



X-ray photoelectron spectroscopy study of $\text{HgBa}_2\text{CuO}_{4+\delta}$

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Abstract

X-ray photoelectron spectroscopy was used to investigate the oxidation states of Hg and Cu ions in the $\text{HgBa}_2\text{CuO}_{4+\delta}$ compound. In contrast to the previous report on the scraped samples [C.S. Gopinath and S. Subramanian, *Physica C* 232 (1994) 222], our spectra from the fresh surfaces of fractured samples do not show the unusual 3+ oxidation state of Hg ions, while the satellite structure of the Cu $2p_{3/2}$ core-level spectrum which indicates the 2+ oxidation state of Cu ions is observed. These results confirm that, in the $\text{HgBa}_2\text{CuO}_{4+\delta}$ compound, the Hg atom does not act as an electron reservoir, and that the Cu–O layers are hole-doped due to the extra oxygens in the Hg–O₈ planes.

1. Introduction

The recently discovered high- T_c superconducting compound $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201 hereafter) attracts much interest due to its higher transition temperature T_c of 94 K compared with any other mono Cu–O layer superconductors [1]. The Hg-based superconductors with two or three Cu–O layers (denoted as Hg-1212 and Hg-1223, respectively) with even higher T_c have also been synthesized [2,3], and the observation of superconductivity at 165 K in Hg-1223 under pressure increases the interest in these compounds for technological applications and the underlying mechanism of high T_c [4].

Hg-based superconductors are isostructural with the Tl-based superconductors $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$,

except that the oxygen site O₈ at the center of four Hg atoms is partially occupied. It is widely believed that the oxygen content at the O₈ site affects the T_c of the Hg-based superconductors. One peculiar phenomenon of these Hg-based superconductors is that the optimum doping level seems to be higher than in most other high- T_c cuprates. The values of O₈ content measured by neutron powder diffraction techniques for the highest- T_c samples are approximately 0.06 in Hg-1201, 0.22 in Hg-1212 and 0.4 in Hg-1223 [5]. If we assume purely ionic configurations, these oxygen doping levels correspond to 0.12, 0.22 and 0.27 holes per Cu atom for Hg-1201, Hg-1212 and Hg-1223, respectively. These values for Hg-1212 and Hg-1223 are considerably higher than those found in most other high- T_c cuprates.

However, the O₈ content and the charge carrier density have close relations with the valence of the neighboring ions, especially Hg ions. Therefore, it is essential to investigate the valence of Hg atoms as

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well as the O_s content in evaluating the density of charge carriers and understanding the electronic structure of these systems. Recently, Singh and Pickett [6] performed self-consistent local density approximation calculations of $(HgBa_2Ca_2Cu_3O_8)_2O$ compound in order to understand the role of the Hg– O_s layer, especially in relation to the doping behavior. They found that the hybridization between mercury and the extra oxygen O_s is so strong that there is considerable Hg 5d–O 2p antibonding-state-derived weight at and above the Fermi level. Hence, some of the holes created by the oxygen doping reside in these Hg 5d–O 2p antibonding states, and thus the number of holes in the Cu–O layers is smaller than that expected from ionic considerations.

If Hg 5d states participate strongly in these antibonding states near the Fermi level and become partially depopulated, we should expect to see the signature of Hg^{3+} ions (5d⁹ configuration) in the Hg-based cuprate superconductors. X-ray photoelectron spectroscopy (XPS) is an ideal tool for this purpose, since Hg core levels would show complicated satellite structures, as found in many transition metal or rare-earth metal compounds with strongly correlated unfilled bands [7]. Recent XPS studies of Hg-1201 by Gopinath and Subramanian (GS) [8] indeed reported complicated structures of Hg core-level spectra, and were interpreted to show the signature of Hg^{3+} ions. In the Hg 4f core-level spectrum they were able to identify three peaks by deconvolution, two of which were attributed to the Hg ions with 2+ oxidation state and the other to an unusual oxidation state of 3+ which has a higher binding energy than the other two. Furthermore, their Cu 2p_{3/2} core-level spectrum did not show any satellite structure typical of Cu^{2+} ions, and was interpreted as showing some mixed-valent character of Cu(I), Cu(II) and Cu(III) states. From these facts, they suggested that the Cu–O layer may not be hole-doped but electron-doped, which is contradictory to the results of thermopower measurements [9].

Since it is an important issue whether the charge carrier is a hole or an electron, and whether Hg ions actively participate in the doping behavior of Hg-based superconductors, we performed an XPS core level study of all major core levels including Hg 4f, Cu 2p_{3/2}, Ba 3d_{5/2} and 4d of the Hg-1201 samples. We find that all the core-level spectra are very

sensitive to surface treatments. For the cleanest spectra taken from freshly fractured surfaces, the Hg 4f core-level spectrum does not show a 3+ oxidation state of Hg ions, whereas the Cu 2p_{3/2} core-level spectrum shows a satellite structure which is typical for Cu^{2+} ions, in contrast to GS's results on the scraped surfaces. Our results imply that the Hg 5d states do not participate strongly in the states near the Fermi level and the Cu–O layers of Hg-1201 are hole-doped rather than electron-doped.

2. Experimental

Hg-1201 samples were prepared by solid-state reaction of mixtures of yellow HgO and precursor powders of $Ba_2CuO_{3+\delta}$ in an evacuated quartz tube. Details of the sample preparation method have been published previously [10]. Before XPS measurements, samples were characterized by X-ray diffraction and micro-Raman measurements. X-ray diffraction data did not show any indication of impurity phases. Raman spectra showed pure Hg-1201 phases with no signal from HgO or the $Ba_2CuO_{3+\delta}$ precursor. Superconducting properties were examined magnetically by using a SQUID magnetometer (Quantum Design). All the samples showed a sharp single transition temperature at 92 K.

All XPS measurements were done in the ESCA/AES system manufactured by VSW Scientific Instruments. We used non-monochromatic Mg K α lines as an excitation source and the hemispherical electron analyzer with a multichannel detector. The energy scale was calibrated by fixing the binding energy of the Ag 3d_{5/2} core level to be 368.5 eV. The experimental resolution as determined by the full-width-at-half-maximum (FWHM) of the Ag 3d_{5/2} core level was 1.1 eV. During experiments the pressure of the experimental chamber was maintained between mid 10^{-10} and mid 10^{-9} Torr for the spectra presented in this paper.

Two methods were tried in order to obtain clean surfaces of the sample. First, sample surfaces were scraped in situ with a diamond file. However, the spectra obtained from the scraped surfaces were found not to be reproducible. Therefore, a method of fracturing the sample in situ was tried to reveal fresh surfaces. The XPS core-level spectra taken from the

freshly fractured surfaces were very clean and reproducible in contrast with the spectra from scraped samples. However, during the XPS measurements we observed that the chamber pressure gradually became worse, eventually rising up to 10^{-8} Torr if left alone. In some cases, moreover, Hg 4f core-level spectra changed as a function of time in several tens of minutes. Therefore, we obtained the spectra as soon as possible after fracturing in order to minimize the effect of any possible contamination of the fresh surface, and we discarded the spectra if any noticeable changes were observed during the experiments. During the XPS measurements, surface degradation might have been promoted as a result of heating by X-rays or by the X-ray gun which was close to the sample. In this regard, scraping Hg-1201 samples may have caused severe surface degradation by local heating and as a result the XPS spectra are not reproducible at each scraping procedure. It may also be noted that a Raman study by Chang et al. on the surface chemical decomposition of Hg-1201 by high-power laser irradiation shows that Ba_2CuO_3 phase is formed on the sample surface by local heating [11].

We also obtained the Hg 4f core-level spectrum of HgO which was commercially purchased as a reference of Hg^{2+} ions. Since HgO is an insulator, the charging effect causes some difficulty in determining the binding energies of core levels. Hence, we used as a reference the binding energy 284.8 eV of the C 1s core level of colloidal graphite which was partially coated onto the HgO powder.

3. Results and discussion

Fig. 1 shows the XPS core-level spectra of (a) Hg 4f, (b) Cu $2p_{3/2}$, (c) Ba $3d_{5/2}$, and (d) Ba 4d of the Hg-1201 samples. The X-ray satellite has been removed, but the inelastic background correction has not been performed. A fractured sample is denoted as #1 and two typical cases of scraped samples are denoted as #2 and #3. The spectrum denoted as #3 in Fig. 1 is from the sample scraped more than the sample for #2. In the Hg 4f core-level spectra of Fig. 1(a), we also present the HgO spectrum as a reference of Hg^{2+} ions.

A noticeable feature in this figure is that the XPS spectra of Hg-1201 are strongly affected by the method of surface treatment. The core-level spectra of the fractured sample are sharper than those of scraped samples, and the spectra from the scraped samples, especially #3, show more than one component. We can see that the intensity of the peak at higher binding energy (by ~ 5 eV) rises in all spectra as a result of further scraping. The origin of this peak is not yet clear. One possibility is that the scraping procedure causes severe surface degradation so that insulating phases such as Ba_2CuO_3 and BaCuO_2 are formed, shifting the core-level spectra towards higher binding energies due to the local charging effect. This means that the scraping procedure which is normally used to clean the surface of the high- T_c superconducting samples is not a good method for the Hg-1201 compound. The spectra

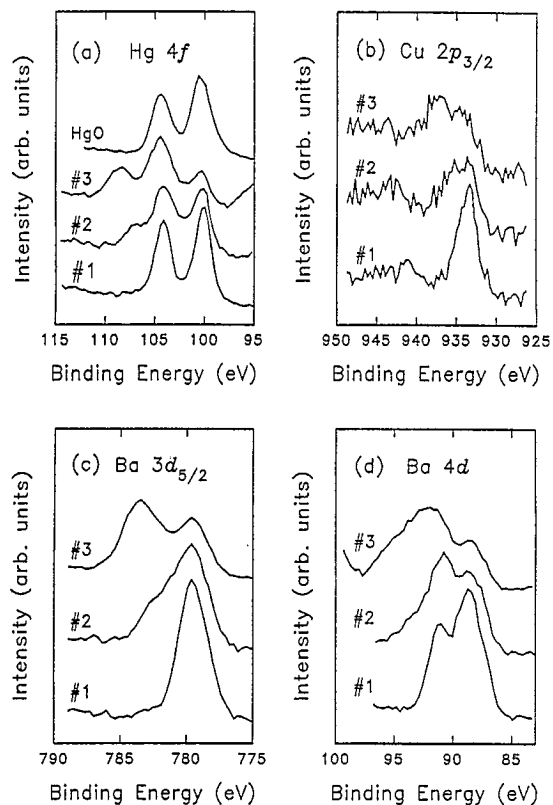


Fig. 1. XPS core-level spectra of $\text{HgBa}_2\text{CuO}_{4+\delta}$. (a) Hg 4f. (b) Cu $2p_{3/2}$. (c) Ba $3d_{5/2}$. (d) Ba 4d. #1 is from a fresh surface of fractured samples, and #2 and #3 are from the surfaces cleaned by scraping. Fracturing and scraping were done in situ.

denoted as #2 are similar to those reported in Ref. [8], and thus we can conjecture that the sample surface measured by GS might have been damaged by the scraping procedure. Although GS observed a Fermi edge in their XPS spectra, this does not exclude the possibility of surface damage due to scraping with metallic residues left on the sample surfaces.

As for the question of the existence of Hg^{3+} ions, the Hg 4f core-level spectrum shown in Fig. 1(a) for the fractured sample shows only a single component within our experimental resolution, and we do not find any extra high-binding-energy feature that can be ascribed to the unusual 3+ oxidation state. Furthermore, the binding energy of the main peak of Hg 4f core-level spectra of Hg-1201 is almost identical with that of HgO, which indicates that the main peak originates from Hg^{2+} ions.

The Cu $2p_{3/2}$ core-level spectra shown in Fig. 1(b) have poorer signal-to-noise ratios in comparison with other core-level spectra. This is due to the fact that the intensity of the Cu $2p_{3/2}$ spectrum is much smaller than those of others. The intensity ratio of Cu $2p_{3/2}$ spectrum to Ba $3d_{5/2}$ spectrum was estimated by considering the number of ions in the unit cell and the photoionization cross section of Cu 2p and Ba 3d core levels [12], and we found that the intensity of the observed Cu $2p_{3/2}$ spectrum is about half of the expected value [13]. It is noted that the Ba:Cu ratio determined by energy-dispersive X-ray microanalysis on crushed Hg-1201 is 2:1 [14]. However, if we assume that the sample surface is not exposed at the Cu–O layer but at the Hg or Ba–O layer and consider the fact that photoelectrons in this kinetic energy are very surface-sensitive, we could expect such a reduction of the intensity of the Cu $2p_{3/2}$ spectrum.

Despite the weak signal-to-noise ratio for the Cu $2p_{3/2}$ spectrum, we can clearly notice the satellite structure which is commonly observed in the core-level spectra of Cu^{2+} ions. The intensity ratio of the satellite to the main peak obtained by the curve-fitting procedure is about 0.2, which is smaller than those of other cuprates [15]. This may be due to the experimental error caused by the poor signal-to-noise ratio or due to the smaller charge transfer energy in the analysis of the Cu $2p_{3/2}$ core-level spectrum within the configuration interaction model [16].

The Ba $3d_{5/2}$ and 4d core-level spectra of the fractured sample also imply the good quality of the sample surface, in comparison with the scraped samples which show extra components. However, even in the spectrum denoted as #1 of Figs. 1(c) and (d), we can observe a shoulder peak at lower binding energy. As is well known from the XPS studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO), Ba core-level binding energies are strongly affected by the oxygen environment [17]. For its origin, the hybridization between Ba 5d and O 2p as an initial state effect or the difference of the density of screening charge as a final state effect has been suggested. Whichever scenario we may follow, the more oxygen ions are present around Ba ions, the lower the binding energies of the Ba core levels. We could therefore expect some structures in Ba core-level spectra for this oxygen-rich Hg-1201 compound. To analyze this, we performed curve fittings of Ba $3d_{5/2}$ and 4d core-level spectra. The

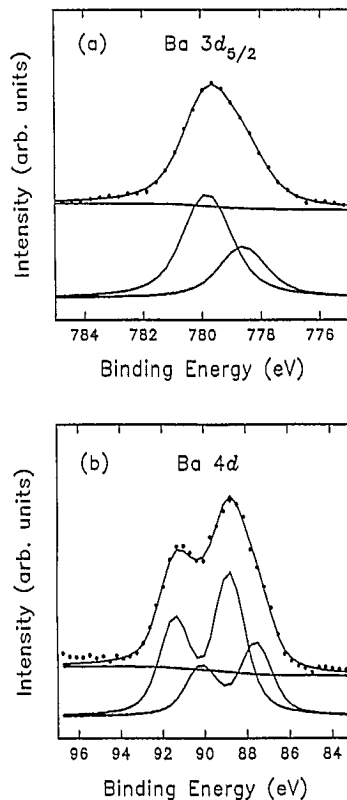


Fig. 2. Curve fitting of (a) Ba $3d_{5/2}$ and (b) Ba 4d XPS core-level spectra using Lorentzians convoluted with a Gaussian. For details of parameters, see the text.

curve form used in this process was a Lorentzian convoluted with a Gaussian. In order to remove arbitrariness of the curve fitting procedure, we fixed the values of Lorentzian and Gaussian widths. Gaussian width was determined from the fitting of the measured Ag $3d_{5/2}$ spectrum, whose Lorentzian broadening due to lifetime is known to be 0.28 eV and the singularity index α of 0.059 [18]. The Gaussian broadening due to our instrumental resolution thus determined was 1.1 eV (FWHM). For the values of Lorentzian widths which are related to the core-hole lifetime, we used the estimated values of 1.13 eV for Ba $3d_{5/2}$ core level and 0.78 eV for Ba 4d core level which had been used successfully in the analyses of Ba core-level spectra of YBCO [19].

As we can see in Fig. 2, all the spectra are well fitted using two curves whose binding-energy difference is 1.2 eV. We could assign the component at lower binding energy as coming from Ba ions surrounded by more oxygen ions. The intensity ratios of the component at lower binding energy to the component at higher binding energy are about 0.5 for both $3d_{5/2}$ and 4d spectra. Since the surface sensitivity of a core-level spectrum depends on the kinetic energy of the photoelectron, the Ba $3d_{5/2}$ spectrum is more surface sensitive than the Ba 4d spectrum. Hence, the uniformity of the intensity ratio of the two components in Ba core-level spectra implies that the two-component structure of Ba core-level spectra is not related to the surface of Hg-1201 but is intrinsic to the Hg-1201 bulk. Similar behaviors were also observed in the XPS studies of YBCO [19].

Based on the absence of unusual 3+ oxidation state of Hg ions in Hg 4f core-level spectra and the presence of a satellite structure in Cu $2p_{3/2}$ core-level spectra from the fractured Hg-1201 surfaces, we can conclude that the Cu–O layer in Hg-1201 is doped with holes by excess oxygen. This is in contrast to the conclusions by Gopinath and Subramanian [8]. However, our conclusion is consistent with the result of theoretical calculations by Singh and Pickett [6], who find that although in Hg-1223 there is considerable Hg 5d–O 2p antibonding-state-derived weight at and above the Fermi level, the Hg ion maintains almost +2 ionic configuration according to the charge distribution analysis, and the extra hole in the Hg–O₈ layer mainly goes into the O₈ site. Furthermore, the optimum doping level for superconductiv-

ity in Hg-1201 is not much different from other cuprates. In this regard, it will be interesting to study Hg-1212 and Hg-1223 compounds of the optimum doping level by electron spectroscopic techniques to reveal the role of the Hg–O₈ layer in these Hg-based compounds. For more evidence, X-ray absorption spectroscopy studies would also be useful.

4. Conclusions

In these XPS studies, it is shown that all the core-level spectra of Hg-1201 superconductors are very sensitive to the surface treatments. The usual scraping procedure produces spectra that are not reproducible, while the fracturing method gives reliable XPS spectra for the Hg-1201 samples. XPS spectra of the fractured sample surface disprove the existence of Hg³⁺ ions, and confirm the presence of the well-known satellite structure of Cu²⁺ ions in the Cu $2p_{3/2}$ core-level spectrum, which assures that the doping nature of the Hg-1201 compound is similar to other mono Cu–O layer hole-doped cuprates.

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