

## Micro-Raman study of the role of pressure in mercury-based superconductors

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Understanding the role of pressure in increasing  $T_c$  is a crucial issue in mercury-based superconductors. We report on the effect of pressure on the Raman frequency ( $\omega$ ) of the apical oxygen ( $O_A$ ) in Hg- $O_A$ -Cu bonds of HgBa<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+2+ $\delta$</sub>  superconductors. For both Hg-1201 and Hg-1223,  $\Delta(\omega^2/\omega_0^2)/\Delta P$  is found to be strongly correlated with  $\Delta T_c/\Delta P$ , where  $\omega_0$  is the frequency at ambient pressure. Together with our local-density approximation total-energy phonon study of the  $O_A$ - $A_{1g}$  Raman mode, it is concluded that the change of the  $O_A$  Raman frequency is due to the change in Hg- $O_A$  bond strength, which may be directly related to the charge transfer between the CuO<sub>2</sub> planes and the Hg-O layers.

The superconducting transition temperature ( $T_c$ ) of the mercury-based superconductors increases by  $\sim 30$  K under high pressure, the largest among oxide high-temperature superconductors. The highest recorded  $T_c$  so far is known to be 164 K for HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+ $\delta$</sub>  (Hg-1223) at 30 GPa.<sup>1</sup> Investigating the mechanism of the pressure-induced increase of the  $T_c$  is important both in understanding the nature of high-temperature superconductivity and in achieving even higher  $T_c$  values. Structural investigations in these superconductors under pressure have been carried out by neutron powder diffraction<sup>2</sup> and energy-dispersive x-ray diffraction.<sup>3</sup> From the structural investigations, Hunter *et al.*<sup>2</sup> suggested a possible pressure-induced charge transfer between CuO<sub>2</sub> planes, but could not find any conclusive evidence for it. There has been a theoretical study of the effects of pressure on electronic structure and  $T_c$  using local-density approximation (LDA) total-energy calculations.<sup>4</sup> However, there is no experimental result available for directly probing the changes in the electronic structure of the mercury-based superconductors under pressure. While photoemission spectroscopy and electronic Raman studies under pressure might be helpful, such measurements are hampered by the impurity phases unless sizable single crystals are available. On the other hand, the micro-Raman technique requires only micrometer-sized crystals and thus it is less prone to impurities, although it is limited in polarization configurations.

In this article, results of micro-Raman measurements on polycrystalline HgBa<sub>2</sub>CuO<sub>4+ $\delta$</sub>  (Hg-1201) and Hg-1223 samples under pressure up to 10 GPa are presented. The results show that the Raman frequency ( $\omega$ ) of the  $O_A$ - $A_{1g}$  mode increases from 592 cm<sup>-1</sup> at 1 atm to 626 cm<sup>-1</sup> at 7.4 GPa for Hg-1201 and from 585 cm<sup>-1</sup> at 1 atm to 649 cm<sup>-1</sup> at 9.0 GPa for Hg-1223.

It is striking to observe that increases in the rates  $\Delta(\omega^2/\omega_0^2)/\Delta P$  and  $\Delta T_c/\Delta P$  are strongly correlated, where  $\omega_0$  is the frequency at ambient pressure. For Hg-1223, there exists a noticeable change in both  $\Delta(\omega^2/\omega_0^2)/\Delta P$  and  $\Delta T_c/\Delta P$  near  $P \approx 5$  GPa. Incidentally, earlier LDA total-energy calculations<sup>4</sup> suggest that at this pressure the Hg- $O_A$  orbital energy crosses the Fermi energy  $E_F$  for Hg-1223. In contrast to the case of Hg-1223,  $\Delta(\omega^2/\omega_0^2)/\Delta P$  for Hg-1201 does not show such an anomaly up to 10 GPa. Together with our LDA total-energy phonon study of the  $O_A$ - $A_{1g}$  Raman mode, it is concluded that the change of  $O_A$  Raman frequency is due to the change of the Hg- $O_A$  bond strength, which may be directly related to the charge transfer between the CuO<sub>2</sub> planes and the Hg-O layers. In addition, it is remarkable to note that the increased rate is found to be nearly the same for both Hg-1201 and Hg-1223 below  $P \approx 5$  GPa. This suggests that the same mechanism may be increasing the Raman frequency for both Hg-1201 and Hg-1223 below  $P \approx 5$  GPa.

Single-phase Hg-1201 and Hg-1223 samples were prepared in a manner described elsewhere.<sup>5,6</sup> Magnetic susceptibility and resistance versus temperature measurements of these samples showed that there exists only one superconducting phase in each set of samples. The onset temperatures are 92 and 134 K for Hg-1201 and Hg-1223, respectively. Complete transition to the zero-resistance state occurs within 3 K for both sets of samples. Among the Hg-12( $n-1$ ) $n$  ( $n=1,2,3$ ) superconducting phases, the Hg-1223 phase is the most difficult to make as a single phase. Based on x-ray powder diffraction, our Hg-1223 samples consist mostly of the Hg-1223 phase with a BaCuO<sub>2</sub> impurity phase. Traces of a CaHgO<sub>2</sub> phase were detected only in Raman measurements.<sup>7</sup> In addition, Auger electron microprobe analysis and thermoelectric power measurements confirmed the

high quality of the samples.<sup>8</sup>

Polycrystalline samples were loaded at room temperature into a gasketed diamond anvil cell with the sample itself serving as a pressure medium. Any other pressure media would greatly reduce the already poor signal-to-noise ratio. The dimensions of the sample chamber were approximately 300  $\mu\text{m}$  in diameter and 150  $\mu\text{m}$  in thickness. Pressures were determined by the well-known ruby-fluorescence technique.<sup>9</sup>  $R$  lines of the fluorescent spectra of ruby chips, incorporated into the sample space, were recorded before and after each Raman measurement. The uniformity of the quasihydrostatic condition below 10 GPa inside the pressure cell was determined using the ruby fluorescence lines.

Raman spectra were excited using the 514.5-nm line of an Ar-ion laser through a metallurgical microscope with ultra-long-working-distance objective lenses. The light was focused onto specific crystal(s) in the cell, and the backscattered light was dispersed using a Jobin Yvon U1000 double monochromator. The overall resolution of our Raman spectrometer was 4.6  $\text{cm}^{-1}$ . The lateral dimension of the measured crystals was in the range of 2–10  $\mu\text{m}$ , while the diameter of the probing beam spot was 3–5  $\mu\text{m}$ . The exact orientation of the crystals under pressure is not known.

Figure 1 shows typical Raman spectra of the Hg-1223 samples under pressure. The spectra are shown in the measured sequence, with the first at the bottom and the last at the top. A slight deterioration in the intrinsic Hg-1223 spectra was detected after the full cycle of pressure measurements. In the pressure cell, only the strong peaks of the  $O_A A_{1g}$  mode are distinguishable due to background fluorescence of the diamond anvils. As noted above, the Hg-1223 samples in these measurements do have impurity phases like  $\text{CaHgO}_2$  and  $\text{BaCuO}_2$ . Studies of pressure effects on the Raman spectra of Hg-1201 and Hg-1212 single-phase samples and several impurity phases were also carried out. Details of the results will be published in a separate paper.

Figure 2 shows the peak positions of the  $O_A A_{1g}$  modes of Hg-1201 (circles) and Hg-1223 (squares). Different types (filled, open, hatched) of circles and squares represent different batches of samples, indicating the reproducibility of the data. Representative error bars of the selected peak positions are shown in the figure, and they are rather large due to the poor signal-to-noise ratio of the spectra. Uncertainty in the magnitude of the applied pressure is about the size of the legends, except for the highest pressure, whose uncertainty is drawn in the figure.

To probe the pressure dependencies of the  $O_A A_{1g}$  mode, we plotted our Raman data as  $(\omega^2/\omega_0^2)$  vs  $P$  for both Hg-1201 and Hg-1223 (Fig. 3).  $\omega^2$  represents effectively the force constants of the bonds between  $O_A$  and its neighboring Hg and Cu atoms (i.e.,  $\text{Hg-O}_A$  and  $\text{Cu-O}_A$  bonds). It is noted that the change of  $(\omega^2/\omega_0^2)$  can be regarded as being proportional to  $P$  and the rates of increase of  $(\omega^2/\omega_0^2)$  for both Hg-1223 and Hg-1201 are the same up to  $P \approx 5$  GPa. The Hg-1223 shows a sharp increase of the rate above  $P \approx 5$  GPa. Shown in the inset are  $T_c$  data for Hg-1223 from electrical measurements by

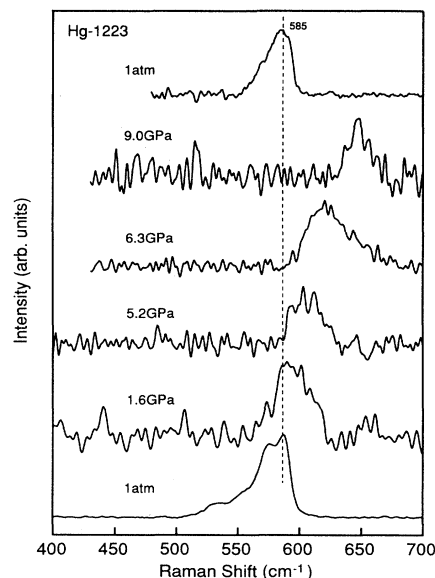


FIG. 1. Typical Raman spectra of Hg-1223 at various pressures. The spectra are presented in the measuring sequence, the first at the bottom and the last at the top.

Gao *et al.* and Chu *et al.*<sup>1</sup> and from magnetic measurements by Takahashi *et al.*<sup>10</sup> It is noted that the slope in  $T_c$  vs  $P$  also changes in both sets of data at  $P \approx 5$  GPa. Table I summarizes our experimental results for  $\Delta(\omega^2/\omega_0^2)/\Delta P$  and estimated values of the Grüneisen parameters<sup>11</sup> using the values of bulk moduli given in Refs. 2 and 3 for low and high pressures, respectively.

In order to understand the dependence of the  $O_A A_{1g}$  Raman frequency on the pressure in relation to the shortening of each  $\text{Hg-O}_A$  and  $\text{Cu-O}_A$  bond, a first-principles LDA-FLAPW (full-potential linearized augmented-plane-wave<sup>12</sup>) total-energy calculation of the  $O_A A_{1g}$

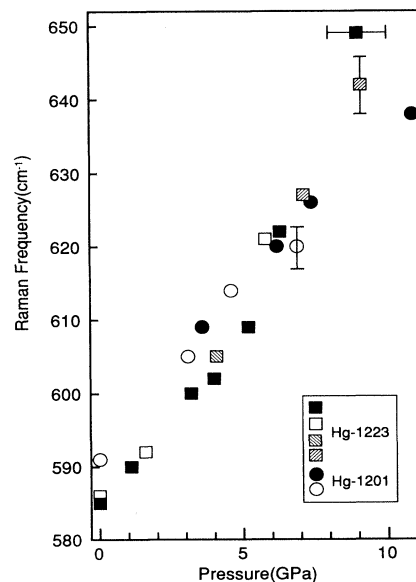


FIG. 2. Raman frequencies of the  $O_A A_{1g}$  modes of Hg-1201 (circles) and Hg-1223 (squares) at various pressures. Different types of circles (squares) are for different batches of samples. Error bars are discussed in the text.

phonon frequency was carried out. As a model calculation, we took two different sets of neutron diffraction data on the Hg-1201 lattice parameters by Hunter *et al.*<sup>2</sup> The results of the calculations for Hg-1201 are shown in Table II, in comparison with experiment, where the set *A* is for the results obtained from the equilibrium lattice parameters at ambient pressure, and the set *B* is from the lattice constants at 0.6 GPa—but for the set *B* only the position of the  $O_A$  ion is relaxed in the present calculation. First, the calculated  $O_A A_{1g}$  Raman frequency of  $587 \text{ cm}^{-1}$  for Hg-1201 shows excellent agreement with the observed value of  $592 \text{ cm}^{-1}$ .<sup>6,13</sup> However, the calculated value of  $631 \text{ cm}^{-1}$  at  $P=0.6 \text{ GPa}$  is much higher than the observed value of  $\sim 595 \text{ cm}^{-1}$ . Such a large discrepancy may arise due to the lack of *full-scale* relaxation of lattice parameters and other ionic positions, except the  $O_A$  site, in our calculations. Detailed results of our total-energy calculations will be published elsewhere.

Despite the lack of full-scale relaxation in the higher-pressure calculation, it is notable to observe that the Hg- $O_A$  bond length,  $d_{\text{Hg-}O_A}$ , changes little with the increase of pressure, while that of Cu- $O_A$ ,  $d_{\text{Cu-}O_A}$ , changes most. That is, as shown in Table II,

$$\frac{\Delta d_{\text{Cu-}O_A}}{\Delta c} \gg \frac{\Delta d_{\text{Hg-}O_A}}{\Delta c} \approx 0, \quad (1)$$

which is indeed consistent with earlier LDA calculations by Novikov, Mryasov, and Freeman<sup>4</sup> and measurements for Hg-1201 by Hunter *et al.*<sup>2</sup> Using a simple force-constant model, we may write the increase of the force acting on  $O_A$  by its neighboring atom  $X$  ( $X = \text{Hg}$  or  $\text{Cu}$ ) due to the reduced bond length  $\Delta d_{X-O_A}$  as

$$\Delta F_{X-O_A} = k_{X-O_A}^0 \Delta d_{X-O_A} + \Delta k_{X-O_A} d_{X-O_A}^0, \quad (2)$$

where  $k_{X-O_A}^0$  and  $d_{X-O_A}^0$  represent the equilibrium force

TABLE I. Estimated rate of increase in the force constants  $\Delta(\omega^2/\omega_0^2)/\Delta P$  (in  $\text{GPa}^{-1}$ ) and the Grüneisen parameter (Ref. 11)  $\gamma$  for Hg-1201 and Hg-1223.

Pressure	Hg-1201		Hg-1223	
	$\Delta(\omega^2/\omega_0^2)/\Delta P$	$\gamma$	$\Delta(\omega^2/\omega_0^2)/\Delta P$	$\gamma$
Below 5 GPa	0.015	0.52	0.015	0.68
Above 5 GPa	0.015	0.52	0.040	1.28

constants and bond lengths of Hg- $O_A$  and Cu- $O_A$  bonds, respectively. Therefore an equilibrium condition at high pressure (or reduced bond lengths) becomes

$$(k_{\text{Hg-}O_A}^0 \Delta d_{\text{Hg-}O_A} + \Delta k_{\text{Hg-}O_A} d_{\text{Hg-}O_A}^0) - (k_{\text{Cu-}O_A}^0 \Delta d_{\text{Cu-}O_A} + \Delta k_{\text{Cu-}O_A} d_{\text{Cu-}O_A}^0) = 0. \quad (3)$$

Our calculation gives  $\Delta d_{\text{Cu-}O_A} \gg \Delta d_{\text{Hg-}O_A} \approx 0$  in agreement with previous results,<sup>2,4</sup> from which it follows that

$$\Delta k_{\text{Hg-}O_A} \approx \left[ \frac{\Delta d_{\text{Cu-}O_A}}{d_{\text{Hg-}O_A}^0} \right] k_{\text{Cu-}O_A}, \quad (4)$$

assuming  $\Delta k_{\text{Cu-}O_A} \approx 0$ .<sup>14</sup> From the force-constant model, we know that

$$\omega_{O_A}^2 = \frac{k_{\text{Cu-}O_A} + k_{\text{Hg-}O_A}}{M_{O_A}} \quad (5)$$

for the  $O_A A_{1g}$  mode frequency  $\omega$ . Thus, the increase of the Raman frequency has the following dependence

$$\Delta(\omega^2) \approx \frac{\Delta k_{\text{Hg-}O_A}}{M_{O_A}} \approx \left[ \frac{\Delta d_{\text{Cu-}O_A}}{d_{\text{Hg-}O_A}^0} \right] \omega_{O_A}^2, \quad (6)$$

which is proportional to  $\Delta c$ , i.e., the decrease in lattice constant  $c$ .

Once we assume that this simple model can be applied to both Hg-1201 and Hg-1223, then the linear dependence of  $\Delta(\omega^2/\omega_0^2)$  on  $\Delta P$  (i.e.,  $\Delta c$ ), shown in Fig. 3, can be understood as a direct consequence of the change of the Hg- $O_A$  bond strengths. In other words, for both Hg-1201 and Hg-1223, the increase of  $(\omega^2/\omega_0^2)$  arises from the change of bond strength,  $\Delta k_{\text{Hg-}O_A}$ , which is dependent on the electronic structure of the Hg- $O_A$  orbital states. Interestingly,  $\Delta(\omega^2/\omega_0^2)/\Delta P$  for Hg-1223 has a sharp change near  $P \approx 5 \text{ GPa}$  and shows a strong correlation with a similar anomaly in the rate  $\Delta T_c/\Delta P$  as shown in Fig. 3. Since this change of  $\Delta(\omega^2/\omega_0^2)$  is directly relat-

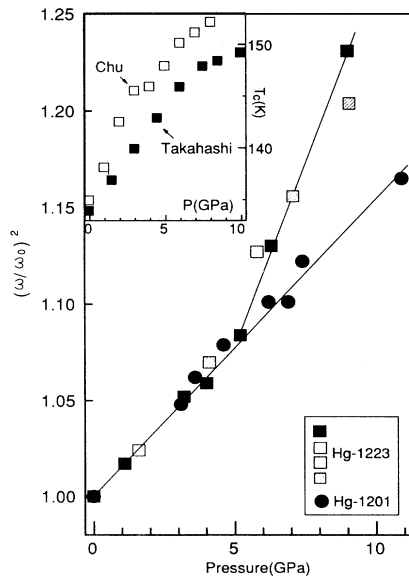


FIG. 3. Raman peak frequency  $\omega$  plotted as  $(\omega^2/\omega_0^2)$  vs  $P$  for both Hg-1201 (circles) and Hg-1223 (squares). The lines are guides to the eye. In the inset are  $T_c$  vs  $P$  plots for Hg-1223, using data from Refs. 1 and 10.

TABLE II. Results of LDA total-energy calculations of the  $O_A A_{1g}$  mode frequencies, the corresponding bond lengths in Hg-1201 at two different pressure points, and a comparison with experimental values.

	Bond lengths (Å)		$O_A A_{1g}$ Raman freq. ( $\text{cm}^{-1}$ )	
	$d_{\text{Hg-}O_A}$	$d_{\text{Cu-}O_A}$	$\omega_{O_A}$ (calc.)	$\omega_{O_A}$ (expt.)
<i>A</i> ( $P=1 \text{ atm}$ )	2.00	2.76	587	592
<i>B</i> ( $P=0.59 \text{ GPa}$ )	2.00	2.74	631	$\sim 595$
Difference ( <i>B</i> - <i>A</i> )	0.00	-0.02	44	$\sim 3$

ed to  $\Delta k_{\text{Hg-O}_A}$ , such anomalies in both  $\Delta(\omega^2/\omega_0^2)$  and  $\Delta T_c/\Delta P$  near  $P \approx 5$  GPa can arise from a change of  $\Delta k_{\text{Hg-O}_A}$  as pressure goes through  $P \approx 5$  GPa. In fact, at this pressure, the calculated Hg-O<sub>A</sub> orbital energy ( $E_{\text{Hg-O}_A}$ ) crosses Fermi energy  $E_F$  for Hg-1223.<sup>4</sup> Such a level crossing of  $E_{\text{Hg-O}_A}$  and  $E_F$  may initiate a large charge transfer from the CuO<sub>2</sub> planes to the Hg-O layers as the pressure increases. Consequently, such a charge transfer may lead to a decrease of  $\Delta T_c/\Delta P$  and an increase of  $\Delta(\omega^2/\omega_0^2)/\Delta P$ .

In Hg-1201, on the other hand, there is no signature of such an anomaly within the pressure range studied (i.e., below 10 GPa). It is remarkable, however, that  $\Delta(\omega^2/\omega_0^2)/\Delta P$  for Hg-1201 is the same as that for Hg-1223 below  $P \approx 5$  GPa, which strongly indicates that the same mechanism is responsible for the change of  $(\omega^2/\omega_0^2)$  for both Hg-1201 and Hg-1223. That is, the increase of  $k_{\text{Hg-O}_A}$  drives  $\Delta\omega^2$  for both Hg-1201 and Hg-1223 below  $P \approx 5$  GPa. From  $T_c$  vs  $P$  measurements also, it was suggested that a common mechanism is responsible for the pressure-induced increase in  $T_c$  in all Hg-12( $n-1$ )n ( $n=1,2,3$ ) compounds.<sup>1,15</sup>

Initially the increase of the O<sub>A</sub>  $A_{1g}$  Raman frequencies was thought to be directly related to the shortening of bond lengths between O<sub>A</sub> and neighboring atoms resulting from the applied pressure (i.e., compression of the bonds). By neutron powder diffraction, Hunter *et al.*<sup>2</sup> investigated the changes of such bond lengths in the crystal structures of Hg-1201 and Hg-1212 up to 0.6 GPa, and for Hg-1223 to 9.2 GPa. By comparing structural data at pressures below 0.6 GPa, they concluded that the Cu-O<sub>A</sub> bonds are more compressible in Hg-1201 and Hg-1212, while the Hg-O<sub>A</sub> bonds are more compressible in Hg-1223. The Cu-O<sub>A</sub> bond compressibility of Hg-1223 was nearly zero up to 9.2 GPa. If this is the case, then one might expect the pressure dependence of the O<sub>A</sub> Raman frequencies of Hg-1201 to be different from that of Hg-

1223. On the contrary, the behavior of the O<sub>A</sub> Raman frequencies of Hg-1201 and Hg-1223 is nearly the same below  $P \approx 5$  GPa. It is possible that the data of Hunter *et al.* may have been influenced by the presence of impurity phases, as noted in their paper.

In conclusion, effects of pressure on the Raman frequencies of the apical oxygen O<sub>A</sub>  $A_{1g}$  modes of the HgBa<sub>2</sub>CuO<sub>4+δ</sub> and HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+δ</sub> superconductors are studied. The results show that the Raman frequencies of the apical oxygen  $A_{1g}$  modes increase from 592 to 626 cm<sup>-1</sup> at 7.4 GPa for Hg-1201 and from 585 to 649 cm<sup>-1</sup> at 9.0 GPa for Hg-1223. It is striking to observe that the increased rates of the force constants,  $\Delta(\omega^2/\omega_0^2)$ , and the variation of  $T_c$ ,  $\Delta T_c$ , under pressure are strongly correlated for both Hg-1201 and Hg-1223. For Hg-1223, both  $\Delta(\omega^2/\omega_0^2)$  and  $\Delta T_c$  show anomalous slope changes near  $P \approx 5$  GPa. Incidentally, this pressure ( $\approx 5$  GPa) corresponds to the energy level crossing of the Hg-O<sub>A</sub> orbital energy and the Fermi energy  $E_F$  as reported for earlier LDA total-energy calculations.<sup>4</sup> In addition, it is remarkable to note that the increased rate  $\Delta(\omega^2/\omega_0^2)/\Delta P$  is found to be nearly the same for both Hg-1201 and Hg-1223 below  $P \approx 5$  GPa. This implies that the same mechanism works to increase the Raman frequency of both Hg-1201 and Hg-1223 below  $P \approx 5$  GPa. Together with our LDA total-energy phonon study of the O<sub>A</sub>  $A_{1g}$  Raman mode, it is concluded that the change of O<sub>A</sub> Raman frequency is due to the change of Hg-O<sub>A</sub> bond strength and the Hg-O<sub>A</sub> orbital energy relative to  $E_F$ , which may be directly related to the charge transfer between the CuO<sub>2</sub> planes and the Hg-O layers.

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<sup>2</sup>B. A. Hunter *et al.*, Physica C **221**, 1 (1994).

<sup>3</sup>J. H. Eggert *et al.*, Phys. Rev. B **49**, 15 299 (1994).

<sup>4</sup>D. L. Novikov, O. N. Mryasov, and A. J. Freeman, Physica C **222**, 38 (1994).

<sup>5</sup>Sergey Lee, Mi-Ock Mun, Myoung-Kwang Bae, and Sung-Ik Lee, J. Mater. Chem. **4**, 991 (1994).

<sup>6</sup>N. H. Hur, H.-G. Lee, J.-H. Park, H.-S. Shin, and In-Sang Yang, Physica C **218**, 365 (1993).

<sup>7</sup>In-Sang Yang *et al.*, Physica C **222**, 386 (1994).

<sup>8</sup>G. T. Jeong *et al.*, Phys. Rev. B **49**, 15 416 (1994); Y. S. Ha *et al.*, J. Mater. Chem. (to be published).

<sup>9</sup>H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

<sup>10</sup>H. Takahashi *et al.*, Physica C **218**, 1 (1993).

<sup>11</sup>The Grüneisen parameter  $\gamma$  for these superconductors can be estimated from the Raman frequency increase of the O<sub>A</sub>  $A_{1g}$  mode and the bulk modulus in pressure measurements,

$$\gamma = -\frac{d \ln \omega}{d \ln V} = K_V \frac{d \ln \omega}{d P},$$

where  $\omega$  is the Raman frequency and  $K_V$  is the bulk modulus of these superconductors.

<sup>12</sup>H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984), and references therein.

<sup>13</sup>Y. T. Ren *et al.*, Physica C **217**, 273 (1993).

<sup>14</sup>In the case of  $\Delta k_{\text{Cu-O}_A} \neq 0$ , we have

$$\Delta k_{\text{Hg-O}_A} = \left[ \frac{\Delta d_{\text{Cu-O}_A}}{d_{\text{Hg-O}_A}^0} \right] k_{\text{Cu-O}_A}^0 + \Delta k_{\text{Cu-O}_A} \left[ \frac{d_{\text{Cu-O}_A}^0}{d_{\text{Hg-O}_A}^0} \right].$$

Here, if we assume  $\Delta k_{\text{Cu-O}_A} > \Delta k_{\text{Hg-O}_A} \approx 0$  instead, then we get

$$\Delta k_{\text{Cu-O}_A} \approx - \left[ \frac{\Delta d_{\text{Cu-O}_A}}{d_{\text{Cu-O}_A}^0} \right] k_{\text{Cu-O}_A}^0 < 0,$$

which means that the O<sub>A</sub>  $A_{1g}$  Raman frequency should decrease at high pressure, which is not consistent with our observations.

<sup>15</sup>A.-K. Klehe, J. S. Schilling, J. L. Wagner, and D. G. Hinks, Physica C **223**, 313 (1994).