



COLLÈGE  
DE FRANCE  
—1530—



UNIVERSITÉ  
GRENOBLE  
ALPES

*Chaire de Physique de la Matière Condensée*

# Matériaux et dispositifs à fortes corrélations électroniques

*“Ingénierie quantique” = vers le contrôle  
de leurs fonctionnalités*

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Cycle 2014-2015  
4 mai 2015 – I.1/Intro

# MENU DU JOUR

- Introduction: pourquoi s'intéresser aux matériaux a fortes corrélations électroniques ?
- Blocage de Coulomb vs. Quasiparticules
- Transition de Mott et théorie de champ moyen dynamique
- Introduction a la structure électronique des oxydes de métaux de transition

# Menu des autres jours...

- 18 mai: Hétéro-structures, Contrôle par la lumière: vers de nouvelles fonctionnalités des oxydes de métaux de transition.
- 1<sup>er</sup> juin: Effets thermoélectriques: petits systèmes quantiques et gaz d'atomes froids

# INTRODUCTION

*Pourquoi s'intéresser aux  
matériaux a fortes corrélations  
électroniques ?*

# MATERIALS – THE PLAYGROUND:

Los Alamos National Laboratory Chemistry Division

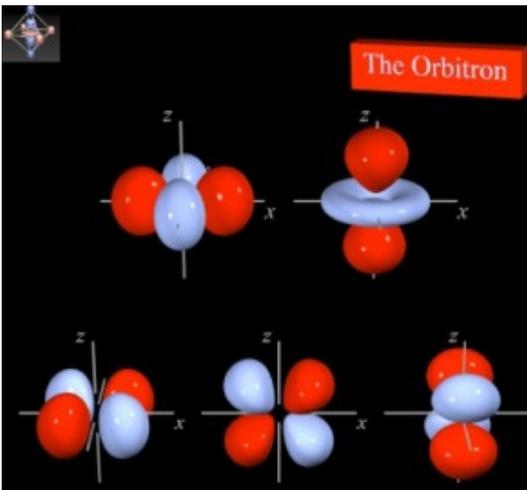
## Periodic Table of the Elements

### Transition Metals

1A 1 <b>H</b> hydrogen 1.008	2A 4 <b>Be</b> beryllium 9.012											3A 5 <b>B</b> boron 10.81	4A 6 <b>C</b> carbon 12.01	5A 7 <b>N</b> nitrogen 14.01	6A 8 <b>O</b> oxygen 16.00	7A 9 <b>F</b> fluorine 19.00	8A 2 <b>He</b> helium 4.003																		
3 <b>Li</b> lithium 6.941	11 <b>Na</b> sodium 22.99	12 <b>Mg</b> magnesium 24.31	13 <b>Al</b> aluminum 26.98	14 <b>Si</b> silicon 28.09	15 <b>P</b> phosphorus 30.97	16 <b>S</b> sulfur 32.07	17 <b>Cl</b> chlorine 35.45	18 <b>Ar</b> argon 39.95	19 <b>K</b> potassium 39.10	20 <b>Ca</b> calcium 40.08	21 <b>Sc</b> scandium 44.96	22 <b>Ti</b> titanium 47.88	23 <b>V</b> vanadium 50.94	24 <b>Cr</b> chromium 52.00	25 <b>Mn</b> manganese 54.94	26 <b>Fe</b> iron 55.85	27 <b>Co</b> cobalt 58.93	28 <b>Ni</b> nickel 58.69	29 <b>Cu</b> copper 63.55	30 <b>Zn</b> zinc 65.39	31 <b>Ga</b> gallium 69.72	32 <b>Ge</b> germanium 72.58	33 <b>As</b> arsenic 74.92	34 <b>Se</b> selenium 78.96	35 <b>Br</b> bromine 79.90	36 <b>Kr</b> krypton 83.80									
37 <b>Rb</b> rubidium 85.47	38 <b>Sr</b> strontium 87.62	39 <b>Y</b> yttrium 88.91	40 <b>Zr</b> zirconium 91.22	41 <b>Nb</b> niobium 92.91	42 <b>Mo</b> molybdenum 95.94	43 <b>Tc</b> technetium (98)	44 <b>Ru</b> ruthenium 101.1	45 <b>Rh</b> rhodium 102.9	46 <b>Pd</b> palladium 106.4	47 <b>Ag</b> silver 107.9	48 <b>Cd</b> cadmium 112.4	49 <b>In</b> indium 114.8	50 <b>Sn</b> tin 118.7	51 <b>Sb</b> antimony 121.8	52 <b>Te</b> tellurium 127.6	53 <b>I</b> iodine 126.9	54 <b>Xe</b> xenon 131.3	55 <b>Cs</b> cesium 132.9	56 <b>Ba</b> barium 137.3	57 <b>La*</b> lanthanum 138.9	72 <b>Hf</b> hafnium 178.5	73 <b>Ta</b> tantalum 180.9	74 <b>W</b> tungsten 183.8	75 <b>Re</b> rhenium 186.2	76 <b>Os</b> osmium 190.2	77 <b>Ir</b> iridium 192.2	78 <b>Pt</b> platinum 195.1	79 <b>Au</b> gold 197.0	80 <b>Hg</b> mercury 200.6	81 <b>Tl</b> thallium 204.4	82 <b>Pb</b> lead 207.2	83 <b>Bi</b> bismuth 208.9	84 <b>Po</b> polonium (209)	85 <b>At</b> astatine (210)	86 <b>Rn</b> radon (222)
87 <b>Fr</b> francium (223)	88 <b>Ra</b> radium (226)	89 <b>Ac~</b> actinium (227)	104 <b>Rf</b> rutherfordium (261)	105 <b>Db</b> dubnium (262)	106 <b>Sg</b> seaborgium (263)	107 <b>Bh</b> bohrium (264)	108 <b>Hs</b> hassium (265)	109 <b>Mt</b> meitnerium (266)	110 <b>Ds</b> darmstadtium (271)	111 <b>Uuu</b> (272)	112 <b>Uub</b> (277)	114 <b>Uuq</b> (296)	116 <b>Uuh</b> (298)	118 <b>Uuo</b> (?)																					

### Rare earths and Actinides

Lanthanide Series*	58 <b>Ce</b> cerium 140.1	59 <b>Pr</b> praseodymium 140.9	60 <b>Nd</b> neodymium 144.2	61 <b>Pm</b> promethium (147)	62 <b>Sm</b> samarium (150.4)	63 <b>Eu</b> europium 152.0	64 <b>Gd</b> gadolinium 157.3	65 <b>Tb</b> terbium 158.9	66 <b>Dy</b> dysprosium 162.5	67 <b>Ho</b> holmium 164.9	68 <b>Er</b> erbium 167.3	69 <b>Tm</b> thulium 168.9	70 <b>Yb</b> ytterbium 173.0	71 <b>Lu</b> lutetium 175.0
Actinide Series~	90 <b>Th</b> thorium 232.0	91 <b>Pa</b> protactinium (231)	92 <b>U</b> uranium (238)	93 <b>Np</b> neptunium (237)	94 <b>Pu</b> plutonium (242)	95 <b>Am</b> americium (243)	96 <b>Cm</b> curium (247)	97 <b>Bk</b> berkelium (247)	98 <b>Cf</b> californium (251)	99 <b>Es</b> einsteinium (254)	100 <b>Fm</b> fermium (253)	101 <b>Md</b> mendelevium (258)	102 <b>No</b> nobelium (259)	103 <b>Lr</b> lawrencium (260)



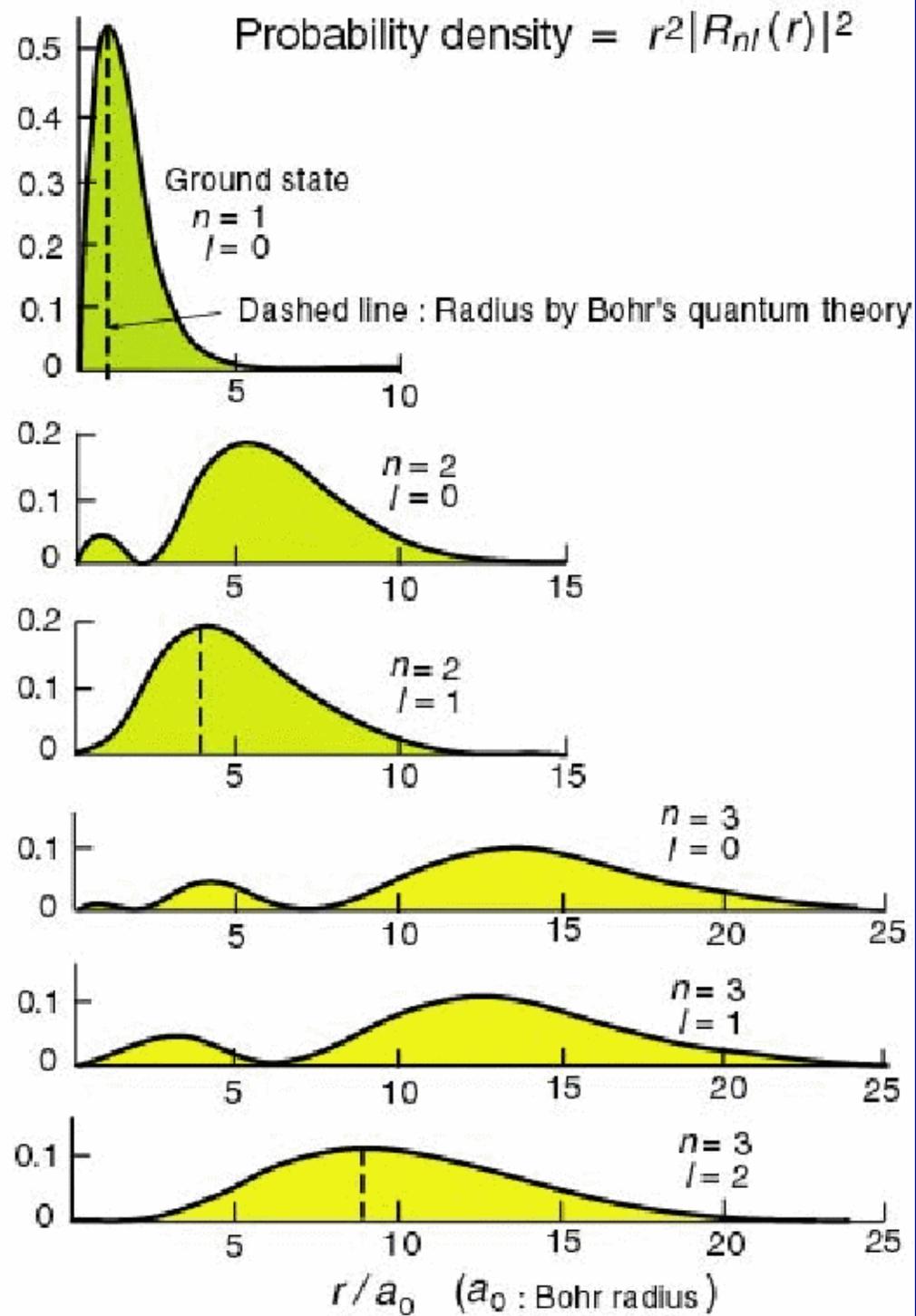
# “Strong Correlations” ↔ Localized orbitals !

d- or f- orbitals are quite close to ions nuclei  
(particularly 3d and 4f: radial wavefunction does not extend very far, for orthogonality reasons)

**They do not behave as regular band-forming orbitals (e.g sp-bonding) and retain atomic-like aspects**

→ **Electrons “hesitate” between localized and itinerant behaviour !**

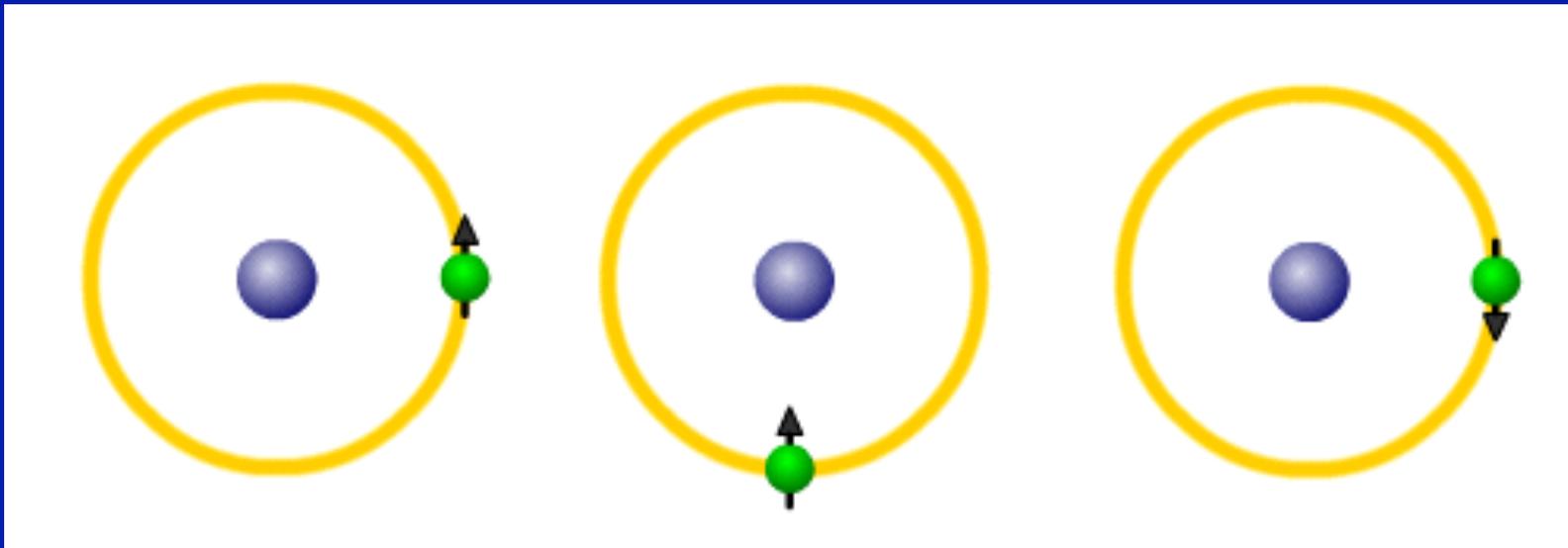
**Materials:** transition-metals and their oxides, rare-earth/actinides and their compounds, but also some organic materials (molecular solids)



# Two competing energy scales:

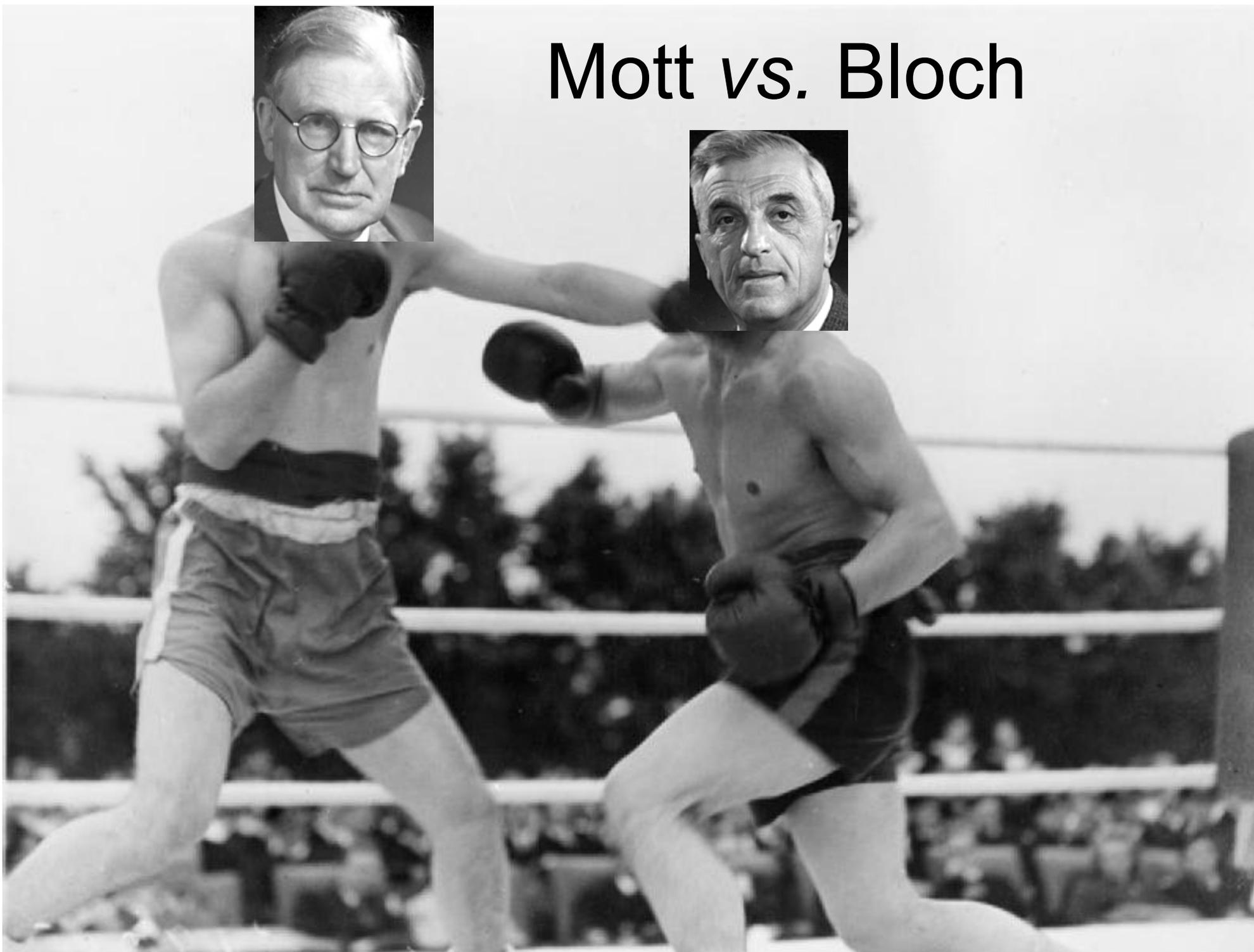
- Kinetic energy of electrons/Bandwidth ('t')  
(Controlled by inter-atomic overlap of orbitals)
- Typical size of Coulomb interaction matrix element(s) in the atomic shell ('U')  
(Strongly affected by screening and drastically reduced from its value in the isolated atom)

Electrons “hesitate”  
between being localized  
on short-time-scales  
and itinerant on long time-scales



*As seen in many spectroscopies: see later in these lectures*

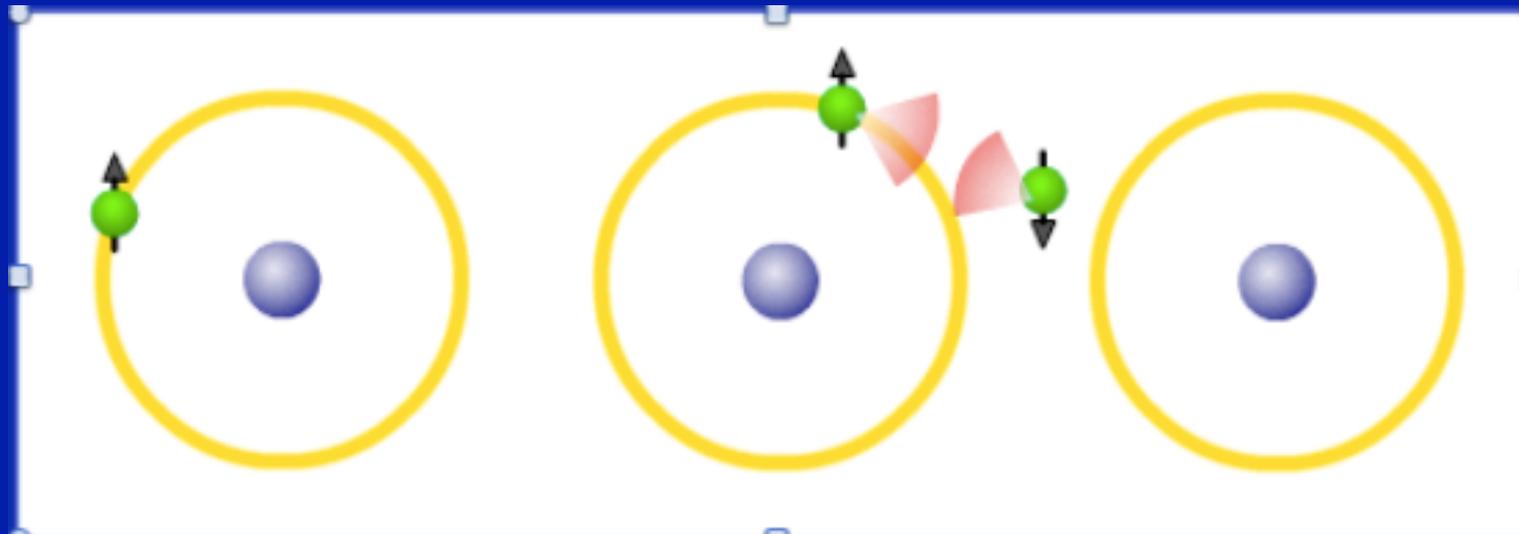
# Mott vs. Bloch



# Simplest « toy model »: The Hubbard model



$$H = -t \sum_{\langle ij \rangle} (c_i^\dagger c_j + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$



$t$ : Tunnel amplitude  $\rightarrow$  bandwidth

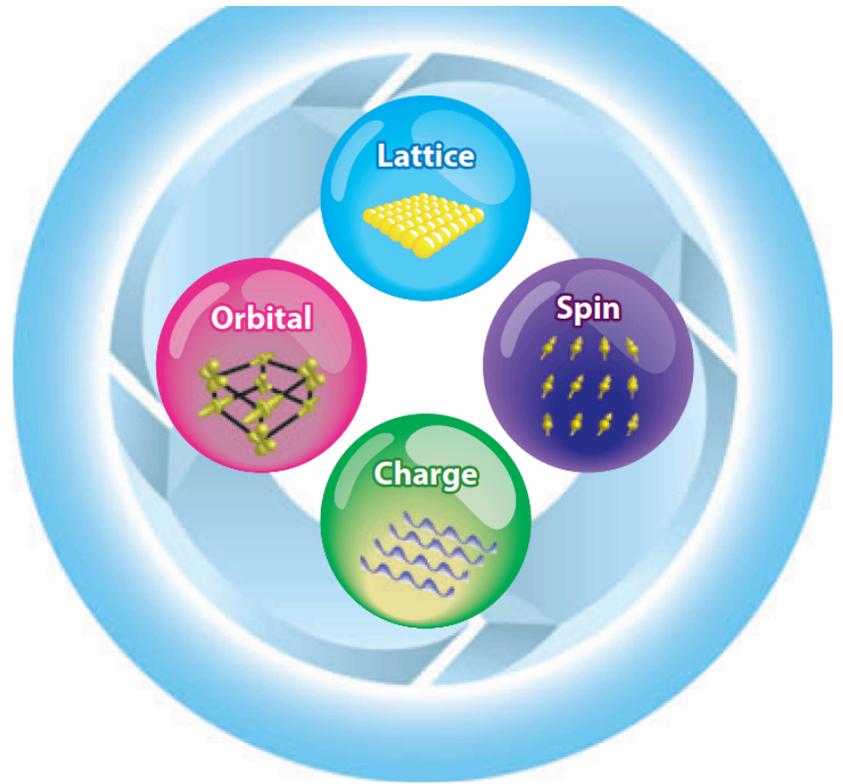
$U$ : On-site matrix element of screened Coulomb interaction

# The physics of this model is surprisingly rich and complex

- Why is this so ? – Physical reasons
- Emergence of energy scales which are (much) smaller than the bare scales ( $t, U$ )
- e.g.: Superexchange  $J \sim t^2/U$  ( $\sim t$  or smaller)
- Energy scale below which coherent quasiparticles are formed  $T_F^* \ll t$
- *This –and several more technical reasons– implies that theory has a hard time...*

# But the physics of real materials is even richer... and more interesting

Other degrees of freedom...



- Other important energy scales, e.g.:
- Crystal-field splitting
- Other matrix elements of Coulomb matrix elements (e.g. Hund's and spin-orbit coupling)
- Lattice energy scales
- etc...

# Materials with Strong Electron Correlations do “BIG THINGS”

- Because of the strong interdependence of electrons, collective phenomena take place
- Materials can be easily switched between these different states
- Competing states with small energy differences between them

# Metal-Insulator Transitions

# Metal-Insulator Transitions:

$V_2O_3$  : a time-honored example displaying a rich variety of phenomena

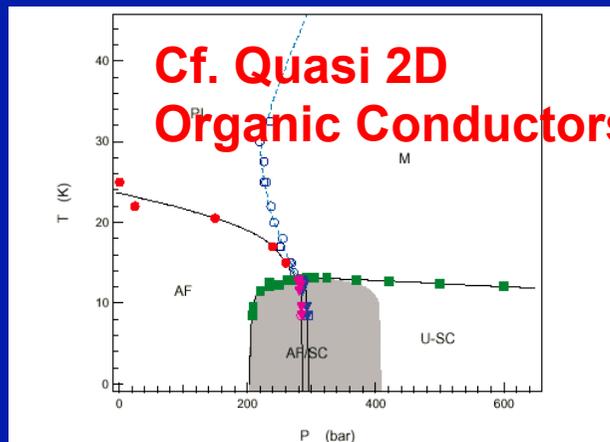


FIG. 1. Temperature vs pressure phase diagram of  $\kappa$ -CI. The antiferromagnetic (AF) critical line  $T_N(P)$  (dark circles) was determined from NMR relaxation rate while  $T_c(P)$  for unconventional superconductivity (U-SC: squares) and the metal-insulator  $T_{MI}(P)$  (MI: open circles) lines were obtained from the AC susceptibility. The AF-SC boundary (double dashed line) is determined from the inflexion point of  $\chi'(P)$  and, for 8.5K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence (shaded area).

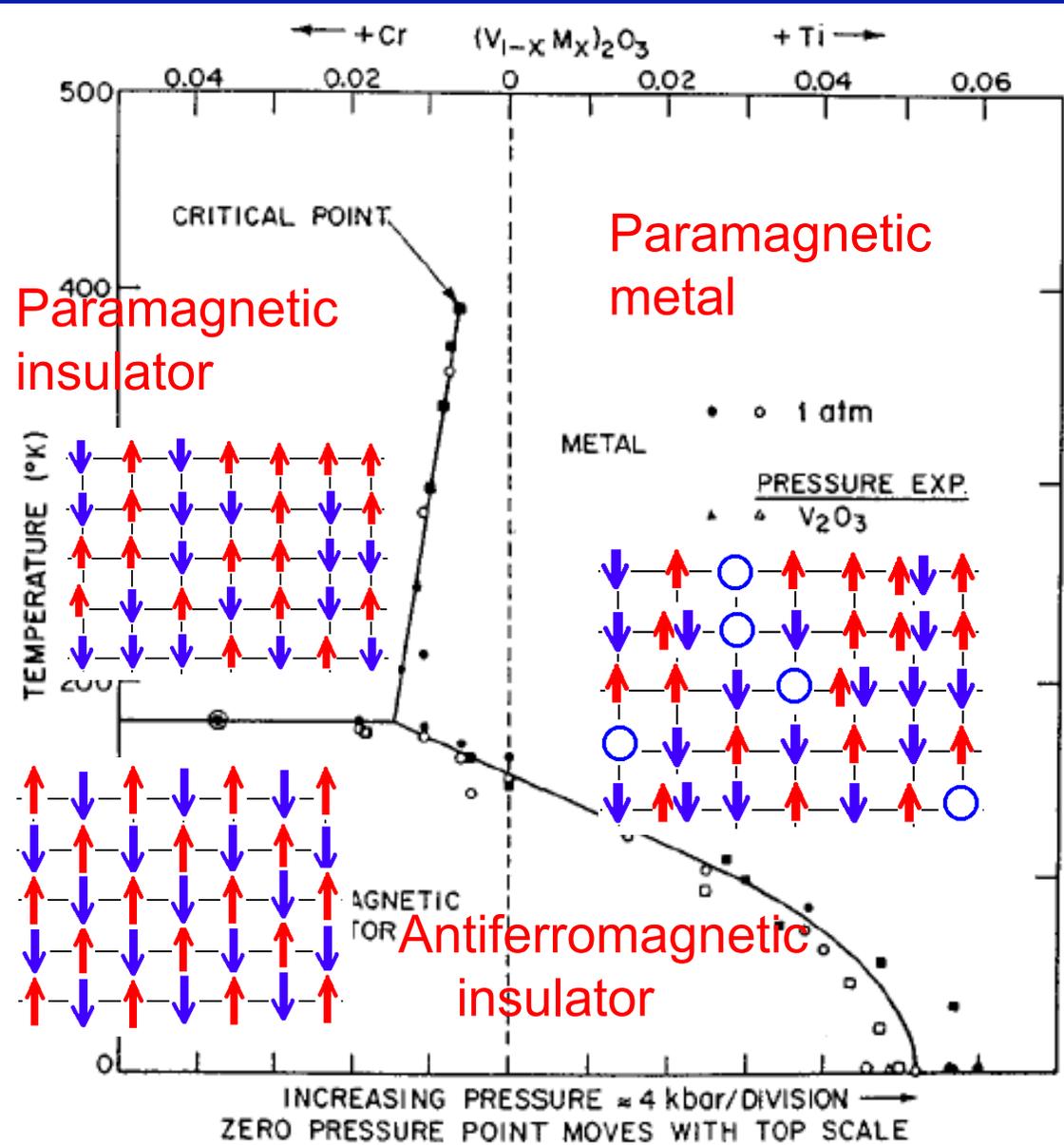
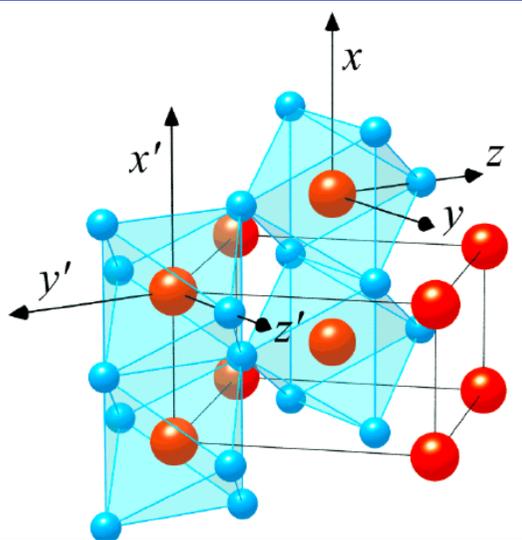


FIG. 70. Phase diagram for doped  $V_2O_3$  systems,  $(V_{1-x}Cr_x)_2O_3$  and  $(V_{1-x}Ti_x)_2O_3$ . From McWhan *et al.*, 1971, 1973.

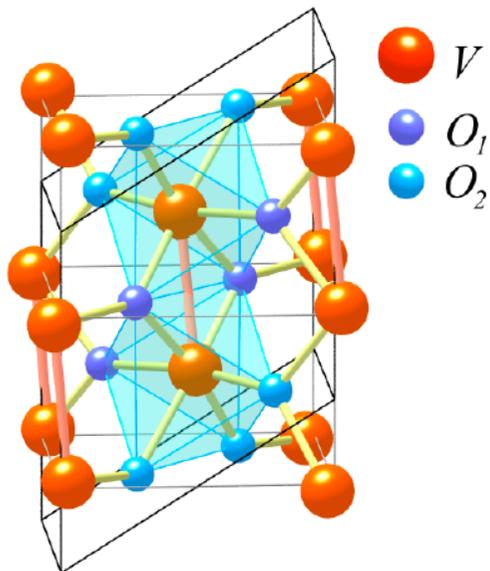
# An application of room-temperature MIT of Vanadium Dioxide $\text{VO}_2$

“Intelligent windows”

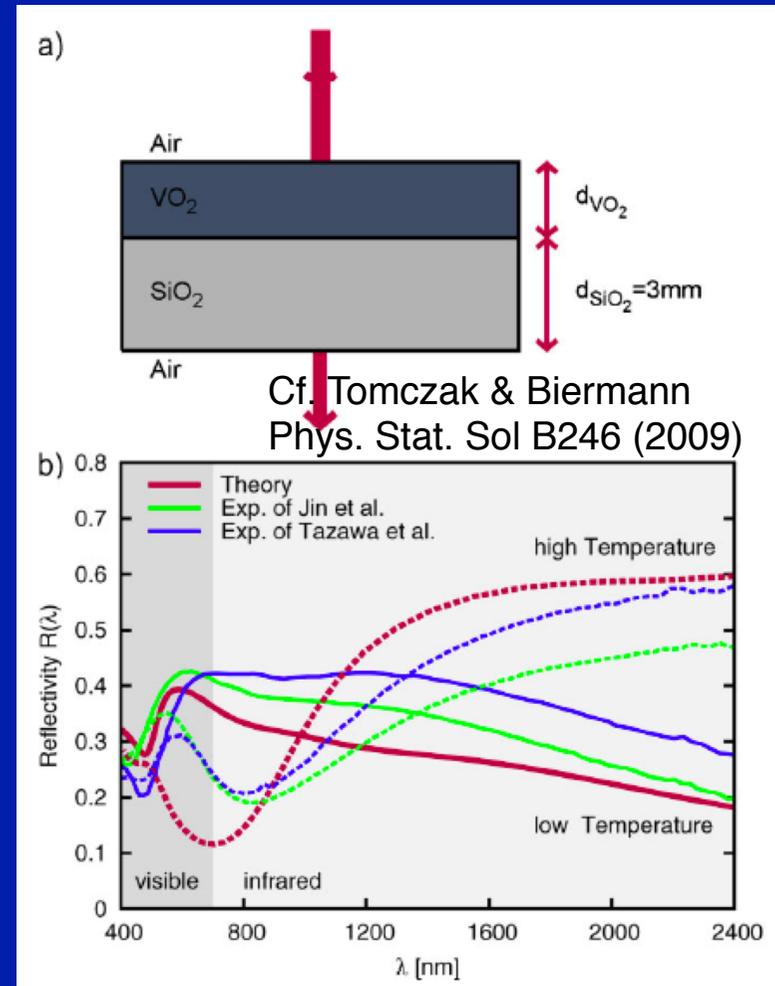


Hi-T rutile structure:  
~ Metal  
→ Reflects infra-red

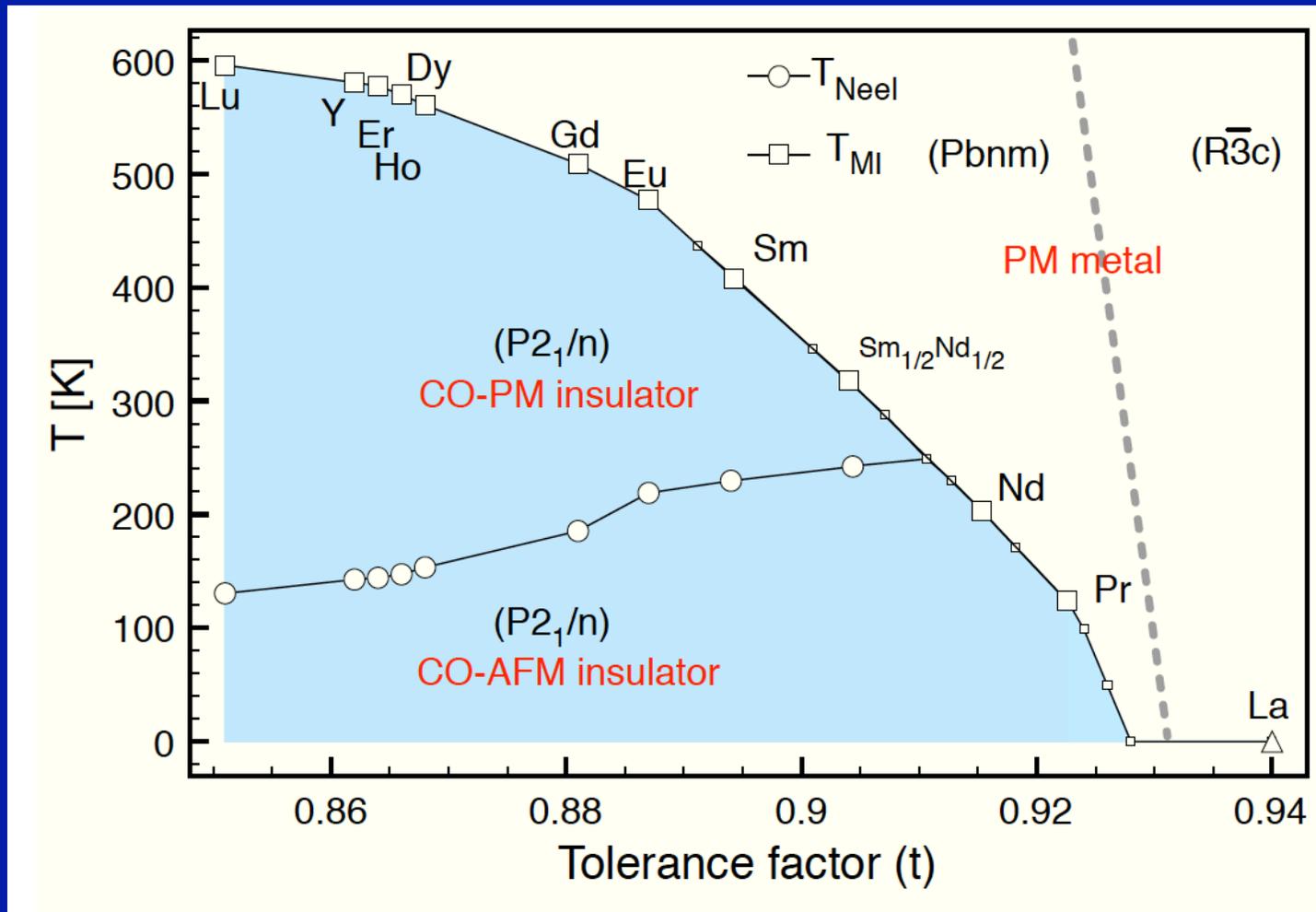
$T_{\text{MIT}} \sim$  room temperature



Low-T monoclinic structure:  
Insulator  
→ Transparent in infra-red

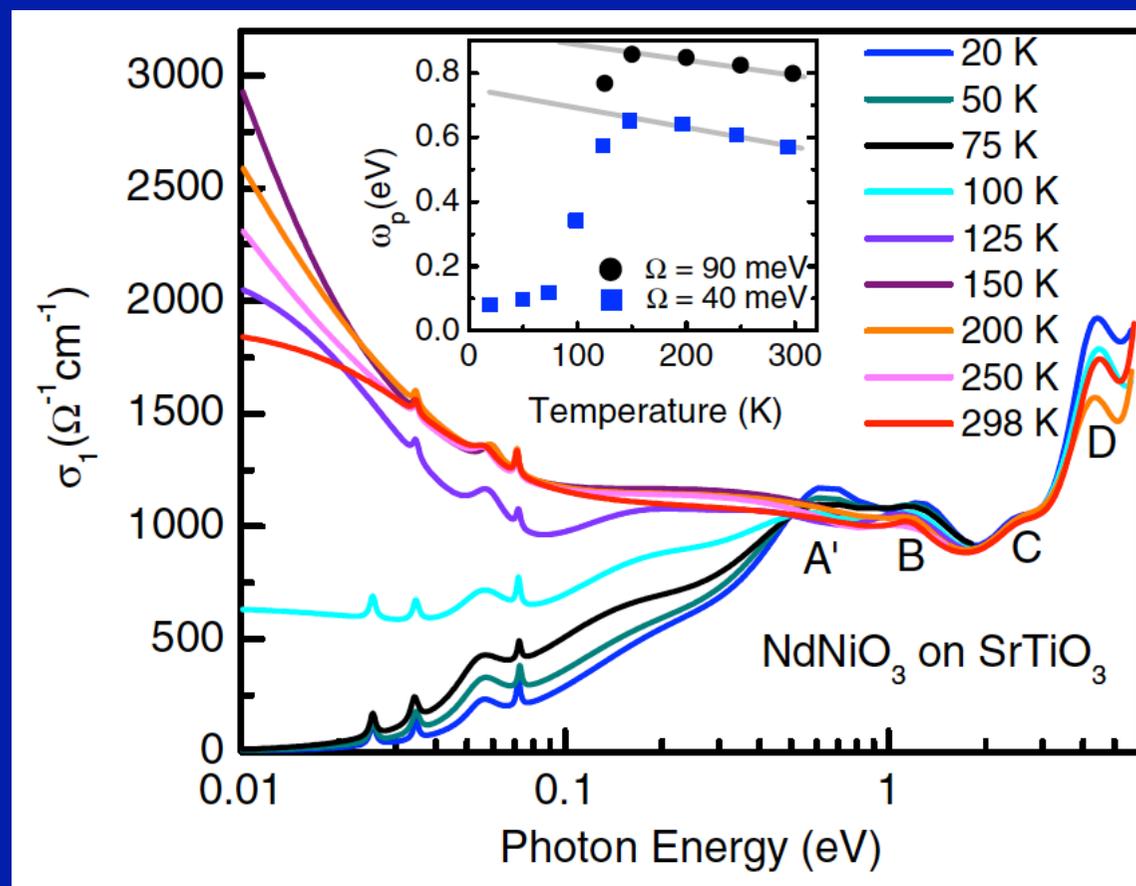


# Nickelates $R\text{NiO}_3$ : tunable MIT



Control by strain/hetero-structuring, and possible applications:  
→ Lecture 2 on May 18

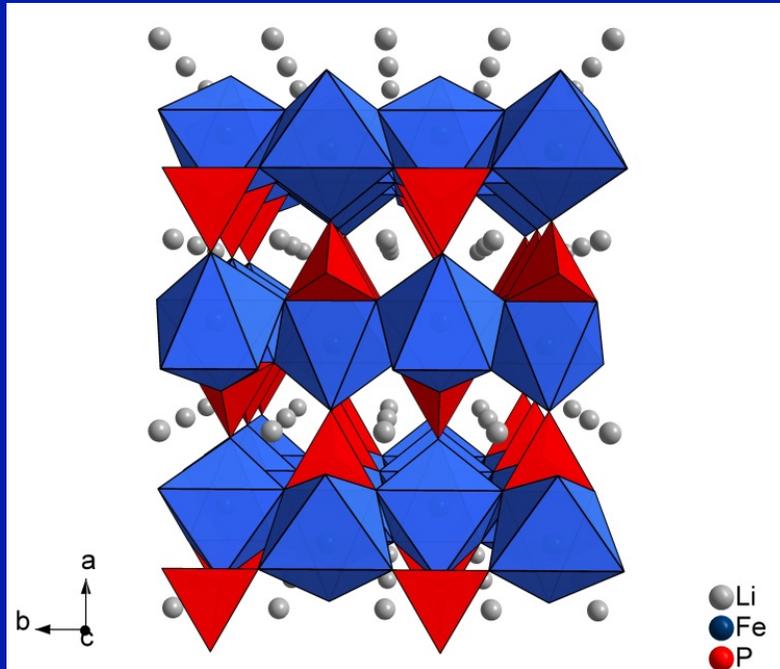
# Transfers of spectral weight over very large energy range !



Optical conductivity NNO on STO - Stewart et al. PRL 107, 176401 (2011)

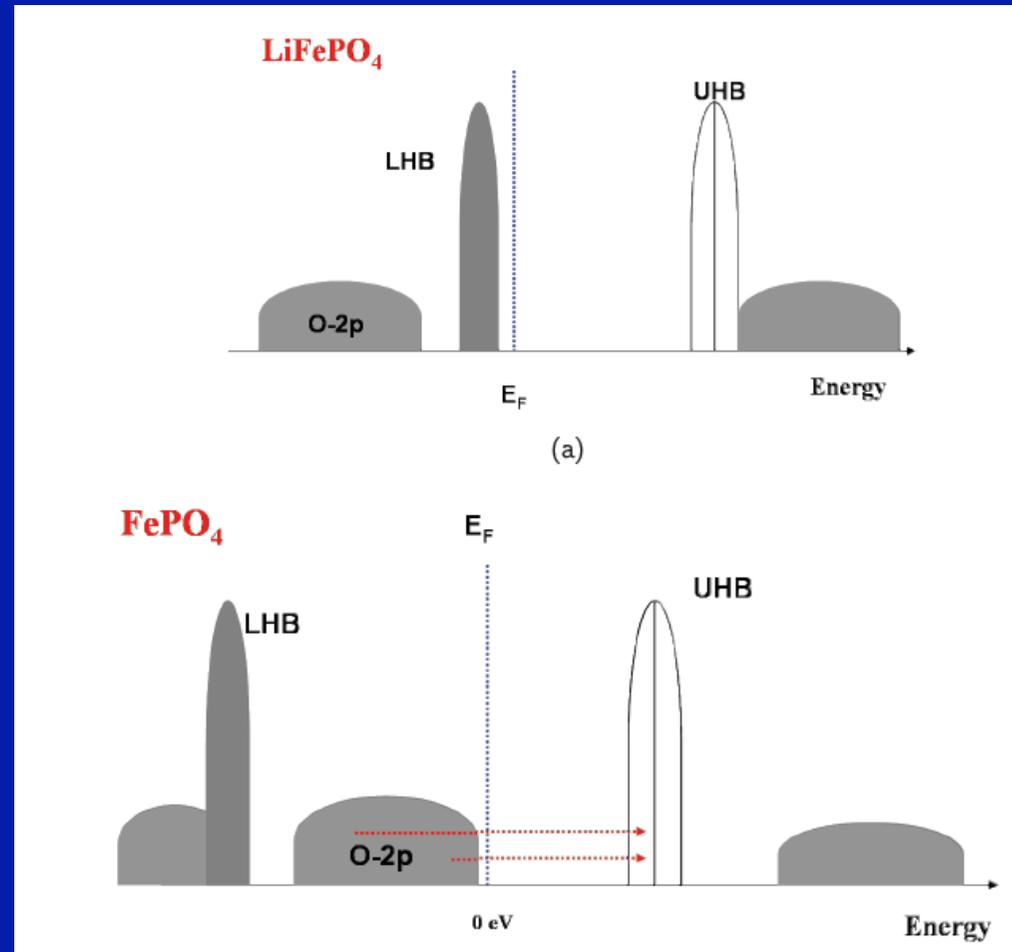
Despite small energy difference between the two states,  
reshuffling of states/weights over large energy range: multi-scale problem

# Current Battery (cathode) materials



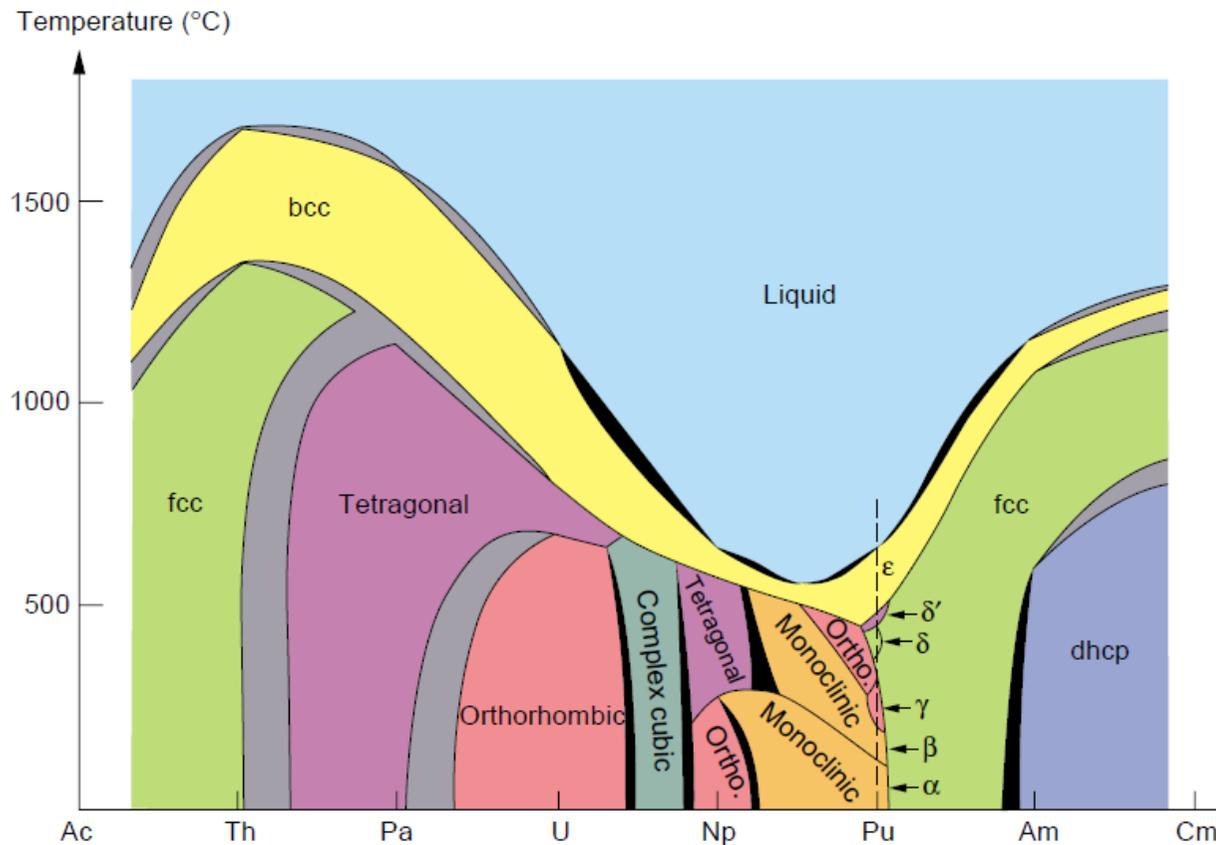
LFPO: Mott insulator  
FPO: Charge-transfer insulator

Kinyanjui, PhD, Ulm 2010



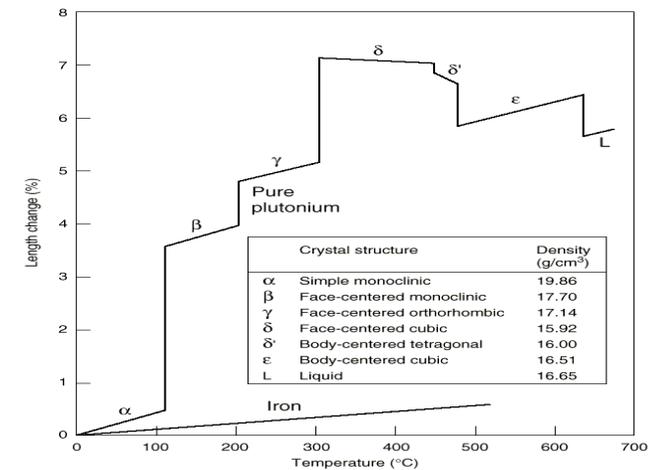
Relevance of the localization/  
delocalization competition  
( $\sim$  Mott transition)  
to f-electron materials  
(rare earths and actinides)

Plutonium has the most complex phase diagram of all pure elements, because it is just on the frontier separating itinerant/localized behaviors (here, of 5f electrons)



**Figure 10. Connected Binary-Phase Diagram of the Actinides**

The binary-phase diagrams (temperature vs composition) for adjacent actinide elements are connected across the entire series to demonstrate the transition from typical metallic behavior at thorium to the enormous complexity at plutonium and back to typical metallic behavior past americium. Two-phase regions are in black; uncertain regions are in gray.



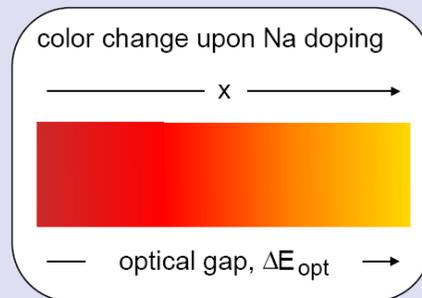
Note:  
bandstructure  
(such as DFT-GGA)  
methods fail completely  
at predicting unit-cell  
volume of delta-phase  
(error ~ 35% too small)

# $\gamma$ -cerium sulfides: red/orange pigment (Rhodia's 'Neolor') ...due to the Mott phenomenon !

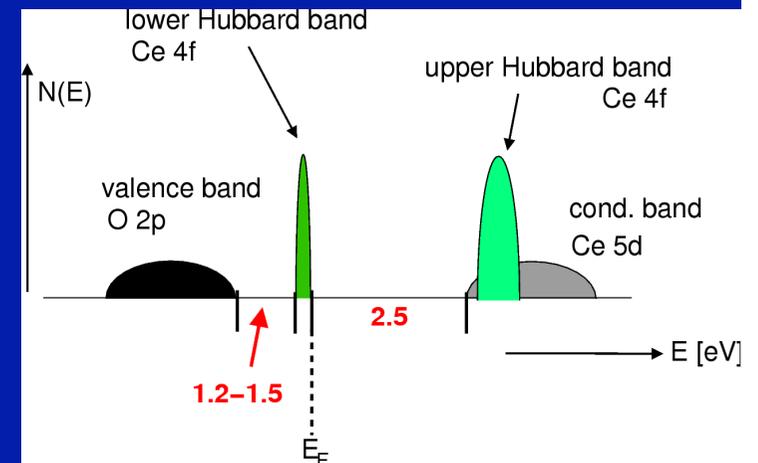


Industrial pigments which can be viewed as 'f-electron Mott insulators', whose colour is tuned by the position of the localised f-orbitals

Environmentally-responsible pigments (NEOLOR™, Rhodia)



[http://www.rhodia-rare-earths.com/site\\_ec\\_us/other\\_markets/index\\_neolor.htm](http://www.rhodia-rare-earths.com/site_ec_us/other_markets/index_neolor.htm)



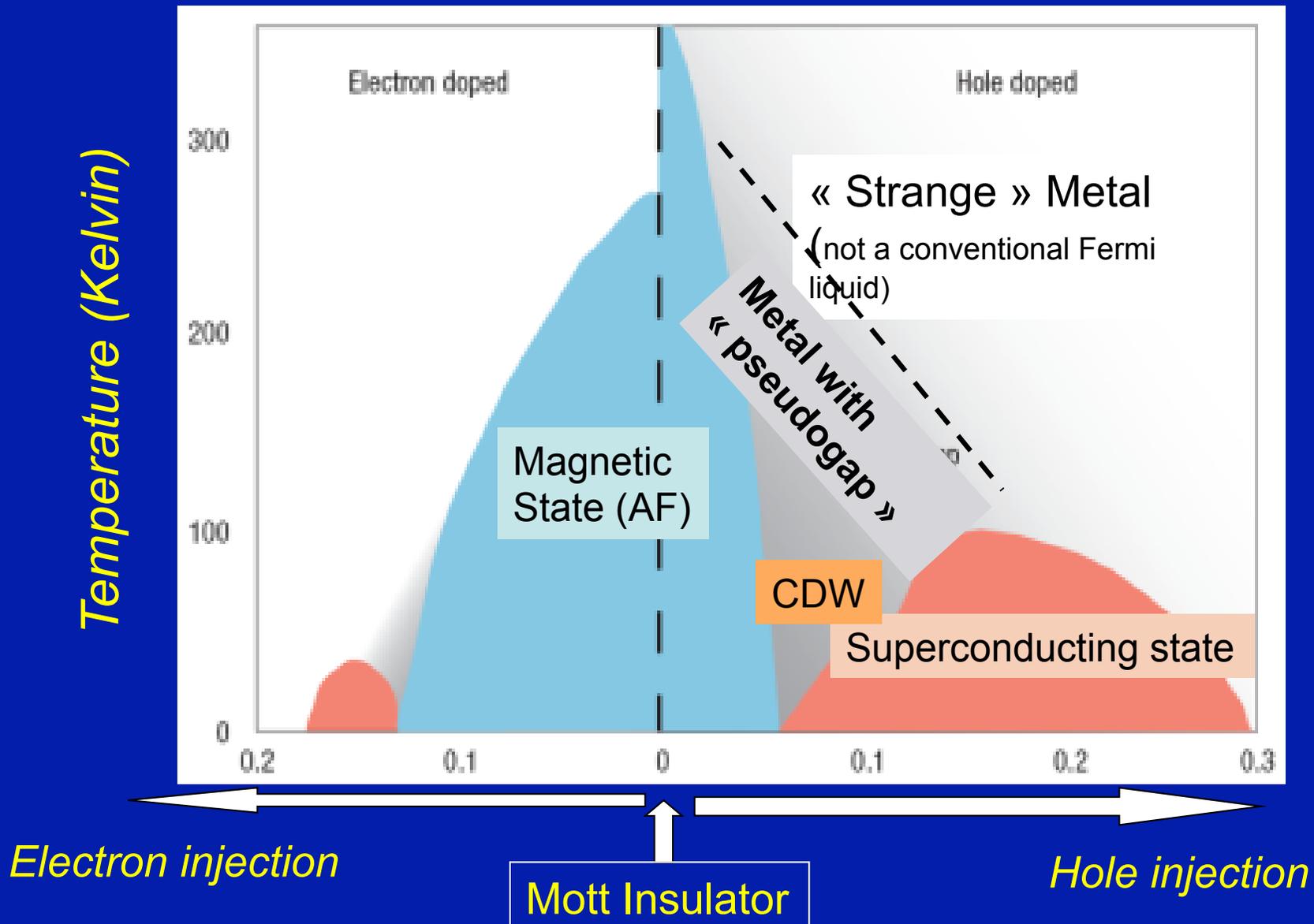
Ce<sub>2</sub>O<sub>3</sub>: R. Windiks et al.,  
J. Phys Chem Sol

Ces exemples (et bien d'autres)  
soulignent qu'il est absurde  
de ne pas soutenir une recherche de  
pointe sur les matériaux  
à fortes corrélations électroniques  
(du fondamental aux applications)  
**si on veut pouvoir faire face  
aux enjeux actuels  
dans le domaine de l'énergie  
(ou de l'électronique)...**

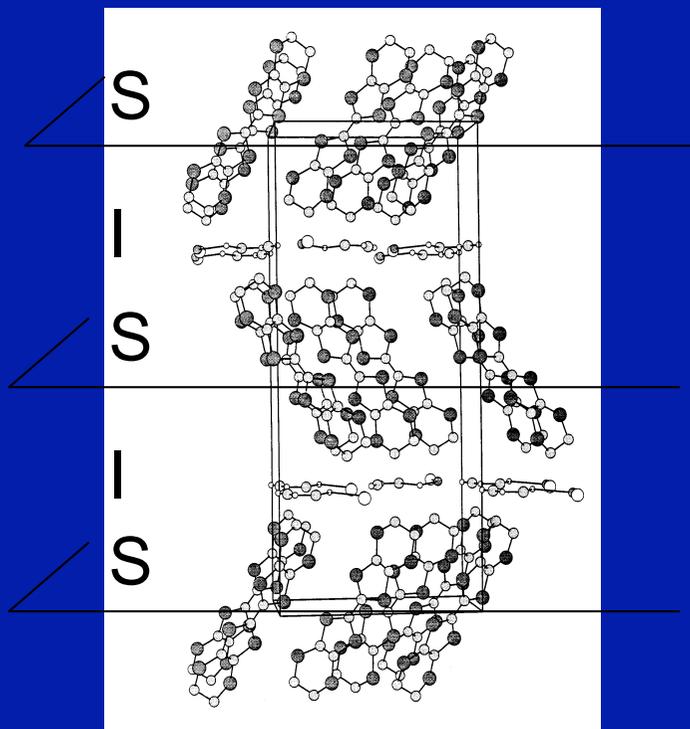
# High-Tc Superconductivity

# Copper-oxide superconductors:

*A headache for theorists - Rich phase diagram with mysterious electronic phases*



# Quasi 2D organic conductors



From NMR experiments

Sherbrooke/Orsay

S.Lefebvre et al. : PRL 85 (2000) 5420;

Limelette et al. PRL 91, 016401 (2003)

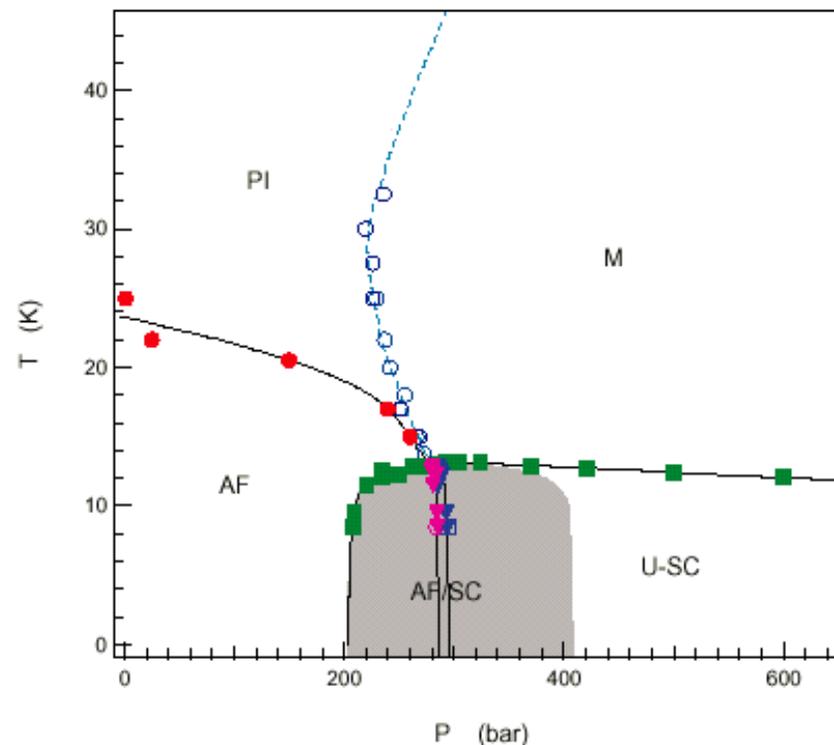
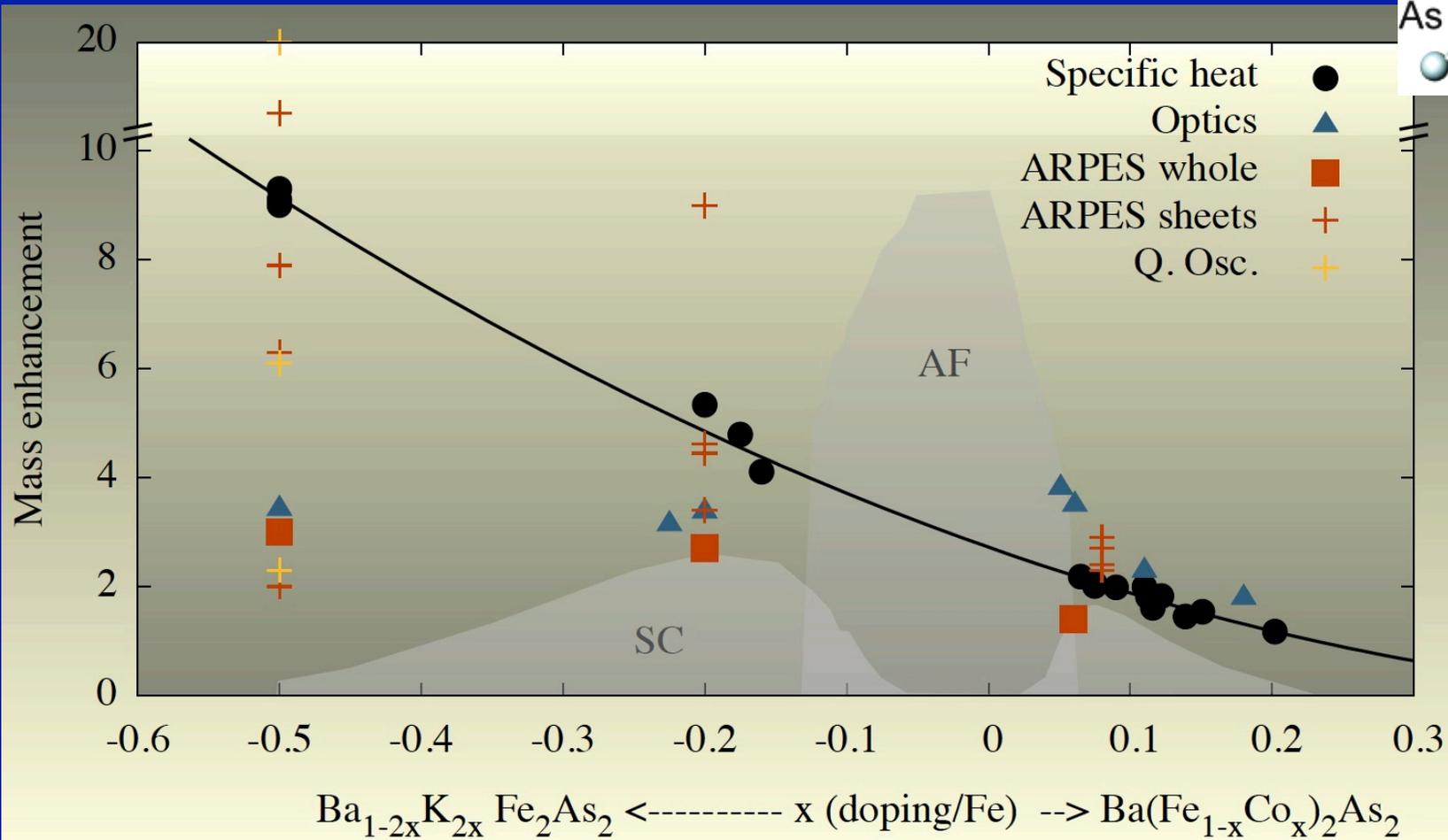
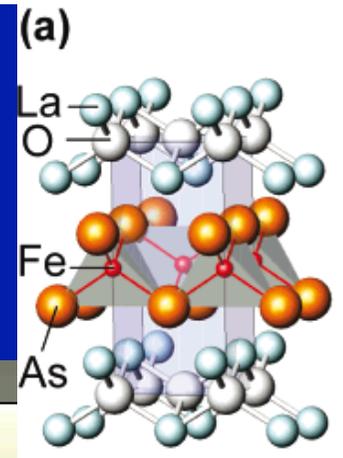
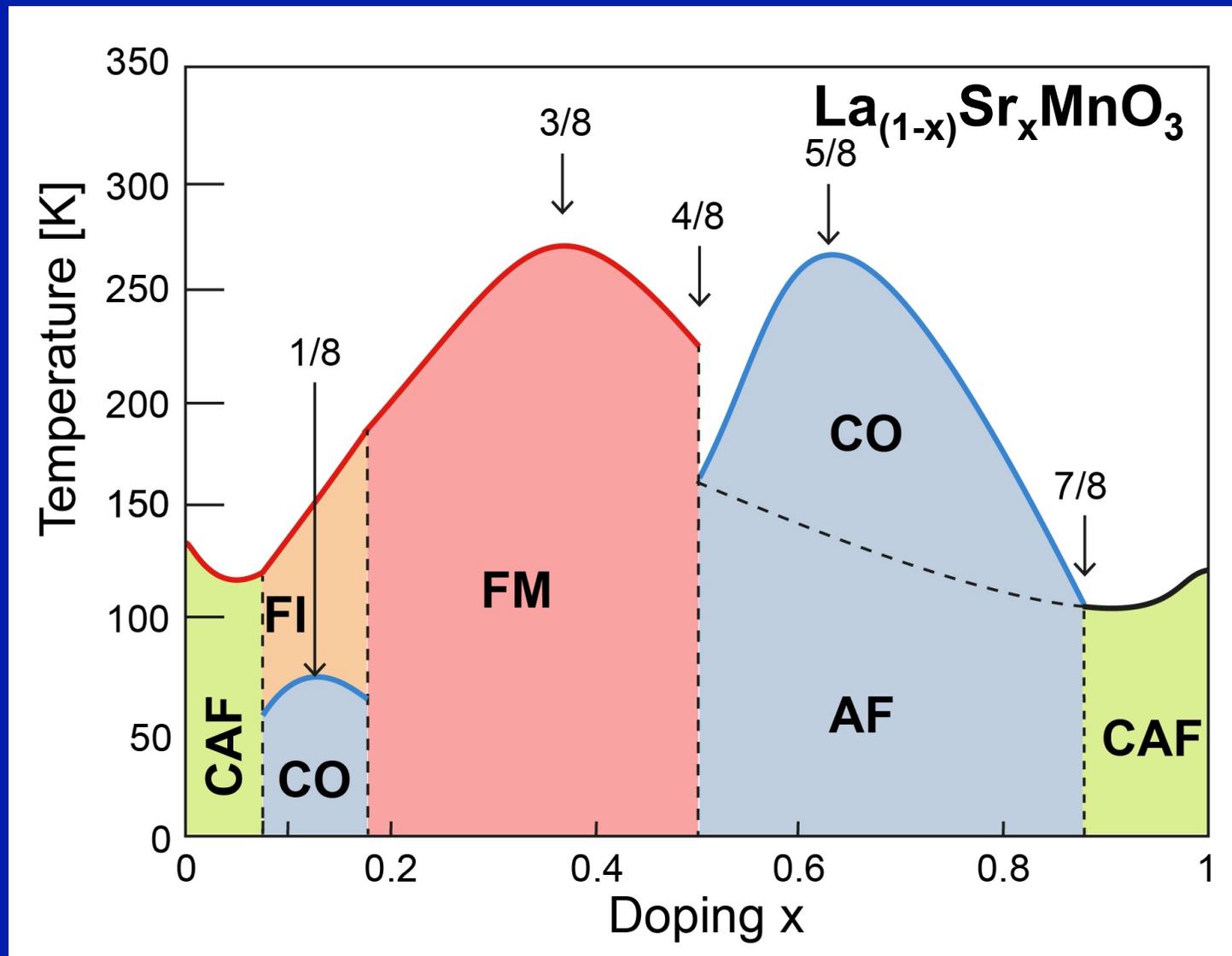


FIG. 1. Temperature *vs* pressure phase diagram of  $\kappa\text{-Cl}$ . The antiferromagnetic (AF) critical line  $T_N(P)$  (dark circles) was determined from NMR relaxation rate while  $T_c(P)$  for unconventional superconductivity (U-SC: squares) and the metal-insulator  $T_{MI}(P)$  (MI: open circles) lines were obtained from the AC susceptibility. The AF-SC boundary (double dashed line) is determined from the inflexion point of  $\chi'(P)$  and, for 8.5K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence (shaded area).

# Fe-based superconductors (2008→)



# Manganites – Multiple Electronic Phases and ‘Colossal Magnetoresistance’



# Take-home:

- Many degrees of freedom: charge, spin, orbitals, lattice
- Many competing phases
- Small energy differences
- → CONTROL is desirable
- Small emerging energy scales (smaller than bare electronic scales)

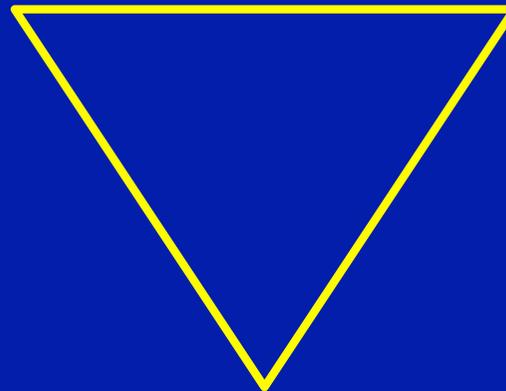
# Keys to success...

## Experiments

Pushing the limits  
New Instrumentation  
New Techniques

## Theory

Simple concepts  
and basic mechanisms  
Quantitative methods



## Materials Science and Chemistry

New materials, bulk or `artificial`  
High quality samples  
New elaboration methods

# What is needed from theory (in my opinion...)

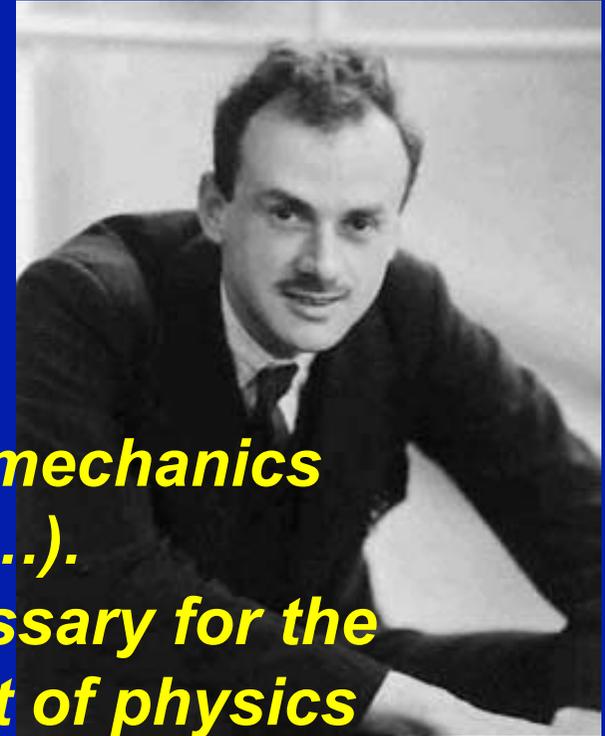
- Understanding of basic physical mechanisms
- Development of better quantitative methods and algorithms to cope with interacting electrons
- Taking advantage of basic progress on the above: go beyond simple models and take into account realistic aspects of materials.
- Never loose sight of experiments and materials science

# When can we tell that we have a theory of cuprates ?

(Given that it has been solved so many times already 😊 )

- When we understand for sure WHY two single layers cuprates such as LSCO and Hg1201 have such a different  $T_c$
- When we can take advantage of this to guide materials design (optimistically)

Paul Dirac, 1929  
`Quantum Mechanics  
of Many-Electron Systems`



***“The general theory of quantum mechanics  
is now almost complete (...).  
The underlying physical laws necessary for the  
mathematical theory of a large part of physics  
and the whole of chemistry  
are thus completely known,  
and the difficulty is only that  
the exact application of these laws  
leads to equations much too complicated to be soluble.”***

P. A. M. Dirac, "Quantum Mechanics of Many-Electron Systems",  
Proceedings of the Royal Society of London, Series A, Vol.123,  
April 1929, pp 714.

# Sounds like a `reductionist' joke ?

*`Biologists think they are Biochemists,*

*Biochemists think they are Physical Chemists,  
Physical Chemists think they are Physicists,*

*Physicists think they are Gods, ...*

*And God thinks he is a Mathematician''*



*“ It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. ”*

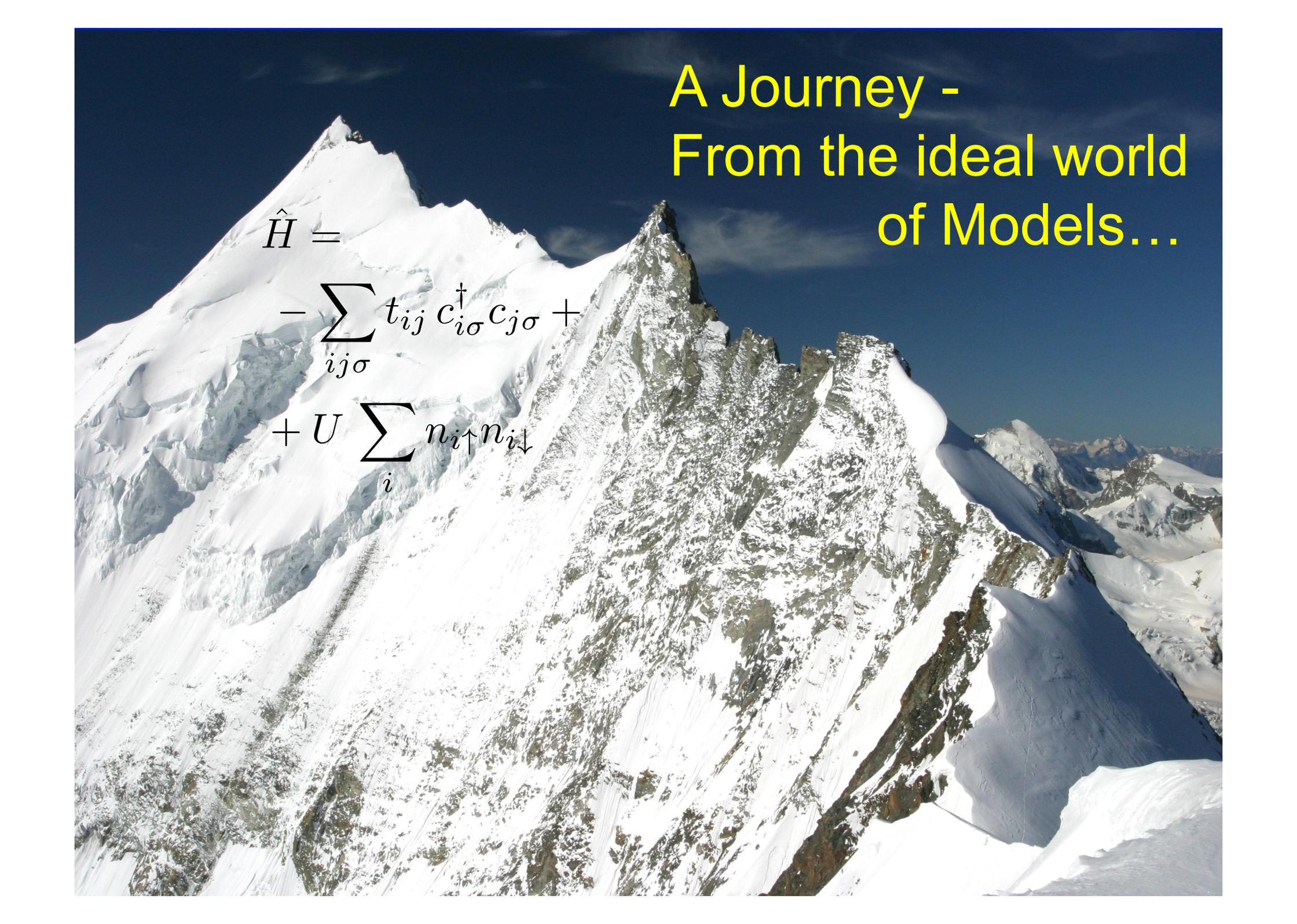
Dirac's program is not yet fully implemented but very significant progress has been made.  
Note that *“without too much computation”* has an entirely different meaning now than in the 1930's 😊

# Why are interacting fermion systems still hard problems ?

- Exponential size of the Hilbert space
  - Exact diagonalisation only handles (very) small systems
- Alternating sign of fermionic quantum-mechanical amplitudes
  - (Direct) Quantum Monte-Carlo is in trouble

Example: Hubbard model (the simplest model in the field)  
4<sup>N</sup>-dimensional Hilbert space, physics still not established in  
d=3, and especially d=2...

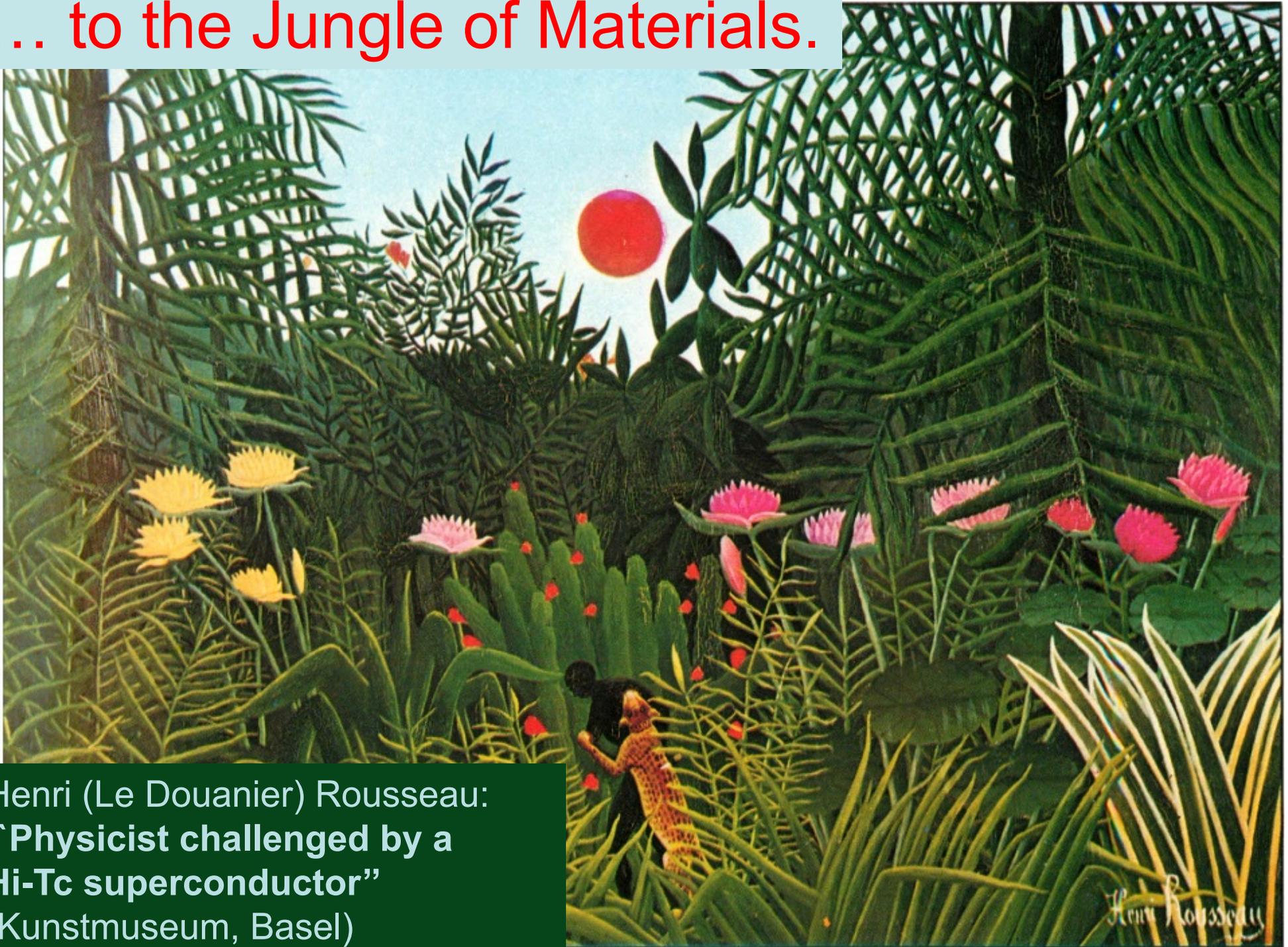
$$\hat{H} = -t \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



# A Journey - From the ideal world of Models...

$$\hat{H} = - \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

... to the Jungle of Materials.



Henri (Le Douanier) Rousseau:  
“Physicist challenged by a  
Hi-Tc superconductor”  
(Kunstmuseum, Basel)