Mott insulators

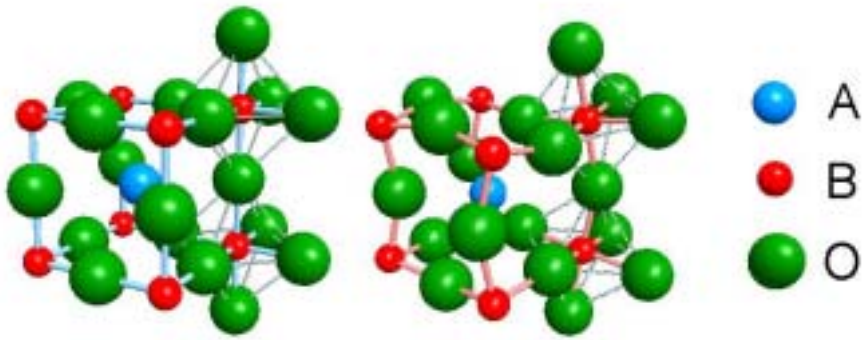
- Mott-Hubbard type *vs* charge-transfer type
- Cluster-model description
- Chemical trend
- Band theory
- Self-energy correction
- Electron-phonon interaction

Mott insulators

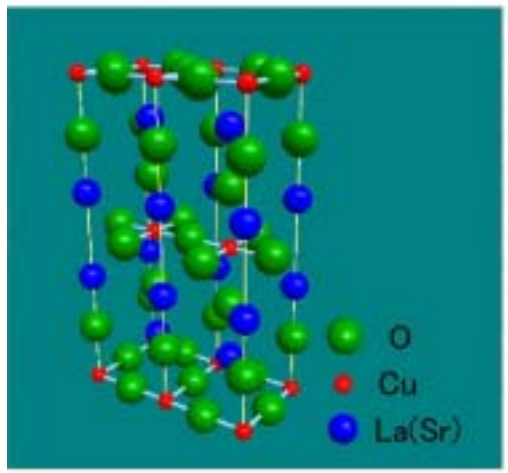
- Mott-Hubbard type *vs* charge-transfer type

Correlated electron systems/ Complex materials

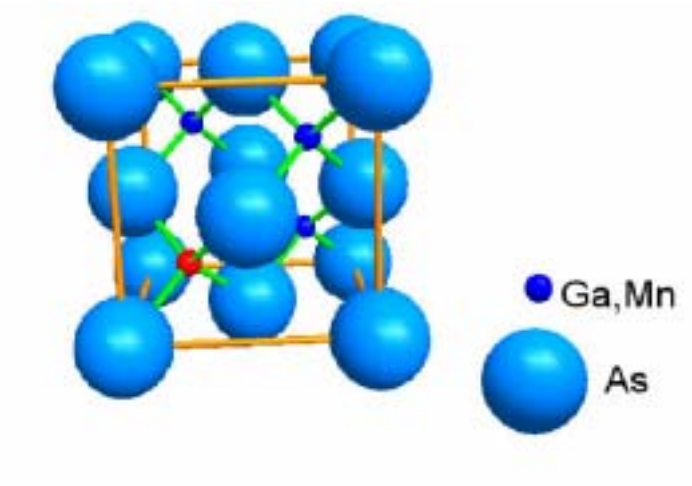
ABO_3



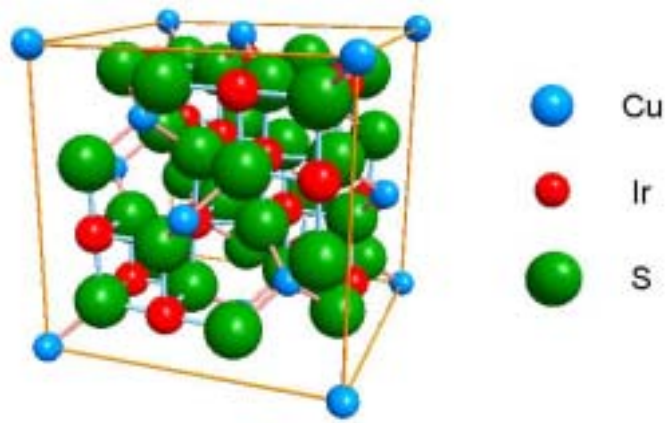
$La_{2-x}Sr_xCuO_4$



$Ga_{1-x}Mn_xAs$



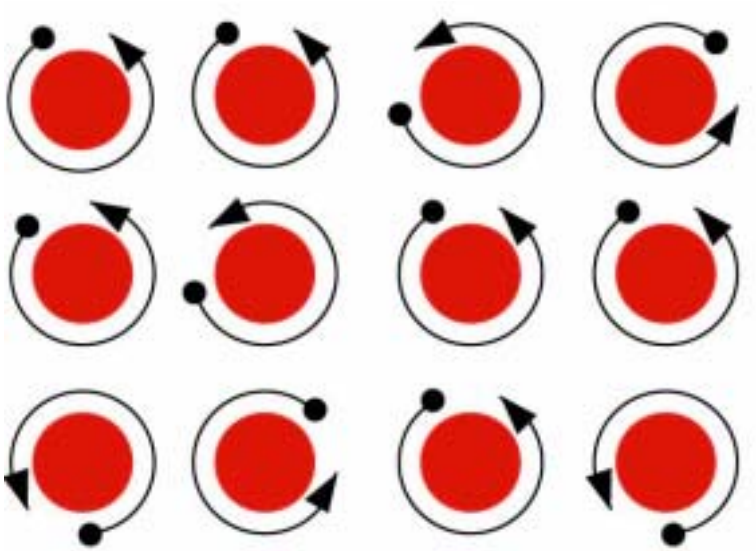
$CuIr_2S_4$

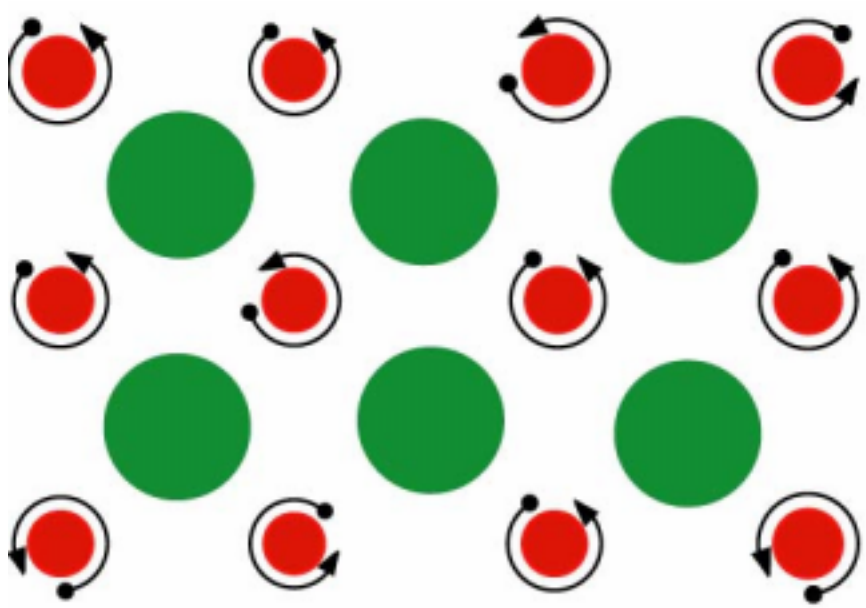


Lattice models for transition-metal compounds

Hubbard model

p-d model





Transition metal ion (with d orbitals)

Non-metal anion (with p orbitals)

Lattice models for transition-metal compounds

(degenerate) Hubbard model

$$\mathcal{H}_{DH}=\mathcal{H}_{Dt}+\mathcal{H}_{DU}+\mathcal{H}_{DV}+\mathcal{H}_{DUJ},$$

$$\mathcal{H}_{Dt}=-\sum_{\substack{\langle ij\rangle\\ \sigma,v,v'}} k(t_{ij}^{v,v'}c_{i\sigma v}^{\dagger}c_{j\sigma v'}+\mathrm{H.c.}),$$

$$\mathcal{H}_{DU}=\sum_{\substack{iv v'\\ \sigma,\sigma'}}(1-\delta_{vv'}\delta_{\sigma\sigma'})U_{vv'}n_{i\sigma v}n_{i\sigma' v'},$$

$$\mathcal{H}_{DV}=\sum_{\substack{\sigma,\sigma'\\ v,v'\langle ij\rangle}} V_{ij}^{vv'}n_{i\sigma v}n_{j\sigma' v'},$$

$$\mathcal{H}_{DUJ}=-\sum_{\cdot} J_{0vv'}[(1-\delta_{vv'})c_{iv\sigma}^{\dagger}c_{iv\sigma'}c_{iv'\sigma'}^{\dagger}c_{iv'\sigma}$$

t-*J* model

$$\mathcal{H}_{t\text{-}J}=-\sum_{\substack{\langle ij\rangle\\ \sigma}} P_d(t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\mathrm{H.c.})P_d+J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j,$$

no double occopancy

p-*d* model

$$\mathcal{H}_{dp}=\mathcal{H}_{dpt}+\mathcal{H}_{dpU}+\mathcal{H}_{dpV},$$

$$\mathcal{H}_{dpt}=-\sum_{\langle ij\rangle\sigma} t_{pd}(d_{i\sigma}^{\dagger}p_{j\sigma}+\mathrm{H.c.})+\varepsilon_d\sum_i n_{di}$$

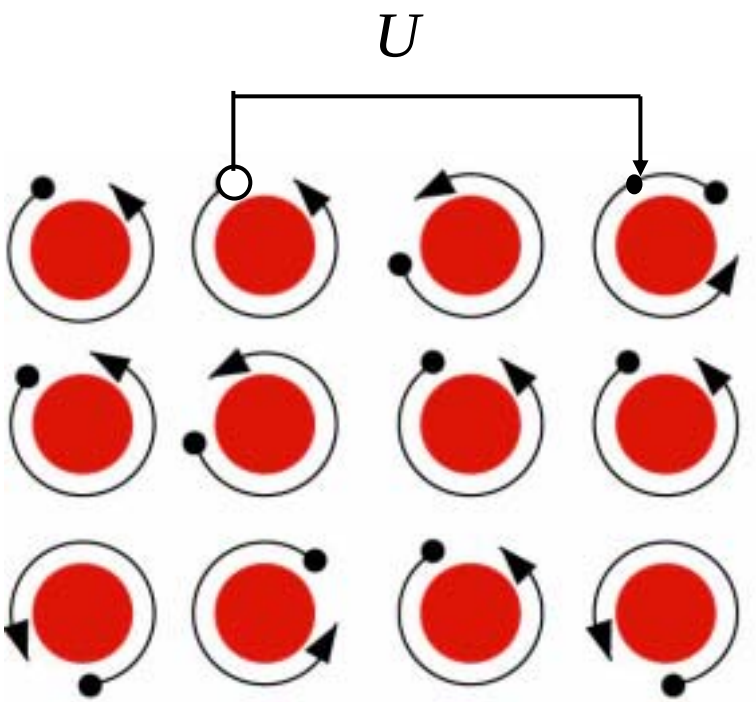
$$+\varepsilon_p\sum_j n_{pj},$$

$$\mathcal{H}_{dpU}=U_{dd}\sum_i n_{di\uparrow}n_{di\downarrow}+U_{pp}\sum_i n_{pi\uparrow}n_{pi\downarrow},$$

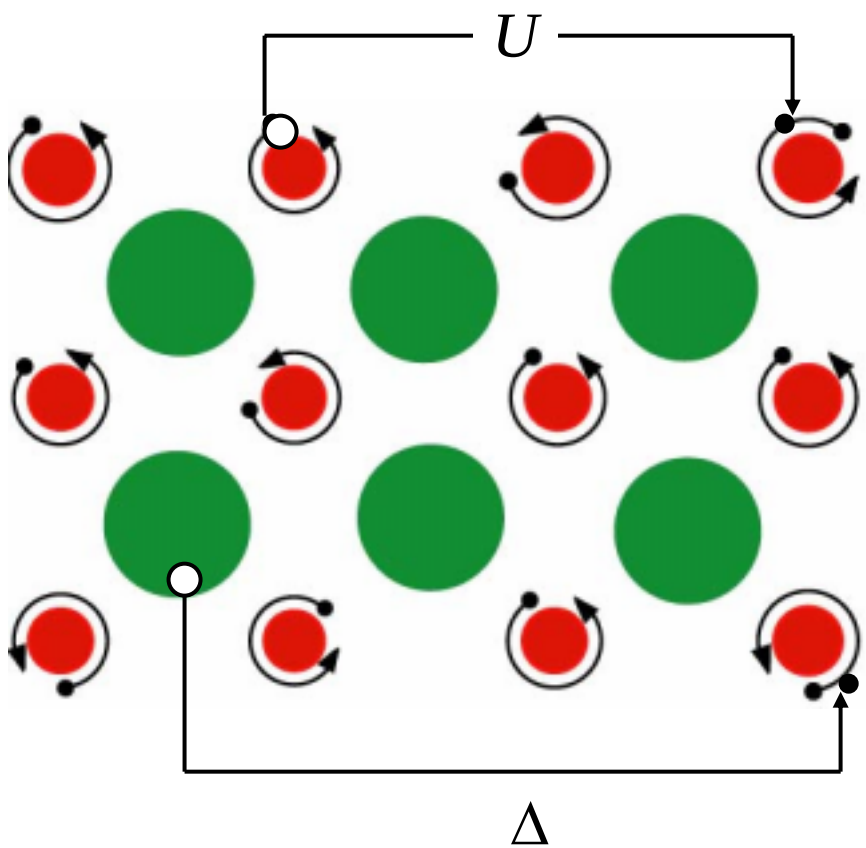
$$\mathcal{H}_{dpV}=V_{pd}\sum_{\langle ij\rangle} n_{pi}n_{dj}.$$

Band gap excitations - relevant to charge transport

Hubbard model

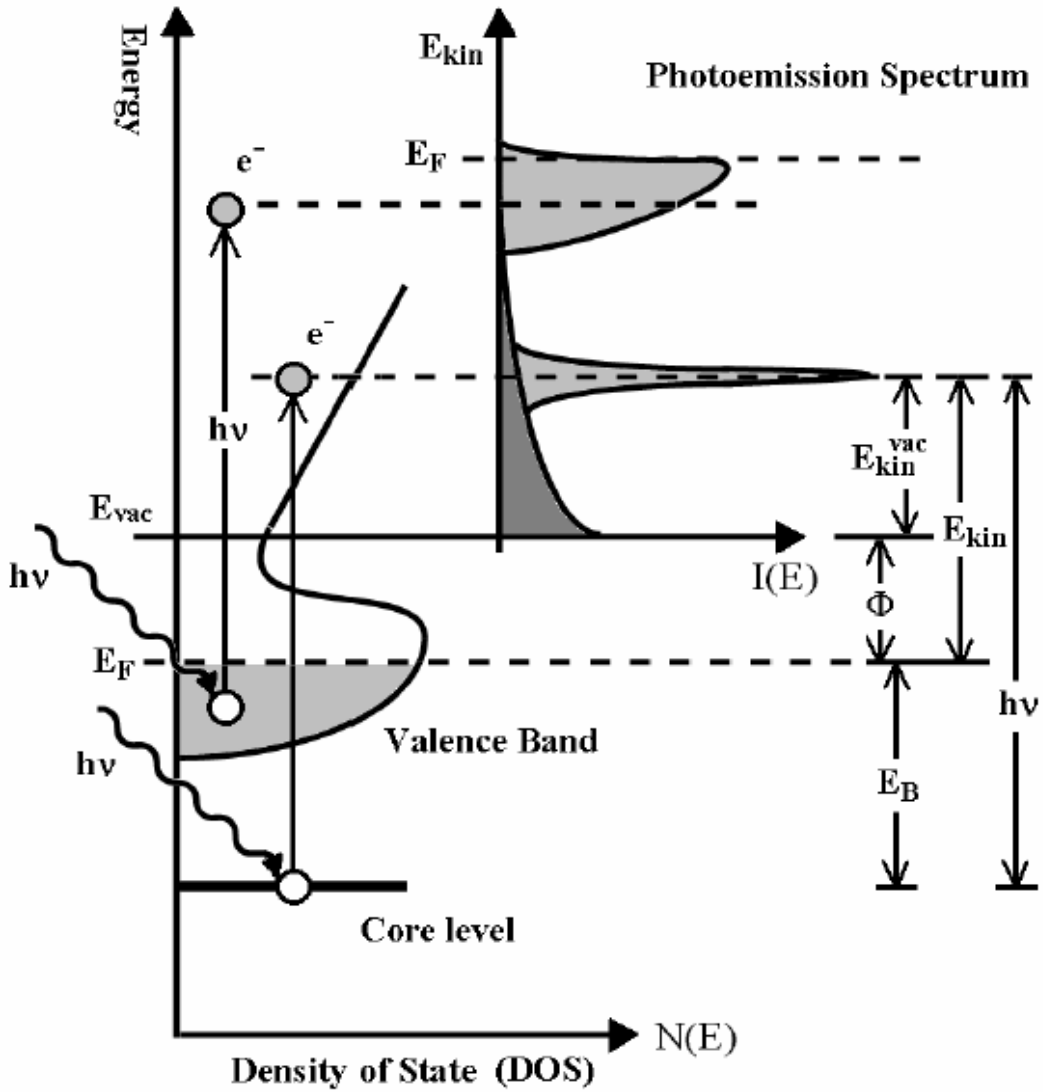


p-d model

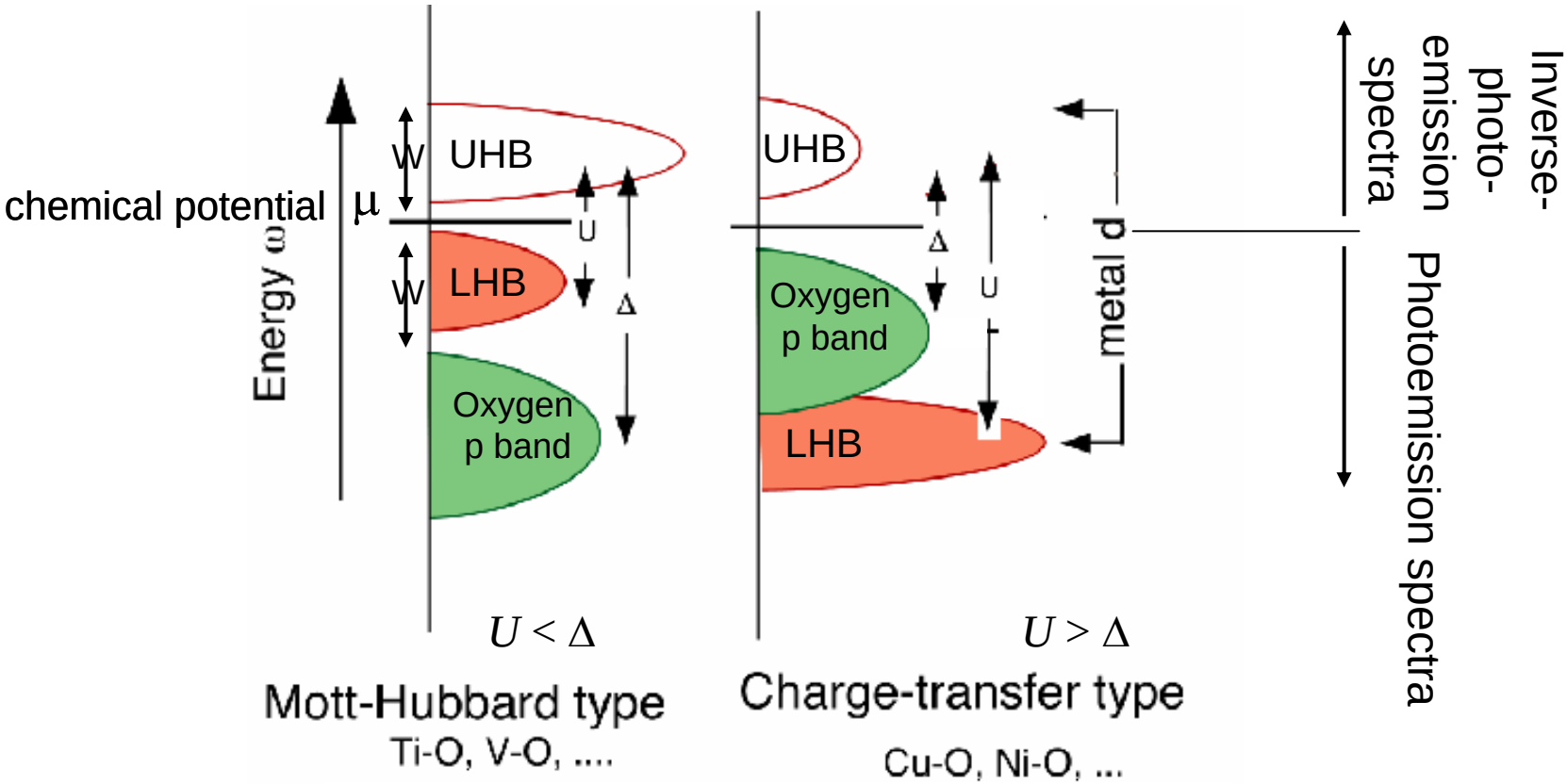


Charge transfer energy: Δ
on-site Coulomb energy: U

Photoemission spectroscopy



Mott-Hubbard-type insulators *vs* charge-transfer-type insulators



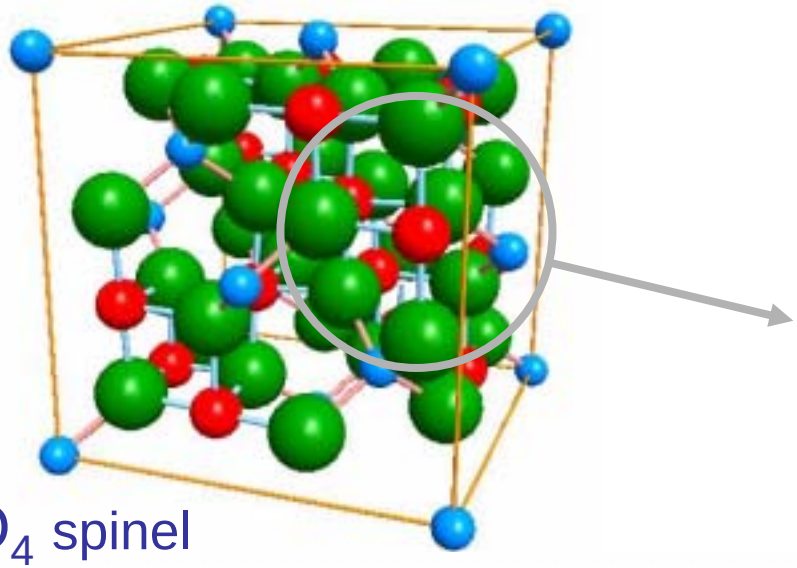
UHB: upper Hubbard band
LHB: lower Hubbard band

Charge transfer energy: Δ
on-site Coulomb energy: U
Band width: W

Mott insulators

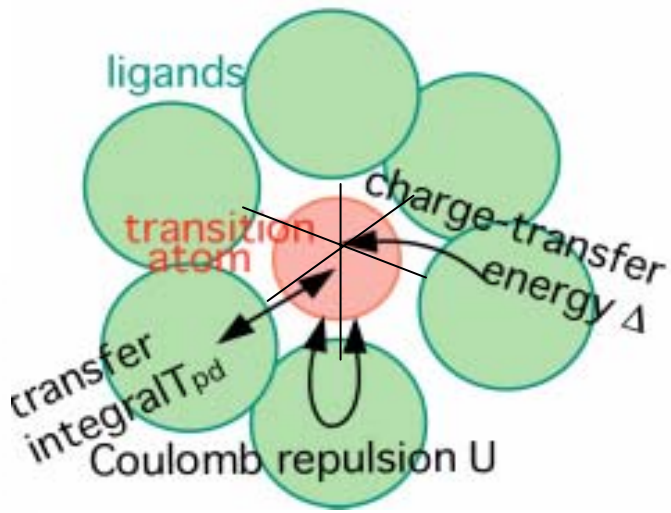
- Cluster-model description

Cluster model for transition-metal oxides

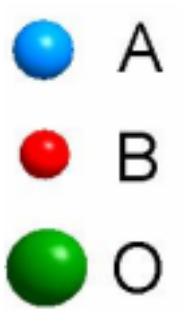


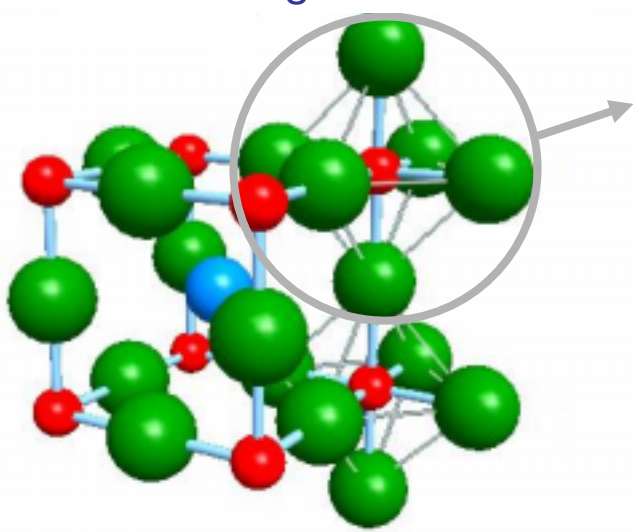
AB_2O_4 spinel

BO_6 cluster model



ABO_3 perovskite



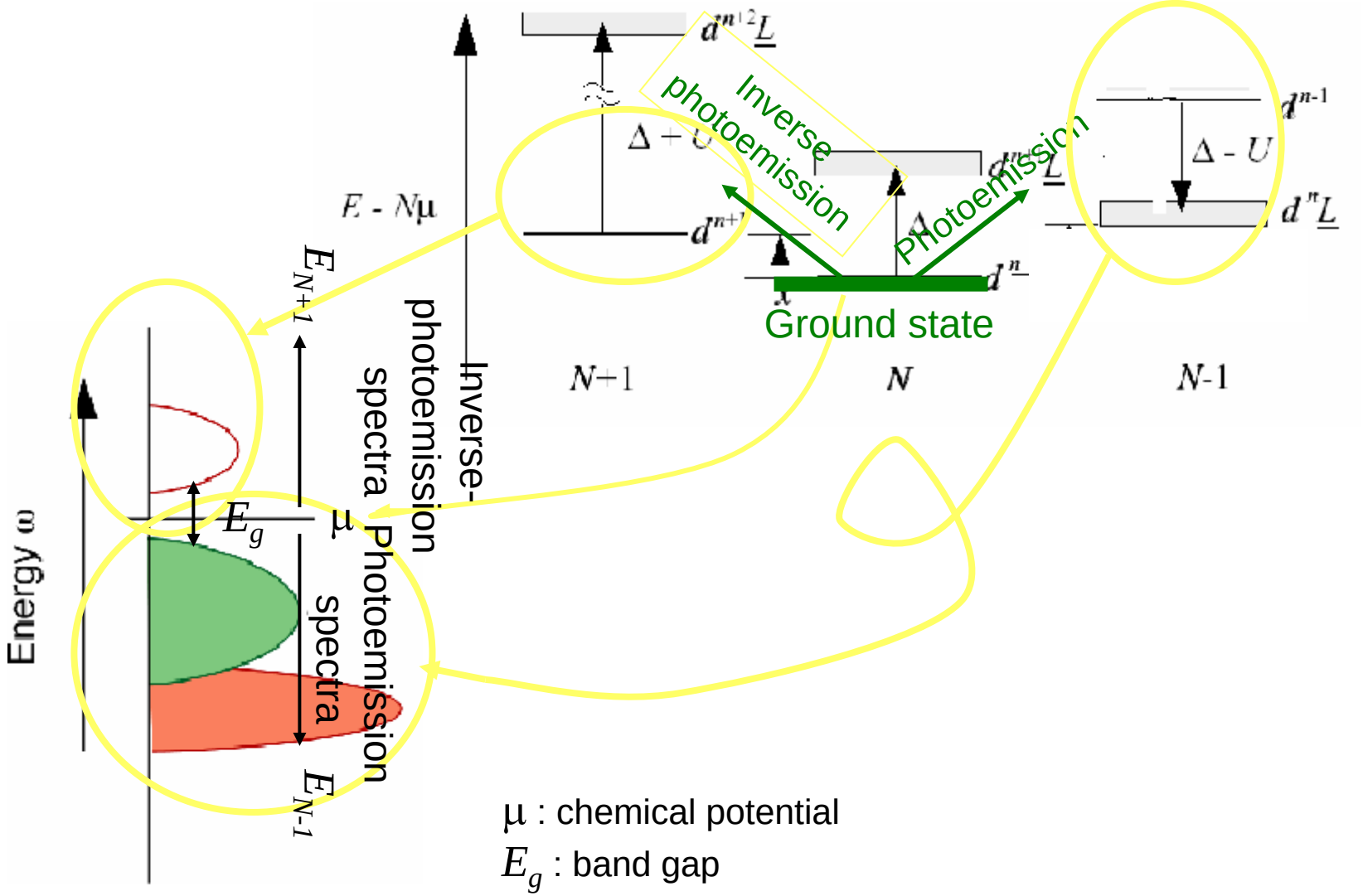


$$\Delta = E(d^{n+1}\underline{L}) - E(d^n)$$
$$U = E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$$
$$T = \langle d_\alpha | H | L_\alpha \rangle$$

are treated as adjustable parameters

$\underline{L}$: ligand (p) hole

Many-electron energy levels *vs* single-particle energy level



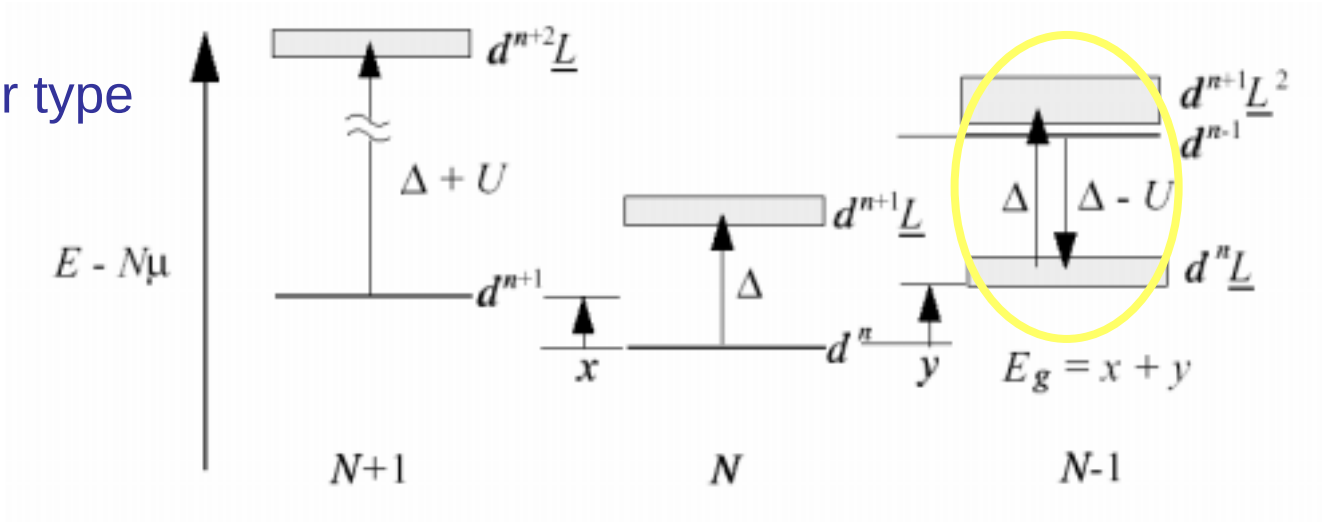
μ : chemical potential

E_g : band gap

Mott-Hubbard type *versus* charge-transfer type many-electron energy level scheme

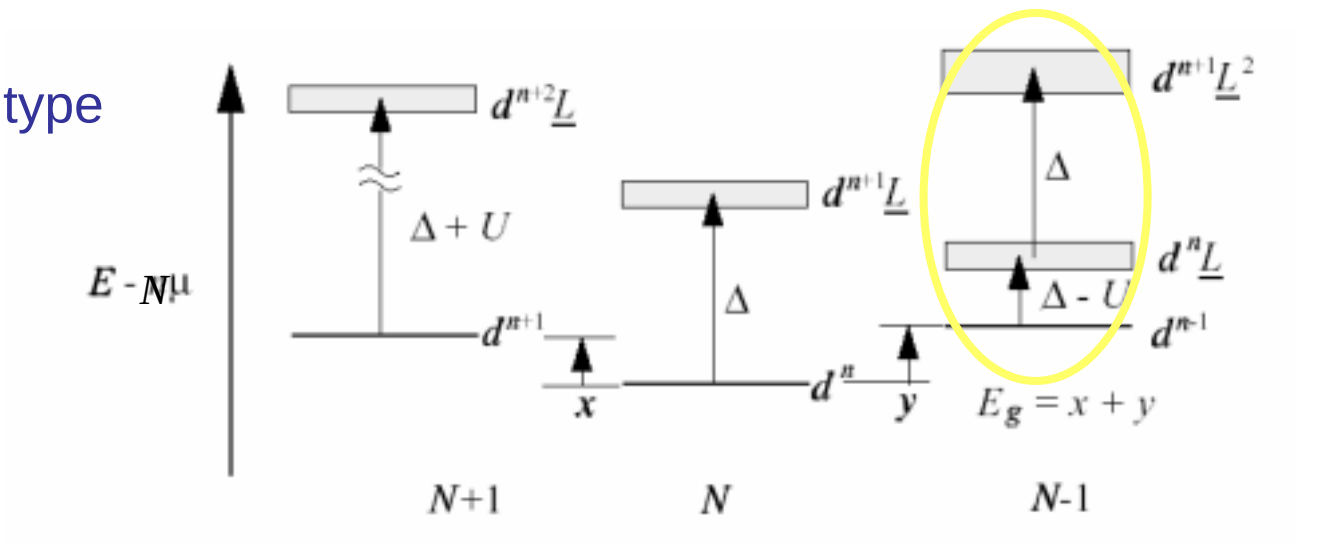
Charge-transfer type insulator

$U > \Delta$

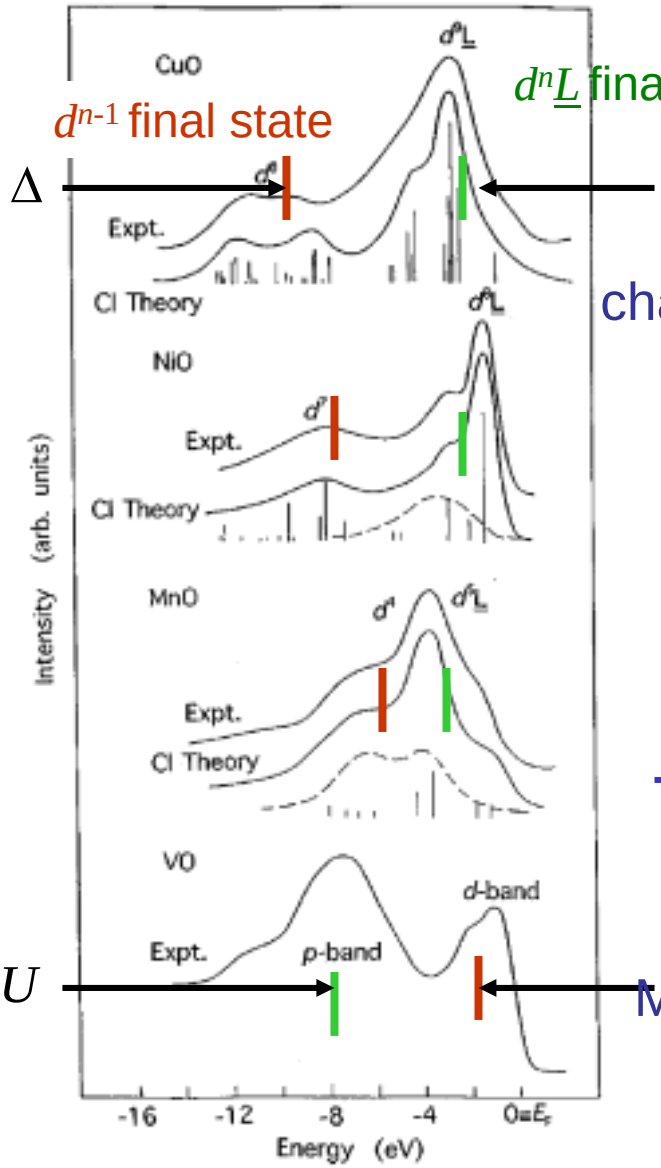


Mott-Hubbard type insulator

$U < \Delta$



Configuration-interaction cluster-model analysis of *d*-electron photoemission satellites



d^{n-1} final state

$d^n\underline{L}$ final state

$U - \Delta$

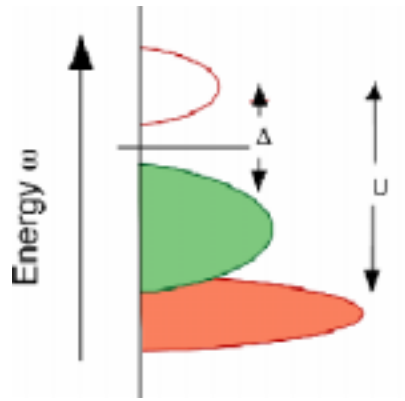
$\Delta - U$

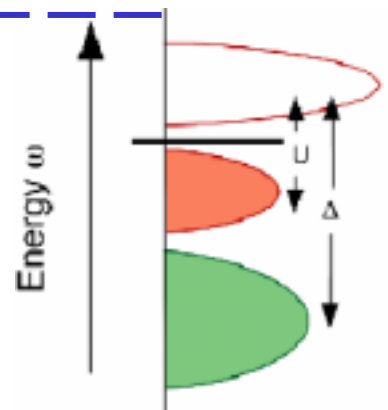
charge-transfer type

$U > \Delta$

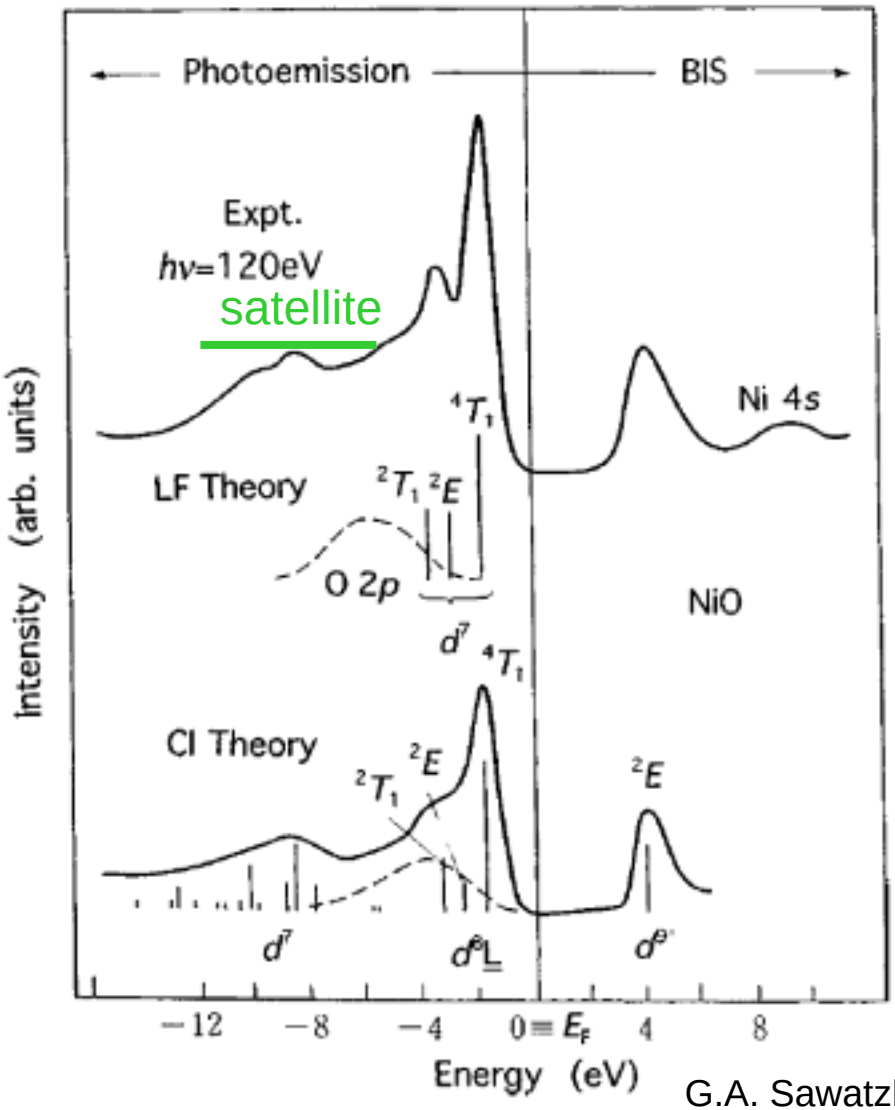
Mott-Hubbard type

$U < \Delta$

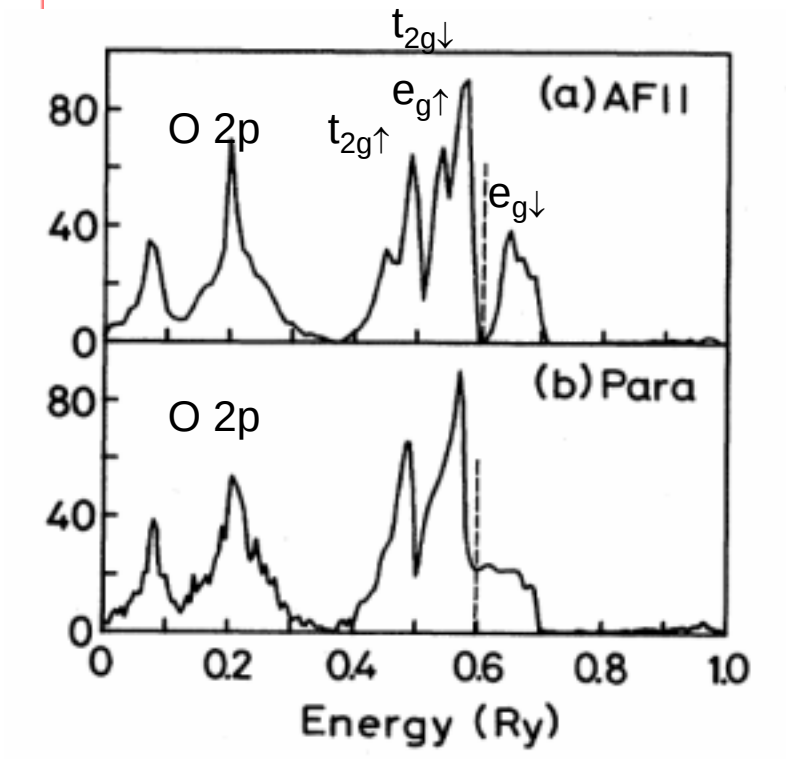




Configuration-interaction cluster-model analysis *vs* LDA band theory for NiO



LDA band calc.



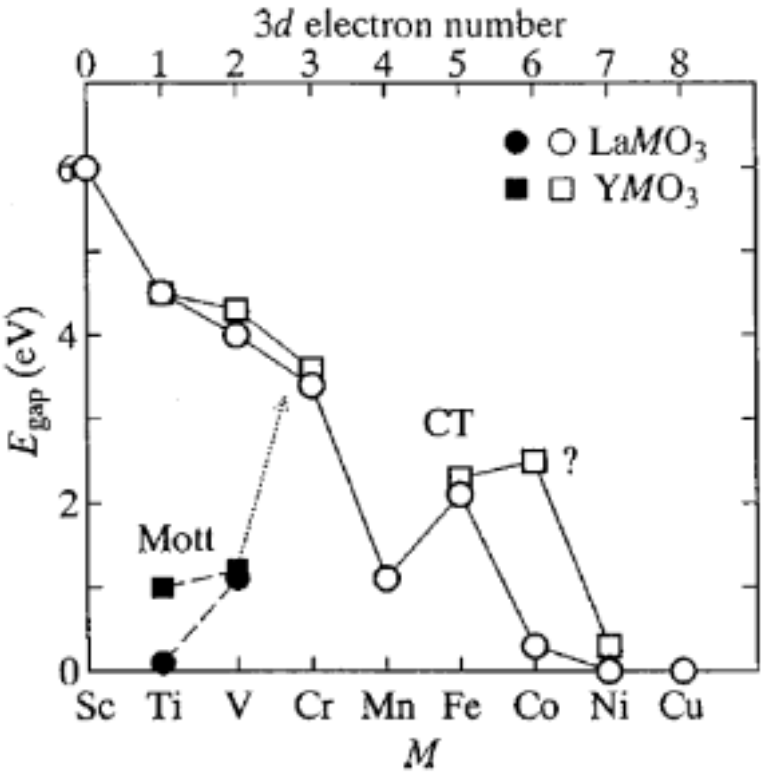
T. Oguchi et al., PRB ‘83

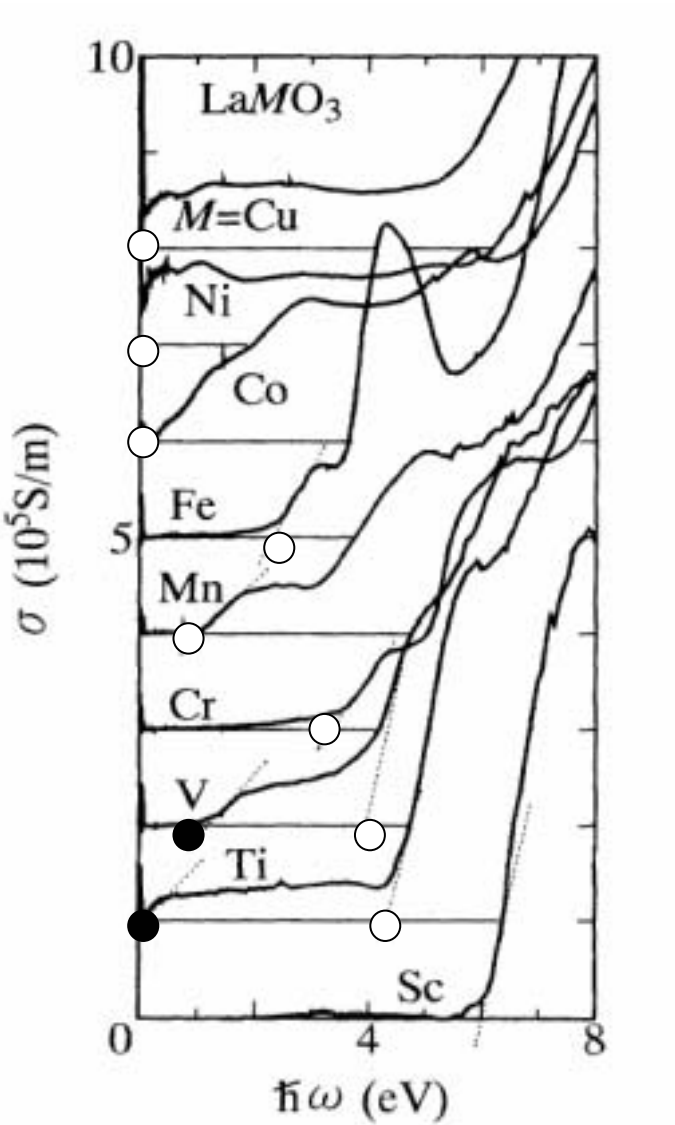
G.A. Sawatzky and J.W. Allen, PRL ‘84
A. Fujimori and F. Minami, PRB ‘83

Mott insulators

- Chemical trend

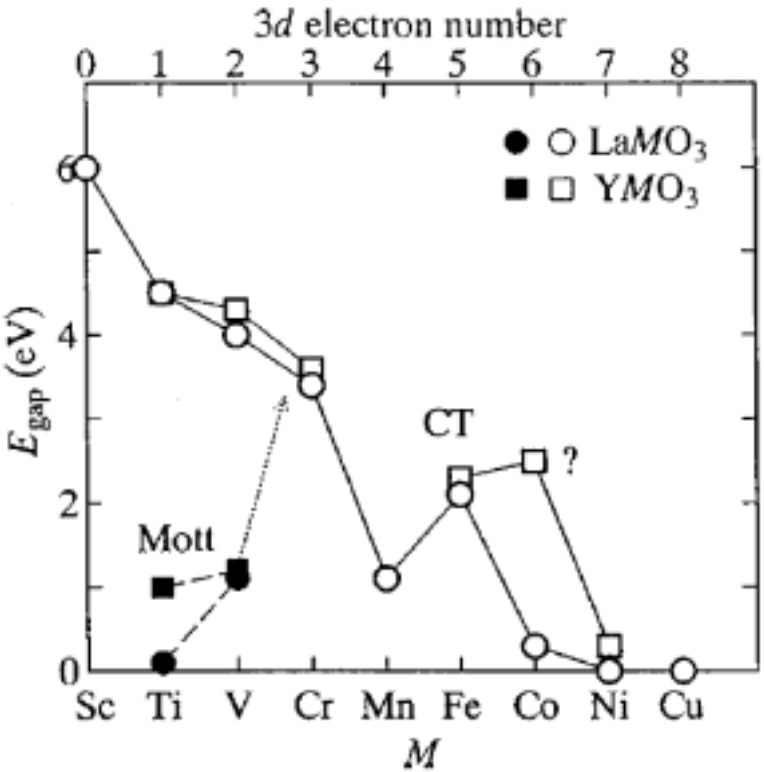
Systematic variation of band gaps in transition-metal oxides

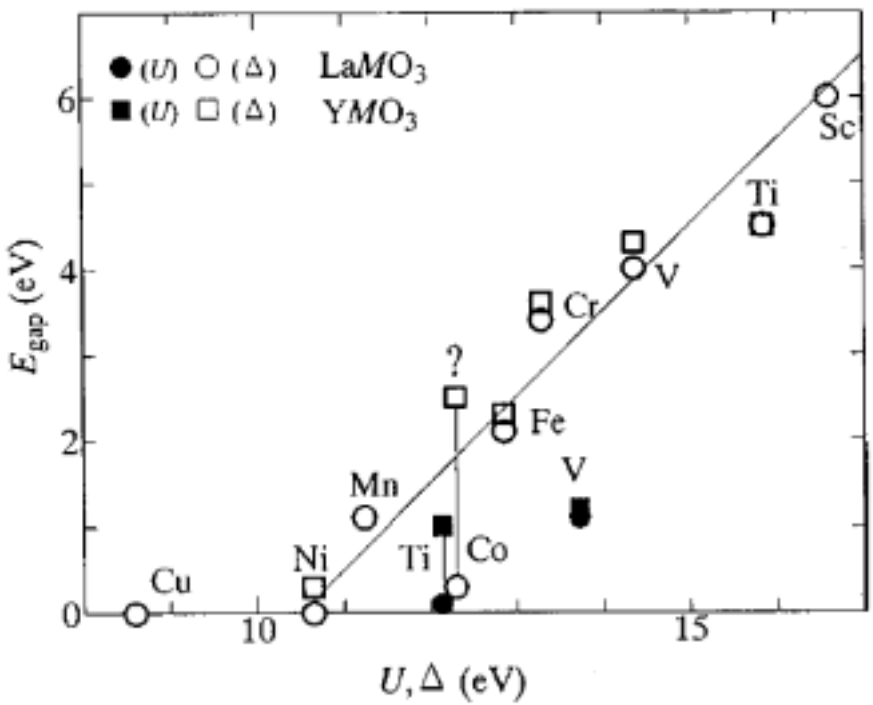




T. Arima et al., PRB '93

Systematic variation of band gaps in transition-metal oxides





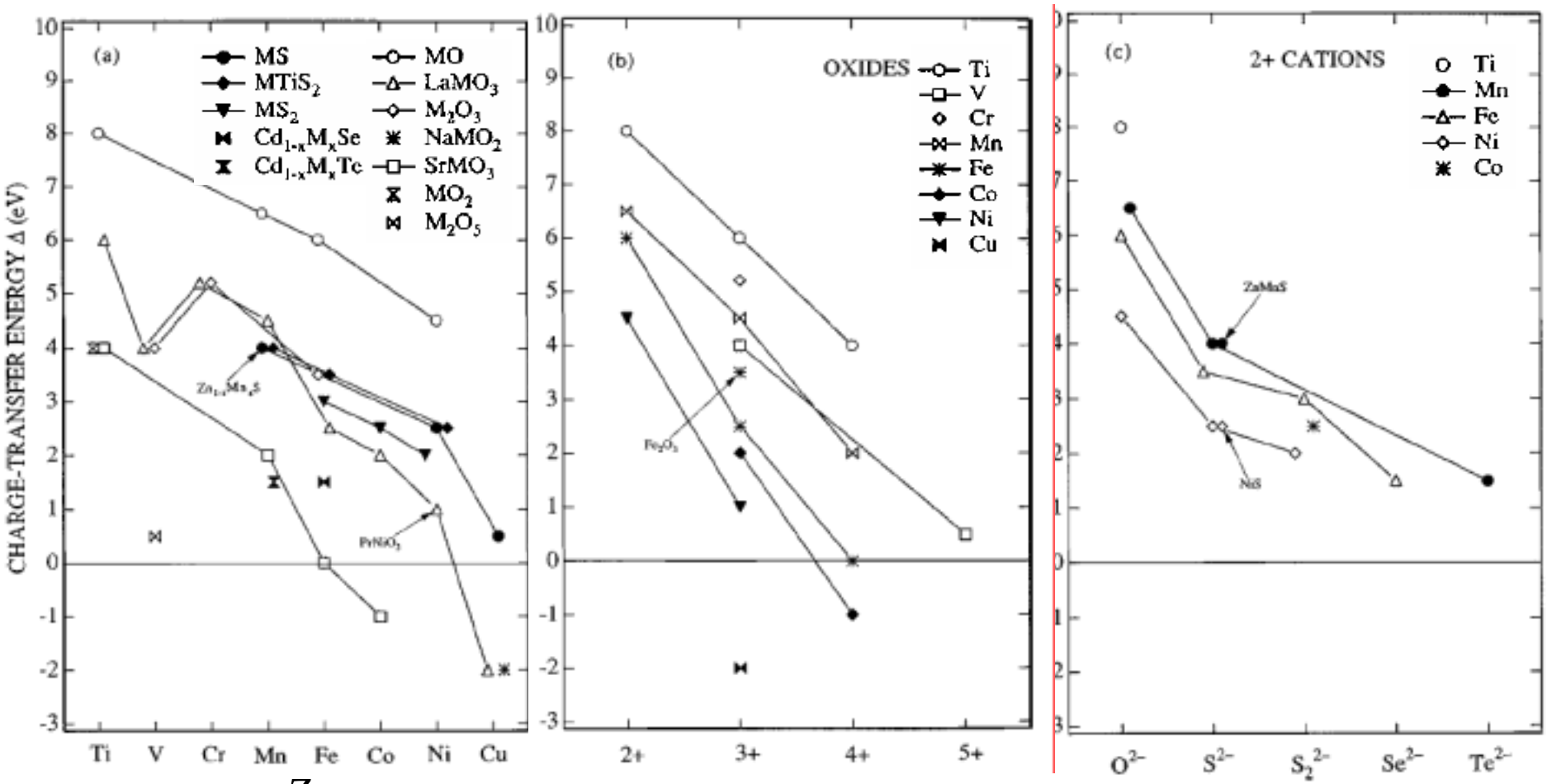
U_{eff}, Δ_{eff}: Eestimated from ionic model

$$U_{\mathrm{eff}} = I(M^{v+}) - A(M^{v+}) - \frac{e^2}{\quad},$$

$$\Delta_{\mathrm{eff}} = e\Delta V_{\mathrm{Mad}} + I(\mathrm{O}^{2-}) - A(M^{v+}) - \frac{e^2}{d_{M-\mathrm{O}}}$$

T. Arima et al., PRB ‘93

Systematic materials dependence of charge-transfer energy Δ



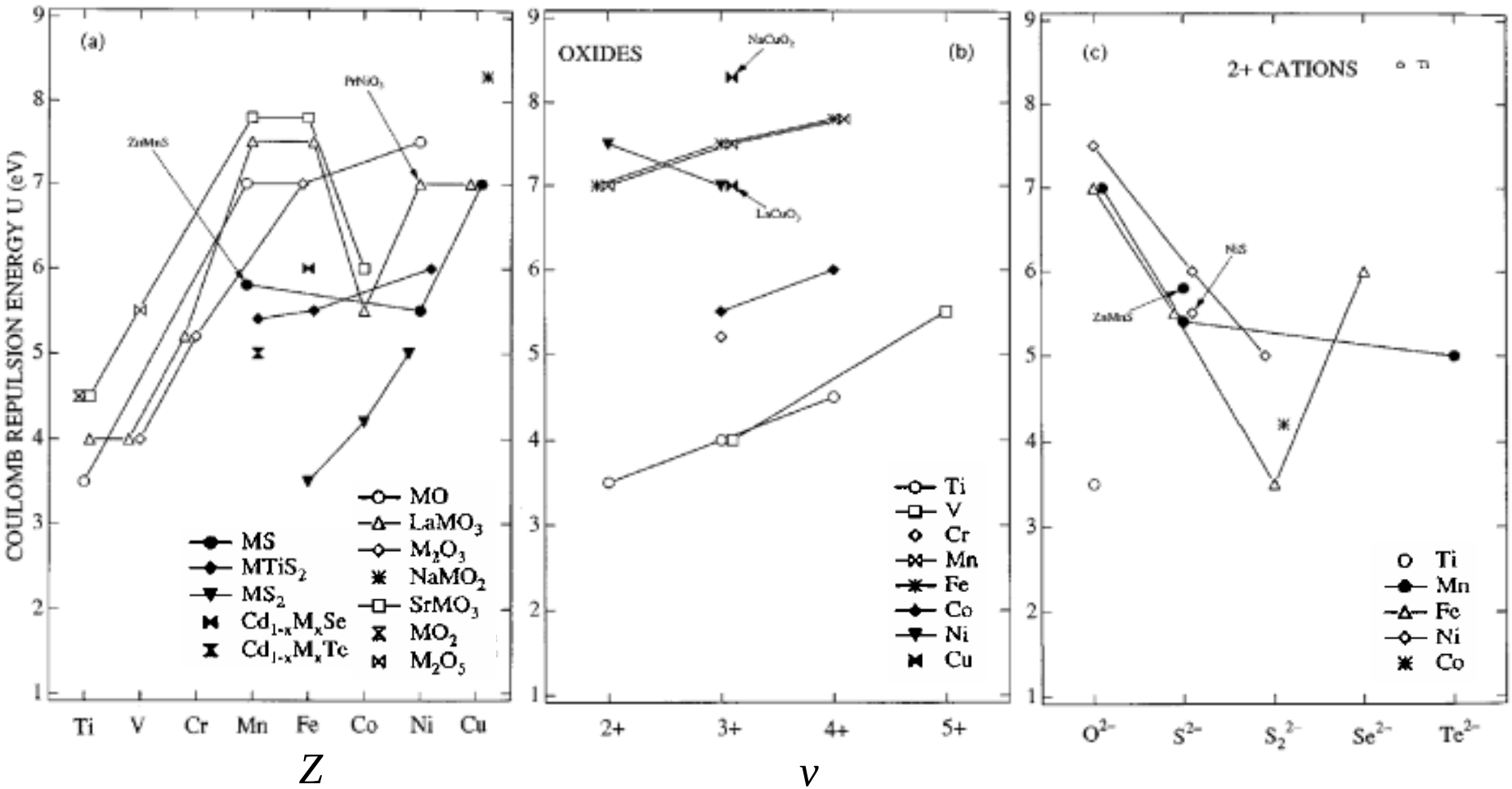
$$\Delta \sim \Delta_0 - 0.6Z - 2.5v, \quad \Delta_0 \sim 26\ \text{eV} \quad \text{for oxides}$$

$$\sim 23.5\ \text{eV} \quad \text{for sulfides}$$

~ 23 eV, 22.5 eV for selenides, tellurides

A.E. Bocquet et al., PRB '92

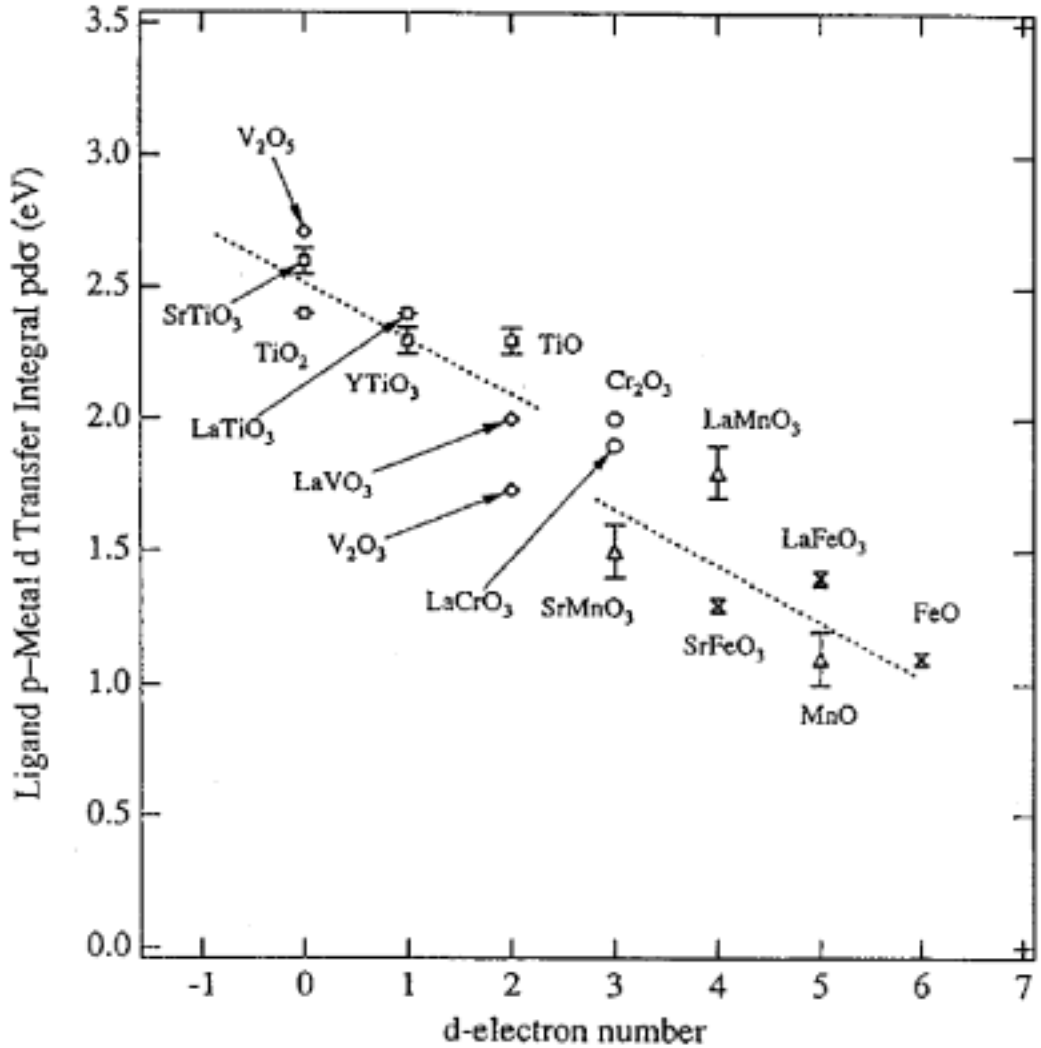
Systematic materials dependence of on-site Coulomb energy U



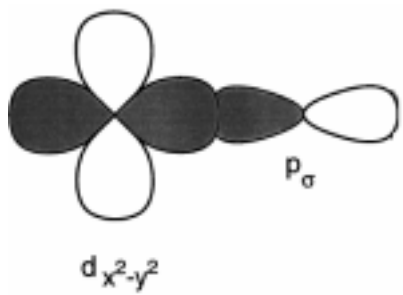
$$U \sim U_0 + 0.3Z + 0.5v \quad U_0 \sim -2.5\ \text{eV} \text{ for oxides}$$
$$\sim -4.5\ \text{eV} \text{ for sulfides}$$

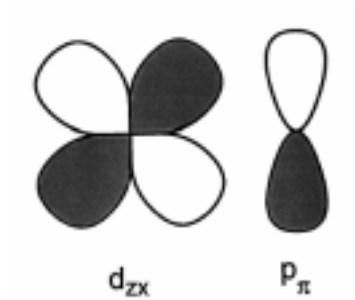
A.E. Bocquet et al., PRB '92

Systematic materials dependence of *p-d* transfer integral



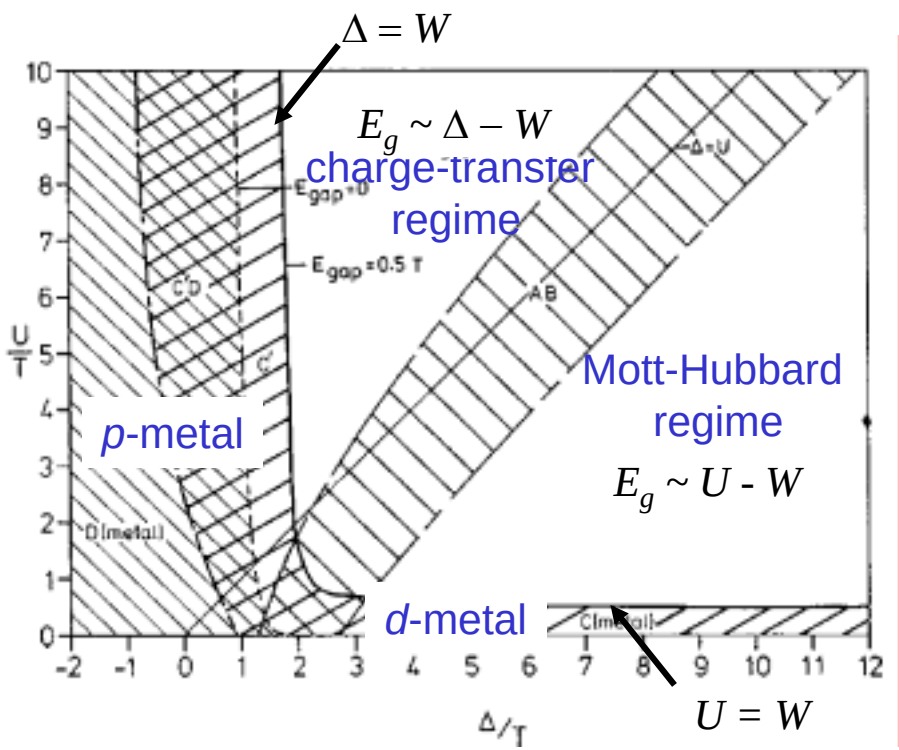
$$T_{pd} \equiv \sqrt{3}(pd\sigma),\ 2(pd\pi)$$

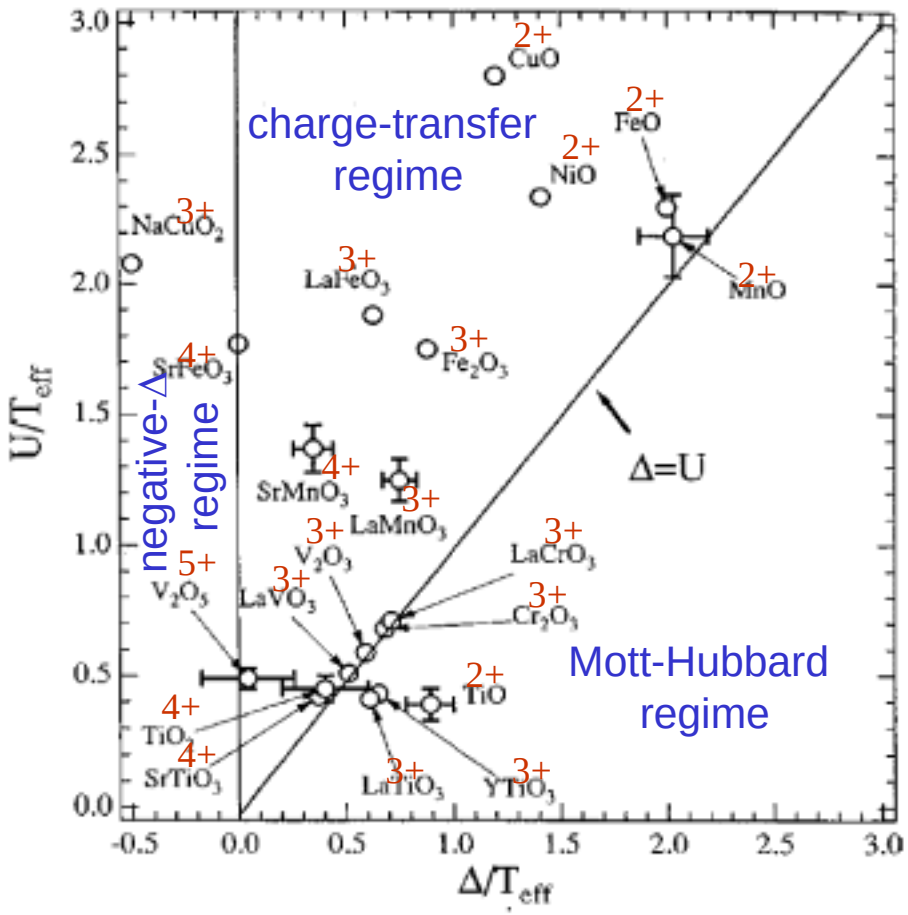




A.E. Bocquet et al., PRB ‘92

Zaanen-Sawatzky-Allen diagram

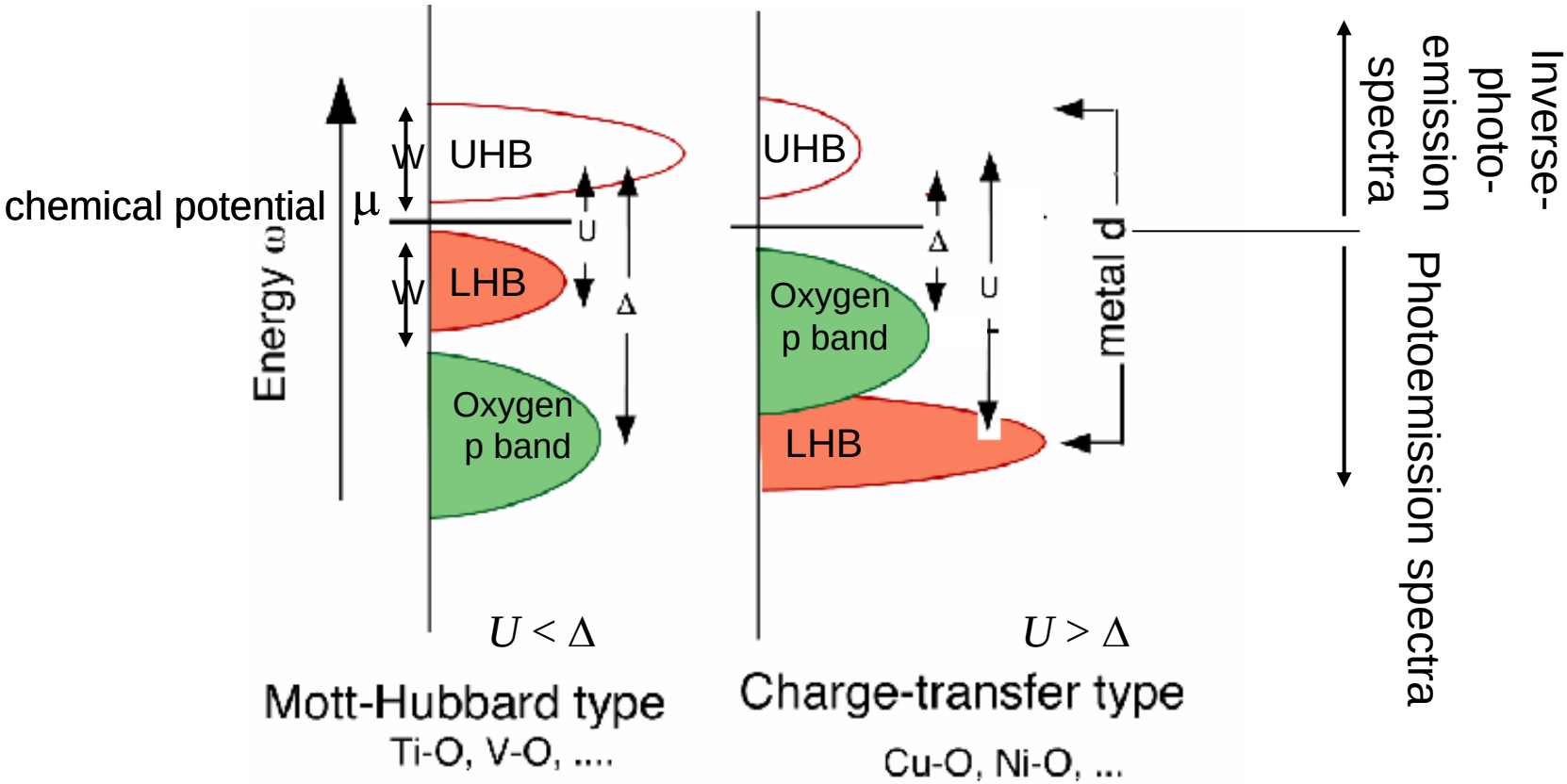




J. Zaanen, G.A. Sawatzky, J.W. Allen, PRL ‘85

A.E. Bocquet et al., PRB ‘96

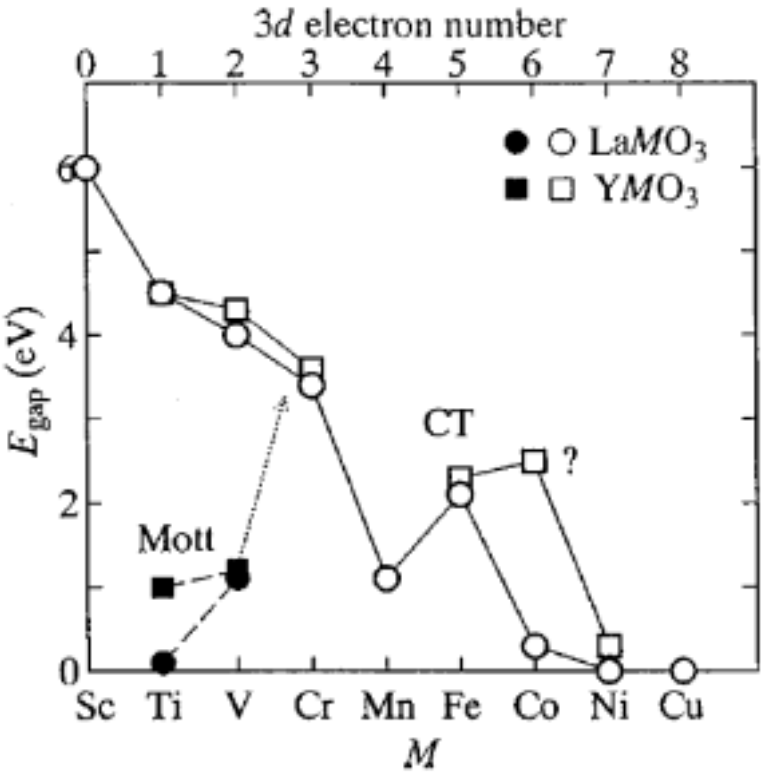
Mott-Hubbard-type insulators *vs* charge-transfer-type insulators

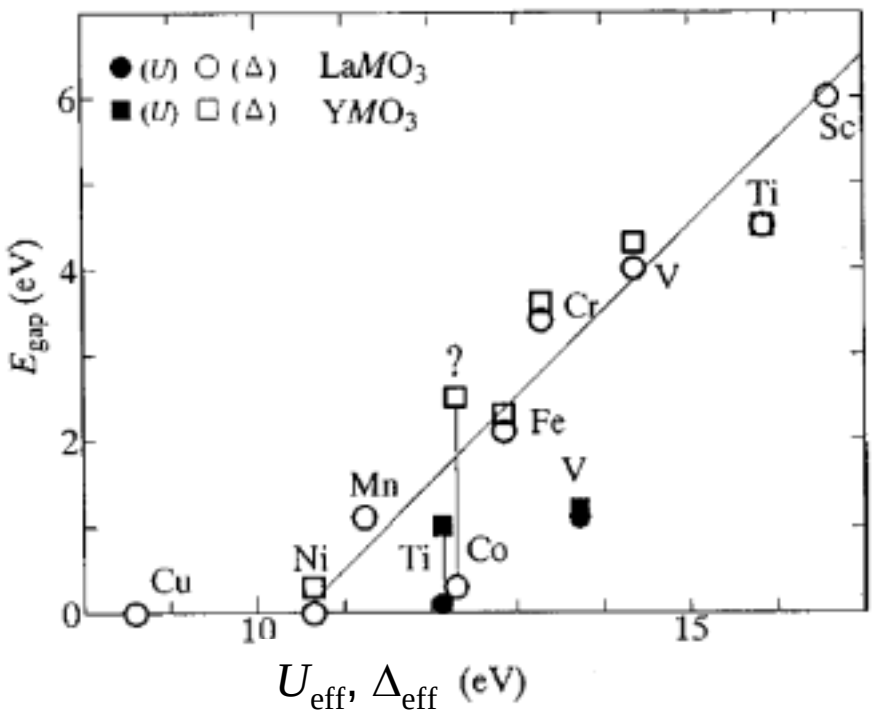


UHB: upper Hubbard band
LHB: lower Hubbard band

Charge transfer energy: Δ
on-site Coulomb energy: U
Band width: W

Systematic variation of band gaps in transition-metal oxides





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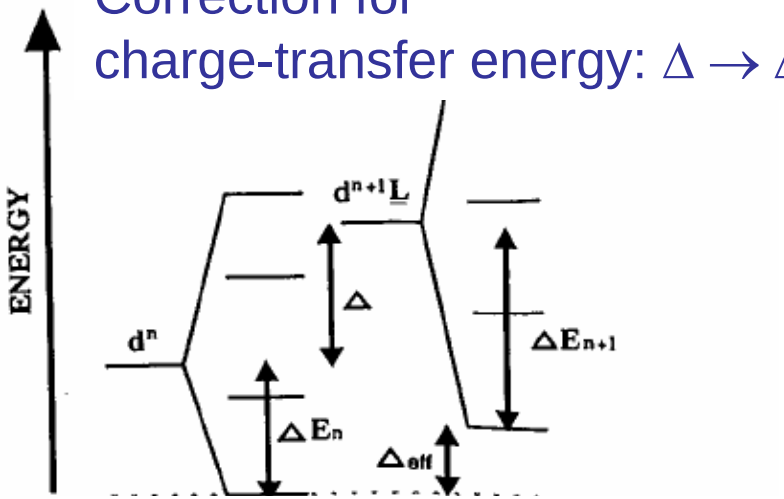
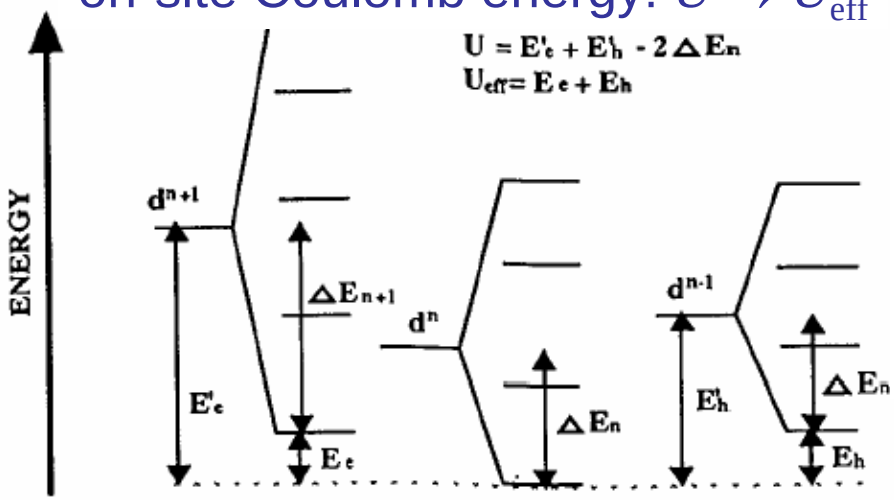
T. Arima et al., PRB ‘93

Multiplet corrections for Mott-Hubbard gap and charge-transfer gap

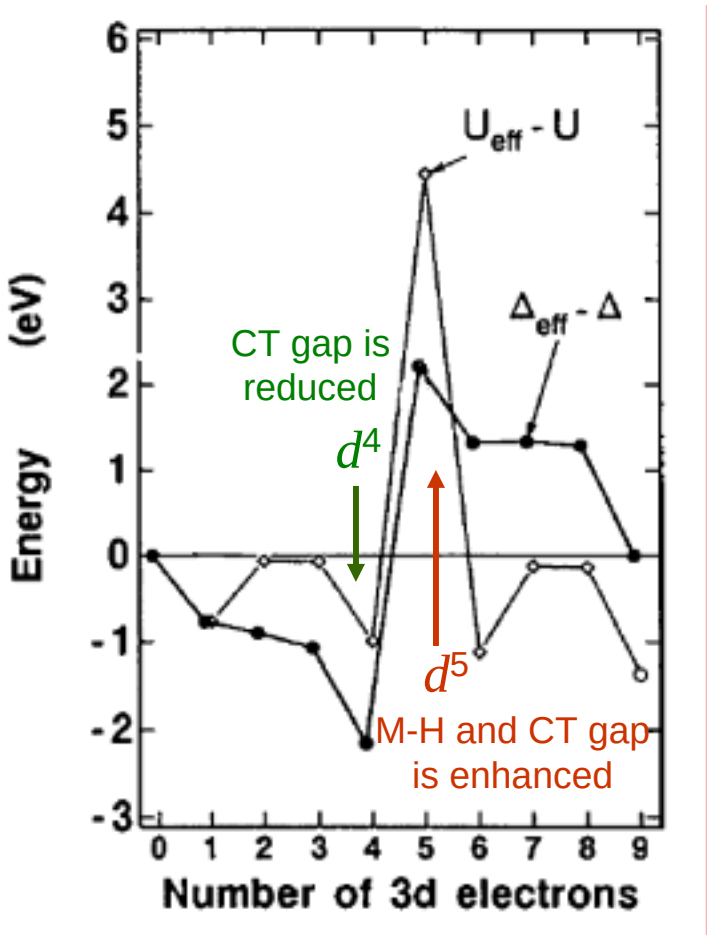
Correction for
charge-transfer energy: $\Delta \rightarrow \Delta_{\mathrm{eff}}$



Correction for
on-site Coulomb energy: $U \rightarrow U_{\mathrm{eff}}$



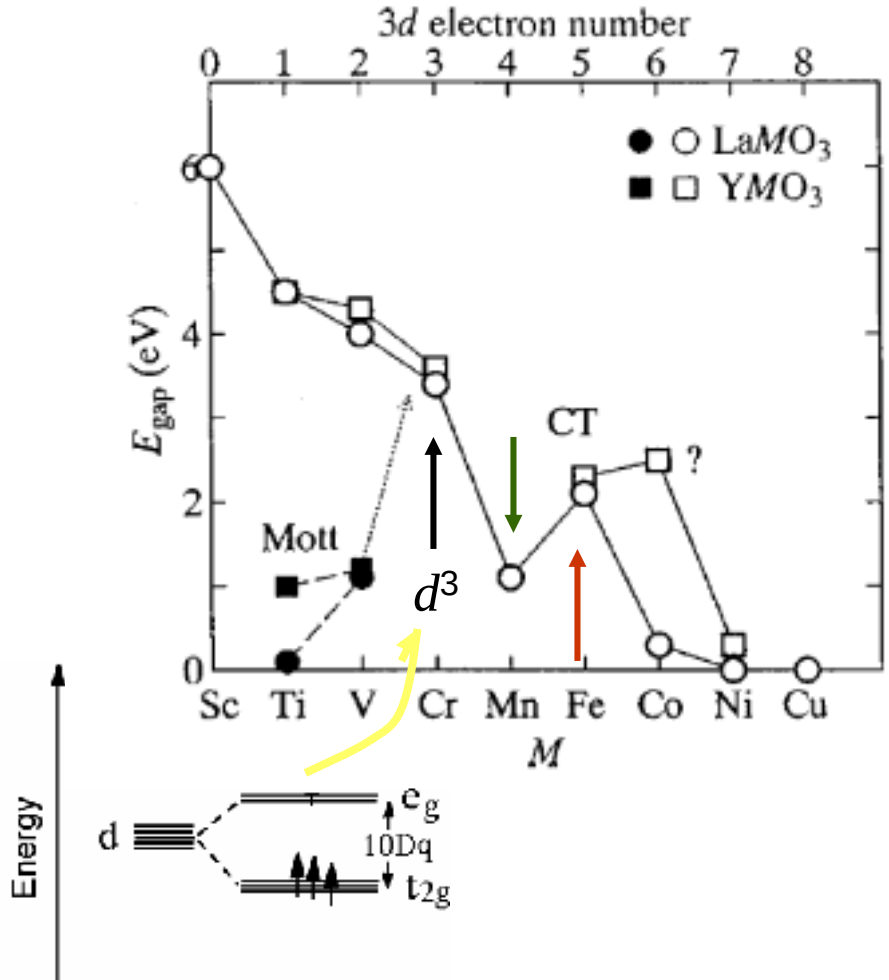
Multiplet corrections for Δ and U



T. Saitoh et al., PRB '95

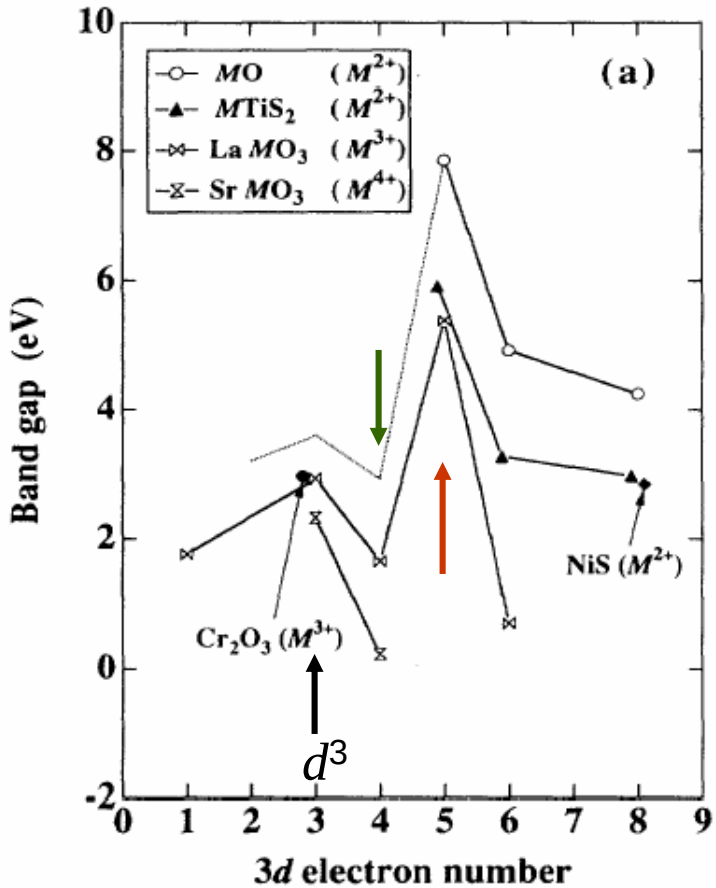
Multiplet corrections for Mott-Hubbard gap and charge-transfer gap

Optical gaps



T. Arima et al., PRB '93

Calculated band gaps



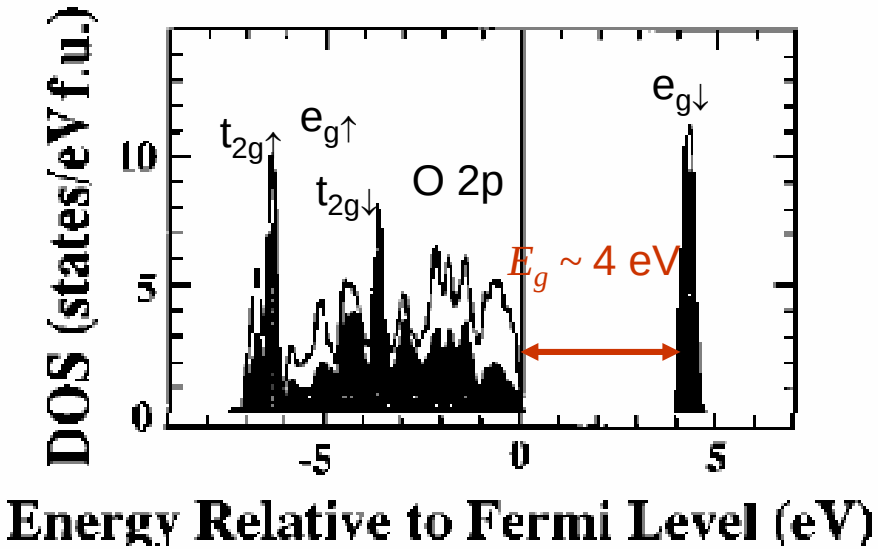
T. Saitoh et al., PRB '95

Mott insulators

- Band theory

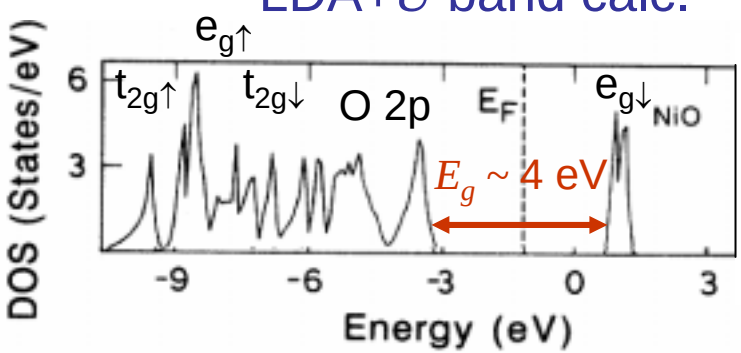
Hartree-Fock and LDA+U band calculations - failure of LDA in NiO -

Hartree-Fock band calc.



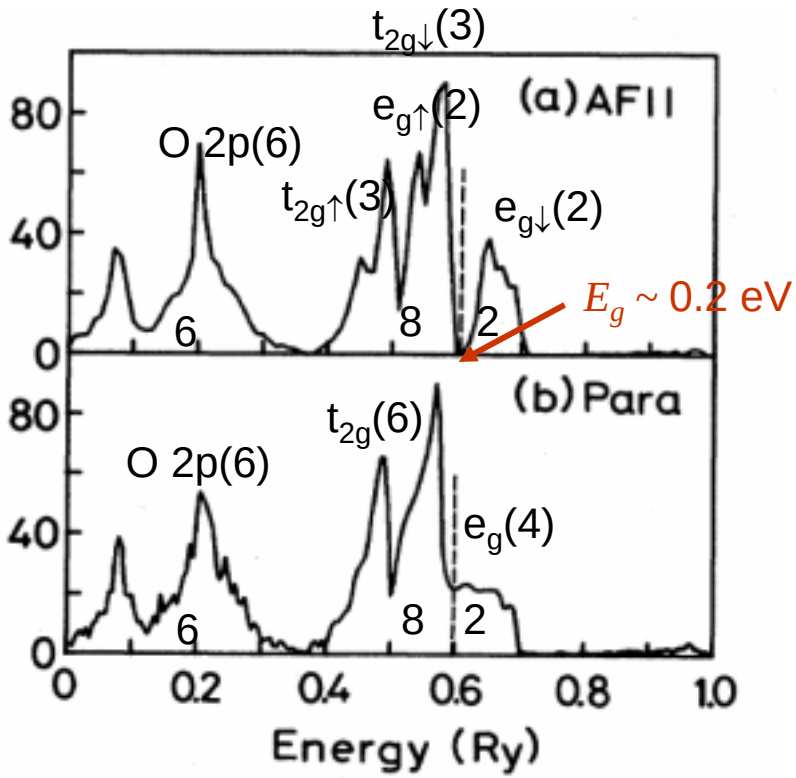
T. Mizokawa and A.F., PRB '96

LDA+U band calc.



V.I. Anisimov et al., PRB '91

Local-density-approximation (LDA) band calc.- NiO (14 valence electrons)



CoO, FeO: metallic !

T. Oguchi et al., PRB '83

Failure of LDA in Mott insulators

Hartree-Fock potential energy (also for LDA+U)

$$E_{\mathrm{LDA}+U} \sim E_{\mathrm{HF}} \sim \tfrac{1}{2} U \sum_{i \neq j} n_i n_j$$

n_i : occupation number of orbital i

→ orbital-dependent self-consistent potential
→ positive feedback toward orbital polarization

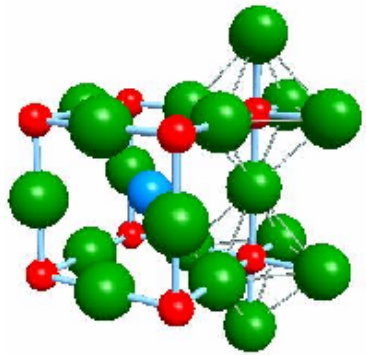
Local-density approximation (LDA) potential energy

$$E_{\mathrm{LDA}} \sim UN(N-1)/2 \,, \quad N = \sum_i n_i$$

N: total occupation number (local density)

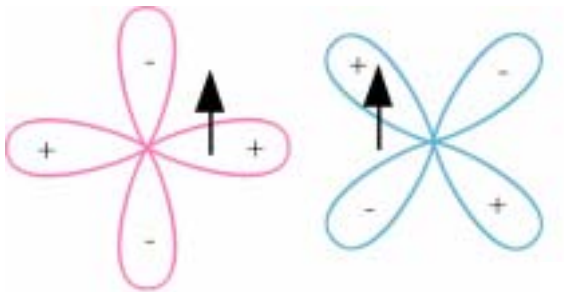
→ "spherically" averaged potential, unphysical self-interaction
→ orbital polarization suppressed

Orbital ordering in perovskite-type ABO_3 compounds

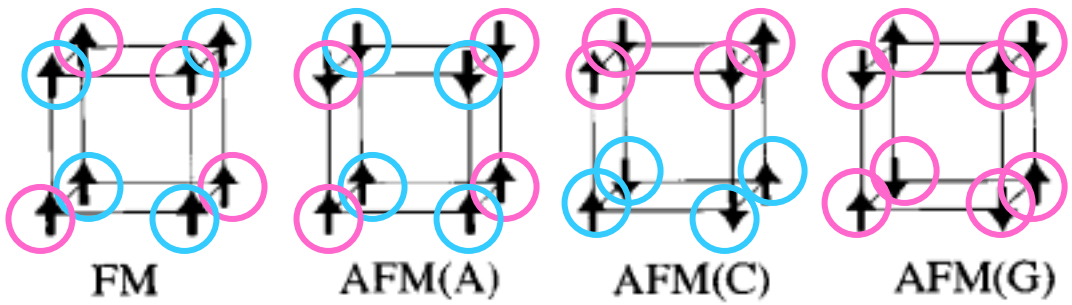


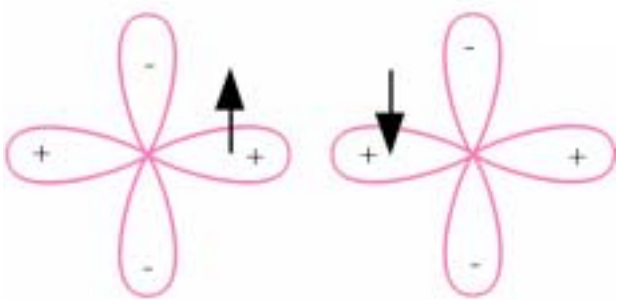
orbital 1

orbital 2



Ferromagnetic

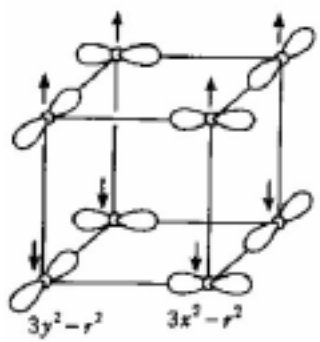




Antiferromagnetic

ex) $LaMn^{3+}O_3$

d^4: $t_{2g}\uparrow^3 e_g\uparrow$



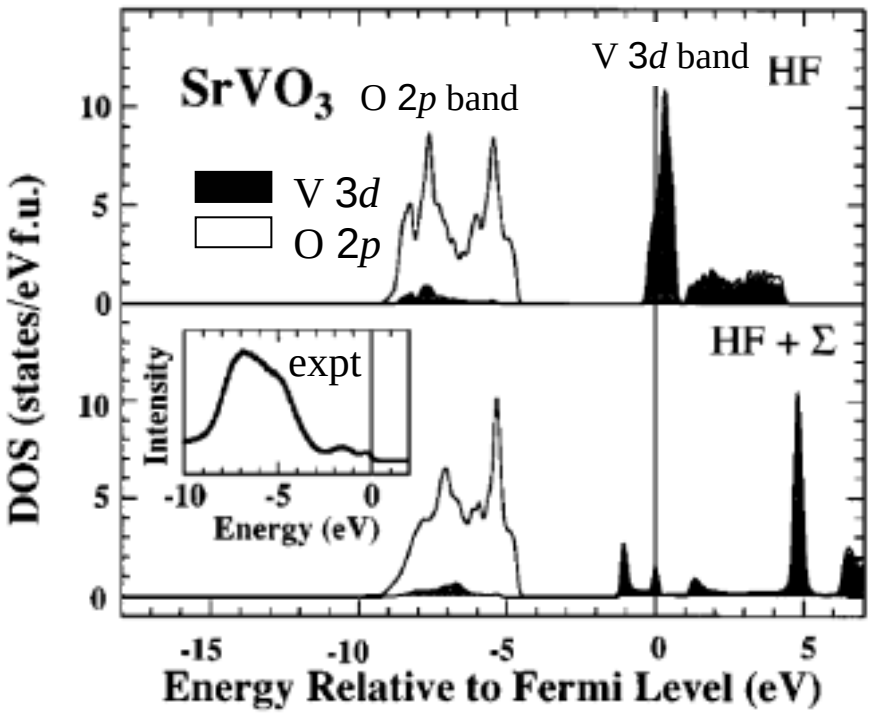
Jahn-Teller distortion

Mott insulators

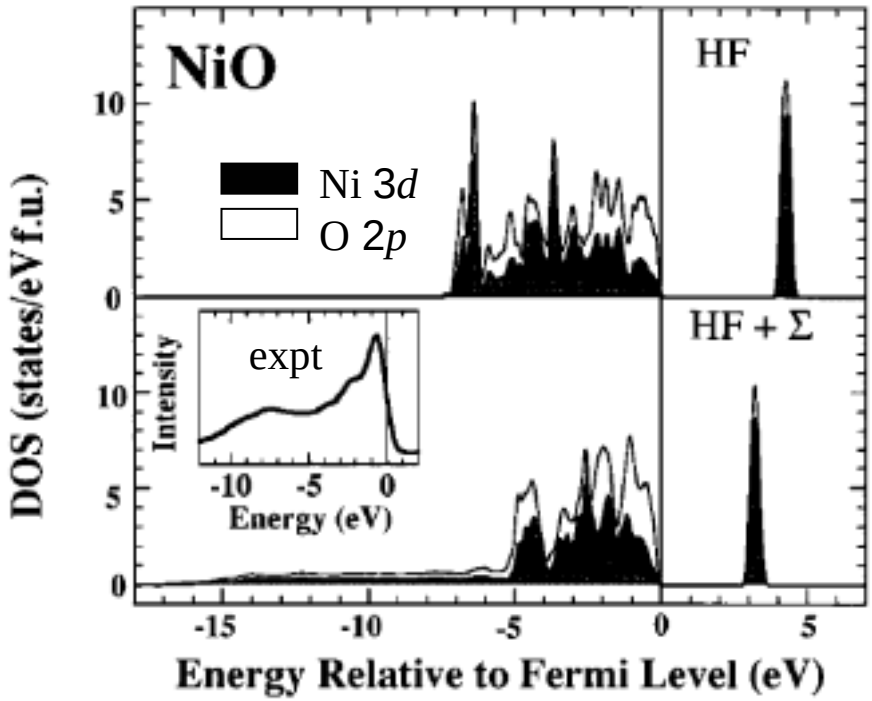
- Self-energy correction

Hartree-Fock band calculation + self-energy correction $\Sigma(\omega)$

Mott-Hubbard type



Charge-transfer type



Green's function:

$$G(\mathbf{k},\omega) = \frac{1}{\omega - \varepsilon^0_{\mathbf{k}} - \Sigma(\omega)}$$

Spectral function:

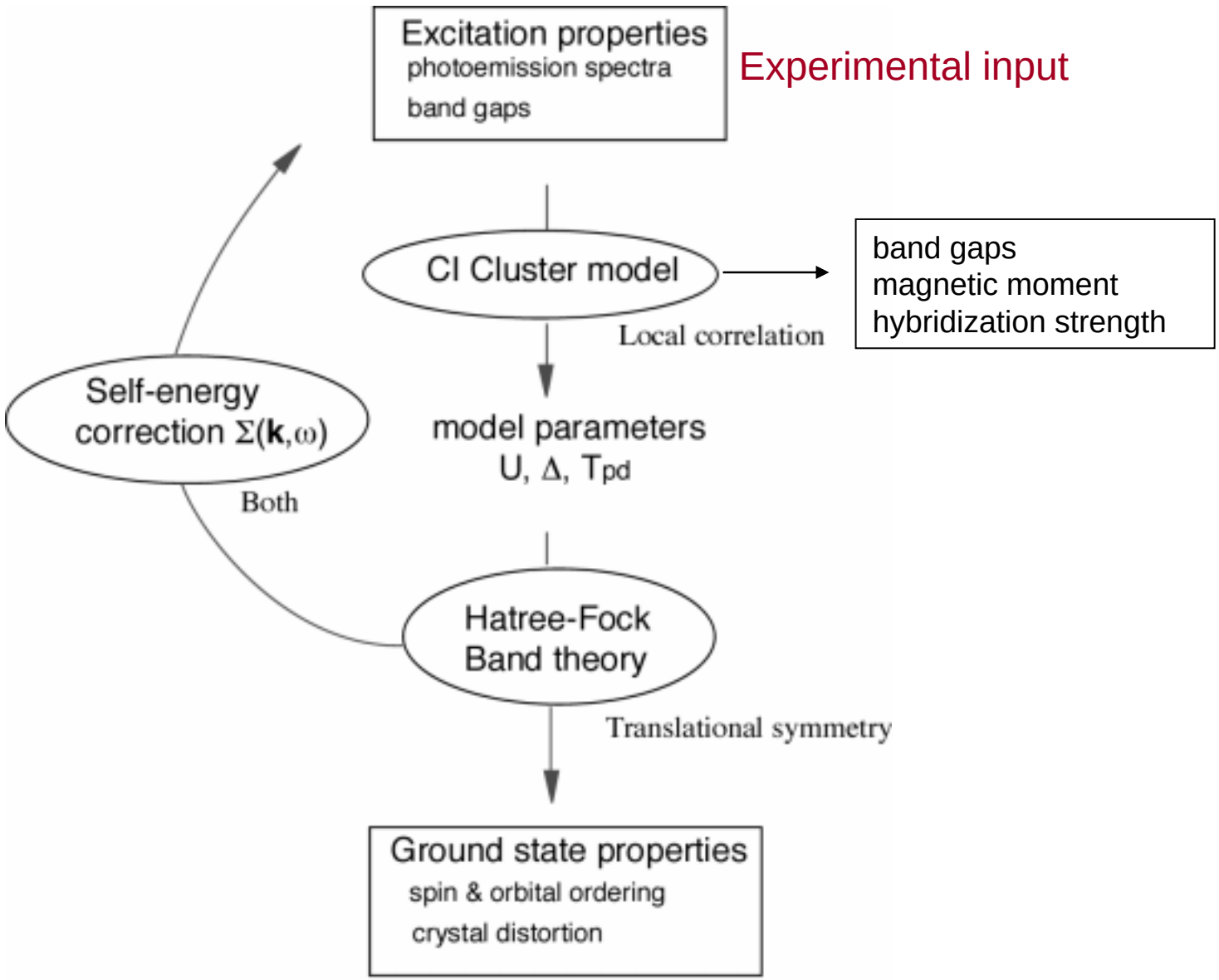
$$A(\mathbf{k},\omega) = -\frac{1}{\pi}\mathrm{Im}G(\mathbf{k},\omega)$$

calculated with 2nd order perturbation

Hartree-Fock eigenvalue

T. Mizokawa and A. Fujimori, PRB '96

CI cluster model, Hartree-Fock band theory and photoemission spectra

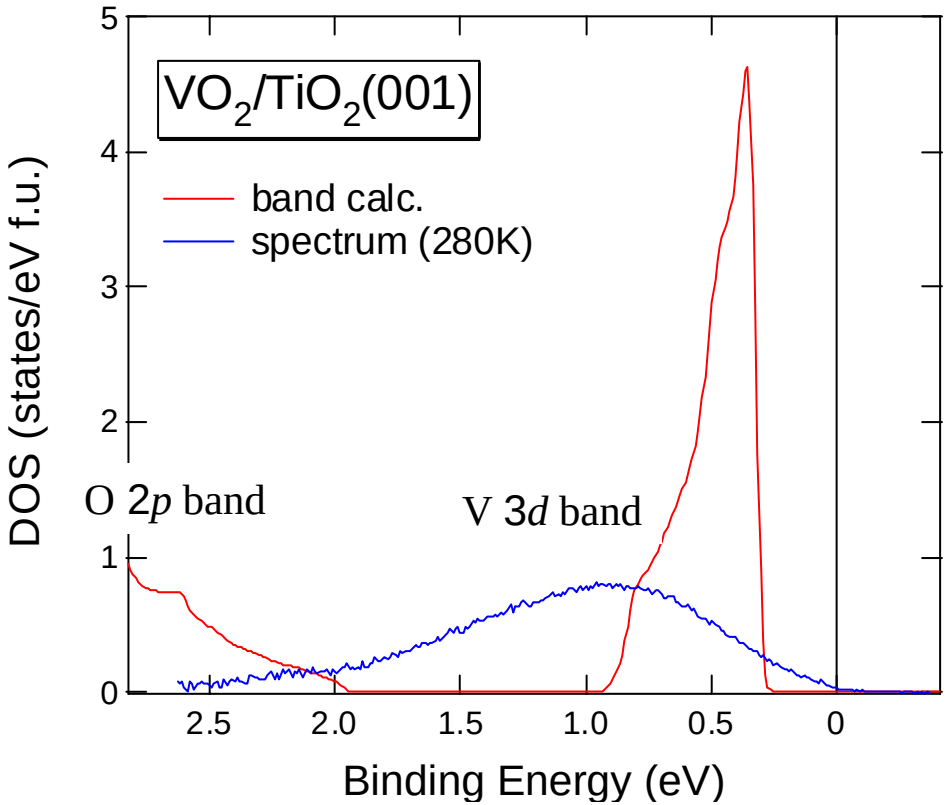


Mott insulators

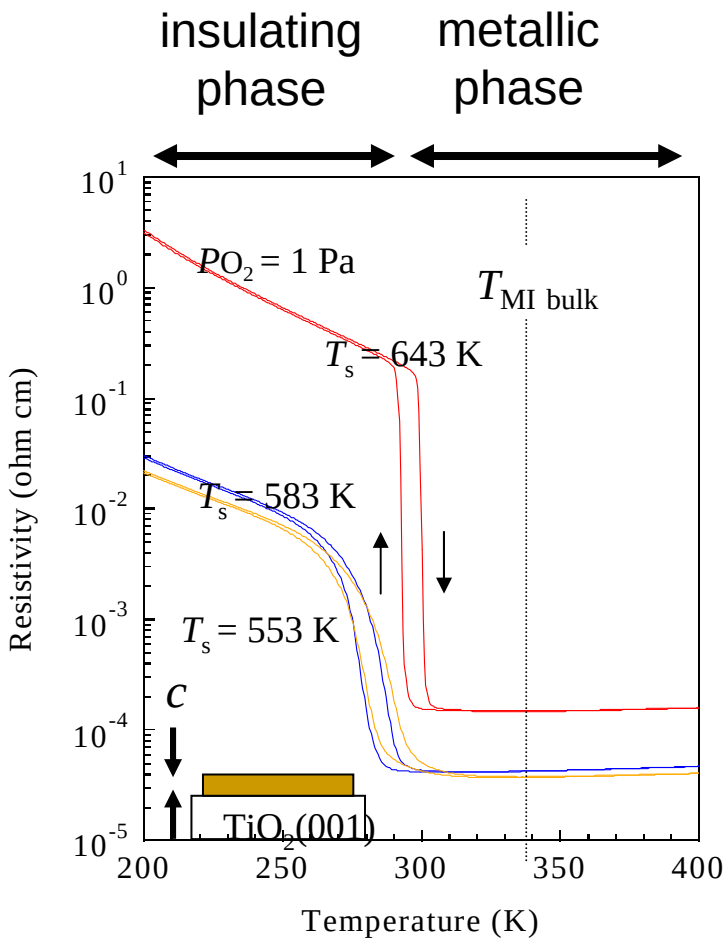
- Electron-phonon interaction

Discrepancy of spectral line shapes between band theory and photoemission spectra

Mott-Hubbard type insulator VO_2



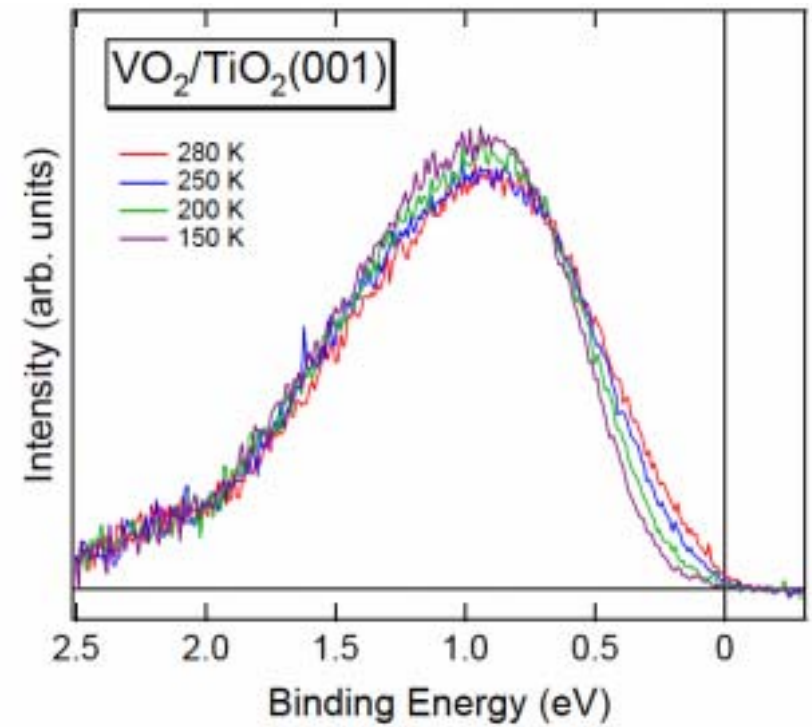
LDA+U band-structure calculation,
X. Hunag, et al., cond-mat/98

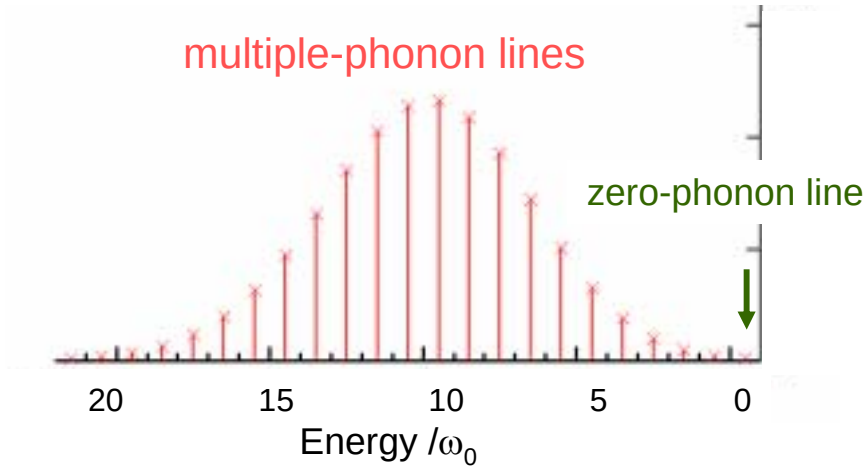


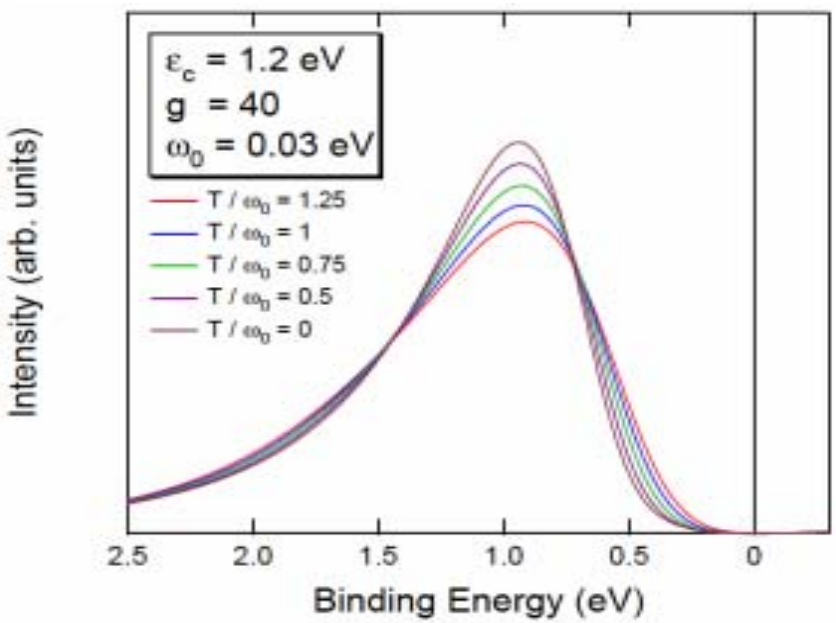
Y. Muraoka et al.

Electron-phonon interaction in the insulating phase of VO_2

Simulations using independent-boson model







K. Okazaki et al. PRB '04

Electron-phonon interaction in the insulating phase of VO_2

Simulations using independent-boson model