Electronic Structure from the top down

Predicting the behavior of materials starting from high temperature

Using Dynamical Mean Field theory

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Electronic Structure from the bottom up (starting at low T)

Key words:
Order
Energy

Elementary excitations
– phonons, ,magnons, . . .

Ground State – T=0

In principle -- well -understood

Advantage – most straightforward to treat ordered systems

Goal for this talk

In much of the field of electronic structure, all the theory and methods for calculation are formulated at zero temperature

This is sufficient for much of the work. I am NOT trying to criticize present calculations!!

But consider the goal that electronic structure calculations can predict the transition temperature of ferromagnetic Fe --- and many other cases where temperature is crucial

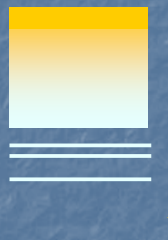
Electronic Structure from the top down (starting at high T)

In principle -- well -understood

Advantage – Higher T – less correlation, shorter range

High temperature
(T >> energy scale /k_b)

Key Words:
Disorder
Entropy



Uncorrelated
at high T

Correlation functions
– spin, charge, . . .

Electronic Structure from the top down

In principle -- well -understood

Idea – Higher T – less correlation, shorter range

High temperature
(T >> energy scale /k_b)

Key Words:
Disorder
Entropy

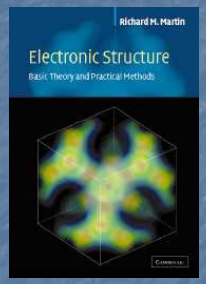
Uncorrelated at high T

T

Correlation functions – spin, charge, . . .

Nice Description by Walter Kohn
"Nearsighted"

The big picture in perspective "Nearsightedness"



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Locality and linear scaling $O(N)$ methods

Nearsightedness

W. Kohn

Throwing out k-space

V. Heine

- Nearsightedness is a property of a many-body system . . .
- In insulators and metals at non-zero temperature, . . .

Electronic Structure The big picture

High temperature
(> energy scale /k_b)

Key Words:
Disorder
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Key words:
Order
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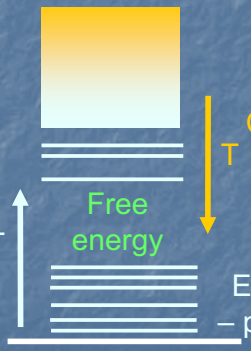
Ground State – T=0



Uncorrelated at high T

T

Correlation functions – spin, charge, . . .

T

Free energy

Elementary excitations – phonons, ,magnons, . . .

Theoretical formulation

Partition Function --- $Z = \Sigma_i \exp(- \beta E_i)$, $\beta = 1/kT$

$= Tr \exp(- \beta H)$

Free energy -- $F = - kT \ln Z$

Starting from low T --- more difficult as T increases

→ more eigenstates required

Starting from high T --- more difficult as T decreases

→ longer correlation lengths required

Electronic Temperature scales

Natural --- Hartree/k_b ~ 200,000 K

Large effects of valence electronic excitations in typical materials

--- eV/k_b ~ 8,000 K

Good reasons to ignore effect of temperature for electronic excitations in many materials for ordinary T

Practical reasons to ignore effect of temperature for electronic excitations

Questions for audience

Electronic Properties where temperature matters

My list

Magnetism – spins are really electrons

T_c ~ 1K – 1000 K sets scale for magnetism

Other scales – band width ~ exchange ~ eV

Metal – insulator transitions

Transition metal oxides

Kondo Effect -- magnetic impurities in metals

T_K can be ~ 10^{-3} K

Also can be ~ 10^{+3} K

-- Can cause change in volume by ~ 15% (Ce)

In every case there are also high energy scales – band widths – exchange energies – multiplet energies --

Electronic Temperature scales

Why is it difficult to treat electronic states in "real materials" at non-zero T ?

Difficult to carry out trace --- $Z = Tr \exp(- \beta H)$

Feasible for small number of states

Applies to a "real material" only if one can establish that a small number of states is relevant for the interesting properties

Questions for audience

Low energy excitations in magnetic system

Magnetic moments form on atomic sites – disordered at high temperature

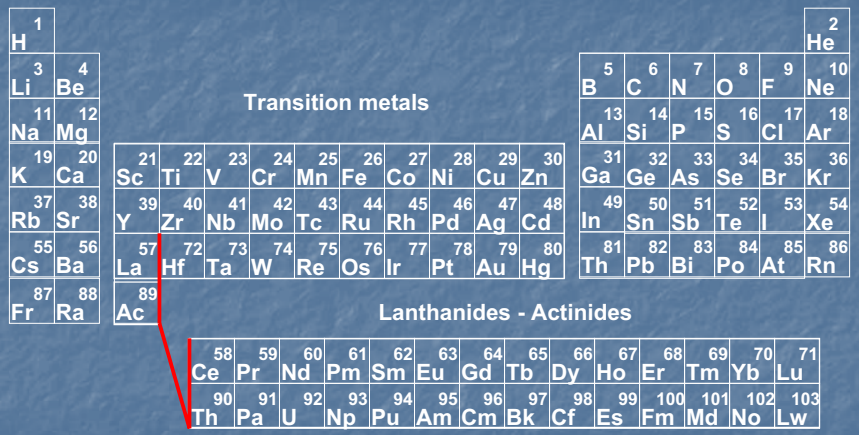
Moments order at a critical temperature to form magnetic order

Ferromagnet

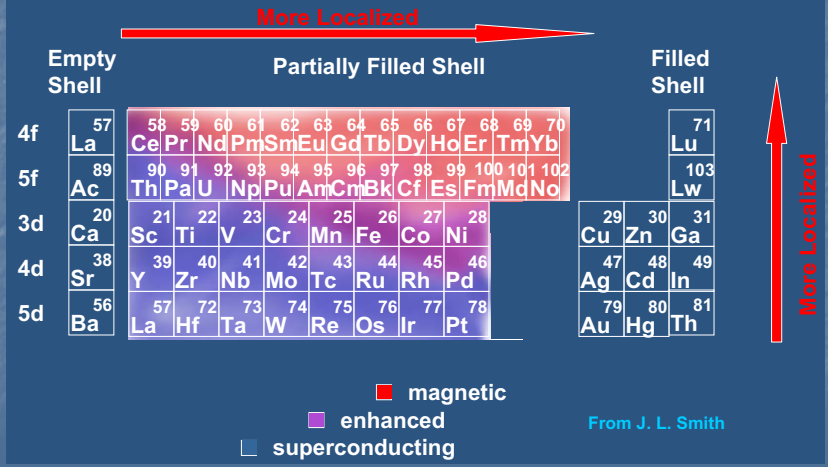
Antiferromagnet

Model: Heisenberg Spin Model – appropriate for Lanthanides – reasonable for 3d transition metals (Fe, Ni, …)

Periodic Table

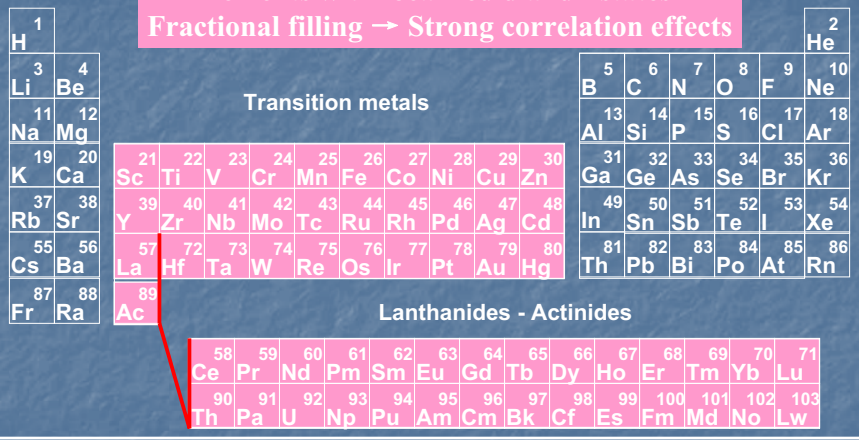


Transition & Rare Earth Elements



Periodic Table

Elements with localized d and f states
Fractional filling → Strong correlation effects



Need method to treat strong correlation on each atom
and
Correlation between sites that determines order, phase transitions, …

What is "U" in "LDA + U"

How to treat the localized states?

Selection of a few orbitals

Partially filled --- "Open Shell"

Two energy scale -- strong interactions -- U

low energy excitations -- magnetic moments

U is a screened interaction – must be determined

Is the resulting problem unique?

No! – depends upon choice of the localized state

Reasonable choices give reasonable, useful results

This is the problem in making LDA+U quantitative

Impotant – the same problem limits other methods such as DMFT discussed later!

LDA+U

In LDA + U the system is treated as ordered
Assumes the system is ordered – e.g., antiferromagnetic order

This is correct for T=0
very valuable results – e,.g., correcting the usual density functionals (like LDA) which often predict a metal when the correct state is an ordered antiferromagnetic insulator.

What about disordered states?

Characteristic issues and applications

What about "U" in disordered` states at high temperature?

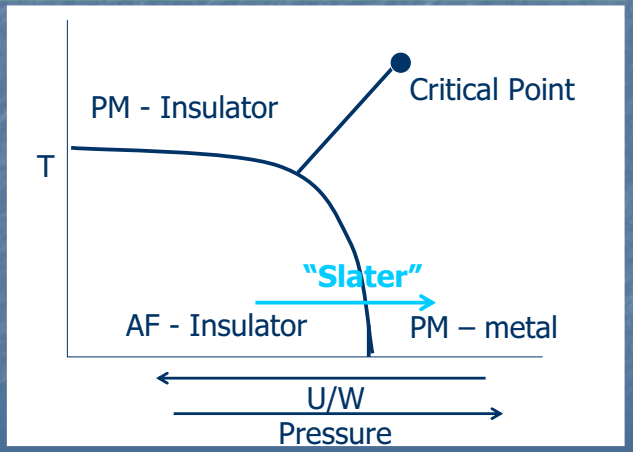
U does not go away with disorder
Large energy scale
Determined by atomic properties

This is where DMFT provides a systematic approach

Starting from High T and working down!

Metal-Insulator Transition

Classic Case --- V_2O_3



Bottom Up

Metal-Insulator Transition

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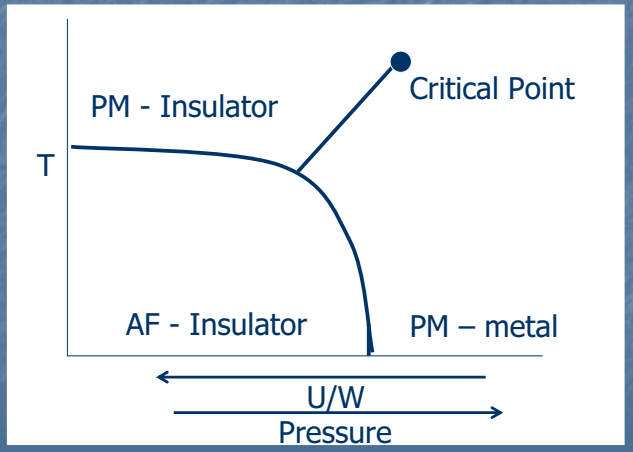

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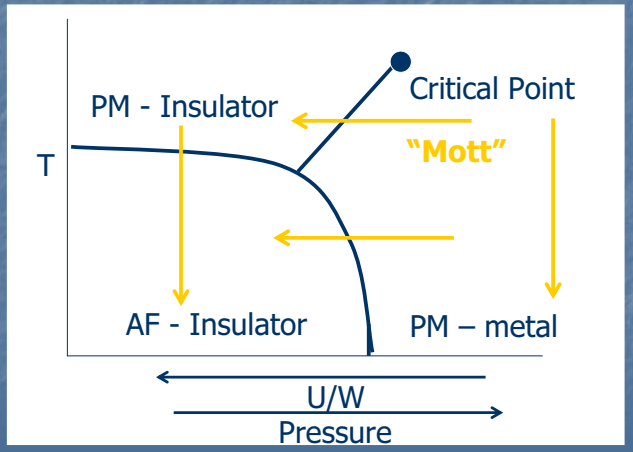

Top Down

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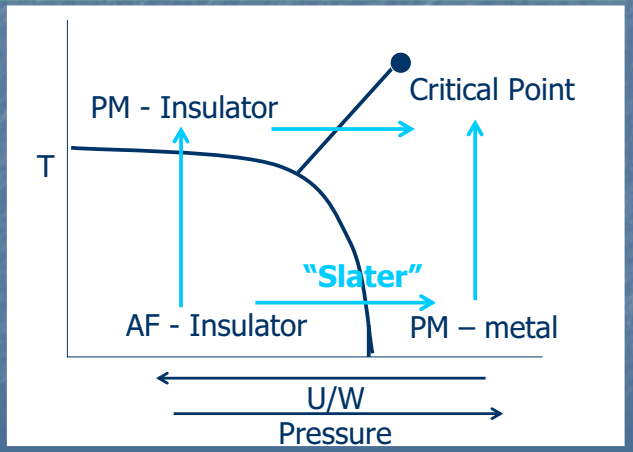
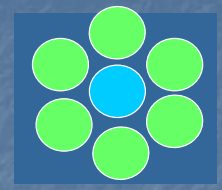


Bottom Up

How to treat Correlation?

- **Atom in a "bath" of surrounding atoms**
  - Treat correlation on central atom
  - Treat bath as independent electrons
- **Old idea** – solve for one atom with some method of averaging over the environment



- **Curie-Weiss Mean field for magnetism**
- Applied idea for spins in a mean field that is the thermal average of neighboring spins -- each spin is in a "bath' that is an average effect on the spin
- Increased correlation as T is decreased – leads` to a phase transition at some T (Must have ordered` structure at T=0 to have zero entropy)

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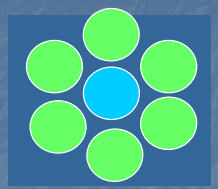


• Gutzwiller – Hubbard – 1960's

- Applied idea at T=0 ---- open shell systems
- Correlation included in a clever way –
  Each atom treated as strongly correlated
  Assume no correlation with surrounding atoms
- Kinetic energy - W – reduced due to restriction of hopping by the price of the repulsive interactions

•Metal-insulator transition (bootstrap effect)

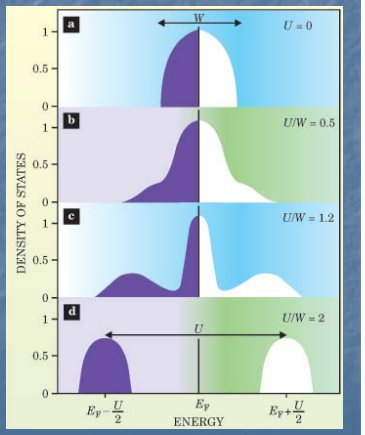
Characteristic energy scales shown by spectra of electron excitations

Evolution with increasing interaction U:

•Top: Small U - Band-like spectrum
- **W ~ E_{Fermi} ~ 10 eV ~ 10^5 K**
  - **•Increases with pressure**

•Bottom: Large U >>W
- **•- Localized, correlated atom-like**
- **Two types of excitations**
- **High energy ~ U ~ 10 eV ~ 10^5 K**
  - **•Increases for more localized states**
- **Low energy magnetic ~J ~ 10^2 K**
  - **•Decreases for more localized states**

• Middle: Multiple energy scales
- **High energy ~ U ~ 10^5 K**
  - **•Increases for more localized states**
- **Intermediate ~ 10^{-3} K - 10^5 K**
  - **•Can vary over range – low to high**



Kotliar and Vollardt, Physics Today 2004

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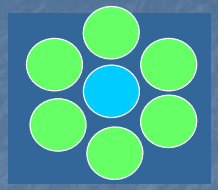


•Dynamical Mean Field Theory – 1980's - Present

- Applied idea at high T – decreasing to low T

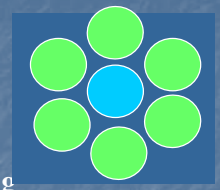
•Each atom treated as strongly correlated
Neglect of correlation with surrounding atoms – **Justified at high T**

- Kinetic energy - W – reduced … due to restriction of hopping –
  ---- **Treated by Self-Consistent Green's function**
- **Add correlation between sites as T decreases**
- **Phase Transitions -- Metal-insulator transition, magnetism, …..**

Dynamical Mean Field Theory

•Basic idea – Exact calculation for local system In presence of "dynamical mean field"

- **What is dynamical?**
  - **•Electrons can enter and leave site**
  - **•Dynamics comes from the dependence upon the time difference for entering, leaving**
  - **•Spectra of the site – which can be calculated exactly (or to a good approximation) Easier at high T !**

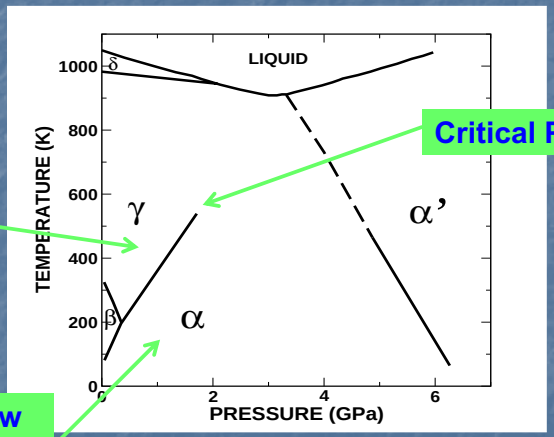


•But in a crystal the bath is due to other atoms that are the same as the central atom

•DMFT results from the requirement that the spectrum of the bath are consistent with spectrum of the site

- •The limitation is that correlations between sites are ignored
- •These can be included using clusters - expensive in computer time!

Phase Diagram
Anomalous Lanthanide -- Ce



Critical Point

γ - High volume

α - Low volume

15% volume change at low T!
No change in symmetry – fcc metals

Electronic Spectrum
Anomalous Lanthanide -- Ce

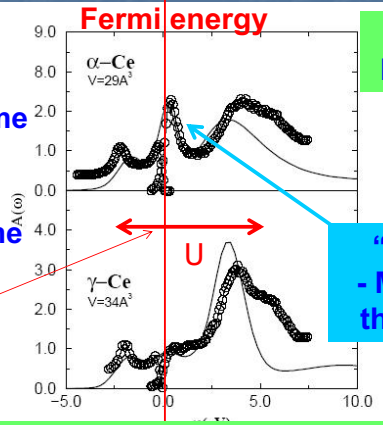
Fermi energy

Photoemission

Inverse Photoemission

Low volume

High volume



Split bands due to interaction U - Much wider than DFT bands

"Kondo" peak - Much narrower than DFT bands

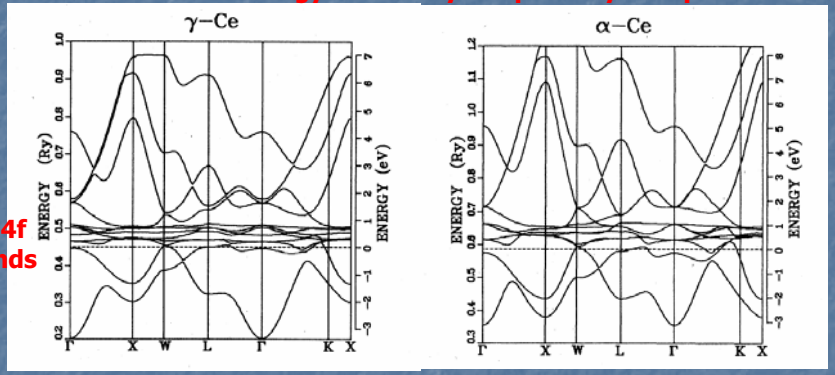
Cannot be explained by the usual KS theory
"LDA + DMFT" calculation explains:
Phase diagram, Driven by entropy of moments at high T,
Electronic spectrum

McMahan, et al., 2005

Calculated Bands of Ce
Local Density Approximation

There are 7 4f bands (not counting spin. The 4f bands MUST be at the Fermi energy since they are partially occupied

14 4f bands

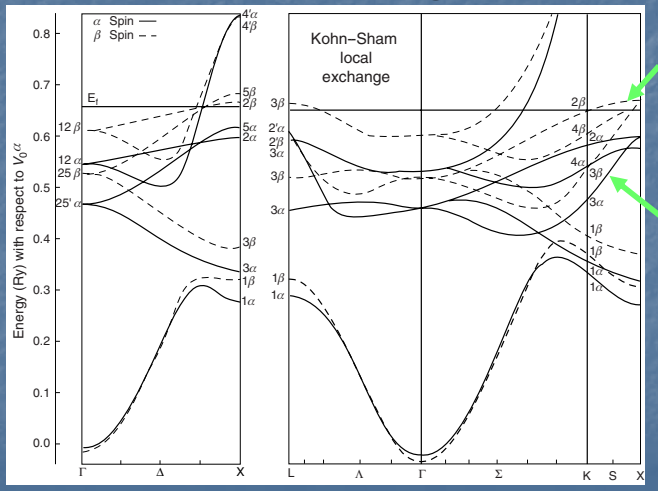


Large volume Gamma phase -- Magnetic (experimental fact)

Low volume Alpha phase Non-magnetic (experimental fact)

From: W. E. Pickett, et al., PRB 23, 1266 (1981).

T=0 Approach -- Spin polarized bands in ordered magnetic state - Ni



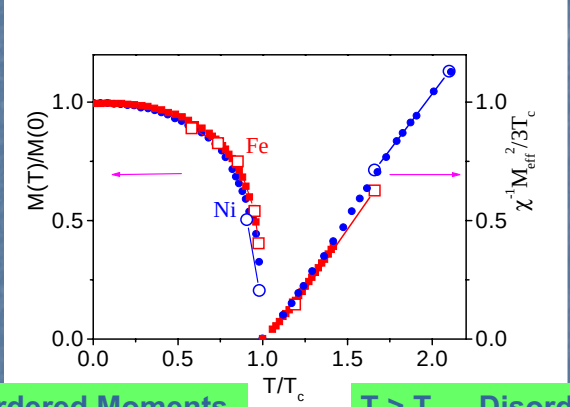
Spin down

~ 1.5 eV

Spin up

What happens for T > Tc – where spin polarization = 0 ?

T≠0 -- Magnetism of Fe and Ni calculated from electronic structure theory



T < T_c -- Ordered Moments
T=0 Moment scaled to DFT
Close to experiment

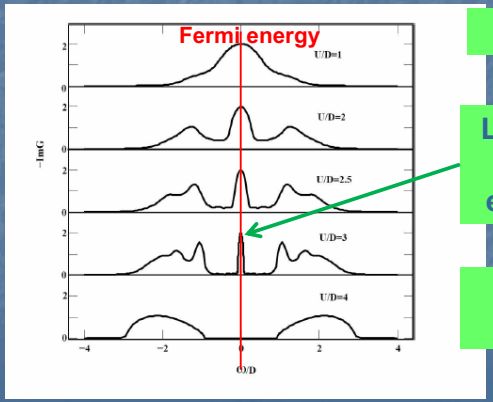
T > T_c -- Disordered Local Moments
Curie-Weiss $\chi^{-1} \sim (T - T_c)$

"LDA + DMFT" calculations

Lichtenstein, et al., 2001

The problem in making DMFT quantitative U is not uniquely defined!

Simple model for bands - half-filled - D = band width
for independent electrons – U = interaction



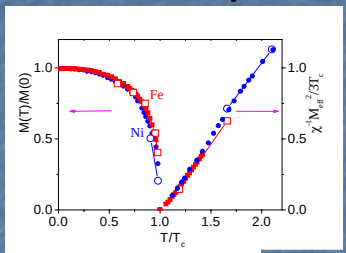
U=0 metal

Low energy spin excitations

Large U insulator

Magnetism of Fe and Ni calculated from electronic structure theory

Quantitative successes:
Ordered Moment
Local Moments at high T



What about T_c ?

	Calculated	E
Ni	700	
Fe	1900	1031

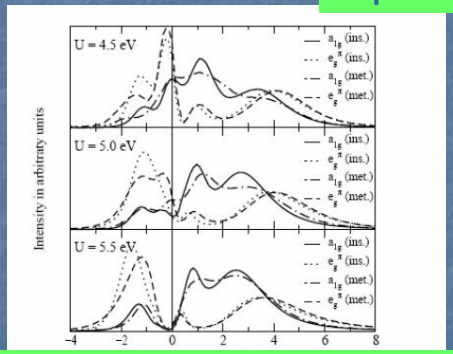
Why is Fe off so much?
Spin wave fluctuations reduce T_c in Fe – not taken into account by the localized calculation

Lichtenstein, et al., 2001

Metal insulator transition Qualittative explanation from DMFT

SrVO3
Meat or insulator?

Photoemission clearly shows correlation effects – peak at Fermi energy



"LDA + DMFT" calculations --- the results are very sensitive to the value of U!

Lichtenstein, et al., 2001

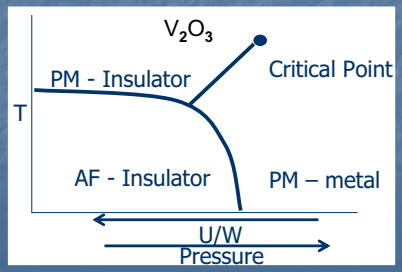
Electronic Structure
The big picture

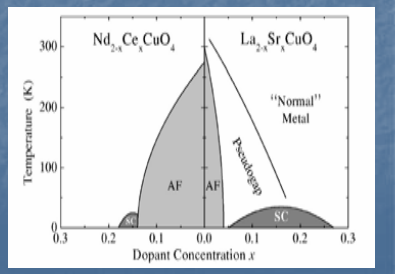
- Starting from Low T or high T:

•The limits – small U/W, large U/W - are relatively straightforward to understand and to treat

• The intermediate cases – "strongly correlated" – multiple energy scales -- are the great challenges

"Classic" examples





Conclusions

- Starting from Low T or high T
- **Low T approach completely justified in many cases**
  - **Si – no electronic excitations below 1.1 eV ~10,000K**
  - **Phonons are the important excitations – use T=0 phonons to calculate specific heat – hard problem at melting requires high T approach for atomic motion**
- High T approach completely justified in many cases
  - Magnetism at temperature ~ Curie temperature limits
  - "Kondo effect" – low energy crossover from zero entropy state at T=0 to thermally fluctuating spins at T>TK that is often very low ~ 1-10 K