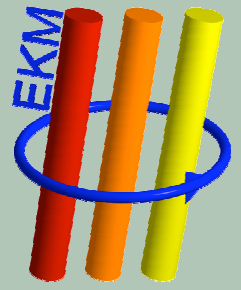
Fluctuating valence and valence transition in Yb



J. Kuneš

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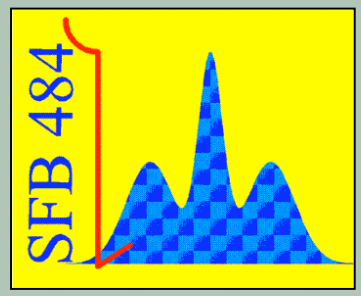


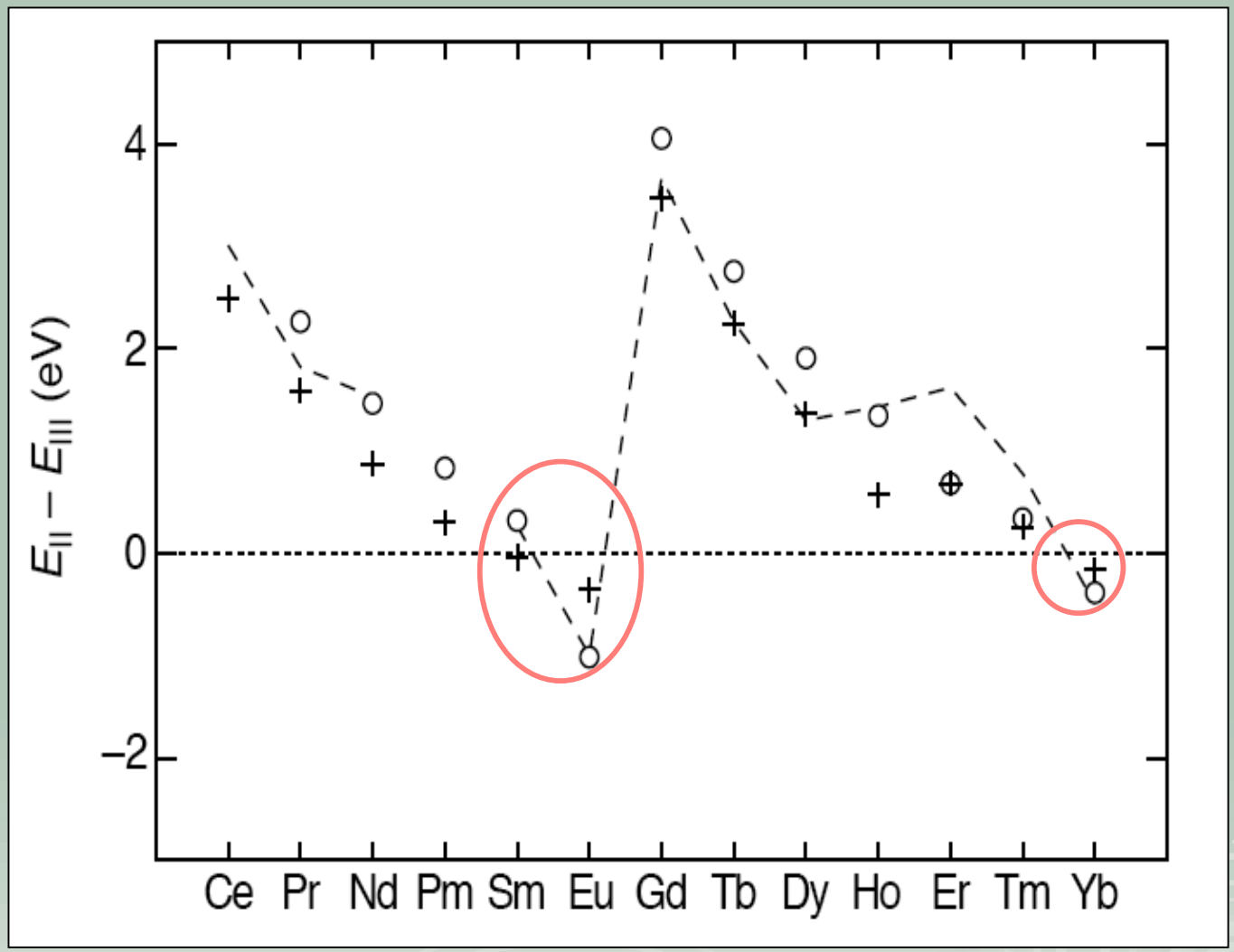
in collaboration with:

W.E. Pickett, E.R. Ylvisaker *UC Davis*

A.K. McMahan *Lawrence Livermore Nat. Lab.*

special thanks to P. Werner

Valence across the rare earth series



*Strange et al., Nature **399**, 756 (1999)*

Outline

- Motivation - fluctuating vs intermediate valence
- Elemental Yb - experimental overview
- DMFT results & discussion:

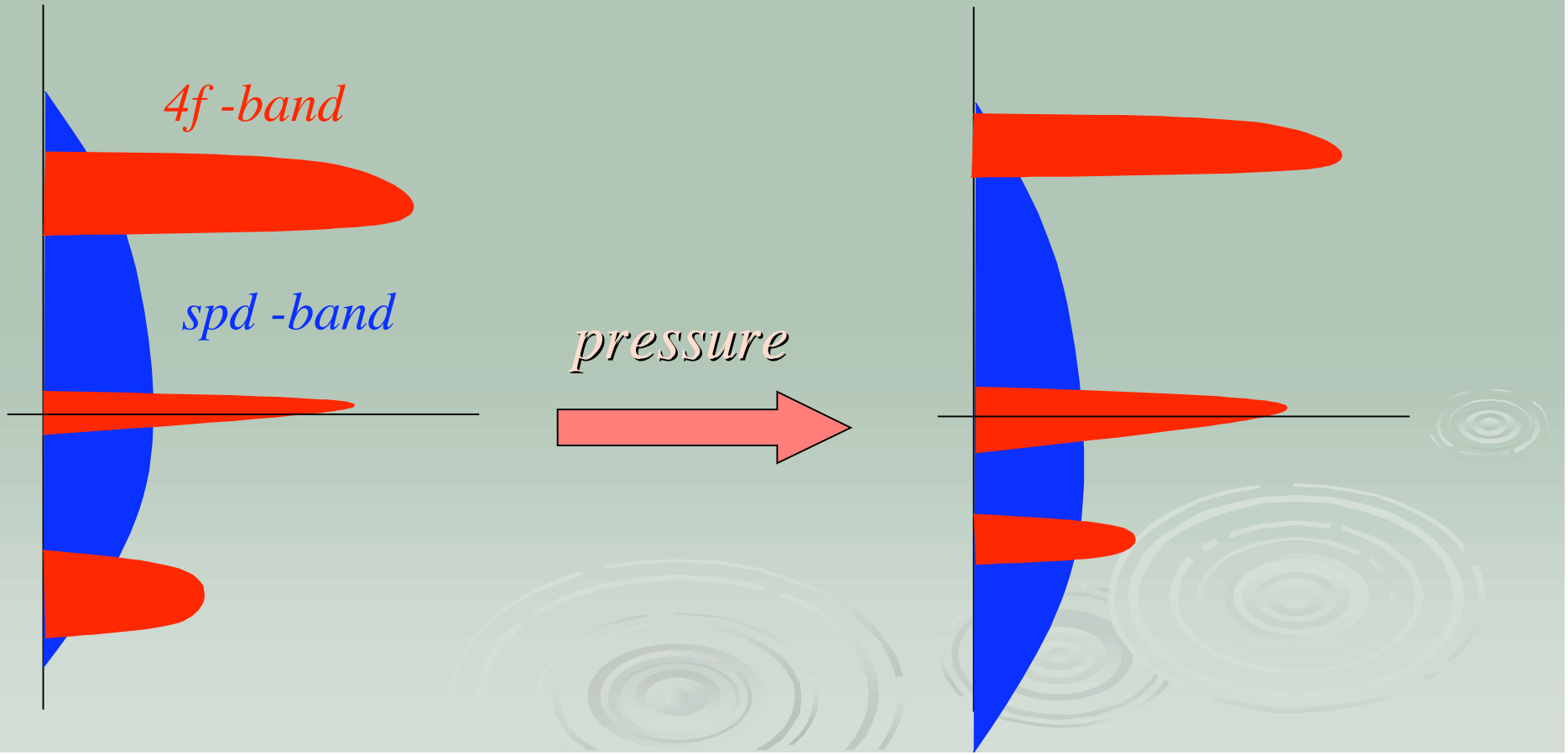
  f-shell occupancy

  single-particle spectrum

  local charge susceptibility

4f - metal typical situation

- single local (*4f*) groundstate
- pressure -> increased *f-spd* hybridization
  relative band shifts

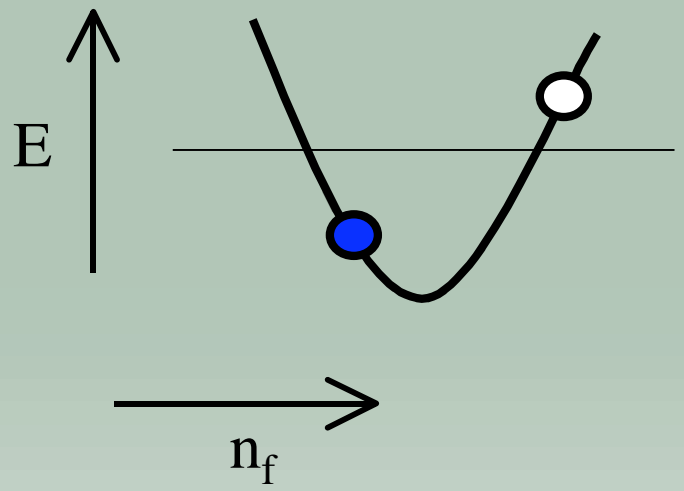


Degenerate charge states

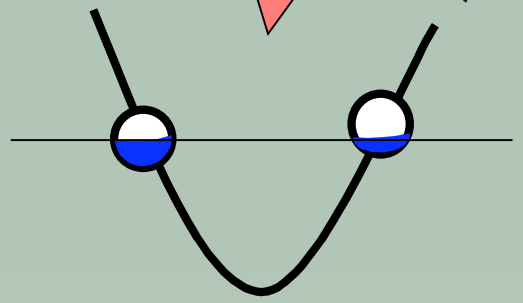
Atom in equilibrium with particle/energy reservoir:

$E(n_f) = (\varepsilon_f - \mu)n_f + Un_f(n_f-1)/2$

E - non-monotonous

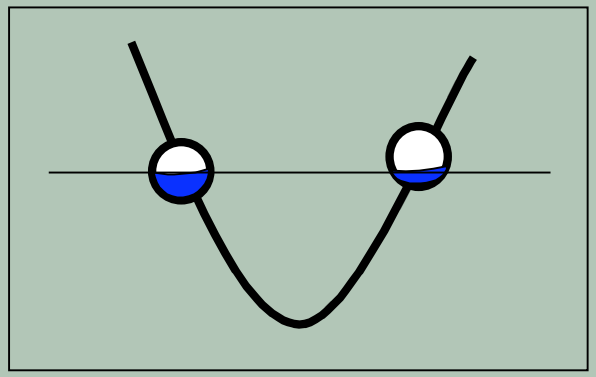


Single valence state



Degenerate states of different valence

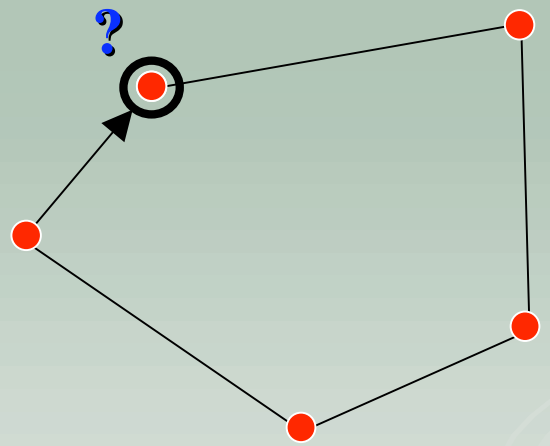
Fluctuating vs intermediate valence



non-integer $\langle n_f \rangle$ =>

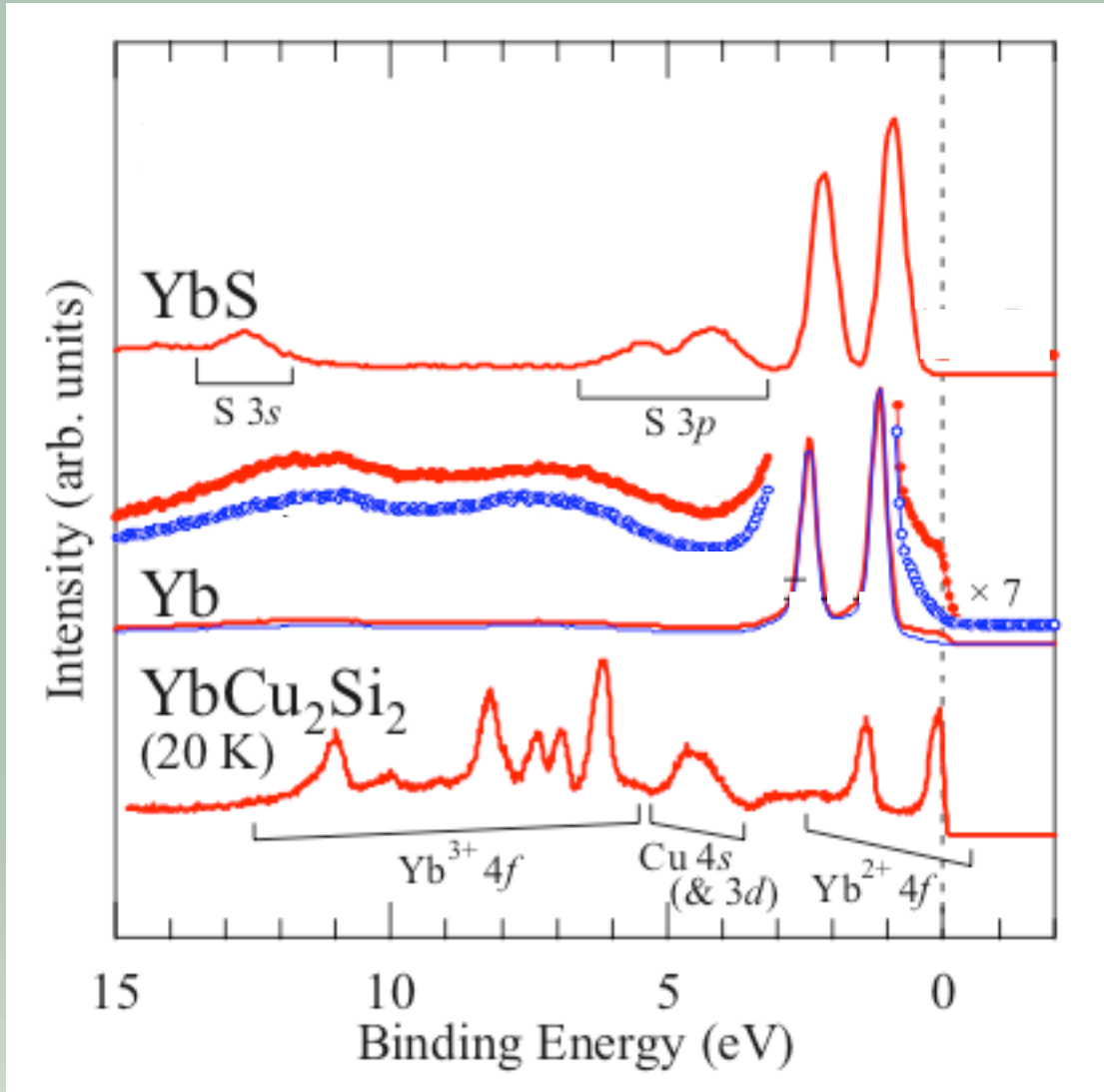
local charge fluctuations

Explicit coupling to the bath:



Coherent	intermediate valence
?	
Incoherent	fluctuating valence

Yb in compounds - different valence states

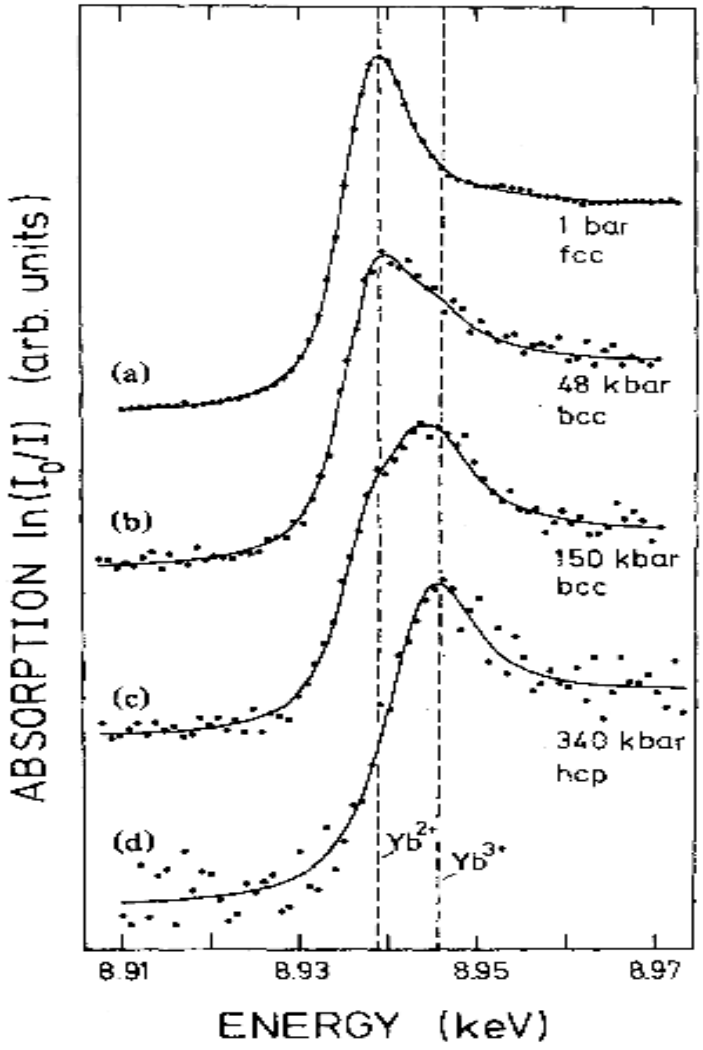


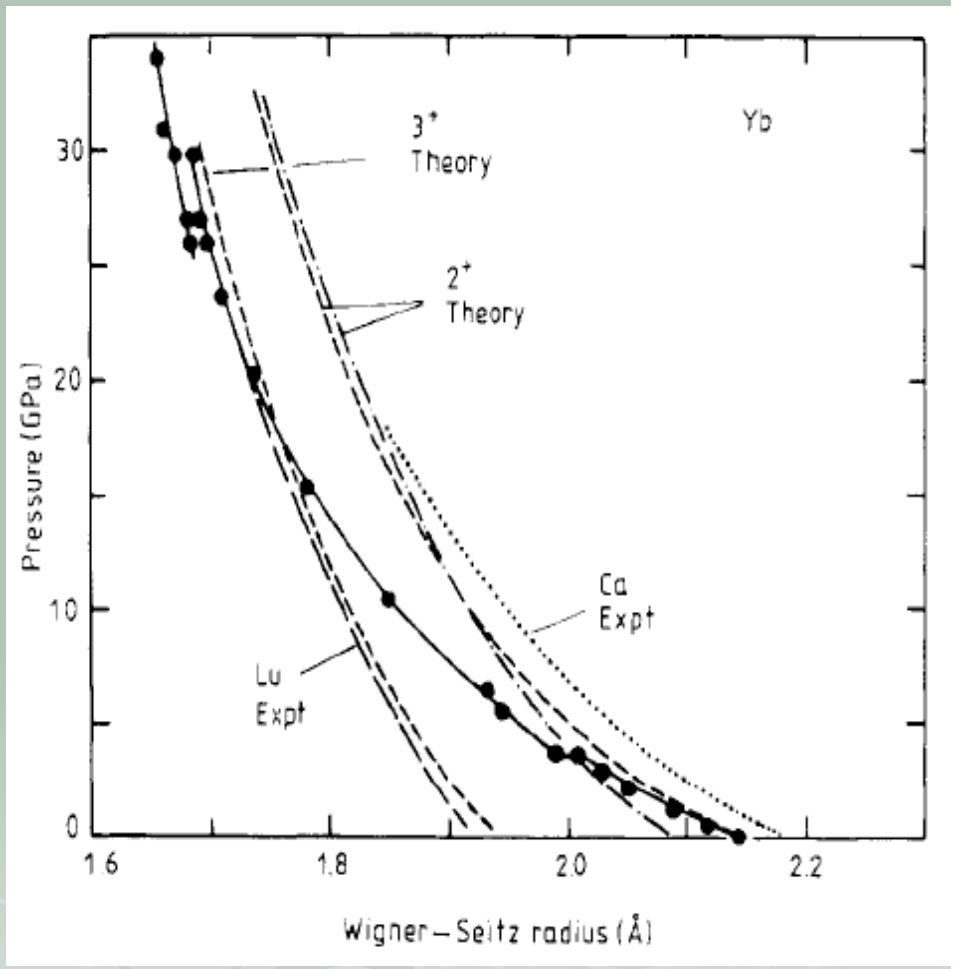
*Matsunami et al., Phys. Rev. B **78**, 195118 (2008)*

Yb valence transition under pressure

L_{III} edge x-ray absorption ($2p \rightarrow 5d,6s$)
*Syassen et al., Phys. Rev. B **26**, 4745 (1982)*

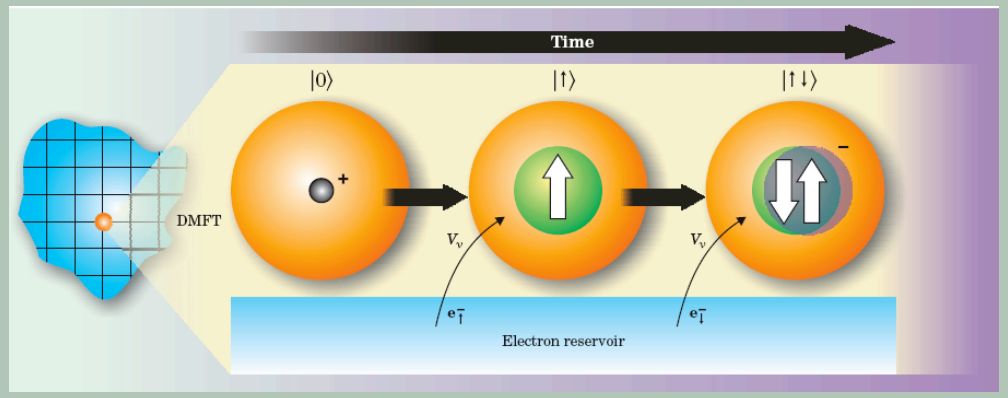
p-V curve
*Takemura & Syassen, J. Phys. F **15**, 543 (1985)*





Yb is softer than its chemical relatives.

Dynamical Mean-Field Theory



Kotliar &Vollhardt
Physics Today (March 2004)

*Georges et al. RMP **68**, 13 (1996)*

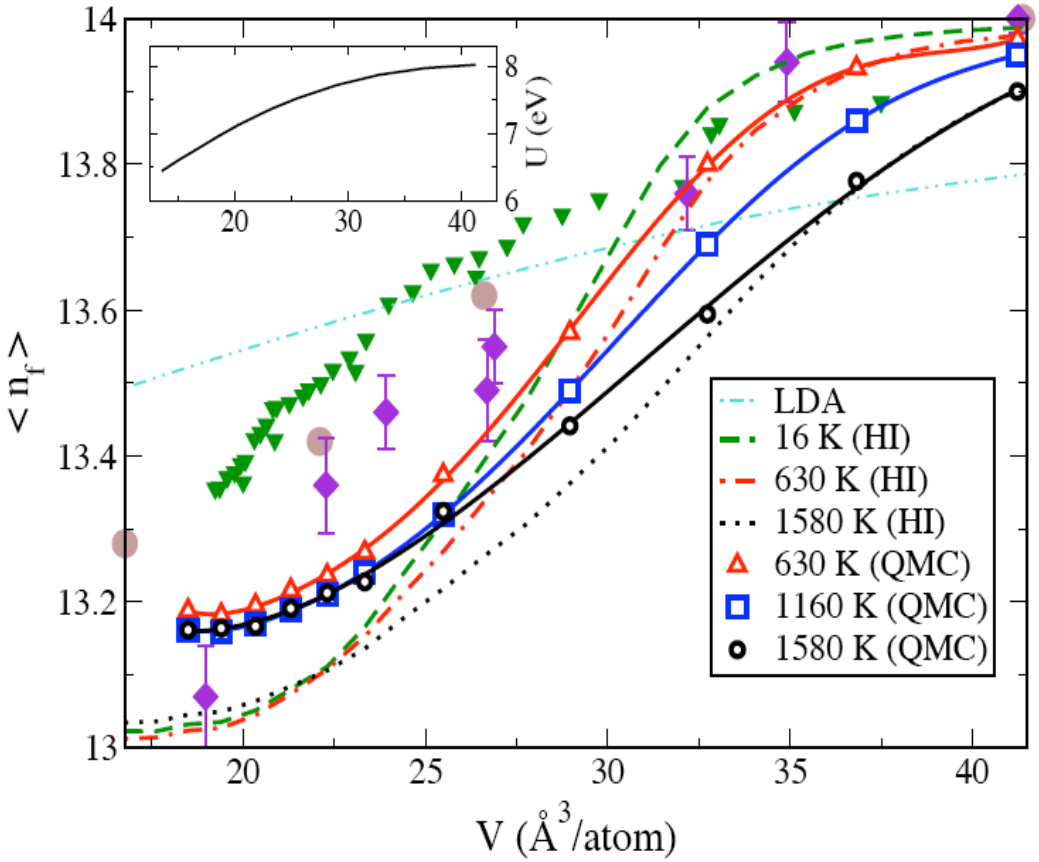
Computational details:

- *spdf* Wannier function basis (LMTO bandstructure code)
- spin-orbit coupling
- G_{local} and Σ only diagonal terms in jj-basis
- SU(N) symmetric interaction $U \sum n_i n_j$
- CT-QMC (hybridzation expansion), Hirsch-Fye and Hubbard I impurity solvers

Valence transition - *4f* occupancy

Change of $\langle n_f \rangle$ with specific volume

(not a transition in thermodynamic sense)



Three imputity solvers:

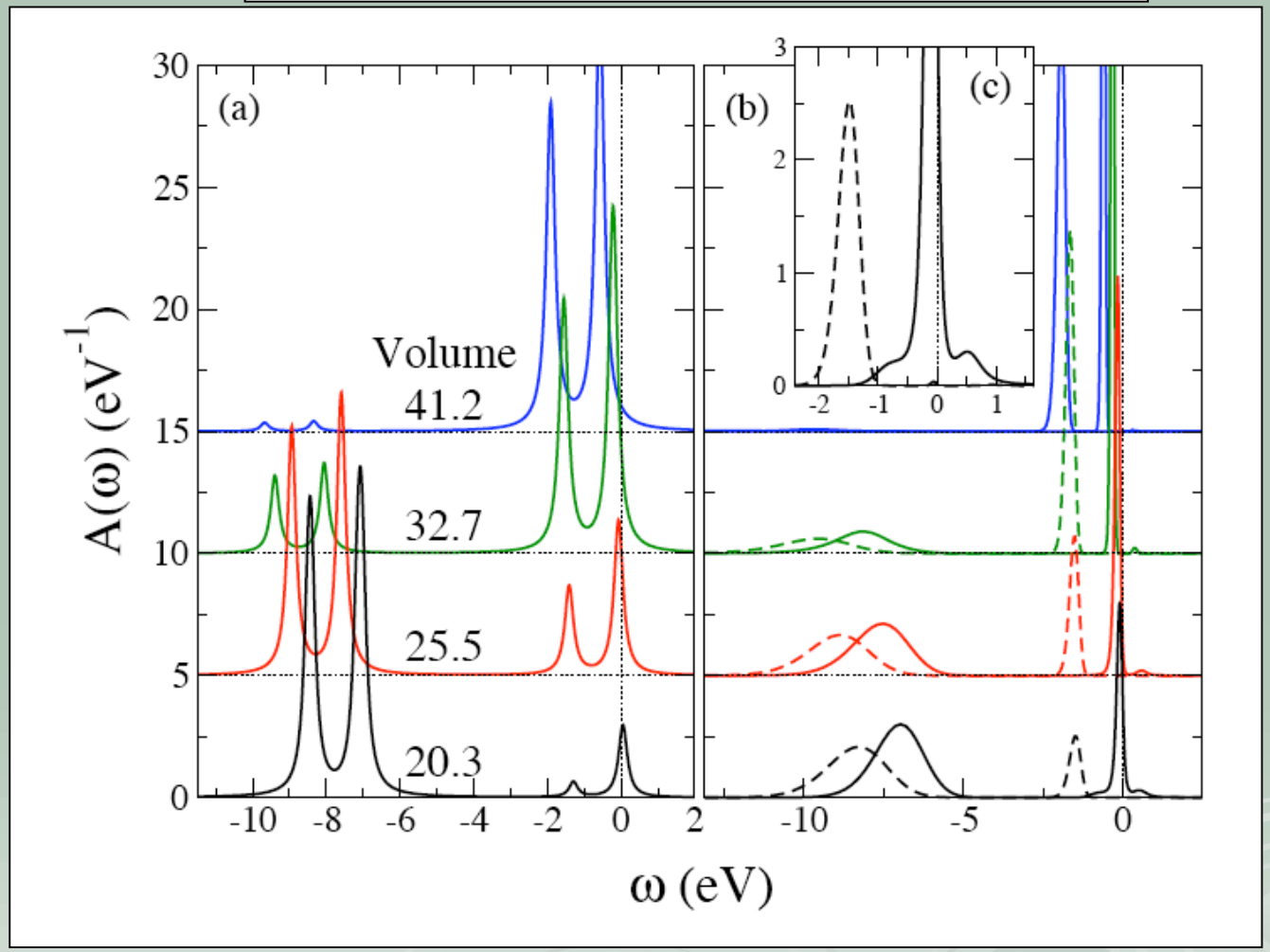
1) Hubbard I (HI) - atomic limit

2) CT-QMC

3) Hirsch-Fye QMC

Valence transition - single-particle spectra

Hubbard I CT-QMC

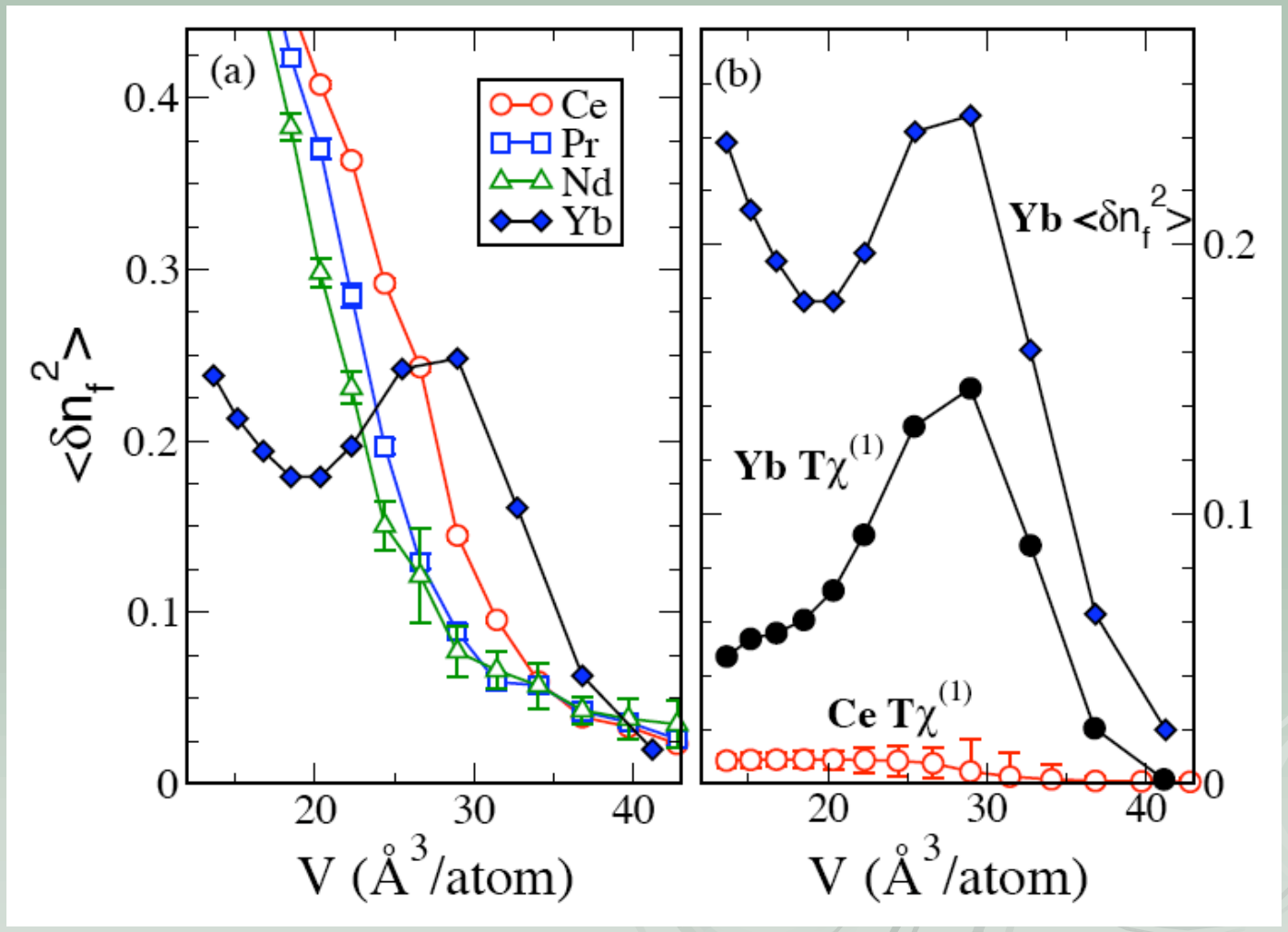


Gradual change of relative weights of f^{13} and f^{14} valence states.

Charge fluctuations in the *4f* shell

$\langle \delta n_f^2 \rangle = \langle n_f^2 \rangle - \langle n_f \rangle^2$

Local charge susceptibility $\chi^{(1)} = \partial \langle n_f \rangle / \partial V_i$



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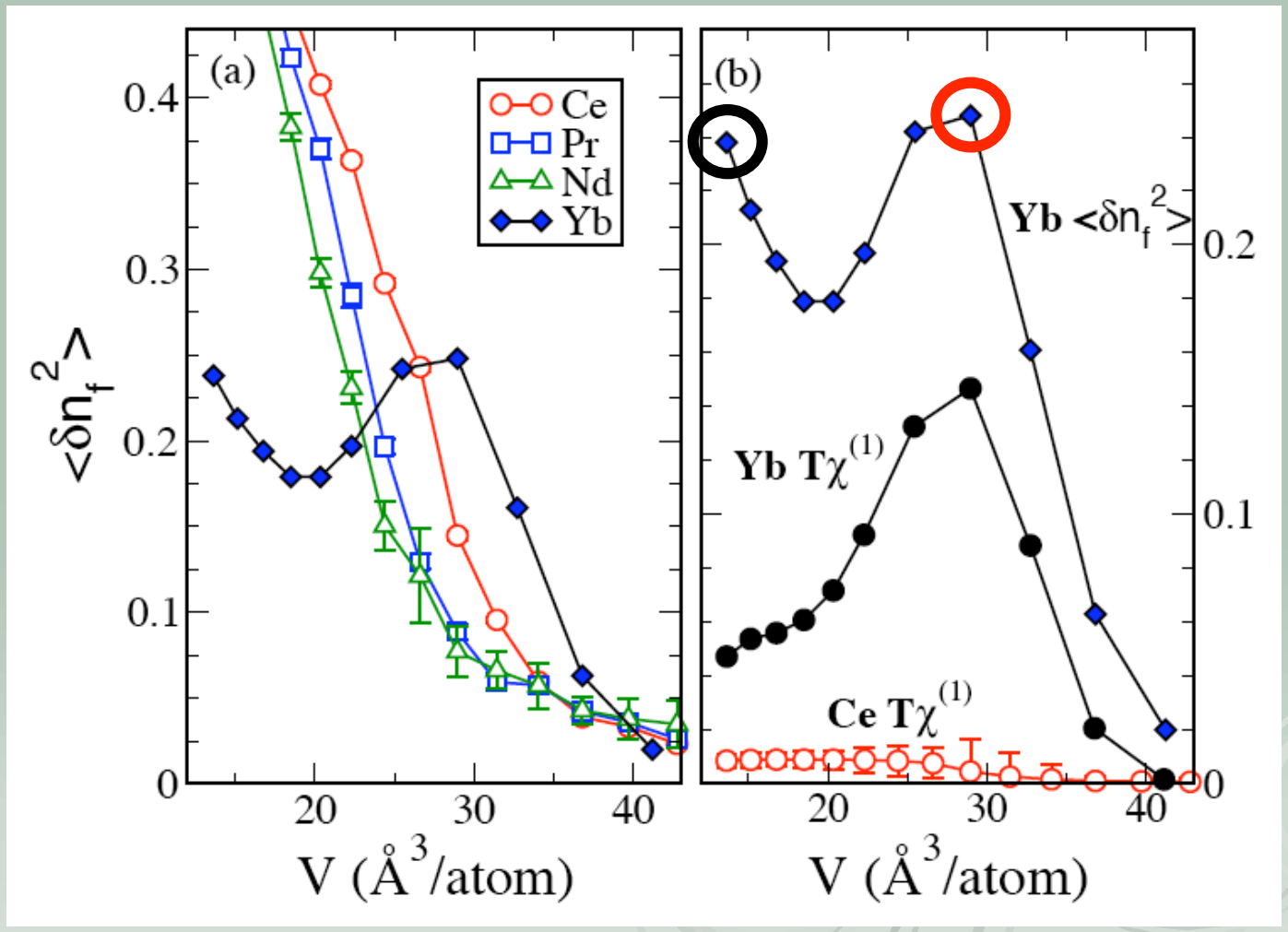
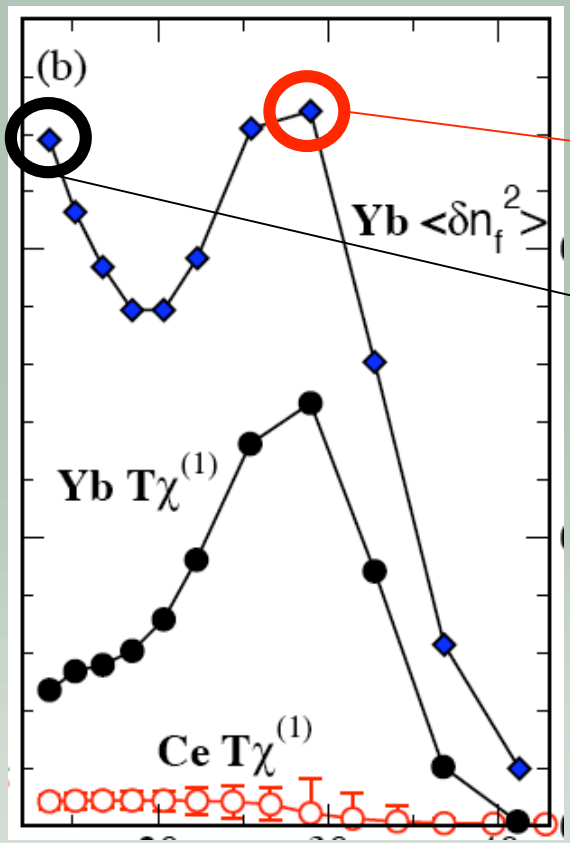
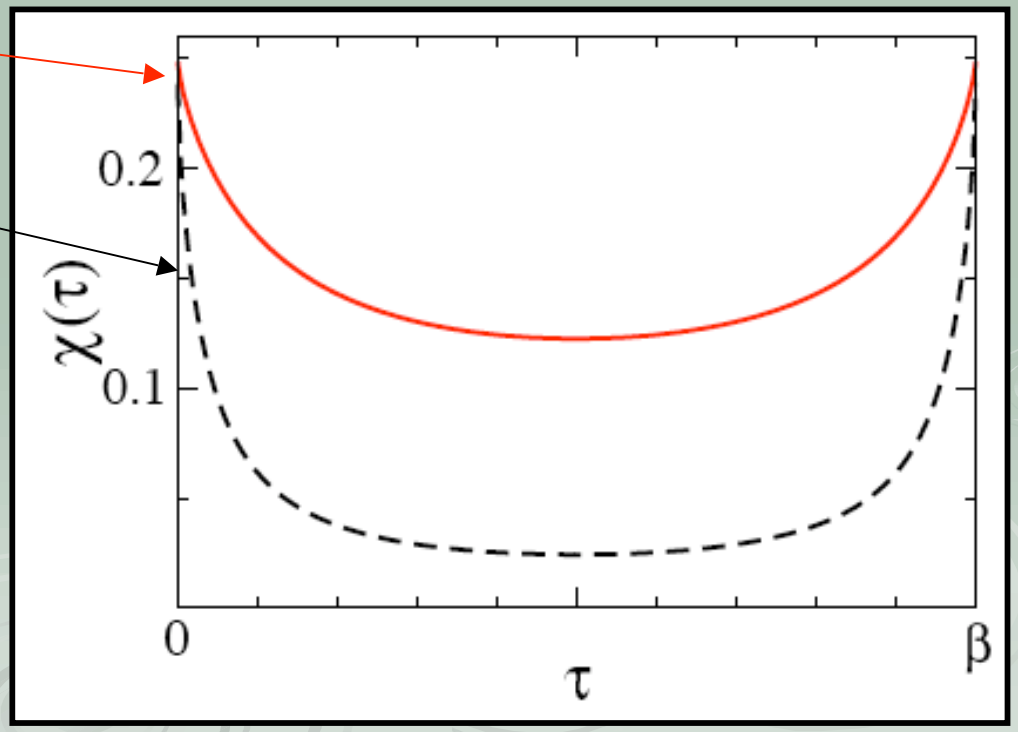


Local charge susceptibility (static)

τ charge-charge correlation function:
$\chi_{ff}(\tau) = \langle n_f(\tau) n_f(0) \rangle - \langle n_f \rangle^2$

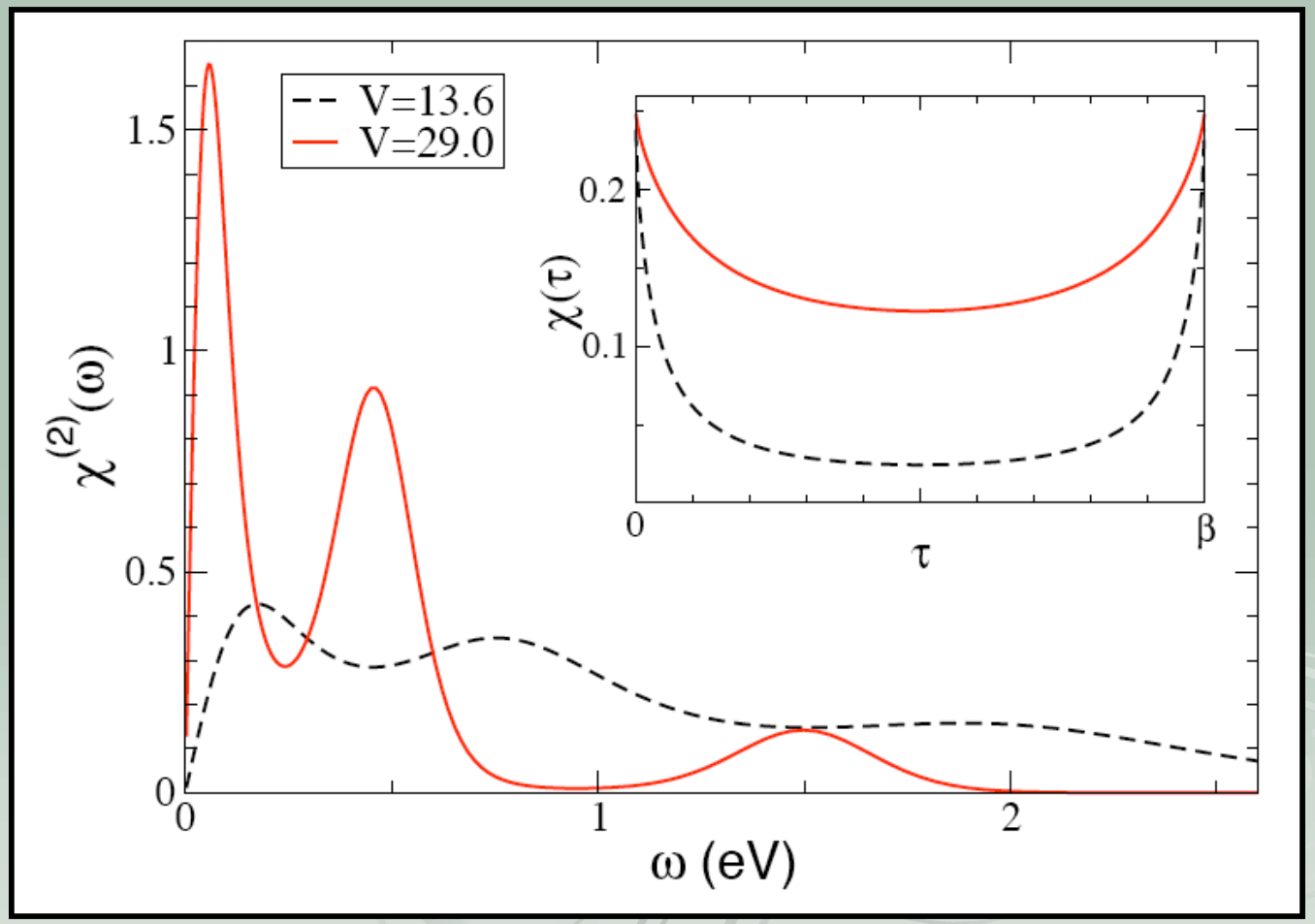
Local charge susceptibility:
$\chi^{(1)} = \int d\tau \, \chi_{ff}(\tau)$



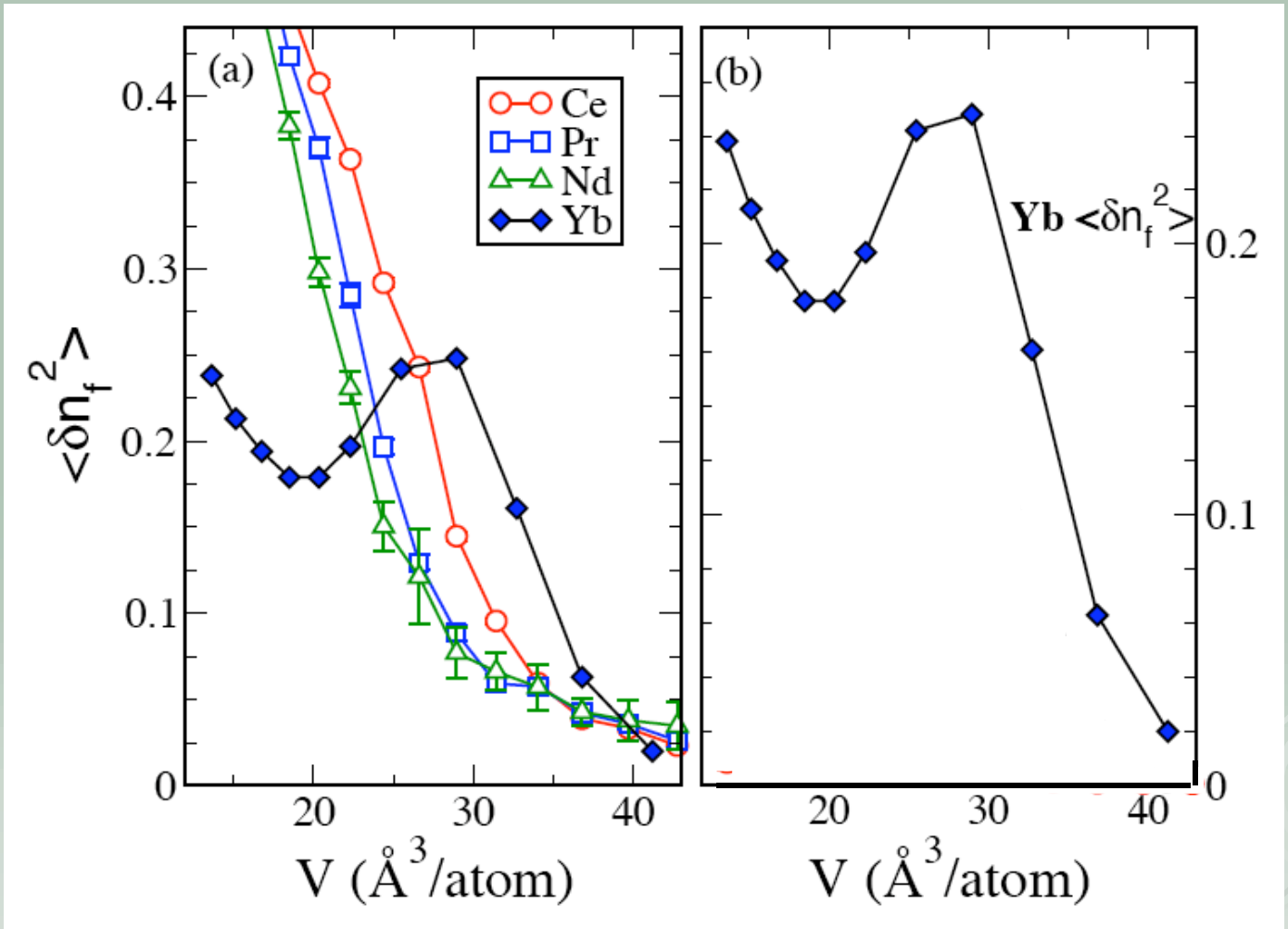


Local charge susceptibility (dynamic)

Dynamical susceptibility:
$\chi_{ff}(\tau)$ - analytic continuation $\rightarrow \chi^{(2)}(\omega)$

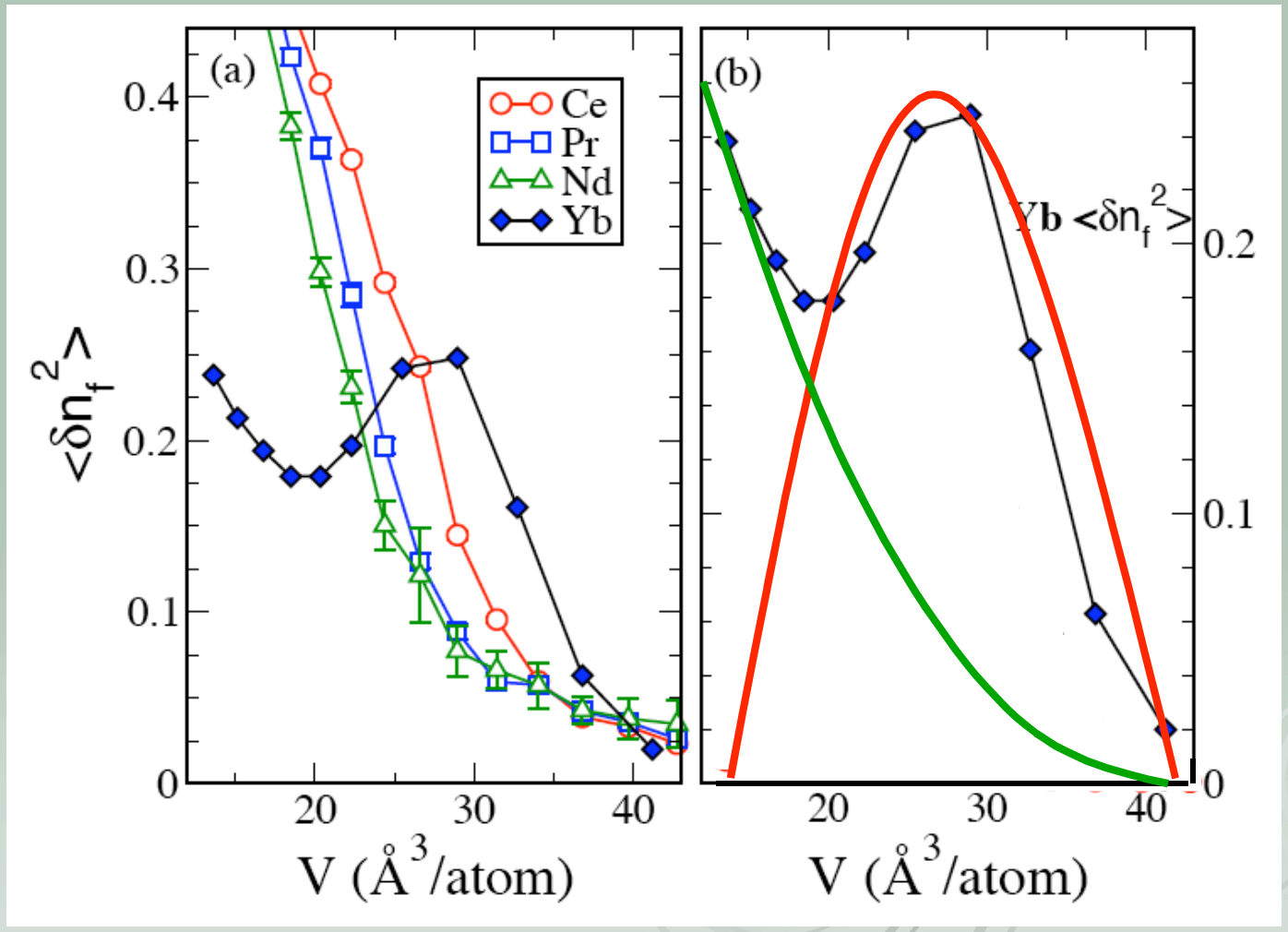


Yb summary


(a)
Ce
Pr
Nd
Yb
0.4
0.3
0.2
0.1
0
20
30
40
V (Å^3/atom)
$\langle \delta n_f^2 \rangle$
(b)
Yb $\langle \delta n_f^2 \rangle$
0.2
0.1
0
20
30
40
V (Å^3/atom)

Yb summary

- incoherent atomic physics - variable chem. potential
- coherent formation of a narrow quasi-particle band



Conclusions

- Charge susceptibility provides a tool to distinguish intermediate and fluctuating valence systems

- Fluctuating valence behavior -> large charge susceptibility leads to unusually low bulk modulus of Yb

- DMFT can capture the smooth crossover between different valence states as well as departure from fluctuating towards intermediate valence behavior.

*Ylvisaker, JK, McMahan, and Pickett PRL **102**, 246401 (2009)*