative* motion of atomic pairs, which is usually approximated by harmonic vibrations of the pair, leading to a harmonic Debye-Waller factor.¹ This approximation however, is invalid when the vibrations of the pair sample anharmonic regions of the interatomic potentials.² For cases of weak to moderate anharmonicity, perturbative treatments in which the first few cumulants to the Debye-Waller factors are retained have been successfully applied.^{3,4} However, for systems which exhibit strong anharmonicity (whenever $k\sigma \sim 1$, where k is the photoelectron wave vector and σ the second order cumulant of the Debye-Waller factor) the cumulant expansion diverges, and it is necessary to consider the effect of anharmonicity in a nonperturbative manner.

Attempts to address the effects of anharmonicity in a non-perturbative manner have used non-gaussian radial distribution functions (RDF's).⁵⁻⁸ The relation between these non-gaussian RDF's and interatomic potentials has been discussed in the classical limit, and interatomic potentials were derived for superionic conductors, giving the first illustration of the capability of XAFS as a probe of interatomic potentials.⁸

We have generalized the derivation of the XAFS equation, considering a general pair potential, to the finite-temperature quantum regime. In this approach we consider a RDF directly derived from a model potential, which is parameterized in terms of variables determined from nonlinear least-squares fits between calculated XAFS and experimental data. This generalization thus, allows the use of XAFS as a technique to characterize pair-interatomic potentials along bonding directions. The use of a quantum formalism yields the full vibrational spectrum associated with the pair potential and the corresponding eigenfunctions, allowing comparisons with optical spectroscopic results. This approach also permits the use of XAFS to obtain reliable quantitative structural information in systems that exhibit highly anharmonic motion which cannot be addressed using series expansions of the Debye-Waller factor (cumulant expansions).^{3,4}

In Sec. 2 we present the general formalism used to study XAFS of systems which exhibit strong anharmonicity and extract interatomic pair potentials from XAFS spectra. In Sec. 3 we present an application of this method to the analysis of the oxygen contribution to the Fe K-edge XAFS of the ferrosilicates andradite and magnesiowustite. Using these results we show that a change in the coordination of the Fe-O in the mineral fayalite is predicted across the melting transition. In Sec. 4 we show the application of this method to the axial oxygen (O(4)) contribution to polarized Cu K-edge XAFS of $\text{YBa}_2\text{Cu}_3\text{O}_7$, where the Cu-O(4) potential shows a double-well character and discuss the implication of such finding for the mechanism of superconductivity in these materials. Finally, in Sec. 5, we summarize the results obtained, and present general conclusions.

2. XAFS FROM AN ANHARMONIC SYSTEM

In order to consider the effect of the relative motion of a given atomic pair in an arbitrary pair potential, we consider the statistical average of the XAFS from a single bond. In the *single*

particle approximation, this can be represented by

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

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

$$g(z) = \frac{\sum_i |\psi_i(z)|^2 e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} \quad . \quad (2)$$

The temperature of the system T is introduced through $\beta = 1/k_B T$, and z denotes the relative displacement along the bond from the bond equilibrium position, i.e., $\vec{r} = \vec{R} + z\hat{R}$. The wave-functions $\{\psi_i(z)\}$ are determined by solving the Schrödinger equation using the reduced mass for the isolated pair of interest, and a model potential, $V(z)$. For the Fe-O bond in the systems discussed in Sec. 3 we found that a Lennard-Jones form,

$$V(z) = -V_0[(r_0/r)^\alpha - 2(r_0/r)^\beta], \quad (3)$$

leads to the best fits to experiment, and yields consistent results for the observed bond-length expansion, bond dissociation energies, and available optical spectroscopical data. Here, V_0, r_0, α , and β are used as parameters determined by fitting $\langle \chi(k) \rangle$ to experiment at the highest available temperature and then kept fixed when calculating $\langle \chi(k) \rangle$ at lower temperatures. For the Cu-axial oxygen bond in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and related compounds, discussed in Sec. 4, we found that the functional form,

$$V(z) = \frac{a}{2}(z - z_1)^2, z \leq z_0; \quad \frac{b}{2}(z - z_2)^2, z \geq z_0 \quad , \quad (4)$$

where z_0 is determined by the continuity condition $V(z_0^+) = V(z_0^-)$, and a, b, z_1, z_2 are fitting parameters, lead to the best fits to experiment.

In the standard harmonic analysis of XAFS data, $g(z)$ is assumed to have a Gaussian form that leads to the usual quadratic form for the Debye-Waller factor.⁹ We note that the *single* particle approximation that leads to an effective pair potential is equivalent to the commonly used Einstein approximation.

3. XAFS FROM MATERIALS AT HIGH TEMPERATURES

We have employed this method to the analysis of Fe K-edge XAFS O contributions in andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) and magnesiowustite ($\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$) for temperatures $80 \leq T \leq 1073\text{K}$. Sample preparation and the reduction of the XAFS signal have been presented elsewhere.¹¹ A model potential as described in Eq. 3 was used, determining V_0, r_0, α, β by fitting $k^3 \langle \chi(k, r) \rangle$ to the

Fourier-filtered Fe-O experimental XAFS at 1073 K, in the range $3 \leq k \leq 11 \text{ \AA}^{-1}$, using amplitude and phase functions extracted from the data at 80K. At lower temperatures $\langle \chi(k, r) \rangle$ was calculated using the values of V_0, r_0, α , and β determined at 1073 K, using Eqs. 1 and 2 with the appropriate temperature T. For the Fe^{3+} -O bond in andradite we found $V_0 = 15326 \text{ K}$, $\alpha = 5.03$, $\beta = 3.50$, and $r_0 = 2.00 \text{ \AA}$. For the Fe^{2+} -O bond in magnesiowustite we found $V_0 = 14928 \text{ K}$, $\alpha = 5.65$, $\beta = 2.77$, and $r_0 = 2.14 \text{ \AA}$. It is important to note that for the general form of the potential that we use $V(r_0) \neq -V_0$. The potential and vibrational energy levels are shown in Fig. 1. We note that in the case of andradite, a Raman active mode associated with the Fe-O vibration has been identified at 440 cm^{-1} (630 K) which is in good agreement with the fundamental vibrational frequency estimated from XAFS, $\omega = [\epsilon_1 - \epsilon_0]/\hbar = 570 \text{ K}$.¹² In the case of magnesiowustite an infrared active mode at 300 cm^{-1} (434 K) has been associated with the Fe-O vibration, which is in excellent agreement with the XAFS derived frequency $\omega = 430 \text{ K}$.¹² However, in order to assess the accuracy of XAFS in the determination of vibrational spectra it is necessary to carry out a detailed comparison between the energy levels derived from the XAFS data and overtones of the fundamental frequency modes determined using spectroscopic techniques. The values obtained for the depth of the potential well are in good agreement with estimated bond dissociation energies, and show the expected trend of a stronger Fe^{3+} -O bond compared with the Fe^{2+} -O bond.¹² The corresponding RDF's, for different temperatures (Fig. 2) show the softer character of the Fe^{2+} -O potential leading to faster bond length expansion for magnesiowustite compared to andradite. The fits to the XAFS data reproduce crystallographic distances (See Fig. 3), and explain the apparent bond length contraction obtained using harmonic fits.

Fig. 1a: Potential and vibrational levels for the Fe^{3+} -O bond in andradite. Fig. 1b: Potential and vibrational levels for the Fe^{2+} -O in magnesiowustite.

Using these model compounds we have estimated a temperature dependent anharmonic correction to the Fe-O bond length of about 0.1 radians at 1573 K. Using this estimate in the analysis of the O contributions to the Fe K-edge XAFS of fayalite (Fe_2SiO_4) at 1573 K we have concluded that the local Fe-O coordination changes from six in the solid phase to four in the liquid phase. This result has important implications for the dynamical behavior of the geologically important low velocity zone of the lower earth's mantle.¹³

Fig. 2a: RDF for the Fe^{3+} -O bond in andradite at $T = 80, 273, 413, 673, 873, 1073, 1573$ K (last temperature not measured). Fig. 2b: RDF for the Fe^{2+} -O in magneslowustite at $T = 80, 673, 873, 1073, 1573$ K. (last temperature not measured).

Fig. 3a: Fe-O nearest neighbor distance as a function of temperature in andradite, derived from diffraction measurements (dashed line), anharmonic fits (solid line), harmonic fits (dotted line). Fig. 3b: Fe-O nearest neighbor distance as a function of temperature in magneslowustite, derived from anharmonic fits (solid line), and harmonic fits (dotted line).

4. THE AXIAL OXYGEN IN $\text{YBa}_2\text{Cu}_3\text{O}_7$

The axial oxygen, O(4), which serves as a bridge between the Cu(1)-O(1) chains and Cu(2)-O(2,3) planes in $\text{YBa}_2\text{Cu}_3\text{O}_7$, provides a natural way by which structural and electronic changes in the basal Cu(1)-O(1) planes (or equivalent planes in other materials) can influence the superconductivity occurring in the Cu(2)-O(2,3) planes. More specifically, O(4) vibrations are expected to couple to charge transfer between chains and planes.¹⁴ Experimentally, several studies have shown that the O(4) site is involved in structural changes which also affect the superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.¹⁵⁻¹⁹ Infrared reflectivity studies indicate an anomalously large strength for the 155 cm^{-1} phonon mode associated with the $[\text{Cu}(1)+\text{O}(4)]-\text{Cu}(2)$ vibration,¹⁵ and excess intensity and frequency shift of the Cu(1)-O(4) 580 cm^{-1} mode that correlate with the superconducting order parameter.¹⁶ Raman profiles also suggest that a structural instability related to the A_g ($\sim 500 \text{ cm}^{-1}$) Cu(1)-O(4) stretching vibration could be coupled to charge transfer.¹⁷ Diffraction studies have shown a correlation between the Cu-O(4) bond lengths and T_c .¹⁸

Direct evidence for O(4) lattice anomalies across T_c , comes from ion channeling experiments.¹⁹ We recently presented XAFS from $\text{YBa}_2\text{Cu}_3\text{O}_7$ which indicate that the O(4) atom moves in a double-well potential that softens in a fluctuation region around T_c .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),^{20,21} and dynamical Jahn-Teller coupling models.²² These models lead to anharmonic potentials for the Cu-O(4) relative motion in $\text{YBa}_2\text{Cu}_3\text{O}_7$, predicting a more harmonic motion of the O(4) atom as the stoichiometry changes from $\text{YBa}_2\text{Cu}_3\text{O}_7$ to $\text{YBa}_2\text{Cu}_3\text{O}_8$.²⁰ Our analysis provides evidence of a dynamical coupling between the O(4) vibrations and in-plane electronic degrees of freedom involved in the superconductivity.

The samples, experimental methods, and XAFS data reduction have been described elsewhere.²³ We only note that as the listed temperatures T_{nom} are those of the cold finger of the cryostat used in the experiment, the actual temperature of the sample may be as much as 5-10 K higher.

4.1 The Cu-O(4) RDF as a function of temperature

Diffraction studies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ have shown large anisotropic thermal ellipsoids for the O(4) ion, hinting at anharmonicity associated with this ion.²⁴ Also unpolarized XAFS studies on unoriented samples have shown anomalies in the Debye-Waller factors across T_c .²⁵ Polarized XAFS measurements separate the Cu-O(4) contributions from those arising from Cu-equatorial oxygens, allowing a more quantitative analysis of the Cu-O(4) signal.

The presence of a beat in the Cu-O(4) XAFS contribution around $k = 12 \text{ \AA}^{-1}$, signals two Cu(1)-O(4) distances, indicative of a double-well (Fig. 4). This beat disappears for temperatures near T_c . A nonlinear squares fit, including *both* the Cu(1)-O(4) and Cu(2)-O(4) contributions was performed over the range $k = 3 - 14 \text{ \AA}^{-1}$ on Fourier-filtered data (filtered over the ranges $1.0 \leq R \leq 2.0 \text{ \AA}$, $k = 2 - 15 \text{ \AA}^{-1}$) measured at $T_{nom} = 10, 83, 86, 88, 95$, 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 XAFS amplitude and phase functions in $\chi(k, r)$ were obtained from the XAFS of Cu-O bonds in the $a-b$ plane, and the number of O(4) atoms at an average distance R from Cu(1) was fixed at 2. The comparison between experiment and the achieved fits is shown in Fig. 4, and the resulting Cu(1)-O(4) parameters are presented in Ref. 9. These results indicate that the effect of the Cu(2)-O(4) signal is negligible in the beat region, indicating the two positions for the O(4) ion.

From these fits a potential, $V(z)$, and a RDF, $g(z)$, for the Cu(1)-O(4) ¹ - ¹ were extracted at the measured temperatures. These results 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 $T_{nom} = 105 \text{ K}$. The beat disappears in a fluctuation region around T_c because the separation between the minima of the potential $V(z)$ decreases by $\sim 0.02 \text{ \AA}$. This small change in distance is well within the sensitivity of these data because it moves the beat from $k = 12$ to beyond $k = 14 \text{ \AA}^{-1}$; the structural change lowers the potential barrier between the two wells (Fig. 5a). As shown in Fig. 5a $g(z)$ exhibits 2 maxima located $0.13 \text{ \AA}$ apart for $T_{nom} \sim 10 \text{ K}$ and $T_{nom} > 86 \text{ K}$. Within the fluctuation region, $T_{nom} = 83$ and 86 K , the separation between maxima decreases by $\sim 0.02 \text{ \AA}$ leading to a decrease in the root mean square deviations of the

Cu(1)–O(4) bond length, consistent with ion channeling results.¹⁹ We do not yet have data to establish the lower limit of the fluctuation 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 is in good agreement with crystallographically determined values,²⁶ and it does not show appreciable variations as a function of temperature.

Fig. 4 Cu–O(4) XAFS, experimental data (dashed line) and calculated XAFS (solid line), at (a) $T_{nom} = 10$ K, (b) $T_{nom} = 86$ K, and (c) $T_{nom} = 105$ K.

Fig. 5a: RDF (solid line) and potential $V(z)$ (dashed line) for Cu-O(4) in $\text{YBa}_2\text{Cu}_3\text{O}_7$, at (a) $T_{\text{nom}} = 10$ K, (b) $T_{\text{nom}} = 86$ K, and (c) $T_{\text{nom}} = 105$ K. **Fig. 5b:** RDF (solid line) and potential $V(z)$ (dashed line) for Cu-O(4) in (a) $\text{YBa}_2\text{Cu}_3\text{O}_7$, (b) $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$, (c) $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$, at $T_{\text{nom}} = 10$ K

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 $\hbar\omega_T = \hbar\omega_1 - \hbar\omega_0$. Unlike a ferroelectric system at the order-disorder limit, where a double-well potential also occurs, for the fluctuation we observe, both sides of the well are nearly equally occupied over the entire temperature range, but the splitting between levels increases within the fluctuation region. Fig. 6a shows the tunneling frequency ω_T as a function of temperature. An increase of ~ 80 K in ω_T is observed for $T_{\text{nom}} = 83$ and 86 K. Since the local potential description of the Cu-O(4) motion does *not* correspond to the normal modes of the system, a precise identification of this increase in the tunneling frequency with frequency shifts in related Raman and infrared modes is *not* correct. Calculations, based on electron-phonon models with on-site anharmonicity derived from double-well potentials obtained from XAFS and biphonon-electron coupling, predict the anomalously large strength and correct frequency shifts of the infrared active mode at 155 cm^{-1} .²⁷

Fig. 6a: Tunneling frequency between two well sites as a function of temperature in $\text{YBa}_2\text{Cu}_3\text{O}_7$. **Fig. 6b:** Tunneling frequency versus critical temperature in $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$, $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$.

We note that 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. We assume a coupling between the proposed two level system and the superconducting order parameter Ψ , leading to a free energy F of the form:

$$F = \frac{\omega_T^0}{2} \langle \phi | \sigma_z | \phi \rangle - A |\Psi|^2 + \frac{B}{2} |\Psi|^4 + C |\Psi|^2 \langle \phi | \sigma_z | \phi \rangle, \quad (5)$$

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 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 which agrees qualitatively with Fig. 6a however, a detailed quantitative comparison will require more experimental data in the fluctuation region. 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 the two equations that result from the minimization of the free energy F (cf. Eq. 5) must be solved self-consistently.

4.2 Effect of doping and oxygen content on the Cu(1)–O(4) bond

The main local structural changes achieved by the removal of the O(1) atoms from the $\text{YBa}_2\text{Cu}_3\text{O}_7$ orthorhombic phase (for $\delta \leq 0.55$) are a decrease of the Cu(1)–O(4) bond length ($\sim 0.03 \text{ \AA}$) and a large increase of the Cu(2)–O(4) bond length ($\sim 0.08 \text{ \AA}$).²⁸ At low doping levels, Co substitutes specifically for Cu(1) and induces similar structural changes in the Cu–axial O bonds, such as those obtained by oxygen removal.²⁹ The Cu–O contribution to the polarized ($\hat{\epsilon} \parallel c$) Cu K-edge XAFS signal was isolated by Fourier filtering within the ranges $3 \leq k \leq 15 \text{ \AA}^{-1}$, and $1.0 \leq r \leq 2.0 \text{ \AA}$. Anharmonic fits, including both the Cu(1)–O(4) and Cu(2)–O(4), were performed in the range $4 \leq k \leq 14 \text{ \AA}^{-1}$, using the model potential in Eq. 4, and the same potential fitting parameters used in the study described in the previous section. The XAFS phase and amplitude functions derived from the Cu–O signal from the $\hat{\epsilon} \perp c$ data were used in these fits. The coordination number for the Cu–O pairs was fixed at $N = 2$. The agreement between experimental data and the fits is similar to the one shown in Fig. 4.³⁰ These fits and the resulting parameters for the Cu(1)–O(4) bond are presented in Ref. 30.

In going from $\text{YBa}_2\text{Cu}_3\text{O}_7$ to $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$, we observe the following changes: a) the minima of the double-well potentials move further apart – from $\Delta R = 0.13 \text{ \AA}$ in $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\Delta R = 0.14 \text{ \AA}$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, to $\Delta R = 0.145 \text{ \AA}$ in $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$; b) the RDF, $g(z)$, becomes more asymmetric in the same progression, going from near equal populations for both sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$, to a ratio 2:1 for the population of the shorter site, compared with the longer site in $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$ (See Fig. 5b). These structural changes produce an increase in the height and 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 as shown in Fig. 6b. Although, there are not enough cases to establish quantitative trends, we can conclude that the tunneling frequency systematically decreases as the critical temperature decreases. 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 $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$ ($T_c = 25\text{K}$) it was possible to fit the $\epsilon \parallel c$ data using a purely harmonic treatment.³⁰

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 anharmonic phonons derived with potentials obtained from the XAFS fit. Other parameters, i.e., the density of electronic

states at the Fermi level and the (bare) electron-phonon interaction parameter were kept fixed in this calculation. We found that the predicted changes in T_c were much smaller than the actual variation in T_c in the studied materials. This suggests that the coupling between nonlinear phonons (derived from the double-well potential) and electrons is not the sole factor determining T_c .³¹ As mentioned in the previous section *not* only on-site anharmonicity, but *also* multiphonon-electron coupling terms seem to be important to describing spectroscopical data and possibly other properties.²⁷

In going from anharmonic motion to the case of more harmonic motion, a decrease in the elastic-electronic coupling is expected.^{20,21} Consequently, elastic anomalies across T_c involving the O(4) atom are expected to be smaller for the more harmonic systems, i.e., a smaller change in the tunneling frequency across T_c , should be observed in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7+\delta}$ compared with that observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$, discussed in the previous section. This trend has been observed in the anomalous frequency shift and intensity peak of the 580 cm^{-1} infrared active mode in $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7+\delta}$.¹⁶ As the Co content is increased and T_c decreases, the observed anomalies decrease in magnitude. Also, specific heat measurements in $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7+\delta}$ have reported the same trend for the anomalous contribution to the specific heat across T_c .³²

Our analysis of the axial oxygen contribution to the Cu K-edge XAFS of $\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11}$ has shown the presence of two oxygen positions in the Tl-based materials.³³ This study suggests the presence of two different charge states of the Tl ion, with evidence for charge transfer between the Tl-O planes and the Cu-O planes around the superconducting transition. This analysis points out the fact that the axial oxygen atom in Tl-based superconductors plays a similar role to that played by the O(4) atom in $\text{YBa}_2\text{Cu}_3\text{O}_7$, i.e., it serves as a vehicle for charge transfer between Tl-O and Cu-O planes, and its motion reflects electronic changes taking place in the Cu-O planes during the superconducting transition.

4.3 Connection to superconductivity

The three studies discussed here present a unified view of the role of the axial oxygen in high- T_c materials. These studies show two different positions for the axial oxygen, which can be explained in terms of Cu-O(4) motion in an anharmonic double-well potential. These potentials arise naturally in electron-phonon models that allow charge transfer between the (mixed valence) cations and the highly polarizable O^{2-} ions. In the oxygen deficient and Co-doped samples, the tendency of the cation to a full shell configuration suppresses charge fluctuations leading to a more harmonic motion for the cation-oxygen pair. The observed temperature behavior of the Cu-O(4) RDF can be explained consistently as a result of the coupling between anharmonic phonons and the superconducting order parameter. These results show the influence of electronic degrees of freedom entering in the superconducting transition on the phononic degrees of freedom related with the axial oxygen. To address the relevance of the observed anharmonic phonons to the superconducting mechanism, it is necessary to formulate a microscopic model that includes the Cu-O in-plane electronic degrees of freedom and their interactions with electronic and phononic degrees of freedom related with the axial oxygen. We note, however that changes in the electronic properties of the Cu(2) planes are suggested by fluctuations in the XANES, which may support dynamic Jahn-Teller coupling.

5. SUMMARY AND CONCLUSIONS

We have developed a method to use XAFS as a tool to determine interatomic potentials, allowing the analysis of XAFS in systems which exhibit strong anharmonicity.

Besides the conclusions presented for the specific materials used to exemplify the use of this method, we have shown that XAFS can be used as tool to extract pair interatomic potentials which lead to: i) accurate determinations of bond length expansion as a function of temperatures, ii) consistency with bond dissociation energies and optical vibrational spectra, iii) give quantitative descriptions of structural anomalies observed in certain materials.

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