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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 $La_xSr_{1-x}TiO_3$, electron doping induces new photoemission feature within the band gap of $SrTiO_3$. For the $3d^1$ 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 $La_xSr_{1-x}TiO_3$, where La substitution introduces electrons into the empty conduction band of $SrTiO_3$. 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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2. Experiment and results

Polycrystalline samples of $La_xSr_{1-x}TiO_3$ were prepared by melt-quenching a stoichiometric mixture of $SrCO_3$, La_2O_3, TiO_2 and Ti_2O_3 powders in a floating-zone furnace, and were checked by X-ray diffraction. All these samples show metallic conductivity at room temperature. However, it is difficult to control the oxygen stoichiometry of $LaTiO_3$, and this sample is metallic at room temperature probably due to a small amount of excess oxygen ($LaTiO_{3.01\pm0.01}$), although the stoichiometric sample is found to be insulating [4].

Photoemission experiments of $La_xSr_{1-x}TiO_3$ and $YTiO_3$ were carried out at BL-2 of the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, and also on an instrument equipped with a He discharge lamp ($h\nu = 21.2$ and 40.8 eV). Photoemission experiments of $SrVO_3$ were performed at BL-11 of the Photon Factory, Laboratory for High-Energy Physics. X-ray absorption measurements were performed at BESSY in Berlin with the SX700/II monochromator. The samples were cleaned in situ by scraping with a diamond file. In order to avoid surface degradation, the samples were cooled down to liquid-nitrogen temperature.

Valence band photoemission and oxygen K-edge XAS spectra of $La_xSr_{1-x}TiO_3$ are shown in fig. 1. In the PES spectra, the dominant feature at 4–9 eV is the oxygen 2p band. It is found that the E_F does not shift

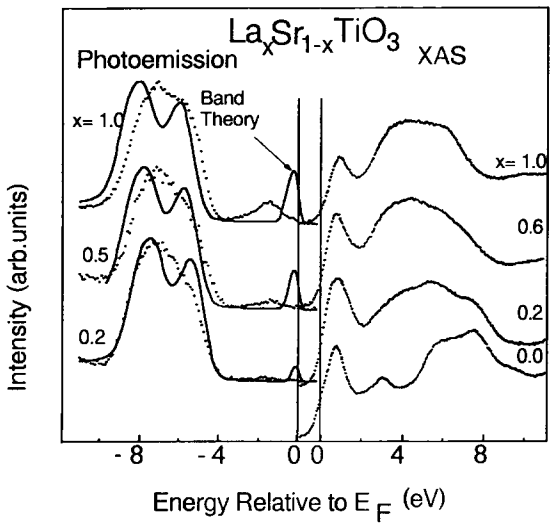

Fig. 1. Photoemission ($h\nu = 48$ eV, dots) and XAS spectra (dots) of $La_xSr_{1-x}TiO_3$ compared with calculated spectra (solid curves) using the DOS derived from the LDA band-structure calculation under a rigid-band assumption.

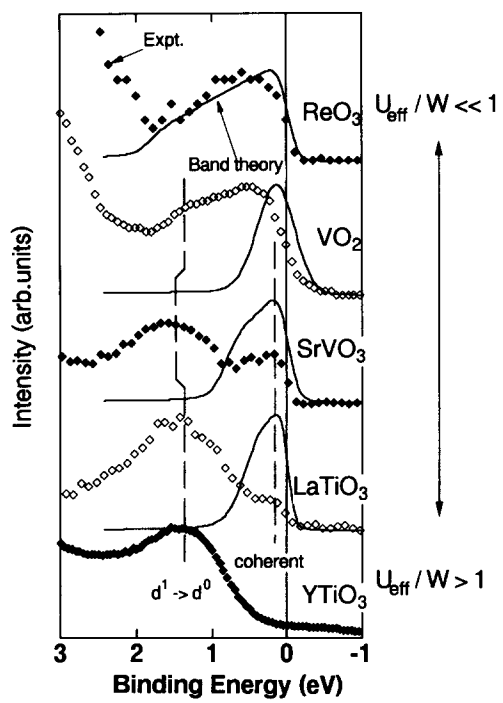

Fig. 2. Photoemission spectra (dots) of $YTiO_3$ (insulating, $h\nu = 21.2$ eV), $LaTiO_3$ ($h\nu = 48$ eV), and $SrVO_3$ (metallic, $h\nu = 55$ eV) in the d-band region. The spectra of VO_2 (metallic phase, $h\nu = 60$ eV) and ReO_3 (metallic, $h\nu = 40.8$ eV) are taken from refs. [6] and [7], respectively. They are compared with the DOS given by band-structure calculations [8,9] (solid curves).

appreciably with different x. The weaker feature within ~4 eV of E_F (within the band gap of the parent compound $SrTiO_3$) increases in intensity with La concentration x. Simultaneously, the XAS spectra seem to show that the structure at ~1 eV above E_F diminishes its intensity with electron doping x, although the absolute intensity normalization is not possible in the present spectra.

The PES spectra near E_F consist of two parts: one is the ~1.5 eV feature (we call it the 'incoherent part'), the other is the state very close to E_F (we call it the 'coherent part'). It is found that the ratios of the two features are not changed between samples with different x.

These two features are found in several formal d^1 oxides, as shown in fig. 2. When U/W increases, the intensity of the 'coherent part' decreases, the 'incoherent part' grows in intensity and the system becomes insulating, i.e., becomes a so-called 'Mott insulator'. From this, $LaTiO_3$ seems to be located close to the metal–insulator boundary.

3. Discussion

The PES and XAS spectra are compared to the local density approximation (LDA) band-structure calculations for the end compounds $SrTiO_3$ and $LaTiO_3$ in fig. 1. For PES, we take the density of states (DOS) of $SrTiO_3$ 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 appropriated photoionization cross sections with Gaussian and Lorentian 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 ~1.5 eV peak of $LaTiO_3$ in the experimental spectra seems to be a remnant of the lower Hubbard band. However, the Fermi level μ moves as the hole is doped in the Hubbard model, whereas μ 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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