

# Spectral functions in doped transition metal oxides

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## Abstract

We present experimental photoemission and inverse photoemission spectra of  $\text{SrTiO}_{3-\delta}$  representing electron doped  $d^0$  systems. Photoemission spectra in presence of electron doping exhibit prominent features arising from electron correlation effects, while the inverse photoemission spectra are dominated by spectral features explainable within single-particle approaches. We show that such a spectral evolution in chemically doped correlated systems is not compatible with expectations based on Hubbard or any other similar model. We present a new theoretical approach taking into account the inhomogeneity of the *real* system which gives qualitatively different results compared to standard *homogeneous* models and is in quantitative agreement with experiments. PACS numbers: 79.60.Bm, 79.60.Ht, 71.30.+h

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Following the discovery of high  $T_c$  oxides [1], there has been a resurgence of interest in doped transition metal oxides. Recent investigations have revealed some very unusual physics in these systems [2–4].  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  [2] is a system containing Ti  $3d$  electrons where the carrier concentration can be varied in a controlled fashion. At one end,  $\text{LaTiO}_3$  is a Mott-Hubbard insulator with a  $3d^1$  configuration, while at the other end of the solid solution,  $\text{SrTiO}_3$  is a band insulator with a  $3d^0$  configuration. Thus, varying  $x$  tunes the electron configuration continuously between 0 and 1. For large values of  $x$ , the transport and magnetic properties [2] as well as the experimentally observed spectral weights behave as a correlated doped Mott insulator. For small values of  $x$  ( $\approx 0$ ), the system represents small amount of electron doping in a  $3d^0$  configuration, and thus, it should behave as a *doped band insulator* and is expected to show little correlation effects. This expectation is also consistent with transport and magnetic properties of such compounds [2,5] which exhibit an essentially free-electron like behavior.

Interestingly however, ultra-violet photoemission spectra (UPS) of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  with small  $x$  ( $= 0.1$  and  $0.2$ ) exhibit two features: a coherent low energy feature and a very prominent incoherent feature which is in fact found to be *more intense* than the coherent feature [4]. The observation of a large fraction of incoherent to coherent spectral weight suggests the presence of very strong correlation effects, in contrast to transport and magnetic properties, as well as to the theoretical expectations of an uncorrelated behavior close to the  $d^0$  configuration. Coherent features at low energies and incoherent features at around 1.4 eV are also seen in systems with one d electron per unit cell [3]. The evolution of the redistribution of spectral weight as a function of interaction strength in the half filled system can be accounted by zero temperature large  $d$  calculations based on the Hubbard model [6]. The doping dependence of these features, however, has not been accounted within this framework.

In order to clarify these important issues, we have reinvestigated the electronic structure of lightly doped  $d^0$  systems both experimentally and theoretically. We supplement the already existing UPS of  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  with those of  $\text{SrTiO}_{3-\delta}$ , where the oxygen deficiency

( $\delta$ ) introduces electrons into the stoichiometric  $d^0$  system. We have also carried out inverse photoemission experiments in these systems. Since we expect that the strength of the incoherent features is more visible in the unoccupied part of the spectrum in systems which have a small number of  $d$  electrons, this technique is ideal for settling the importance of correlations here. The present results conclusively establish that the observed spectral function is inconsistent with the *homogeneous* Hubbard model which is normally used in the interpretation of these kinds of experiments. We present a new theoretical treatment of inhomogeneity (arising from disorder in the real system) within a Hubbard-like model to establish qualitatively new descriptions for the evolution of spectral functions in chemically substituted systems, in very good agreement with experimental results. Whereas substituted compounds have been extensively investigated in recent times, the role of disorder has almost always been neglected; thus, our findings have important implications for a large number of compounds.

Polycrystalline ingots of oxygen deficient  $\text{SrTiO}_{3-\delta}$  with  $\delta = 0.0, 0.08$  and  $0.28$  were prepared by melt quenching required amounts of  $\text{Sr}_2\text{TiO}_4$ ,  $\text{TiO}$  and  $\text{TiO}_2$  in an inert gas arc furnace. Oxygen contents were determined thermogravimetrically. The sample surfaces were cleaned by *in-situ* scraping using an alumina file at liquid nitrogen temperature to avoid surface degradation. UPS and bremsstrahlung isochromat (BI) spectra were obtained with 0.1 and 0.8 eV resolutions respectively, in a commercial VSW spectrometer [7]. Self-consistent semi-relativistic *ab-initio* calculations with the linearized muffin-tin orbital method within the atomic sphere approximation (LMTO-ASA) for  $\text{SrTiO}_{3-\delta}$  with oxygen vacancies were carried out by considering a cubic supercell consisting of eight formula units of  $\text{SrTiO}_3$  with empty spheres at oxygen vacancy sites and 216  $k$ -points in the irreducible part of the Brillouin zone.

In Fig. 1 we show the experimental He I UPS of  $\text{SrTiO}_{3-\delta}$  for  $\delta = 0.0, 0.08$  and  $0.28$  near the Fermi energy ( $E_F$ ) region; the inset shows a typical spectrum over a wider energy range, being very similar for all the compositions with the intense doublet feature at about 7 eV arising from primarily oxygen  $2p$  derived states. Expectedly, the wide band gap material,

SrTiO<sub>3</sub> shows no intensity at  $E_F$ . On introducing oxygen vacancies ( $\delta > 0$ ), it is clear that two spectral features emerge in the near  $E_F$  region, one appearing at  $E_F$  and another at about 1.3 eV, in striking similarity to those of La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> [4]. While the feature at  $E_F$  is due to electron doping and the consequent movement of the Fermi energy  $E_F$  into the conduction band as confirmed by our band structure results on SrTiO<sub>3- $\delta$</sub> , the calculations do not have any counterpart of the experimentally observed 1.3 eV feature (see later in the text). Furthermore, this higher binding energy feature in Fig. 1 (and also in La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> [4]) is similar to the incoherent feature observed in LaTiO<sub>3</sub> [3] which is an end member of the solid solution La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>. These observations along with the absence of this feature in single-particle calculations, would strongly suggest correlation effects being responsible for the origin of this peak in these lightly doped electron systems.

In Fig. 2 we show BI spectra of SrTiO<sub>3</sub> and SrTiO<sub>2.72</sub> compared to the theoretically calculated BI spectrum of SrTiO<sub>3</sub> obtained from band structure calculations and calculated matrix elements [7]. The calculated spectrum provides a good description of the experimentally observed one for SrTiO<sub>3</sub> within the first 10 eV of  $E_F$ ; the mismatch at higher energies arises from the well-known limitation of linearized band structure methods. This agreement is consistent with the fact that SrTiO<sub>3</sub> with a  $d^0$  configuration is primarily a band insulator with correlation effects playing no major role. However, it is interesting to note that the BI spectrum of SrTiO<sub>2.72</sub> is almost identical to that of SrTiO<sub>3</sub>, except for a small shift ( $\approx$  0.5 eV) of the peaks and some overall broadening of the spectral features. The shift is consistent with electron doping of the system and thus, is explainable within a rigid shift of  $E_F$  with respect to the one-electron results for SrTiO<sub>3</sub> with no perceptible signature of any correlation induced features in contrast to the occupied spectral features (Fig. 1). We, however, cannot rule out the presence of weak intensity features corresponding to the upper Hubbard band which may be considerably broadened if it coexists in the region of 4-9 eV with extended O and Sr states which have a much larger intensity.

The above results of the presence of correlation induced feature in the occupied parts and the simultaneous absence of any such feature in the unoccupied parts, are very sur-

prising. It is well known that for few electrons in the band (such as Ce and U containing systems), correlation induced features appear most prominently in the unoccupied spectral function, whereas in Ni based systems with few holes in the band, the correlation effects are prominent only in the occupied parts. We demonstrate explicitly that the evolution of the photoemission and inverse photoemission spectra as a function of doping cannot be accounted by one band or a multiband homogeneous model by incorporating self-energy corrections to the calculated Ti  $d$  density of states (DOS) in SrTiO<sub>3- $\delta$</sub>  ( $\delta = 0.125$ ) within a second order perturbative treatment of correlation [8]. The results for  $U = 0$  and 4.6 eV are shown in Fig. 3. It is clear from this figure that a correlation induced satellite appears outside the one-electron ( $U = 0$ ) bandwidth in the unoccupied parts with increasing  $U$  and no such distinct feature can be seen in the occupied parts. Similar results are also found within exact diagonalization studies of the Hubbard model [9] and in the solution of the Hubbard in infinite dimensions, while an *exactly opposite trend* is observed in the experimental results in Figs. 1 and 2.

In order to understand this surprising result, we first note that the Hubbard model represents a homogeneous system, whereas in real systems electron (or hole) doping is brought about by chemical substitution; *this invariably introduces disorder or inhomogeneity at some length scale*. In this paper we propose that it is essential to use a spatially *inhomogeneous* picture to model these systems. The basic idea is that in these systems the electrons experience different local environments. The angle integrated photoemission spectrum, as a local probe, captures a suitable average of the Green's function over the local environments. In principle the degree of inhomogeneity can vary between two limits. If the system is disordered on a microscopic scale (termed microscopic inhomogeneity here), but homogeneous on a macroscopic scale, i.e. the impurities do not form clusters, a model of uncorrelated disorder is appropriate. If there is a tendency of the defects to form clusters, this may reinforce the natural tendency of strongly correlated systems to phase separate as pointed out in ref [10] and a model of macroscopic inhomogeneities is more suitable. Recent developments in the treatment of correlated electrons by using a mean field theory that becomes exact in the

limit of infinite spatial coordination [11] allows us to make these ideas more quantitative. We study the evolution of photoemission spectra in these two well defined limits. We expect that the physical situation is somewhere in between. We stress that in both limits we find the photoemission spectrum as a function of  $x$  to be very different from the predictions of the Hubbard model and very similar to what is observed experimentally.

In the microscopically inhomogeneous situation we describe  $\text{SrTiO}_{3-\delta}$  or  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  using a Hubbard model with diagonal disorder. The Hamiltonian is given by:

$$H = - \sum_{(ij)} t_{ij\sigma} C_{i\sigma}^+ C_{j\sigma} + \sum_i (\epsilon_i - \mu) C_{i\sigma}^+ C_{i\sigma} + \sum_i n_{i\uparrow} n_{i\downarrow} U_i$$

To get a bounded density of states and a well defined limit as the lattice coordination gets large, we take the hopping matrix elements  $t_{ij}$  to be defined on a Bethe lattice and scale them as  $\frac{t}{\sqrt{d}}$ . The full bandwidth  $2D = 4t$ , is estimated to be 2.5 eV from our band structure calculations. The  $\epsilon_i$  are random variables which take the values  $\epsilon_A$  with probability  $P_A$  and  $\epsilon_B$  with probability  $P_B$ ;  $P_A$  and  $P_B$  are given by the composition, as  $2\delta$  and  $(1-2\delta)$  in  $\text{SrTiO}_{3-\delta}$  and  $x$  and  $(1-x)$  in  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  respectively. Supercell calculations for  $\text{SrTiO}_{2.875}$  and  $\text{SrTiO}_{2.75}$  showed that several bands are pulled down compared to  $\text{SrTiO}_3$  due to the presence of vacancies by about 1.5 - 3.0 eV which provides an estimate for  $(\epsilon_B - \epsilon_A)$ . We use  $(\epsilon_B - \epsilon_A) \sim 2.4$  eV; however, the qualitative features of the calculations do not depend on this exact value.  $U_A = U_B = 4.6$  eV was estimated from earlier spectroscopic analysis. The chemical potential  $\mu$  is chosen so that the number of  $d$  electrons is equal to  $x$  in  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  or  $2\delta$  in  $\text{SrTiO}_{3-\delta}$ .

The mean field theory which is exact in the  $d \rightarrow \infty$  limit determines the local Green's functions at the A and B sites as the local  $f$  electron Green's function of an Anderson impurity model

$$H = \sum_k \epsilon_k a_{k\sigma}^+ a_{k\sigma} + U f_{\uparrow}^+ f_{\uparrow} f_{\downarrow}^+ f_{\downarrow} + \sum_k V_k (a_{k\sigma}^+ f_{\sigma} + f_{\sigma}^+ a_{k\sigma}) + \epsilon_f f_{\sigma}^+ f_{\sigma} \quad (1)$$

Here the  $f$  level position  $\epsilon_f$  is given by  $E_A - \mu$  or  $E_B - \mu$  respectively. The hybridization

function  $\Delta(i\omega_n)$

$$\Delta(i\omega_n) = \sum_k \frac{V_k^2}{(i\omega_n - \epsilon_k)} \quad (2)$$

has to be determined self consistently from the local Green's functions via the equation:

$$\Delta(i\omega_n) = t^2 G_{av}(i\omega_n) = t^2 (P_A G_A(i\omega_n) + P_B G_B(i\omega_n))$$

It is to be noticed that the A and B sites are connected by the same hybridization function which depends on the local physics at both sites. Thus we have a coupled system of equations. To solve the mean field equations we used the recent extension of the IPT method [12] to extract real frequency information. On the imaginary axis identical results are obtained with the exact diagonalization algorithm of Caffarel and Krauth [13].

We now turn to the case where the inhomogeneities occur on a macroscopic scale. In this scenario the density of electrons is inhomogeneous on a more macroscopic scale. A fraction  $f_1$  is in an insulating phase with the local concentration of the Mott insulating phase  $n_{ins} = 1$  and a fraction  $1 - f_1$  with the metallic concentration  $n_{met}$ . The total density  $n = f_1 n_{ins} + (1 - f_1) n_{met}$ , and the measured Green's function is given by

$$\bar{G} = f_1 G_{n_{ins}} + (1 - f_1) G_{n_{met}} \quad (3)$$

$G_{n_{ins}}$  and  $G_{n_{met}}$  can again be calculated using the mean field theory now in the respective homogeneous phases. To explore this scenario we took  $n_{met} = .1$  (which corresponds to a chemical potential  $\mu = -.78$ ) and varied the density  $n$  by varying the volume fraction  $f_1$  in equation (3). The spectral function in these two scenarios for a density close to  $n = .2$  are shown in Fig. 4 a and b including a finite broadening to model the finite experimental resolutions. Fig. 4 a and b are in very good agreement with the experimental spectra (Figs. 1 and 2); this is more striking so, when we keep in mind that we expect the real system to be somewhere in between the two limiting cases theoretically considered here. For example, the calculation correctly predicts the existence of an intense incoherent feature at about 1.3 eV arising from the local Green's function for site A with a band-like coherent feature

near  $E_F$  due to the local Green's function for site B. This is in perfect agreement with the experimentally observed features in the photoemission spectra of  $\text{SrTiO}_{3-\delta}$  (Fig. 1) and  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$  [4]. Moreover, it is clear from the calculated results that unoccupied parts of the spectral function will be entirely dominated by coherent band-like features arising from site B as observed in Fig. 2. Here we once again draw attention to the fact that these results are in sharp contrast to those expected on the basis of Hubbard and similar homogeneous models (see Fig. 3). While there have been past attempts to deal with substoichiometric correlated systems [14], effects of disorder inevitably present in such systems have not been addressed so far.

To summarize, in this paper we studied high-energy spectroscopic data of compounds with close to  $3d^0$  configuration. We presented explicit calculations of the spectral function of correlated electrons at different dopings in an inhomogeneous picture. We considered two cases, in one the inhomogeneity is present only on a microscopic scale while in the other the system was assumed to be macroscopically inhomogeneous. Both models give similar angle integrated spectra which therefore cannot determine the length scale over which the system is inhomogeneous. The spectra of the inhomogeneous models, however are qualitatively different from that of a homogeneous system, conclusively establishing the need to go beyond the standard theories to describe spectral functions in a class of doped transition metal compounds.



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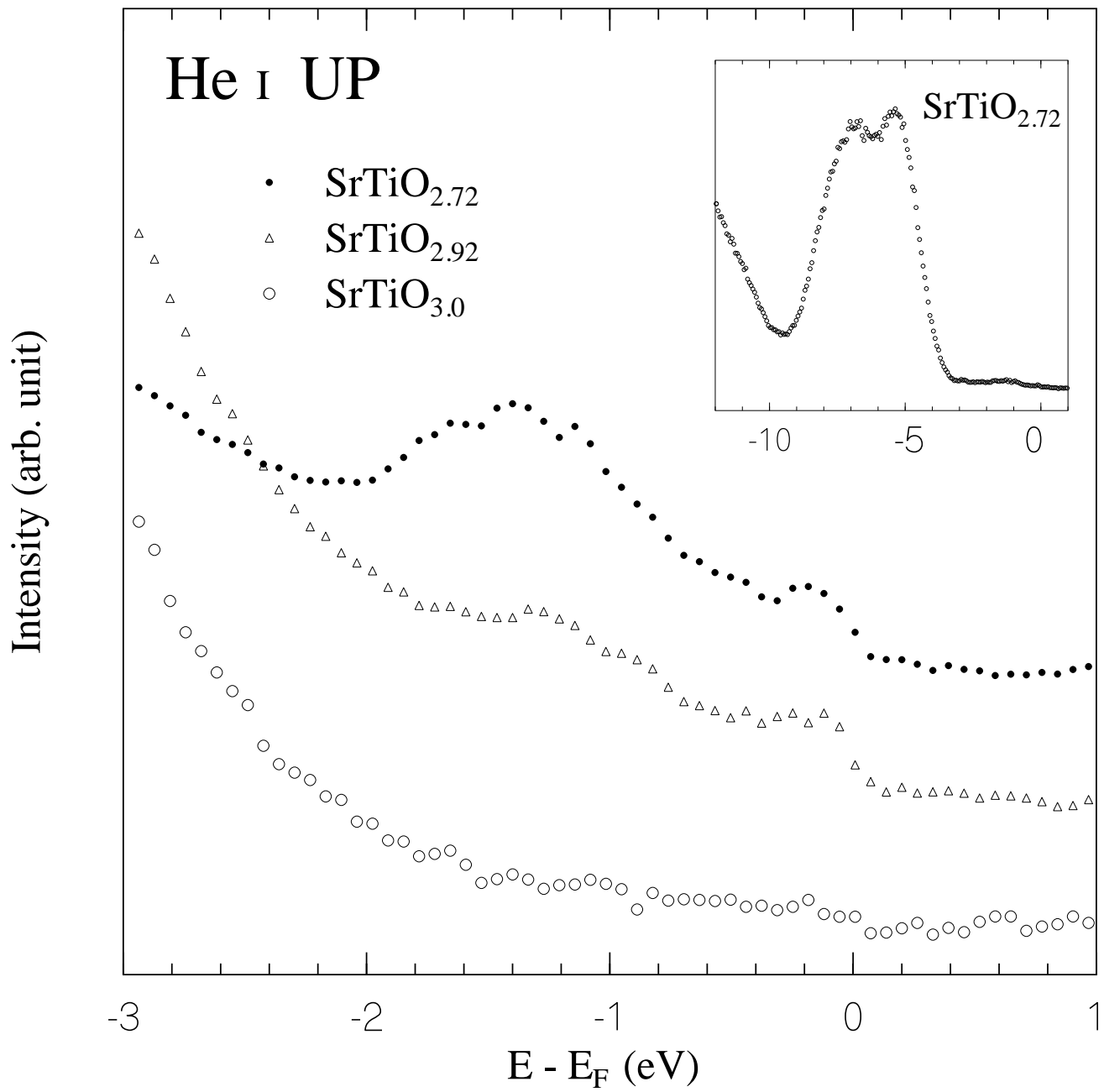
FIGURES:

Fig. 1 He I photoemission of  $\text{SrTiO}_{3-\delta}$  for three values of  $\delta$ .

Fig. 2 Bremsstrahlung isochromat spectra of  $\text{SrTiO}_3$  and  $\text{SrTiO}_{2.72}$ .

Fig. 3 2nd order perturbation applied to the DOS obtained from LMTO supercell calculations for  $\text{SrTiO}_{2.875}$ .

Fig. 4 Spectral functions of the disordered Hubbard model for density  $n=.2$  in the case of (a) microscopic and (b) macroscopic inhomogeneities. The separate contributions from the A and B sites to the total are also shown. The occupied parts of the spectral functions are expanded for clarity, as shown in the figures.



**SrTiO<sub>3-y</sub> : BI**

- Expt.
- Calc. total
- - - Ti *d*
- - - Sr *p*
- Sr *d*
- △ O *s*

SrTiO<sub>2.72</sub>

SrTiO<sub>3.0</sub>

Intensity (arb. unit)

