

# Electronic structure of $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$ : Comparison between substitutional and vacancy doping

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The change of the electronic structure across the metal-insulator transition in a Mott-Hubbard system  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  has been investigated by x-ray absorption and photoemission spectroscopy. The results are compared with  $\text{CeTiO}_{3+\delta}$ , where hole doping is achieved by excess oxygen instead of Sr substitution. It is found that additional doped-hole states are created in the insulator gap for both cases, while the density of states at the Fermi level in  $\text{CeTiO}_{3+\delta}$ , is nearly half of that in  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  at the same nominal doping. This suggests a strong reduction in the mobility of carriers due to cation vacancies produced by excess oxygen. [S0163-1829(99)03803-5]

## I. INTRODUCTION

Stimulated by the discovery of high-temperature superconductors, physical properties of perovskite-type transition-metal (TM) oxides have been intensively studied in the last few years. This has led to an understanding of their rich physical properties,<sup>1</sup> and has also provided an opportunity to investigate the anomalous electronic structure of TM oxides further near the metal-insulator (MI) transition. Photoemission spectroscopy of early TM oxides revealed that there are two electronic features, coherent and incoherent parts, at and near the Fermi level ( $E_F$ ), respectively. The intensity ratio changes as a function of  $U/W$  ( $U$  is the on-site Coulomb energy, and  $W$  is the bandwidth),<sup>2-4</sup> and the experimental results are consistent with dynamical mean-field theory results.<sup>5</sup>

In early studies, the doping level was controlled mainly of the substitution of atoms having different valencies, e.g.,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , etc. The doping level can also be controlled by changing the oxygen content, e.g.,  $\text{La}_2\text{CuO}_{4+\delta}$  shows a MI transition, and the excess oxygen tends to locate at interstitial sites in the layered perovskite structure,<sup>6</sup> while it leads to a cation vacancy in materials with a three-dimensional perovskite structure as in  $\text{LaMnO}_{3+\delta}$ ,<sup>7</sup>  $\text{CeTiO}_{3+\delta}$ , etc. The difference in transport properties between substitutional doping and vacancy doping has been recognized in recent times.<sup>8</sup> Recent study shows that the calculated electronic structure is different between  $\text{SrTiO}_{3-\delta}$  and  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ , where  $\text{SrTiO}_3$  is a band insulator.<sup>9</sup> These results give rise to the question of whether vacancy doping causes different modifications of electronic states as compared to substitutional doping.

In order to study the difference of the electronic structure between substitutional doping and vacancy doping in the vicinity of the Mott-Hubbard insulating state, we have studied the electronic structure of  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  by using x-ray-absorption (XAS) as well as ultraviolet photoemission spec-

troscopy (UPS), and compared the result with that of  $\text{CeTiO}_{3+\delta}$  (Ref. 10).  $\text{CeTiO}_3$  is a Mott-Hubbard insulator with an on-site  $U$  of about 2–3 eV,<sup>10-12</sup> but with a variable-range-hopping-like resistivity due to defects. On substituting Ce with Sr, or increasing the oxygen content, the system exhibits an insulator-to-metal transition.<sup>8</sup> Ce-based systems are thus similar to La-based systems, namely  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  and  $\text{LaTiO}_{3+\delta}$  in terms of MI transitions caused by hole doping due to Sr substitution or excess oxygen.<sup>13</sup> However, the Ce systems show differences in their transport and thermodynamic properties such as electrical resistivity, magnetic susceptibility, etc.<sup>8,14</sup> Oxygen 1s XAS shows that hole states with substantial O 2p character evolve as a function of  $x$ , while UPS results show that the gap (<100 meV) observed for the  $x=0$  compound closes across the MI transition due to the doped-hole states. Both vacancy-doped and substituted systems exhibit a coherent feature at  $E_F$  and an incoherent feature away from  $E_F$  which corresponds to the lower Hubbard band. Importantly, we found that the relative density of states (DOS) at  $E_F$  for the vacancy doping is half of that for the substitutional doping at the same doping content. In conjunction with the electrical resistivity data, we conclude that the mobility of carriers is strongly reduced in the vacancy doping case, to give an order-of-magnitude higher resistivity beyond the carrier density contribution.

## II. EXPERIMENT

Polycrystalline specimens of  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x=0, 0.05$ , and 0.2) and  $\text{CeTiO}_{3.1}$  were prepared from congruent melt in an Ar arc furnace, using  $\text{CeO}_2$  (99.9% purity),  $\text{SrO}$  (99% purity),  $\text{TiO}_2$  (99.9% purity), and Ti metal (99.9% purity). The oxygen concentration and the cation concentrations were estimated by thermogravimetric analysis and electron-probe microanalysis, respectively, to an accuracy of  $\pm 0.01$  of the nominal concentrations.

XAS measurements were carried out at the synchrotron

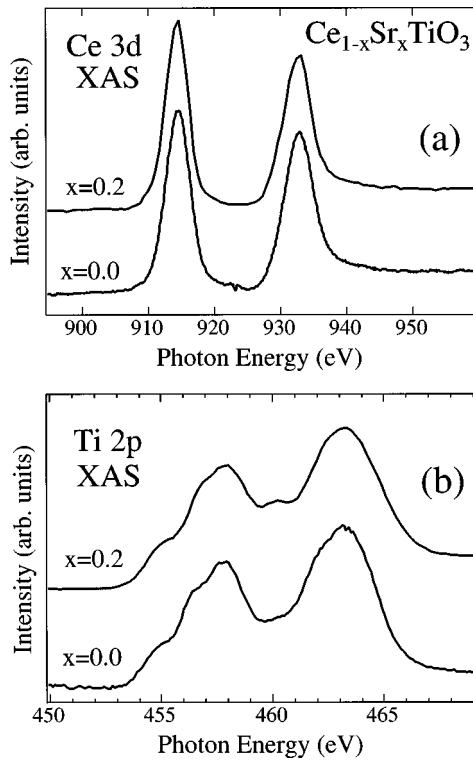


FIG. 1. (a) Ce  $3d$ - $4f$  XAS spectra of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0$  and  $0.2$ ), which confirm the trivalent nature of Ce ions by the absence of the  $Ce^{4+}$  satellite. (b) Ti  $2p$ - $3d$  XAS spectra of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0$  and  $0.2$ ).

radiation facility (UVSOR) of the Institute for Molecular Science (IMS), Okazaki, by using BL2b1 in the total electron yield mode at a resolution of 1 eV. Samples were scraped *in situ* with diamond files to obtain clean surfaces. UPS measurements with better energy resolution (0.1 eV) were performed using a home-built spectrometer with a He discharge lamp (He I, 21.2 eV). For UPS measurements, samples were scraped *in situ* at about 60 K to obtain clean surfaces.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows Ce  $3d$ - $4f$  XAS spectra of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0$  and  $0.2$ ). The spectra for  $x=0.0$  and  $0.2$  are very similar to each other, and show two peaks due to the spin-orbit splitting at 915 and 933 eV, respectively. An important point to note in both spectra is the absence of a satellite feature 6 eV above the main peak, which is characteristic of tetravalent Ce. The spectra for both compositions thus correspond only to a trivalent Ce ion. This indicates that the change in valency due to Sr substitution, and thus, carrier number, takes place only in the Ti  $3d$ -O  $2p$  manifold.

In order to study these changes, we have performed Ti  $2p$ - $3d$  XAS as shown in Fig. 1(b). The Ti  $2p$  spectrum for  $x=0.0$  is very similar to that of  $LaTiO_3$ .<sup>15,16</sup> The spectral features of  $x=0.0$  correspond to  $Ti^{3+}$ , and are well explained by a cluster calculation.<sup>14</sup> Upon Sr substitution, we see small changes at higher photon energy but a negligible change in the leading edge of the spectrum. This suggests that hole doping due to Sr substitution up to  $x=0.2$  results in negligible changes in the Ti  $3d$  partial DOS near  $E_F$  in the unoccupied part.

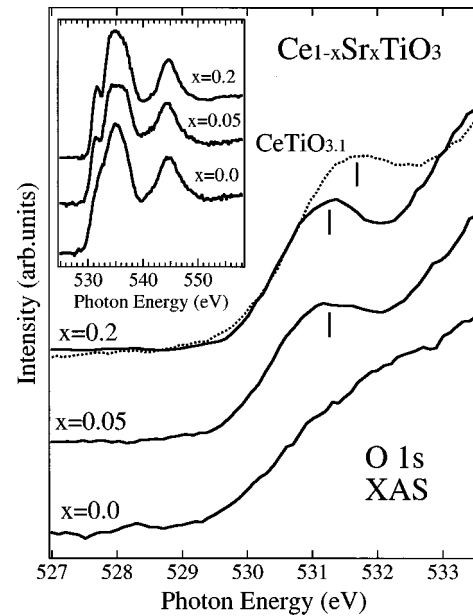


FIG. 2. O  $1s$ - $2p$  XAS spectra of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0, 0.05$ , and  $0.2$ ) and  $CeTiO_{3.1}$  (dotted line) (Ref. 10). The inset shows the same over a wide energy scale.

The O  $1s$ - $2p$  XAS spectra of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0, 0.05$ , and  $0.2$ ) are shown in Fig. 2. The overall features of the O  $1s$  XAS spectra for three compounds (shown in the inset) are similar, having three structures at about 532-, 535-, and 544-eV photon energy. By comparing the experimental result with that of  $LaTiO_3$ ,<sup>17</sup> the structure around 544 eV is assigned to the Ti  $4sp$  band. The prominent peak centered at 535 eV is due to Ce  $5d$  states with an O  $2p$  admixture, while the small structure around 532 eV is ascribed to O  $2p$  states hybridized with the upper Hubbard band. We find that the weak feature around 532 eV in the  $x=0.0$  spectrum evolves systematically with Sr substitution.

Since the O  $1s$  XAS spectra represent an O  $2p$  partial DOS hybridized with an unoccupied Ti  $3d$  partial DOS, it is obvious that the additional doped-hole states, having substantial O  $2p$  character, grow at the bottom of conduction band as a function of  $x$  across the MI transition.<sup>18</sup> To see this more clearly, we enlarge the O  $1s$  XAS spectra near  $E_F$  in Fig. 2, where we clearly see the weak broad feature at 532 eV at  $x=0.0$  showing a strong and systematic enhancement at  $x=0.05$  and  $0.2$ . These spectral changes are caused by the hole doping due to substitution of Ce atoms with Sr atoms. The XAS result indicates that these doped-hole states with substantial O  $2p$  character increase with substitution, and may cause a MI transition beyond a critical concentration  $x \sim 0.05$ . While early TM compounds are usually thought to be Mott-Hubbard (MH) insulators in the Zaanen-Sawatzky-Allen scheme,<sup>19</sup> the present results indicate substantial charge-transfer nature of early TM compounds due to strong hybridization, as theoretically pointed out earlier.<sup>20</sup>

In order to confirm whether the evolution of the DOS observed with XAS corresponds to the MI transition, we have performed UPS measurements. Figure 3 shows UPS spectra in the vicinity of  $E_F$  of  $Ce_{1-x}Sr_xTiO_3$  ( $x=0.0, 0.05$ , and  $0.2$ ) obtained using He I resonance line (21.2 eV). The spectrum of  $CeTiO_3$  has a broad structure around 1.2-eV

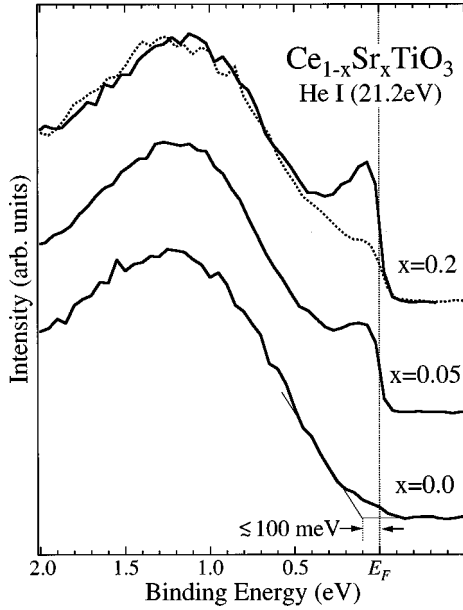


FIG. 3. UPS spectra of  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x=0.0, 0.05, \text{ and } 0.2$ ) measured with He I photons (21.2 eV), showing the MI transition as a function of  $x$ . The dotted line shows the UPS result of  $\text{CeTiO}_{3.1}$  (Ref. 10). The thin line on the  $x=0$  spectrum is a model DOS.

binding energy, and no Fermi-edge cutoff. The latter indicates an energy gap, and the upper-limit value of the gap was estimated to be about 100 meV by using a model DOS as shown in Fig. 3.<sup>21</sup> On increasing  $x$ , a feature evolves at  $E_F$  and, as a result, closes the gap in  $x=0.05$ , consistent with the transport measurements.<sup>8</sup> In  $x=0.2$ , in addition to the broad structure around 1.2 eV, we clearly see a sharp peak at  $E_F$ . This result confirms that the spectral changes in XAS in Fig. 2 correspond to the MI transition.

$\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  and  $\text{CeTiO}_{3+\delta}$  systems provide a very good case to study the change in the DOS due to substitutional and/or vacancy doping in the same parent MH insulator  $\text{CeTiO}_3$ . To compare the evolution of electronic structure through the MI transition controlled by excess oxygen ( $\delta$ ) or Sr content ( $x$ ), we show UPS and XAS results on  $\text{CeTiO}_{3.1}$  in Figs. 2 and 3, respectively, with broken lines. Note that the nominal hole concentrations of  $\text{CeTiO}_{3.1}$  and  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  are the same. We find that the changes in XAS and UPS spectra across the MI transition are similar as a whole for both cases; that is, doping causes a closure of the gap at  $E_F$ . However, we notice that the intensity at  $E_F$  in the UPS spectrum of  $\text{CeTiO}_{3.1}$  is smaller than that of  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ , while the intensity of the doped-hole states in the XAS spectrum of  $\text{CeTiO}_{3.1}$  is higher than that in  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ . This indicates that the position of the center of the doped-hole states is different between the two systems, and we note that the prepeak in the XAS spectrum is nearly 0.4 eV higher in the  $\text{CeTiO}_{3.1}$  spectrum (Fig. 2).

The observed UPS spectral change in Fig. 2 is consistent with previous reports on early TM oxides with  $d^1$  configurations as a function of hole concentration.<sup>17,22,23</sup> In particular, the broad peak around 1.2 eV for the semiconducting phase is assigned to the lower Hubbard band, and the binding energy (1.2 eV) is a measure of half of the on-site Coulomb energy ( $U$ ). Thus the structures at  $E_F$  and around 1.2 eV, for

$x=0.05$  and 0.2, are ascribed to the coherent part of spectral weight derived from Ti 3d states and the incoherent part corresponding to the remnant of the lower Hubbard band, respectively. We notice that the states near  $E_F$  is sharper than that reported in earlier studies<sup>17,22,23</sup> because of the higher resolution and lower measurement temperature. The appearance of a feature in the occupied DOS due to Sr substitution is surprising, simply because hole doping by Sr substitution should create states in the unoccupied DOS. Thus the spectral changes in the occupied DOS confirm that Sr substitution also results in increasing the bandwidth ( $W$ ) or reducing  $U/W$ , and gives rise to the coherent feature at  $E_F$ , as predicted from the dynamical mean-field theory calculation.<sup>5</sup> On the other hand, in  $\text{CeTiO}_{3.1}$ , we know that the perovskite lattice cannot accommodate excess interstitial oxygen, and the system actually has cation vacancies. For small  $\delta$  ( $<0.06$ ), where the resistivity data exhibit a semiconducting behavior,<sup>8</sup> the induced holes are expected to be localized at the cation defects because the defect sites may have relatively negative potential. When more holes are induced, the localized states gradually broaden and change into delocalized states around  $\delta=0.1$ , where the resistivity shows a metallic behavior.<sup>8</sup> An important observation to be noted is that UPS results show that the DOS at  $E_F$  in  $\text{CeTiO}_{3.1}$  is half of that in  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ , though the nominal hole concentration is the same between the two compounds.<sup>24</sup> In summarizing the observed spectroscopic changes in relation to the substitutional doping vis-à-vis vacancy doping, we find that the observed changes can be due to (1) the  $U/W$  ratio difference between  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  and  $\text{CeTiO}_{3.1}$ , with the Sr-doped case having a larger bandwidth compared to the vacancy doped case; and (2) the formation and position of the new doped hole states as discussed earlier. The ratio of the occupied and unoccupied states in the quasiparticle band at  $E_F$  should be constant for a given doping level, provided that the change is solely caused by a  $U/W$  change in the absence of additional doped-hole states. However, in the present case, we observe that the additional doped-hole states are formed and positioned at different energies for  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  and  $\text{CeTiO}_{3+\delta}$ , as shown by the XAS. We believe this is an important difference in substitutional doping compared to vacancy doping, leading to the observed differences in the properties of the two systems.

At the temperature of measurement, the resistivity of  $\text{CeTiO}_{3.1}$  is  $\sim 30$  times larger than that of  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ .<sup>8</sup> This result, in conjunction with the present results, shows that if we assume a single-band model for the carriers, the mobility of the carriers is reduced by an order of magnitude in  $\text{CeTiO}_{3.1}$  compared to  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ . This shows that vacancy doping strongly reduces the mobility compared to the substitutional doping probably due to the increased disorder in  $\text{CeTiO}_{3+\delta}$  with cation vacancies.<sup>8</sup>

#### IV. CONCLUSION

We have presented XAS and UPS results on  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  across the MI transition as a function of Sr content ( $x$ ), and compared them with those of  $\text{CeTiO}_{3+\delta}$ . The O 1s XAS spectrum shows hole states with substantial O 2p character which evolve across the MI transition. UPS

shows that the energy gap ( $<100$  meV) observed at  $x=0$  closes due to the doped-hole states. These observations are quite similar to those reported on  $\text{CeTiO}_{3+\delta}$ . However, the intensity at  $E_F$  of UPS spectrum is only two times larger in  $\text{Ce}_{1-x}\text{Sr}_x\text{TiO}_3$  than in  $\text{CeTiO}_{3+\delta}$ , in spite of the 30-times difference in the electrical resistivity. This result indicates that vacancy doping strongly reduces the mobility of carriers compared to substitutional doping.

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- <sup>24</sup>Note also that the reduced intensity near  $E_F$  in UPS for  $\text{CeTiO}_{3,1}$  is compensated for by the increased intensity in XAS compared to the  $\text{Ce}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  spectra. The relative DOS at  $E_F$  was obtained by two independent normalization methods, using (1) the area under the curve or (2) the peak height of the lower Hubbard band. Both results are nearly identical to one another.