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Electronic structure of early transition metal oxides, $Ca_{1-x}Sr_xVO_3$ and $La_{1-x}Ca_xVO_3$: What can we learn from photoelectron spectroscopy

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Abstract

Photoemission spectroscopy offers the unique possibility of mapping out the electronic structure of the occupied electron states. However, the extreme surface sensitivity of this technique ensures that only the surface and the near-surface regions of any sample are probed. An important question arises in this context—Is the electronic structure of the surface region the same as that of the bulk? We address this issue using two different series of vanadium oxides, $Ca_{1-x}Sr_xVO_3$ and $La_{1-x}Ca_xVO_3$. Our results clearly establish that the electronic structure of the surface region is drastically different from that of the bulk in both these cases. We provide a method to separate the two contributions: one arising from the near-surface region and the other representative of the bulk. This separation allows us to deduce some very unusual behaviors of the electronic structures in these systems.

Keywords: Electron correlation; Surface and interface states; Photoelectron spectroscopy

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1. Introduction

The electronic structure of strongly correlated transition metal oxides has attracted a great deal of attention both theoretically [1] and experimentally [2] due to many exotic properties exhibited by these systems such as high temperature superconductivity and colossal magnetoresistance. The Hubbard Hamiltonian $H=\sum t_{ij}c_{i\sigma}^{+}c_{j\sigma}+U\sum n_{i\uparrow}n_{i\downarrow}$ provides a simplistic quantitative description of the electron correlation, which displays explicitly the competition between the itinerant behavior of electrons via the hopping amplitude, t and the localization effects due to Coulomb repulsion, U. The bandwidth, W of the system is directly related to t ($W\sim 2zt$; z=coordination number). Thus, the effective correlation strength can be expressed as a function of a single parameter, U/W. Experimentally, photoemission spectroscopy has been extensively employed due to its ability to probe the electronic structure directly. While this technique is highly surface sensitive, leading to a substantial contribution from the surface electronic structure, as observed in rare earth intermetallics [3], its extensive use to understand the bulk properties of transition metal (TM) oxides has been based on the implicit assumption of very similar electronic structures at the surface and in the bulk. This is in general a reasonable assumption in many systems, as has often been demonstrated by a good agreement between experimentally obtained photoemission spectra and calculated ones on the basis of the bulk electronic structures [4], most notably for the late (Mn–Ni) transition metal oxides. Interestingly, the early transition metal oxides exhibit a spectacular failure of the assumption of similar surface and bulk electronic structure. Notably, the late transition metal oxides exhibit large covalent mixing of the TM d levels with the ligand p levels. Early TM oxides, however, exhibit a different scenario. Large charge-transfer energy [5], Δ, defined by the energy required to transfer an

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electron from O *p* levels to TM *d* levels, compared to the hopping strength, *t*, leads to a substantially reduced overlap of the ligand levels with the transition metal *d* levels. This allows one to investigate the effect of electron correlation as well as of charge carrier doping in the TM *d* band with the ligand levels playing only a minor role. In order to extract meaningful information from photoemission studies of early transition metal oxides, it is, however, necessary to separate the surface and the bulk contribution to the experimentally obtained spectra.

In this article, we review the detail electronic structure of a typical early transition metal oxide family, $Ca_{1-x}Sr_xVO_3$, as a function of electron interaction strength, followed by a discussion on another system, $La_{1-x}Ca_xVO_3$, with changing carrier concentration. In $Ca_{1-x}Sr_xVO_3$, Ca and Sr are homovalent (2+). The V–O–V bond angle is 160° in $CaVO_3$ and 180° in $SrVO_3$ [3]. Thus, the change in composition, x in $Ca_{1-x}Sr_xVO_3$ leads to a change in U/W without any change in charge carrier concentration. This is the simplest strongly correlated transition metal oxide system, since it remains paramagnetic down to the lowest temperature measured so far (T=50 mK), exhibit typical Fermi-liquid behavior and has nominally just one conduction electron per site of V^{4+}. On the other hand, the substitution of Ca^{2+} in place of La^{3+} in $La_{1-x}Ca_xVO_3$ dopes holes in the valence band without any significant change in V–O–V bond angle [7–10]. Thus, these compounds are well suited for the experimental realization of a continuous tuning of U/W and doping, respectively and consequently, provide good testing ground for the predictions of the Hubbard model.

2. Experimental details

Single crystalline samples of $Ca_{1-x}Sr_xVO_3$ were prepared by floating zone method and characterized by X-ray diffraction, Laue photography and thermogravimetric analysis. Polycrystalline samples of $La_{1-x}Ca_xVO_3$ were prepared from congruently molten states which gives rise to large grains with strong inter grain bonding and <1% of the impurity phases at the grain boundaries. The characterizations exhibit the samples to be stoichiometric, homogeneous and single phasic [6,7]. Experiments were carried out using monochromatic sources at a base pressure of 2×10^{-10} mbar with a resolution of 0.45 eV for X-ray photoemission (XP), and 14 meV and 22 meV with He I and He II photons, respectively. Experiments at soft-X-ray energies were carried out using synchrotron radiation from the VUV beamline (Elettra, Trieste). The cleanliness of each sample surface was maintained by repeated in-situ scrapings with an alumina file or cleaving, thereby exposing fresh sample surfaces, and was monitored by O 1*s* and C 1*s* spectra in case of the XPS study, as well as by analyzing the spectra in the 9–12-eV binding-energy region in the UPS study. No chemical-impurity feature was observed for any of the compositions studied. Reproducibility of the spectra with repeated cleaning processes was confirmed for each composition.

3. Results and discussion

In Fig. 1, the V $2p_{3/2}$ core level spectra of $Ca_{1-x}Sr_xVO_3$ exhibit three distinct features as marked in the figure for every composition in contrast to the single peak structure, expected from a homogeneous single-phase V^{4+} compound. Least-squared error analysis showed that the positions of the components, as well as the corresponding full widths at half maximum (FWHM) remain essentially the same across the series. Most significantly, the intensity ratio between the first and the last components are always approximately in the ratio of 1:1. The energy separations and the spectral widths of these three components agree with the V $2p_{3/2}$ signals from V_2O_3, VO_2 and V_2O_5, suggesting that the peaks 1, 2 and 3 arise from V^{3+}, V^{4+} and V^{5+} entities. The equal intensities of the V^{3+} and V^{5+} signals suggest that a fraction of V^{4+} ions spontaneously phase separate, $2V^{4+}\rightarrow V^{3+}+V^{5+}$, maintaining the charge balance. Since the escape depth of the photoelectrons strongly depends on their kinetic energies, one can tune the surface sensitivity of the technique by changing the photon energies. We, thus, investigate V $2p_{3/2}$ feature as a function of the photon energy in Fig. 2. Interestingly, the relative intensity of V^{4+} signal reduces monotonically with the decrease in photon energy. This observation establishes that the charge dis-

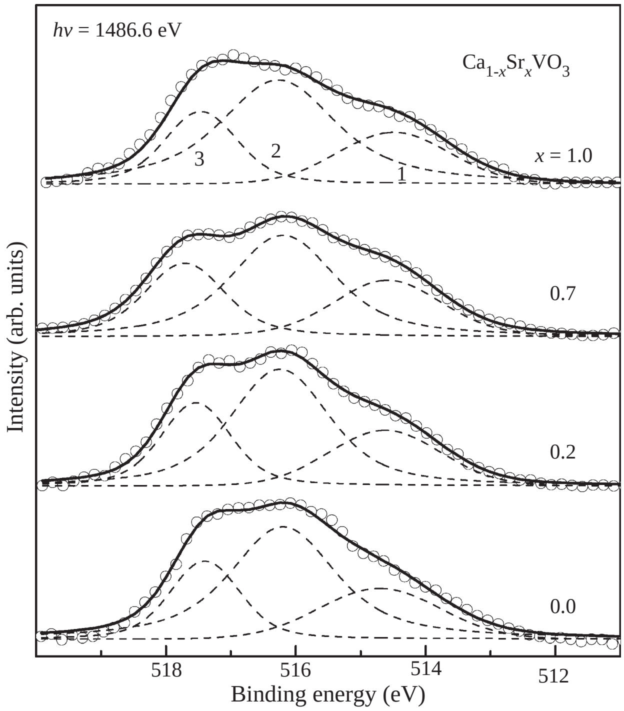

Fig. 1. V $2p_{3/2}$ spectra at Al Kα photon energy for different values of x in $Ca_{1-x}Sr_xVO_3$.