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Characterization of a split axial-oxygen site in $TlBa_2Ca_3Cu_4O_{11}$ by extended x-ray-absorption fine-structure spectroscopy

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The Cu K-edge extended x-ray-absorption fine structure (EXAFS) of $TlBa_2Ca_3Cu_4O_{11}$ ($T_c = 118$ K) is analyzed in the range $10 \le T \le 156$ K. Nonlinear-least-squares fits to the EXAFS Cu–axial-oxygen contributions show the presence of two equally populated axial-oxygen sites at $R_1 = 2.57$ Å and $R_2 = 2.74$ Å for temperatures above T_c and at 10 K. The corresponding Tl–axial-oxygen distances are 2.18 and 2.01 Å, which are similar to those found in other thallium superconducting phases. In a fluctuation region below T_c ($T = 100$, 117 K), the separation between the two sites decreases to less than 0.10 Å. This effect is analogous to the one previously reported in $YBa_2Cu_3O_7$, suggesting a similar coupling between elastic degrees of freedom and superconductivity. We note, however, that both the separation between the sites and the decrease in this separation within the fluctuation region are greater than in $YBa_2Cu_3O_7$.

INTRODUCTION

We have recently presented an extended x-ray-absorption fine-structure (EXAFS) analysis on $YBa_2Cu_3O_7$ which showed the presence of a lattice instability associated with the axial oxygen atoms, O(4), across the superconducting transition.[1] This analysis indicated the existence of two different O(4) sites whose separation decreases in a fluctuation region near T_c. This result has recently been confirmed by Yacoby *et al.*[2] These observations were explained in terms of the motion of the O(4) ion in an anharmonic double-well potential, which changes in the vicinity of T_c due to its coupling to the superconducting order parameter.

Several other experiments on high-T_c materials support the existence of lattice instabilities in these compounds and their possible relation to superconductivity.[3] Ion-channeling experiments in $ErBa_2Cu_3O_7$ have shown a lattice instability signaled by a sudden change in the mean-square displacements of the Cu and the O(4) ions in the vicinity of the superconducting transition.[4] Heat-capacity measurements have revealed anomalous behavior around T_c for $YBa_2Cu_3O_7$ and some Ti- and Bi-based materials.[5] There is also vibrational evidence in $YBa_2Cu_3O_7$ from infrared reflectivity studies which show unusually high oscillator strengths for phonon modes parallel to the c axis and from Raman profiles which suggest the presence of a structural instability related to the Cu-O(4) stretching vibration.[6,7] Another study involving pair-distribution function (PDF) analysis of pulsed neutron-scattering data in $Tl_2Ba_2CaCu_2O_8$ found changes in the local structure of the [Cu-O] planes across the superconducting transition.[8] In a similar experiment it was shown that Tl and O ions in the [Tl-O] planes are displaced from their ideal high-symmetry positions, creating two possible configurations.[9] It has been suggested that the observed short-range ordering of these configurations is likely to affect charge fluctuations between the [Tl-O] and [Cu-O] planes.[9] A detailed model of these charge fluctuations has been presented by Bishop *et al.*[10] More recently, PDF analysis of elastic- and inelastic-neutron-scattering data on $Tl_2Ba_2CaCu_2O_8$ has found a split axial oxygen position, supporting the dynamical interpretation of Ref. 1.[11]

Recent studies of Tl-based high-T_c materials including $TlBa_2Ca_{n-1}Cu_nO_{3+2n}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ types have reported crystal structures for a variety of these phases. However, the uncertainty in the position of the axial-oxygen atoms is often an order of magnitude larger than for other atoms.[12–15] This uncertainty is reflected in discrepancies which exist between reported atomic positions from x-ray- and neutron-diffraction studies in addition to the anomalously large thermal parameters reported for the axial-oxygen atoms.[12–16] For the compound reported in this paper, $TlBa_2Ca_3Cu_4O_{11}$, a crystal structure was reported, but the positions of the O(4) atoms were not detailed.[17] The lack of definitive structural parameters for the axial-oxygen atoms in these materials suggests a degree of structural "disorder" associated with these atoms.

EXAFS provides an appropriate means for investigating the local structure related to the axial oxygen. In both EXAFS and diffraction experiments, the resolution in real space bears a direct dependence on the value of the momentum transfer, $\mathbf{q}$. However, the momentum transfer in EXAFS is given by $\mathbf{q} = 2\mathbf{k}$, where $\mathbf{k}$ is the photoelectron wave vector. As a result, despite its lower absolute accuracy, EXAFS has an intrinsically higher resolution to split positions and is very sensitive to structures of this type and small changes in them. In this paper, we have analyzed Cu K-edge EXAFS results for $TlBa_2Ca_3Cu_4O_{11}$ to determine the temperature dependence of the average Cu site in this compound for $10 \le T \le 156$ K. These results augment our previous findings of a lattice fluctuation below T_C,[1] indicating that this instability occurs at the axial oxygen and involves softening of a double-well configuration at this site. This data adds to that noted above and supports the generic role of axial-oxygen-mediated charge transfer in high-T_C materials.[18]

EXPERIMENT

The standard preparation of $TlBa_2Ca_3Cu_4O_{11}$ has been described elsewhere.[17] An overpressure of thallium was employed before the final O_2 anneal in a MgO tube. The material was determined to be ~85% pure by x-ray powder-diffraction analysis (the remainder being the $Tl_2Ba_2Ca_2Cu_3O_{10}$ phase). The sample showed a $T_c = 118$ K, $T_{1/2} = 103$, K and 100% flux exclusion below 4 K. The sample was mounted on an aluminum holder which was attached to the cold finger on an open-cycle liquid-helium refrigerator. The EXAFS spectra were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line I-5, using Si(220) crystals. The monochromator crystals were detuned 50% with respect to θ, the orientation between the faces of the two crystals, in order to reduce the harmonic content of the beam. The synchrotron was running under dedicated operating conditions (electron energy, 3.0 GeV; stored current, 15–50 mA).

EXAFS data reduction and analysis were accomplished through standard procedures.[19] The data were measured out to $\mathbf{k} = 17$ Å^{-1} at six different temperatures: 10, 100, 117, 127, 135, and 156 K. Raw data were collected in transmission mode and four individual scans were averaged for a given temperature to improve the signal-to-noise ratio. The files were calibrated using the first inflection point of a Cu-foil standard defined as 8980.3 eV and an ionization threshold defined as 9000 eV. The data were normalized by setting the edge jump equal to unity over a specific range at the edge. Background subtraction was performed by fitting the preedge region with a smooth second-order polynomial and by fitting the post-edge region with an adjustable spline function. In order to isolate the neighboring atoms of interest for curve fitting, the EXAFS was Fourier transformed from $\mathbf{k} = 3$ to 17 Å^{-1} and back transformed from $R = 1.40$ to 3.85 Å using Guassian window functions with a half-width of 0.05 Å^{-1} and 0.05 Å, respectively. Nonlinear-least-squares fits were performed on the filtered EXAFS data over the range $\mathbf{k} = 3.5$–16.5 Å^{-1}.

RESULTS

In Fig. 1 we present the raw EXAFS data as a function of temperature. The overall similarity of the data indicates no *dramatic* change in the structure over this temperature range (10–156 K). An expansion of the Fourier transforms of these data over $R = 2$–3 Å are shown in Fig. 2. The full range transforms have been shown in a previous report.[3] From a qualitative standpoint, the Fourier-transformed data are very similar in every region with the exception of the region from $R = 2$–3 Å. In this region, *two different* patterns are observed. The 100- and 117-K transforms show only one broad shoulder just to the left of the main peak at $R = 2.8$ Å. In contrast, the 10-, 127-, 135-, and 156-K data all possess two shoulders to the left of the 2.8-Å peak. This is the region where the axial oxygen makes its contribution, so that changes in the axial-oxygen position are most likely the source of the observed changes. The regions where the main contributions of other atoms lie do not show any significant change.

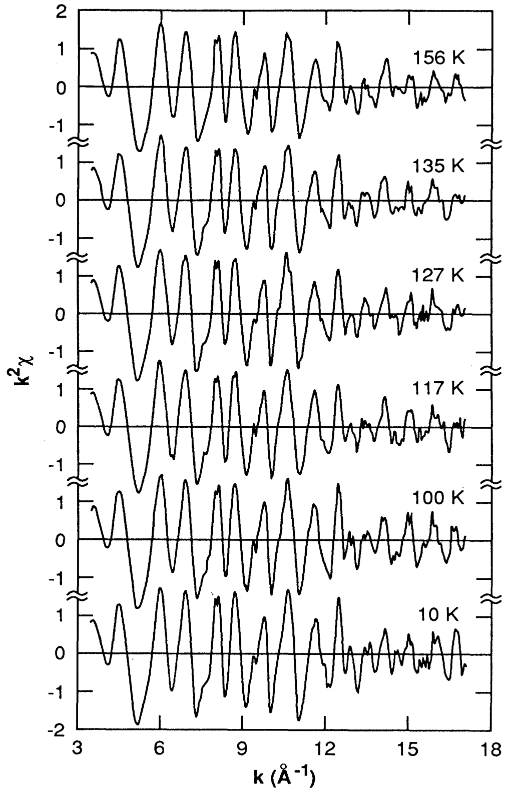

FIG. 1. Cu *K*-edge EXAFS ($k^2\chi$) of $TlBa_2Ca_3Cu_4O_{11}$ as a function of temperature.

The curve-fitting results are summarized in Table I. In these fits, contributions from six shells of atoms were included; equatorial oxygens [O(2)], Ca, Ba, Cu, and two axial oxygens, [O(4)]. Empirical phases and amplitudes from model compounds were used for the O(2) and Cu atoms. Theoretical phases and amplitudes calculated using the program FEFF were employed to fit the O(4), Ca, and Ba atoms.[20] For each shell the following parameters were allowed to vary: Ca: N, R, σ; Ba: N, R, σ; Cu: N, R; O(2): N, R; O(4): N, R; O(4): N, R, where N is the

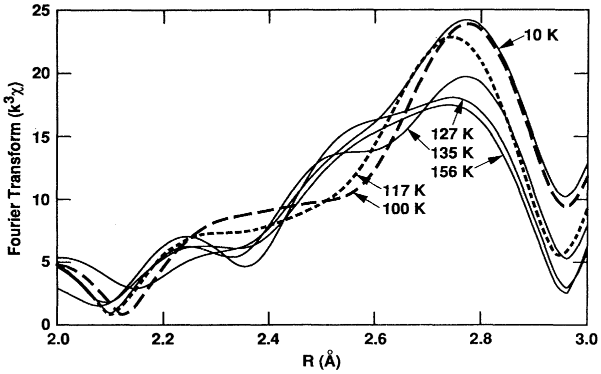

FIG. 2. An expanded view of the Fourier transforms ($k^3\chi$) of the Cu *K*-edge EXAFS of $TlBa_2Ca_3Cu_4O_{11}$ as a function of temperature, over the region where the O(4) atoms reside.

coordination number, R is the bond length, and σ is the Debye-Waller factor. Thus, the total number of adjustable parameters is 14 while the total number of independent points is given by $(2/\pi)\Delta k \Delta R = 20$. Therefore, the true number of independent points is six and represents a reasonable value for an EXAFS curve-fitting analysis.[21]

In $TlBa_2Ca_3Cu_4O_{11}$, there are four [Cu-O] planes which are separated into two types. Two of the planes are in contact with [Ba-O] layers and the other two lie between the first two. Thus, there are two types of Cu environments in this material which are present in a 1:1 ratio. Since EXAFS sees only an average structure, the curve-fitting results represent average coordination environments of the two Cu sites. The only shells which are not affected by averaging are the O(2) and Cu shells which are identical in the two Cu environments. One point to note from Table I is the constancy of bond lengths and coordination numbers for the Ca, Ba, Cu, and O(2) shells. The positions of these shells remain fixed independent of temperature. On the other hand, the O(4) atoms seem to be present in two different configurations depending on the temperature. At 10, 127, 135, and 156 K, the curve fits indicate two different O(4) sites with Cu-O(4) distances of 2.57 and 2.74 Å. On the contrary, the data at 100 and 117 K show little or no evidence for two O(4) sites. Instead, the curve fits demonstrate only one O(4) site having $R = 2.62$ Å. If the main contributions of the other shells do not vary, then minor contributions (i.e., side lobes) will not vary either. Therefore, the curve-

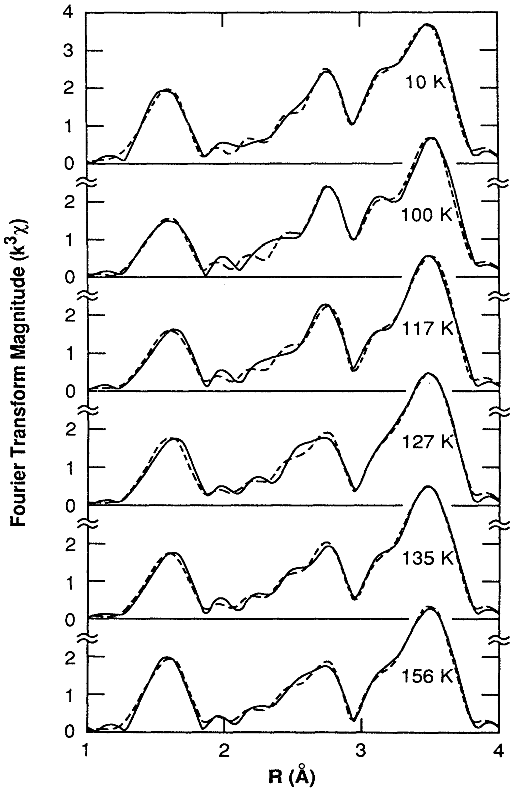

FIG. 3. Comparison of the Fourier transforms of the filtered data (solid line) with the corresponding fits (dashed line), which exclude the O(4) atom contributions.

TABLE I. Six-shell calcium, barium, copper, equatorial oxygen, axial-oxygen curve-fitting results for $TlBa_2Ca_3Cu_4O_{11}$.

	Calcium shell[a]			Barium shell[a]			Copper shell[b]		Equatorial oxygen[b]		Axial oxygen[c]		Axial oxygen[c]	
Temperature (K)	Cu-Ca distance (Å)	rms deviation (Å)	No. of atoms	Cu-Ba distance (Å)	rms deviation (Å)	No. of atoms	Cu-Cu distance (Å)	No. of atoms	Cu-O(2) distance (Å)	No. of atoms	Cu-O(4) distance (Å)	No. of atoms	Cu-O(4) distance (Å)	No. of atoms
10	3.172	0.067	6.00	3.374	0.066	2.00	3.803	4.00	1.901	4.00	2.574	0.22	2.748	0.23
100	3.174	0.065	5.47	3.366	0.058	1.33	3.809	4.03	1.904	3.16	2.616	0.52		
117	3.167	0.066	5.45	3.366	0.082	2.20	3.807	3.76	1.907	3.24	2.598	0.54		
127	3.170	0.085	7.12	3.379	0.073	1.77	3.804	3.70	1.907	3.60	2.563	0.36	2.749	0.39
135	3.172	0.078	6.32	3.374	0.069	1.58	3.807	3.77	1.912	3.57	2.569	0.32	2.712	0.32
156	3.169	0.082	6.51	3.371	0.075	1.80	3.806	3.55	1.904	3.98	2.573	0.29	2.735	0.25

[a] The small variations of the number of atoms and rms deviations are due to correlations between these parameters in determining the overall amplitude.

[b] Empirical amplitudes derived from La_2CuO_4 (with built-in rms deviations) were held fixed for these shells.

[c] The rms deviation was held fixed at 0.05 Å.

fitting results for the O(4) atoms are not simply an artifact of fitting other features related to the other shells. The good agreement of the O(4) parameters at 10, 127, 135, and 156 K indicates the negligible effect of random noise in the fits, e.g., the estimated error in the Cu-O(4) distance is $\sim<0.01$ Å. The presence of $\sim 15\%$ $Tl_2Ba_2Ca_2Cu_3O_{10}$ only modifies the coordination number(s) for the axial-oxygen site(s). The expected deviations are within the uncertainties of these coordination numbers ($\sim 25\%$). Consequently, they do not modify the curve-fitting results.

Figure 3 shows a comparison of the Fourier transforms of the filtered data with the corresponding fits, which exclude the axial-oxygen atom contribution. From this figure one can see that the fits are consistently poorer in the $R = 2-3$ Å range, the region where the axial-oxygen atoms reside. This demonstrates that the O(4) atom is making a contribution despite being only-half of an atom on average. This result is reinforced if one looks at the phase information obtained from the O(4) contributions. In order to isolate the O(4) contributions, we have obtained a residual EXAFS signal by taking the difference between the data and fits which exclude the O(4) shells. The residuals obtained in this manner should include all contributions not fitted—specifically those of the axial-oxygen atoms. We have Fourier transformed the residual EXAFS from this series of fits and subsequently back transformed over the range of 2–3Å. In Fig. 4 we plot the phases of the filtered residuals. It is apparent that again the 10-, 127-, 135-, and 156-K data sets agree while the 100- and 117-K data are distinctly different. Upon closer examination, it is seen that the phase of the data sets outside the fluctuation region ($T = 100$ and 117 K) is shifted $\sim\pi$ rad from the phase at 100 and 117 K for $\mathbf{k} > 10$ Å^{-1}. This is in agreement with the estimate for the position of a beat calculated from the relation $\mathbf{k} = \pi/2\Delta R = 10$ Å^{-1}, where ΔR refers to the separation between two shells.[22] Using this relation, we also conclude that an upper limit for the separation of two shells at $T = 100$ and 117 K is $\Delta R \leq \pi/2\mathbf{k}_{\max} = 0.10$ Å where $\mathbf{k}_{\max} = 17$ Å^{-1}.

We have also performed fits to the filtered residual EXAFS. These fits, which incorporate only the axial-oxygen atoms, give bond lengths and coordination numbers in close agreement with those from the six shell fits. In Fig. 5, we show the overlays of the fits with the filtered residuals at 10, 100, and 156 K. These fits demonstrate the good agreement obtained using theoretical oxygen phases. The relatively poorer agreement in the low-k region is a result of the poor chemical transferability of theoretical phases and amplitudes in addition to uncertainties inherent in the background removal procedure.

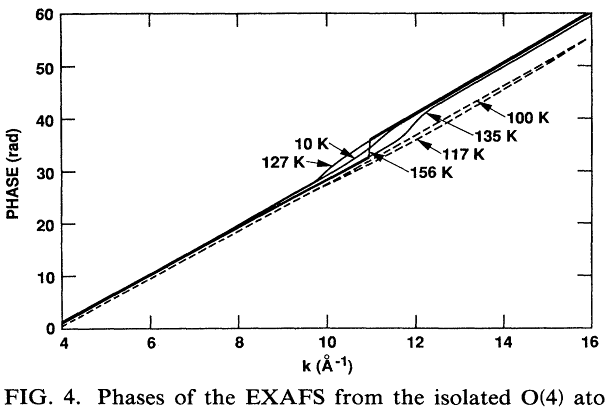

FIG. 4. Phases of the EXAFS from the isolated O(4) atom contributions as a function of temperature.

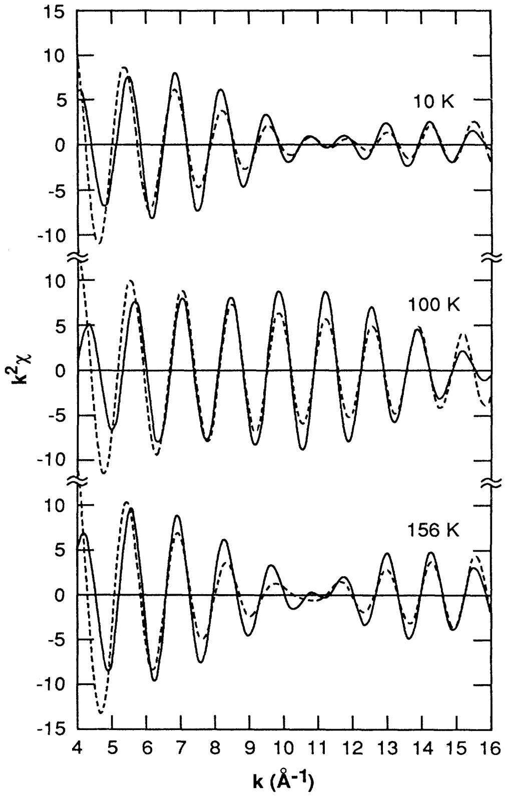

FIG. 5. Comparison of the EXAFS from the isolated O(4) atom contributions ($k^2\chi$, solid line) with the corresponding fits (dashed line) at 10, 100, and 156 K.

DISCUSSION

The results of our analysis here can be explained on the basis of previous EXAFS and diffraction studies. We note that the longer Cu-O(4) distance, $R = 2.74$ Å, which we obtain from curve fitting agrees closely with the single Cu-O(4) distances reported in essentially every high-T_c thallium phase studied thus far.[12–15] There is additional evidence to support the existence of the shorter Cu-O(4) distance, $R = 2.57$ Å, in a PDF analysis of neutron-scattering data.[8] This latter study, although primarily concerned with displacements within the [Cu-O] planes, reveals that the axial-oxygen atoms are displaced along the c axis toward the [Cu-O] plane by approximately 0.15 Å, a value close to the splitting we see. Moreover, a recent analysis by Egami *et al.* has found two axial-oxygen positions to be present in $Tl_2Ba_2CaCu_2O_8$.[23] Since the separation between the Tl and Cu atoms was found to be 4.75 Å by Ihara *et al.*,[17] the corresponding Tl-O(4) distances are 2.01 and 2.18 Å. The shorter of these agrees well with diffraction results. In general, both distances are reasonable values for Tl^{+3}-O bond lengths as evidenced by the known structure of Tl_2O_3.[24] Based on these distances, the ionicity of the thallium atoms in this phase is much closer to +3 than it is to +1. This is consistent with an x-ray photoemission study, which shows the trivalent state to be predominant in the $TlBaCa_3Cu_2O_7$ phase.[25]

The observation of a split O(4) site and the subsequent decrease in the splitting between the sites in a fluctuation region near T_c has also been observed in $YBa_2Cu_3O_7$.[1] The similarity in these findings points to a common origin of the split site and its decreased separation around T_c. In this context, the split oxygen site and its subsequent collapse have been described by a double-well potential whose intrawell barrier height decreases in a fluctuation region near T_c. Such a rigid double well is a convenient model concept, of course,[26,31–33] and in $YBa_2Cu_3O_7$, its variation around T_c was attributed microscopically to a coupling between nonlinear phonons, derived from this double-well potential, and the superconducting order parameter. In this scenario, charge fluctuations along the *c* axis and between the [Cu-O] planes and the polarizable layer ([Cu-O] or [Tl-O]) induce the formation of anharmonic phonons associated with the motion of axial-oxygen atoms. These nonlinear phonons then synergystically couple to the in-plane pairing mechanisms which give rise to the superconductivity.[27,28] Elsewhere,[29] we have introduced a shell model, appropriate for highly polarizable perovskite structures, which leads naturally to the *correlated* aspects of structural and optical anharmonicity, as well as a novel biphonon-electron coupling. The latter coupling strength is enhanced by the proximity of a softening phonon mode (associated with a structural phase transition) and can lead to a substantial superconducting phase-transition temperature, as well as anomalous isotope dependence, an anisotropic pairing gap, etc. The shell-model representation is closely related to dynamic Jahn-Teller and to bipolaron formalisms. An interesting aspect of the present data is that the elastic-superconducting coupling [leading to the softening of the split O(4) structure around T_C] appears to extend well below T_C. This is suggestive of a coupling to the superconducting order parameter itself analogous to a specific-heat anomaly.

One important point to note is that the splitting seen here, $\Delta R = 0.17$ Å, is larger than that reported in $YBa_2Cu_3O_7$ ($\Delta R = 0.13$ Å). There is also a greater degree of collapse between the two sites in $TlBa_2Ca_3Cu_4O_{11}$. We can expect this based on the fact that the separation between the [Cu-O] planes and the [Tl-O] layer (4.75 Å) is larger than the corresponding distance in $YBa_2Cu_3O_7$ (4.12 Å). Since this difference cannot be accounted for solely on the basis of different ionic radii of $Cu^{+2,3}$ and Tl^{+3}, it is likely that a greater degree of disorder exists with respect to the axial-oxygen atoms in $TlBa_2Ca_3Cu_4O_{11}$. As suggested in Ref. 10, there may be charge fluctuations associated with the [Tl-O] layer analogous to those proposed in the [Cu-O] chains in $YBa_2Cu_3O_7$. Evidence for this proposal exists in the observation of lattice displacements of Tl and O(3) atoms from their ideal high-symmetry sites in $Tl_2Ba_2CaCu_2O_8$ which would create an inhomogeneous distribution of charge carriers.[9] This disorder is not simply a property of double [Tl-O] layer compounds but is also present in single [Tl-O] layer phases.[12–15] In addition, the photoemission study mentioned earlier points to the possibility of charge transfer involving the thallium atoms:[25] In this study, x-ray photoelectron spectra (XPS) from a series of thallium-based high-T_c materials were compared to XPS data from the reference compounds Tl_2O and Tl_2O_3. The study included data from one single [Tl-O] layer material and two double [Tl-O] layer materials; $TlBaCa_2Cu_2O_7$ ($T_c = 73$ K), $Tl_2Ba_2CaCu_2O_8$ ($T_c = 98$ K), and $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($T_c = 114$ K). There is a potentially important trend in the photoemission data. As T_c increases, the thallium atoms are progressively more reduced so that the resulting valence is between Tl^{+3} and Tl^{+1}. Therefore, it is reasonable to expect that $TlBa_2Ca_3Cu_4O_{11}$ ($T_c = 118$ K) may, in fact, contain thallium in an oxidation state between Tl^{+3} and Tl^{+1}. If this is the case, then charge transfer is likely to be present both within the [Tl-O] layers and between the adjacent [Cu-O] planes.

In summary, EXAFS data for $TlBa_2Ca_3Cu_4O_{11}$ has been presented and analyzed at $10 \leq T \leq 156$ K. The data demonstrate a clear change in a fluctuation region around T_c both qualitatively and quantitatively. In particular, curve fitting has shown the change to be one of a structural origin involving the presence of two unique axial-oxygen sites whose separation has decreased around T_c. It is postulated that the decrease in site separation can be explained in the context of a double-well potential which softens as a result of coupling to phonon-mediated charge transfer. Coupled with evidence in other high-T_c materials,[1,30–33] the present data strengthens our proposal[10] that this off-plane polarizability is a generic feature of high-T_c materials. To explore the potential significance for superconductivity itself[29] will require a coordinated series of optical and structural experiments.

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[1] J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. Lett. **65**, 1678 (1990).

[2] Y. Yacoby, E. A. Stern, M. Qian, and S. M. Heald (unpublished).

[3] S. Conradson, I. Raistrick, and A. R. Bishop, Science **248**, 1394 (1990).

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

[5] F. Seidler *et al.*, Physica (Amsterdam) C **157**, 375 (1989).

[6] L. Genzel *et al.*, Phys. Rev. B **40**, 2170 (1989).

[7] R. Zamboni *et al.*, Solid State Commun. **70**, 813 (1989).

[8] B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, Phys. Rev. Lett. **64**, 2414 (1990).

[9] W. Dmowski *et al.*, Phys. Rev. Lett. **61**, 2608 (1988).

[10] A. R. Bishop, R. L. Martin, K. A. Muller, and Z. Tesanovic, Z. Phys. B **76**, 14 (1989).

[11] B. H. Toby, T. Egami, C. Janot, M. De Boissieu, and M. A. Subramanian, Bull. Am. Phys. Soc. **36**, 990 (1991).

[12] C. C. Torardi *et al.*, Phys. Rev. B **38**, 225 (1988).

[13] D. E. Cox *et al.*, Phys. Rev. B **38**, 6624 (1988).

[14] M. A. Subramanian *et al.*, J. Solid State Chem. **77**, 192 (1988).

[15] N. N. Kolesnikov *et al.*, Physica (Amsterdam) C **162-164**, 1663 (1989).

[16] C. C. Torardi *et al.*, Science **240**, 631 (1988).

[17] X. Ihara *et al.*, Phys. Rev. B **38**, 11 952 (1988).

[18] J. Mustre de Leon, S. D. Conradson, P. G. Allen, A. R. Bishop, and I. Batistic, in *Electronic Structure and Mechanisms of High-Temperature Superconductivity,* edited by J. Ashkenazi and G. Vezzoli (Plenum, New York, in press).

[19] P. A. Lee *et al.*, Rev. Mod. Phys. **53**, 679 (1981).

[20] J. J. Rehr, J. Mustre de Leon, S. Zabinsky, and R. C. Albers, J. Am. Chem. Soc. **113**, 5135 (1991); J. Mustre de Leon, J. J. Rehr, S. Zabinsky, and R. C. Albers, Phys. Rev. B **44**, 4146 (1991).

[21] F. W. Lyttle, E. A. Stern, and D. E. Sayers, Physica (Amsterdam) B **158**, 701 (1989).

[22] P. G. Allen, J. Mustre de Leon, S. D. Conradson, A. R. Bishop, and I. Batistic, Bull. Am. Phys. Soc. **36**, 989 (1991).

[23] T. Egami *et al.*, in *Electronic Structure and Mechanisms of High-Temperature Superconductivity,* edited by J. Ashkenazi and G. Vezzoli (Plenum, New York, in press).

[24] P. Papamantellos, Z. Kristallogr. **126**, 143 (1968).

[25] T. Suzuki *et al.*, Physica (Amsterdam) C **162-164**, 1387 (1989).

[26] We have considered an electron-phonon Hamiltonian (Ref. 27), which takes into account charge transfer within the cluster O(4)-Cu(1)-O(4). For large enough values of the electron-phonon coupling parameter, exact diagonalization of this system leads to a phonon spectrum similar to that of the proposed double-well potential (Ref. 31). This double well is associated with the infrared-active mode in which the two O(4) ions move asymmetrically with respect to the Cu(1), leading to the split site observed in EXAFS (Ref. 32). We note that the associated Raman-active symmetric vibraton does *not* exhibit a double-well character, consistent with the harmonic behavior inferred from Raman measurements of the ~ 500-cm^{-1} mode (Ref. 33).

[27] I. Batistic *et al.*, Phys. Rev. B **40**, 6896 (1989).

[28] A. R. Bishop, in *Earlier and Recent Aspects of Superconductivity,* edited by J. G. Bednorz and K. A. Muller (Springer-Verlag, Berlin, 1990).

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

[30] J. Mustre de Leon, S.D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. B **44**, 2422 (1991).

[31] J. Mustre de Leon, I. Batistic, S.D. Conradson, and A.R. Bishop (unpublished).

[32] J. Mustre de Leon, S.D. Conradson, I. Batistic, and A.R. Bishop (unpublished).

[33] G. Burns, F. H. Dacol, C. Feild, and F. Holtzberg, Solid State Commun. **75**, 893 (1991).