

## Effect of oxygen vacancies on electronic states of $\text{CaVO}_{3-\delta}$ and $\text{SrVO}_{3-\delta}$ : A photoemission study

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There are two structures in the photoemission spectra of  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  in the  $d$ -band region. One peak is within  $\sim 1$  eV of the Fermi level and has a sharp Fermi cutoff. The other is a broad peak centered at  $\sim 1.6$  eV. From our photoemission spectra of  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  both with oxygen vacancies ( $\delta \sim 0.1$ ) and without vacancies ( $\delta = 0$ ), it is shown that the relative intensity of the peak near the Fermi level for  $\text{CaVO}_{3-\delta}$  drastically decreases with decreasing oxygen vacancy concentration ( $\delta$ ). In contrast, no such drastic change in intensity is observed for  $\text{SrVO}_{3-\delta}$ . This difference in the effect of oxygen vacancies between  $\text{SrVO}_{3-\delta}$  and  $\text{CaVO}_{3-\delta}$  reflects the fact that a metal-insulator phase transition induced by bulk oxygen vacancies takes place in  $\text{CaVO}_{3-\delta}$  but not in  $\text{SrVO}_{3-\delta}$ .

### I. INTRODUCTION

Stimulated by the discovery of superconductivity in Cu oxides with doped carriers,<sup>1</sup> the effect of doped carriers on the electronic state of transition-metal (TM) oxides has once again become a subject of extensive study.<sup>2</sup> Many spectroscopic studies of Cu oxides have shown that carrier doping induces a spectral feature known as an "in-gap" state within the band gaps of the parent compounds.<sup>3</sup> Recently, it has been shown that carrier doping induces a similar spectral feature with cation  $3d$  character near the Fermi level ( $E_F$ ) in some Mott-Hubbard-type TM oxides.<sup>4,5</sup> Because of the difficulty of oxygen control, however, the effect of oxygen vacancies on electronic states in TM oxides has not yet been sufficiently studied. We believe that this oxygen effect plays an important role in realizing superconducting states in many Cu oxides,<sup>1-3</sup> and controls physical properties in TM oxides.

Until recently, it has been believed that  $\text{CaVO}_{3-\delta}$  is a typical metallic TM oxide. From our detailed x-ray-diffraction, dc-conductivity, and magnetic-susceptibility measurements, however, we have found that the stoichiometric material is an insulator.<sup>6</sup> In contrast,  $\text{SrVO}_{3-\delta}$  remains metallic even with stoichiometric oxygen content ( $\delta = 0$ ). To understand why oxygen vacancies induce a metal-insulator phase transition in  $\text{CaVO}_{3-\delta}$  but not in  $\text{SrVO}_{3-\delta}$ , it is important to study how the changes in the electronic structure due to oxygen vacancies differ between the two compounds.

In this Brief Report, we present the results of a photoemission spectroscopy (PES) study of  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  with some oxygen vacancies ( $\delta \sim 0.1$ ) and without vacancies ( $\delta = 0$ ). The formation of an electronic state due to oxygen vacancies near  $E_F$  is discussed in terms of the band model and the "in-gap"-state model.

### II. EXPERIMENTAL PROCEDURE

Single crystals of  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  were made by an infrared image furnace with double halogen lamps, as described elsewhere.<sup>6</sup> The oxygen content ( $3-\delta$ ) of the obtained as-cast  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  samples were determined by thermogravimetric analysis (TGA) to be 2.9 and 2.85, respectively. Electric resistivities of both as-cast samples show a metallic temperature dependence. However, after oxidation by annealing in air at 660°C for 1 h, the  $\text{CaVO}_{3-\delta}$  sample becomes an insulator. The oxygen content ( $3-\delta$ ) in this insulating phase is exactly 3.0. On the other hand,  $\text{SrVO}_{3-\delta}$  remains metallic even after oxidation ( $3-\delta = 3.0$ ).

Experiments were performed at the Photon Factory (Beam Lines 11C and 11D), National Laboratory for High-Energy Physics, using a double-pass cylindrical mirror analyzer. Total instrumental energy resolution was 0.1–0.3 eV full width at half maximum (FWHM), depending on the photon energies ( $h\nu$ 's) in the range 15–60 eV. The samples were cleaned *in situ* by scraping with a diamond file. The PES spectra were measured at room temperature. The cleanliness of the sample surfaces was confirmed by Auger electron spectroscopy and PES for the absence of extra features arising from contamination.

### III. EXPERIMENTAL RESULTS

#### A. Photoemission spectra

Figure 1 shows the PES spectra of as-cast  $\text{CaVO}_{2.9}$  (upper side) and  $\text{SrVO}_{2.85}$  (lower side) taken with photon energies ( $h\nu$ ) in the V  $3p \rightarrow 3d$  core adsorption region ( $h\nu = 50$  and 51.5 eV for  $\text{CaVO}_{2.9}$  and  $\text{SrVO}_{2.85}$ , respectively; crosses) and out of it ( $h\nu = 45$  eV for both oxides; open circles). Figure 2 shows the constant-initial-state

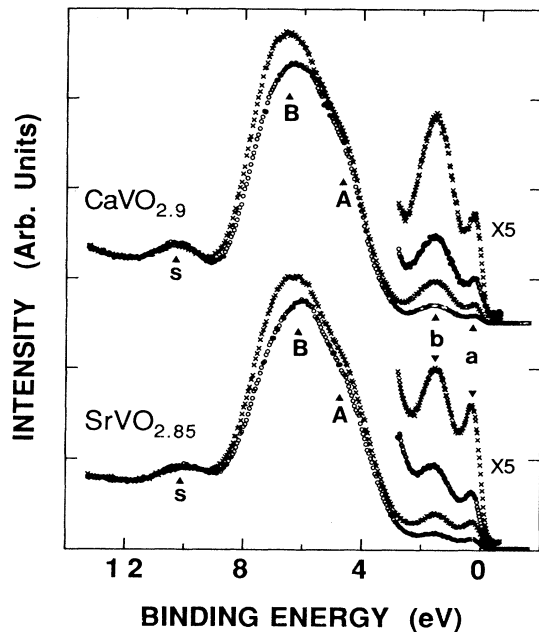


FIG. 1. Photoemission spectra of as-cast  $\text{CaVO}_{2.9}$  (upper side) and  $\text{SrVO}_{2.85}$  (lower side) samples taken with photon energies inside the V  $3p \rightarrow 3d$  core adsorption region ( $h\nu = 50$  and  $51.5$  eV for  $\text{CaVO}_{2.9}$  and  $\text{SrVO}_{2.85}$ , respectively; crosses) and outside it ( $h\nu = 45$  eV for both oxides; open circles).

(CIS) spectra of  $\text{CaVO}_{2.9}$  measured using photon energies from 25 to 60 eV. The spectra ( $a, b, A, B, s$ ) are taken at the binding energies of the peak positions in Fig. 1. As the photon energy reaches the  $3p-3d$  adsorption threshold, the V  $3d$ -electron emission is enhanced due to quantum interference between the direct photoemission process ( $3p^6 3d^n + h\nu \rightarrow 3p^6 3d^{n-1} + e$ ) and an Auger decay process following the  $3p$ -core photoadsorption ( $3p^6 3d^n + h\nu \rightarrow 3p^5 3d^{n+1} \rightarrow 3p^6 3d^{n-1} + e$ ).

Figure 3 shows the PES spectra taken with  $h\nu = 50$  eV

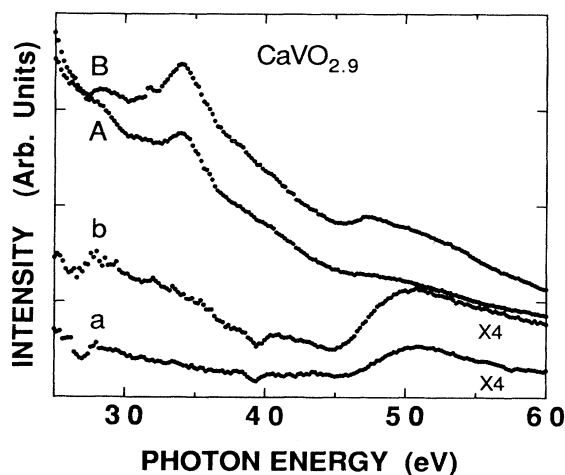


FIG. 2. Constant-initial-state spectra of  $\text{CaVO}_{2.9}$  for the photon energies from 25 to 60 eV. The spectra ( $a, b, A, B, s$ ) are taken at the binding energies of the peak position in Fig. 1.

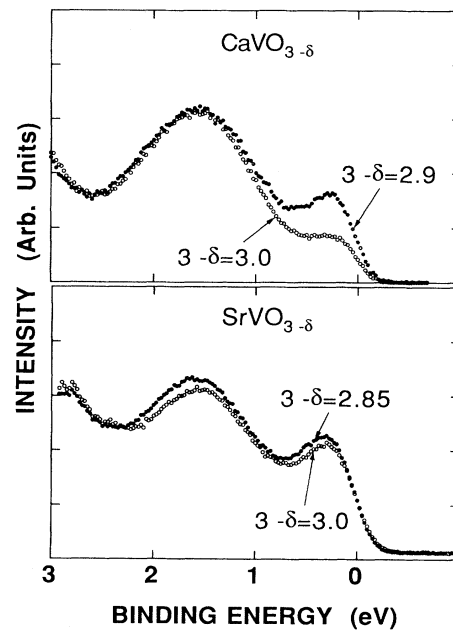


FIG. 3. Photoemission spectra of  $\text{CaVO}_{3-\delta}$  (upper side) and  $\text{SrVO}_{3-\delta}$  (lower side) samples with oxygen vacancies ( $\delta = 0.1$  and  $0.15$  for  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$ , respectively; solid circles) and without vacancies ( $\delta = 0$ ; open circles) in the V  $3d$ -band region ( $h\nu = 50$  eV).

in the V  $3d$ -band region of  $\text{CaVO}_{3-\delta}$  (upper side) and  $\text{SrVO}_{3-\delta}$  (lower side) with oxygen vacancies ( $\delta = 0.1$  and  $0.15$  for  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$ , respectively; solid circles) and without oxygen vacancies ( $\delta = 0$ ; open circles). In the spectra, a peak less than  $\sim 1$  eV below  $E_F$  with a sharp Fermi cutoff and a broad one centered at  $\sim 1.6$  eV are observed. Moreover, it is clear that the relative intensity of the peaks near  $E_F$  in  $\text{CaVO}_{3-\delta}$  becomes drastically weak with decreasing oxygen vacancy concentration ( $\delta$ ), but does not change in  $\text{SrVO}_{3-\delta}$ .

### B. Electronic structures of $\text{CaVO}_{3-\delta}$ and $\text{SrVO}_{3-\delta}$

A clear enhancement at the V  $3p$  core adsorption threshold can be seen in the PES spectra in Fig. 1 and the CIS spectra in Fig. 2. This resonance behavior indicates that the emission within  $\sim 3$  eV of  $E_F$  results from the occupied state of the V  $3d$  band.

From theoretical<sup>7</sup> and experimental<sup>8</sup> studies, it is well known that the O  $2p$  cross section gradually decreases with increasing photon energy above  $h\nu = \sim 20$  eV, while the V  $3d$  cross section resonantly increases at the photon energy corresponding to the V  $3p$  core excitation ( $h\nu = \sim 34$  eV) may be caused by a quantum interference between the direct photoemission process and an Auger decay process following the Ca  $3p \rightarrow 3d$  core adsorption. The CIS spectra in Fig. 2, therefore, indicate that the valence band in the binding energy 3–9 eV consists of bands having O  $2p$ , Ca  $3d$ , and V  $3d$  orbital components: the valence-band structures in the lower and higher binding-energy region

( $A$  and  $B$ , respectively, in Fig. 1) are identified as a nonbonding O  $2p$  structure and a bonding structure due to hybridization between the V  $3d$  and O  $2p$  orbitals, respectively. Small contributions from the Ca  $3d$  band are also observed in both valence structures.

The PES spectra of  $\text{SrVO}_{3-\delta}$  observed here is almost the same as previously reported PES spectra measured at low-temperature,<sup>9,10</sup> except for a slight difference in the feature at a binding energy of 9–12 eV (indicated by  $s$  in Fig. 1). This difference may arise from oxygen vacancies near the surface. Smith and Henrich<sup>11,12</sup> have observed from single-crystalline  $\text{V}_2\text{O}_3$  and  $\text{Ti}_2\text{O}_3$  that there is a distinct valence-band satellite in the PES spectra at higher binding energy than the O  $2p$  valence band in  $\text{V}_2\text{O}_3$ , but no satellite in  $\text{Ti}_2\text{O}_3$ . They have ascribed the lack of a valence-band satellite in  $\text{Ti}_2\text{O}_3$  to the presence of only one  $d$  electron per cation, which would imply a low intensity for this satellite feature. Since as-cast  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  have a  $3d^{1+2\delta}$  configuration, we expect to be able to observe a valence-band satellite in these as-cast materials. In the PES spectra of stoichiometric  $\text{CaVO}_3$  and  $\text{SrVO}_3$ , on the other hand, we do not observe any clear spectral features at a binding energy of 9–12 eV. We therefore infer that the stoichiometric materials have only one  $d$  electron per cation like  $\text{Ti}_2\text{O}_3$ .

#### IV. DISCUSSION

It is suggested from the calculated band structure<sup>13</sup> that strong bonding bands between V  $3d/4s$  and O  $2p$  orbitals exist in the higher binding-energy region of the valence band, and that an almost nonbonding O  $2p$  band exists in the lower binding-energy region of the valence band. The PES and CIS spectra of the valence band agree with the calculated band structure except for a slight difference in the energy position between the calculated and measured valence bands.

We now discuss the origin of the spectral feature near  $E_F$  in off-stoichiometric  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$ . In previous studies of similar spectral features near  $E_F$  in metallic TM oxides, two alternative explanations have been given. One is the coherent band model<sup>9</sup> and the other is the “in-gap”-state model.<sup>14</sup> We consider each of these in turn.

From an analysis of PES measurements of perovskitetype  $\text{Ti}^{3+}$  and  $\text{V}^{4+}$  oxides, Fujimori *et al.*<sup>9</sup> have suggested that the emission within  $\sim 1$  eV of  $E_F$  should be assigned to itinerant  $d$ -band states (corresponding to quasiparticle excitations or renormalized  $d$ -band states) and that the higher-energy structure in the  $d$ -band region is assigned to a remnant of the lower Hubbard band. They have argued that, with decreasing  $U/W$ , the upper and lower Mott-Hubbard bands approach each other and the spectral weight is transferred from both Hubbard bands to a region near  $E_F$ , where  $U$  and  $W$  are the  $d$ - $d$  Coulomb repulsion energy and the one-electron  $d$ -band width, respectively.

In the stoichiometric oxygen region, it has been shown from x-ray-diffraction measurements<sup>6,15</sup> that metallic  $\text{SrVO}_3$  has a cubic perovskite structure and insulating  $\text{CaVO}_3$  has an orthorhombically distorted perovskite

structure. The orthorhombic distortion in  $\text{CaVO}_3$  will give rise to a narrower  $W$  compared with that of the cubic  $\text{SrVO}_3$ .<sup>15</sup> Assuming that  $U$  is the same for both oxides, the ratio  $U/W$  for  $\text{CaVO}_3$  is larger than for  $\text{SrVO}_3$ . If this is indeed the case, then the coherent band model<sup>9</sup> predicts that the spectral weight in  $\text{SrVO}_3$  will be more strongly transferred from the upper and lower Hubbard bands to the region near  $E_F$ . Hiroi and Takano<sup>15</sup> have recently shown that metallic  $\text{CaVO}_{3-\delta}$  has a cubic structure. Therefore, it may be possible that the spectral feature near  $E_F$  in off-stoichiometric  $\text{CaVO}_{3-\delta}$  can be assigned to an itinerant  $d$ -band state like that observed for stoichiometric  $\text{SrVO}_3$ .<sup>9</sup> A similar metal-insulator phase transition induced by the effect of the crystal distortion has been observed for  $\text{VO}_2$ .<sup>16</sup>

Alternatively, in many insulating TM oxides (including the parent compounds of Cu-oxide superconductors) doped with extra carriers (by the substitution of metal ions or the introduction of oxygen vacancies), it can be argued<sup>14</sup> that an “in-gap” state appears near the top of the valence band and that  $E_F$  is located just above it. Hence the spectral feature near  $E_F$  in off-stoichiometric  $\text{CaVO}_{3-\delta}$  may also be assigned to the “in-gap” states induced by oxygen vacancies.

If we assume that the spectral feature near  $E_F$  consists of an itinerant  $d$ -band state, the spectral weight centered at  $\sim 1.6$  eV, which is a remnant of the lower Hubbard band, should be proportional to  $U/W$ , while the spectral feature just below  $E_F$  should exhibit rigid band behavior. However, these expected changes in the observed PES spectra of the V  $3d$ -band region have not been observed, as shown in Fig. 3. Therefore, we think that the spectral feature near  $E_F$  may be an “in-gap” state induced by oxygen vacancies.

Recently, similar results have been obtained in PES and x-ray-adsorption spectroscopy (XAS) for  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ .<sup>17</sup> Electron doping through Sr substitution for La induces a new peak at  $\sim 1.5$  eV below  $E_F$  with predominantly Ti  $3d$  character in the band gap of  $\text{SrTiO}_3$ , which cannot be interpreted using one-electron band theory.<sup>17</sup>

The spectral feature near  $E_F$  should not be observed in insulating  $\text{CaVO}_3$ . We think that the observed spectral weight near  $E_F$  in insulating  $\text{CaVO}_3$  can be attributed to extrinsic states induced by oxygen vacancies at the surface. There has been a great deal of PES work on light TM oxides  $\text{TiO}_2$ ,<sup>18–22</sup>  $\text{SrTiO}_3$ ,<sup>18,23</sup>  $\text{Ti}_2\text{O}_3$ ,<sup>22,24–27</sup> and  $\text{V}_2\text{O}_3$ ,<sup>22,26,28,29</sup> having formal  $d^0$ – $d^2$  configurations. Significant changes in the electronic structure near  $E_F$  induced by surface oxygen vacancies has been observed in these PES results. However, the metal-insulator phase transition in  $\text{CaVO}_{3-\delta}$  is not induced by surface oxygen vacancies, but by bulk ones. To perform a more detailed analysis for the metal-insulator phase transition in  $\text{CaVO}_{3-\delta}$ , structural information for both bulk and surface oxygen vacancies is also essentially important.

#### V. CONCLUSION

We observed the PES spectra of  $\text{CaVO}_{3-\delta}$  and  $\text{SrVO}_{3-\delta}$  with and without oxygen vacancies

( $\delta=0-0.15$ ). In the PES spectra of the V 3d-band region for both oxides, a peak within  $\sim 1$  eV of  $E_F$  with a sharp Fermi cutoff and a broad one centered at  $\sim 1.6$  eV are observed. We find that the relative intensity of the peaks near  $E_F$  becomes drastically weak with decreasing concentration of oxygen vacancies ( $\delta$ ) in  $\text{CaVO}_{3-\delta}$  but not in  $\text{SrVO}_{3-\delta}$ . This difference in the effect of oxygen vacancies between  $\text{SrVO}_{3-\delta}$  and  $\text{CaVO}_{3-\delta}$  should reflect the fact that a metal-insulator phase transition induced by

oxygen vacancies takes place in  $\text{CaVO}_{3-\delta}$  but not in  $\text{SrVO}_{3-\delta}$ . Our experimental results for the states near  $E_F$  are favorable to the "in-gap" state model in comparison with the coherent model.

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