Genuine Electronic States of Vanadium Perovskites Revealed by High-Energy Photoemission

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Bulk-sensitive high-resolution photoemission was carried out on a prototype $3d^3$ metallic Sr$_{1-x}$Ca$_x$VO$_3$. In a strong contrast to so far reported results, the bulk spectral functions are revealed to be insensitive to $x$. The conservation of the density of states at the Fermi level in spite of the electron correlation is clarified by the successful suppression and deconvolution of the surface contribution. Our study has demonstrated the importance of high-energy and high-resolution photoemission spectroscopy for revealing detailed bulk electronic states of transition metal oxides.

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The effect of the electron correlation to electronic states of transition metal (TM) oxides is still one of the most important and essential topics in condensed matter physics. The electronic structures of insulating TM oxides are basically understood in a framework of the Hubbard model and/or Mott insulator description. The occupied (unoccupied) $d$ orbitals hybridized with the neighboring O $2p$ orbitals form the lower (upper) Hubbard band in the presence of the electron correlation. The electron correlation is scaled by the on-site Coulomb repulsion between the $d$ electrons $U$ over a transfer integral $t$ between the mutually neighboring TM $3d$ states via the O $2p$ orbitals, namely, $U/t$. In metallic but correlated TM oxides, it has been recognized that the lower and upper Hubbard bands remain as the so-called incoherent parts reflecting the electron correlation. A renormalized band crossing $E_F$ (coherent part) is located between the occupied and unoccupied incoherent parts. Here reported Sr$_{1-x}$Ca$_x$VO$_3$ is one of the metallic Mott-Hubbard systems. The occupied $3d$ electronic structures are expected to be simple because of the nominal $3d^1$ ($V^{4+}$) configuration. SrVO$_3$ has a cubic structure with the V-O-V bond angle of 180° whereas the angle is about 160° in CaVO$_3$ due to the smaller ionic radius of Ca$^{2+}$ than that of Sr$^{2+}$. It is generally thought that $t$ is smaller in CaVO$_3$ than in SrVO$_3$ due to the V-O-V distortion whereas $U$ is fairly independent of $x$. Therefore one might expect that $U/t$ is larger for CaVO$_3$ than for SrVO$_3$. However, measurements of the electron specific heat and magnetic susceptibility suggest that the mass-enhancement does not change appreciably with $x$, casting a serious question on the above scenario. On the other hand, accumulated theoretical studies have shown that the density of states (DOS) at $E_F$ is conserved irrespective of the presence of the electron correlation in the Fermi liquid if momentum dependence of the self-energy is negligible. This theorem has been proposed for a long time, but not experimentally confirmed yet, as far as our knowledge is concerned.

Photoemission spectroscopy (PES) can directly probe occupied electronic structures of solids reflecting DOS. Valence-band PES studies of Sr$_{1-x}$Ca$_x$VO$_3$ so far performed at $h\nu < 120$ eV have shown that the intensity at $E_F$ as well as the relative spectral weight of the coherent part to the incoherent part is systematically suppressed with increasing $x$. It has been believed that such a behavior originates from the change of $U/t$ with $x$. The change of the spectral weight at $E_F$ by the effect of $U/t$ suggests an essential role of a momentum-dependent self-energy, which is derived from the strong electron correlation. However, these PES spectra are very sensitive to the surface electronic states due to a short photoelectron mean free path. The high-resolution valence-band PES at high-$h\nu$ near 1000 eV is a more direct and important technique to reveal the bulk electronic states near $E_F$ owing to its longer $\lambda$ of photoelectrons. In this Letter we demonstrate that genuine bulk spectral functions revealed by virtue of the high-energy and high-resolution PES for Sr$_{1-x}$Ca$_x$VO$_3$ on fractured surfaces are nearly independent of the Ca concentration $x$. This fact has been overlooked for a long time in low energy photoemission by the contribution of surface states which strongly changes with $x$. 
The PES at \( h\nu = 900 \) and 275 eV was performed at BL25SU in SPring-8, where the PES spectra were measured by using a GAMMADATA-SCIENTA SES-200 spectrometer. Single crystals of SrVO\(_3\) and Sr\(_{0.5}\)Ca\(_{0.5}\)VO\(_3\), and polycrystalline CaVO\(_3\) were employed for the measurements. The overall energy resolution was set to about 140 and 80 meV at \( h\nu = 900 \) and 275 eV, respectively. The results were compared with the low-energy PES spectra taken at \( h\nu = 40.8 \) and 21.2 eV by using a He discharge lamp, which were measured by using a VG CLAM4 spectrometer in Osaka University. The energy resolution was set to 50-80 meV. The samples were cooled to 20 K for all the measurements. Clean surfaces were obtained by fracturing the samples in situ at measuring temperatures and the surface cleanliness was confirmed before and after the measurements. The base pressure was about 4 \( \times 10^{-8} \) Pa.

Figures 1 and 2 show the high-resolution PES spectra near \( E_F \) measured at low- and high-energy excitations. In all the spectra, the peak near \( E_F \) and the broad peak centered at about 1.6 eV are corresponding to the coherent and incoherent parts, respectively. These structures are drastically enhanced in a V 2p - 3d resonance PES (not shown) and therefore originate predominantly from the V 3d electronic states. On going from CaVO\(_3\) to SrVO\(_3\), the coherent part is clearly enhanced in the low-energy PES spectra at \( h\nu = 40.8 \) eV as shown in Fig. 1(a). This tendency is consistent with the previous low-energy PES studies. However, this spectral difference among the compounds becomes noticeably smaller in the spectra measured at \( h\nu = 900 \) eV in Fig. 1(b). The photon-energy dependence of the V 3d spectral weights for Sr\(_{1-x}\)Ca\(_x\)VO\(_3\) is summarized in Fig. 2. The coherent spectral weight increases drastically with the photon energy for all the compounds. One might consider that the relatively strong incoherent spectral weight of the 1.6 eV peak at low-\( h\nu \) originates possibly from a large O 2p weight in this peak because the low-energy PES of TM oxides is generally more sensitive to the O 2p states than the TM 3d states. However, the observed behavior with \( h\nu \) is rather independent of the relative photoionization cross section of the V 3d to O 2p states, which should be the largest at 275 eV among \( h\nu = 21.2, 40.8, 275 \) and 900 eV. Therefore the monotonous increase of the coherent part with \( h\nu \) should originate from the increased sensitivity to the bulk 3d states at higher \( h\nu \). Namely, the V 3d spectra at low-\( h\nu \) mainly reflect the surface electronic states which are more localized than the bulk states caused by the broken V-O-V topological connectivity and/or structural surface relaxations at the surface.

We have estimated the bulk and surface V 3d spectral functions of Sr\(_{1-x}\)Ca\(_x\)VO\(_3\) from the experimental spectra at \( h\nu = 900 \) and 275 eV by the following procedure: (1) The mean free path \( \lambda \) has been calculated as \( \sim 17 \) and \( \sim 7 \) Å at \( h\nu = 900 \) and 275 eV. (2) The bulk weight \( R \) (depending on \( h\nu \)) should be determined as \( \exp(-s/\lambda) \) where \( s \) is a "surface thickness", therefore \( R's \) at 900 eV \( (R_{900}) \) and 275 eV \( (R_{275}) \) are related as \( R_{275} = R_{900}^{2/3} \). (3) The observed V 3d spectrum \( I(E_B) \) at \( h\nu = 900 \) eV is represented as \( I_{900}(E_B) = R_{900}(E_B)R_{900}^{2/3} + surf(E_B)(1 - R_{900}) \) while \( I_{275}(E_B) = R_{275}(E_B)R_{900}^{2/3} + surf(E_B)(1 - R_{900}) \), where
bulk($E_B$) [surf($E_B$)] is the bulk (surface) 3d spectral function and $E_B$ stands for the electron binding energy.

(4) If $s$ is assumed as 7.5 Å corresponding to about twice the V-O-V distance. \[ R_{900} (R_{275}) \] is determined as $\sim 0.64$ ($\sim 0.34$). The bulk and surface 3d spectral functions bulk($E_B$) and surf($E_B$) are consequently obtained from the observed spectra measured at $h\nu = 900$ and 275 eV. It should be noted that the line shapes of bulk($E_B$) have hardly changed even when we assume $s$ as from 5.4 to 11 Å. If $s$ is assumed to be less than 5.4 Å, unrealistic “negative” intensities are seen in some binding energy region for surf($E_B$). The uncertainty of $s$ (5.4–11 Å) yields the error for $R_{900}$ and $R_{275}$ as $\pm 0.12$, by which the error of the intensity in the vicinity of $E_F$ in the bulk spectra is estimated to be less than 15 %. The results for the bulk states are shown in Fig. 3(a). In contrast to the previous PES studies, the bulk 3d spectral functions are almost equivalent among the three compounds and the intensity in the vicinity of $E_F$ does not change for different $x$. These results indicate that the effect of the V-O-V distortion is not influential in the bulk 3d electronic states in Sr$_{1-x}$Ca$_x$VO$_3$. Our bulk-sensitive results are consistent with the behavior of the electron specific heat and magnetic susceptibility measurements. This fact has never been revealed by so far reported low-energy PES. It should be even noticed that the bulk spectral functions nearly independent of $x$ could not be obtained on scraped sample surfaces. [10]

In order to know the genuine effect of the electron correlation in the bulk for this system, we compare the bulk spectrum with a V 3d partial DOS for SrVO$_3$ obtained from a band-structure calculation [18] as shown in Fig. 3(b). Here, the partial DOS broadened by the instrumental resolution (dashed curve) is normalized to the bulk 3d spectral function of SrVO$_3$ by the integrated intensity from $E_F$ to 2.6 eV. This comparison shows us two obvious discrepancies. At first, the band-structure calculation cannot reproduce the incoherent spectral weight centered at 1.6 eV at all. Secondly, the width of the observed coherent part is about 60 % of the predicted value. These features indicate that the vanishing coherent spectral weight due to the narrowing is transferred to the incoherent part. Our study has revealed that the bulk electron correlation effect, which cannot be fully taken into account in the band-structure calculation, is strongly modifying the predicted bulk spectral function resulting in the spectral narrowing and redistribution. Nonetheless, it is found that the band-structure calculation really well reproduces the spectral intensity in the vicinity of $E_F$. This result provides the first experimental evidence for the conservation of DOS at $E_F$ against the electron correlation, suggesting that the self-energy has nearly no momentum dependence in Sr$_{1-x}$Ca$_x$VO$_3$. [20] Thus such a treatment as a dynamical mean-field theory (DMFT), \[ \text{in which the momentum dependence of the self-energy is not taken into account, can be a useful approach.} \]

In Fig. 4 are summarized the estimated surface 3d spectral functions by symbols. We notice that the coherent part near $E_F$ increases on going from CaVO$_3$ to SrVO$_3$. Figure 4 also demonstrates that these spectra coincide well with the broadened 3d spectra measured at $h\nu = 21.2$ eV as shown by solid curves, verifying that the surface contribution is predominant in the $h\nu = 21.2$ eV spectra. [21] Some people believe that $\lambda$ generally takes a minimum in the kinetic energy region of $\sim 100$ eV and becomes longer again at low kinetic energies, e.g. $\sim 20$ eV. Such an energy dependence has been known as a “universal curve”. [11] On the other hand, Figs. 2 and 4 suggest that the mean free path of the V 3d photoelectrons decreases with kinetic energy down to $\sim 20$ eV even in the low kinetic energy region. In this respect, a previous photoemission study of rare earth metals has indicated that $\lambda$ of 4f photoelectrons decreases also with the kinetic energy down to $\sim 20$ eV, [22] being again completely inconsistent with the so-called universal curve. The surface-sensitivity of photoemission spectroscopy depends upon the individual orbital of individual material at low-$h\nu$. Therefore bulk electronic structures should be re-examined by high-resolution high-energy photoemission spectroscopy especially for strongly correlated 3d and 4f electrons systems.

![Graph](image-url)
In summary, our results have demonstrated for the first time the importance of the high-energy and high-resolution photoemission spectroscopy for revealing the genuine bulk electronic states of the correlated 3d TM oxides. We have confirmed that the intensity of the spectral function at $E_F$ is not much changed in the bulk spectra even when the electron correlation is effective in the TM oxides. Future theoretical studies will clarify why the surface 3d electronic states change appreciably with $x$ whereas the bulk states are insensitive to $x$.

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[1] J. Hubbard, Proc. Roy. Soc. A 276, 238 (1963).
[2] N. F. Mott, Metal-insulator transitions. Second Edition (Taylor and Francis, London, 1990).
[3] A. Fujimori et al., Phys. Rev. Lett. 69, 1796 (1992).
[4] I. H. Inoue et al., Phys. Rev. B 58, 4372 (1998).
[5] A. Khurana, Phys. Rev. B 40, 4316 (1989).
[6] X. Y. Zhang, M. J. Rozenberg, and G. Kotliar, Phys. Rev. Lett. 70, 1666 (1993).
[7] R. Bulla, T. A. Costi, and D. Vollhardt, Phys. Rev. B 64, 045103 (2001).
[8] I. H. Inoue et al., Phys. Rev. Lett. 74, 2539 (1995).
[9] K. Morikawa et al., Phys. Rev. B 52, 13711 (1995).
[10] A. Fujimori et al., Spectroscopy of Mott Insulators and Correlated Metals, A. Fujimori, Y. Tokura, Eds. (Springer-Verlag, Berlin, 1995), p. 174.
[11] D. A. Shirley, Photoemission in Solids I, M. Cardona, L. Ley, Eds. (Springer-Verlag, Berlin, 1978).
[12] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Sci. 192, L849 (1987).
[13] A. Sekiyama et al., Nature 403, 396 (2000).
[14] Y. Saitoh et al., Rev. Sci. Instrum. 71, 3254 (2000).
[15] K. Maiti, P. Mahadevan, and D. D. Sarma, Phys. Rev. Lett. 80, 2885 (1998).
[16] K. Maiti et al., Europhys. Lett. 55, 246 (2001).
[17] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables 32, 1 (1985).
[18] The band-structure calculation performed by using a full-potential linearized augmented plane wave (FLAPW) method within the local density approximation. This method is one of the most reliable methods in the band-structure calculations.
[19] This theorem is applicable only at zero temperature. According to the finite temperature DMFT method within the local density approximation, an effect of the finite temperature $T = 20$ K ($0.0017$ eV) in our measurements is negligible compared with the band width $W (\sim 1$ eV) when bulk SrVO$_3$ is far from the Mott transition.
[20] According to the band-structure calculation in Ref. [8], the V 3d partial DOS of CaVO$_3$ is very similar to that of SrVO$_3$. Therefore the conservation of DOS at $E_F$ should also be applicable to CaVO$_3$ from our results.
[21] The surface contributions in the spectra measured at $h\nu = 40.8$ eV are estimated as at least 70 % from our results.
[22] F. Gerken et al., Physica Scripta 32, 43 (1985).