

## Evolution of the spectral function in Mott–Hubbard systems across metal–insulator transitions

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The electronic structure of Mott–Hubbard-type Ti and V oxides have been studied by photoemission and X-ray absorption spectroscopy. The evolution of the spectra across the Mott transition indicates characteristic transfer of spectral weight from the incoherent to the coherent part of the spectral function. Across the metal–insulator transitions induced by carrier doping, new spectral weight is shown to fill the band gaps of the parent compounds.

### 1. Introduction

Electron correlation in narrow-band systems has been studied using the Hubbard model [1]. According to the model, the magnitude of the on-site Coulomb energy  $U$  and the one-electron band width  $W$  control the physical properties of the system: for integer band filling, the system undergoes a phase transition (Mott transition) at  $U/W \approx 1$  between a Mott insulator and a correlated metal. Through carrier doping, the band filling is changed from an integer to intermediate ones and the system becomes conducting even for  $U/W > 1$ . Carrier doping of Mott insulators has recently attracted considerable interest as a model for the high-temperature superconductors.

The single-particle spectral function  $\rho(\omega)$  is one of the most basic quantities of interacting electron systems and can be measured by photoemission and inverse-photoemission spectroscopy (BIS). No widely accepted picture for the  $\rho(\omega)$  of the Hubbard model, however, exists at present. In particular, it has been controversial whether carrier doping induces new spectral weight or so-called ‘gap states’ within the

original Hubbard gap. These complications arise from the nature of the splitting between the lower and upper Hubbard bands, which is fundamentally different from the splitting of one-electron energy bands [2].

In order to elucidate the above controversial issues, we have made photoemission and X-ray absorption (XAS) studies on various Ti and V oxide systems, which we consider typical Mott–Hubbard-type systems. Oxygen 1s core-level XAS yields the spectral function above the Fermi level ( $E_F$ ) as BIS does although it probes only the oxygen p component.

### 2. Materials

In perovskite-type Ti and V oxides, the metal 3d band is split into the  $e_g$  and  $t_{2g}$  sub-bands. Because of the degeneracy of the  $t_{2g}$  band, we will use  $U_{\text{eff}}$ , which includes intra-atomic exchange contribution, instead of  $U$ . For the d-band filling  $n = 1$  or 2, a Mott transition occurs at  $U_{\text{eff}}/W \approx 1$ , where  $W$  is the width of the  $t_{2g}$  band. In fig. 1, we have plotted various Ti and V oxides against  $U_{\text{eff}}/W$  and  $n$ . Compounds with  $U_{\text{eff}}/W > 1$  for  $n = 1$  or 2 are Mott insulators whereas compounds with  $n = 0$  are ordinary band insulators. Carrier doping in these insulators induces insulator-to-metal transitions. It should be noted that the insulating region with intermediate  $n$ 's are due to Anderson

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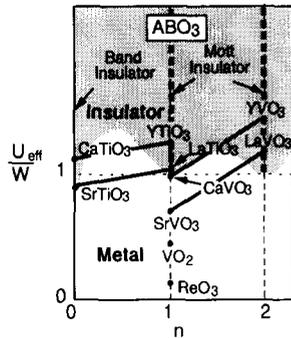


Fig. 1. Perovskite-type Ti and V oxides plotted against the d-band filling  $n$  and  $U_{\text{eff}}/W$ .

localization rather than to Mott localization since these states would be metallic if there were no potential disorder.

We have studied some  $\text{Ti}^{3+}$  and  $\text{V}^{4+}$  perovskite-type oxides shown in fig. 1 as model Mott–Hubbard systems with integer band filling, namely  $n = 1$ . In going from  $\text{YTiO}_3$  to  $\text{LaTiO}_3$  to  $\text{SrVO}_3$ , the crystal structure approaches from distorted perovskite structures to the ideal cubic one [3], which increases the overlap between neighboring d orbitals and hence  $W$ . In addition, the p–d hybridization increases in going from the  $\text{Ti}^{3+}$  to  $\text{V}^{4+}$  compounds, which in turn increases  $W$  and decreases  $U_{\text{eff}}$ . Thus,  $U_{\text{eff}}/W$  will decrease in the order  $\text{YTiO}_3 \rightarrow \text{LaTiO}_3 \rightarrow \text{SrVO}_3$ . Indeed,  $\text{YTiO}_3$  is a ferromagnetic Mott insulator [4],  $\text{LaTiO}_3$  is a ‘barely metallic’ antiferromagnet (weakly ferromagnetic) [5] and  $\text{SrVO}_3$  is a paramagnetic metal [6]. We also compare the spectra of other  $d^1$  systems,  $\text{VO}_2$  [7] and  $\text{ReO}_3$  [8], with those of the perovskites. The  $U_{\text{eff}}/W$  of  $\text{VO}_2$  is expected to be smaller than that of  $\text{SrVO}_3$  because of the much shorter V–V distance. For the normal metal  $\text{ReO}_3$ , certainly  $U_{\text{eff}}/W \ll 1$  because of the large Re 5d band width.

As a valence control system, we have studied  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ , in which the Ti valence is varied between  $\text{Ti}^{4+}(d^0)$  and  $\text{Ti}^{3+}(d^1)$ . Electron doping through La substitution makes the system metallic except for  $x \ll 0.1$  [9,10].

### 3. Composition-dependent Mott transition

Photoemission spectra of the  $d^1$  oxides are shown in fig. 2 [11]. One notices in fig. 2 that the d band consists of two parts: One is within  $\sim 1$  eV of  $E_F$  with a sharp Fermi cut-off and the other is a broad peak centered  $\sim 1.5$  eV below  $E_F$ ; with increasing  $U_{\text{eff}}/W$ , the  $\sim 1.5$  eV peak becomes more intense whereas the feature near  $E_F$  becomes weaker and vanishes in the

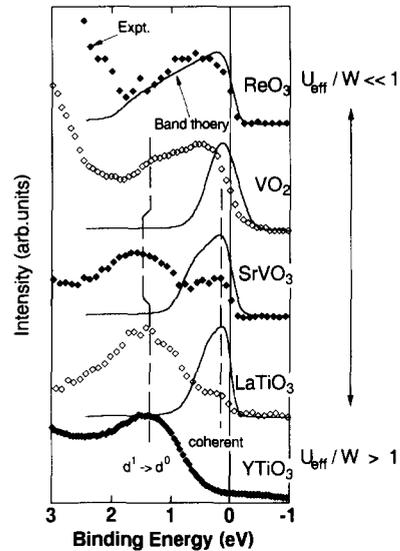


Fig. 2. Photoemission spectra ( $h\nu = 21.2\text{--}48$  eV) of  $\text{Ti}^{3+}$  and  $\text{V}^{4+}$  oxides with  $d^1$  configuration with varying  $U_{\text{eff}}/W$  [11]. They are compared with the DOS given by LDA band-structure calculations (solid curves).

insulating limit  $\text{YTiO}_3$ . The spectra are compared with the local-density approximation (LDA) band-structure calculations in fig. 2. The emission within  $\sim 1$  eV of  $E_F$  seems to correspond to the density of states (DOS) given by the calculations, and are attributed to itinerant d-band states or quasi-particle excitations; we will refer to this part as the ‘coherent part’ of the spectral function. The  $\sim 1.5$  eV peak in each compound is located close to that of the lower Hubbard band of  $\text{YTiO}_3$  and has no corresponding feature in the calculated DOS. We therefore attribute this feature to a remnant of the lower Hubbard band and refer to it as the ‘incoherent part’ of the spectral function. For  $\text{ReO}_3$ , the spectrum does not show any evidence for incoherent spectral weight.

Although we do not yet have systematic  $U_{\text{eff}}/W$ -dependent data above  $E_F$ , we speculate that the spectral function as a whole of the degenerate Hubbard model behaves like fig. 3 for integer d-band filling. This behavior is not necessarily consistent with recent theoretical calculations on the spectral function of the Hubbard model: Monte Carlo simulation [12] and exact diagonalization [13,14] studies predict rather rigid-band-like shifts of the upper and lower Hubbard bands toward  $E_F$  with decreasing  $U/W$ . A weak-coupling perturbation study on the infinite-dimension Hubbard model [15] seems to show structures corresponding to the incoherent spectral weight in the metallic state although the vicinity of the Mott transition has not been investigated there.

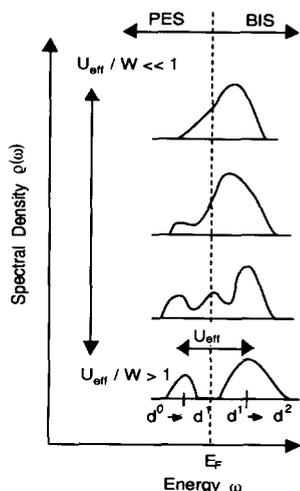


Fig. 3. Schematic representation of the single-particle spectral function for the d band with integer band filling, as a function of  $U_{\text{eff}}/W$ .

#### 4. Doping-induced metal–insulator transition

Figures 4 and 5 show the valence-band photoemission and O 1s XAS spectra of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  [16]. Upon La substitution, new spectral weight of Ti 3d-character appears within the band gap of  $\text{SrTiO}_3$  and its intensity increases with  $x$ . The line shape of this feature essentially does not change with  $x$  down to  $x \approx 0.1$ . From the upper edge of the O 2p band

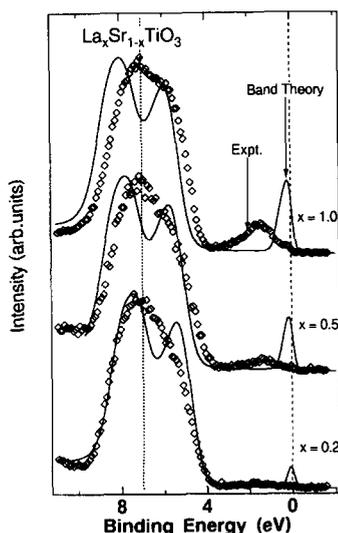


Fig. 4. Photoemission spectra ( $h\nu = 48 \text{ eV}$ ) of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  compared with LDA band-structure calculation [16]. The O 2p band is located 4–9 eV below  $E_F$ .

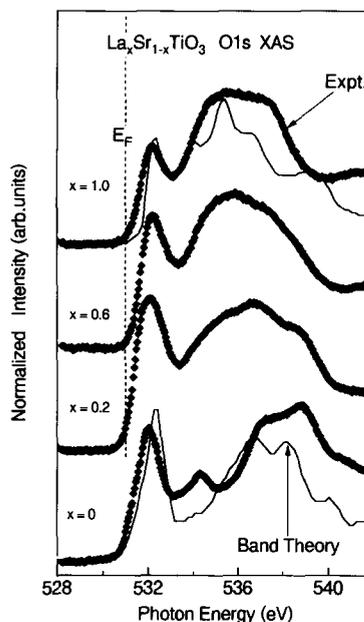


Fig. 5. Oxygen 1s XAS spectra of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  compared with band-structure calculation [16]. La 5d and Sr 4d bands are seen at  $\sim 536 \text{ eV}$  and  $\sim 538 \text{ eV}$ .

( $\sim 3.8 \text{ eV}$  below  $E_F$ ) and the optical band edge of  $\text{SrTiO}_3$  ( $\sim 3.2 \text{ eV}$ ), we conclude that  $E_F$  in  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  is located near or slightly above the bottom of the Ti 3d conduction band and does not shift appreciably with  $x$ .

From these results, we show schematically in fig. 6 the electronic structure of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  as a function of doping concentration  $x$ : upon electron doping, new spectral weight appears below  $E_F$  within the band gap of the parent insulator. For a hole-doped Mott–

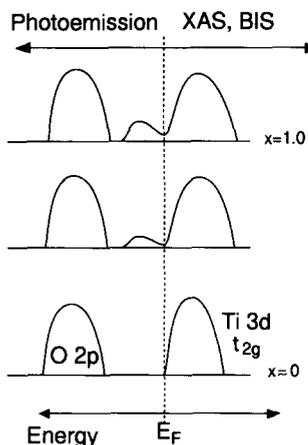


Fig. 6. Schematic representation of the single-particle spectral function of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  as a function of  $x$ .

sulator  $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$ , on the other hand, new spectral weight is induced above  $E_F$  within the band gap (Hubbard gap in this case) of  $\text{ZnV}_2\text{O}_4$  [17,18]. These observations imply that there is essentially electron–hole symmetry in the spectral functions of carrier doped Mott insulators.

The present result is in distinct disagreement with the one-electron rigid-band model as can be seen from the comparison of the photoemission spectra with the band-structure calculation shown in fig. 4. This can be easily understood for  $x \approx 1$  ( $\text{LaTiO}_3$ ) where d electrons are almost localized due to electron correlation. The disagreement for small  $x$ 's, however, is difficult to interpret because electron correlation should become unimportant with decreasing  $x$  and the one-electron rigid-band model should be recovered. Indeed, an exact diagonalization study of the single-band Hubbard model [19] has demonstrated an apparent rigid-band shift of  $E_F$  with doping. Also, the optical properties of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  are free-electron-like for carrier concentrations below  $x \sim 0.5$  [9].

### 5. Limitation of the Hubbard model

Our spectroscopic results are thus not necessarily consistent with the prediction of the recent theoretical results on the Hubbard model. The discrepancies would be attributed to effects not included in the model: (i) orbital degeneracy, (ii) multiplet effects, (iii) long-range Coulomb interaction, (iv) impurity/disordered potential due to the substituted cations at the A site, or (v) electron–phonon interaction. Among these, multiplet effects are excluded in the present study since our photoemission probes final states with  $d^0$  or  $d^1$  configuration. Long-range Coulomb interaction alone will also be unable to explain the results since it should diminish at low electron concentration  $x$ , but a complex combination of long-range Coulomb interaction, electron–phonon coupling and potential disorder might be responsible for the observed anomalous behavior.

As we do not have microscopic theories with which one can consistently interpret the experimental data at present, we take a phenomenological analysis in which all interaction effects are included in the self-energy  $\Sigma(\omega, \mathbf{k})$  of quasi-particles. It can be shown that a local ( $\mathbf{k}$ -independent) self-energy with constant renormalization factor  $z(\omega) \equiv [1 - \text{Re} \partial \Sigma(\omega) / \partial \omega]^{-1}$  is unable to explain the low spectral density at  $E_F$  compared to those calculated by the LDA calculations. One possible origin of the low spectral density at  $E_F$  is the strong  $\omega$ -dependence of the renormalization factor: If we assume  $z(\omega) \ll 1$  in the vicinity of  $E_F$  and  $z(\omega) \sim 1$  otherwise, the spectral density at  $E_F$  is apparently reduced unless the energy resolution of photoemission

spectroscopy is high enough. Another possible origin is the  $\mathbf{k}$ -dependence of the self-energy [20] and will have to be investigated in future.

If the local  $z(\omega)$  had such an energy dependence as stated above, a Kramers–Kronig relation may lead to  $\text{Im} \Sigma(\omega) \sim -|\omega|$  near  $E_F$  as in marginal Fermi-liquid phenomenology [21] except for the very vicinity of  $E_F$ . Indeed, the recent optical study of  $\text{LaTiO}_3$  ( $h\nu > 0.1$  eV) [9] has indicated that the mass steeply increases toward  $h\nu \rightarrow 0$  and the relaxation time behaves rather linear in  $h\nu$ .

### 6. Conclusion

We have demonstrated the evolution of the single-particle spectral function across the Mott transition and the metal–insulator transitions induced by carrier doping. The results show characteristic transfer of spectral weight and doping-induced filling of the band gaps. These findings cannot be satisfactorily explained by existing theories, necessitating improved description of interacting electron systems.

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