

Doping-induced changes in the electronic structure of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$: Limitation of the one-electron rigid-band model and the Hubbard model

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The electronic structure of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ has been studied by photoemission and x-ray absorption spectroscopy. Electron doping through La substitution induces a new photoemission feature of Ti 3d character within the band gap of SrTiO_3 ; the Fermi level is located near the bottom of the conduction band of SrTiO_3 . The experimental results are incompatible with the rigid-band behavior predicted by one-electron band theory or Hubbard-model calculations.

The evolution of electronic states in Cu-oxide superconductors with carrier doping has been the subject of much controversy. Optical¹ and photoemission^{2,3} studies have shown that carrier doping induces spectral weight or so-called "gap states" within the bands gaps of the parent compounds, whereas oxygen 1s core-level absorption spectra have been interpreted in terms of the rigid-band filling of the O 2p band by doped holes or that of the Cu 3d-derived upper Hubbard by doped electrons.⁴ Moreover, it has been reported that in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, the position of the Fermi level (E_F) is located well inside the band gaps of the parent compounds with a minimal shift with doping³ whereas a rigid-band shift has been observed for $\text{Ba}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{CuO}_8$.⁵

In this paper, we report on the results of photoemission and x-ray absorption (XAS) studies of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$, where La substitution introduces electrons into the conduction band of SrTiO_3 . This system differs from the Cu oxides in that the parent compound has the empty Ti 3d band and therefore that the band gap is not due to electron correlation. This offers a possibility of clarifying the role of electron correlation in the formation of the gap states. The results clearly show the formation of gap states, inconsistent with the rigid-band behavior predicted by one-electron band theory and a recent exact diagonalization study of the Hubbard model⁶ although the E_F is found near the bottom of the conduction band as in the rigid-band model.

SrTiO_3 is an *n*-type semiconductor having the cubic perovskite-type structure. LaTiO_3 is a Pauli-paramagnetic metal at room temperature and orders antiferromagnetically below $T_N \approx 125$ K;⁷ it has a distorted perovskite (GdFeO₃-type) structure.⁸ La doping makes $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ metallic for *x* as small as <0.1 .⁹ All the doped samples studied here are therefore metallic. Polycrystalline samples were synthesized by melt-quenching

stoichiometric mixtures of La_2O_3 , TiO_2 , and SrO powders in a floating-zone furnace, and were checked by x-ray diffraction. Photoemission experiments performed at beamline BL-2 of the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, and also using a spectrometer equipped with a helium discharge lamp ($h\nu=21.2$ eV) and a Mg x-ray source. The total resolution of the ultraviolet photoemission spectra was 0.2–0.4 eV depending on the photon energy. X-ray absorption measurements were carried out at Berliner Elektronen-speicherrung Gesellschaft für Synchrotronstrahlung (BESSY) with the SX700/II monochromator. The instrumental resolution was better than 0.1 eV in the O 1s absorption range. In order to obtain clean surfaces, the samples were scraped *in situ* with a diamond file in a vacuum of 1×10^{-10} Torr. Photoemission measurements were made at liquid-nitrogen temperature in order to prevent surface degradation in ultrahigh vacuum.

Band-structure calculations were performed for stoichiometric SrTiO_3 and LaTiO_3 using the localized-spherical-wave method¹⁰ in the local-density approximation. A minimal basis set of orbitals was used to achieve the self-consistency and to obtain low-energy states probed by photoemission. An extended basis set was then included to permit an accurate calculation of high-energy states probed by XAS. For simplicity, the cubic perovskite structure has been assumed for LaTiO_3 . We do not think this assumption will significantly influence the comparison below.

The Ti 2p XAS study of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ (Ref. 11) has indicated that extra electrons introduced by La substitution enter the Ti 3d orbitals and that the system is in the Mott-Hubbard regime. The dipole selection rules indicate that O 1s XAS spectra of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ correspond to transitions into O 2p character hybridized into the unoccupied metal states. Accordingly, in Fig. 1 the O 1s

spectra are compared with the calculated oxygen *p* partial density of states (DOS), which has been broadened by Gaussian and Lorentzian functions in order to simulate the instrumental and life-time broadening. The E_F marked in the figure is determined from the binding energy of the O 1s x-ray photoemission peak. (For $x=0$, we have not measured photoemission spectra because of charging effects, and the calculated DOS and XAS spectrum have been tentatively aligned at the leading peak.) The broad peak around ~ 538 eV in SrTiO₃ is attributed to Sr 4*d* bands with O 2*p* character mixed in, and that around ~ 536 eV in LaTiO₃ to La 5*d* bands. The peak at ~ 532 eV is the t_{2g} subband of the Ti 3*d* states; the e_g subband is obscured by the overlapping La 5*d* or Sr 4*d* bands. Thus good overall agreement has been obtained between the experiment and calculated DOS except for the peak at ~ 524 eV for $x=0$, which might be due to the effect of the O 1s core-hole potential. It should be noted that electron doping does not induce a "pre-edge peak" in the O 1s XAS as in the electron-doped Nd_{2-x}Ce_xCuO₄.¹² If we regard La_xSr_{1-x}TiO₃ as a hole-doped LaTiO₃, no such peak grows because the gap is already closed in LaTiO₃.

Figure 2 shows the valence-band photoemission spectra of La_xSr_{1-x}TiO₃. The dominant feature located at 4–9 eV is formed by bands of primarily O 2*p* character. The emission within ~ 4 eV of E_F increases intensity with x and is attributed to Ti 3*d* states. This assignment was confirmed by its resonance enhancement above the Ti

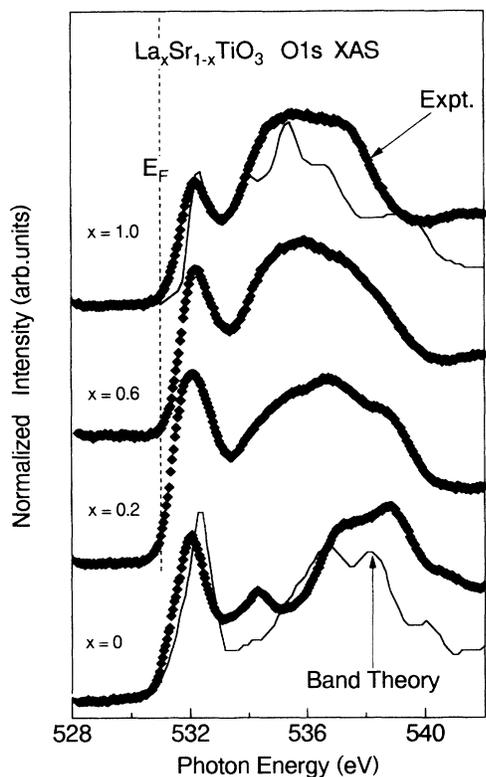


FIG. 1. Oxygen 1s x-ray absorption spectra compared with the oxygen *p* partial DOS derived from the band-structure calculation.

3*p* → 3*d* absorption threshold. The line shape of this feature essentially does not change with x down to $x \approx 0.1$ as illustrated in Fig. 3. Since the optical band gap of SrTiO₃ is ≈ 3.2 eV,¹³ we conclude from the position of the O 2*p* band that E_F in La_xSr_{1-x}TiO₃ is located slightly above the bottom of the Ti 3*d* conduction band. The E_F of La_xSr_{1-x}TiO₃ does not shift appreciably with x although it is higher than that of Nb-doped semiconducting SrTiO₃ by ≈ 0.8 eV.¹⁴ The spectral weight of the doping-induced emission is probably transferred from the Ti 3*d* band above E_F , although the decrease in the intensity of the Ti 3*d* band with x is not clear from the O 1s XAS spectra (Fig. 1) because of the difficulty in absolute intensity normalization and the possible x dependence of the Ti 3*d*–O 2*p* hybridization strength. (The XAS spectra have tentatively been normalized at $h\nu \sim 550$ eV, where the intensity is assumed to be independent of composition.) Here, we note that doping-induced photoemission feature has been clearly observed at and below E_F for Nd_{2-x}Ce_xCuO₄.¹⁵

The above results deviate from the rigid-band model. This is more clearly illustrated in the detailed comparison of the photoemission spectra with the band-structure calculation shown in Fig. 2. Since the band structures of SrTiO₃ and LaTiO₃ are essentially the same apart from the Sr- and La-related high-energy states and the magnitude of the O 2*p*–Ti 3*d* separation (calculated to be ≈ 2.0 eV for SrTiO₃ and ≈ 3.0 eV for LaTiO₃), we take the DOS of SrTiO₃ and assume a rigid-band filling of the conduction band by doped electrons. The Ti *d* and O *p* partial DOS have been multiplied by corresponding photoionization cross sections and broadened with Gaussian and Lorentzian functions. The calculated O 2*p*–Ti 3*d*

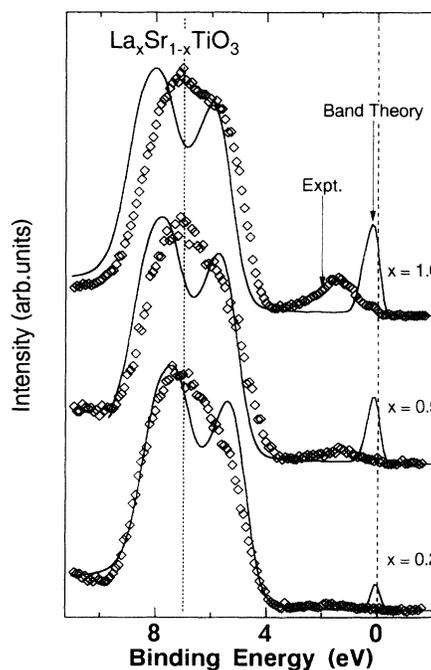


FIG. 2. Photoemission spectra ($h\nu=48$ eV) compared with the band-structure calculation. The vertical line shows the fixed position of the O 2*p* band.

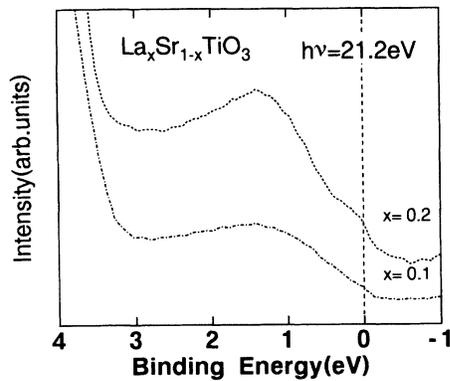


FIG. 3. Photoemission spectra ($h\nu=21.2$ eV) near the Fermi level on an expanded scale for small doping concentrations.

separation has been adjusted so that the experimental and calculated positions of the O $2p$ band coincide for $x \approx 0.2$. The theoretical spectra indicate that the partial filling of the t_{2g} band would lead to the appearance of a narrow emission with a sharp Fermi cutoff, in obvious disagreement with experiment. Also, the rigid-band model predicts a E_F shift of ≈ 0.5 eV between $x \approx 0$ and $x=1$ whereas the observed position of the O $2p$ band is almost fixed.

The discrepancy between the photoemission spectra and band theory for $x=1$ arises from strong d -electron correlation since LaTiO_3 is close to a Mott insulator.⁹ The emission peak at ~ 1.5 eV has been attributed to the remnant of the lower Hubbard band.¹⁶ The same discrepancy, however, persists down to $x \approx 0.1$. This is difficult to understand along the same line because, for small doping concentration, electron correlation due to short-range Coulomb repulsion could become less important and the one-electron rigid-band model is expected to be recovered. Indeed, an exact diagonalization study of the single-band Hubbard model⁶ has demonstrated an apparent rigid-band shift of E_F with doping. Also, the optical properties of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ show free-electron-like behavior below ~ 0.5 .⁹ As a possible origin for the discrepancy between theory and experiment, we consider effects which are not included in the one-electron band theory nor in the Hubbard model.

(i) Multiplet effects invoked to explain the XAS and bremsstrahlung isochromat spectra of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (Ref. 17) cannot account for the present results since the photoemission final state is simply d^0 .

(ii) Impurity potential due to the La^{3+} ions substituting

Sr^{2+} produces donor levels, but the binding energy of such a donor level would be orders of magnitude too small to account for the ~ 1.5 -eV peak.

(iii) Long-range Coulomb interaction combined with potential disorder might cause a pseudogap in metallic systems¹⁸ since it is known to produce a Coulomb gap in insulators.¹⁹ Such an effect, however, depends on the mean distance between doped electrons and hence should diminish with decreasing x .

(iv) If there exists strong coupling between the doped electrons and lattice distortion or vibration, the lattice motion cannot follow the sudden disappearance of the photoelectron, leading to high binding energy features. Such a coupling, however, would lead to a heavy electron mass, apparently inconsistent with the optical properties.⁹

Although the origin of the peak shift to ~ 1.5 eV for small x still remains unclear, we note that similar photoemission results have been previously reported for reduced samples of SrTiO_3 (Ref. 20) and TiO_2 ,²¹ where electrons are doped via oxygen vacancies: In these compounds, Ti $3d$ -derived emission appears showing a peak at ~ 1 eV below E_F . Similar non-rigid-band doping behaviors have been found for a hole-doped Mott-Hubbard insulator $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$.¹⁸

In conclusion, electron doping in SrTiO_3 induces a new spectral feature of Ti $3d$ character predominantly below E_F as in the case of the electron-doped superconductor $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. The position of E_F shows a minimal shift with doping; it is clearly located near the bottom of the conduction band of SrTiO_3 , unlike the ambiguous situations of Cu oxides. The new spectral feature is spread over the band gap of SrTiO_3 with a peak ~ 1.5 eV below E_F . The persistence of the peak down to $x \approx 0.1$ cannot be explained by either the Hubbard model or the one-electron rigid-band model, suggesting that electron correlation is not the only origin of the formation of gap states in doped transition-metal oxides.

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