

## XAFS measurements of negatively correlated atomic displacements in $\text{HgBa}_2\text{CuO}_{4+\delta}$

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We have investigated the local structure about the Cu, Ba, and Hg atoms in  $\text{HgBa}_2\text{CuO}_{4+\delta}$  using the x-ray absorption fine structure (XAFS) technique. We find that most of the local structure results are consistent with the diffraction measurements except for two peaks in the XAFS spectra corresponding to the Cu-O(2) and Ba-O(2) atom pairs. These peaks are exceptionally broad, much broader than expected from the diffraction results. Our analysis, which includes neutron-diffraction results, indicates that the atomic displacements for the Cu and O(2) atoms are negatively correlated. The Ba and O(2) atoms may also be negatively correlated. Although this anticorrelation could be static or dynamic, we consider that it may be the result of the rapid hopping of charge between the apical O(2) ion and the  $\text{CuO}_2$  plane; this hopping may also provide a coupling mechanism for the formation of Cooper pairs.

Since the first high- $T_c$  materials were discovered,<sup>1</sup> a major question has remained unanswered—what is the mechanism for the formation of Cooper pairs? Another related and potentially important question is—does structure play an important role in high- $T_c$  superconductivity? The recently discovered Hg series of high- $T_c$  compounds<sup>2</sup> provide yet another opportunity to address these questions. These materials have the highest  $T_c$ 's to date ( $T_c=164$  K for the three  $\text{CuO}_2$  under quasihydrostatic pressure<sup>3</sup>). More importantly, they also have the largest change in  $T_c$  with pressure<sup>3</sup> which indicates that local structural distortions may be playing a larger role than in most other high-temperature superconductors. The one  $\text{CuO}_2$  layer compound, Hg 1201 ( $\text{HgBa}_2\text{CuO}_{4+\delta}$ ), has a relatively simple structure (see Fig. 1 for definitions of sites); it has no Cu-O chains as found in the Y-Ba-Cu-O family and, although the structure is very similar to the Tl series, there is very little O in the Hg layer.

Conventional wisdom assigns superconductivity to the  $\text{CuO}_2$  plane while the heavy-metal oxide layer (the BaO and Hg layer in Hg 1201) provides a charge carrier reservoir. Over the last five years there has been increasing evidence that structural distortions in this heavy-metal oxide layer play an important role. Consequently, models that involve coupling the superconducting pairs to this layer have received increased attention; for a review of charge transfer, excitonic, and polaronic models, see Ref. 4. If the coupling involves local correlated atomic positions in pairs of atoms, diffraction experiments will not provide a measure of this correlation because diffraction can only measure average positions and broadening parameters over a macroscopic piece

of a crystal. Only experiments which are sensitive to correlated displacements, such as ion channeling, pair correlation measurements from neutron scattering, and XAFS, can measure such effects.

In this article we present XAFS measurements that can be viewed as evidence for a large negative correlation in the relative displacements of the Cu and axial O(2) atoms, and possibly also for the Ba and O(2) atoms. These results can be interpreted in terms of a local, quasistatic, antiferroelectric (or ferroelectric) order, possibly induced by the defect O(3)

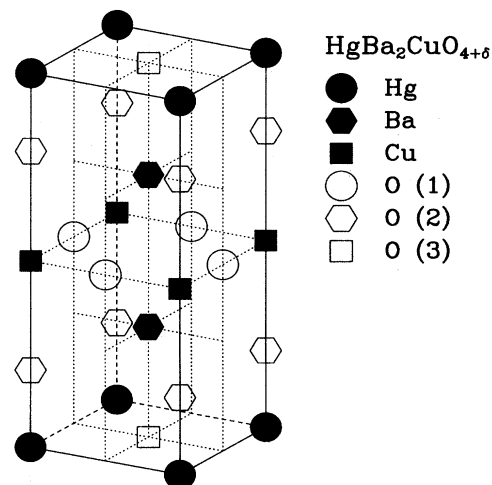


FIG. 1. The crystal structure for  $\text{HgBa}_2\text{CuO}_{4+\delta}$ . The O(3) site is a defect site and has a small occupation.

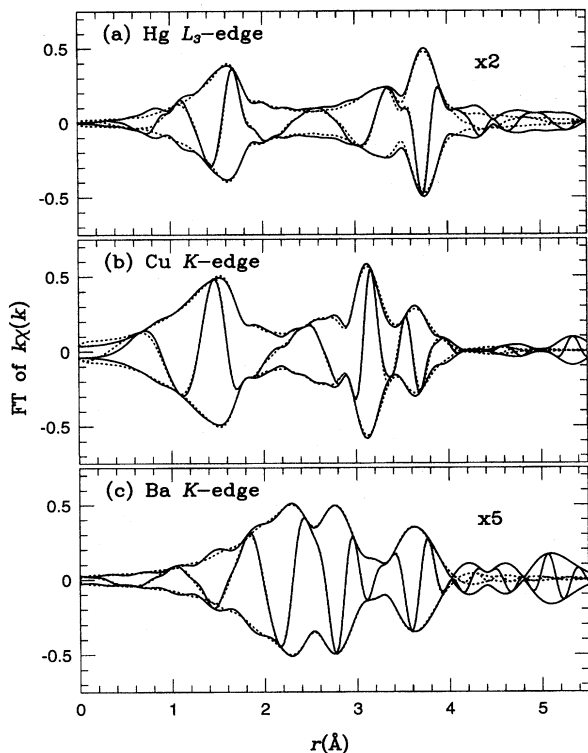


FIG. 2. Fourier transforms (FT) of  $k\chi(k)$  for Hg 1201 ( $T_c=96$  K) at various edges. The top panel (a) is Hg  $L_3$ -edge data (solid) and fit (dotted), both transformed from  $3.5$  to  $16.5 \text{ \AA}^{-1}$ . The middle panel (b) is Cu  $K$ -edge data (solid) and fit (dotted), both transformed from  $3.0$  to  $16.5 \text{ \AA}^{-1}$ . The bottom panel (c) is Ba  $K$ -edge data (solid) and fit (dotted), both transformed from  $3.5$  to  $12.5 \text{ \AA}^{-1}$ . All transform windows are Gaussian broadened by  $0.3 \text{ \AA}^{-1}$ . The Hg and Ba data and fits have been multiplied by a constant factor as indicated in order to compare with the Cu data.

site. Alternatively, it may be caused by a dynamic process in which the atoms are moving together or apart in a correlated manner. These measurements add to the collection of reports of small anomalies involving the axial oxygen.<sup>5–8</sup> Several of these anomalies occur near or at  $T_c$ , suggesting that these anomalies arise from a lattice coupling to the superconducting pairs.

Transmission x-ray absorption data were collected at 80 K for the Cu  $K$  and the Hg  $L_3$  edge on Hg 1201 samples using a Si(220) monochromator and the Ba  $K$  edge using a Si(400) monochromator on beamlines 4-2 and 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). Complete measurements were obtained for two powder samples:  $T_c$ 's of 96 K (optimal O concentration,  $\delta = 0.18$ ) and 45 K (slightly O depleted,  $\delta = 0.12$ ). Cu and Hg edge data were also collected for a 30 K sample (O overdoped,  $\delta = 0.23$ ). The XAFS sample preparation, data reduction, and analysis procedures have been described in detail elsewhere.<sup>9–11</sup> We note that for the Ba and Hg edges, there is significant structure in the background and we have used our iterative method<sup>10</sup> to remove it. Neutron diffraction measurements indicate the samples were essentially single phase. Further details of the neutron diffraction study are provided in Ref. 12.

The Fourier transformed XAFS data and fits for the  $T_c=96$  K sample are shown in Fig. 2. The  $T_c = 45$  K data and fits are similar. For the Hg edge the first peak corre-

sponds to two axial O(2) neighbors while the multiplex in the 3–4 Å range is the sum of the Hg-Ba and Hg-Hg contributions. A comparison of the data to a simple simulation calculated by the FEFF code<sup>13</sup> (using calculated Debye-Waller factors and assuming no distortions) shows that the amplitude of the Hg-Ba/Hg-Hg peak is about a factor of 2 smaller than expected. This reduction in amplitude indicates that there is some disorder in one or both of these peaks. The disorder is similar for the 96 K and 45 K samples but increases for the 30 K material. The 30 K sample also has a small peak corresponding to the Hg-O(3) atom pair which is not observable for the other samples.

For the Cu edge, the first peak corresponds to the four planar O(1) atoms while the multiplex over the 3–4 Å region arises from the eight Ba and four planar Cu neighbors. The positions and amplitudes of these peaks are consistent with the structure obtained from diffraction studies on other samples.<sup>2,14,15</sup> However there should be another O peak in the XAFS spectra, near 2.2 Å (corresponding to a distance of 2.77 Å in the crystal) from the two axial O(2) atoms. This peak is not obviously present in the spectra shown in Fig. 2, which can be fit reasonably well without it. To explain its low amplitude when several diffraction studies<sup>2,12,14,15</sup> as well as our Hg  $L_3$ -edge data show this O(2) site to be fully occupied, requires a very broad Cu-O(2) peak. A constrained fit requiring two O(2) neighbors, improves the fit compared to removing the O(2), and yields a very large Debye-Waller parameter (Table I).

The Ba  $K$ -edge data are similar to the Cu  $K$ -edge data in that the Ba-O(1) peak and the Ba-Cu peaks are consistent with the diffraction results while the Ba-Hg is broadened. However, the Ba-O(2) peak with four O(2) neighbors at  $\sim 2.8$  Å also has a very low amplitude. Again, a constrained fit yields a large Debye-Waller factor.

As mentioned earlier, XAFS measurements of the broadening factors are fundamentally different from the corresponding diffraction measurements. Diffraction measures the mean-square deviation of a given atom from its average site in the crystal. However, in XAFS we measure the broadening of the distance between atoms  $a$  and  $b$ :

$$\sigma_{ab} = \sqrt{\langle (\delta r_a - \delta r_b)^2 \rangle}, \quad (1)$$

where  $\delta r_a$  and  $\delta r_b$  are the instantaneous deviations from the average atomic positions for atoms  $a$  and  $b$ . XAFS therefore measures a *correlated* Debye-Waller factor. A comparison of the XAFS Debye-Waller parameters with the uncorrelated ones obtained in diffraction<sup>12</sup> for similar samples and measurement temperatures, allows a measure of the degree of correlation of the displacements of the neighboring atoms. If we assume that the XAFS measurements of  $\sigma_{ab}$  are absolute, and we define the uncorrelated widths ( $\sqrt{U}$  in diffraction) to be  $\sigma_a$  and  $\sigma_b$ , then we can define a correlation parameter  $\phi$  by

$$\sigma_{ab}^2 = \sigma_a^2 + \sigma_b^2 - 2\sigma_a\sigma_b\phi. \quad (2)$$

If  $\phi$  is near +1 we have a highly correlated width, as expected for well-ordered materials at low (but not zero) temperatures; if  $\phi$  is zero we have the uncorrelated result which often applies to more distant neighbors. However if  $\phi$  is negative, the atom positions are anticorrelated, as found for

TABLE I. Fit results for  $\sigma_{ab}$  and  $R$  from XAFS at the Hg  $L_3$  edge, and the Cu and Ba  $K$  edges of a  $T_c=96$  K sample of  $\text{HgBa}_2\text{CuO}_4$ . All the results reported here are consistent with the measurements on the  $T_c=45$  K sample. The values of  $\sigma_a$  and  $\sigma_b$  are from Ref. 12.  $\phi$  was calculated via Eq. (2). Both the XAFS and the diffraction data were collected at 80 K. Quoted errors do not include any possible sample differences between the XAFS and the diffraction samples. A single value of the amplitude reduction factor  $S_0^2$  was used for the Ba and Cu edges. The Hg edge data required a separate reduction factor for the first peak. The fit to the Hg-Hg and the Hg-Ba peaks is of poor quality, indicating distortions exist which we are currently unable to model. The Ba-O(2) pair distance had to be held fixed in the fit, so no error was determined.

Bond	$R$ (Å)	$S_0^2$	$\sigma_{ab}$ (Å)	$\sigma_a$ (Å)	$\sigma_b$ (Å)	$\phi$
Hg-O(2)	1.98(1)	0.83	0.034(8)	0.099(5)	0.095(7)	0.94(3)
Hg-Hg	3.83(4)	1.1	0.09(2)	0.099(5)	0.099(5)	0.6(2)
Hg-Ba	3.97(4)	1.1	0.08(1)	0.099(5)	0.073(7)	0.6(1)
Cu-O(1)	1.93(1)	0.80	0.047(10)	0.05(1)	0.081(8)	0.9(2)
Cu-O(2)	2.76(4)	0.80	0.21(4)	0.05(1)	0.095(7)	-3(2) <sup>a</sup>
Cu-Ba	3.34(2)	0.80	0.064(3)	0.05(1)	0.073(7)	0.5(1)
Cu-Cu	3.88(2)	0.80	0.055(6)	0.05(1)	0.05(1)	0.4(2)
Ba-O(1)	2.77(1)	0.925	0.075(2)	0.073(7)	0.081(8)	0.53(7)
Ba-O(2)	2.87	0.925	0.17(4)	0.073(7)	0.095(7)	-1(1) <sup>a</sup>
Ba-Cu	3.34(1)	0.925	0.069(5)	0.073(7)	0.05(1)	0.4(2)
Ba-Ba	3.91(4)	0.925	0.062(4)	0.073(7)	0.073(7)	0.64(7)

<sup>a</sup>Since large values of  $\sigma_{ab}$  (required for negative values of  $\phi$ ) have large errors, the uncertainty in  $\phi$  for these cases is very large.

small off-center displacements in an antiferroelectric system, or for an optical phonon mode (Fig. 3).

We expect measurements of  $\phi$  to have fairly large systematic errors. First, the parameters  $\sigma_{ab}$  must be determined absolutely; the standards used to fit the data must have well-known Debye-Waller factors. We have recently shown that fits to the XAFS of model compounds, using theoretical standards calculated from the FEFF code,<sup>13</sup> give values of  $\sigma_{ab}$  that agree with the correlated-Debye model (the method used by the program) generally within 10%.<sup>11</sup> Second, the samples used in the neutron diffraction experiment are dif-

ferent than the ones used in the XAFS experiment. This problem is potentially much more serious, since measurements of the diffraction width parameters vary considerably from sample to sample. The best comparisons are for the 96 K sample; the diffraction and XAFS samples were both made in the same laboratory using the same technique, both have the same  $T_c$  and the measurements were made at the same temperature. However, we obtain the same qualitative results for the measurements of  $\phi$  even when we use other published diffraction data.<sup>15</sup> Significant errors may also be present in the diffraction measurements of  $\sigma_a$  and  $\sigma_b$ , especially in measurements of oxygen atoms. These studies employ neutron diffraction (as opposed to x-ray diffraction) to help minimize this problem. Finally, errors may occur in the diffraction measurements if the atomic broadening is highly anisotropic. The results presented here all assume isotropic broadening factors. Some measurements of the O(2) atom (for instance, Ref. 15) indicate that it is more disordered in the  $ab$  plane than along the  $c$  axis. Using such measurements does not qualitatively change the results of this study.

To check that the values of  $\sigma_a$ ,  $\sigma_b$ , and  $\sigma_{ab}$  are reasonably consistent, we expect  $\phi$  for well-defined nearest-neighbor bonds to be near unity for  $T = 80$  K. In Table I the values of  $\phi$  for Hg-O(2) and Cu-O(1) (the two shortest bonds in this material) are indeed close to unity within 20%. In particular, we note that the Hg-O(2) bond is exceptionally narrow ( $\sigma=0.034$  Å) even though diffraction shows the Hg width to be quite broad ( $\approx 0.1$  Å). Another simple check is that the further neighbors generally should have smaller  $\phi$ 's than the near neighbors. The most correlated atom pairs in these fits are the nearest-neighbor pairs, as expected. The more striking result of the data in Table I is that *only* the Cu-O(2) and Ba-O(2) pairs are negatively correlated—these bond distances fluctuate by roughly 0.3 Å. However, such large Debye-Waller factors also have large errors. The errors

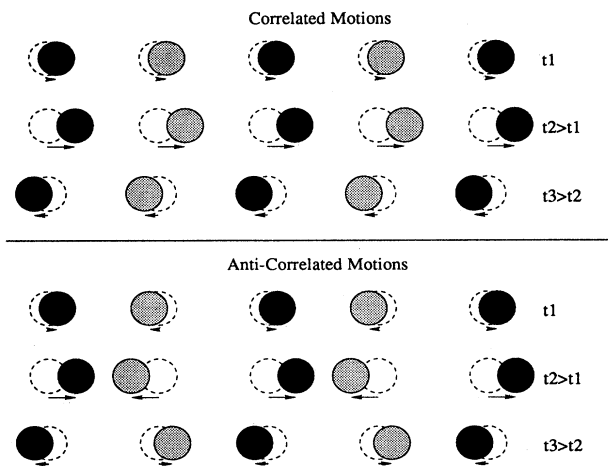


FIG. 3. Snapshots in time of two vibrational modes that illustrate correlated broadening measurements. The top panel shows a long wavelength acoustical phonon at three different times. Notice that while the average displacements of the individual atoms may be significant, the bond length does not change with time. The bottom panel shows a short wavelength optical phonon. Here, the bond length changes twice as much as the average site positions.

on the Ba-O(2) pair are large enough to allow for the possibility that the Ba and O(2) atom positions are merely uncorrelated. Also, the Cu and O(2) atom pair has a value for  $\phi$  that is larger than  $-1$ . This seemingly unphysical result can be attributed to using a single-pair Gaussian distribution function in the harmonic approximation to model a more complicated pair distribution function in both the XAFS and diffraction data. In order to obtain a positive value of  $\phi$ ,  $\sigma_{ab}$  for this peak would have to be  $\leq 0.11$  Å. Such a peak would be easily observable in our fits, therefore we must conclude that the positions of the Cu and the O(2) atoms are negatively correlated at least to some degree. This together with the positive correlation for the Hg-O(2) pair suggests that the displacements of the Cu and Hg atoms may also be negatively correlated.

A natural way to explain these anticorrelations is to consider a charge redistribution of the valence electrons on the O(2)<sup>2-</sup> ion. The Hg-O(2) bond is short and has a narrow width, suggesting that one of the electrons on the O(2)<sup>2-</sup> ion is tightly bound in that bond. The second electron on the O(2)<sup>2-</sup> ion is weakly bound to four Ba atoms and one Cu atom. If the probability of finding this electron in an orbital linked to Ba or Cu is fluctuating (perhaps because of polaron formation), we expect the positions of the Cu-O(2) and Ba-O(2) pairs to be anticorrelated. Such fluctuation may occur if, for instance, the *c*-axis conductivity involves electrons hopping on and off the O(2)<sup>2-</sup> ion. However, XAFS is not sensitive to whether the displacements are static or dynamic, because it is a very fast probe and the lattice is essentially frozen for times as short as the fluorescence lifetime. If the distortions were static, one might expect well-defined off-center displacements as found in ferroelectrics, which would lead to a split nearest-neighbor peak [e.g., if the O(2) position was different depending on whether the adjacent O(3) site was occupied]. In fact, recent Raman studies have shown two  $A_{1g}$  modes which involve the O(2),<sup>16</sup> with a dominant mode at 592 cm<sup>-1</sup> and a smaller peak at 570 cm<sup>-1</sup>, indicating two possible sites for the O(2) atom. The fit to the XAFS data did not improve significantly when a split peak was included; however we cannot differentiate between two broad peaks and one broad peak. Thus there is either a distribution of static displacements, or the atoms are moving, driven dynamically by some local charge redistribution as discussed above, at a rate somewhat faster than parts of the unit cell can respond.

This hopping process may produce a coupling mechanism between pairs of holes in the CuO<sub>2</sub> plane which is a combination of the polarization and excitonic models. A hole in the CuO<sub>2</sub> plane on a neighboring site to a given O(2)<sup>2-</sup> ion may cause a redistribution of the electron charge, resulting in increased negative charge density in the Cu-O(2) bond or induce an electron on the O(2)<sup>2-</sup> ion to hop into the CuO<sub>2</sub> layer. This negative charge will attract a second hole in much the same way as a negative polarization of the lattice would in the usual phonon coupling model, but with a higher cut-off frequency (electronic vs ionic displacements) beneficial for a stronger pair coupling. As the electronic polarization must be coupled to (anticorrelated) movements of the atoms to explain our observations, the hopping time should not be much shorter than the period of the highest optical phonon frequency involving the Cu, Ba and O(2) atoms to allow the lattice to partially respond. If the phonon frequency and the hopping frequency are closer in this material it may enhance the pair coupling. This idea is in rough agreement with the relatively high frequency  $A_{1g}$  mode mentioned above<sup>16</sup> and its pressure dependence.<sup>17</sup>

In conclusion, we have analyzed XAFS data on HgBa<sub>2</sub>CuO<sub>4+ $\delta$</sub>  at the Hg, Cu, and Ba edges. The extracted pair distances agree reasonably well with diffraction studies. Most of the Debye-Waller factors obtained in XAFS at 80 K, are smaller than the corresponding factors from diffraction measurements, indicating that most near-neighbor bonds involve positively correlated motions of their atomic constituents. Exceptions are the Cu-O(2) and possibly the Ba-O(2) atom pairs. For these pairs, anticorrelated motions of the atoms are needed to describe the data. Such anticorrelation has been observed in other systems (notably the TI compounds) and is further evidence of an antiferroelectric-like distortion occurring in a high- $T_c$  superconductor. The nature of this distortion prompted us to outline a simple electron-hopping model that might explain both the distortion and a possible pairing mechanism.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory, which is operated by the U.S. Department of Energy, Division of Chemical Sciences, and by the NIH, Biomedical Resource Technology Program, Division of Research Resources. The experiment was partially carried out on UC/National Laboratories PRT beam time. The work was supported in part by NSF Grant No. DMR-92-05204.

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