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ESRF

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: HE-2375** (proposal ref. 14842) Angle-resolved temperature dependent photoemission on $3d^1$ Mott-insulators	**Experiment number**: HE-2375
Beamline: ID08	**Date of experiment**: from: 20/06/07 to: 26/06/07	**Date of report**: 29/02/08
Shifts: 18	**Local contact(s)**: Nick Brookes, Júlio Criginski Cezar	*Received at ESRF:*

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Report:

One of the long standing topics in theoretical solid state physics concerns the single-particle spectral weight distribution in Mott-Hubbard systems in the vicinity of the metal-insulator transition. The class of d^1 perovskites has been recognized in the last decade as a materialization of this topic on which experimental tests using photoelectron spectroscopy can be carried out [1-8]. However, reliable data are often lacking because most photoemission spectra were take with low (UV) photon energies resulting in spectra which originate more from the surface region rather than the bulk. The consequences are severe since the electronic structure of the surface can be quite different from the bulk especially for strongly correlated materials. This is illustrated for instance in Fig.1 for $LaTiO_3$ and $YTiO_3$: the spectra for the O 2p valence bands taken with UV light do not match at all to those of the band theory, and also the Ti 3d spectral weight in both compounds look very similar while in reality they should be different due to differences in the band width.

Fujimori *et al*. PRB **46**, 9841 (1992) Morikawa *et al*. PRB **54**, 8446 (1996)

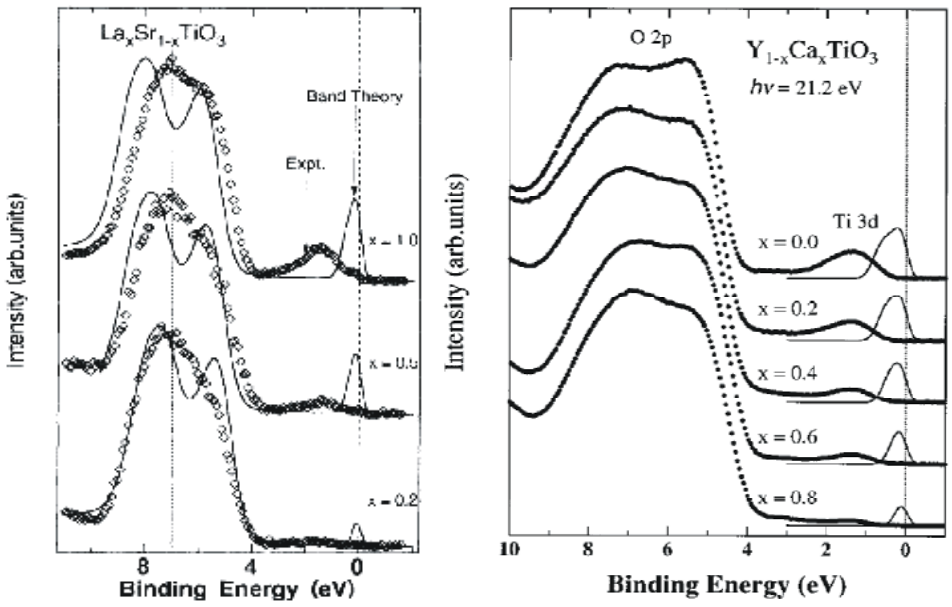

Fig. 1: Literature results of PES studies on $LaTiO_3$ and $YTiO_3$.

Bulk-sensitivity is the key issue here. We therefore have carried the experiments using soft-x-rays (700 eV) at the ID-12 beamline and the Al-Ka source (1486 eV) in our Institute. The results are shown in Fig. 2. Now the lineshapes of the experimental O-2p valence bands match nicely to those from band theory, and the differences between the two compounds are also clearly visisble, not only in the O 2p but also in the Ti 3d bands. This on the one hand confirms the quality and bulk sensitivity of our results, and on the other

hand evidences the need to reinvestigate the photoemission of this system. Important is that only now we are in the position to study reliably the many body effects in the Ti 3d spectral weight distribution as a function of the one-electron band width. To investigate to what extent correlation effects play a role in these two titanates, we compare the Ti 3d spectra with the occupied Ti 3d density of states as calculated using the GGA. The top curves of Fig. 3 reveal first of all that such a one-electron approach predicts the system to be a metal, in stark contrast to reality. The second point which calls for attention is the narrowness of the calculated occupied band: it is about a factor three too small as compared with the experiment. While the first point indicates that correlation effects are indeed sufficiently strong to open up a band gap and make these titanates to be Mott insulators, the second point requires a more subtle explanation, as we will describe below.

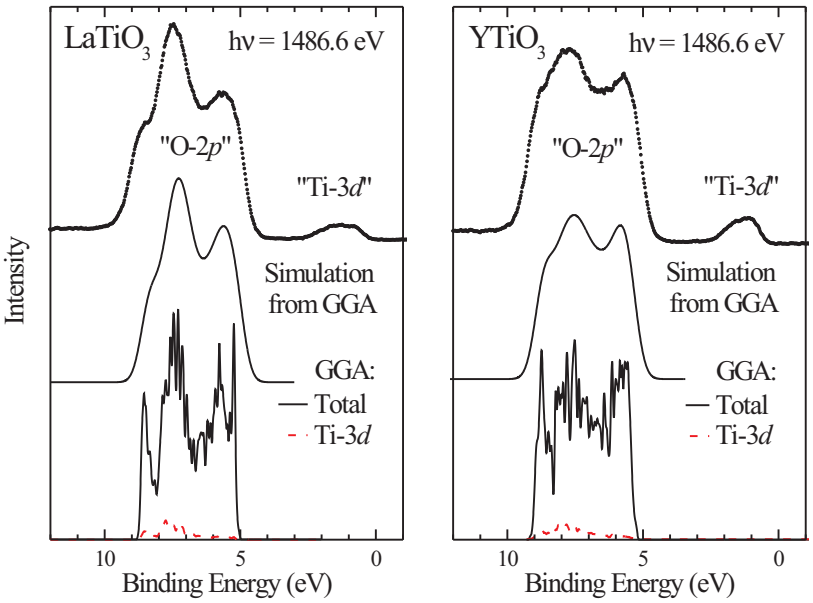

Fig. 2: Valence band of $LaTiO_3$ (left panel) and $YTiO_3$ (right panel). Top: experimental spectra taken at 100 K with 1486.6 eV photons and 0.35 eV overall resolution. Middle: simulation for the O 2*p* region based on the GGA. Bottom: total (black/solid), and Ti 3*d* (red/dashed) GGA density of states.

As an ansatz to take into account correlation effects, we perform GGA+U calculations with the Hubbard U set at 3 eV and the Hund exchange J at 0.7 eV for the Ti 3d electrons. We find a band gap of 0.4 eV for antiferromagnetic (AFM) $LaTiO_3$ and 0.8 eV for ferromagnetic (FM) $YTiO_3$, in close agreement with the optical data. The calculated Ti 3d densities of states are plotted in Fig. 2 and labelled by GGA+U. One can clearly see that they do not reproduce the experimental spectra at all as they are much too narrow. This failure can be traced back to the inherent flaw of methods which include electron correlations in a mean field manner: those methods cannot calculate spectral weight distributions properly ("not dynamic enough").

A quite different approach is offered by methods based on the DMFT. Aiming to describe both the low and high energy excitations simultaneously, one projects self-consistently the electronic structure of the solid with its dynamic response onto a solvable impurity problem. The price to pay is that the *k*-dependence of the self-energy is lost. This could be a serious omission for cases where, for instance, the effective band width is affected by the significant Hund's rule exchange via the inter-site exchange interactions, but perhaps this causes less of an error for the propagation of a hole in a d^1 system. In Fig. 3 we reproduce the results of the LDA+DMFT obtained very recently by Pavarini et al. [7]. Here we took the liberty to align the theoretical spectra in energy so that the leading edge near E_F coincides with that of the experiment. One can observe the very good correspondence between theory and experiment. The large width of the spectra is well reproduced. This is a major improvement in comparison to the GGA and GGA+U.

With the encouraging agreement between the DMFT results and the experiment, there is also the finding that these titanates are Mott insulators having strongly polarized orbital occupations. The question therefore arises to what extent charge fluctuations, which the DMFT is designed to handle, are relevant here. To answer this, we show in the bottom of Fig. 2 the *entire* GGA t_{2g} band of $LaTiO_3$ and $YTiO_3$, i.e. both the occupied and unoccupied parts. It is surprising how well these one-electron band widths W fit to the widths of the experimental spectra, including the 20% larger width in $LaTiO_3$ as compared to $YTiO_3$.

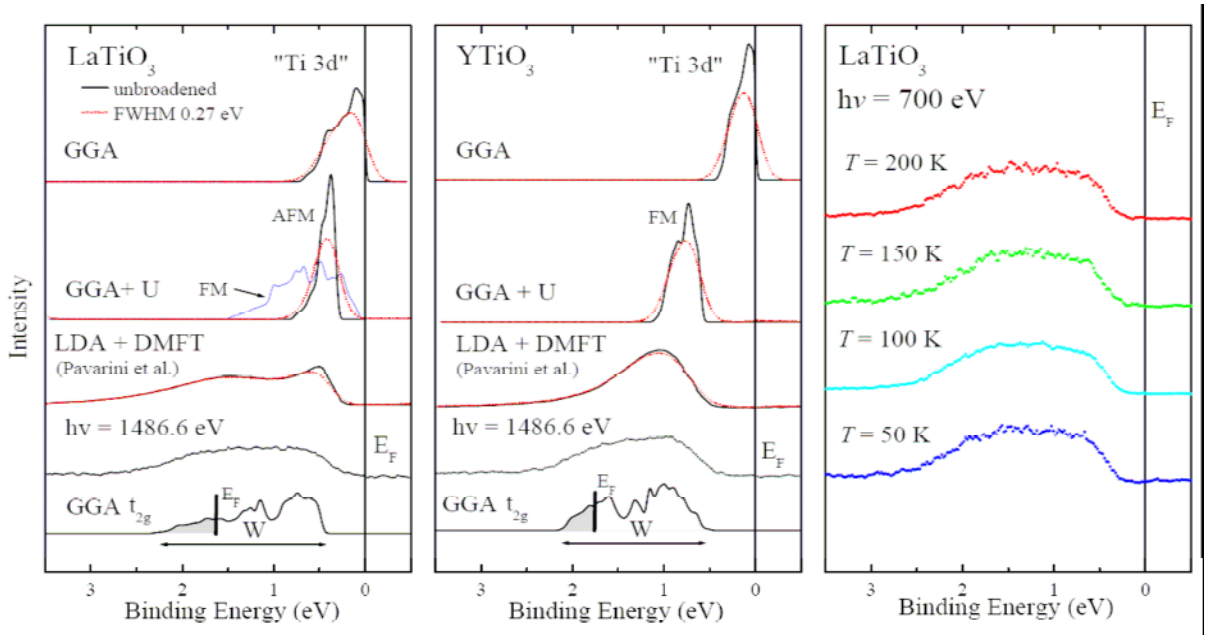

Fig. 3: Ti 3*d* region of the valence band of $LaTiO_3$ (left panel), $YTiO_3$ (middle panel). Top two curves: occupied total density of states from GGA and GGA+U calculations (unbroadened/black, 0.27 eV FWHM broadened/red-dashed). The GGA+U result for an artificially ferromagnetic (FM) $LaTiO_3$ is also included (thin-blue-line). Middle curves: spectral weight from LDA+DMFT calculations as reproduced from E. Pavarini *et al.* [16]. Bottom two curves: experimental spectra taken at 100 K with 1486.6 eV photons and 0.27 eV overall resolution, together with the occupied (filled-grey) and unoccupied GGA t_{2g} density of states (shifted and unbroadened). Right panel: Experimental spectra of $LaTiO_3$ taken at 50, 100, 150 and 200 K.

To see the astonishing implications of this observation, we consider the case of the ferromagnetic half-filled single-band Hubbard insulator in the large U limit. In this simple system, an extra hole, once injected by PES, can propagate without experiencing additional Coulomb repulsions and with transfer integrals given by the one-electron band width. In other words, the valence band of this correlated insulator is the same as the combined occupied and unoccupied band of the uncorrelated metal. It is extremely surprising that these characteristics fit the titanates since they have electronically quite distinct orbital-and/or spin (super-) structures. One would at least expect that the propagation of an extra hole would lead to a wake of wrongly oriented orbitals and/or spins, thereby reducing the quasi-particle or the coherent band width in a manner which may be explained by the well known t-J models.

Nevertheless, the entire band width, i.e. including the incoherent part, may very well be given by the bare one-electron band width. The question is then why the nearest-neighbor spin and orbital correlations in such a t-J like d^1 system do not show up clearly in the *k*-integrated photoemission experiment. Our assertion is that the energy scale associated with these inter-site correlations (typically much less than 0.1 eV), is too small in comparison with the total band width (1.5-2.0 eV) and the experimental broadening (0.3 eV). To support this idea experimentally, we measured the valence band of $LaTiO_3$ as a function of temperature (50--200 K) as to go from the antiferromagnetic to the paramagnetic phase. The results are shown in the right panel of Figure 3. The data reveal essentially no detectable temperature dependence. Again, this is surprising by itself since we know that the spin-spin correlations change considerably across the Neel temperature, but it is consistent with and confirming our assertion about the energy scales involved.

This work is submitted for publication to Physical Review Letters.

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