

This is the accepted manuscript made available via CHORUS. The article has been published as:

# Electronic properties of $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ ( $x=0,0.2,1$ ) studied using hard x-ray photoelectron spectroscopy

S. Dash, M. Okawa, T. Kajita, T. Yoshino, R. Shimoyama, K. Takahashi, Y. Takahashi, R. Takayanagi, T. Saitoh, D. Ootsuki, T. Yoshida, E. Ikenaga, N. L. Saini, T. Katsufuji, and T. Mizokawa

Phys. Rev. B **95**, 195116 — Published 9 May 2017

DOI: [10.1103/PhysRevB.95.195116](https://doi.org/10.1103/PhysRevB.95.195116)

# Electronic properties of $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ ( $x = 0, 0.2$ , and $1$ ) studied by using hard x-ray photoelectron spectroscopy

S. Dash,<sup>1</sup> M. Okawa,<sup>2</sup> T. Kajita,<sup>3</sup> T. Yoshino,<sup>1</sup> R. Shimoyama,<sup>2</sup> K. Takahashi,<sup>2</sup> Y. Takahashi,<sup>2</sup> R. Takayanagi,<sup>2</sup> T. Saitoh,<sup>2</sup> D. Ootsuki,<sup>4</sup> T. Yoshida,<sup>4</sup> E. Ikenaga,<sup>5</sup> N. L. Saini,<sup>6</sup> T. Katsufuji,<sup>3</sup> and T. Mizokawa<sup>1</sup>

<sup>1</sup>*Department of Applied Physics, Waseda University, Shinjuku, Tokyo 169-8555, Japan*

<sup>2</sup>*Department of Applied Physics, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan*

<sup>3</sup>*Department of Physics, Waseda University, Shinjuku, Tokyo 169-8555, Japan*

<sup>4</sup>*Department of Interdisciplinary Environment, Kyoto University, Sakyo, Kyoto 606-8501, Japan*

<sup>5</sup>*Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198, Japan*

<sup>6</sup>*Department of Physics, University of Roma "La Sapienza" Piazzale Aldo Moro 2, 00185 Roma, Italy*

(Dated: April 18, 2017)

We have studied the electronic structure of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  ( $x = 0, 0.2$ , and  $1$ ) at different temperatures across the trimerization and charge order transitions by using hard x-ray photoemission spectroscopy (HAXPES) experiment. The V  $2p$  HAXPES indicates  $\text{V}^{2+}/\text{V}^{3+}$  charge order and fluctuation in the high-temperature tetramer phase, low-temperature trimer phase, and intermediate-temperature charge order phase in the series of  $x = 0, 0.2$ , and  $1$ . In the valence-band HAXPES, although the spectral weight at the Fermi level tends to be suppressed in all the phases due to strong charge order or fluctuation, it increases in the trimer phase at  $x = 0.2$  in agreement with the decrease of resistivity and the increase of itinerant electrons in the trimer phase. Interestingly, in the most conducting  $x = 1$  without the charge order phase, the spectral weight at the Fermi level is strongly suppressed even in the trimer phase, indicating charge fluctuation in the trimer phase is different between  $x = 0.2$  and  $1$ .

PACS numbers: 71.30.+h, 75.25.Dk, 71.28.+d, 79.60.-i

## I. INTRODUCTION

3d transition-metal oxides exhibit various interesting physical properties like metal-insulator transition (MIT), colossal magneto-resistance, and spin-charge-orbital ordering.<sup>1</sup> The origin of such behaviors is quite attractive and compelling to understand. Among them, there are various origins of insulating states in transition-metal oxides including on-site Coulomb interaction for Mott insulators with integer number valence, inter-site Coulomb interaction for charge order insulators with non-integer number valence, Peierls transition with structural distortion, and Anderson localization with disorder effect. The MITs are usually accompanied by spin and/or charge and/or orbital ordering of  $3d$  electrons. For the case of orbital ordering with integer number of valence, there are several differences between the orbital orderings in  $\text{LaMnO}_3$  and  $\text{LiVO}_2$ : in  $\text{LaMnO}_3$ , the electrons responsible for the orbital ordering exist at each Mn site, whereas in  $\text{LiVO}_2$ , the electrons exist at each V-V bond. Furthermore, in  $\text{LaMnO}_3$ , the electron with orbital degrees of freedom also has spin degrees of freedom whereas in  $\text{LiVO}_2$ , the spin degrees of freedom are suppressed by the spin-singlet bond formation.<sup>2</sup> Such spin-singlet trimers are common building blocks for the  $\text{V}^{3+}$  oxidation state on the triangle-based lattice.<sup>3,4</sup>

$\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  and  $\text{BaV}_{10}\text{O}_{15}$  are among this category<sup>5,6</sup> with orbital degree of freedom like  $\text{LaMnO}_3$  and with trimerization like  $\text{LiVO}_2$ . In addition, among the various charge ordering phenomena, the charge order with  $\text{V}^{2+}$  and  $\text{V}^{3+}$  sites in  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ <sup>5,6</sup> and  $\text{BaV}_{10}\text{O}_{15}$ <sup>7,8</sup> is quite rare compared to the  $\text{V}^{3+}$  and  $\text{V}^{4+}$

charge order insulating state in various vanadates.<sup>9-13</sup>  $\text{BaV}_{10}\text{O}_{15}$  forms triangle-based lattice with a structural phase transition with anomaly of electrical conductivity at around 130 K. Electronic properties of  $\text{BaV}_{10}\text{O}_{15}$  is recently reported with  $\text{V}^{2+}$  and  $\text{V}^{3+}$  charge ordering<sup>7</sup> with V trimerization. Other studies are also obtained from the resonant x-ray scattering experiments,<sup>14</sup> V NMR<sup>15</sup> as proposed by Pen *et al.*,<sup>16</sup> time-resolved spectroscopy,<sup>17</sup> and Raman spectroscopy.<sup>18</sup> On the other hand, there are a few studies on  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ .  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  forms rock-salt lattice with periodically missing V and O sites<sup>19,20</sup> and V atoms are on the fcc lattice as the stacking of the triangular lattices with the ABCABC periodicity along the diagonal direction. The side view of the crystal structure of  $\text{BaV}_{13}\text{O}_{18}$  parallel to ab-plane is shown in the Fig. 1 (a) and the top view along the c-axis is shown in the Fig. 1 (b). Ikeda and coworkers have found that low-temperature phase is dominated by V trimers [Fig. 1 (c)] and high-temperature phase by V tetramers [Fig. 1 (d)] in the series of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  for  $0 \leq x \leq 1$ .<sup>5,6</sup>

The schematic of temperature dependent phase transition from V tetramers to V trimers is shown in Fig. 2(a). There is a strong competition between the tetramer phase and the trimer phase in the series of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ , and the electronic structure substantially changes in association with the phase transition.  $T_{tr}$  corresponds to the transition temperature from the tetramer to trimer phase.  $\text{BaV}_{13}\text{O}_{18}$  takes the same crystal structure as that of  $\text{SrV}_{13}\text{O}_{18}$  and exhibits an intermediate charge order phase followed by the low-temperature trimer phase. The charge order phase exists for lower values of  $x$  ( $0 < x < 1$ )

0.3) in  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ .  $T_{co}$  is defined as the transition temperature to the intermediate charge order phase. Although the details of the crystal structure and the transport properties (including resistivity  $\rho$ , magnetic susceptibility  $\chi$ , Seebeck coefficient  $S$ , and thermal conductivity  $K$ ) of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  have been reported,<sup>5,6</sup> the electronic structure and the valence state of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  are not studied yet by spectroscopic methods. The schematics of resistivity  $\rho$  [Fig. 2(b)], Seebeck coefficient  $S$  [(Fig. 2(c)], and magnetic susceptibility  $\chi$  [(Fig. 2(d)] across the transition temperatures are drawn for  $x = 0, 0.2$ , and 1. These properties are associated with the presence of tetramers in the high temperature phase and trimers in the low temperature phase. The intermediate-temperature charge order phase is also dominated with tetramers and shows interesting physical behaviors.<sup>5,22</sup> Since the average valence of V is  $\sim +2.62$ ,  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  is expected to show an interesting interplay between V charge order and fluctuation with V trimerization or tetramerization. It has been proposed that the high temperature phase contains 31 electrons within 3 tetramers (10 electrons per tetramer) and centrally localized  $\text{V}^{4+}$  (one electron). The low temperature phase contains 3 trimers and one tetramers i.e.,  $31 - (3 \times 6 + 10) = 3$  itinerant  $3d$  electrons give metallic nature.<sup>6</sup>

In order to clarify the electronic structural change across the phase transitions and to reveal the relationship between the V tetramers or trimerization and the rare  $\text{V}^{2+}$  and  $\text{V}^{3+}$  charge ordering, we have performed hard x-ray photoemission spectroscopy (HAXPES) of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$ . Since charge ordered systems tend to exhibit surface electronic states different from bulk ones, HAXPES is more important to understand the bulk properties and hence useful to compare with the previously studied bulk characterizations such as magnetic and transport properties.<sup>5,6</sup> Although there is a disadvantage of low cross section with high photon energies, it is more reliable because the information is coming from the bulk irrespective of surface condition. On the other hand, angle-resolved photoemission spectroscopy with low photon energies is surface sensitive and useful to study layered materials with well defined cleavage plane. Since the present system has no well defined cleavage plane, surface sensitive experiments with soft x-ray are not appropriate to compare with bulk sensitive measurements. The V  $2p$  spectrum is split into two components at the high-temperature tetramer, the low-temperature trimer, and intermediate-temperature charge order phases for  $x = 0, 0.2$ , and 1, indicating the presence of  $\text{V}^{2+}$  and  $\text{V}^{3+}$  charge fluctuation and charge order ( $\text{V}^{2+}$  and  $\text{V}^{3+}$  ratio is approximately 5 : 8). Based on the proposed charge order or fluctuation, relationship between the electronic properties and various physical properties will be discussed.

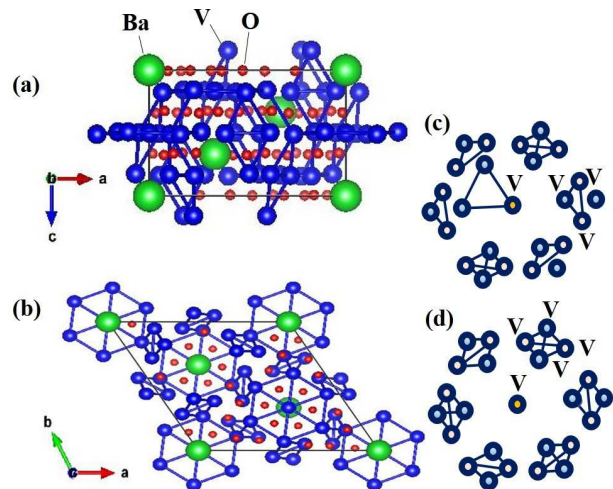


FIG. 1: (Color online) The crystal structure of  $\text{BaV}_{13}\text{O}_{18}$  (a) along the hexagonal  $ab$ -plane and (b) from the  $c$ -axis is drawn from Iwasaki *et al.*,<sup>19</sup> by using VESTA.<sup>21</sup> (c) The schematics of the low temperature trimer phase and (d) high temperature tetramer phase of V atoms. Barium, vanadium, and oxygen atoms are shown by filled circle with different color.

## II. EXPERIMENTAL DETAILS

The single crystals of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  ( $x = 0, 0.2$ , and 1) were grown as reported in the literature.<sup>5,6</sup> HAXPES measurements were performed at BL09XU of SPring-8.<sup>23</sup> HAXPES with 7930 eV of source energy gives more bulk information with probing depth around 10 nm.<sup>24–27</sup> The incidence and detection angles are set to about 10 degrees and 90 degrees, respectively, to increase photoelectron yield. The surface contamination was removed by fracturing the single crystals under ultrahigh vacuum of  $10^{-6}$  Pa at 300 K. The electronic state of the topmost surface layer (width of about 1 nm) would be different from that of the bulk. With the probing depth around 10 nm, more signals (above 90 percent) is expected from the bulk region.<sup>28</sup> Sample charging effects are removed with conducting carbon surroundings. Photoelectrons excited with photon energy of 7930 eV were collected and analyzed by OMICRON-SCIENTA R4000. With such high photon energy, the cross sections at the O 1s and V 2p edges are decreased by magnitude of 148.148 and 221.694 times, respectively from those with Al  $K\alpha$  source.<sup>29</sup> On the contrary, the advantages of HAXPES measurements are bulk sensitivity and high resolution with the third-generation synchrotron light sources (SPring-8). The pass energy was set to 200 eV and the total energy resolution was about 270 meV. The binding energy was calibrated using the Fermi edge of Au reference.

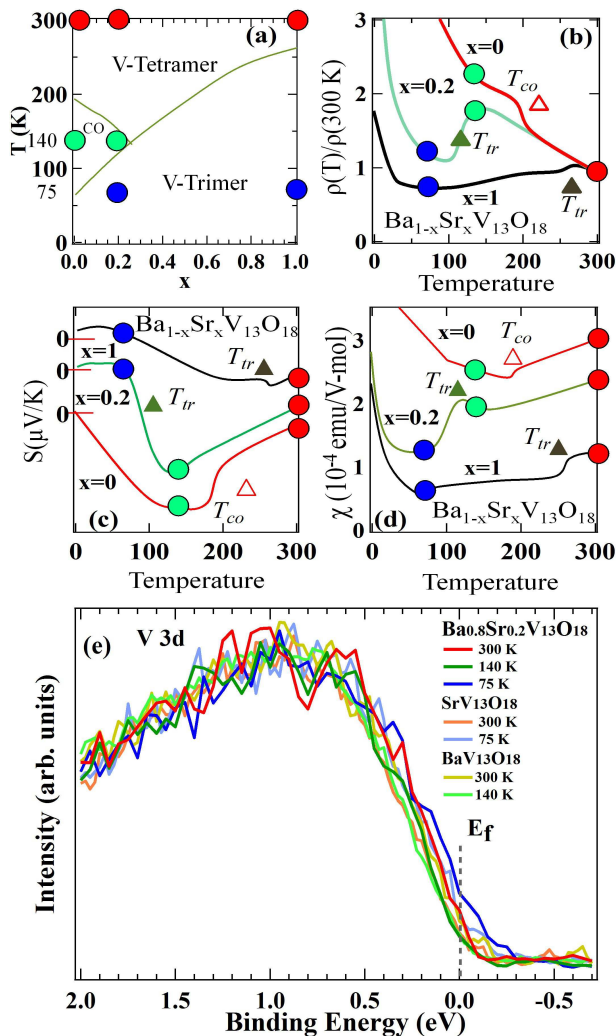


FIG. 2: (Color online) The schematics of (a) phase diagram for V tetramer to V trimer and charge order phases, (b) resistivity  $\rho$ , (c) Seebeck coefficient  $S$ , (d) magnetic susceptibility  $\chi$  for  $\text{AV}_{13}\text{O}_{18}$  ( $A = \text{Ba}, \text{Sr}$ ), and mixed compound  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$  obtained from Ikeda *et al.*<sup>6</sup> (e) Valence band HAXPES spectra collected around V 3d region.  $T_{tr}$  is shown with filled triangle and  $T_{co}$  is shown by open triangle. Each circle indicates the temperature for the HAXPES measurement.

### III. RESULTS AND DISCUSSION

Figure 2(e) shows the HAXPES results collected across V 3d of  $\text{AV}_{13}\text{O}_{18}$  ( $A = \text{Ba}, \text{Sr}$ ),  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$  at different temperatures across the transitions. Each spectrum is normalized with the V 3d intensity (total area). Firstly, the spectral weight at the Fermi level tends to be suppressed in all the compositions and the temperatures. The spectral weight suppression would be related to the charge order or fluctuation obtained from the V 2p HAXPES that will be discussed later. The spectral weight at the Fermi level is slightly enhanced for  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$  and  $\text{SrV}_{13}\text{O}_{18}$  at 75 K. This enhancement could be the

signature of the metallic trimer phase due to itinerant 3d electrons. However, spectral weight across the Fermi edge of  $\text{SrV}_{13}\text{O}_{18}$  collected at 75 K is relatively suppressed than  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$ . The valence-band HAXPES spectra of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  for  $x = 0.2$  are shown in Fig. 3(a) and 3(b). In the high-temperature phase (300 K) and the intermediate-temperature charge order phase (140 K), the spectral weight at the Fermi level is strongly suppressed likely with a pseudogap that can be associated with the tetramer formation and the charge order. On the other hand, the spectral weight at the Fermi level is enhanced at 75 K indicating that the number of the itinerant electrons is increased in the trimer phase. However, the pseudogap still remains and can be related to the charge fluctuation in the trimer phase observed by the V 2p HAXPES. The increase in spectral weight at the Fermi level can be comparable with the decreases in resistivity [Fig. 2(b)] and the behavior of Seebeck coefficient  $S$  approaching zero [Fig. 2(c)]. The O 1s HAXPES is shown in Fig. 3(c). The O 1s can be fitted to a Doniach-Sunjic profile.<sup>30</sup>

Figure 4 shows the V 2p HAXPES spectra taken at 300, 140 and 75 K (indicated by the thick solid curves) for  $x = 0.2$ . Each of the V 2p spectra is subtracted with Shirley type background excluding O 1s with reference to Silversmith *et al.*,<sup>31</sup> and is fitted to five Voigts (mixture of Gaussian and Lorentzian). The V  $2p_{3/2}$  peak can be decomposed with  $\text{V}^{2+}$  and  $\text{V}^{3+}$  contributions which are included in the fit considering the fact that average V valence of  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  is  $\sim +2.62$ . From V  $2p_{3/2}$ ,  $\text{V}^{2+}$  peak is fitted with two Voigts and  $\text{V}^{3+}$  is fitted with one Voigt. In V  $2p_{1/2}$ , each  $\text{V}^{2+}$  and  $\text{V}^{3+}$  components are fitted with one Voigt, respectively. The energy separation between the  $\text{V}^{3+}$  and  $\text{V}^{2+}$  components in all temperatures is large compared to the typical values.<sup>35,37</sup> In the V 2p HAXPES of various metallic V oxides such as  $\text{SrVO}_3$ ,<sup>32</sup>  $\text{VO}_2$  (metallic phase),<sup>33</sup> and  $\text{V}_2\text{O}_3$  (metallic phase),<sup>34-38</sup> it has commonly been reported that the V  $2p_{3/2}$  peaks are very broad and are extended from 519 eV to 512 eV. At 75 K, the low binding energy side of the V  $2p_{3/2}$  branch reaches 512 eV. Also, broadening due to phonons<sup>38</sup> are possible. We also tried curve fittings with five Voigts similarly as described earlier and four Doniach-Sunjic profiles on the V 2p spectra with Shirley background removed from the broad region including O 1s.<sup>31</sup> The estimated  $\text{V}^{2+}/\text{V}^{3+}$  intensity ratio is summarized in Table I. As for the Doniach-Sunjic fitting, the asymmetric parameter is set to the same as that obtained from O 1s for each temperature.<sup>30</sup> At 300 K, the V  $2p_{3/2}$  peak becomes less broad and is relatively shifted towards higher binding energy. The V 2p binding energy decreases with cooling and may be related with band bending in the interface of the coexisting phases.<sup>40</sup> The intensity ratio between the low-energy and high-energy components which correspond to  $\text{V}^{2+}$  and  $\text{V}^{3+}$  components is obtained from fitted results of V  $2p_{3/2}$  rather than V  $2p_{1/2}$  since the V  $2p_{1/2}$  peak overlaps with the charge-transfer satellites of V  $2p_{3/2}$  peak in V oxides.<sup>39</sup> The in-

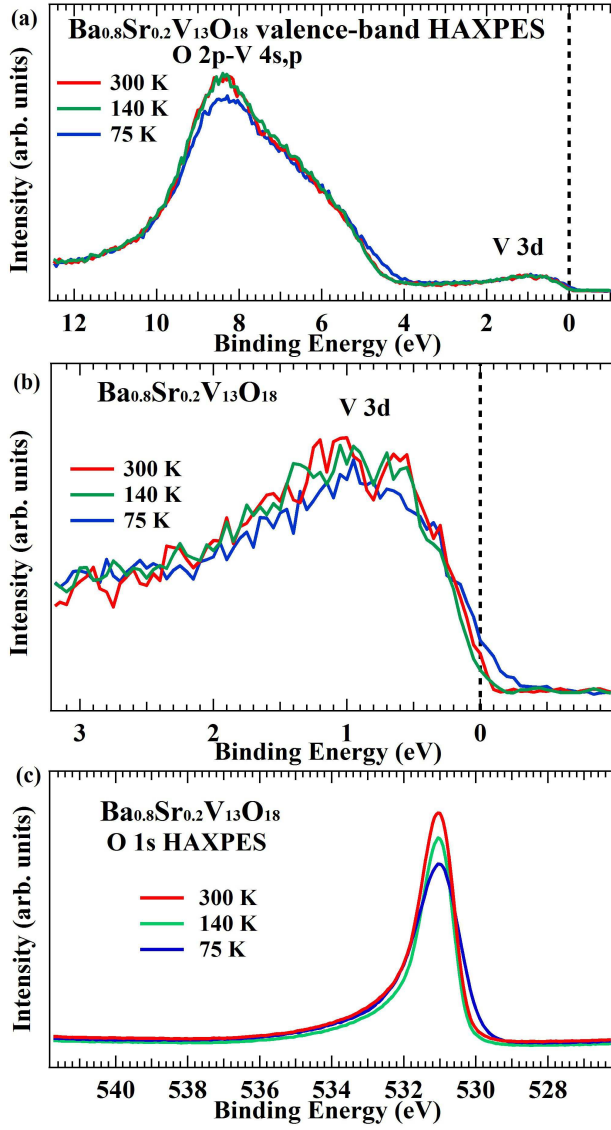


FIG. 3: (Color online) HAXPES spectra of  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$  at 300, 140, and 75 K for (a) valence band, (b) V 3d, and (c) O 1s.

tensity ratio between  $\text{V}^{2+}$  and  $\text{V}^{3+}$  fluctuates around 0.6 at the temperatures across the phase transitions and is shown in Table I. The values are found consistent for the charge order or fluctuation with average valency of +2.62 or  $\text{V}^{2+} : \text{V}^{3+} = 5 : 8$ . This leads to the suppression of spectral weight at the Fermi level.

The temperature dependence of magnetic susceptibility  $\chi$  is schematically drawn in Fig. 2(d). The reduction in magnetic susceptibility  $\chi$  in trimer phase can be understood on the basis of charge fluctuation of  $\text{V}^{2+}$  and  $\text{V}^{3+}$  associated with the competition between tetramerization and trimerization. Since the  $\text{V}^{2+}$  and  $\text{V}^{3+}$  components are well separated in the V 2p HAXPES taken at 300 K (Fig. 4), two (or one)  $\text{V}^{2+}$  and two (or three)  $\text{V}^{3+}$  form the tetramer at 300 K and a kind of Zener double exchange interaction provides ferromagnetic coupling be-

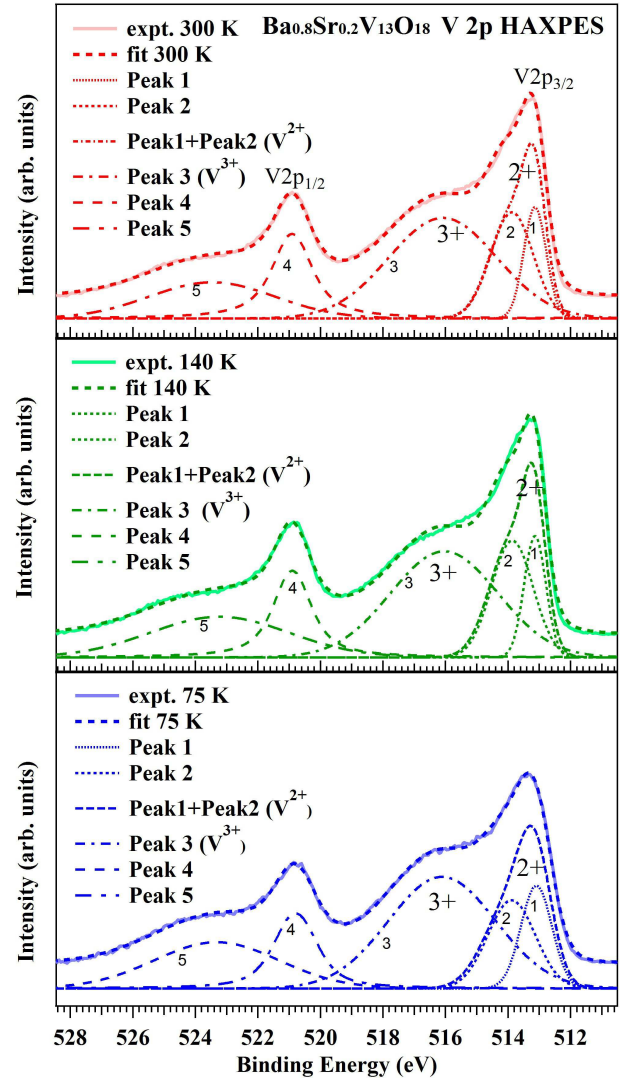


FIG. 4: (Color online) V 2p HAXPES spectra fitted with five Voigt functions for 300, 140, and 75 K. Peak 1 and 2 represent for  $\text{V}^{2+}$ , and peak 3 represents for  $\text{V}^{3+}$  component in the V  $2p_{3/2}$ . Peak 4 and 5 are fitted for the V  $2p_{1/2}$  region. Peak 1 and 2 of V  $2p_{3/2}$  collected at 75 K are broadened and shifted towards lower binding energy side.

tween the  $\text{V}^{2+}$  and  $\text{V}^{3+}$  sites and  $\chi$  can be enhanced.<sup>7</sup> The magnetic susceptibility  $\chi$  decreases slowly with cooling till  $T_{co}$  and increases upto  $T_{tr}$  like Curie-Weiss behavior that is assigned to the localized V 3d electron at the central site.<sup>6</sup> Here, it should be noted that one cannot exclude the possibility of one  $\text{V}^{4+}$  among 13 V sites in the present analysis since the  $\text{V}^{3+}$  peak is extremely broad. Below  $T_{tr}$ ,  $\chi$  falls down sharply as seen in Fig. 2(d) because the charge order phase breaks down and  $\chi$  is somehow reduced with trimerization where spin singlet states between  $\text{V}^{3+}$ - $\text{V}^{3+}$  are realized in some of the trimers. However, most of the trimers are constructed from  $\text{V}^{2+}$  and  $\text{V}^{3+}$  with ferromagnetic coupling and contribute to the residual component of  $\chi$ . Below 75 K, the



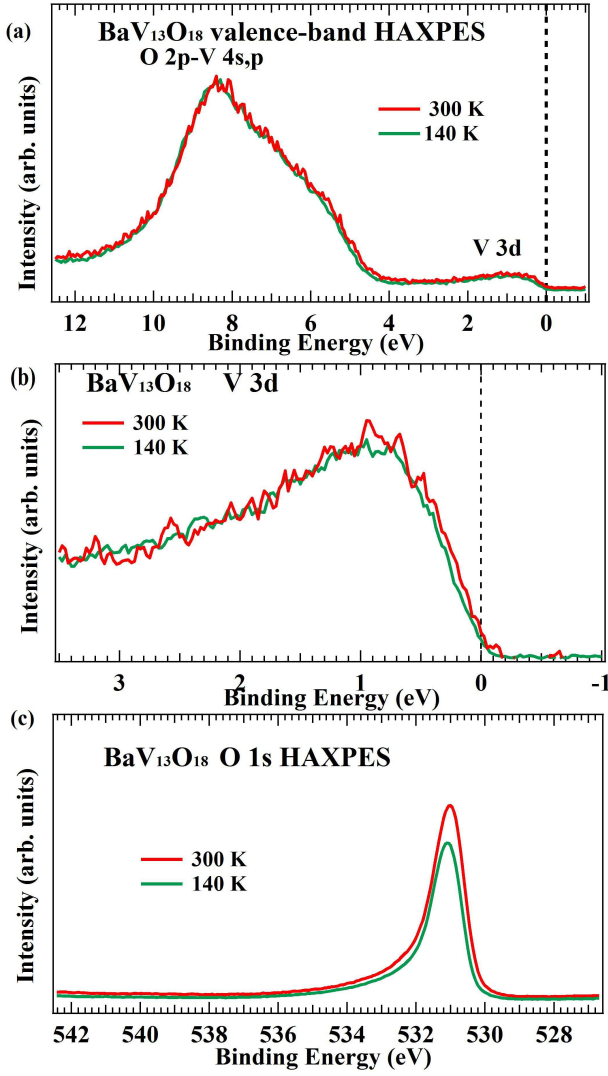


FIG. 5: (Color online) HAXPES spectra of  $\text{BaV}_{13}\text{O}_{18}$  at 300 and 140 K for (a) valence band, (b) V 3d, and (c) O 1s.

TABLE I: Intensity ratio  $\text{V}^{2+}/\text{V}^{3+}$  in  $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$  for ( $x = 0, 0.2$ , and 1) at different phases across the transitions. V1: Voigt profile on V 2p subtracted with Shirley background excluding O 1s region, V2: Voigt profile on V 2p subtracted with Shirley background including O 1s region, DS: Doniach-Sunjc profile on V 2p subtracted with Shirley background including O 1s region.<sup>31</sup>

Fittings	T(K)	$\text{V}^{2+}/\text{V}^{3+}$ ratio in $\text{Ba}_{1-x}\text{Sr}_x\text{V}_{13}\text{O}_{18}$		
		$x=0$	$x=0.2$	$x=1$
V1	300	0.62	0.64	0.64
	140	0.64	0.64	-
	75	-	0.62	0.79
V2	300	0.64	0.64	0.68
	140	0.64	0.65	-
	75	-	0.67	0.81
DS	300	0.72	0.71	0.60
	140	0.70	0.74	-
	75	-	0.68	0.82

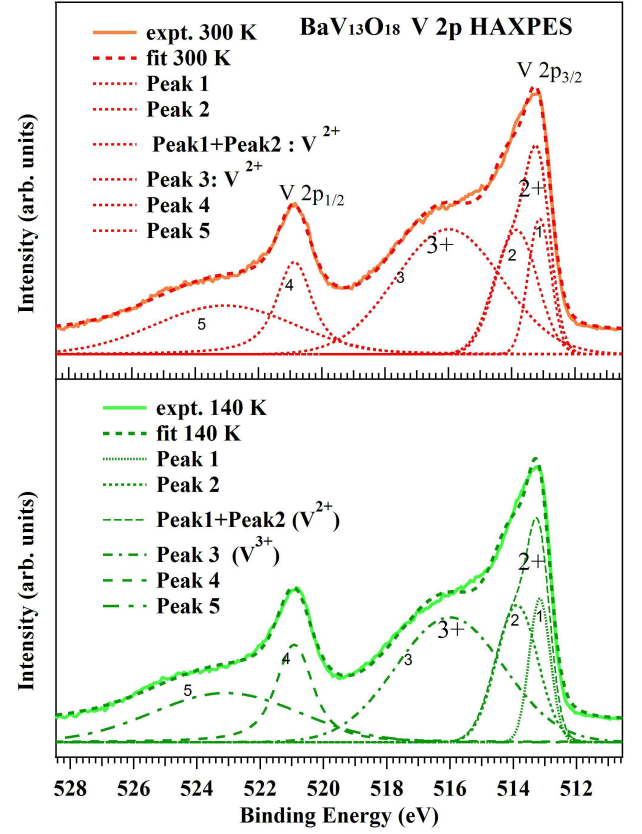


FIG. 6: (Color online) V 2p HAXPES spectra fitted with five Voigt functions for 300 and 140 K. Peak 1 and 2 represent for  $\text{V}^{2+}$ , and peak 3 represents for  $\text{V}^{3+}$  component in V  $2p_{3/2}$ . Peak 4 and 5 are fitted for the V  $2p_{1/2}$  region.

increase in  $\chi$  is already ascribed to impurity spin of the sample.<sup>6</sup>

Figures 5(a) and 5(b) show the valence-band HAXPES spectra of  $\text{BaV}_{13}\text{O}_{18}$  across the charge order transition. At 140 K, spectral weight at the Fermi level is relatively dropped compared to 300 K. This agrees to the increases of resistivity at 140 K as shown in the Fig. 2(b). The presence of localized electrons at the central V site surrounded with tetramers could be the common origin of such behavior in the charge order phase. Also, the Seebeck coefficient is negative at room temperature and its absolute value further increases with lowering temperature as seen from Fig. 2(c). This can be associated to the relative increase of the V 3d and O 1s binding energies with cooling seen in Figs. 5(b) and 5(c). Figure 6 shows the V 2p HAXPES spectra taken at 300 and 140 K (indicated by the thick solid curves). Each of the V 2p spectra at both temperatures is subtracted with Shirley type background and fitted to five Voigts similarly as described above for  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$ . From the fit parameters, the low binding energy peak of the V  $2p_{3/2}$  at 300 K is relatively broader and shifted towards lower binding energy compared to the spectrum at 140 K. Intensity ratio between the low-energy and high-energy components

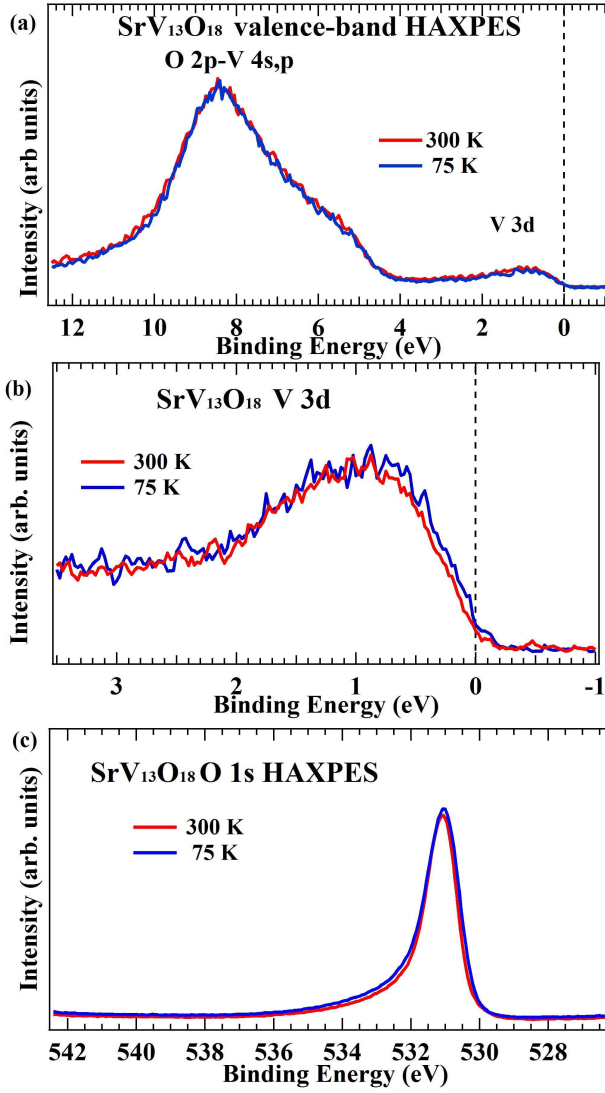


FIG. 7: (Color online) HAXPES spectra of  $\text{SrV}_{13}\text{O}_{18}$  at 300 and 75 K for (a) valence band, (b) V 3d, and (c) O 1s.

which correspond to  $\text{V}^{2+}$  and  $\text{V}^{3+}$  components fluctuates around 0.6 – 0.7 at different temperatures, is obtained from the Voigt fits and the Doniach-Sunjc fits<sup>30</sup> as shown in Table I. The behavior of magnetic susceptibility around 140 K, as seen in the schematic of phase diagram in Fig. 2(d), could be related to the central V atom of the hexagonal plane and the charge order with  $\text{V}^{2+} : \text{V}^{3+} = 5 : 8$ .

Figures 7(a) and 7(b) show the valence-band HAXPES spectra of  $\text{SrV}_{13}\text{O}_{18}$  collected above and much below  $T_{tr}$ . The resistivity drops below  $T_{tr} \approx 250$  K, where the 3d electrons become itinerant as explained earlier.<sup>6</sup> A relative increase in spectral weight at the Fermi level of  $\text{SrV}_{13}\text{O}_{18}$  is seen at 75 K [Fig. 7(b)] as a signature of the metallic nature due to the presence of 3d itinerant electrons. However, the higher charge fluctuation at 75 K (Table I) suppresses the spectral weight at the Fermi level in comparison to the case of  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{V}_{13}\text{O}_{18}$ . In

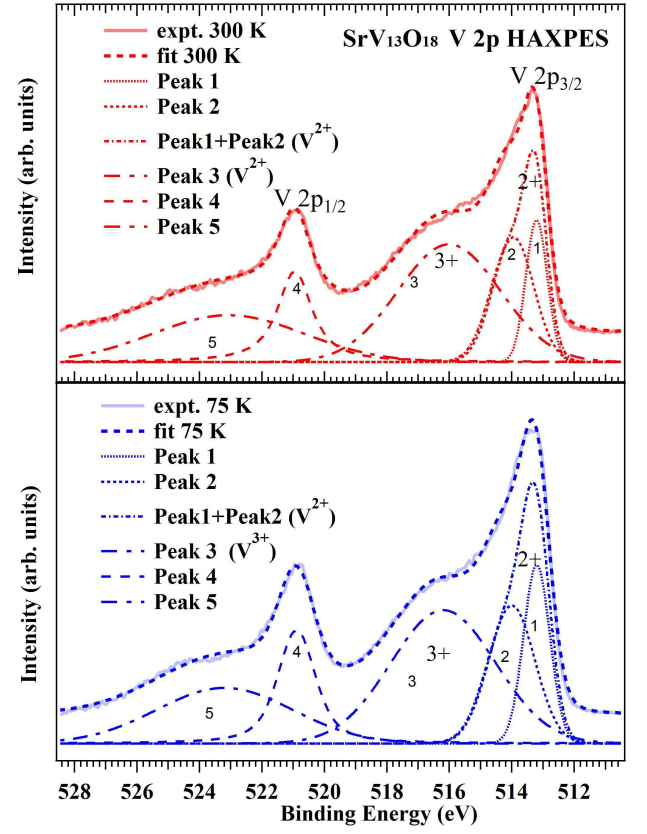


FIG. 8: (Color online) V 2p HAXPES spectra fitted with five Voigt functions for 300 and 75 K. Peak 1 and 2 represent for  $\text{V}^{2+}$ , and peak 3 represents for  $\text{V}^{3+}$  component in V  $2p_{3/2}$ . Peak 4 and 5 are fitted for the V  $2p_{1/2}$  region.

Fig. 7(c), the O 1s HAXPES of the metallic phase at 75 K exhibits the slight increase of asymmetry due to the screening effect from such itinerant 3d electrons. The relative increase in spectral weight at the Fermi level can be compared with the decrease in resistivity [Fig. 2(b)] and the behavior of Seeback coefficient [Fig. 2(c)]. Figure 8 shows the V 2p HAXPES spectra taken at 300 and 75 K (indicated by the thick solid curves). The V 2p spectrum at each temperature is fitted to five Voigts similarly as described earlier. The intensity ratio between the low-energy and high-energy components which correspond to  $\text{V}^{2+}$  and  $\text{V}^{3+}$  components obtained from the Voigt fits increases from 0.64 for 300 K to 0.79 for 75 K as shown in the section V1 in Table I. The increase is also seen with other set of fittings as shown in the sections V2 and DS in Table I. This shows that charge fluctuation in the trimer phase is different between  $x = 0.2$  and  $x = 1$ . At  $x = 0.2$ , the  $\text{V}^{2+}$  peak becomes broad at 75 K without drastic change of the intensity ratio. Therefore, the itinerant electrons are derived from extra electrons at the  $\text{V}^{2+}$  site and/or extra holes at the  $\text{V}^{3+}$  site, and the population of  $\text{V}^{2+}$  and  $\text{V}^{3+}$  sites is almost locked. On the other hand, at  $x = 1$ , the intensity ratio between the  $\text{V}^{2+}$  and  $\text{V}^{3+}$  peaks is changed at 75 K without broadening of the peak.

Therefore, although the population of  $V^{2+}$  and  $V^{3+}$  sites is flexible at  $x = 1$ , the carriers are rather localized and a kind of polaronic transport would be responsible for the metallic behavior. This is consistent with the valence-band HAXPES in which the spectral weight suppression in the trimer phase is different between  $x = 0.2$  and 1.

#### IV. CONCLUSIONS

We conclude that core level HAXPES measurements have shown the unusual metallic states with mixed valence between  $V^{2+}$  and  $V^{3+}$  in the series of  $x = 0, 0.2$ , and 1 in  $Ba_{1-x}Sr_xV_{13}O_{18}$ . The  $V^{2+/3+}$  charge fluctuation or charge order is confirmed in the V  $2p$  core-level HAXPES results. This charge fluctuation or charge order suppresses the spectral weight at the Fermi level and creates the pseudogap as observed in the valence-band HAXPES. The valence-band HAXPES results are almost

consistent with the transport behaviors seen across the transitions. Although the pseudogap remains probably due to the charge fluctuation, the spectral weight at the Fermi level is slightly enhanced for the presence of  $3d$  itinerant electrons at the low temperature trimer phase. In general, various physical properties across the transition of  $AV_{13}O_{18}$  ( $A = Ba, Sr$ ), and  $Ba_{0.8}Sr_{0.2}V_{13}O_{18}$  are well ascribed to the charge fluctuation of  $V^{2+}$  and  $V^{3+}$  which would be related to the competition between the tetramer and trimer phases.

#### Acknowledgment

This work was supported by CREST-JST and KAKENHI from JSPS (No. 26400321 and No. 16H04020). The synchrotron radiation experiment was performed with the approval of SPring-8 (2016B1005).

- 
- <sup>1</sup> M. Imada, A. Fujimori, Y. Tokura, *Rev. Mod. Phys.* **70**, 4 (1998).
  - <sup>2</sup> D. I. Khomskii, *Transition Metal Compounds*, (Cambridge University Press, 2014).
  - <sup>3</sup> G. Liu and J.E. Greedan, *J. Solid State Chem.* **122**, 416 (1996).
  - <sup>4</sup> C. A. Bridges and J. E. Greedan, *J. Solid State Chem.* **177**, 1098 (2004).
  - <sup>5</sup> M. Ikeda, Y. Nagamine, S. Mori, J. E. Kim, K. Kato, M. Takata, and T. Katsufuji, *Phys. Rev. B* **82**, 104415 (2010).
  - <sup>6</sup> M. Ikeda, T. Okuda, K. Kato, M. Takata, and T. Katsufuji, *Phys. Rev. B* **83**, 134417 (2011).
  - <sup>7</sup> T. Yoshino, M. Okawa, T. Kajita, S. Dash, R. Shimoyama, K. Takahashi, Y. Takahashi, R. Takayanagi, T. Saitoh, D. Ootsuki, T. Yoshida, E. Ikenaga, N. L. Saini, T. Katsufuji, and T. Mizokawa, *Phys. Rev. B* **95**, 075151 (2017).
  - <sup>8</sup> T. Kajita, T. Kanzaki, T. Suzuki, J. E. Kim, K. Kato, M. Takata, and T. Katsufuji, *Phys. Rev. B* **81**, 060405(R) (2010).
  - <sup>9</sup> A. V. Mahajan, D. C. Johnston, D. R. Torgeson, and F. Borsa, *Phys. Rev. B* **46**, 10973 (1992).
  - <sup>10</sup> G. Jackeli, and G. Khaliullin, *Phys. Rev. Lett.* **101**, 216804 (2008).
  - <sup>11</sup> Y. Ishige, T. Sudayama, Y. Wakisaka, T. Mizokawa, H. Wadati, G. A. Sawatzky, T. Z. Regier, M. Isobe, and Y. Ueda, *Phys. Rev. B* **83**, 125112 (2011).
  - <sup>12</sup> A. C. Gossard, J. P. Remeika, T. M. Rice, H. Yasuoka, K. Kosuge, and S. Kachi, *Phys. Rev. B* **9**, 1230 (1974).
  - <sup>13</sup> A. S. Botana, V. Pardo, D. Baldomir, A. V. Ushakov and D. I. Khomskii, *Phys. Rev. B* **84**, 115138 (2011).
  - <sup>14</sup> K. Takubo, T. Kanzaki, Y. Yamasaki, H. Nakao, Y. Murakami, T. Oguchi, and T. Katsufuji, *Phys. Rev. B* **86**, 085141 (2012).
  - <sup>15</sup> Y. Shimizu, K. Matsudaira, M. Itoh, T. Kajita, and T. Katsufuji, *Phys. Rev. B* **84**, 064421 (2011).
  - <sup>16</sup> H. F. Pen, J. van den Brink, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. Lett.* **78**, 1323 (1997).
  - <sup>17</sup> A. Nogami, K. Takubo, T. Kajita, M. Hoshino, and T. Katsufuji, *Phys. Rev. B* **84**, 214442 (2011).
  - <sup>18</sup> T. Kanzaki, R. Kubota, T. Katsufuji, *Phys. Rev. B* **85**, 144410 (2012).
  - <sup>19</sup> K. Iwasaki, H. Takizawa, K. Uheda, T. Endo, and M. Shimada, *J. Solid State Chem.* **158**, 61 (2001).
  - <sup>20</sup> K. Iwasaki, H. Takizawa, H. Yamane, S. Kubota, J. Takahashi, K. Uheda, and T. Endo, *Mater. Res. Bull.* **38**, 141 (2003).
  - <sup>21</sup> K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
  - <sup>22</sup> T. Katsufuji, T. Okuda, R. Murata, T. Kanzaki, K. Takayama, and T. Kajita, *J. Phys. Soc. Jpn.* **85**, 013703 (2016).
  - <sup>23</sup> E. Ikenaga, M. Kobata, H. Matsuda, T. Sugiyama, H. Daimon, and K. Kobayashi, *J. Electron Spectrosc. Relat. Phenom.* **190**, 180-187 (2013).
  - <sup>24</sup> S. Ouardi, G. H. Fecher, C. Felser, *J. Electron Spectrosc. Relat. Phenom.* **190**, 249267 (2013).
  - <sup>25</sup> K. Kobayashi, M. Yabashi, Y. Takata, T. Tokushima, S. Shin, K. Tamasaku, D. Miwa, T. Ishikawa, H. Nohira, T. Hattori, Y. Sugita, O. Nakatsuka, A. Sakai, and S. Zaima, *Appl. Phys. Lett.*, **83**, 1005 (2003).
  - <sup>26</sup> K. Kobayashi, *Nucl. Instr. Meth. Phys. Res. A*, **601**, **32** (2009).
  - <sup>27</sup> K. Kobayashi, *Nucl. Instr. Meth. Phys. Res. A*, **547**, **98** (2005).
  - <sup>28</sup> M. Sacchi, F. Offi, P. Torelli, A. Fondacaro, C. Spezzani, M. Cautero, G. Cautero, S. Huotari, M. Grioni, R. Delaunay, M. Fabrizioli, G. Vankó, G. Monaco, G. Paolicelli, G. Stefani, and G. Panaccione, *Phys. Rev. B* **71**, 155117 (2005).
  - <sup>29</sup> J. J. Yeh and I. Lindau, *Atomic Data and Nuclear Data Tables*, **32**, 1-155 (1985).
  - <sup>30</sup> See Supplemental Materials for fittings with Doniach-Sunjic profiles.
  - <sup>31</sup> G. Silversmit, D. Depla, H. Poelman, G. B. Marin, R. D. Gryse, *J. Electron Spectrosc. Relat. Phenom.* **135**, 167175 (2004).
  - <sup>32</sup> J. Laverock, J. Kuyyalil, B. Chen, R. P. Singh, B. Karlin, J. C. Woicik, G. Balakrishnan, and K. E. Smith, *Phys.*



- Rev. B **91**, 165123 (2015).
- <sup>33</sup> S. Suga, A. Sekiyama, S. Imada, T. Miyamachi, H. Fujiwara, A. Yamasaki, K. Yoshimura, K. Okada, M. Yabashi, K. Tamasaku, A. Higashiya, and T. Ishikawa, New J. Phys. **11**, 103015 (2009).
  - <sup>34</sup> G. Panaccione, M. Sacchi, P. Torelli, F. Offi, G. Cautero, R. Sergo, A. Fondacaro, C. Henriquet, S. Huotari, G. Monaco, L. Paolasini, J. Electron Spectrosc. Relat. Phenom. **156-158**, 64 (2007).
  - <sup>35</sup> G. A. Sawatzky and D. Post, Phys. Rev. B **20**, 1546 (1979).
  - <sup>36</sup> T. Uozumi, K. Okada, A. Kotani, R. Zimmermann, P. Steiner, S. Hener, Y. Tezuka, S. Shin, J. Electron Spectrosc. Relat. Phenom. **83**, 9 (1997).
  - <sup>37</sup> M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, Appl. Surf. Sci. **257**, 887898 (2010).
  - <sup>38</sup> P. H. Citrin, P. Eisenberger, and D. R. Hamann, Phys. Rev. Lett. **33**, 965 (1974).
  - <sup>39</sup> A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. R. Barman, K. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda Phys. Rev. B **53**, 1161 (1996).
  - <sup>40</sup> Z. Zhang and J. T. Yates Jr, Chem. Rev. **112**, 55205551 (2012).