Electronic structure and metal–insulator transitions in Ti and V oxides

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The electronic structures of various Ti and V oxides have been studied by photoemission and X-ray absorption spectroscopy. For \( \text{La}_x\text{Sr}_{1-x}\text{TiO}_3 \), electron doping induces new photoemission feature within the band gap of \( \text{SrTiO}_3 \). For the 3d systems, as the Hubbard gap collapses and \( U/W \) becomes small, a new spectral feature grows around the Fermi level.

1. Introduction

Since the discovery of high-\( T_c \) superconductors, the behavior of holes or electrons doped in the transition metal oxide has attracted considerable interest. In high-\( T_c \) oxides, optical [1] and photoemission [2,3] studies have shown that carrier doping induces new spectral weight or so-called ‘gap states’ within the band gaps of the parent compounds. It is then interesting to see how Mott–Hubbard-type oxides behave when they are doped with extra carriers.

In this paper, we report on the results of photoemission (PES) and X-ray absorption (XAS) studies of \( \text{La}_x\text{Sr}_{1-x}\text{TiO}_3 \), where La substitution introduces electrons into the empty conduction band of \( \text{SrTiO}_3 \). With an integral number of electrons per atomic site, on the other hand, the system remains insulating when \( U/W > 1 \), and becomes metallic when \( U/W < 1 \), where \( U \) is the on-site Coulomb repulsion, and \( W \) is the one-electron bandwidth. In order to investigate the electronic states of the integer-filling system when the quantity \( U/W \) is changed, we have also studied several Ti\(^{3+} \) and V\(^{4+} \) compounds ranging from a Pauli-paramagnetic metal to a Mott insulator, which all formally have the d\(^{1} \) configuration.

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Fig. 1. Photoemission ($h\nu = 48\text{ eV}$, dots) and XAS spectra (dots) of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ compared with calculated spectra (solid curves) using the DOS derived from the LDA band-structure calculation under a rigid-band assumption.

Fig. 2. Photoemission spectra (dots) of $\text{YTiO}_3$ (insulating, $h\nu = 21.2\text{ eV}$), $\text{LaTiO}_3$ ($h\nu = 48\text{ eV}$), and $\text{SrVO}_3$ (metallic, $h\nu = 55\text{ eV}$) in the d-band region. The spectra of $\text{VO}_2$ (metallic phase, $h\nu = 60\text{ eV}$) and $\text{ReO}_3$ (metallic, $h\nu = 40.8\text{ eV}$) are taken from refs. [6] and [7], respectively. They are compared with the DOS given by band-structure calculations [8,9] (solid curves).

3. Discussion

The PES and XAS spectra are compared to the local density approximation (LDA) band-structure calculations for the end compounds $\text{SrTiO}_3$ and $\text{LaTiO}_3$ in fig. 1. For PES, we take the density of states (DOS) of $\text{SrTiO}_3$ and assume a rigid-band filling of the conduction band by doped electrons. In order to compare the calculated DOS with the experimental spectra, the Ti 3d and O 2p partial DOS is multiplied by appropriate photoionization cross sections with Gaussian and Lorentzian broadening. Instead of a sharp cut-off at the Fermi level expected from the rigid-band model, this 'band-like' or 'coherent' peak is suppressed and the spectral weight is transferred to the 'incoherent' one.

As for the XAS spectra, on the other hand, it is possible to fit the experimental data with the calculated unoccupied DOS.

A Monte Carlo simulation study for the two-dimensional single-band Hubbard model has been performed by Dagotto et al. [5]. In this model, upper and lower Hubbard bands appear at half filling. So the $\sim1.5\text{ eV}$ peak of $\text{LaTiO}_3$ in the experimental spectra seems to be a remnant of the lower Hubbard band. However, the Fermi level $\mu$ moves as the hole is doped in the Hubbard model, whereas $\mu$ is fixed in the experimental spectra and the peak remains and becomes the so-called 'gap state' for small $x$. Although the dimensionality differs between the calculation and experiment, these experimental features show fun-
damental disagreement with the single-band Hubbard model calculation.

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References


