COLLÈGE DE FRANCE
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Chaire de Physique de la Matière Condensée

Des oxydes supraconducteurs aux atomes froids

- la matière à fortes corrélations quantiques -

Antoine Georges

Cycle 2009-2010
Cours 6 – 9 juin 2010

Cours 6: Introduction à la transition metal-isolant de Mott dans les oxydes de métaux de transition (1)

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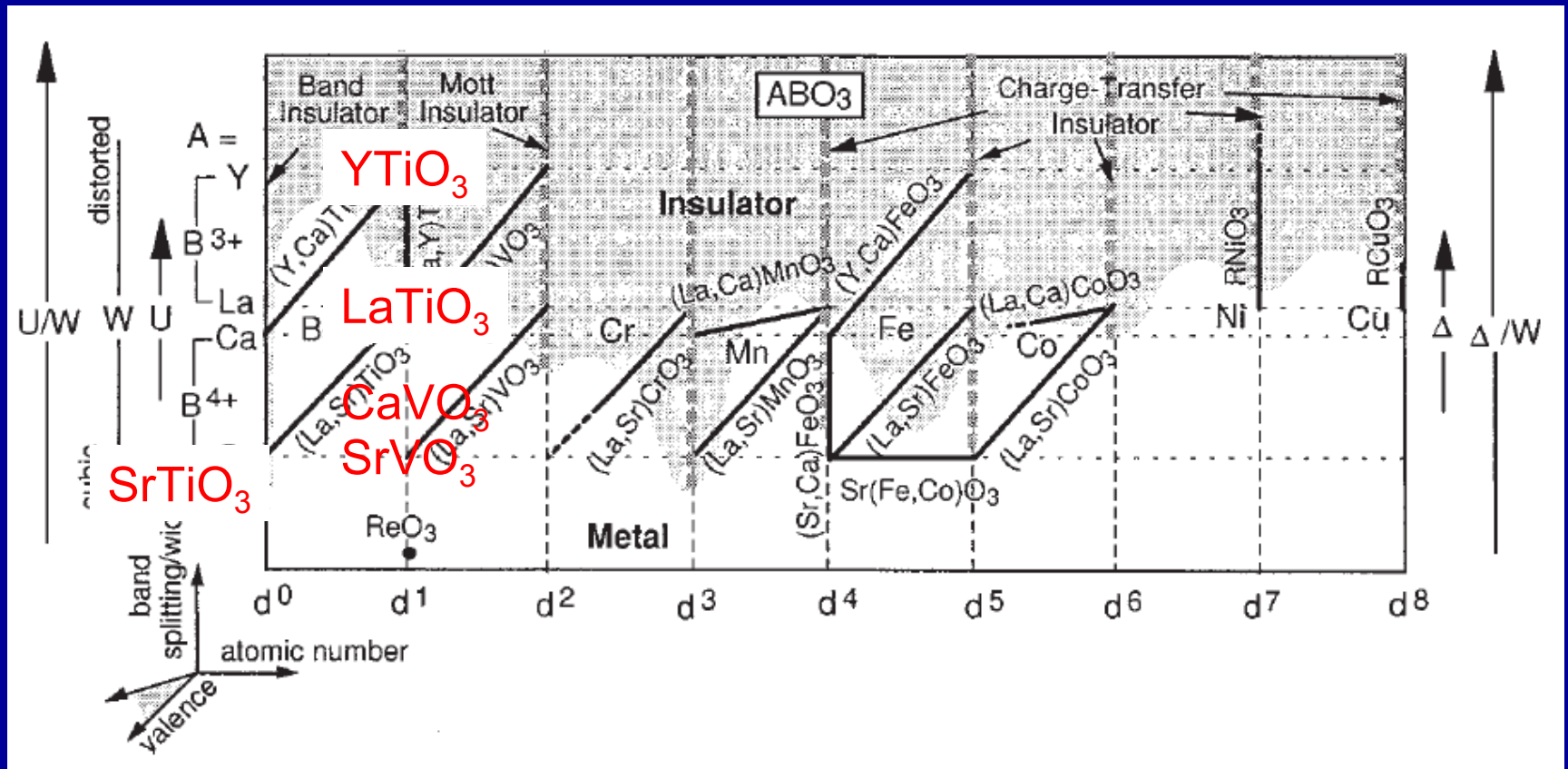
Séminaire:

Antoine MAIGNAN

Laboratoire de Cristallographie et Sciences des Matériaux (CRISMAT), Caen

Oxydes des métaux de transition : réseaux carrés et triangulaires pour générer de nouvelles fonctionnalités.

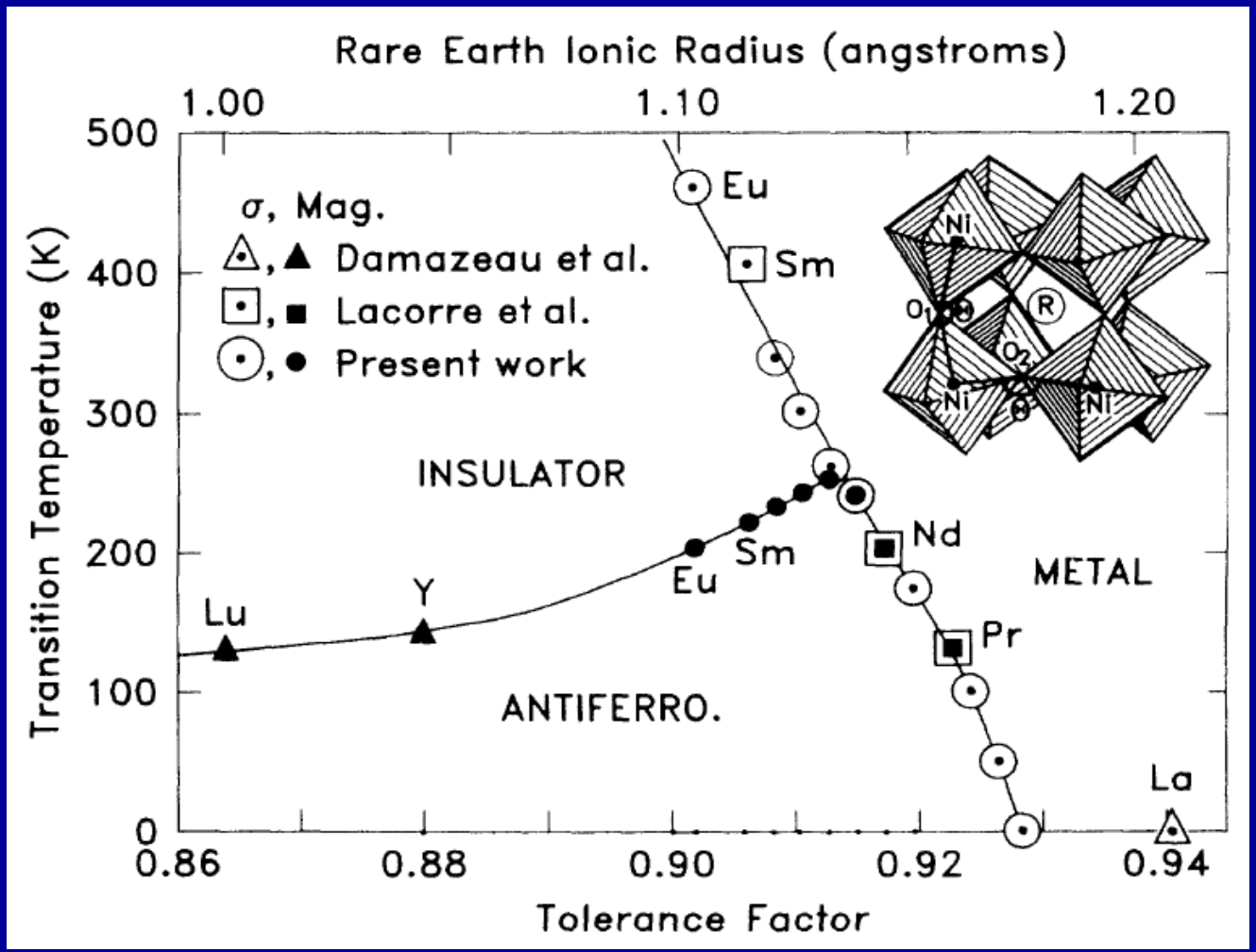
The Mott phenomenon plays a key role



``Atsushi Fujimori's map of RMO_3 perovskites''
J.Phys Chem Sol. 53 (1992) 1595

Partially filled d-shells… and yet often insulators

The $RNiO_3$ $3d^7$ compounds: metal-insulator transition in a `late' TMO



Torrance at al. Phys Rev B 45 (1992) 8209

OUTLINE

- 1. Interactions: the `Hubbard U'
- 2. Mott and charge-transfer insulators
- 3. Mott transition: the Brinkman-Rice description
- 4. BR confronts experiments: $La_{1-x}Sr_xTiO_3$
- 5. A derivation of Brinkman-Rice (and beyond)

1.Interactions: the `Hubbard U'

Dominant interaction: Coulomb repulsion for putting two electrons in the same orbital : **the famous Hubbard U**
(Similar, but smaller matrix element for two electrons in different orbitals, with parallel or antiparallel spins
→ cf. lecture 8 (exchange and Hund's coupling)

(Very) naively:

$$U = \int d^3r |\phi_m(r)|^2 \frac{e^2}{4\pi\varepsilon_0 |r - r'|} |\phi_m(r')|^2 \equiv F_0$$

But this is HUGE ! (~20 eV)

What did we forget ? → **SCREENING** by other electrons !

A scheme to calculate U including screening: `constrained' RPA

F.Aryasetiawan et al.
PRB 70 (2004) 195104

RPA (GW) scheme: calculate polarisability from a single particle-hole excitation

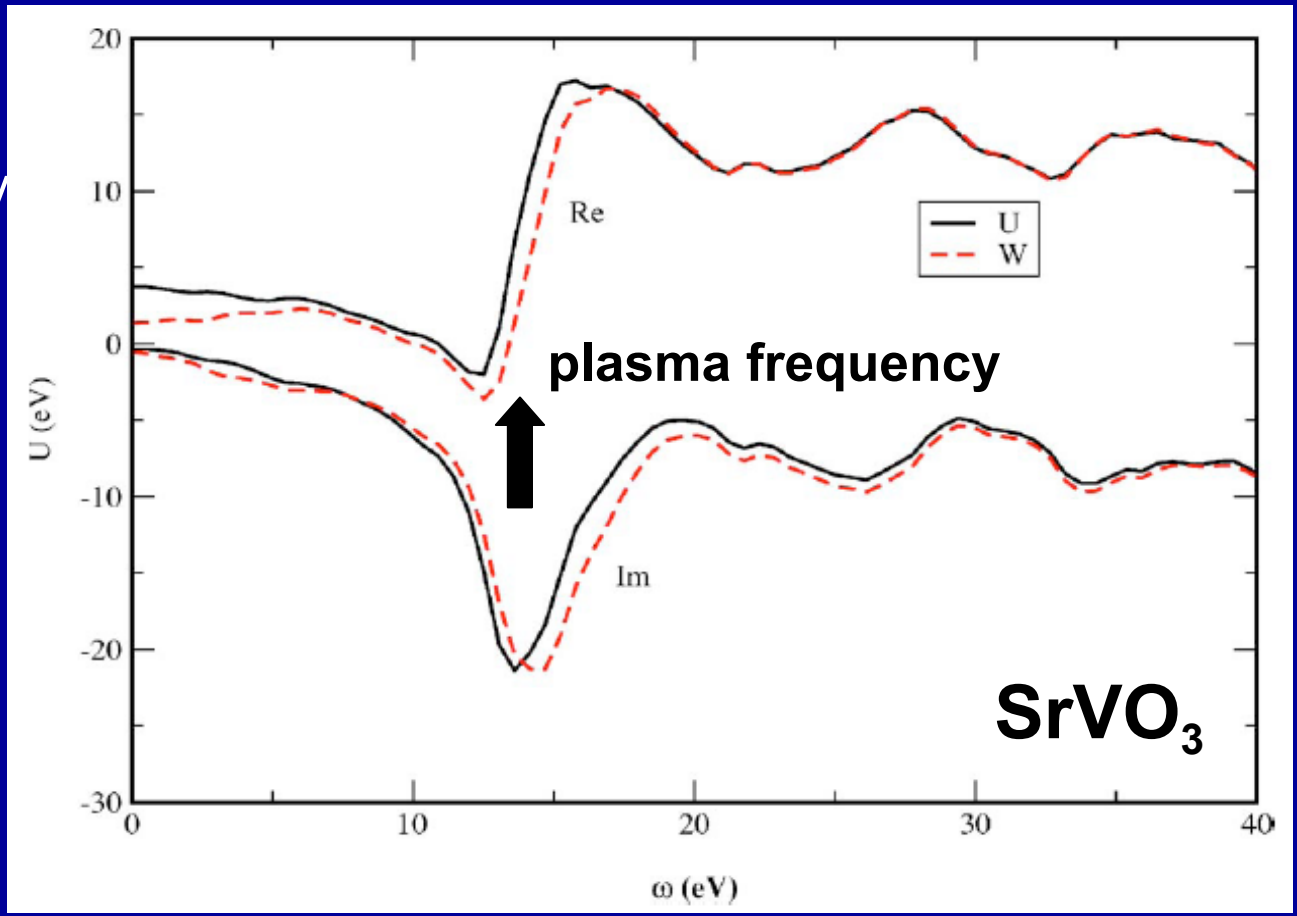
$$W = V_c/[1 - PV_c] \ , \ V_c = \frac{e^2}{4\pi\varepsilon_0 r}$$

$$P(\mathbf{r},\mathbf{r}';\omega) = \sum_{i}^{occ}\sum_{j}^{unocc} \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}') \times \left\{ \frac{1}{\omega - \varepsilon_j + \varepsilon_i + i0^+} - \frac{1}{\omega + \varepsilon_j - \varepsilon_i - i0^+} \right\}$$

When constructing effective screened interaction for low-energy model, truncate all transitions which are within the selected energy window
(e.g. all t2g→t2g transitions if low-energy t2g only model)

This reduces the actual value of U to about 3.5 eV for an effective model including the t2g bands only.

Low-energy Value: ~ 3.5 eV

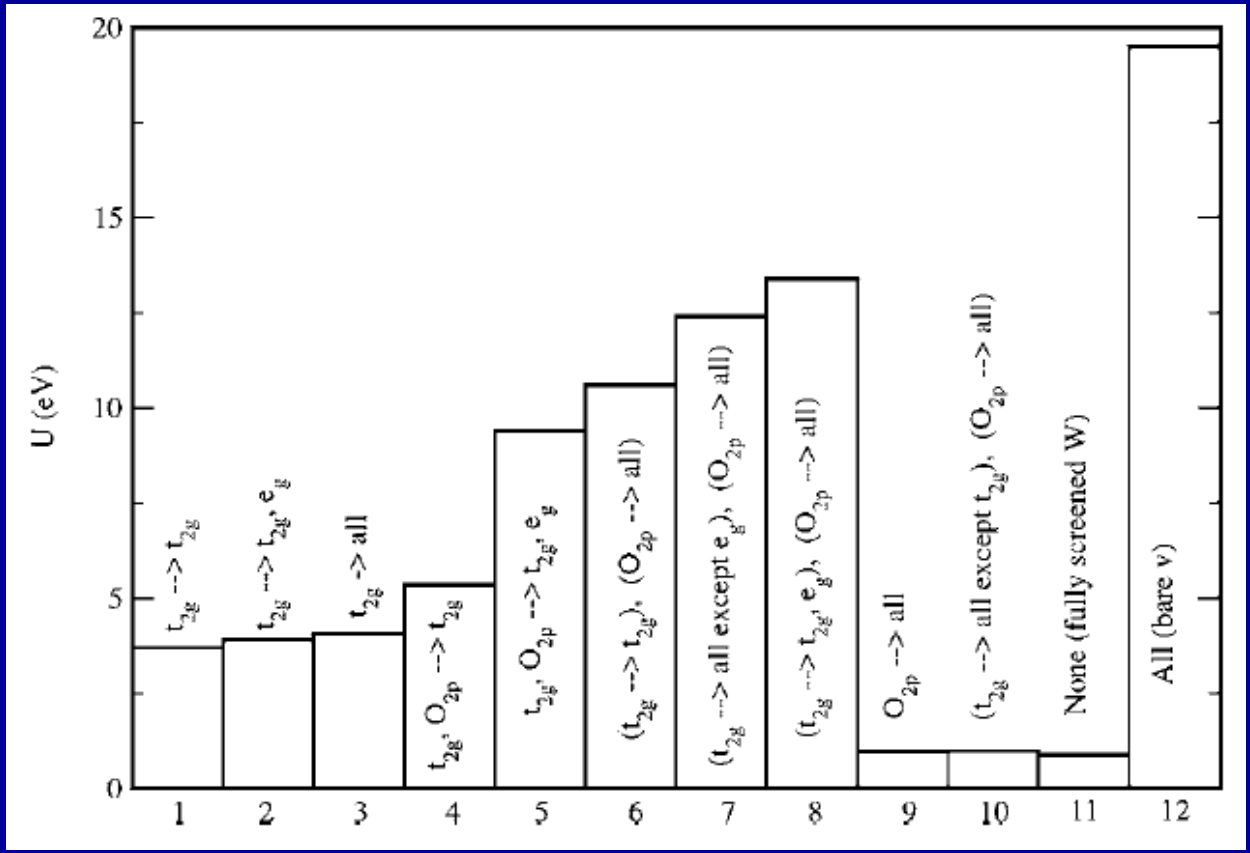


High-energy value: ~ 12 eV

F.Arayasetiawan et al. PRB 74 (2006) 125106

U: an energy-dependent Concept → U(ω)

Plasma frequency (screening) is here mainly dominated by transitions from occupied O-2p bands to other empty bands



Fully screened: ~ 1 eV

Effect of removing various transitions :

FIG. 2. The Hubbard U of $SrVO_3$ obtained by eliminating various transitions as indicated in the picture. For example, case 5 corresponds to eliminating transitions $t_{2g} \rightarrow t_{2g}$, $t_{2g} \rightarrow e_g$, $O_{2p} \rightarrow t_{2g}$, and $O_{2p} \rightarrow e_g$ and case 6 corresponds to eliminating $t_{2g} \rightarrow t_{2g}$ transition and all transitions from O_{2p}. Discussion of the result is described in the text.

Other schemes for evaluating U: `constrained LDA'

$$U_{\alpha\alpha\beta\beta} = E\left[n_{\mathbf{R}\alpha}+1, n_{\mathbf{R}'\beta}-1\right] - E\left[n_{\mathbf{R}\alpha}, n_{\mathbf{R}'\beta}\right]$$

From total energy ion DFT and constraining occupancies on a given site (e.g imposing constraint with Lagrange Multipliers = potentials)

$$E\left[\{n_{\mathbf{R}\alpha}\}\right] = E[\rho] + \sum_{\mathbf{R}\alpha} V_{\mathbf{R}\alpha}\left(\langle \tilde{W}^{\alpha}_{\mathbf{R}}|\hat{\rho}|\tilde{W}^{\alpha}_{\mathbf{R}}\rangle - n_{\mathbf{R}\alpha}\right)$$

Many variants… topics for a detailed lecture !
Usually: this yields rather overestimated values of U
For metals

Measuring U ?
PES +
IPES (BIS),
Auger,
etc…

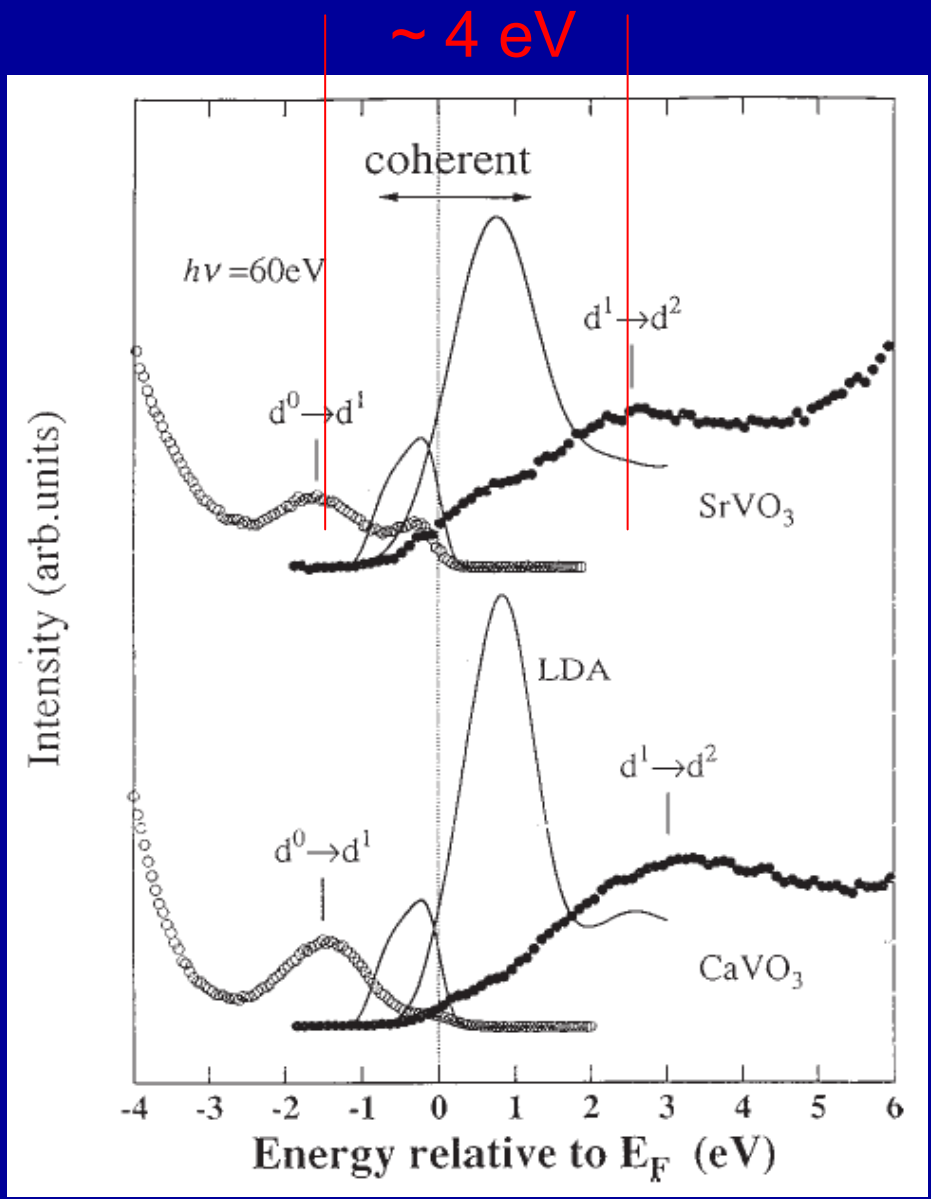


FIG. 99. Photoemission and inverse-photoemission spectra of $SrVO_3$ and $CaVO_3$ in the V $3d$ band region compared with a LDA band-structure calculation of Takegahara (1994). From Morikawa *et al.*, 1995.

Other interactions: see lecture 8

- Actually, the full interaction in a multi-orbital context is a matrix $U_{m1m2m3m4}$
- There is physics in this ! (e.g. Hund's coupling)
- Some multi-orbital effects → lecture 8

2.) Keeping things simple: three key energy scales:

t_{pd} **Metal/Ligand Hybridization**

$\Delta = \varepsilon_d - \varepsilon_p$ **Charge transfer energy**

U **d-orbital on-site repulsion**

Bandwidth controlled by : $t_{eff} \approx t_{pd}^2 / \Delta$

The Mott phenomenon: turning a partially-filled band into an insulator

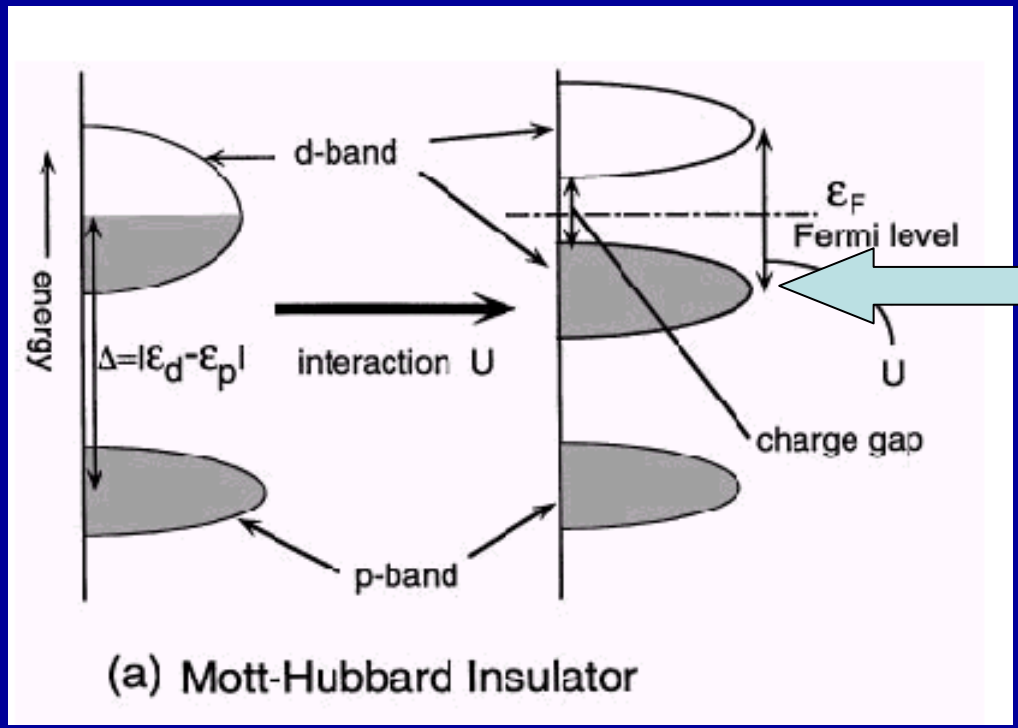
Consider simplest case first: $U<\Delta$

Moving an electron requires creating a hole and a double occupancy: **ENERGY COST U**

This object, once created, can move with a kinetic energy of order the **bandwidth W**

U < W : A METALLIC STATE IS POSSIBLE
U > W : AN INSULATING STATE IS PREFERRED

One-electron (photoemission) spectroscopy of a Mott insulator: Hubbard ``bands''



Lower Hubbard ``band''

From M.Imada's review

Note: not a band, really: can only contain at most one electron per state, not two. A broadened atomic level, in fact.

``Charge transfer'' insulators

U < Δ

e.g. NiO, $RNiO_3$, cuprates

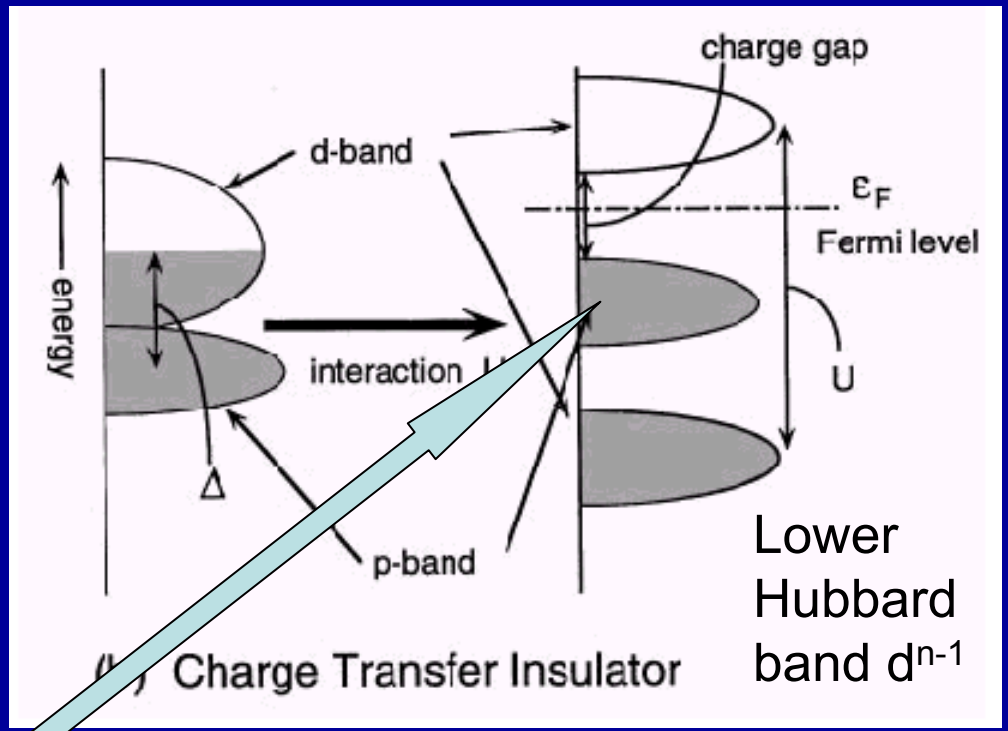
(TMOs with late transition metals)

Gain: $t_{eff} \approx t_{pd}^2 / \Delta$

Cost: $\Delta = \varepsilon_d - \varepsilon_p$

Transition for

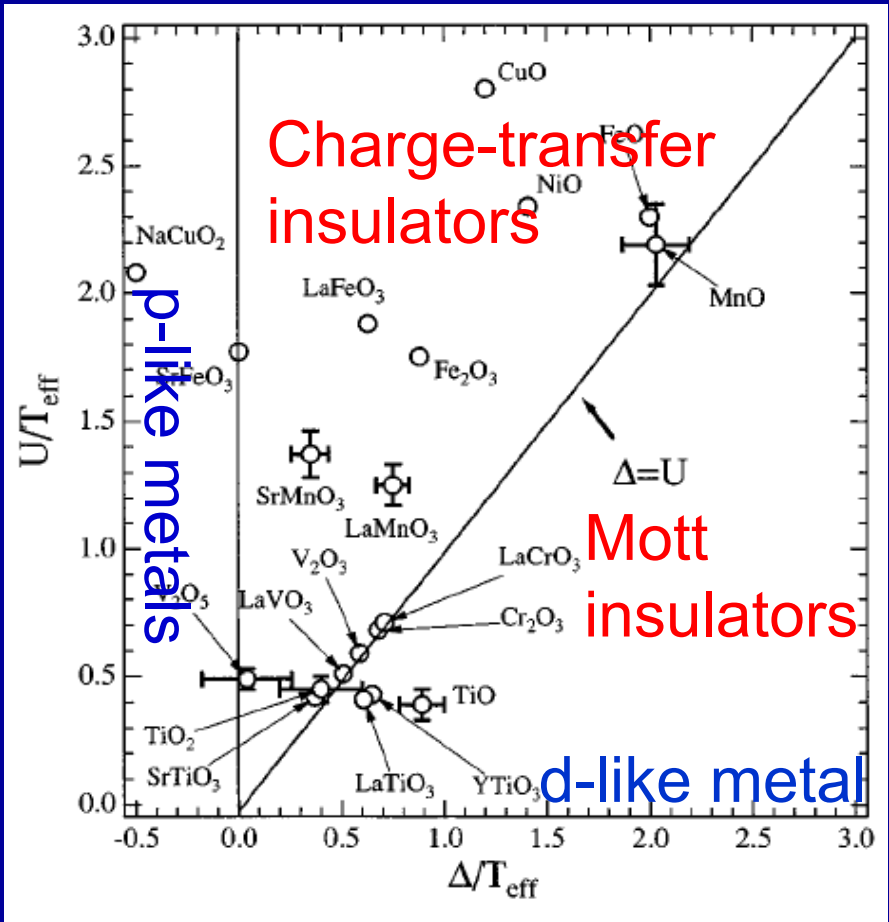
$$\Delta > t_{pd}$$



Doped holes go on oxygen sites (cf. cuprates)

Zaanen, Sawatzky, Allen (1985); Fujimori and Minami (1984)

The ZSA `phase diagram'

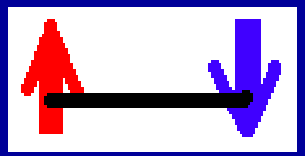


Bocquet et al.
PRB 1996

Reason why U is larger than Δ in late TMOs: attractive potential of nucleus is larger, Hence large electron removal energy $d^n \rightarrow d^{n-1}$

Still another important energy scale, at lower energy : the inter-site magnetic exchange

>>Virtual hopping is blocked (Pauli principle)



>>Virtual hopping is allowed

Inter-site antiferromagnetic exchange:

$$J = \frac{8t_{pd}^4}{(|\varepsilon_d - \varepsilon_p| + V_{pd})^2(|\varepsilon_d - \varepsilon_p| + U_{pp})} + \frac{4t_{pd}^4}{(|\varepsilon_d - \varepsilon_p| + V_{pd})^2 U_{dd}}$$

$$J_{AF} = \frac{4t^2}{U}$$

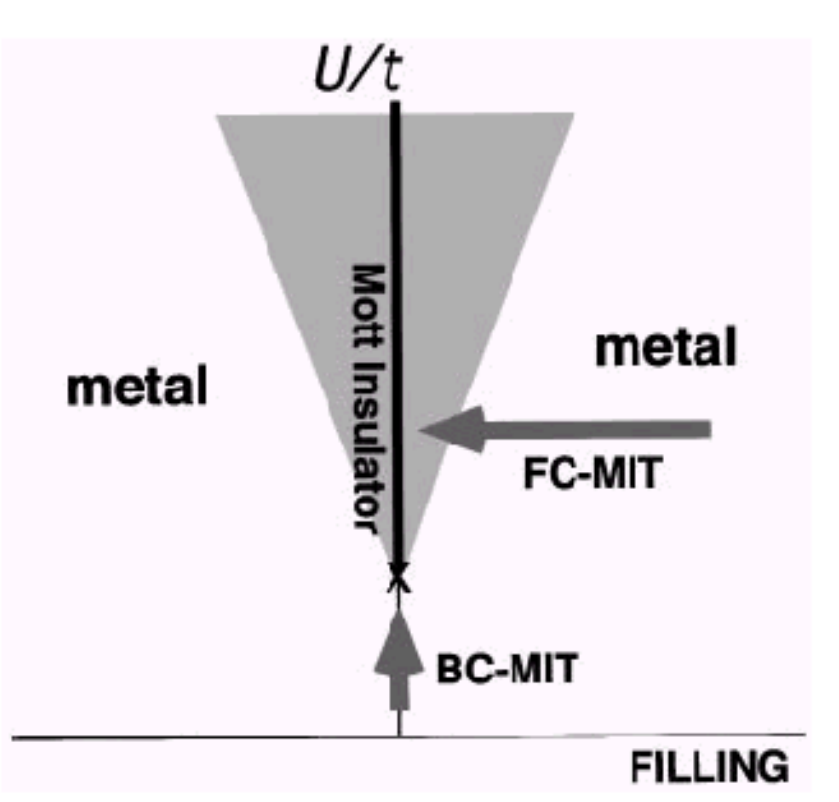
3. Theoretical descriptions of the Mott transition (fermions)

- Why is it a far more difficult problem than for bosons (lecture 3) ?
- For bosons, the superfluid (itinerant) state had a simple static order-parameter: <b>
- Not here !
- A (paramagnetic) metal does not break an obvious symmetry → `order parameter' distinguishing metal from insulator is related to dynamical (time, frequency dependent) response function
- e.g Drude weight, quasiparticle spectral weight…(cf.W.Kohn, Phys Rev 133, 1964)
- → Need a mean field theory based on dynamical correlation function !

Mott transition: the Brinkman-Rice description (simplest mean-field theory)

- Simplest case: one-band Hubbard model, U-controlled or doping-controlled
- **Two key ingredients:**
- 1) Fermi-surface unchanged (cf. Luttinger theorem)
- 2) Quasiparticle spectral weight Z is the order parameter: Z vanishes as the Mott insulating state is reached
- Only quasiparticle states are described w/in this theory: approach from the metallic state
- Magnetic instabilities to be discussed separately

Two routes to the transition:



``Large'' Fermi-surface
For hole-doped system with δ holes:

$$\frac{A_{FS}}{A_{BZ}} = \frac{1-\delta}{2}$$

However, on physical grounds, we expect the Drude weight to be ~ δ

Qualitative features of Brinkman-Rice theory:

- Quasiparticle weight vanishes as transition is reached: $\mathbf{Z \sim U_c - U}$ (BC) or $\mathbf{Z \sim \delta}$ (FC)
- Drude weight **~ Z**
- Effective mass $\mathbf{m^*/m = 1/Z}$: *quasiparticles become heavy as insulator is reached*
- Insulator is incompressible: jump in chemical potential $\mathbf{\Delta\mu \sim (U-U_c)^{1/2}}$
- Local susceptibility diverges at the transition $\chi_{loc} \sim 1/Z$ → insulator has local moments (ln2 entropy)
- Optical gap of insulator and uniform susceptibility not so well-defined in this theory (sometimes identified to $\Delta\mu$ and χ_{loc} , respectively, but see below.

The simplest self-energy which makes all this possible:

$$\Sigma(\omega) = \Sigma(0) + \omega\left(1 - \frac{1}{Z}\right)$$

1) Σ(0) is in charge of making Luttinger happy by insuring a Large Fermi surface: $\mu[n] - \Sigma[\omega = 0; n] = \mu_{U=0}[n]$

2) All the action is in Z ! no k-dependence→ $\frac{m^*}{m} = 1 - \frac{\partial\Sigma}{\partial\omega} = \frac{1}{Z}$

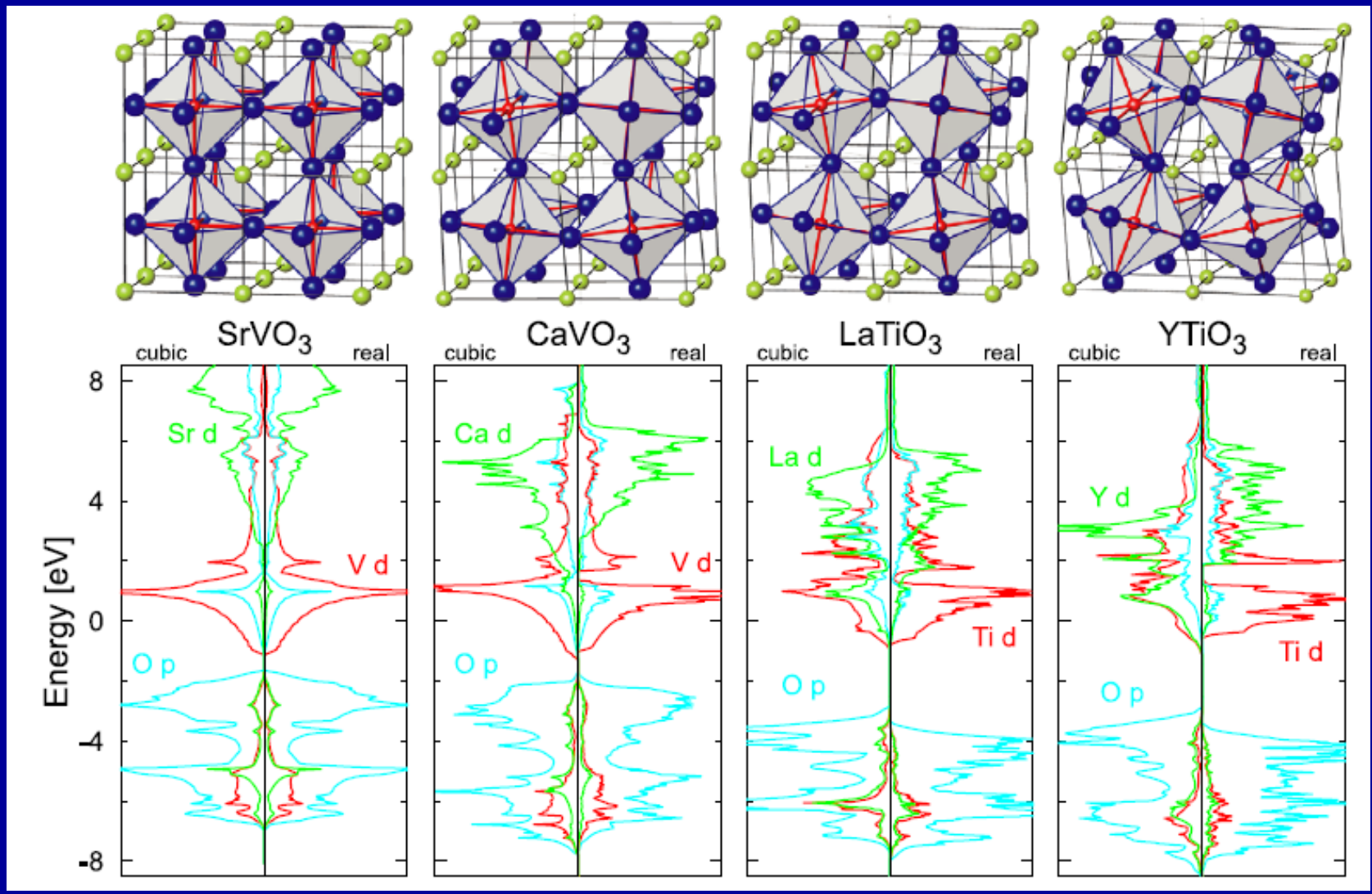
3) This self-energy is both extremely simple and a bit crazy:

- Crazy high-frequency behavior
- Only quasiparticles are described and they have infinitely long lifetime (Σ'' = 0)
-Total spectral weight is Z → incoherent part not included
-Don't even think of checking Kramers-Kronig…

Let me postpone the derivation(s) of Brinkman-Rice theory until the end of the lecture and explore consequences…

- The low-energy description is adequate for quite a few materials e.g $Sr_xLa_{1-x}TiO_3$
- Even for those, it has serious limitations that we shall consider below
- It fails altogether for some materials (e.g. cuprates)

Effects of the orthorombic distortion:
$SrVO_3$, $CaVO_3$,$LaTiO_3$,$YTiO_3$ (all d^1, ***ALL METALS in LDA !)***



Left panels: hypothetical cubic; Right panel: real structure

LaTiO3: AF Mott insulator

AF persists up to ~ 5% hole-doping

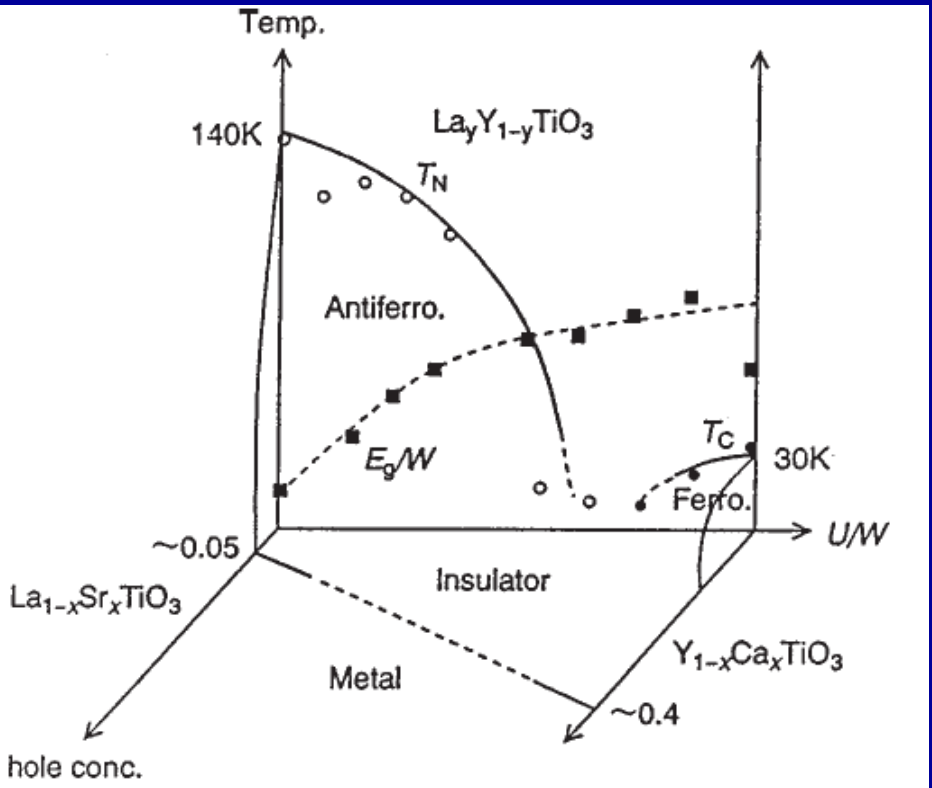
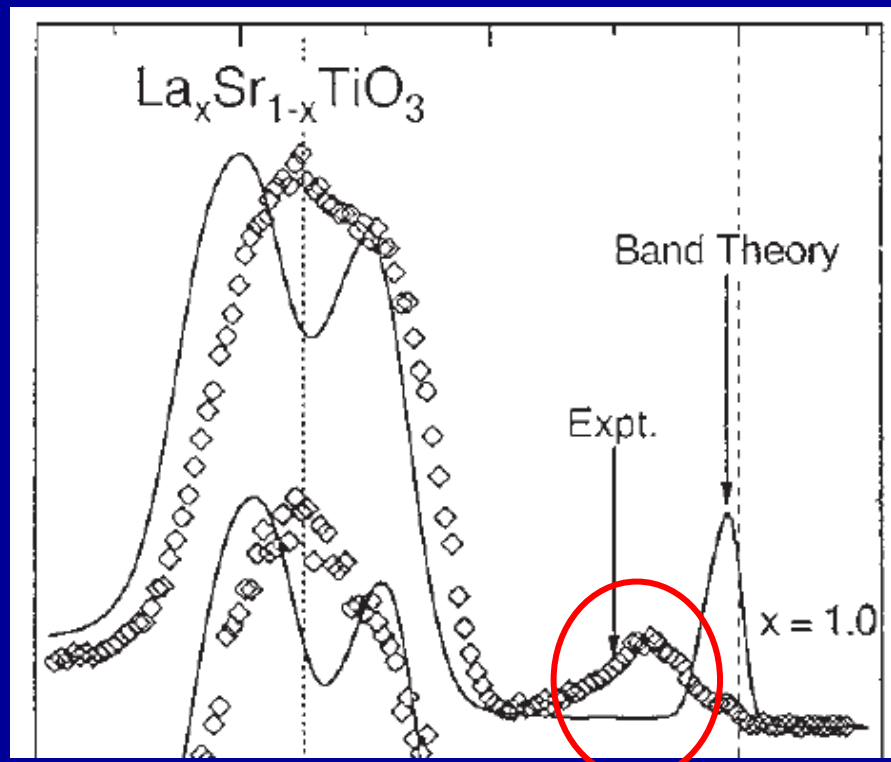


FIG. 101. Electronic and magnetic phase diagram for the $R_{1-x}Sr_xTiO_3$.

Photoemission spectrum: definitely a Mott insulator

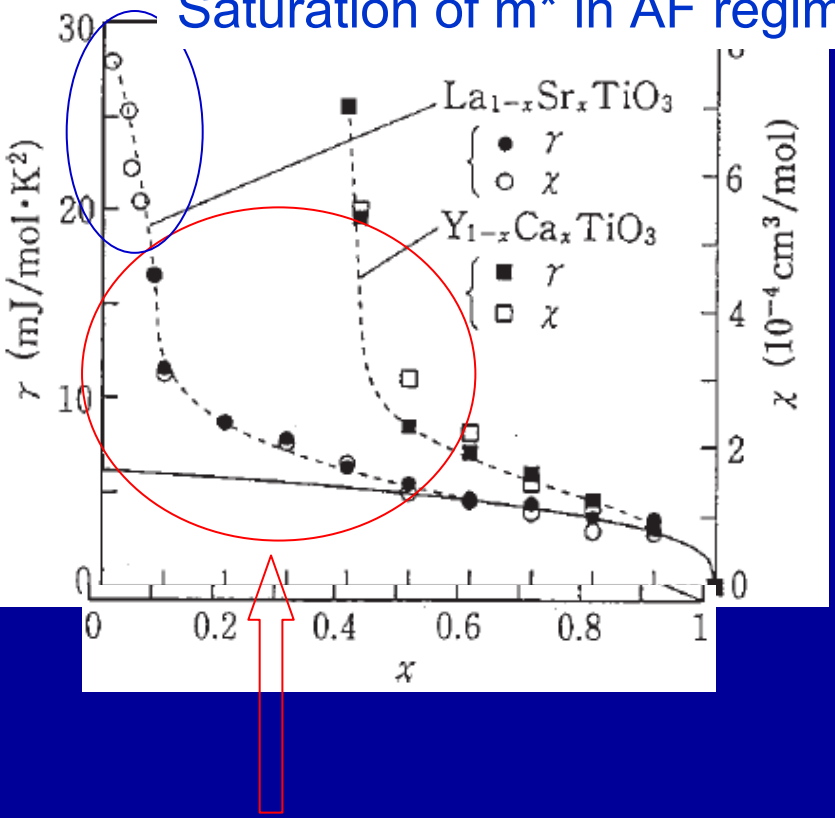


Oxygen states

Lower Hubbard band d1→d0

Approach to the Mott state in titanates

Saturation of m* in AF regime



Increase of effective mass

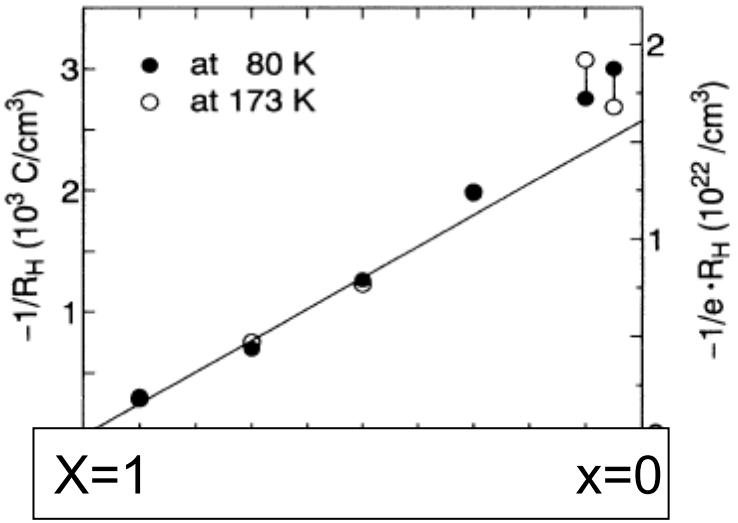
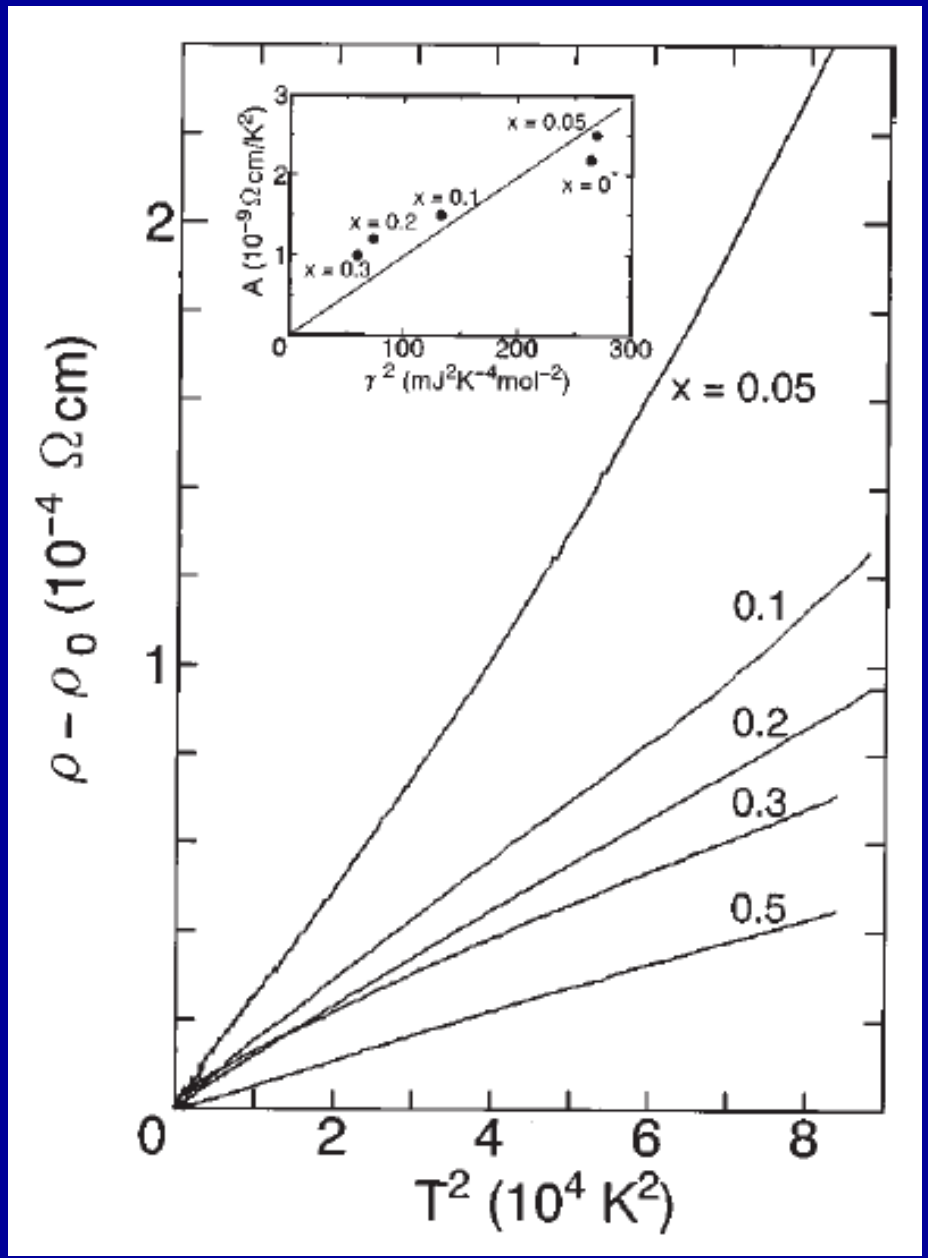
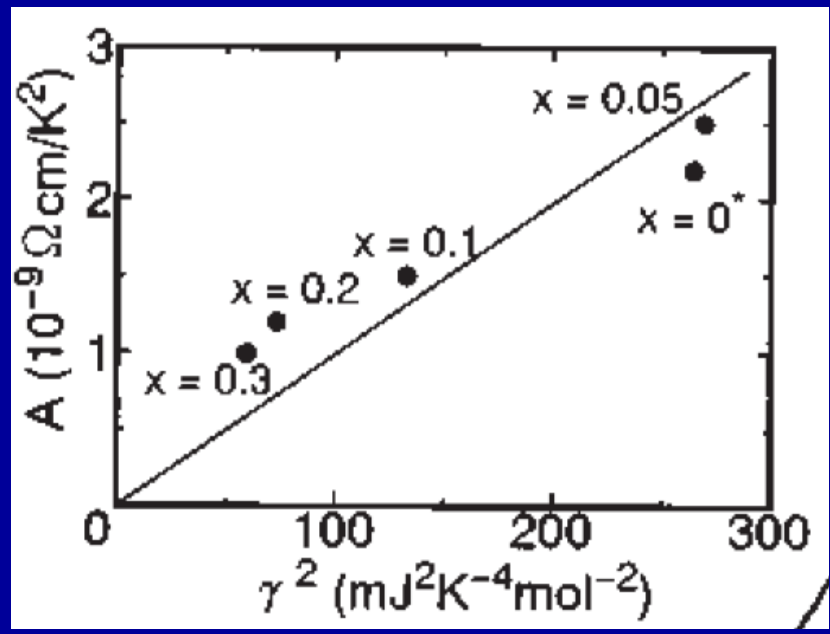


FIG. 2. The filling (x) dependence of the inverse of Hall coefficient (R_H^{-1}) in $Sr_{1-x}La_xTiO_3$. Open and closed circles represent the values measured at 80 K and 173 K, respectively. A solid line indicates the calculated one based on the assumption that each substitution of a Sr^{2+} site with La^{3+} supplies the compound with one electron-type carrier per Ti site.

R_H reported as ~ T-independent and consistent w/ large Fermi surface

Tokura et al.
PRL, 1993





Titanates/transport:

$$\rho_{dc} = AT^2 + \cdots$$

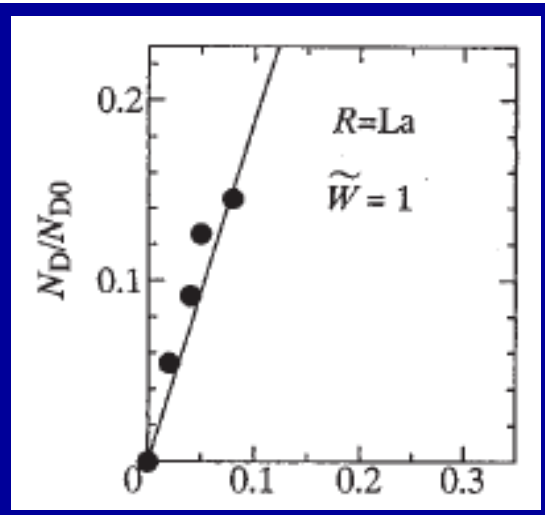
$$A/\gamma^2 \sim \text{const.}$$

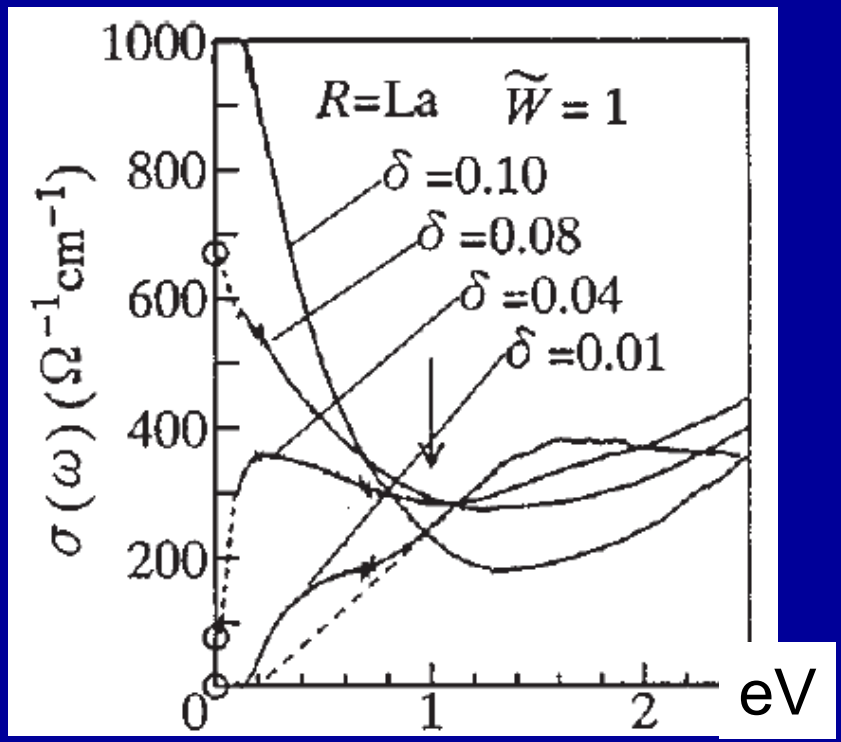
Fermi liquid behavior observed
Below ~ 100K @ 5% doping

Optical conductivity

Drude weight ~ doping

FIG. 108. N_D to N_{D0} as a function of δ (Katsufuji, Okimoto, and Tokura, 1995) for $La_{1-x}Sr_xTiO_3$.





Large transfers of spectral weight

FIG. 107. Optical conductivity spectra in $R_{1-x}Sr_xTiO_{3+y}$ or $R_{1-x}Ca_xTiO_{3+y}$ (R=La, Nd, Sm, and Y). From Katsufuji, Okimoto, and Tokura, 1995.

Limitations of Brinkman-Rice :

- already clear from these experimental results-

- → Must describe lifetime of quasiparticles
  → transport, optics
- Excited states: beyond quasiparticles (Hubbard satellites)
- Transfers of spectral weight
- Superexchange provides a cutoff to the divergence of effective mass (clear from entropic arguments)

Derivation(s) of the Brinkman-Rice approach: MANY

- Historically: [W.Brinkman and T.M.Rice, Phys Rev B 2 (1970) 4302] Gutzwiller approximation to the Gutzwiller wave-function $g^{\hat{D}}|\Psi\rangle_{\rm FS}\ ,\ \ \hat{D} \equiv \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$

  Cf: P.Nozières, lectures at College de France 1986-1987
  D.Vollhardt, Rev. Mod. Phys 56 (1984)

-**``Slave particle'' methods, originally U=infinity**
extended to finite U by Kotliar and Ruckenstein PRL 57 (1986) 1362
→ Comes in many flavors …

Mean-field theory based on `slave-rotor' representation

- Cf. S.Florens and A.G Phys Rev B 70 (2004) 035114
- Close in spirit to the MFT of the bosonic Hubbard model described in lecture 3
- Goes beyond Brinkman-Rice
- Extension (orbital-dependent effects): `slave-spins' cf. de' Medici et al. 72 (2005) 205124

… to be continued and detailed in lecture 7

Main idea: charge is conjugate to phase

Introduce a phase variable, tied (→ `slave') to the fermionic occupancy

$$\hat{L} = -i\frac{\partial}{\partial\theta}$$

$$[\hat{\theta}, \hat{L}] = i$$

Operators: $d_\sigma^\dagger \equiv f_\sigma^\dagger e^{i\theta}, \quad d_\sigma \equiv f_\sigma e^{-i\theta}.$

States:

$$|\uparrow\rangle_d = |\uparrow\rangle_f |0\rangle_\theta$$

$$|\downarrow\rangle_d = |\downarrow\rangle_f |0\rangle_\theta$$

$$|\uparrow\downarrow\rangle_d = |\uparrow\downarrow\rangle_f |+1\rangle_\theta$$

$$|0\rangle_d = |0\rangle_f |-1\rangle_\theta$$

Constraint: $\hat{L} = \sum_\sigma \left[f_\sigma^\dagger f_\sigma - \frac{1}{2} \right]$

Forbids states with
L-values different from 0, -1,+1

Atomic limit:

$$H_{\text{at}} = \sum_{\sigma} \epsilon_0 \, d^{\dagger}_{\sigma} d_{\sigma} + \frac{U}{2}\left[\sum_{\sigma} d^{\dagger}_{\sigma} d_{\sigma} - \frac{N}{2}\right]^2 . \quad \rightarrow \quad H_{\text{at}} = \sum_{\sigma} \epsilon_0 f^{\dagger}_{\sigma} f_{\sigma} + \frac{U}{2}\hat{L}^2 .$$

Constraint treated on average (optimizing over Lagrange multiplier)
Reproduces correctly the Coulomb staircase

Hubbard model: slave rotor representation

$$H = \sum_{i} H_{\text{at}}(i) - \sum_{ij,\sigma} t_{ij} \, d^{\dagger}_{i\sigma} d_{j\sigma}$$

$$\rightarrow \quad H = \sum_{i\sigma} \epsilon_0 f^{\dagger}_{i\sigma} f_{i\sigma} + \frac{U}{2}\sum_{i} \hat{L}_i^2 - \sum_{ij\sigma} t_{ij} \, f^{\dagger}_{i\sigma} f_{j\sigma} \, e^{i(\theta_i - \theta_j)} .$$

+ constraint

No approximation until this point (exact representation)

Now comes the approximation: decouple the r\phase variables and the auxiliary fermions from one another, treat constraint on average

1) Free fermion problem with effective hopping and Lagrange multiplier h:

$$H_f = -\sum_{ij\sigma} t_{ij}^{\text{eff}} f_{i\sigma}^{\dagger} f_{j\sigma} + (\epsilon_0 - h)\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma}$$

2) Charge: Josephson Junction/quantum XY/ bosonic Hubbard

$$H_\theta = -\sum_{ij} \mathcal{J}_{ij}^{\text{eff}} \cos(\theta_i - \theta_j) + \sum_i \left(\frac{U}{2} \hat{L}_i^{\,2} + h\hat{L}_i \right)$$

Couplings determined by:

$$t_{ij}^{\text{eff}} = t_{ij} \langle \cos(\theta_i - \theta_j) \rangle_\theta, \quad \mathcal{J}_{ij}^{\text{eff}} = \sum_\sigma t_{ij} \langle f_{i\sigma}^{\dagger} f_{j\sigma} \rangle_f$$

and h from

$$\langle \hat{L} \rangle_\theta = \sum_\sigma \left(\langle f_{i\sigma}^{\dagger} f_{i\sigma} \rangle_f - \frac{1}{2} \right)$$

Simplest mean-field approximation (almost a.k.a Brinkman-Rice)

Solve bosonic part at mean-field level (cf lecture 3) :

$$H_{\theta}^{\mathrm{MF}} = \sum_i \left[\frac{U}{2} \hat{L}_i^2 + h\hat{L}_i + K \cos\ \theta_i \right]$$

Similar to $\lambda(b + b^{\dagger})$ term in BHM

$$K = 2N\langle \cos\ \theta \rangle \int \mathrm{d}\epsilon\ D(\epsilon)\epsilon\ n_F(Z\epsilon + \epsilon_0 - h),$$

$$\langle \hat{L} \rangle = N \int d\epsilon\ D(\epsilon)\left[n_F(Z\epsilon + \epsilon_0 - h) - \tfrac{1}{2} \right],$$

$$n \equiv \frac{1}{N}\sum_{\sigma} \langle f_{\sigma}^{\dagger} f_{\sigma} \rangle = \int \mathrm{d}\epsilon\ D(\epsilon) n_F(Z\epsilon + \epsilon_0 - h).$$

T=0:

Luttinger theorem !

$$h - \epsilon_0 = Z\ \mu_0(n)$$

$$\langle \hat{L} \rangle = N\left(n - \tfrac{1}{2}\right),$$

$$K = 2N\overline{\epsilon}(n)\langle \cos\ \theta \rangle_{\theta},$$

band kinetic energy:

$$\overline{\epsilon}(n) \equiv \int_{-\infty}^{\mu_0(n)} d\epsilon D(\epsilon)\epsilon$$

Quasiparticle spectral weight: ~ condensed fraction

$$Z \equiv \langle \cos\ \theta \rangle_{\theta}^2.$$

Analysis close to the Mott critical boundary (cf lecture 3)

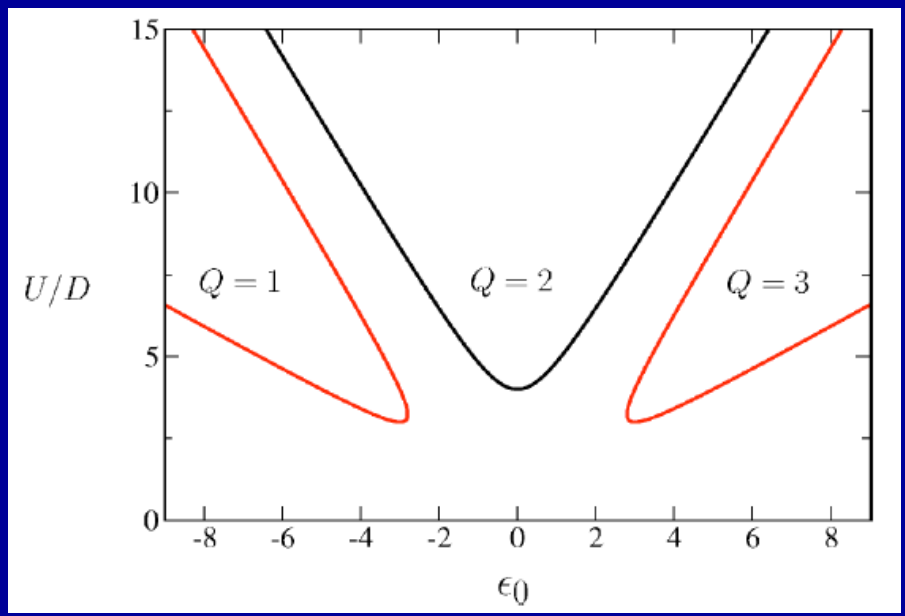
$$\langle \cos\,\theta\rangle_\theta = 2K \sum_{\ell \neq \ell_n} \frac{|\langle \Psi_\ell | \cos\,\theta | \Psi_{\ell_n}\rangle|^2}{E_{\ell_n} - E_\ell}$$

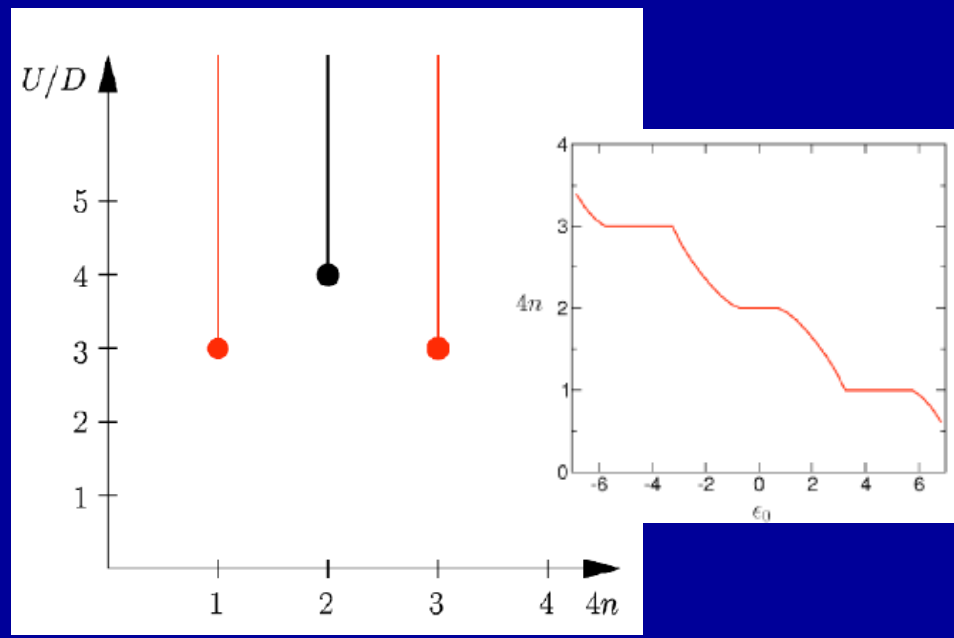
$$= -\frac{2UK}{U^2 - 4(U\ell_n + h)^2} + \mathcal{O}(K^2).$$

Eq. for the critical boundary in (U,chemical potential) plane:

$$U_c(\epsilon_0)^2 - 4[U_c(\epsilon_0)\ell_n + \epsilon_0]^2 + 4N\overline{\epsilon}(n)U_c(\epsilon_0) = 0.$$

$$\ell_n = \mathrm{Int}[1/2 - \epsilon_0/U]$$





Mott insulator boundary for 2 orbitals (with spin)

Beyond Brinkman-Rice: keep the phases and fermions decoupled, but do a better job on XY-model for the phases

Main findings: - Effective mass does not diverge
- Uc is reduced as one lowers dimensionality

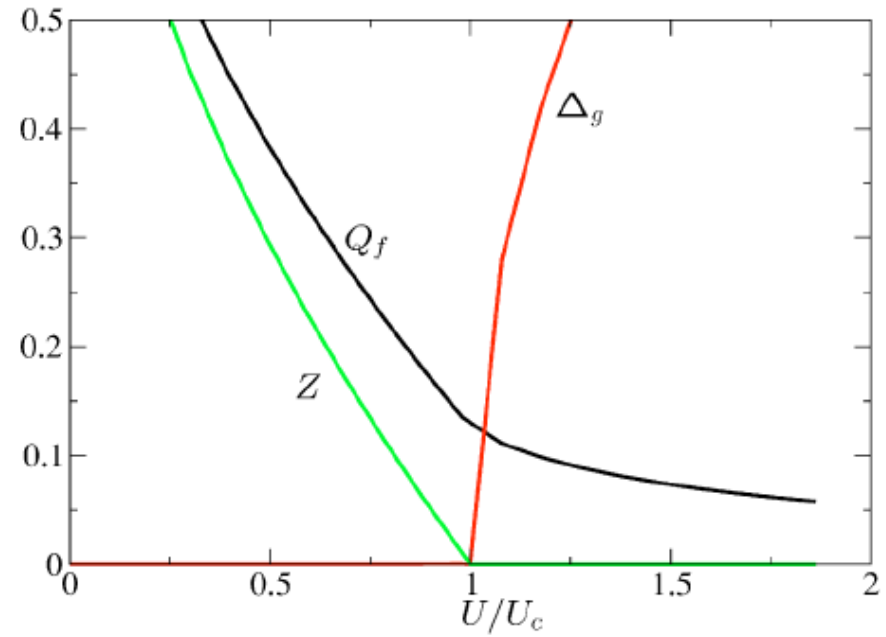


FIG. 9. (Color online) Plot of the quasiparticle weight Z, the effective mass renormalization $Q_f = m/m^*$, and the Mott gap Δ_g as a function of U/U_c across the Mott transition in the three-dimensional case.

$$\frac{m^*}{m} \sim \frac{1}{t/U + \delta} \sim \frac{1}{J/t + \delta}.$$

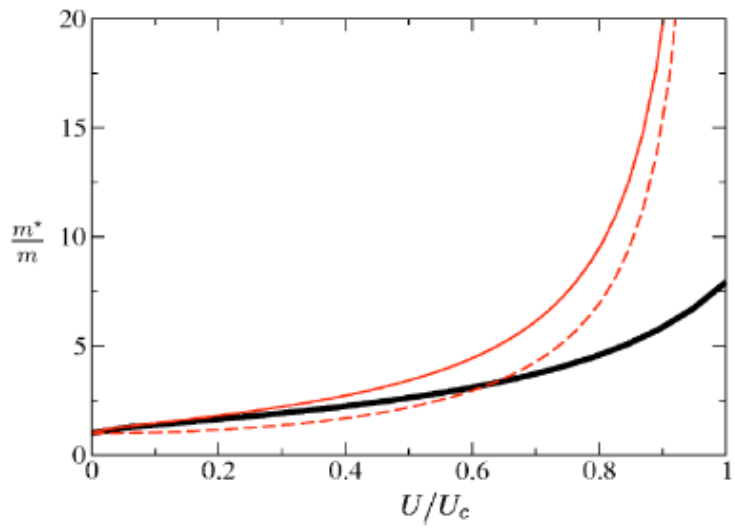


FIG. 10. (Color online) Effective mass $m^*/m = 1/Q$ provided by the mean-field Eqs. (54)–(56) for $d=3$ (bold line) and $d=\infty$ (thin line). For comparison, a DMFT-IPT calculation (dashed line) is also presented.

Critical coupling in this approach:

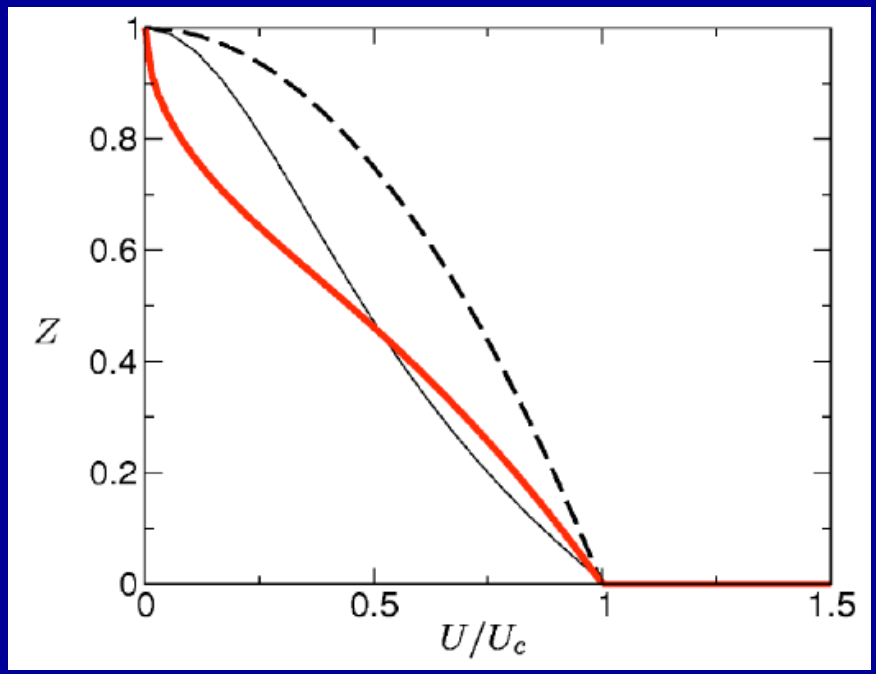
$$U_c(n) = 4N\left|\overline{\epsilon}(n)\right|.$$

$$= 4DNn(1-n)$$ flat band

Increases with orbital degeneracy !

Largest for half-filled band (note: no J_H here !)

Gutzwiller: $$U_c^{GA} = 4(N+2)\left|\overline{\epsilon}(n)\right|$$



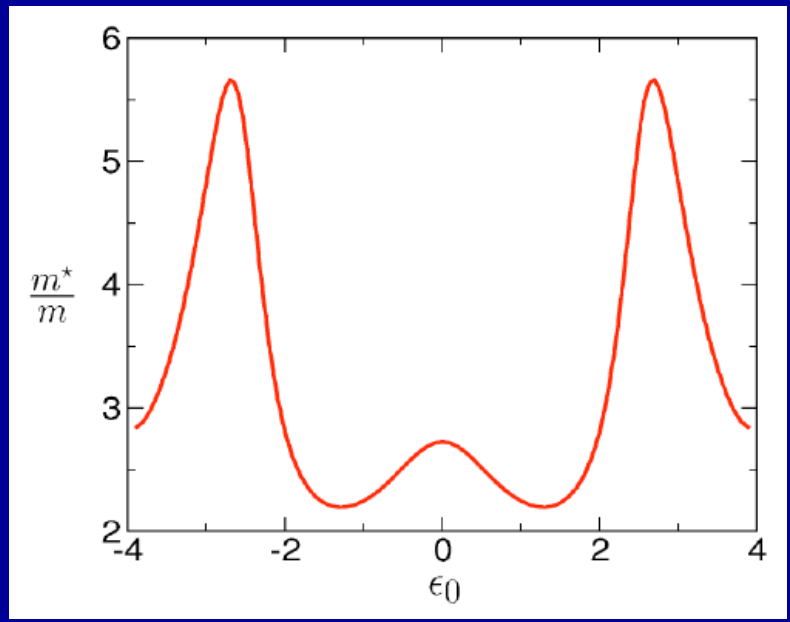


FIG. 6. (Color online) Quasiparticle weight Z as a function of U/U_c at $T=0$; DMFT calculation (thin line), rotor mean-field theory (thick line), and Gutzwiller approximation (broken line).