Lecture Notes

Introduction to Strongly Correlated Electron Systems

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Introduction to strongly correlated electron systems

I. Introduction

Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems

(a) Transition metal compounds: 3d-electrons

- Hubbard model, Mott insulator, metal-insulator transition
- Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials

(b) Heavy fermion systems: 4f (5f) – electrons

- The Kondo effect, heavy fermion systems, non-Fermi liquid behavior,
- Quantum phase transitions, unconventional superconductivity, selected materials

(c) Nanoscale structures:

- Quantum confinement, unusual properties for potential applications

III. Pressure effect on the ground state properties:

- Recent experimental results on heavy fermions and transition metal compounds

IV. Summary and open discussion

Some comments on electrons in Solids:

Theoretical description using **two different approachs/ approximations** without taking into account electon-electron correlations:

- The nearly-free electron model (itinerant electrons in very weak periodic potential)

- The tight-binding model (electrons localized on an atomic site but weakly coupled to all other atoms----use Linear Combination of Atomic Orbitals, LCAO)

Both models qualitatively yield the same results and are well known to most of you in details from the lectures on Solid State Physics by Prof. M. Grüninger and Pd Dr. T. Lorenz .

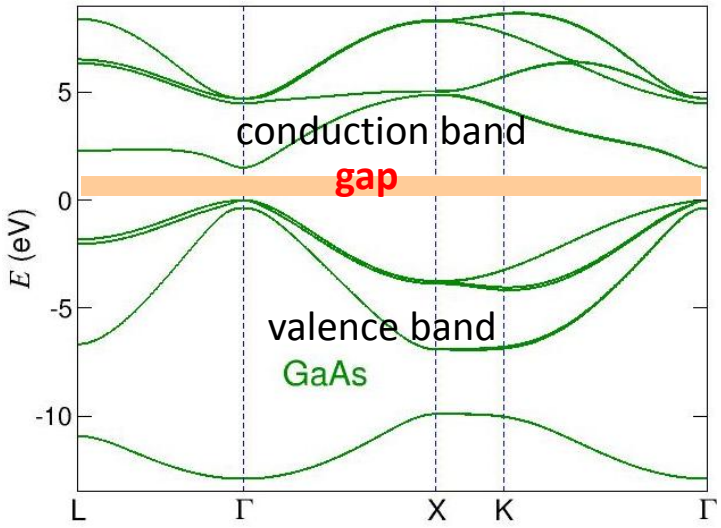
To remind you, I just will go briefly through the two models and stress on some relevant points!

Bloch theorem for non-interacting electrons in a periodic potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r)+U(\vec{r})\psi(r)=E\psi(r)$$

$$U(\vec{r})=U(\vec{r}+R)$$

R is a Bravais lattice vector!



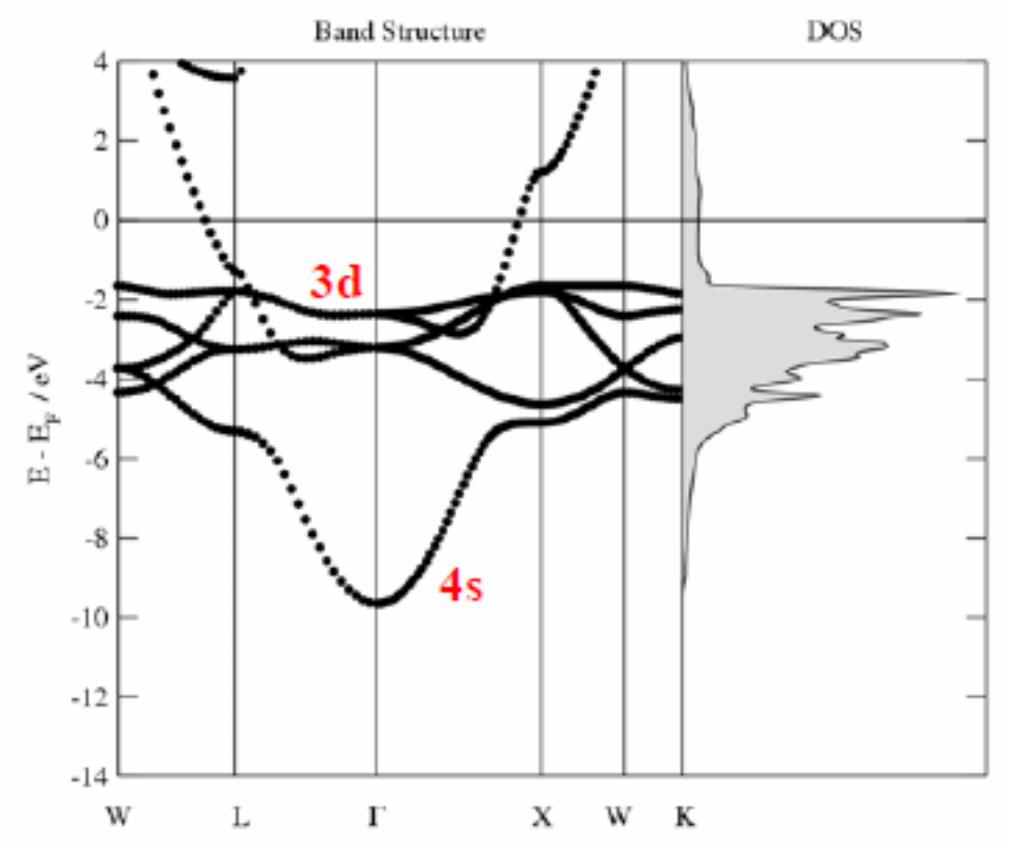
… where $U(\vec{r})$ is a function with the periodicity of the lattice ….

Bloch's theorem tells us that eigenstates have the form

$$\psi(\vec{r})=e^{i\vec{k}\cdot\vec{r}}U(\vec{r})$$

Energy eigenvalues $E_n(\vec{k})$ **Band structure!**

Copper: Valence States



Some comments to the effective mass of electrons

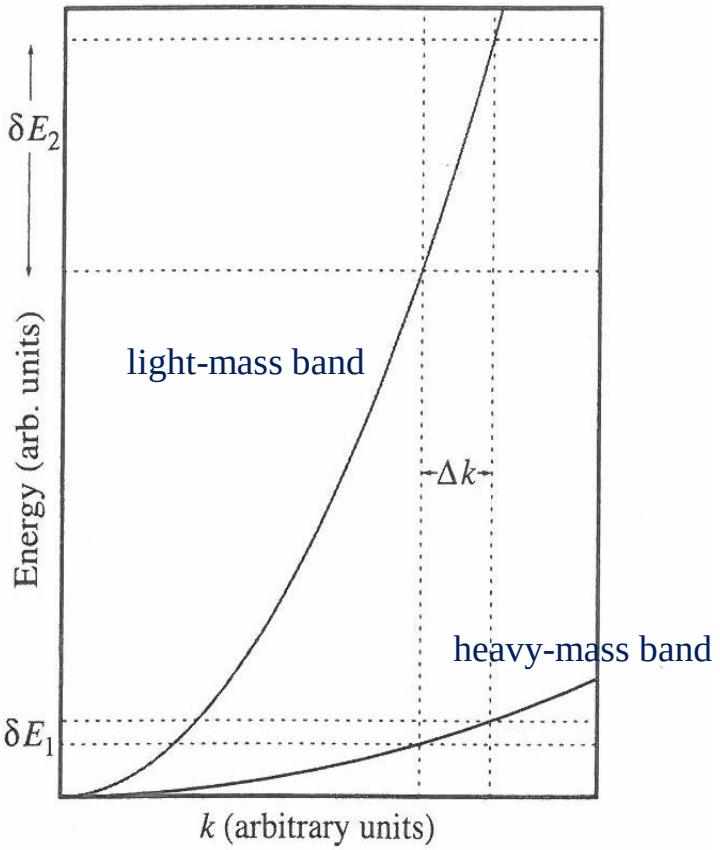
The effective mass of Bloch electrons

The motion of electrons is modified by the crystal potential through which it moves

$$m^* = \left(\frac{1}{\hbar^2} \frac{d^2E}{dk^2} \right)^{-1}$$

1/ curvature of the band is proportional to m^*

Heavy effective mass implies high density of states D(E) and high γ and vice versa ⟹



Electrons in a crystal are accelerated in response to an external force just as though they were free electrons with effective mass m^*

The effective mass of electrons and density of states

$$D(E_F) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{\,1/2}$$

$$C_{el} = \frac{\pi^2}{3} k_B{}^2 D(E_F) T = \gamma T \quad \text{, hence} \quad \boxed{\gamma \propto m}$$

For free electrons γ calculated per mole:

$$\gamma_{th} = \frac{\pi^2}{3} k_B^2 D(E_F) = \frac{\pi^2 k_B^2 m N_0 z}{\hbar^2 (3\pi^2 N/V)^{2/3}}$$

N_0 Avogadro s number and z number of conduction electrons per formula unit

comparison of γ_{th} with experimental γ values

m^*

Metal	γ	γ_{th}	Metal	γ	Metal	γ
Li	1.63	0.749	Fe	5.0	$CeAl_3$	1600
Na	1.38	1.094	Co	4.7	$CeCu_6$	1500
K	2.08	1.668	Ni	7.1	$CeCu_2Si_2$	1100
Cu	0.69	0.505	La	10	$CeNi_2Sn_2$	600
Ag	0.64	0.645	Ce	21	UBe_{13}	1100
Au	0.69	0.642	Er	13	U_2Zn_{17}	500
Al	1.35	0.912	Pt	6.8	YbBiPt	8000
Ga	0.60	1.025	Mn	14	$PrInAg_2$	6500

$$\frac{m^*}{m} \equiv \frac{\gamma}{\gamma_{th}}$$

$\gamma / \gamma_{th} \approx 1 - 1.5$

mainly s-electrons, broad bands

$\gamma / \gamma_{th} \approx 10 - 30$

partially filled d-bands

$\gamma / \gamma_{th} \approx 100 - 1000$

heavy fermion compounds 4 f (5f)-orbitals strong electron-electron correlations SCES

Why m^* is so large in some 4f and 5f electron system?

No answer from the band theory (one electron approximation), neglecting electron-electron interactions. This will be discussed in Chapter II (b).

The tight-binding model

- Electrons (inner shells) are strongly localized and mainly see the atomic potential
  ⇒ use Linear Combination of Atomic Orbitals (LCAO)

- The atomic wave function of level i ϕ_A^i at site $\vec{R}$ ($\vec{R}$ site of Bravais lattice) is defined by

$$\mathcal{H}_A(\vec{r}-\vec{R})\cdot\phi_A^i(\vec{r}-\vec{R}) = E_A^i\,\phi_A^i(\vec{r}-\vec{R}) \qquad (1.1)$$

$$\Rightarrow \quad \mathcal{H}_A(\vec{r}-\vec{R}) = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V_A(\vec{r}-\vec{R})$$

$V_A(\vec{r}-\vec{R})$: Pot. of atom located at $\vec{R}$

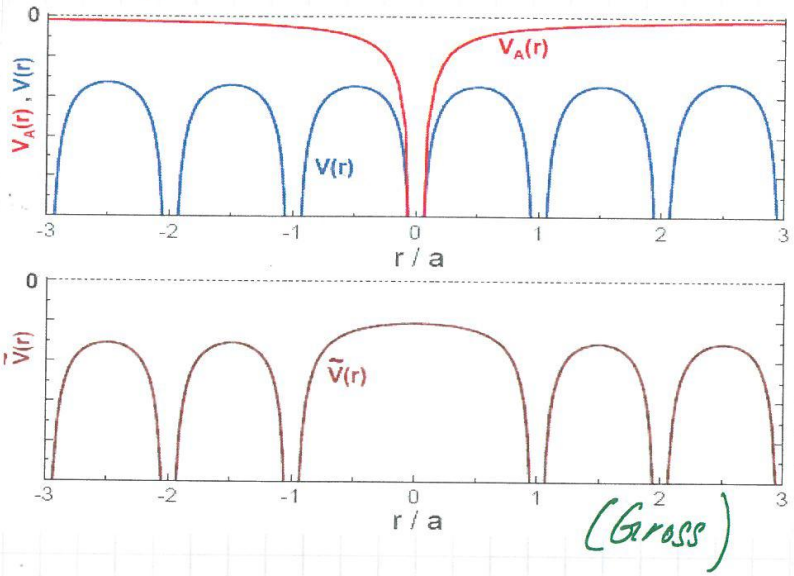
- Lattice periodic potential

$$V(\vec{r}) = \sum_{\vec{R}'} V_A(\vec{r}-\vec{R}')$$

$$= V_A(\vec{r}-\vec{R}) + \sum_{\vec{R}'\neq\vec{R}} V_A(\vec{r}-\vec{R}')$$

$$= \tilde{V}(\vec{r}-\vec{R})$$

⇒ lattice: single atom at $\vec{R}$ + rest!



(Gross)

tight binding energy bands

$$\Rightarrow \boxed{E(\vec{k}) = E_A^i - A - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c)} \quad \text{(B)}$$

t_x, t_y, t_z hopping integrals

E_A^i — atomic level

A — binding energy (electrons at site $\vec{R}$ feel the attraction potential $\tilde{V}(\vec{r}-\vec{R})$ of all other ions)

Bandwidth $W = 12t$ in 3D cubic lattice

(cos from -1 to $+1$)

– dispersion results from finite overlap (hopping)

in general:

$$\Rightarrow t \sim \left\langle \phi_A^i(r-\vec{R}') \middle| \tilde{V} \middle| \phi_A^i(r-\vec{R}) \right\rangle$$

$\vec{R}'$ nearest neighbor

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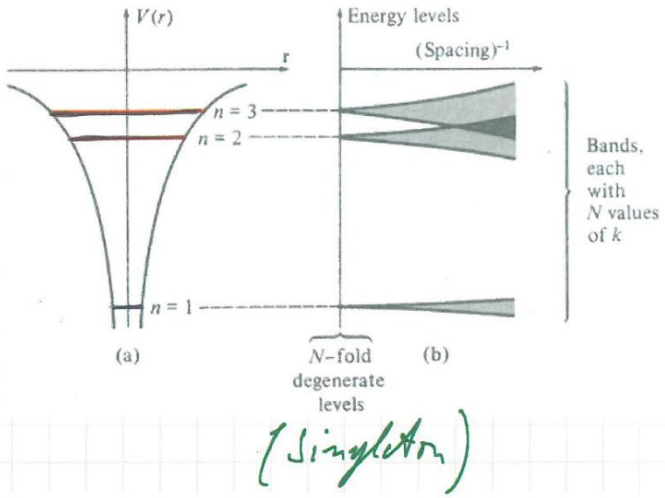
schematic representation of formation of TB bands



(Singleton)

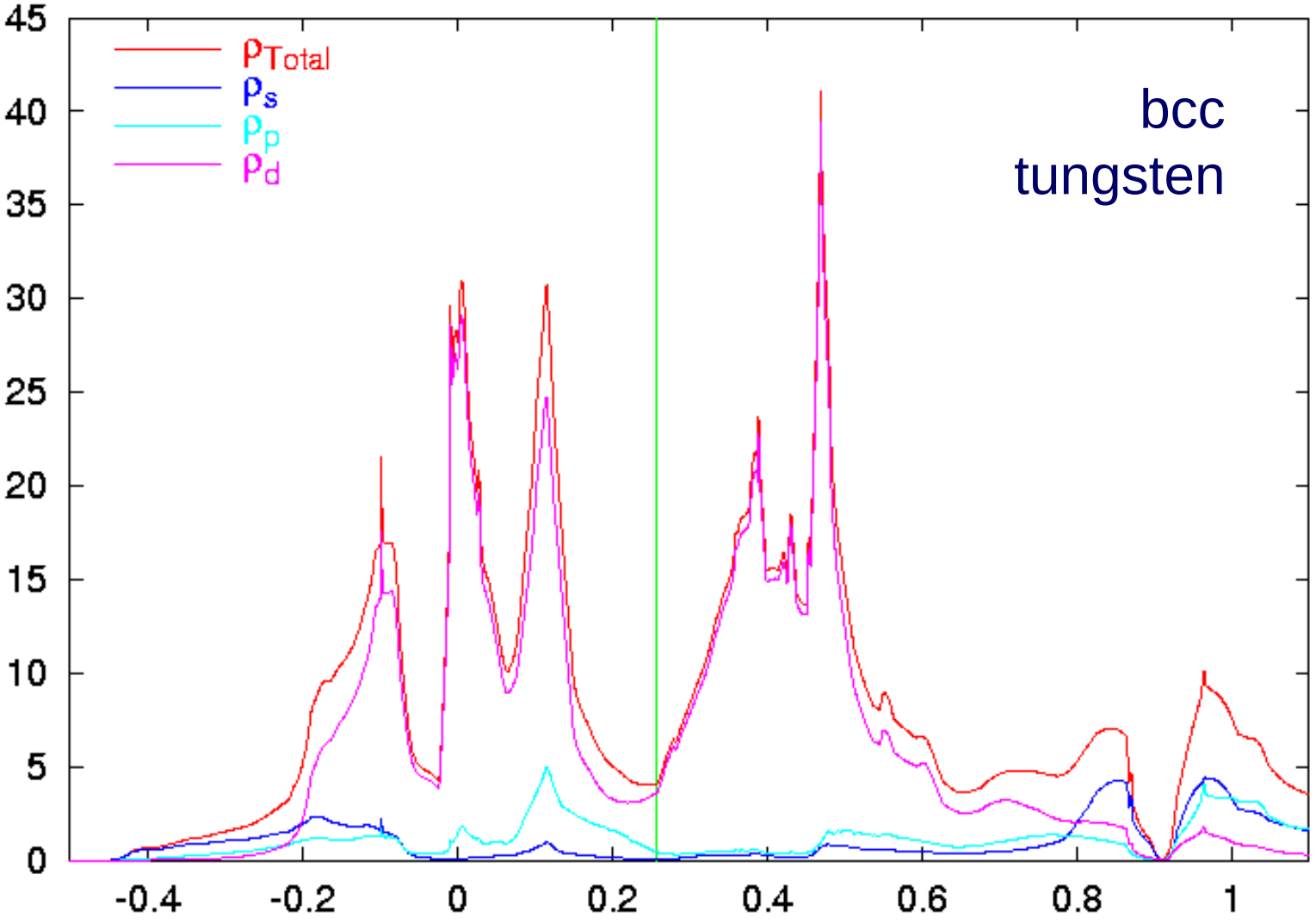
notes: Bandwidth depends on the spatial extent of wf, interatomic distance, and on the number of nearest neighbors (nn)

$W \simeq 2zt$ — z = no. of nn; $z = 2$ for 1D

eqs. (B) for 1D

$$\Rightarrow \epsilon(k) = E_A - 2t \cos k_x x \quad \text{(B')}$$

Electron Density of States: LCAO

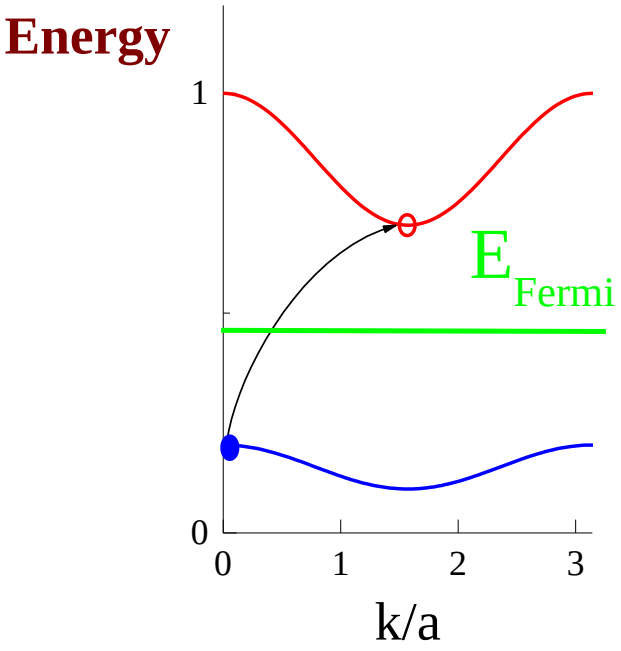


We now discuss the breakdown of the band theory in describing the ground states of strongly correlated transition oxide systems

Insulator vs. Metal

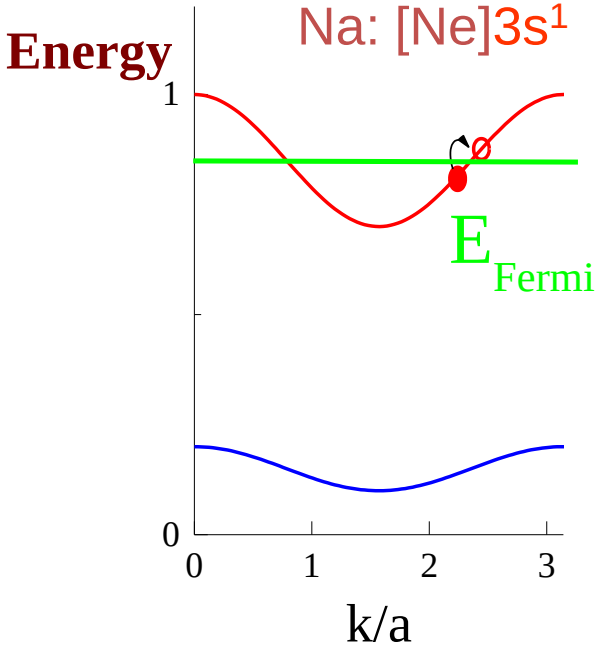
Only full and empty shells

⇒ **Insulator** (NaCl, Si)



Partially filled shells

⇒ **Metal** (Na, Cu)



Examples of correlated Insulators with partially filled shells:

La_2CuO_4: Cu^{2+}: [Ar]$3d^9$ **La^{3+}: [Xe] O^{2-}: [Ne]**

V_2O_3: V^{3+}: [Ar]$3d^2$ **O^{2-}: [Ne]**

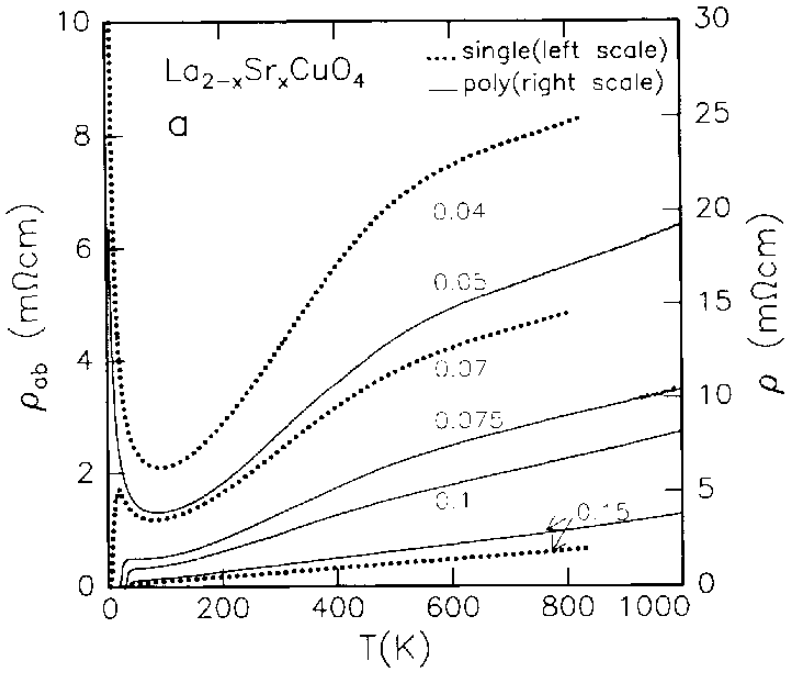
Nd_2O_3: Nd^{3+}: [Xe]$4f^3$ **O^{2-}: [Ne]**

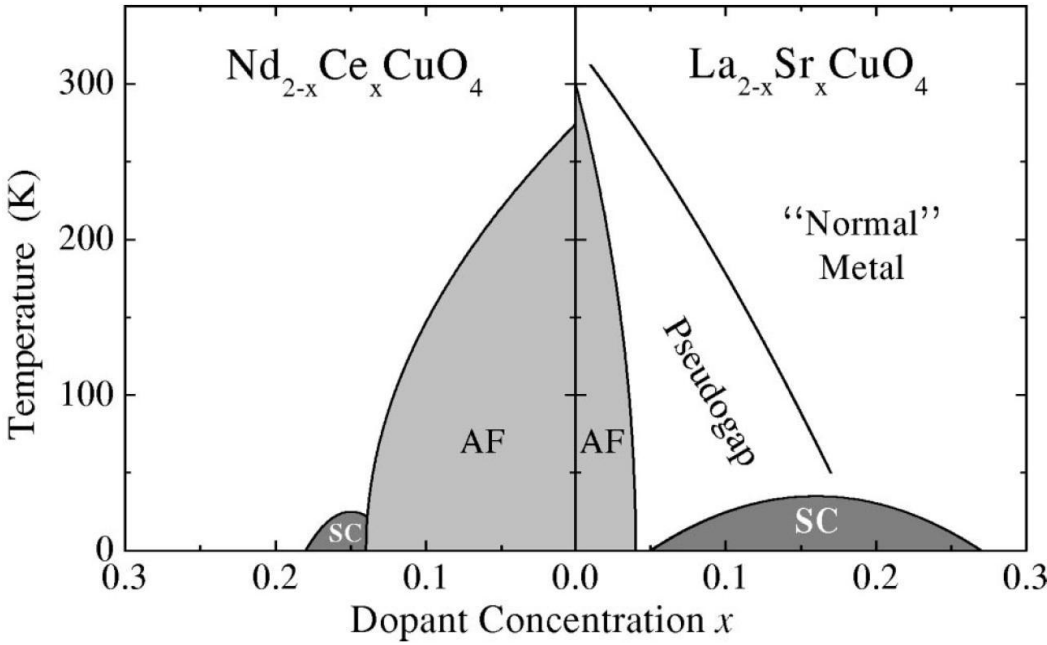
breakdown of band theory ?

High-T_c-Superconductivity in $La_{2-x}Sr_xCuO_4$

La_2CuO_4: antiferromagnetic Mott-Insulator.

Doping with Sr^{2+} for La^{3+} , high-T_c-Superconductor $La_{2-x}Sr_xCuO_4$





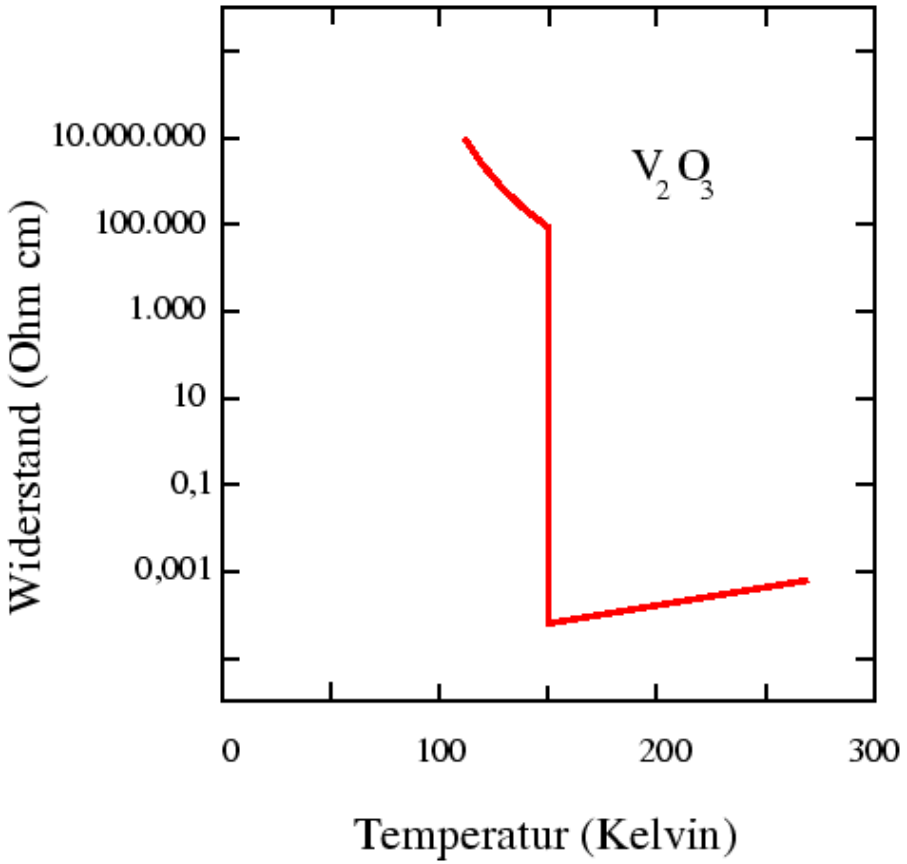
A. Damascelli, Z. Hussain, Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003)

Metal-Insulator transition in V_2O_3

Mott-Hubbard-System: Metal-insulator transition as a function of temperature

(factor 10^8 !) as a function of temperature T ~ **150 K** without structural phase transition!

Energy gap ~ 0.6 eV ~ 7000 K



Mott-Hubbard-Insulators LaMO$_3$

***M* = Cu, Ni: $3d^8$, $3d^7$, Metal**

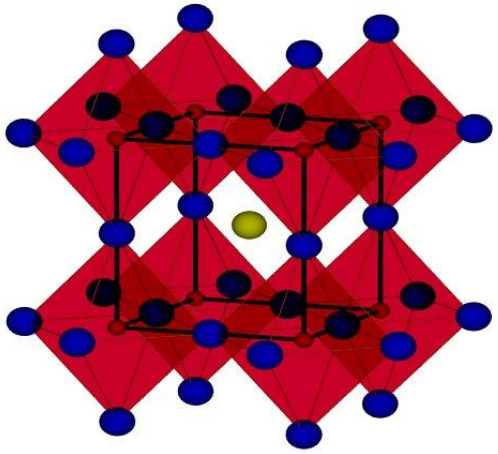
***M* = Sc $3d^0$, Band insulator**

***M* = Ti, V, Cr, Mn, Fe, Co,**

3d partially filled ($3d^1$ – $3d^6$),

Mott-Hubbard insulators

Energy gap ~ 0.2 - 3 eV



Perowskit-structure

(distorted)

La***M***O$_3$

A closer look to "half filling"
Gedankenexperiment

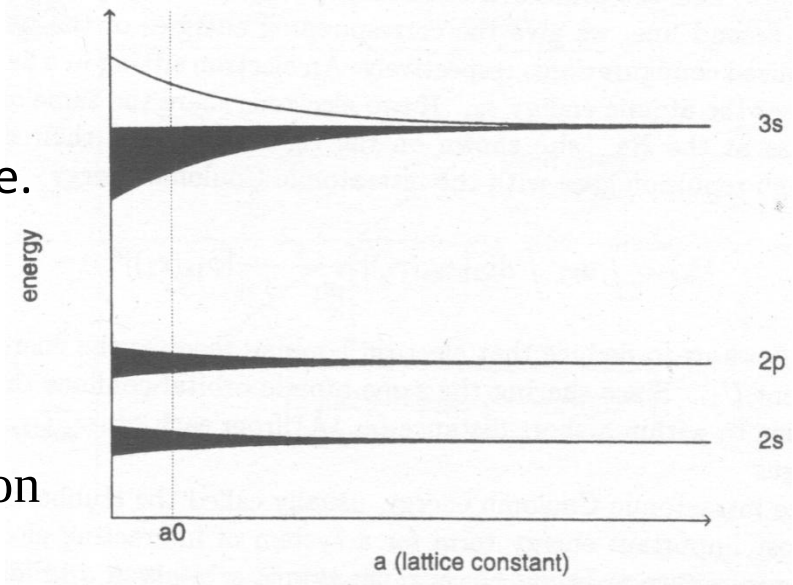
Consider a half-filled band, e.g. Na metal

Na: 1 e in 3s shell with 2 states per atom (spin ↑ ↓)

⟹ **Metallic for any interatomic distance?**
(expected from the band theory)

Obviously not, for a very large distances we have individual atoms ⟹ insulating, not metallic state. The 3s band becomes very narrow, but its always half-filled!!

Question: what suppresses the transfer of an electron from one atom to another atom?



Explanation

small distances: electrons are smeared out (large bandwidth, W) , charge fluctuations do not alter the average occupation (k-space picture)

large distances: electronic transition yields Na+&Na- ⟶ 2 e in same orbital ⟶ large on-site Coulomb repulsion U (local picture)

⟶ **Competion between kinetic energy and on-site energy U determines the nature of the ground state**

⟶ **Metallic state: if W >> U**
Insulating state : If U >> W

In SCES: Coulomb repulsion between 2 electrons at the same atom must be taken into account beyond one electron approximation.

Dealing with electron-electron correlations

Hubbard model

simplest (!) microscopic Model for correlated electrons (1963) introduced at the same time by Gutzwiller, Hubbard und Kanamori

(a) kinetic energy: electron hopping between next nearest neighbors

(b) Interaction only between electrons at the same site:

on-site e-e-repulsion = Hubbard U

Hamiltonian in 2nd quantization:

$$H_{Hubbard} = \sum_{\langle i,j\rangle,\sigma} t\ c^{+}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

$\langle i, j\rangle$ next nearest neighbors sites $c^{+}_{i\sigma}, c_{i\sigma}$ creation, annihilation operators of an occupied electronic state at site i with spin σ

$c^{+}_{i\sigma} c_{i\sigma}$ Electron hops from j to i without spin flip

$n_{i\uparrow} n_{i\downarrow}$ counts doubly occupied sites ($n_{i\uparrow} = c^{+}_{i\uparrow} c_{i\uparrow}$, number operator)

Hubbard model

$$H_{Hubbard} = \sum_{\langle i,j\rangle,\sigma} t\ c^{+}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

kinetic energy

Hopping of e^- between next neighbors

electron interaction

only between e^- on the same site *on-site* e-e repulsion = Hubbard **U (~ eV)**

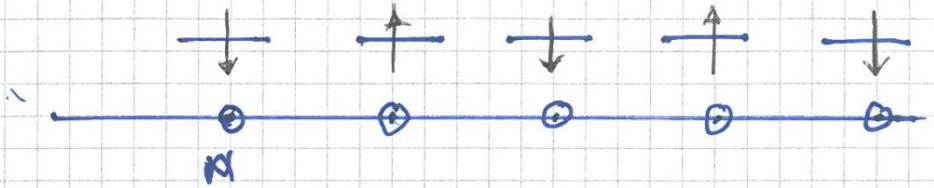
Hopping matrix element *t* large =strong intersite overlap, large W

Hubbard ***U*** **punishes** double occpancy

➡ ***competition:***

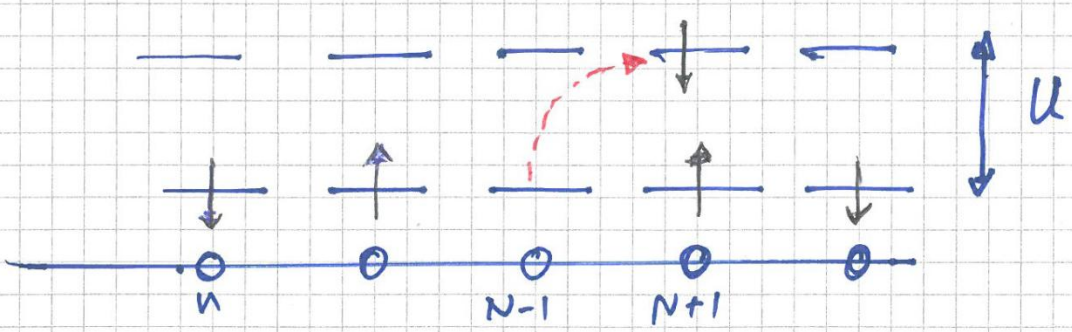
U wants to localize
t rewards delocalization

see Board!



one electron per site
N sites

Total Energy = $N E_N$



$$\Delta E = U = (N-2)\,E_N + E_{N+1} + E_{N-1} - N E_N$$

$$\Rightarrow \boxed{U = E_{N+1} + E_{N-1} - 2E_N}$$ — Hubbard U

Hubbard model describes two opposite limits:

(a) Weak interacting electrons $\Rightarrow U \ll t$; and

(b) Strongly interacting, or Strongly Correlated electrons $\Rightarrow U \gg t$

(a) $U \ll t$ $\Rightarrow$ tight-binding approximation $(U \sim 0)$

$$H_{\text{Hubbard}} \sim t \sum_{\langle i,j \rangle \sigma} c^{+}_{i\sigma} c_{j\sigma}$$

$$\Rightarrow E(k) \simeq 2t \cos(k_x a) - 2t_y \cos(k_y b) + \cdots$$

(see eqs. B)

or in 1D $E(k) = -2t \cos k_x a$ (eqs. B')

(b) $U \gg t$

Collection of isolated atoms; each has 4 electronic many body states:

State $\lvert N, S', S_z \rangle$	total no. of electrons N	total spin S'
$\lvert 0,0,0\rangle = \lvert 0\rangle$	0	0
$\lvert 1, \frac{1}{2}, \uparrow\rangle = c^{+}_{i\uparrow}\lvert 0\rangle$	1	1/2
$\lvert 1, \frac{1}{2}, \downarrow\rangle = c^{+}_{i\downarrow}\lvert 0\rangle$	1	1/2
$\lvert 2,0,0\rangle = c^{+}_{i\uparrow}c^{+}_{i\downarrow}\lvert 0\rangle$	2	0

Hubbard model

$$H_{Hubbard} = \sum_{\langle i,j\rangle,\sigma} t\ c^{+}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

kinetic energy

Hopping of e^- between next neighbors

electron interaction

only between e^- on the same site *on-site* e-e repulsion = Hubbard **U (~ eV)**

Hopping matrix element *t* large =strong intersite overlap, large W

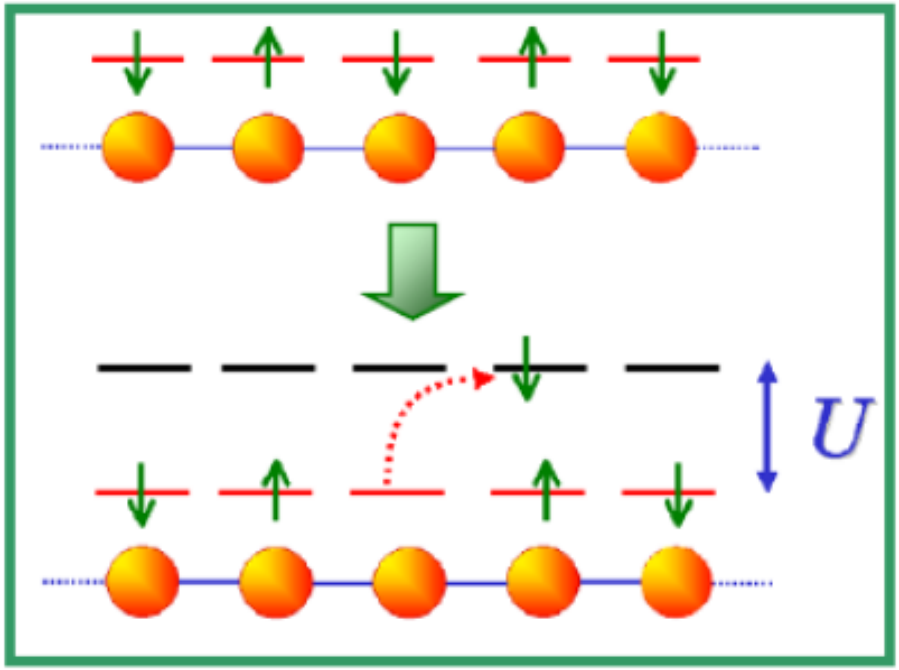
Hubbard ***U*** **punishes** double occpancy

➡ ***competition:***

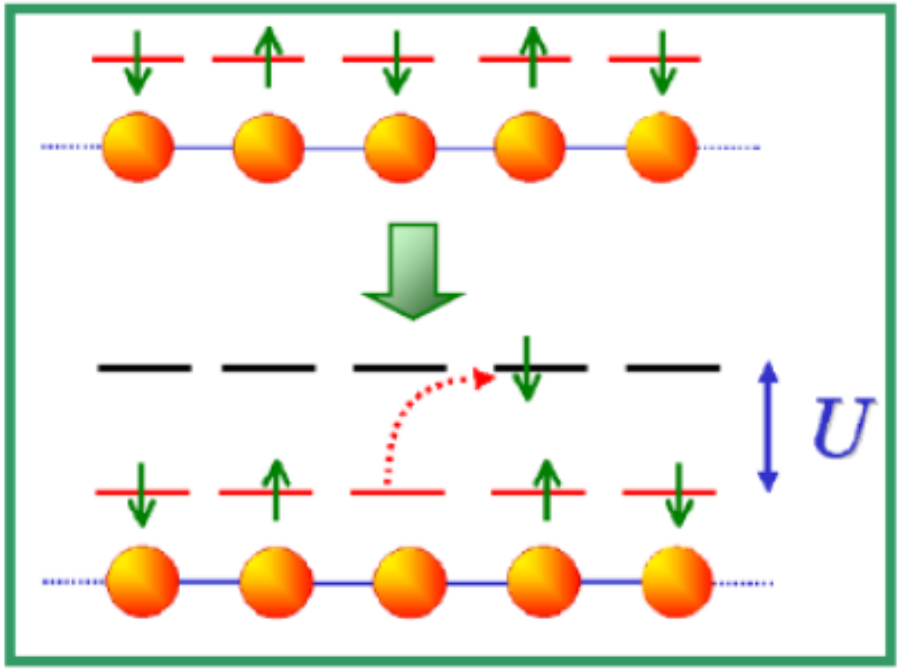
U wants to localize
t rewards delocalization

calculation of Hubbard U

Simple case: one electron per site (half band filling)



Coulomb repulsion between electrons causes localization

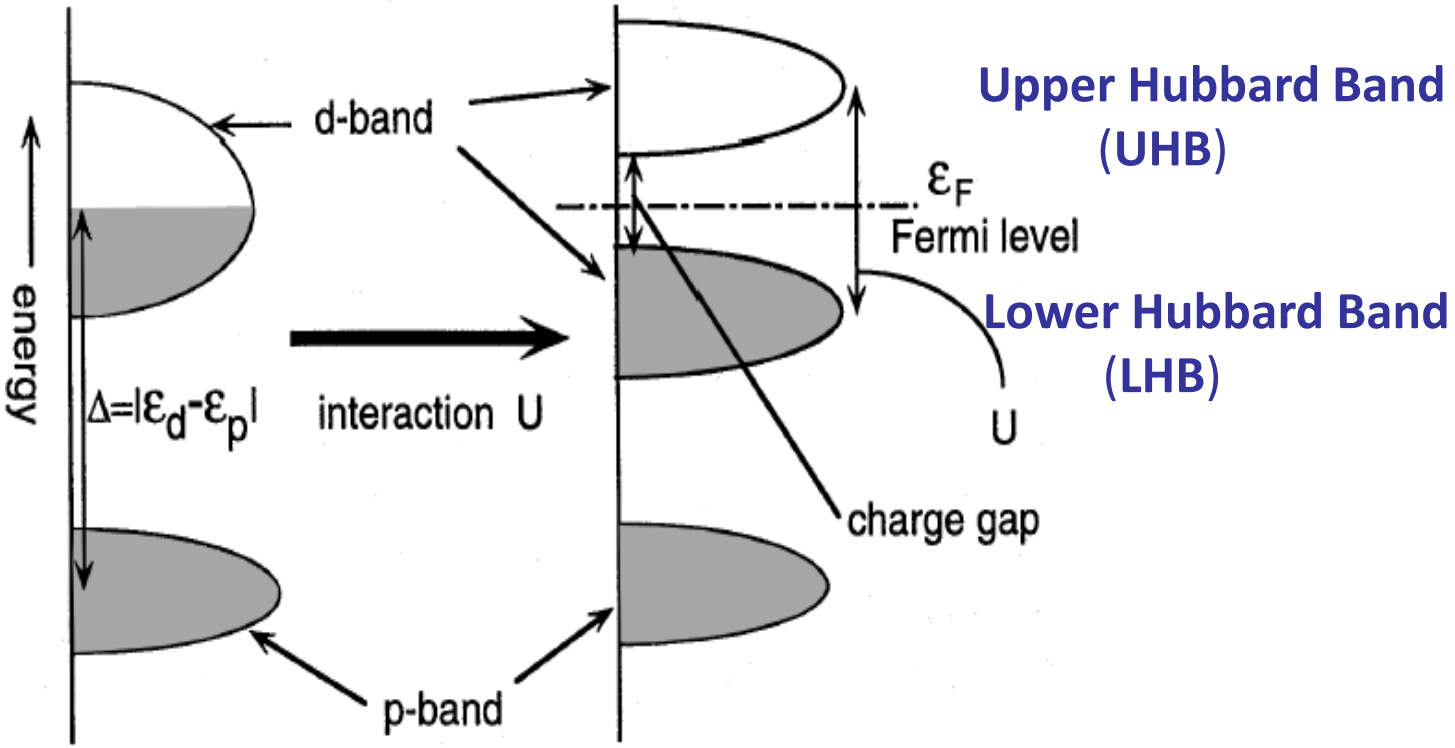


$$U = E_{N+1} + E_{N-1} - 2E_N$$

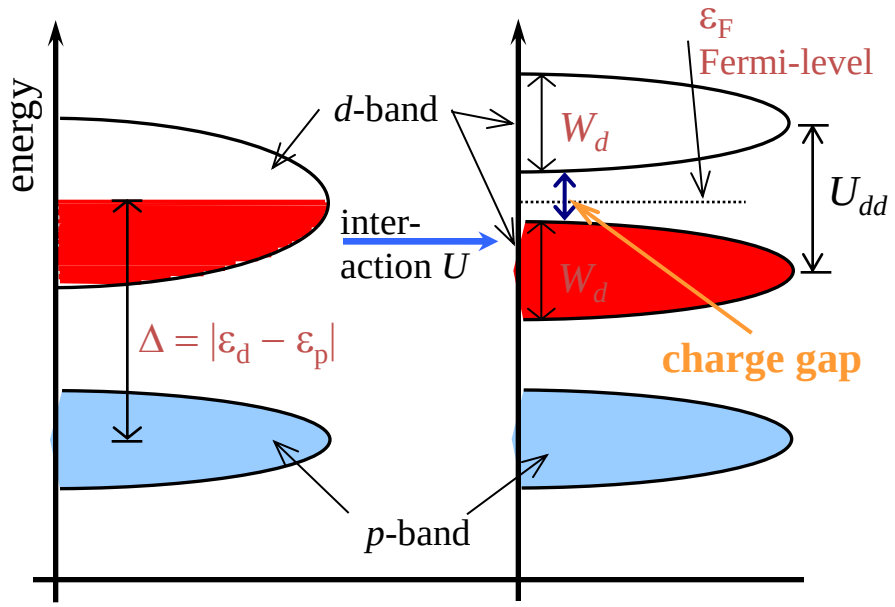
when the intersite interaction and (thus W) is small Coulomb repulsion drives a half-filled band insulating, with Mott-Hubbard gap (U)

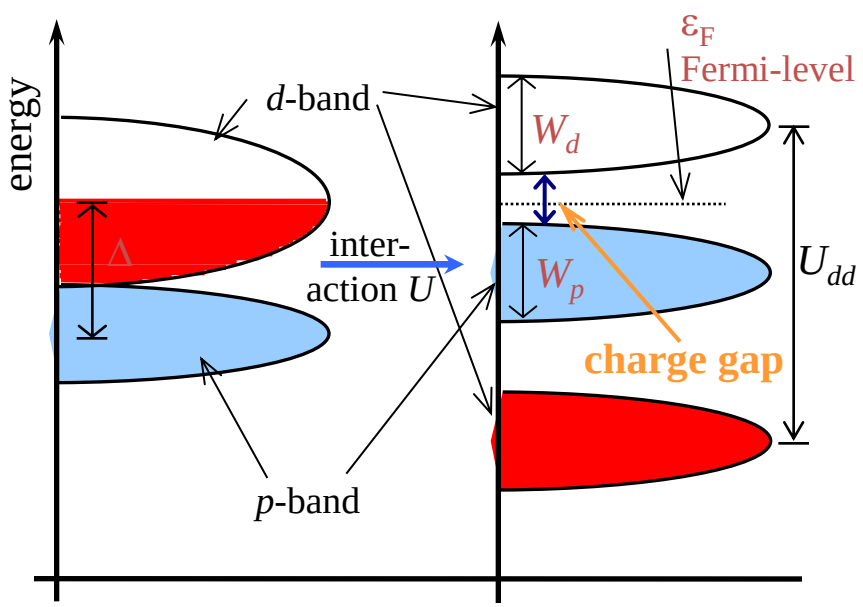
Energy band splitting

Double occupation costs energy (U) ⟹ splitting of the energy band into Upper and Lower Hubbard bands



Types of Mott-Insulators





(a) Mott-Hubbard insulator:

(b) Charge-transfer insulator:

La*M*O3
for M = Co, Fe

***U*, on-site Coulomb interaction**
Δ, charge transfer energy
***W*, bandwidth; (hopping t)**

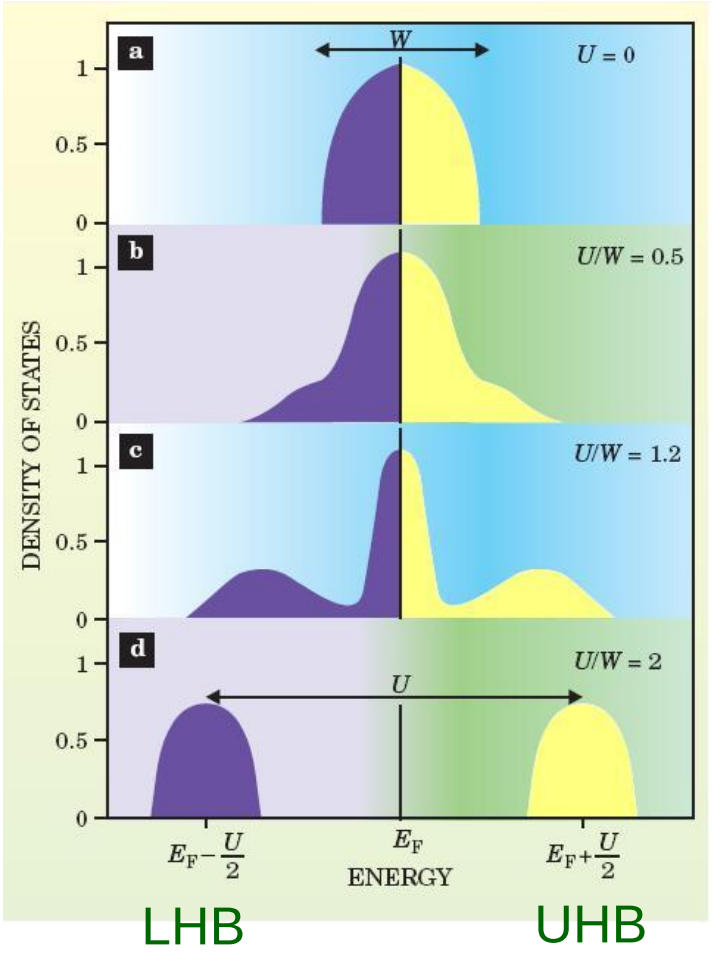
La*M*O3
for M = Ti, V

Metal-insulator transition: Bandwidth

with half filling:

U > W ⟹ LHB full, UHB empty ⟹ Mott-Hubbard-Isolator

U < W ⟹ kinetic energy dominates ⟹ Metal-insulator transition

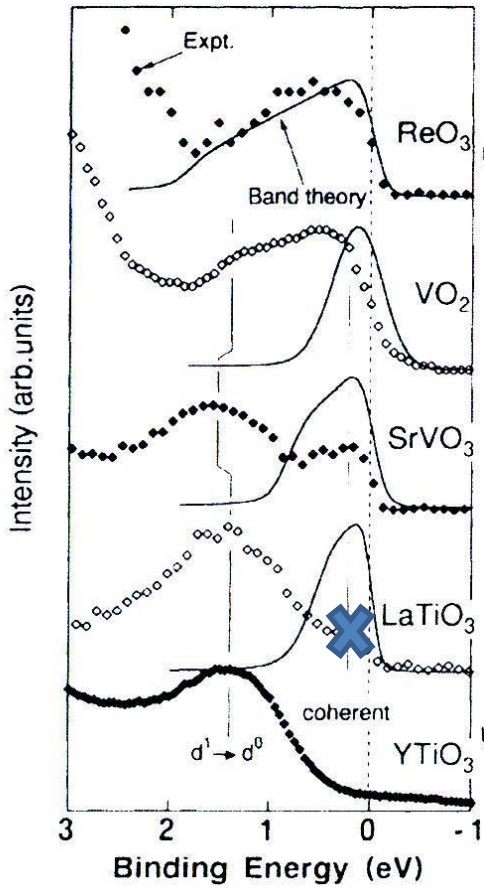


Kotliar, Vollhard, Physics Today, March 2004, 39

U < W

U > W

PES



Ti^{3+}, V^{4+}: **$3d^1$**

Re^{6+}: **$5d^1$**

variation of W (t) with structure (bonding angles) and from 3d to 5d

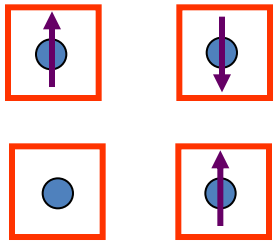
(stoichiometric LaTiO3 is Mott-insulator)

Fujimori et al., Phys. Rev. Lett. 69, 1796 (1992)

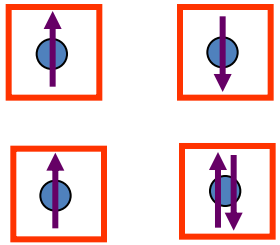
Metal-Insulator-transition : Doping

2) Metal-Insulator transition as a function of doping

e.g.: replace La^{3+} (or Y^{3+}) by Sr^{2+} (or Ca^{2+}) → hole-doping



Hoping of a doped hole costs no energy



Hoping of a doped electron costs no energy

Doping Mott-insulator
Induced a metallic, superconducting state

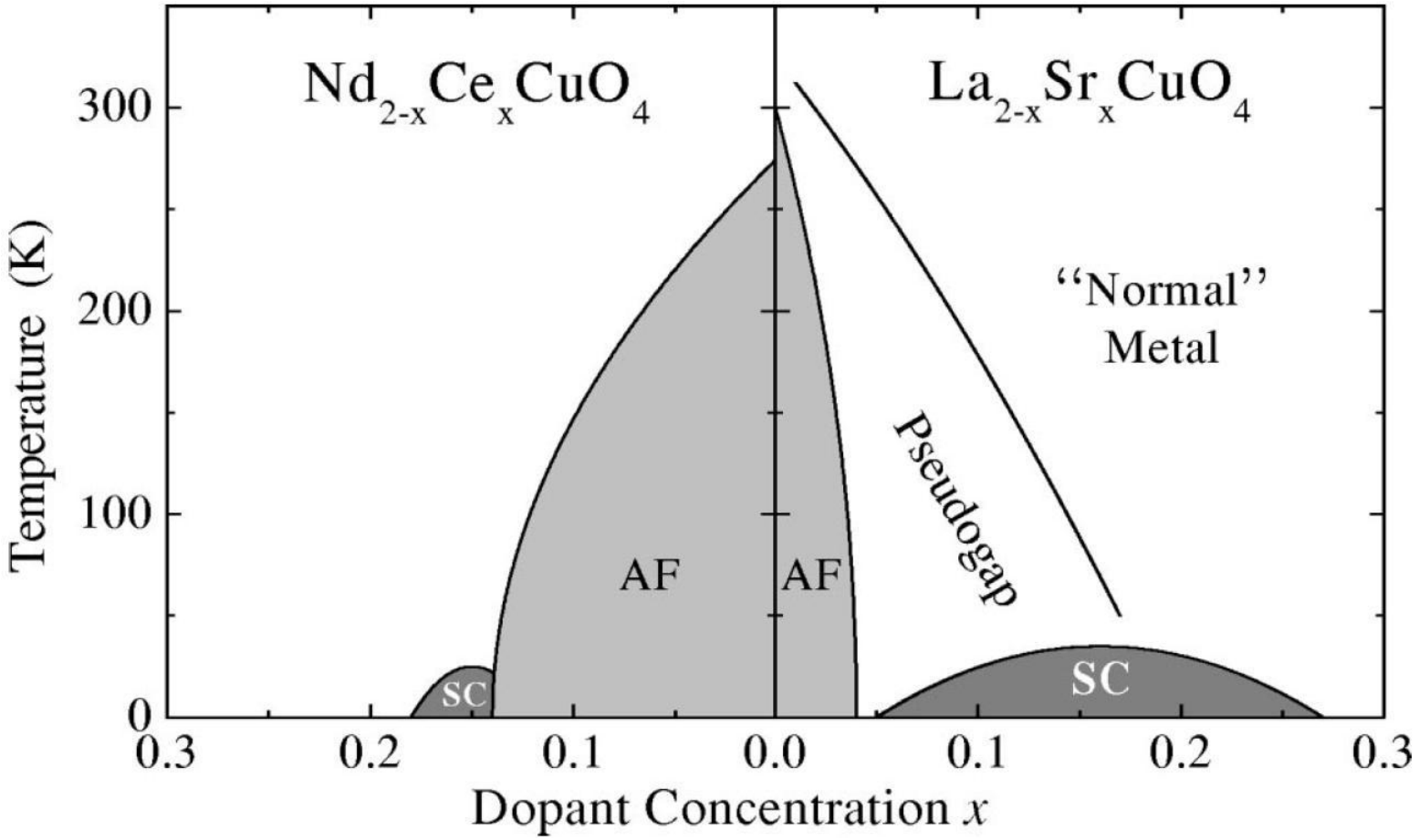
e.g. $La_{2-x}Sr_xCuO4$

Uchida et al, PRB 43, 7942 (91)

More later ….

doped Mott-insulators

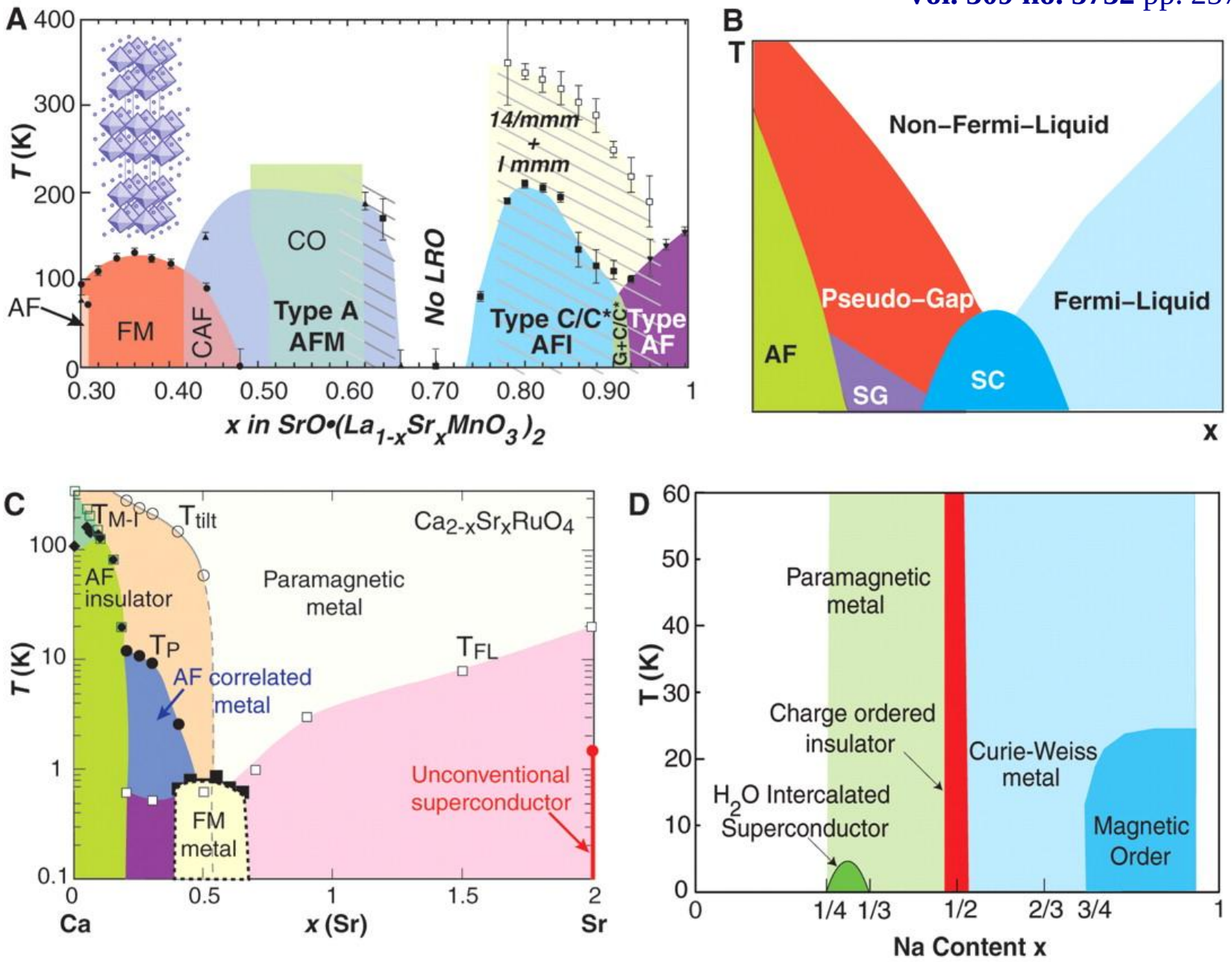
HTC-Superconductors



A. Damascelli, Z. Hussain, Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003)

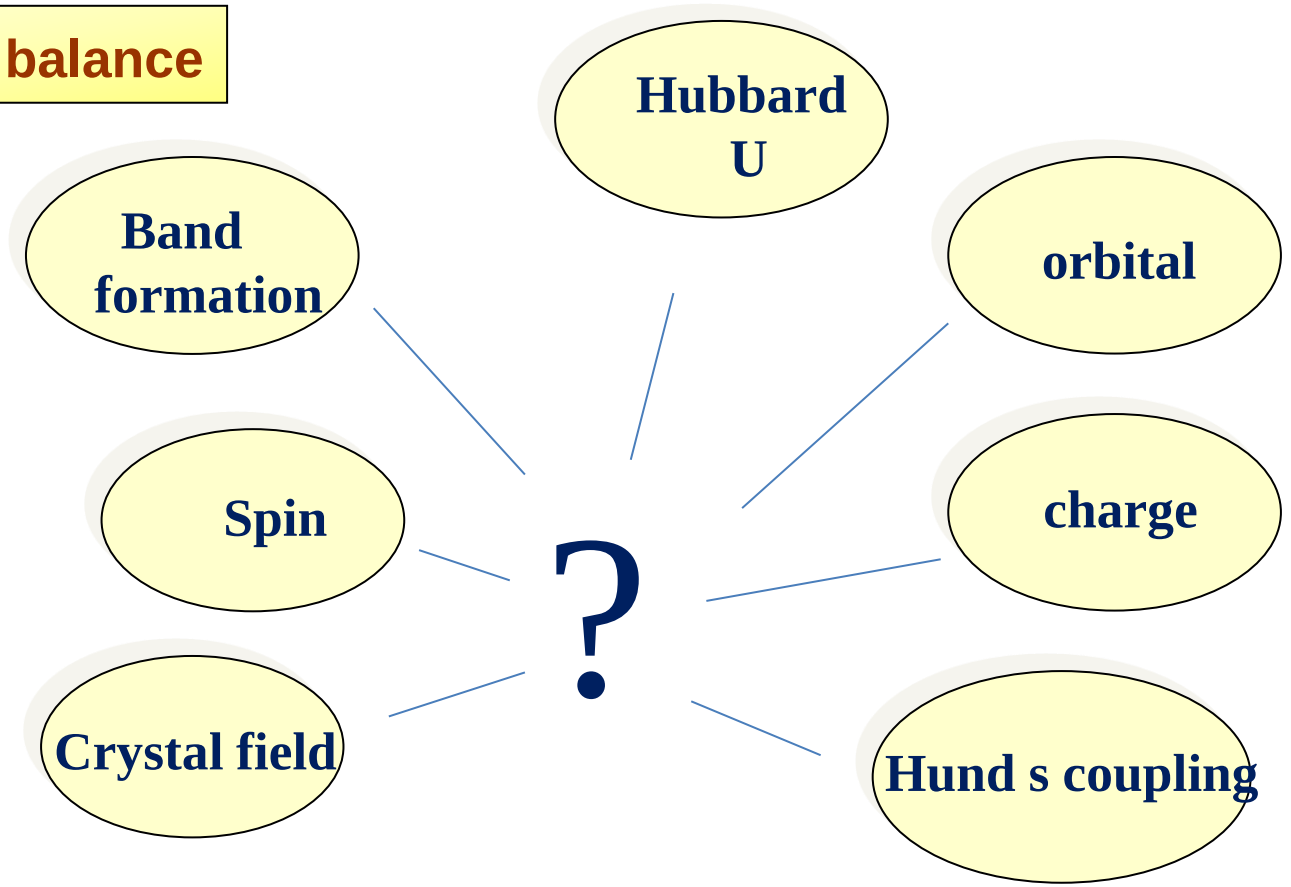
Complexity in Strongly Correlated Electronic Systems

Science 8 July 2005:
Vol. 309 no. 5732 pp. 257-262



Transition metal systems and electron correlations

delicate balance



Systems can be quite close to the borderline U~ W (t)

Thus many interesting transitions can occur by changing T, P, filling, structure, etc

more discussion with examples later!