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Soft-x-ray absorption spectroscopy of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ $(x=0-0.6)$

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O K-edge and Cu L_{23}-edge x-ray-absorption near-edge-structure spectra for the series of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ compounds $(x=0–0.6)$ were measured using a bulk-sensitive x-ray fluorescence yield technique. Near the O $1s$ edge, pre-edge peaks at ~527.5 and ~528.2 eV are ascribed to the excitations of O $1s$ electrons to O $2p$ holes located in the CuO_3 ribbons and CuO_2 planes, respectively. The peak at ~528.2 eV decreases in intensity with increasing the Nd doping, indicating the filling of holes in the CuO_2 planes by the substitution of Nd^{3+} for Ba^{2+} in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system. For low levels of Nd doping, the holes are located mainly in the CuO_2 planes. At higher Nd doping, the holes are located predominantly in the CuO_3 ribbons. The depression in T_c for the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system correlates closely with the hole concentration in the CuO_2 planes and the number of disrupted fourfold-coordinated Cu on the chain sites. The high-energy shoulders in the Cu L_{23}-edge absorption spectra arise from Cu$3d^9L$ defected states to Cu$2p^{-1}3d^{10}L$ excited states, where L denotes the ligand hole on the CuO_3 ribbons and CuO_2 planes. With increasing the Nd doping, the shoulders shift to higher energy ~0.3 eV from $x=0$ to 0.6. [S0163-1829(97)09505-2]

I. INTRODUCTION

Hole concentration in p-type cuprate superconductors has been known as a fundamental parameter in superconductivity. Variation of superconducting properties of cuprate superconductors, such as $YBa_2Cu_3O_{7-\delta}$, has been extensively investigated in relation to oxygen deficiency or oxygen distribution. It was experimentally shown that the hole concentration in the $YBa_2Cu_3O_{7-\delta}$ system is strongly affected by the oxygen content.[1] Recently, considerable attention has been concentrated on the superconducting properties of solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system.[2–4] Nd^{3+} has an ionic radius approaching Ba^{2+}, allowing a high degree of solubility with Ba without forming second phases. In the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ compounds, existence of solid solution has been found in a range from $x=0$ to 0.8.[5] The superconducting properties in this system can be controlled via changing the substitution of divalent Ba by trivalent Nd in addition to changing the oxygen stoichiometry. This system has an advantage over a similar $YBa_2Cu_3O_{7-\delta}$ system with stoichiometric composition because of the large solubility of the Nd^{3+} ions into the Ba^{2+} sites. Moreover, the hole concentration can be systematically varied to control the physical properties.

The orthorhombic $NdBa_2Cu_3O_{7-\delta}$ compound is isomorphic with $YBa_2Cu_3O_{7-\delta}$ (Pmmm). With the increase of Nd content x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ the orthorhombic distortion increases, and the compound becomes tetragonal at $x\sim0.2$ (P/4mmm). The tetragonal structure is isomorphic with the tetragonal form of $YBa_2Cu_3O_6$.[6,7] In general, the orthorhombic system consists of two Cu(2)O(2)O(3) layers separated by a plane of Nd ions. The unit of CuO_2 and Nd planes are separated by a CuO_3 ribbon consisting of a BaO(4) plane, a Cu(1)O(1) chain along the b axis, and another BaO(4) where Nd can substitute for Ba. Depending on the amount of substitution of Nd for Ba, there the nearly filled Cu(1)O(1) chains along the b axis and variable filling of the O(5) sites along the a axis maintain charge balance. The superconducting transition temperatures (T_c) as a function of composition (x) in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ compounds show two plateaus, the first at ~90 K for $0\leq x<0.1$ and the second at approximately 40 K for $0.1<x<0.3$. The compound becomes semiconducting at $x>0.4$.[6,8]

Although the physical properties in this system have been reported by many researchers,[2–8] investigations of the variation of electronic structure on these compounds related to the hole concentration and T_c are still in infancy. Soft x-ray-absorption spectroscopy using synchrotron radiation is a powerful tool for the investigation of unoccupied states at the O and Cu sites in high-T_c cuprates. It is a general agreement that hole states in the p-type superconductors are localized on the oxygen sites. Moreover, there are generally several nonequivalent oxygen sites in the cuprate superconductors. It is therefore expected that the O K-edge x-ray-absorption spectrum shows the multiple pre-edge peaks due to different environments of oxygen. Although the conducting holes were determined to exhibit dominantly in-plane O $2p_{x,y}$ characters,[9,10] several experiments and theories indicate that the out-of-plane oxygen can also play a relevant role in T_c.[11–13] It is our aim in this study to understand the distribution of hole carriers among different sites and their role in superconductivity in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system as a function of the Nd doping. Although the electronic structure of these materials has been measured by electron energy loss spectroscopy (EELS) technique, the energy resolution in those studies is only 1.2 eV.[6] Therefore, the detailed electronic structure near the Fermi level may have been lost. In this paper, we report high-resolution soft-x-ray absorption measurements at the O *K* edge and Cu *L* edge in series of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ samples with x between 0 and 0.6 using a bulk-sensitive x-ray-fluorescence-yield detection method.

II. EXPERIMENTS

Details on the preparation of samples were reported elsewhere.[6] In brief, the materials with the compositions of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ were prepared by solid state reaction of Nd_2O_3, $BaCO_3$, and CuO. These samples were first calcined three times in CO_2 free air at 890 °C for 24 h with intermediate grinding to insure homogenization of the cations. The samples were then annealed in 1% O_2 for 48 h at 950 °C with approximately 48 h at 450 °C in 100% O_2 to fully oxygenate the samples. The samples are all confirmed to be single phase by x-ray diffraction (XRD) and differential thermal analysis.

The x-ray-absorption measurements were carried out using the 6-m high-energy spherical grating monochromator (HSGM) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. The x-ray-fluorescence yield spectra were recorded using a microchannel plate (MCP) detector.[14] This detector consists of a dual set of MCP's with an electrically isolated grid mounted in front of them. For x-ray fluorescence detection the grid was set to a voltage of 100 V, while the front of the MCP's was set to -2000 V, and the rear to -200 V. The grid bias insured that positive ions would not be detected while the MCP bias insured that no electrons were detected. The MCP detector was located ~2 cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon flux (I_0) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All the absorption measurements were normalized to I_0. The photon energies were calibrated within accuracy of 0.1 eV using the O *K*-edge absorption peak at 530.1 eV and Cu L_3 white line at 931.2 eV of CuO compound. The monochromator resolution was set to ~0.22 eV and ~0.45 eV at O 1*s* and Cu 2*p* absorption edges, respectively. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows O *K*-edge x-ray-absorption spectra for a series of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ samples with $x=0$–0.6 obtained using the total x-ray fluorescence yield technique. The prominent features in the O 1*s* absorption edge for samples with $x=0.6$ [Fig. 1(g)], are two strong pre-edge peaks at ~528.2 eV and ~529.2 eV with a shoulder at ~527.5 eV, and a broad peak at ~537.5 eV. The low-energy peaks with energy below 532 eV are ascribed to transitions from the O 1*s* core electrons to holes with 2*p* character on the oxygen sites. The high-energy peaks above 532 eV are attributed to continuum absorption to empty *d* states or *f* states of Nd and Ba hybridized with O 2*p* states and show almost no dependence on the Nd doping. However, due to the energy variation of x-ray penetration depth, the x-ray-absorption spectra via x-ray fluorescence measurements may induce some deviation in peak heights. The O *K*-edge absorption spectra for various compounds with different x values in Fig. 1 were normalized to have the same height at the main peak of ~537.5 eV and were not corrected for this effect.

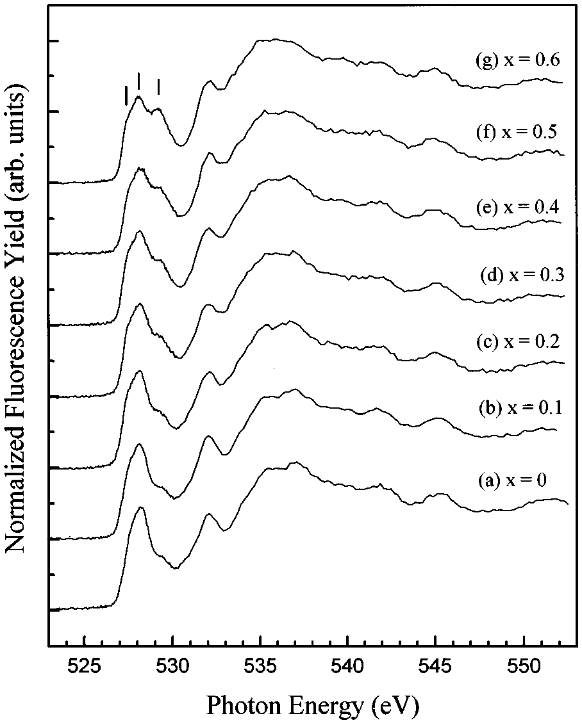

FIG. 1. O *K*-edge x-ray-absorption spectra for the series of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ samples with $x=0$–0.6. The absorption spectra for various compounds with different x values were normalized to have the same height at the main peak of ~537 eV.

In the crystal structure of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$, one expects four nonequivalent oxygen sites, O(2) and O(3) within the $Cu(2)O_2$ layers, O(4) in the BaO planes, and O(1) in the Cu(1)O chains along the *b* axis. Here, we assume that the increase in symmetry has no effect on the binding energies and that the binding energies for O(1) and O(5) are equivalent. The observed multiple pre-edge peaks in Fig. 1 may be related to different binding energies of O 1*s* levels of nonequivalent oxygen sites. The O 1*s* binding energies for the different oxygen sites can be estimated using the band-structure calculations. The $NdBa_2Cu_3O_{7-\delta}$ compound is isomorphic with orthorhombic $YBa_2Cu_3O_{7-\delta}$. According to the calculations in $YBa_2Cu_3O_{7-\delta}$ by Krakauer *et al.*, the relative O 1*s* binding energies decrease relative to O(2) by 0.09, 0.29, and 0.69 eV for O(3), O(1), and O(4), respectively.[15] The lowest O 1*s* binding energy is also assigned to O(4) atom in the apical sites by Zaanen *et al.*[16] In O *K*-edge x-ray-absorption spectra of $YBa_2Cu_3O_{7-\delta}$, the prepeaks at ~527.8 eV are attributed to transitions into O 2*p* holes in the apical oxygen sites and CuO chains. The high-energy pre-edge peak at ~528.5 eV is ascribed to transitions into O 2*p* hole states within the CuO_2 planes.[17,18] When oxygen is removed from $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ compounds, the system behaves analogously to $YBa_2Cu_3O_{7-\delta}$ with a decrease in total hole concentration and a corresponding decrease in T_c.[19] In addition, the O 1s absorption spectrum of $NdBa_2Cu_3O_7$ shows the same features as seen in $YBa_2Cu_3O_{7-\delta}$ with δ=0. We therefore adopt the same scheme in the assignment of present O 1s absorption spectra. The low-energy prepeaks at ~527.5 eV, as shown in Fig. 1, are due to the superposition of O 2p hole states originated from the apical oxygen sites and CuO chains. The high-energy prepeak at ~528.2 eV arises from O 2p holes in the CuO_2 planes. The absorption peak at ~529.2 eV is assigned to a $3d^{10}L \rightarrow$O $1s^{-1}3d^{10}$ transition, i.e., a transition into O 2p states hybridized with the upper Hubbard band (UHB) with predominantly Cu 3d character. Due to the strong on-site correlation on the copper sites in the cuprate compounds, such a band has always been assumed to exist.[20] Because the substitution of Nd^{3+} for Ba^{2+} will donate the electrons, this results in canceling a hole within the CuO_2 planes. As shown in Fig. 1, the peak at ~528.2 eV originated from the O 2p holes states in the CuO_2 layers decreases in intensity with increasing the dopant concentration of Nd. This gives an evidence in support of the filling of holes in the CuO_2 planes by increasing the Nd concentration in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system. As a result, the superconducting transition temperature for the series of samples decreases with increasing the Nd^{3+} doping. Takita *et al.* have measured the Hall number per Cu for these compounds versus Nd concentration.[21] They observed a monotonic decrease in the Hall number with an increase in the Nd content x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$. This data is consistent with our observation (Fig. 1). The present x-ray-absorption data is also consistent with heat-capacity and inelastic-neutron measurements which indicate hole filling with increasing compositional parameter x in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system.[22,23]

In order to investigate the hole distribution among different oxygen sites as a function of Nd doping, these pre-edge features shown in Fig. 1 were analyzed by fitting Gaussian functions to each spectrum. The integrated intensity of each pre-edge peak, normalized against the intensity of the main peak at ~537.5 eV, is plotted as a function of compositional parameter x in Fig. 2. It can be seen from Fig. 2(a) that the hole content from the CuO_2 planes decreases monotonically with increasing the Nd doping, while that from apical oxygen sites and CuO chains increases slowly. For low levels of Nd doping, the holes are located mainly in the CuO_2 planes. Conversely, at higher Nd doping, the holes are located predominantly O(1)/O(5) and O(4) in the CuO_3 ribbons. Furthermore, the peak at ~529.2 eV originated from the upper Hubbard band shows an increase in intensity when the Nd doping increases, as shown in Fig. 2(b). The changing intensity of the structure at ~529.2 eV is related to the well-known transfer of spectral weight from the upper Hubbard band to the doping-induced low-energy prepeak[24] which has also been observed in O 1s absorption spectra of other hole-doped cuprate superconductors.[25,26]

Based on the neutron diffraction studies on the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system, two facts are known.[6] First, the total O content increases to balance the charge of the excess Nd. Second, the number of O(1) atoms at (0,1/2,0) positions on the chain sites decreases by approximately 0.5x while the antichain O(5) site at (1/2,0,0) positions occupancy increases approximately as x. This suggests that a Nd on a Ba site always causes an O to occupy an adjacent O(5) site. In order to maintain charge balance, half of these O are additional atoms incorporated in the structure, while the other half are relocated from O(1) sites. Thus, in addition to the creation of fivefold Cu chain sites by occupancy of the O(5) sites, the removal of a chain O(1) creates two nonfourfold planar coordinated Cu chain atoms. Disruption of fourfold Cu chains by adding extra Nd then becomes analogous to $YBa_2Cu_3O_{7-\delta}$ for increasing δ.[27] Therefore, chemical substitution of Nd for Ba sites creates nonfourfold planar coordinated coppers on the chain sites either by introducing an extra O into the structure corresponding to adding a hole to the chains, or robbing a chain O from elsewhere in the structure. According to the calculations of Gupta *et al.*, these sites do not result in hole transfer from the chains to the conducting CuO_2 planes.[28] The charge transferred to the CuO_2 plane is therefore much lower than that introduced into the chain upon doping. Consequently, the hole concentration in the CuO_3 ribbons increases as the Nd doping increases. The O 1s absorption spectra in Fig. 1 give evidence for such an increase of O 2p hole states from the apical oxygen and CuO chains. It can clearly be seen from Fig. 2 by the increase in intensity for the pre-edge peak at ~527.5 eV when going from x=0 to 0.6.

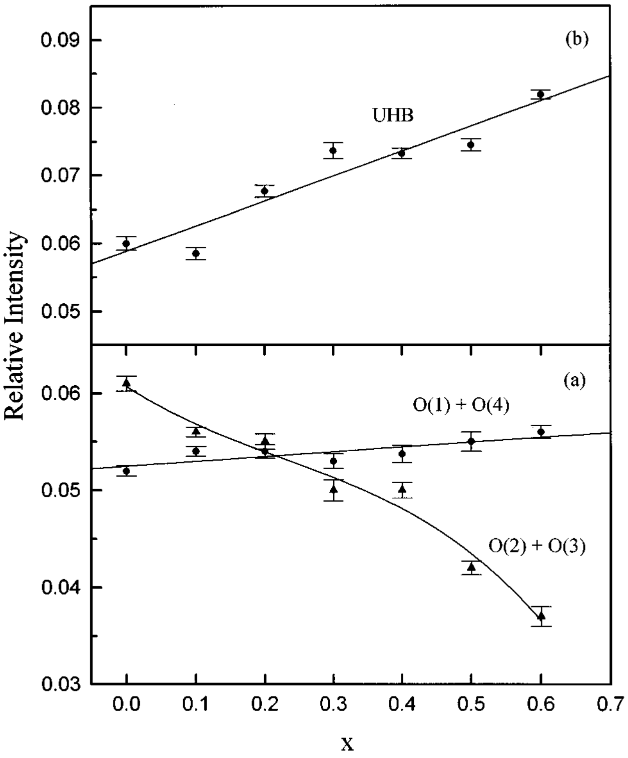

FIG. 2. Dependence on Nd content x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ of the intensity of hole states on oxygen sites originated from the (a) CuO_2 planes [O(2) and O(3)] and CuO_3 ribbons [O(1)/O(5) and O(4)], and (b) upper Hubbard band (UHB). The curves are drawn as a guide for the eyes.

It has been experimentally shown that processing $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ at higher temperatures results in higher T_c's.[6,29] The variability in T_c as a function of processing conditions was explained by the number of fourfold coordinated coppers on the chains which can be varied by differing the amounts of paired and unpaired Nd^{2+} substituted for Ba^{2+}, resulting in more or less hole transfer from the chains to the planes.[6] This hypothesis is further tested by processing

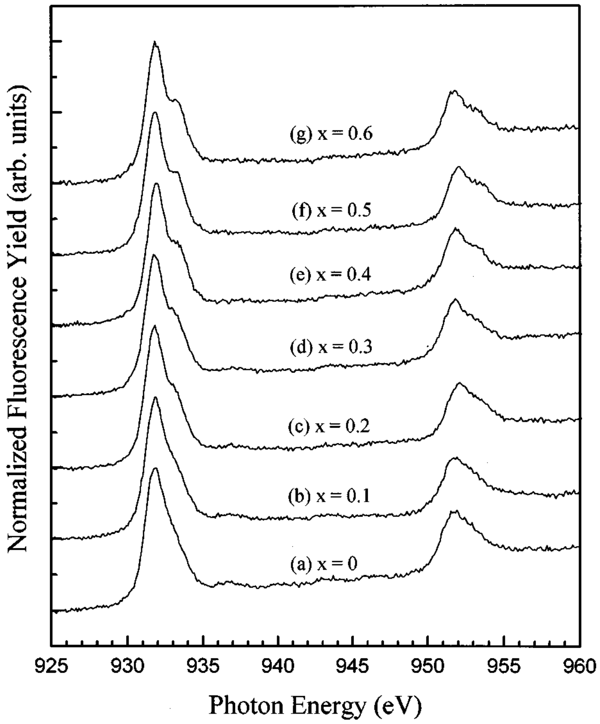

FIG. 3. Copper L_{23}-edge x-ray-absorption near-edge structure spectra of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ for $x=0$–0.6.

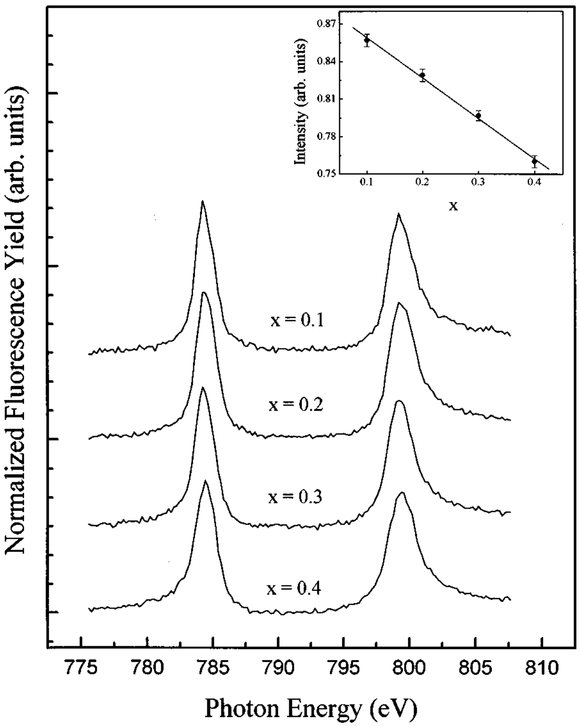

FIG. 4. Ba $3d$-edge x-ray-absorption spectra of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ with $x=0.1$, 0.2, 0.3, and 0.4. Inset is the plot of the intensity at peak ~784.2 eV as a function of the compositional parameter x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$. The curve is drawn as a guide for the eyes.

$Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ at high temperature in a low pressure O_2 where there is a stronger tendency of the excess Nd to pair to preserve charge balance. This results in fewer disrupted fourfold-coordinated coopers on the chain sites corresponding to increased hole transfer from the CuO chains to CuO_2 planes. As a result, processing $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ in a low pressure O_2 at high temperature leads to a higher T_c for a given x.[30]

Therefore, the effect of the excess Nd in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ is to reduce hole concentration in the CuO_2 plane and the number of fourfold coordinated coppers on the chains. Those two effects result in the decrease in T_c with increasing the Nd content x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$.

The peak at ~533.8 eV may be due to surface contamination since this peak changes its intensity from sample to sample and exhibits a greater intensity in surface-sensitive total-electron yield spectra. Existence of surface contamination has been reported by many researchers. Iqbal *et al.* suggested that this peak arises from absorption of hydrides, water, and CO_2 on the surface.[31]

The Cu L_{23}-edge x-ray-fluorescence yield spectra of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ for $x=0$–0.6 in the energy range of 925 to 960 eV are shown in Fig. 3. For $x=0$ shown in Fig. 3(a), the Cu L_3-edge absorption spectrum is asymmetric with a tail extending to higher energies and can be decomposed into two lines at 931.8 eV and ~933.0 eV, respectively. The spectral shape in Cu L_3 absorption edge for samples with $x=0$ is similar to that of single crystalline $YBa_2Cu_3O_{7-\delta}$ for the $E\|ab$ plane.[32] For $x=0.6$, in addition to an excitonic peak at 931.8 eV, a more pronounced shoulder at ~933.3 eV is realized as shown in Fig. 3(g). The samples with $x=0.6$ show the similar spectra features in Cu L_3 absorption spectra as single crystalline $YBa_2Cu_3O_{7-\delta}$ for the $E\|c$ axis.[32] The excitonic peaks at 931.8 and 951.6 eV shown in Fig. 3 are ascribed to the transitions from the $\mathrm{Cu}(2p_{3/2,1/2})3d^9$-O $2p^6$ ground states (formal Cu^{+2} state) to the $\mathrm{Cu}(2p_{3/2,1/2})^{-1}3d^{10}$-O $2p^6$ excited states. The high-energy shoulders, first reported by Bianconi *et al.* for $YBa_2Cu_3O_{7-\delta}$, are assigned as transitions from the $\mathrm{Cu}(2p_{3/2,1/2})3d^9L$ ground state (formal Cu^{+3} state) to the $\mathrm{Cu}(2p_{3/2,1/2})^{-1}3d^{10}L$ excited state, where L denotes the O $2p$ ligand hole.[33] For samples with increasing Nd doping, the shoulders shift to higher energy ~0.3 eV from $x=0$ to 0.6. Because there are two types of Cu sites in the unit cell for the series of compounds, these high-energy shoulders can be identified as the holes in the CuO_2 layers and CuO_3 ribbons. As mentioned previously, for low levels of Nd doping, the holes are located mainly in the CuO_2 planes. Conversely, at higher Nd doping for $x=0.6$, the hole content of the CuO_3 ribbons dominates that of CuO_2 planes. We therefore ascribed the shoulder at ~933.0 eV for sample with $x=0.6$ to transitions predominantly into Cu(1) atoms in the CuO_3 ribbons influenced by holes on O(1) O(5) and O(4) atoms. The shoulder at ~933.3 eV for sample $x=0$ arises from mainly $\mathrm{Cu}(2)3d^9L$ defected states to $\mathrm{Cu}(2)2p^{-1}3d^{10}L$ excited states, where L denotes the ligand hole on O(2) and O(3) atoms in the CuO_2 planes. The energy shift may be due to the fact that holes located in the squares of the CuO_3 ribbons cause a larger energy shift than the more delocalized holes in the CuO_2 planes.

The Ba $3d$ edge x-ray-absorption spectra of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ with $x=0.1$, 0.2, 0.3, and 0.4 are shown in Fig. 4. Two strong peaks at ~784.2 and ~799.4 eV are originated from the transitions of the spin-orbit splitting Ba $3d_{5/2}$,$3d_{3/2}$ states into the empty f states. The overall shape of the Ba $3d$ edge x-ray-absorption spectrum is the same for compounds with different x values, but its intensity decreases linearly with increasing the Nd doping in the compounds as shown in the inset. This confirms the Ba atoms in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system are partially substituted by Nd atoms.

IV. CONCLUSION

X-ray-absorption spectra at the O $1s$ and Cu $2p$ edges of $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ with $x=0$–0.6 were performed to search for the variation of electronic structure related to the superconducting properties. Near the O $1s$ edge, the pre-edge peaks at ~527.5 eV are attributed to O $2p$ holes in the apical oxygen sites and CuO chains. The high-energy pre-edge peak at ~528.2 eV is ascribed to the transitions to O $2p$ hole states within the CuO_2 planes. The chemical substitution of Nd^{3+} for Ba^{2+} in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system results in an increase in oxygen content, a decrease in hole concentration in CuO_2 planes, and a change in the distribution of oxygen ions in the lattice. In addition, the distribution of holes on the different oxygen sites has been derived for $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ in the doping range $0\leqslant x\leqslant 0.6$. For low levels of Nd doping, the holes are located mainly in the CuO_2 planes. At higher Nd doping, the holes are located predominantly in the CuO_3 ribbons. The depression in T_c for the $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ system correlates closely with the hole concentration in the CuO_2 planes and the number of disrupted fourfold coordinated coppers on the chain sites. The high-energy shoulders in the Cu L_{23}-edge x-ray-absorption spectra arise from Cu $3d^9\underline{L}$ defected states to Cu $2p^{-1}3d^{10}\underline{L}$ excited states, where $\underline{L}$ denotes the ligand hole on the CuO_3 ribbons and the CuO_2 planes.

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