

Raman modes of the apical oxygen in mercury-based superconductors

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Recent studies suggest that the apical oxygen plays an important role in high- T_c superconductivity of mercury-based superconductors $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ [Hg-12($n-1$) n]. Among strong Raman peaks at ~ 570 and ~ 585 cm^{-1} , the mode at ~ 585 cm^{-1} has been determined to be the A_{1g} mode of the apical oxygen. However, the origin of the mode near 570 cm^{-1} is still in question. In order to clarify the origin of the 570 cm^{-1} mode, we have carried out Raman measurements on the $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$ systems, where the amount of the oxygen in the Hg/Tl-O plane is controlled by the doping level of Tl ions. The results show that the 570 cm^{-1} peak does not arise from the modes of the interstitial oxygens in the Hg/Tl-O plane, but from the A_{1g} -type mode of the apical oxygen. From our analysis, it is shown that the 570 cm^{-1} mode arises from the apical oxygen O_A with the neighboring interstitial oxygen O_δ , while the 585 cm^{-1} mode is from the O_A without the nearest O_δ neighbor. We conclude that the apical oxygens in the Hg-12($n-1$) n systems can have two distinctive sets of O_δ environment.

The discovery of mercury-based Cu-oxide superconductors has generated a tremendous amount of interest in search of higher- T_c superconductors. Moreover, the highest superconducting transition temperature T_c of ~ 165 K was achieved for Hg-1223 under high pressure,¹ where the bond length between Cu and the apical oxygen O_A was found to be significantly shortened under pressure.² Our earlier work showed a strong correlation between the change of the O_A A_{1g} Raman frequency and the increase of T_c as a function of pressure, indicating a possibility that the apical oxygen O_A plays an important role in high- T_c superconductivity of mercury-based Cu oxides.³ As a continuing effort toward understanding the origin of superconductivity in mercury-based high- T_c superconductors, we performed a detailed study of the structural and vibrational properties of the apical oxygen bridging the Cu-O planes and the Hg layers.

Mercury-based superconductors $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$, Hg-12($n-1$) n hereafter, show strong Raman peaks at ~ 570 and ~ 585 cm^{-1} .⁴⁻⁶ The mode at ~ 585 cm^{-1} has been unambiguously determined to be the A_{1g} mode of the apical oxygen O_A . However, the origin of the mode at ~ 570 cm^{-1} is still in question. Ren *et al.* observed the change of the Raman intensity of the 570 cm^{-1} mode of Hg-1201 samples annealed in different oxygen partial pressures,⁷ and attempted to assign the 570 cm^{-1} mode to the interstitial oxygen O_δ , displaced from the center of the four Hg atoms. However, from the polarization dependence measurements on Hg-1201 samples, Krantz *et al.* suggested that both of the Raman modes near 570 and 590 cm^{-1} are due to apical oxygen vibration,⁶ where the 590 cm^{-1} mode is speculated to be directly coupled to the vibration of apical oxygen, while the 570 cm^{-1} mode is a frequency-shifted apical-oxygen mode. As the reason for the frequency shift of the

apical oxygen mode, two possibilities were proposed. First, the presence of O_δ in the rocksalt Hg-O plane breaks the symmetry of the CuO_2 plane permitting Raman activity of the Cu atom and producing the frequency-shifted apical-oxygen mode. The other possibility is directly related to the possibility of Cu substitution for the Hg site. If the Hg site were partially replaced by Cu,⁸ the 570 cm^{-1} mode would be from the vibration of the $\text{O}_A\text{-Cu}_{\text{Hg-defect}}\text{-O}_A$ bond.

To clarify the origin of the 570 cm^{-1} mode, we have carried out Raman measurements on the Tl-doped Hg-1223 system, $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$, where the amount of the oxygen in the Hg/Tl-O plane is controlled by the doping level of Tl ions. While the O_δ site of the Hg-1223 is mostly empty, the corresponding site of the Tl-1223 is almost filled, unless the samples are heat treated. Therefore, doping Tl in the Hg site of Hg-1223 is regarded as increasing the occupancy of the O_δ site in the Hg-1223 structure.

In this paper, we report experimental evidence for the existence of two different A_{1g} Raman frequencies for the apical oxygen O_A in mercury-based high- T_c superconductors. The presence of the neighboring interstitial oxygens O_δ give rise to a downward shift (by about 15 cm^{-1}) of the apical oxygen vibration at ~ 585 cm^{-1} , producing a double-peak feature commonly observed in Hg-12($n-1$) n superconductors.

$\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$ samples were prepared by solid-state reaction of HgO, Tl_2O_3 , $\text{Ba}_2\text{CuO}_{3+y}$, and $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ mixtures in an evacuated quartz tube. All the sample preparation procedure was carried out in an argon-filled dry box. Details of sample preparation method were published previously.^{9,10}

Samples were characterized by x-ray diffraction (XRD), electron probe microanalysis (EPMA), and thermogravimet-

ric analysis (TGA). Traces of CaHgO_2 and BaCuO_2 impurities were found by the XRD pattern, and the EPMA results show that the starting composition of Hg and Tl remain constant in the products. TGA shows that the samples doped by Tl are stable upto 550°C . All the samples show sharp superconducting transition temperatures (T_c) in the range $124 - 128\text{ K}$. Further details are published in Ref. 10.

Raman measurements were carried out at room temperature using a Jobin Yvon U1000 double monochromator in a backscattering geometry. The spectra were excited with the 514.5 nm line of an Ar-ion laser focused on surfaces of the crystals through an Olympus metallurgical microscope. Further details are explained in our previous publication.⁵

Figure 1 shows Raman spectra of $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) samples, hereafter denoted as $(\text{Hg}_{1-x}\text{Tl}_x)\text{-1223}$. Three distinctive peaks at ~ 520 , ~ 570 , and $\sim 585\text{ cm}^{-1}$ are observed and determined to have the A_{1g} symmetry from the polarization-dependent measurements.^{5,11} In addition, the peak at 147 cm^{-1} is the $\text{Cu}(2)$ (Cu in CuO_2 planes) A_{1g} mode, and the peak denoted by p is a plasma line of the 514.5 nm laser line.

On the basis of previous mode assignments for Hg-1223 and Tl-1223, peaks at 520 and 585 cm^{-1} can be readily assigned to the O_A modes of $\text{Tl-O}_A\text{-Cu}$ and $\text{Hg-O}_A\text{-Cu}$ bonds in $(\text{Hg}_{1-x}\text{Tl}_x)\text{-1223}$, respectively.^{11,5} The mode at $\sim 570\text{ cm}^{-1}$ has been observed for all Hg-12($n-1$) n systems, but the origin of which has not been determined experimentally yet. The relative intensity of the 570 cm^{-1} mode over that of the 585 cm^{-1} mode grows steadily as the amount of the Tl substitution in $(\text{Hg}_{1-x}\text{Tl}_x)\text{-1223}$ increases, although it vanishes completely in the pure Tl-1223, i.e., $x = 1$.

The peak frequencies and the intensities are shown in Fig. 2, as obtained from the least-squares fits using Lorentzians. Two adjacent peaks at 570 and 585 cm^{-1} were analyzed with two Lorentzians as employed by Krantz *et al.* for the Hg-1201 system.⁶ Figure 2(a) shows peak positions of A_{1g} -type modes above 500 cm^{-1} as a function of the Tl content. The peak frequencies of the 585 and 570 cm^{-1} modes shift to lower values, while the peak frequency of the 520 cm^{-1} mode increases, as the Tl content increases. Such continuous changes of the peak frequencies of all the 520 , 570 , and 585 cm^{-1} modes rule out the possibility that the samples are simple mixtures of Hg-1223 and Tl-1223. Furthermore, if it were a simple mixture of the two phases, the relative intensity of the 570 cm^{-1} mode would not change at all, and the peak frequencies would be those of the two domains independent of the Tl content. In fact, as illustrated in Fig. 2(b), the relative peak intensity of the 570 cm^{-1} mode to that of 585 cm^{-1} mode changes continuously as the Tl content, i.e., x , varies from 0 to 1. Therefore, these results strongly suggest that a unique mode at 570 cm^{-1} originates not from any possible impurities but from the $(\text{Hg}_{1-x}\text{Tl}_x)\text{-1223}$ solid solution. Also, it implies that the Tl doping in Hg-1223 occurs in a microscopic scale.

Figure 3 shows analyses of the intensity ratio of three peaks at 520 , 570 , and 585 cm^{-1} as a function of the doping level of both Tl (i.e., x) and Hg (i.e., $1-x$) ions. First, the intensity ratios of the 585 cm^{-1} peak relative to the sum of 520 and 585 cm^{-1} peaks, i.e., $I(585)/I(520+585)$, are plot-

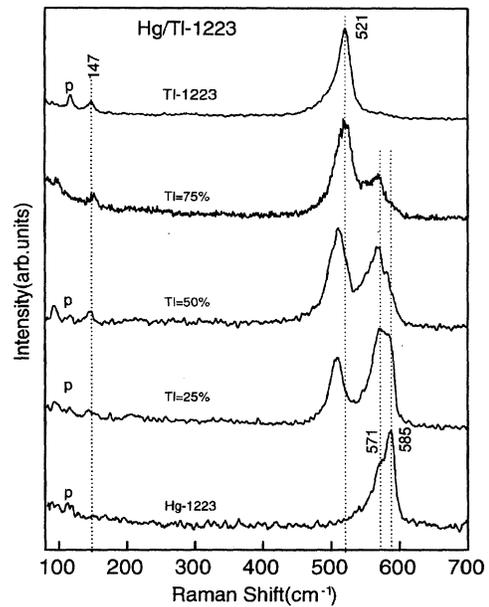


FIG. 1. Raman spectra of $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$ superconductors, where $x = 0.0, 0.25, 0.50, 0.75, 1.0$. The peaks denoted by P are due to the plasma line of the 514.5 nm laser line.

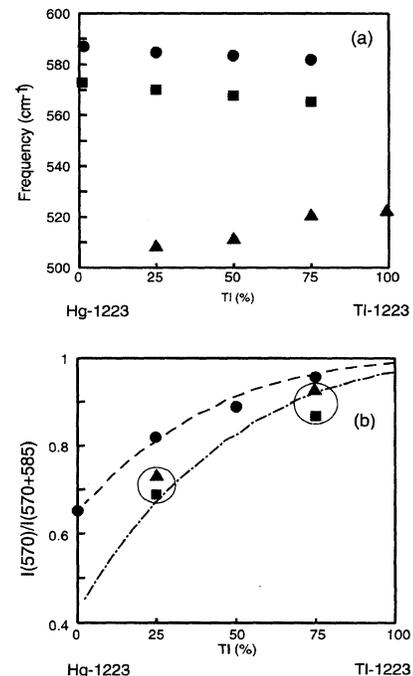


FIG. 2. Results of Lorentzian fitting of the apical oxygen modes and the mode near 570 cm^{-1} , where (a) the peak frequencies of these modes and (b) the relative intensity ratios of $I(570)/I(570+585)$ are plotted as functions of the Tl content. In (b), the filled circles represent the ratio for the as-sintered samples, and the triangles and squares (enclosed by two circles), for that of the annealed samples at 300°C 17 h and at 400°C 40 h, respectively. The dashed and the dot-dashed lines are theoretical fits. (See the text.)

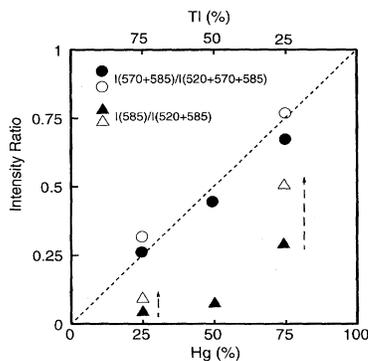


FIG. 3. $I(570+585)/I(520+570+585)$, i.e., the ratio of intensity of the 570 and 585 cm^{-1} modes to the intensity sum of the 520, 570, and 585 cm^{-1} modes as a function of Hg content. For comparison, $I(585)/I(520+585)$, i.e., the ratio of intensity of the 585 cm^{-1} mode to the intensity sum of the 520 and 585 cm^{-1} modes is plotted on the same scale. Open circles and open triangles are for $I(570+585)/I(520+570+585)$ and $I(585)/I(520+585)$, respectively, of the samples annealed in vacuum at 400 °C, 40 h. The arrows indicate that values of $I(585)/I(520+585)$ move toward the linear line.

ted in filled triangles against the Hg contents in %. It is clear that the intensity ratio $I(585)/I(520+585)$ is not linear to the Hg contents, implying that the relative spectral weight of the 585 cm^{-1} mode from O_A is missing as the Hg (or Tl) contents changes. However, the intensity ratios of the sum of the 570 and 585 cm^{-1} modes plotted against the gross sum of the 520, 570, and 585 cm^{-1} modes (filled circles in Fig. 3), $I(570+585)/I(520+570+585)$ shows a nearly perfect linear behavior relative to the Hg contents. Equivalently, the relative intensity of the 520 cm^{-1} mode is linear to the Tl contents only when the intensity of the 570 cm^{-1} mode is properly taken into account in calculating the intensity ratios. This means that both of the 570 and 585 cm^{-1} modes have the same origin, and are due to vibration of the apical oxygen in the Hg- O_A -Cu bond in the $(\text{Hg}_{1-x}\text{Ti}_x)\text{-1223}$ system. In the previous polarized-Raman measurements, the modes at 520, 570, and 585 cm^{-1} were found to have the A_{1g} symmetry.^{5,11} On the other hand, however, from the factor group analysis (FGA) of the crystal structure, only one A_{1g} mode is allowed for the apical oxygen O_A . It means that the presence of the additional 570 cm^{-1} mode is not compatible with the FGA result for the ideal (i.e., either no- O_δ or fully occupied- O_δ) crystal structure.

One plausible resolution for the inconsistency of the FGA results with the presence of additional O_A A_{1g} mode at ~ 570 cm^{-1} may come from the fact that there exist many different local environments for the apical oxygen O_A , generated by the presence of the interstitial oxygen O_δ . Hence, the apical oxygens O_A under different local environments may contribute to different frequencies of the Raman peaks. Assuming that the interstitial oxygens O_δ are randomly distributed, the possible local environments for apical oxygens O_A can be categorized depending on the number of neighboring O_δ around the O_A . As shown in the earlier work,¹² the 585 cm^{-1} peak is assigned to the O_A mode without any neighboring O_δ , while the relatively broad peak at 570

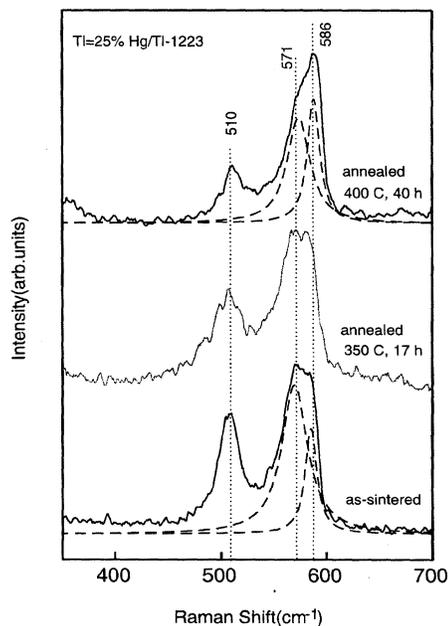


FIG. 4. Raman spectra of $\text{Hg}_{0.75}\text{Ti}_{0.25}\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$ superconductors as-sintered, annealed at 350 °C and 17 h, and annealed at 400 °C and 40 h. The dashed lines represent decomposed Lorentzian spectra.

cm^{-1} can be attributed to the O_A 's with more than one neighboring O_δ . Indeed, the broadness of the 570 cm^{-1} is regarded to be a reflection of the distribution in the number of O_δ neighbors around O_A .

If this is the case, the relative intensity of the 570 cm^{-1} mode to that of 585 cm^{-1} mode should depend on the oxygen content at O_δ site. To investigate such possibility, we have measured Raman spectra of the samples annealed in vacuum at relatively low temperatures. Shown in Fig. 4 are the representative spectra of $\text{Ti}=25\%$ sample, as sintered, annealed at 350 °C 17 h, and annealed additionally at 400 °C 40 h in the pressure of less than 10^{-6} Torr. After post-annealing of the sample under those nonoxidizing conditions, it is expected that the amount of O_δ decrease and, consequently, the number of the O_A sites without O_δ neighbors increase. Therefore, the intensity of the 570 cm^{-1} mode should decrease, while that of the 585 cm^{-1} mode increases as the samples are annealed at higher temperature and for longer time. This is exactly what has been illustrated in Fig. 4.

Using the data obtained during the annealing procedures, we also plotted the intensity ratio of $I(570)/I(570+585)$ in Fig. 2(b), where the triangles represent for the samples annealed at 350 °C and 17 h, and the squares for the samples annealed at 400 °C and 40 h. In the figure, it is clearly demonstrated that the longer the annealing time, the smaller the intensity ratio of $I(570)/I(570+585)$, showing that the intensity of the 570 cm^{-1} mode decreases as the content of O_δ decreases. As the O_δ content decreases, the intensity ratio of the 585 cm^{-1} mode to the sum of the 520 and 585 cm^{-1} modes (open triangles in Fig. 3) is seen to move toward the linear line, while the intensity ratio of the sum of 570 and

585 cm^{-1} to that of 520, 570, and 585 cm^{-1} modes remains on the linear line (open circles in Fig. 3). This seems to be related with the fact that the number of the O_A with O_δ neighbor decreases relative to that of O_A without O_δ neighbors as the O_δ content decreases.

In order to better understand the O_δ dependence of the intensity ratio of $I(570)/I(570+585)$, we have performed a numerical simulation and estimated the ratio of the number of the O_A sites with or without O_δ neighbors as a function of the O_δ filling, where the filling factor of O_δ is assumed to be proportional to the Tl doping. The dashed and dot-dashed lines in Fig. 2(b) are the fits to the experimental data points. However, two fitted lines are indeed the same curves shifted by the offset of the O_δ occupancy, i.e., $\Delta\delta = -0.1$ in $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$. This implies that the shift of $I(570)/I(570+585)$ for the annealed samples is mainly ascribed to the decrease of the O_δ content, and therefore the origin of the 570 cm^{-1} mode arises from the different O_A sites with more than one O_δ neighbor. In other words, the 570 cm^{-1} mode arises from the apical oxygen O_A with different environment due to the presence of the interstitial oxygens O_δ .

Measurement of the values of the O_δ content would be helpful in assessing the 570 cm^{-1} mode quantitatively, but the exact values of the O_δ content are not available at present.¹³ However, regardless of the information on the exact amount of O_δ contents, our argument on the O_δ dependence of the intensity ratio should remain valid, assuming that an enhancement of Tl content increases the O_δ content, and annealing the samples in vacuum reduces the O_δ content in the $(\text{Hg}_{1-x}\text{Tl}_x)$ -1223 system. In fact, similar observations on the behavior of the relative intensity of the 570 cm^{-1} mode under various annealing conditions were made by Ren *et al.* on the Hg-1201 system.⁷ Contrary to our analysis, however, they assigned the 570 cm^{-1} mode directly to the vibration of the interstitial oxygen O_δ .

Interestingly, Bridges *et al.* investigated the local structure about the Cu, Ba, and Hg atoms in Hg-1201 using the x-ray-absorption fine-structure (XAFS) technique.¹⁴ They found exceptionally broad peaks in the XAFS spectra corresponding to the Cu- O_A and Ba- O_A atom pairs. The broad peaks might be a reflection of the fact that there are two different environments for the apical oxygen O_A ; one with an O_δ neighbor and the other without. The O_A might have different

position if the O_δ is occupied, and it may have some distribution of positions due to differences in the number of O_δ neighbors.

As an alternative choice for the origin of the 570 cm^{-1} mode, the Cu defect at the Hg sites has been suggested.⁶ Several neutron or x-ray-diffraction measurements⁸ indicate that part of Hg sites are replaced by Cu ions. But others could not observe clear evidence for the substitution of some Hg atoms by the Cu atoms, and estimated that this replacement cannot be more than 10%.¹⁵ If the Hg site is partially replaced by Cu, the A_{1g} mode at $\sim 570 \text{ cm}^{-1}$ would be from the vibration of the O_A - $\text{Cu}_{\text{Hg-defect}}\text{-O}_A$ bond, as suggested from a theoretical calculation.¹⁶ However, the possibility of the 570 cm^{-1} mode being due to Cu replacement for Hg seems to be rare for the following reason. The observed proportionality of $I(520)/I(520+570+585)$ and the increase of the relative intensity of the 570 cm^{-1} mode with the increase of the Tl content must imply that the content of Cu that replaced Hg should be proportional to the Tl content, which is unlikely.

The replacement of Cu for Hg might produce an additional defect site other than the O_δ site. Wagner *et al.* observed additional oxygen defects on the $[1/2,0,0]$ chain site in the Hg-O planes from their neutron powder-diffraction measurements on Hg-1223.¹⁷ However, the content of such additional oxygen defects was found to be insensitive to reduction or oxygenation of the samples. Therefore, the 570 cm^{-1} mode does not seem to be related to the additional oxygen defects at the $[1/2,0,0]$ site.

In summary, we have done Raman measurements on the Tl-doped Hg-1223 samples, $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{Cu}_3\text{O}_{8+\delta}$, in order to clarify the origin of the 570 cm^{-1} mode in the mercury-based superconductors. The amount of the oxygen in the Hg/Tl-O plane is controlled by the doping level of Tl ions in the solid solution. Our results show that the 570 cm^{-1} mode is not from the motion of the oxygen in the Hg/Tl-O plane, but originates from the A_{1g} -type motion of the apical oxygen. According to our analysis, the 570 cm^{-1} mode arises from the apical oxygens O_A with the neighboring interstitial oxygens O_δ , while the 585 cm^{-1} mode is from the O_A without the nearest O_δ neighbor.

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