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### Angaben zur Veröffentlichung / Publication details:

Sekiyama, A., H. Fujiwara, S. Imada, S. Suga, H. Eisaki, S. I. Uchida, K. Takegahara, et al. 2004. "Mutual experimental and theoretical validation of bulk photoemission spectra of Sr<sub>1-x</sub>CaxVO<sub>3</sub>." *Physical Review Letters* 93 (15): 156402.  
<https://doi.org/10.1103/physrevlett.93.156402>.

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## Mutual Experimental and Theoretical Validation of Bulk Photoemission Spectra of $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$

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(Received 17 December 2003; published 5 October 2004)

We report high-resolution high-energy photoemission spectra together with parameter-free LDA + DMFT (local density approximation + dynamical mean-field theory) results for  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$ , a prototype  $3d^1$  system. In contrast to earlier investigations the bulk spectra are found to be insensitive to  $x$ . The good agreement between experiment and theory confirms the bulk sensitivity of the high-energy photoemission spectra.

DOI: 10.1103/PhysRevLett.93.156402

PACS numbers: 71.20.Be, 71.27.+a, 79.60.Bm

Electronic correlations in transition metal oxides (TMO) are at the center of present solid state research. Among TMO, cubic perovskites have the simplest crystal structure and, thus, may be viewed as a starting point for understanding the electronic properties of more complex systems. Typically, the  $3d$  states in those materials form comparatively narrow bands of width  $W \approx 2\text{--}3$  eV which lead to strong Coulomb correlations between the electrons. Particularly simple are TMO with a  $3d^1$  configuration such as  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  since they do not show a complicated electronic structure.

Intensive experimental investigations of spectral and transport properties of strongly correlated  $3d^1$  TMO started with the paper by Fujimori *et al.* [1]. These authors observed a pronounced lower Hubbard band in the photoemission spectra (PES) measured at low photon energies ( $h\nu \leq 120$  eV) which cannot be explained by conventional band-structure theory. A number of papers [2,3] subsequently addressed the spectral, transport, and thermodynamic properties of  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$ , yielding contradictory results. While the thermodynamic and transport properties (Sommerfeld coefficient, resistivity, and paramagnetic susceptibility) do not change much with  $x$ , low photon energy (low- $h\nu$ ) PES show drastic differences for varying  $x$ . In fact, these spectroscopic data seemed to imply that  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  is on the verge of a Mott-Hubbard transition for  $x \rightarrow 1$ . This is in concordance with the widespread theoretical expectation that the bandwidth  $W$  should decrease strongly with increasing  $x$

since the V-O-V angle is reduced from  $\theta = 180^\circ$  for cubic  $\text{SrVO}_3$  [4] to  $\theta = 154.3^\circ$  (rotation angle),  $171^\circ$  (tilting angle) [5] for orthorhombic  $\text{CaVO}_3$  [6].

With the SPring-8 beam line we are now able to reexamine this puzzling discrepancy by high-resolution high-energy PES which, owing to a longer photoelectron mean free path  $\lambda$  at  $h\nu \approx 1000$  eV, is much more bulk sensitive [7–11]. In this Letter, we show that these bulk-sensitive PES on fractured surfaces with  $\approx 100$  meV resolution are nearly independent of the Ca concentration  $x$  and significantly different from high-energy PES at 0.5 eV resolution on scraped surfaces [11]. The good agreement with LDA + DMFT [12–18] spectra provides an important cross validation: By means of a TMO prototype we show that the two cutting-edge methods employed here are indeed able to determine bulk spectra.

The high-resolution PES are summarized in Fig. 1 [19]. In all spectra, the peak near  $E_F$  and the broad peak centered at about  $-1.6$  eV correspond to the coherent (quasiparticle peak) and incoherent parts (lower Hubbard band), respectively. In contrast to low- $h\nu$  PES of  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  reported so far, including our own, the spectral variation with  $x$  is noticeably smaller in the spectra measured at  $h\nu = 900$  eV as summarized in Fig. 1(b). As shown in Fig. 1(c), the coherent spectral weight decreases drastically with decreasing  $h\nu$  for all 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.

However, both coherent and incoherent parts are drastically enhanced in a V  $2p - 3d$  resonance photoemission (not shown), and are therefore assigned to the effective V  $3d$  states around  $E_F$  [20]. Since the oxygen admixture to these predominantly  $3d$  states is very minor, the relative V  $3d/O\ 2p$  cross section which also changes by only 8% from  $h\nu = 275$  and 900 eV [21] can be neglected. Also note that the effect of PES matrix elements is generally small for high- $h\nu$  angle-integrated spectra. Therefore, the monotonous increase of the coherent part with  $h\nu$  is inevitably attributed to an increased bulk sensitivity.

We have obtained the bulk V  $3d$  [20] PES, Fig. 1(d), of  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  from the data at  $h\nu = 900$  and 275 eV by the following procedure [22]: (i) The mean free path  $\lambda$  has been calculated as  $\sim 17$  and  $\sim 7$  Å at  $h\nu = 900$  and 275 eV [7]. (ii) The bulk weight  $R$  ( $< 1$ , 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  $R_{275} = R_{900}^{2.4}$ . (iii) The observed V  $3d$  PES intensity at  $h\nu = 900$  eV is represented as  $I_{900}(E) = I_B(E)R_{900} + I_S(E)(1 - R_{900})$  while  $I_{275}(E) = I_B(E)R_{900}^{2.4} + I_S(E)(1 - R_{900}^{2.4})$ , where  $I_B(E)/I_S(E)$  is the bulk/surface  $3d$  PES and  $E$  stands for the energy relative to  $E_F$ . (4) If  $s$  is assumed to be 7.5 Å corresponding to about twice the V-O-V distance, [2]  $R_{900}$  ( $R_{275}$ ) is determined as  $\sim 0.64$  ( $\sim 0.34$ ). With this  $R_{900}$  we obtain the  $3d$  bulk PES  $I_B(E)$  shown in Fig. 1(d), noting that  $I_B(E)$  hardly changes ( $< 15\%$  at  $E_F$ ) even when we assume  $s$  to range from 5.4 to 11 Å. In contrast to the previous PES, the bulk  $3d$  PES are almost equivalent among the three compounds, indicating that the V-O-V distortion does not much influence the occupied bulk  $3d$  states in  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$ . This is consistent with the thermodynamic properties. It should be noticed that on scraped sample surfaces nearly  $x$ -independent bulk spectral functions could not be obtained [11].

Figure 2 shows the local-density approximation (LDA) density of states (DOS) for  $\text{SrVO}_3$  and  $\text{CaVO}_3$  which we obtained using the TBLMTO47 code of Andersen and co-workers [23] as well as a full-potential linearized augmented plane wave (FLAPW) method. The van Hove-like peak of the latter can also be obtained by a linear muffin-tin orbital (LMTO) method [24], leading to minor differences which are, however, not important for our LDA + DMFT calculations. Most importantly, the one-electron  $t_{2g}$  bandwidth of  $\text{CaVO}_3$ , defined as the energy interval where the DOS in Fig. 2 is nonzero, is found to be only 4% smaller than that of  $\text{SrVO}_3$  ( $W_{\text{CaVO}_3} = 2.5$  eV,  $W_{\text{SrVO}_3} = 2.6$  eV). The small reduction of the bandwidth

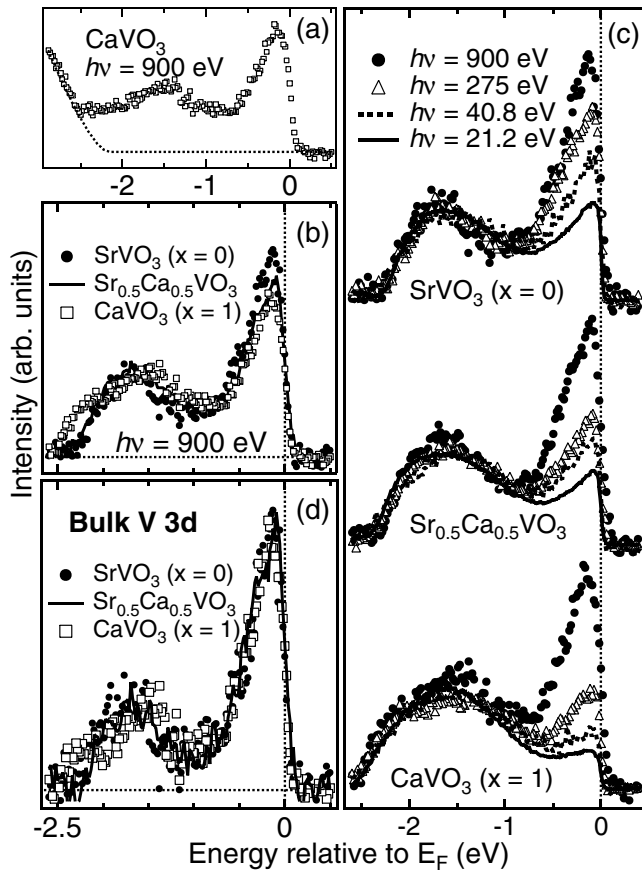


FIG. 1. (a) Raw spectrum of the high-resolution PES near  $E_F$  of  $\text{CaVO}_3$  (squares) and the fitted tails of O  $2p$  contributions. (b) V  $3d$  PES of  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  at  $h\nu = 900$  eV obtained by subtracting the fitted tails of O  $2p$  contributions from the raw spectra as in (a). (c)  $h\nu$  dependence of the V  $3d$  PES normalized by the incoherent spectral weight ranging from  $-0.8$  to  $-2.6$  eV. (d) Bulk V  $3d$  PES of  $\text{Sr}_{1-x}\text{Ca}_x\text{VO}_3$  as obtained by the procedure described in the text.

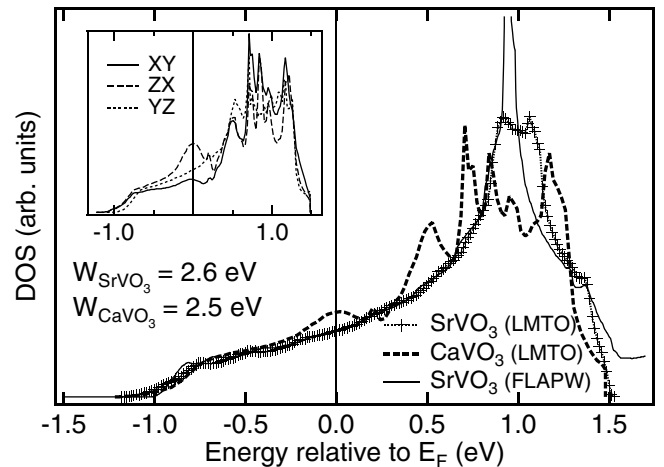


FIG. 2. Comparison of the LDA DOS of the V  $3d\ t_{2g}$  band for  $\text{SrVO}_3$  (line with cross marks) and  $\text{CaVO}_3$  (dashed line) obtained by using the LMTO method. The V  $3d\ (t_{2g} + e_g)$  partial DOS for  $\text{SrVO}_3$  (solid line) obtained by using the FLAPW method is also shown. In  $\text{CaVO}_3$  the degeneracy of the three  $t_{2g}$  bands is lifted (see inset).

well agrees with Ref. [24] and will later turn out to be important.

In order to determine the genuine effect of the electron correlations on the bulk spectra, we first compare in Fig. 3(a) the measured spectrum with a V 3d partial DOS for SrVO<sub>3</sub> obtained by using the FLAPW method. Here, the partial DOS broadened by the instrumental resolution (dashed curve) is normalized to the bulk 3d spectral function of SrVO<sub>3</sub> by the integrated intensity from  $E_F$  to  $-2.6$  eV. This comparison shows that the band-structure calculation does not reproduce the incoherent spectral weight at all and that the width of the observed coherent part is about 60% of the predicted value. Clearly, these deviations originate from electronic correlations which are not treated correctly in the band-structure calculation.

For a more quantitative analysis, we use LDA + DMFT as a nonperturbative approach [12,17,24], in which the local intraorbital Coulomb repulsion  $U$ , the interorbital repulsion  $U'$ , and the exchange interaction  $J$  are explicitly taken into account. We calculated these interaction strengths by means of the constrained LDA method [25] for SrVO<sub>3</sub>. The resulting value of the averaged Coulomb interaction is  $\bar{U} = 3.55$  eV ( $\bar{U} = U'$  for  $t_{2g}$  orbitals [17,26]) and  $J = 1.0$  eV.  $U$  is then fixed by the rotational invariance to  $U = U' + 2J = 5.55$  eV. These calculated values are in agreement with previous calculations of vanadium systems [27] and experiments [28]. We use these values in our LDA + DMFT calculations for both SrVO<sub>3</sub> and CaVO<sub>3</sub> [29] and employ quantum Monte Carlo (QMC) [30] simulations to solve the dynamical mean-field theory (DMFT) self-consistency equation. The resulting LDA + DMFT (QMC) spectra for SrVO<sub>3</sub> and CaVO<sub>3</sub> in Fig. 3(b) show genuine correlation effects, i.e., the formation of lower Hubbard bands at about  $-2$  eV and upper Hubbard bands at about  $2.5$  eV, with well pronounced quasiparticle peaks (coherent part) near  $E_F$ . The results indicate that both SrVO<sub>3</sub> and CaVO<sub>3</sub> are strongly correlated metals, but not on the verge of a Mott-Hubbard metal-insulator transition. The 4% difference in the LDA bandwidth between the compounds is reflected only in some additional transfer of spectral weight from the coherent to incoherent parts. The many-particle spectra of the two systems are seen to be quite similar, especially in the occupied states, in agreement with Ref. [24]. Figure 3(c) shows that the effect of temperature on the spectrum is small for  $T \lesssim 700$  K. The slight differences in the quasiparticle peaks between SrVO<sub>3</sub> and CaVO<sub>3</sub> lead to different effective masses, namely  $m^*/m_0 = 2.1$  for SrVO<sub>3</sub> and  $2.4$  for CaVO<sub>3</sub>, which agree with  $m^*/m_0 = 2-3$  for SrVO<sub>3</sub> and CaVO<sub>3</sub> as obtained from thermodynamics [2] and de Haas-van Alphen experiments [31].

In Fig. 3(d), we compare the experimental bulk V 3d [20] PES to the LDA + DMFT spectra (300 K), which

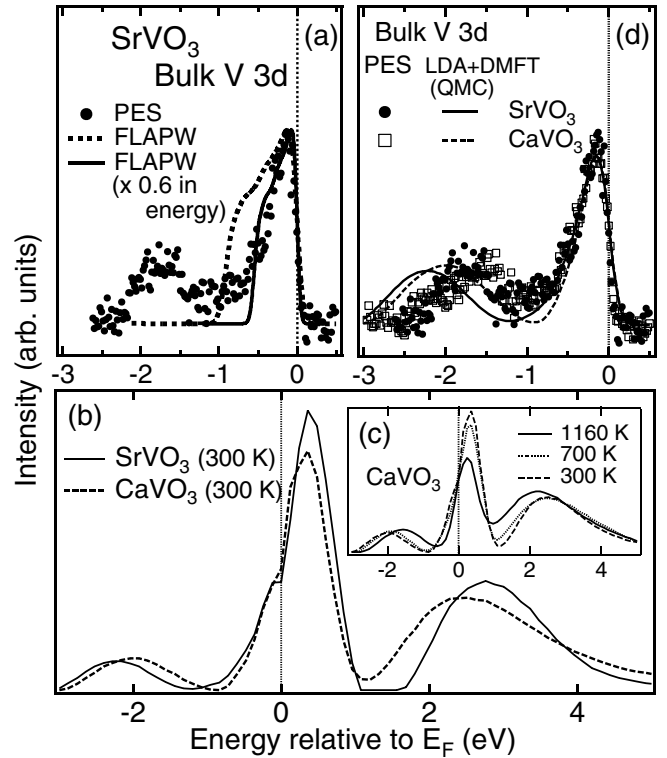


FIG. 3. (a) Comparison of the bulk 3d [20] PES of SrVO<sub>3</sub> (dots) to the 3d DOS obtained by using the FLAPW method (dashed curve), which has been multiplied with the Fermi function at 20 K and then broadened by the experimental resolution of 140 meV. The solid curve shows the same 3d DOS but the energy is scaled down by a factor of 0.6. (b) LDA + DMFT (QMC) spectrum of SrVO<sub>3</sub> (solid line) and CaVO<sub>3</sub> (dashed line) calculated at 300 K. (c) Effect of the temperature in the case of CaVO<sub>3</sub>. (d) Comparison of the bulk PES with the calculated LDA + DMFT spectra for SrVO<sub>3</sub> and CaVO<sub>3</sub>.

were multiplied with the Fermi function at the experimental temperature (20 K) and broadened with the PES resolution. The quasiparticle peaks in theory and experiment are seen to be in very good agreement. In particular, their height and width are almost identical for both SrVO<sub>3</sub> and CaVO<sub>3</sub>. There is some difference in the positions of the incoherent part which may be partly due to uncertainties in the *ab initio* calculations of  $\bar{U}$  or in the oxygen subtraction procedure of Fig. 1. Indeed, some differences have to be expected since both the experimental determination of the bulk spectrum and the LDA + DMFT method involve approximations. Hence, our good overall agreement confirms that the new high-energy high-resolution PES indeed measures bulk spectra which can be calculated quite accurately by LDA + DMFT without free parameters.

This work was supported by a Grant-in-Aid for COE Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, by the Deutsche Forschungsgemeinschaft through SFB 484 and

the Emmy-Noether program, the Russian Foundation for Basic Research through RFFI-01-02-17063 and RFFI-03-02-06126, the Ural Branch of the Russian Academy of Sciences for Young Scientists, Grant of the President of Russia MK-95.2003.02, and the National Science Foundation under Grant No. PHY99-07949. The photoemission at  $h\nu = 275$  and  $900$  eV was performed under the approval of the Japan Synchrotron Radiation Research Institute (1999B0076-NS-np). We thank T. Ushida, A. Shigemoto, T. Satonaka, T. Iwasaki, M. Okazaki, S. Kasai, A. Higashiya, K. Konoike, A. Yamasaki, A. Irizawa, and the staff of SPring-8, especially T. Muro, T. Matsushita, and T. Nakatani for supporting the experiments. We also thank A. Sandvik for making available his maximum entropy code and acknowledge valuable discussions with I. H. Inoue, A. Fujimori, R. Claessen, and M. Mayr.

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