Insulator-metal transition in the doped $3d^1$ transition-metal oxides: a combined LDA+DMFT study

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Motivation

To analyse the Mott-Hubbard insulator-metal transition (IMT) in $3d^1$ TM-oxides $LaTiO_3$ and TiOCl using the *ab initio* LDA+DMFT method. The calculation is performed using real crystal structure and realistic parameters (U, U', J_H) as input.

Model and Method of Solution

Our aim is to provide a multi-orbital correlated *ab initio* description of real materials based on

Model Hamiltonian

$$H = H_{\rm LDA} + H_U \ ,$$

where

$$H_{\rm LDA} = \sum_{\mathbf{k}\alpha\beta\sigma} \epsilon_{\alpha\beta}(\mathbf{k}) c^\dagger_{\mathbf{k}\alpha\sigma} c_{\mathbf{k}\beta\sigma} + \sum_{i\alpha\sigma} \epsilon^0_{i\alpha\sigma} n_{i\alpha\sigma} \ ,$$

$\epsilon^0_{i\alpha\sigma} = \epsilon_{i\alpha\sigma} - U(n_{i\alpha\bar{\sigma}} - \frac{1}{2}) + \frac{1}{2}\sigma J_H (n_{i\alpha\sigma} - 1)$, and

$$H_U = U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + U' \sum_{i\alpha\beta\sigma\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} \ .$$

α, β are orbital indexes; $U' = U - 2J_H$.

Multi-Orbital LDA+DMFT(IPT)

The LDA+DMFT solution involves (i) replacing the lattice model by a multi-orbital Anderson impurity model, and (ii) a self-consistency condition requiring the impurity propagator to be equal to the local (k-averaged) GF of the lattice

$$G_\alpha(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \frac{1}{\omega + \mu - \Sigma_\alpha(\omega) - \epsilon_{\mathbf{k}\alpha}} \ .$$

Local self-energies $\Longrightarrow$ multi-orbital *(extended)* IPT

$$\Sigma_\alpha(\omega) = \frac{\sum_\gamma A_{\alpha\gamma} \Sigma^{(2)}_{\alpha\gamma}(\omega)}{1 - \sum_\gamma B_{\alpha\gamma} \Sigma^{(2)}_{\alpha\gamma}(\omega)} \ .$$

where,

$$\Sigma^{(2)}_{\alpha\gamma}(i\omega) = N_{\alpha\gamma} \frac{U^2_{\alpha\gamma}}{\beta^2} \sum_{nm} G^0_\alpha(i\omega_n) G^0_\gamma(i\omega_m) G^0_\gamma(i\omega_n + i\omega_m - i\omega) \ ,$$

$G^0_\alpha(\omega) = \frac{1}{\omega + \mu_\alpha - \Delta_\alpha(\omega)}$ is the bath propagator,

$A_{\alpha\gamma} = \frac{n_\alpha(1-2n_\alpha) + D_{\alpha\gamma}[n]}{n^2_\alpha(1-n^2_\alpha)}$, $\quad B_{\alpha\gamma} = \frac{(1-2n_\alpha)U_{\alpha\gamma} + \mu - \mu_\alpha}{2U^2_{\alpha\gamma} n^2_\alpha (1-n^2_\alpha)}$.

n_α, n^0_α are particle numbers determined from G_α and G^0_α.

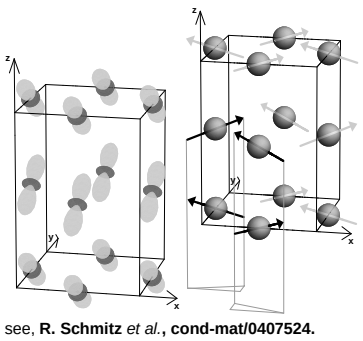
The interorbital correlation function $D_{\alpha\gamma}[n] = \langle n_\alpha n_\gamma \rangle$ is calculated from

$\langle n_\alpha n_\gamma \rangle = \langle n_\alpha \rangle \langle n_\gamma \rangle - \frac{1}{U_{\alpha\gamma}\pi} \int_{-\infty}^{+\infty} f(\omega) Im[\Sigma_\alpha(\omega) G_\alpha(\omega)] d\omega.$

We have used this or similar techniques to study:

CMR manganites, LiV_2O_4, V_2O_3, VO_2, CrO_2, $Ga_{1-x}Mn_xAs$, $LaTiO_3$, TiOCl, and ...

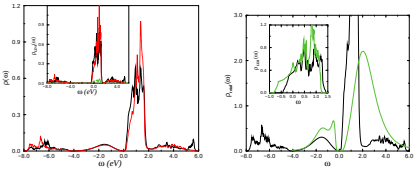
$LaTiO_3$: orbital and magnetic order



see, **R. Schmitz *et al.*, cond-mat/0407524.**

Mott transition in $La_{1-x}Sr_xTiO_{3+y/2}$

Motivation: to demonstrate the nature of the Mott insulating state and the doping-induced insulator-metal in this system.

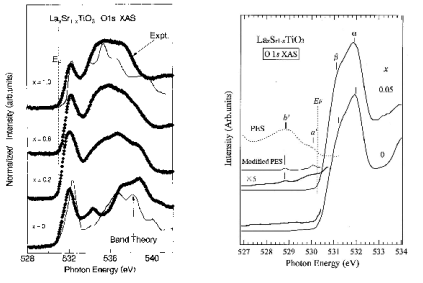


Left: LDA DOS (inset) and LDA+DMFT (orbital resolved) DOS. Right: The inset shows the LDA DOS for the non-degenerate ground-state orbital, ours (black) and downfolded (green). The main panel shows the Total LDA+DMFT DOS for undoped $LaTiO_3$, using in the LDA+DMFT(IPT) [$U = 6$ eV, $J_H = 1$ eV, $T = 0$] and in LDA+DMFT(QMC) [$U = 5$ eV, $J_H = 0.64$ eVat $T = 770$ K]. by E. Pavarini *at al.*, PRL **92**, 176403 (2004).

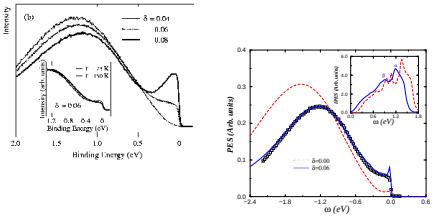
Notes

i) Our solution support ferro-orbital order in the insulating state and a carrier driven (continuous filling induced) IMT in $LaTiO_3$.
ii) Our results imply that $LaTiO_3$ can be described as a Mott-Hubbard system without orbital (liquid) degeneracy.

XAS and PES spectra



Left: A. Fujimori *et al.* PRB **46** 9841 (1992); Right: T. Higuchi *et al.* PRB **61** 12860 (2000).



Left: Valence-band photoemission in the low doping regime by T. Yoshida *et al.* EPL **59**, 258 (2002). Right: PES and IPES (inset) spectra for both, pure (dashed) and Sr-doped (solid) $LaTiO_3$.

Note

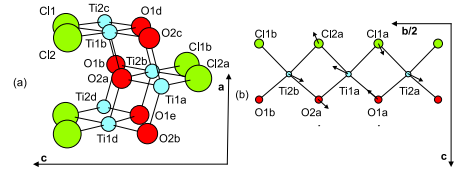
Note the excellent quantitative agreement with photoemission data for $\delta = x = 0.06$. We also resolve the α, β peaks in the XAS spectrum (right inset).

For more details see **L. Craco, M. S. Laad, S. Leoni, and E. Müller-Hartmann, PRB 70, 195116 (2004)**.

Concluding remark

LDA+DMFT(IPT+CPA) scheme gives semiquantitative consistency with a range of experimental observations for $LaTiO_3$.

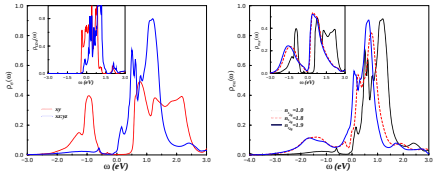
TiOCl crystal structure



Crystal structure of TiOCl: (a) Perspective view of one layer. (b) A chain of Ti atoms. The displacements in the superstructure are given by arrows. Figures taken from **M. Shaz *et al.*, cond-mat/0503203**.

Spectral properties of TiOCl

Motivation: to study the nature of the Mott-Hubbard insulating state and the doping-induced insulator-metal in this system.



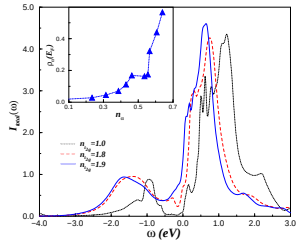
Left: LDA+DMFT(IPT) and LDA (inset) partial DOS. Red line denotes the DOS for the non-degenerate ground-state (xy) orbital. Blue line denotes the DOS for the higher (two-fold degenerate) lying $\alpha \equiv xz : yz$ orbitals. Right: t_{2g} partial DOS for the $3d_\alpha$ and $3d_{xy}$ (inset) orbitals for $U = 3$ eV and $J_H = 1$ eV and different values of the total electron number.

Notes

i) The charge gap shows the Mott-Hubbard character of the insulator. DMFT gives non-trivial renormalization of the crystal field splitting, $\Delta_{t_{2g}} = \epsilon_{xy} - \epsilon_\alpha = 0.12\,eV$ ($\Delta_{LDA} = -0.45\,eV$).

ii) Doping TiOCl with electrons induces a nearly first-order IMT with rapid change in the carrier density around $n_{t_{2g}} = 1.9$. Notice that *only* the d_α bands show metallic behaviour; the d_{xy} DOS still represents almost insulating behaviour.

iii) For $n_{t2g} = 1.9$, the renormalized value of $\Delta^M_{t_{2g}} = -0.011$ $\Rightarrow$ implying *melting* of the (spin) dimerization observed in the insulating phase.



Total spectra for different values of the total electron number. Inset shows the $d_{xz:yz}$ DOS at E_F for different values of the $d_{xz:yz}$ orbital occupation.

We believe that the above results are the first demonstration of the possibility of driving a Mott transition in TiOCl *by electron doping in a realistic scenario.*

For more details see **L. Craco, M. S. Laad, and E. Müller-Hartmann, cond-mat/0410472.**

Concluding remark

Many-body electron-electron interactions introduces non-trivial effects stemming from the *dynamical* nature of electronic systems, leading to large transfer of spectral weight across large energy scales in response to small changes in the *bare* electronic structure. This type of response is at the heart of the anomalous responses of correlated systems.