Realistic Theories of Correlated Electron Materials

Kavli Institute for Theoretical Physics
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Correlation Effects in the Compressed Rare Earth Metals

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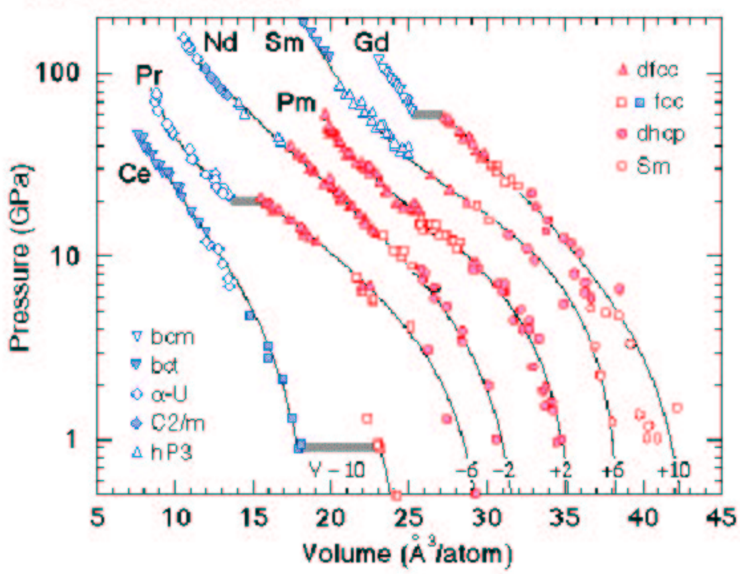
A. K. McMahan, C. Huscroft, R. T. Scalettar, and E. L. Pollock, J. Comput.-Aided Mater. Design 5, 131 (1998).

K. Held, A.K. McMahan, and R.T. Scalettar, Phys. Rev. Lett. **87**, 276404 (2001).

A.K. McMahan, K. Held, and R.T. Scalettar, cond-mat/0208443.

Volume collapse transitions in the rare earth metals

Unusually large volume changes (shaded) — Ce (15%), Pr (9%), Gd (11%) — believed to be driven by change in f electron-electron correlation. This talk reviews recent theoretical efforts to calculate these transitions.



low symmetry, suggests f bonding

↑

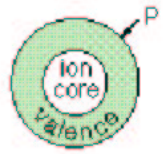
Mott trans.[1] ? | Kondo vol. Collapse[2] ?

close-packed, high symm., seen in non-f metals (Y)

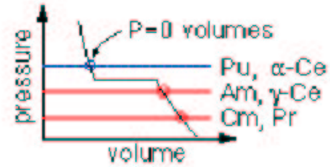
expt: LLNL, Paderborn, U. Ala., Karlsruhe, Carnegie,...

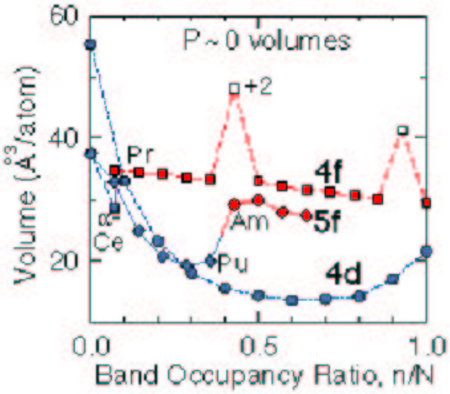
[1]Johansson (74) [2]Allen-Martin (82); Lavagna et. al. (82)

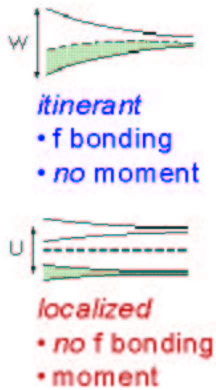
Insights from 1 atm (P ~0) and from mean field

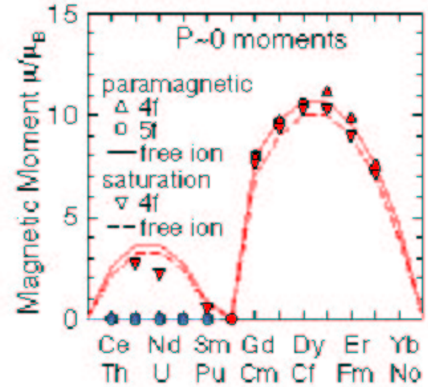


P fixed Z ↔ Z fixed P
(Johansson-Rosengren, 75)









$$\Delta E_W = \int^{\mu} d\varepsilon\, \varepsilon\, D(\varepsilon) - n\,\varepsilon_{\text{atom}} = -\tfrac{1}{2} W N \tfrac{n}{N}\left(1-\tfrac{n}{N}\right)$$

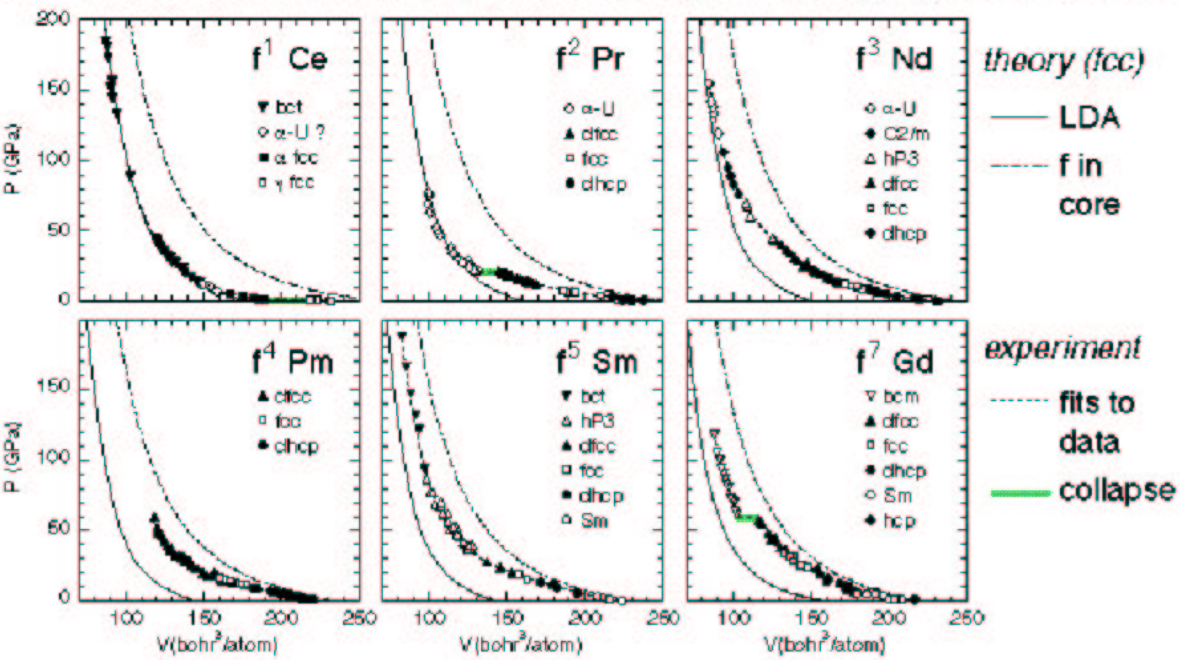
versus

$$\Delta E_U = \left\langle \tfrac{1}{2} U \hat{n}_f (\hat{n}_f - 1) \right\rangle_{HF} - \tfrac{1}{2} U n_f (n_f - 1) = \tfrac{1}{2} U \sum_{\alpha} n_\alpha (1 - n_\alpha)$$

n_α = eigenvalues of $[\langle f^{\dagger}_{m\sigma} f_{m'\sigma'} \rangle]$

How correct is this mean field picture?

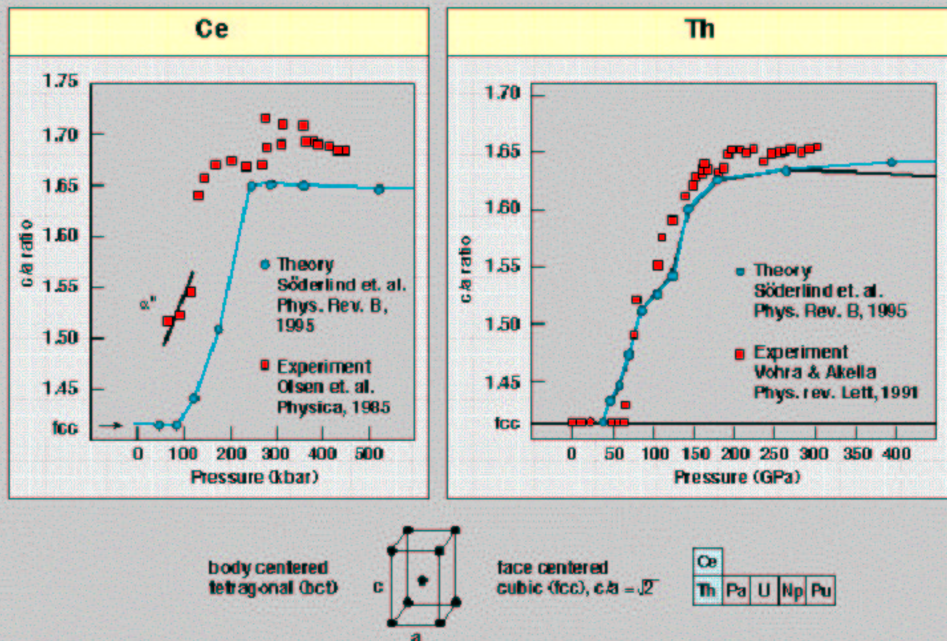
RE's well described by LDA at high enough pressure



- **Ce, Pr, Nd (no collapse!) have reached this point, but not Gd**
- **Continuous phenomenon, only sometimes with volume collapse?**

Exp't: [Ce] Olsen et.al. (85), Vohra et.al. (99); [Pr] Mao et.al. (82), Smith-Akella (82), Grosshans-Holzapfel (84), Hamaya et.al. (93), Yoo et.al. (00); [Nd] Grosshans (87), Akella et.al. (99), Chesnut-Vohra (00); [Pm] Haire et.al. (90); [Sm] Olsen et.al. (90), Vohra et.al. (91), Zhao et.al. (94); [Gd] Akella et.al. (88), Hua et.al. (98)

DFT predictions for fcc → bct transitions in Ce and Th



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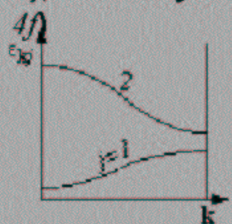
Mean field vs. correlated treatment of electrons

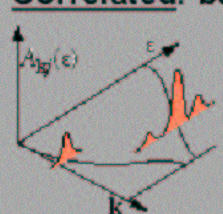
<u>(Static) Mean field</u>: sharp dispersion (energy ε vs. crystal momentum k); as many bands as orbitals per repeating cell (j=*1-16* for *6s, 6p, 5d, 4f*)



Hartree Fock (HF)
Local Density Approx. (LDA)
Self-interaction correction (SIC)
LDA+U, orbital polarization

spectral function
$A_{kj}(\varepsilon) = \delta(\varepsilon - \varepsilon_{kj})$
self energy
const. matrix $\ddot{\Sigma}$

<u>Correlated</u>: bands can have width or be multi-peaked



Configuration interaction
Quantum Monte Carlo (QMC)
Dynamical Mean Field Theory (DMFT), just local correlations, $\Sigma = \ddot{\Sigma}(i\omega)$

spectral function
has structure
self energy
$\Sigma = \ddot{\Sigma}_k(i\omega)$

LDA does well for small volume itinerant regime; correlated treatment imperative for collapse and large volume localized. Fully correlated treatment prohibitive, *<u>local</u>* correlations (DMFT) may be answer.

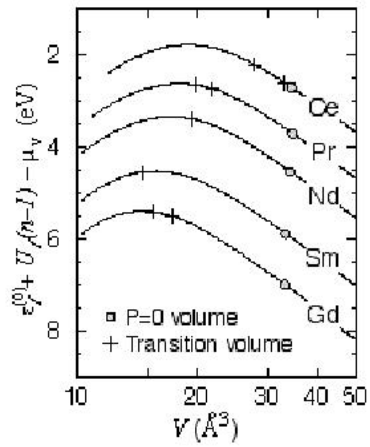
LDA part of LDA+DMFT: effective Hamiltonian

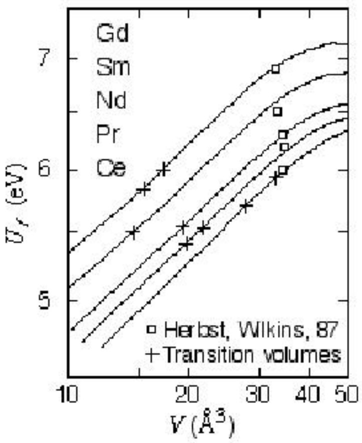
All-valence orbital effective Hamiltonian $(L = lm = 6s, 6p, 5d, 4f)$

$$H = \sum_{\mathbf{k},L,L',\sigma} h^{LDA}_{L,L'}(\mathbf{k}) c^{\dagger}_{\mathbf{k}L\sigma} c_{\mathbf{k}L'\sigma} + \sum_{\mathbf{k},m,\sigma} (\varepsilon_f^{(0)} - \varepsilon_f^{LDA}) c^{\dagger}_{\mathbf{k}fm\sigma} c_{\mathbf{k}fm\sigma} + \tfrac{1}{2} U_f \sum_{\mathbf{i}} \hat{n}_{\mathbf{i}f}(\hat{n}_{\mathbf{i}f} - 1)$$

$$\equiv \sum_{\mathbf{k},L,L',\sigma} h^{0}_{L,L'}(\mathbf{k}) c^{\dagger}_{\mathbf{k}L\sigma} c_{\mathbf{k}L'\sigma} + \tfrac{1}{2} U_f \sum_{\mathbf{i}} \hat{n}_{\mathbf{i}f}(\hat{n}_{\mathbf{i}f} - 1)$$

$h^{LDA}_{L,L'}(\mathbf{k})$ = orthogonalized 16x16 matrix at each $\mathbf{k}$ and each V, the one-electron Hamiltonian from self-consistent LDA calculations





$\varepsilon_f^{(0)}(V), U_f(V)$ from separate self-consistent constrained occupation LDA calculations

Dynamical Mean Field Theory (DMFT)

$\vec{G}_{\mathbf{k}}(i\omega) = [i\omega\vec{I} + \mu\vec{I} - \vec{h}^0(\mathbf{k}) - \Sigma(i\omega)\vec{I}_f]^{-1}$ lattice Green function (16x16 matrix)

$G_f^0(i\omega)^{-1} \equiv \left(\frac{1}{7N}\sum_{\mathbf{k}} Tr[\vec{G}_{\mathbf{k}}(i\omega)\vec{I}_f]\right)^{-1} + \Sigma(i\omega)$ bath Green function

$G_f^0(i\omega), U_f \Rightarrow$ { 7 orbital auxiliary impurity problem; Quantum Monte Carlo (QMC); Hubbard I (H-I), large V, hi T } $\Rightarrow G_f(i\omega)$

$\Sigma(i\omega) = G_f^0(i\omega)^{-1} - G_f(i\omega)^{-1}$ new self energy where $\hat{I}_f \equiv [\delta_{lf}\delta_{l'f}\delta_{mm'}]$

Approximations: scalar U_f; local and scalar $4f$ self energy Σ; no spin orbit yet

Thermodynamics (total energy, entropy)

$$E_{\mathrm{DMFT}}(T,V) = \frac{T}{N}\sum_{\mathbf{k}\sigma}\sum_n Tr[\vec{h}^0(\mathbf{k})\vec{G}_{\mathbf{k}}(i\omega_n)]e^{i\omega_n 0^+} + \frac{1}{2N} U_f \sum_{\mathbf{i}} \sum'_{m\sigma,m'\sigma'} \langle \hat{n}_{\mathbf{i}fm\sigma} \hat{n}_{\mathbf{i}fm'\sigma'} \rangle$$

$$S_{\mathrm{DMFT}}(T,V) = S(\infty,V) - \int_T^{\infty} dT \frac{1}{T} \frac{\partial E_{\mathrm{DMFT}}(T,V)}{\partial T}$$

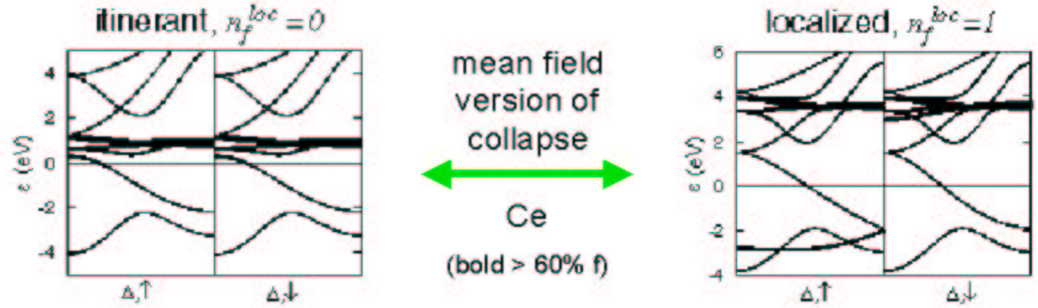
$$E_{tot}(T,V) = E_{\mathrm{LDA}}(V,T) + E_{\mathrm{DMFT}}(T,V) - E_{\mathrm{mLDA}}(V,T)$$

where E_{LDA} is the all-electron LDA energy, and E_{mLDA} ("model" LDA) is an LDA-like solution of effective H, $\Sigma_{\mathrm{mLDA}} = U_f(n_f - 0.5)$, P.E. $= U_f n_f(n_f - 1)/2$.

DMFT: Vollhardt, 93; see review, Georges et al., 96
LDA+DMFT: Anisimov et al., 97; Lichtenstein & Katsnelson, 98; see review, Held et al., 02

Hartree Fock (HF) mean field collapse in f^1 Ce

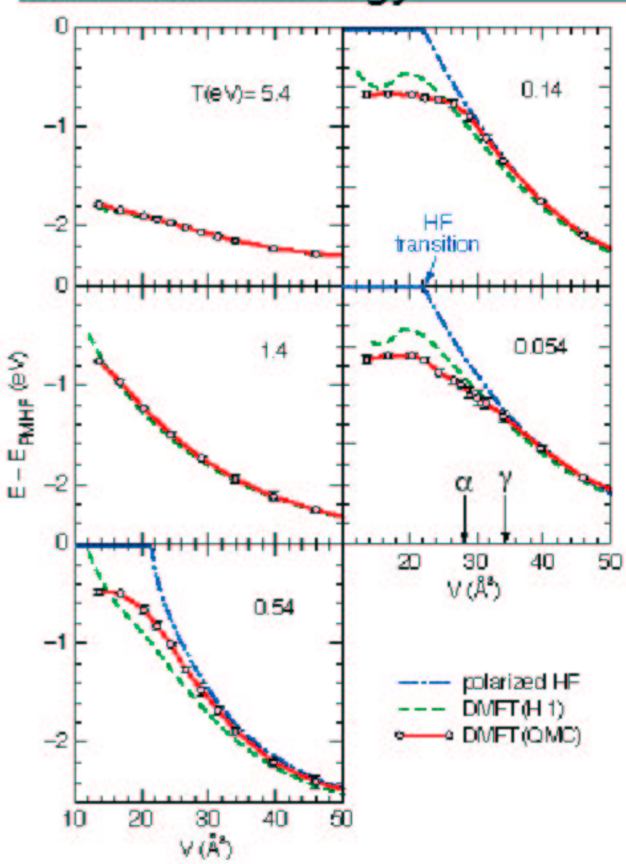
- Localized γ phase has $n_f^{\text{loc}} = 1$ band split off below Fermi level ($\varepsilon_F = 0$). *Snaps* up to joint the other f bands at collapse to the itinerant α phase, $n_f^{\text{loc}} = 0$. Latter bands overlap ε_F slighly so $\langle n_f \rangle$ stays ~ 1.



- Local density (LDA), self-interaction correction (LDA+SIC), LDA+U, and orbital polarization methods behave similarly.

- Correlated solutions resolve two problems via multi-peaked $A_{kj}(\varepsilon)$
  - Localized solution is rotationally invariant
  - Allow a continuous transfer of spectral weight up to ε_F

Correlation energy



- Energy relative to paramagnetic Hartree Fock (PMHF)

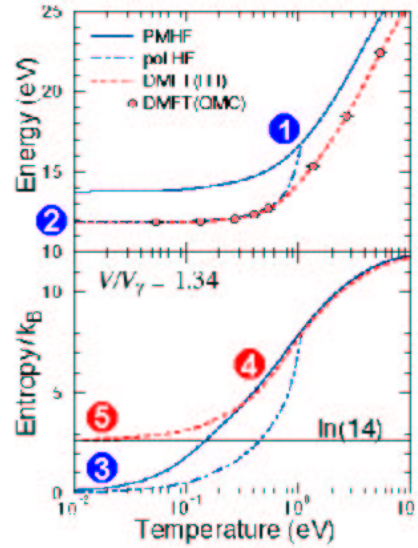
- Polarized HF gives good energy at low T and large V (no stable polarized HF solutions at hightest T's)

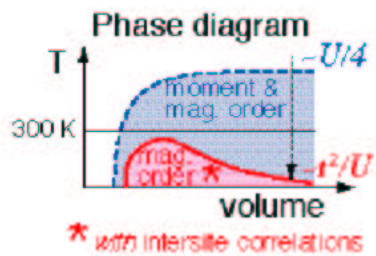
- HF transition at too small V

- DMFT(H-I) (atomic-like Σ) agrees with DMFT(QMC) at large V and at high T

- DMFT(QMC) breaks away from pol HF with decreasing V; more so with decreasing T, and near the observed α–γ transition

Ce energy and entropy vs. T at large V (γ like)





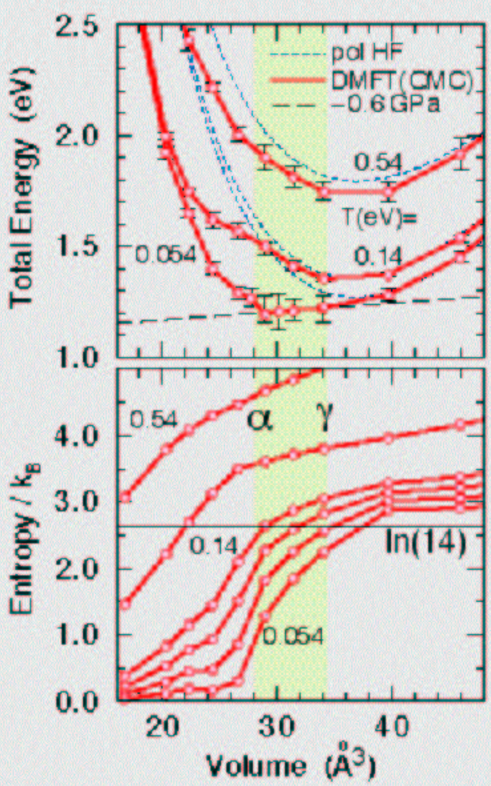
Static mean field (e.g, HF)

1. Spurious 1st order transition: moment formation and magnetic order coincide
2. Low-T polarized HF energy right at large V: multiplet contains at least one single Slater determinant state
3. No rot'l invariance, broken symmetry mistreats other states: bad low-T entropy

Correlated (DMFT, …)

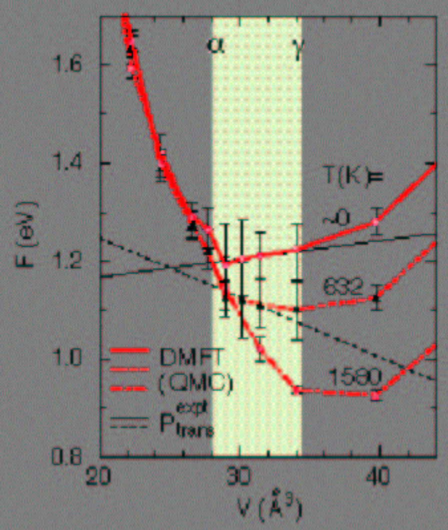
4. Moment formation (continuous) & mag. order (< 300 K if exists, *need* intersite correlations) are *distinct. The volume collapse tran's are about what happens to the moment, not magnetic order!*
5. Low-T entropy $k_B \ln(2J+1)$ = degeneracy in moment direction ($\ln(14)$ since no spin-orbit). Will drop at lower T (x'tal field, …)

Thermodynamic evidence for the γ–α transition



- Note depression of DMFT(QMC) E_{tot} away from the polarized HF result for $V < 35$ Å^3, more dramatic at lower T, leading to shallowness consistent with expt'l transition pressure (extrapolated to T=0)
- Believe T=0.054 eV (632 K) close to low-T limit, as E_{tot}(316 K) agrees for same *finite* time slices $\Delta\tau$ ($\Delta\tau \to 0$ too costly at 316 K).
- Phonon contribution neglected here has small impact (Johansson et al. 95)
- Low-T DMFT(QMC) entropy drops rapidly from $k_B \ln(2J+1)$ [$\ln(14)$ vs. $\ln(6)$ since no spin-orbit] from γ- to α-Ce due to screening or loss of the moment.
- The Fermi level Abrikosov-Suhl resonance also grows rapidly here

Ce free energy

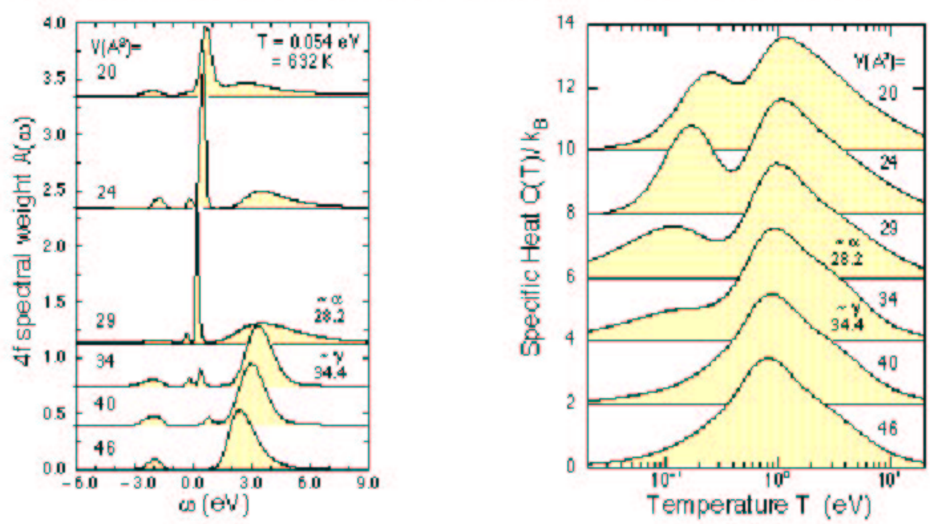


- Evidence that 632-K $E(V,T)$ already close to low-T limit. Take it as $F(V,0)$. Use again at 632 K with $-ST$ added

$$F(V,T) = E(V,T) - S(V,T)\,T$$

- Straight lines show experimental P_{trans} at $T=0$ and ~600 K (critical point). All the action is in the entropy, consistent with Johansson et al., 95
- DMFT(QMC) gives right qualitative features. Need to add spin-orbit to get correct large-V, low-T entropy, and reduce QMC error bars

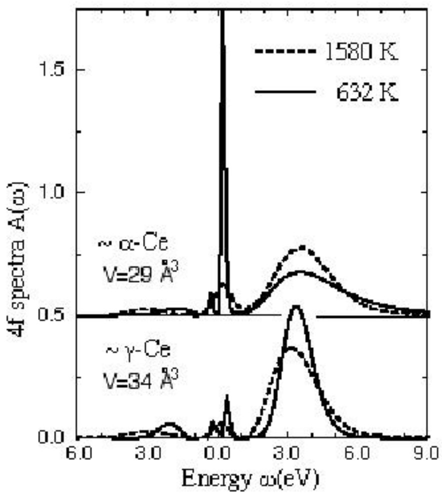
4f spectra and specific heat for Ce from DMFT(QMC)

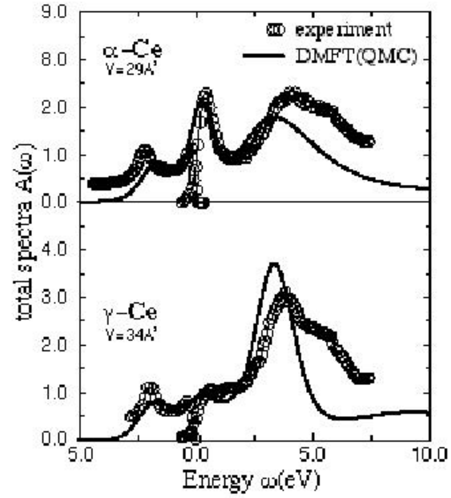


- Hubbard splitting at large volume, signature of moment
- Small Fermi-level (Abrikosov Suhl) resonance at γ volume, grows rapidly by α volume, coincides with energy and entropy signatures of transition
- By smallest volumes this central resonance dominates (like LDA), however small residues of Hubbard side bands still persist (correlation)
- Low-T peak in specific heat coincides with growth of AS resonance

Spectra from maximum entropy method, C(T) from fit to energies

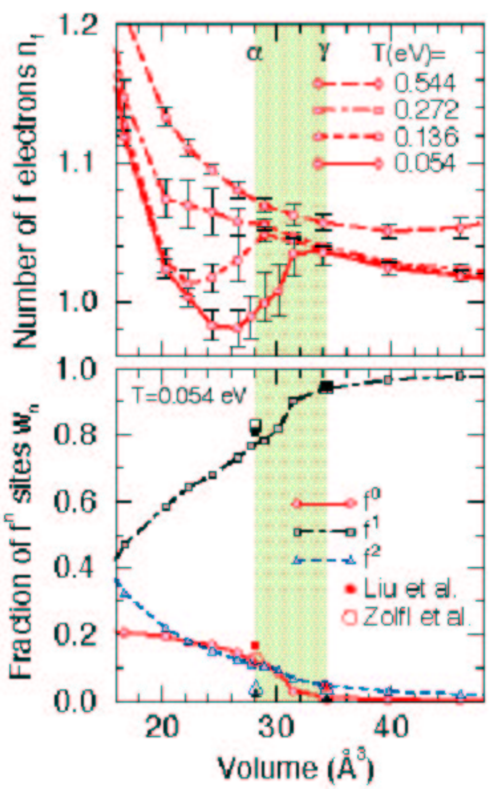
T-dependence of spectra, comparison to experiment





- Kondo temperature: (α-Ce) FWHM suggests $T_K \sim 2000\,\mathrm{K}$, consistent with smearing at higher T and experiment $945\,\mathrm{K}$ (Liu et. al. 92) and $1800–2000$ (Murani et al. 93). (γ-Ce) both T's well above expt 95 and 60 K, respectively
- Agreement of total calculated spectra with experiment is good, especially near the Fermi level. Too narrow theory width of high energy f^2 peak likely due to omission of exchange interaction and thus term structure.

Ce number of f electrons n_f and double occupation d

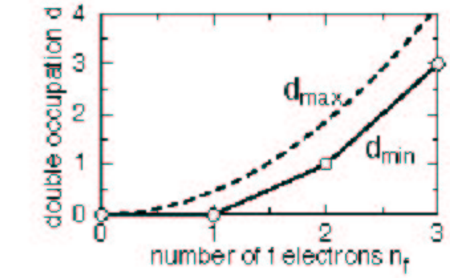


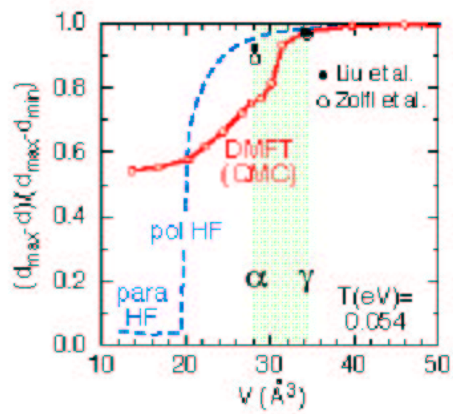
$$n_f = \frac{1}{N}\sum_i \sum_{m\sigma} \langle \hat{n}_{ifm\sigma} \rangle$$

$$d = \frac{1}{2N}\sum_i {\sum_{m\sigma,m'\sigma'}}' \langle \hat{n}_{ifm\sigma}\hat{n}_{ifm'\sigma'} \rangle$$

- n_f increases with T (big empty f DOS) and with decreasing V ($sp \rightarrow df$ transition). Superposed is drop in n_f as d increases (repulsive potential energy Ud)
- Fraction of sites with 0, 1, 2, (3 or more unlikely at low T) f electrons $w_2 = d$
  $w_1 = n_f - 2d$
- Large V: $n_f \sim 1$, avoid $Ud \rightarrow w_1 \sim 1$, $w_0 \sim w_2 \sim 0$
- Decreasing V: growing fv & ff hybridiza- tion, fluctuations $f^1v^3 \rightarrow f^0v^4, f^2v^2$ & $f_i^1 f_j^1 \rightarrow f_i^2 f_j^0$; w_0, w_2 grow at expense of w_1 – particularly dramatic in transition region

Double occupation d quantifies degree of correlation





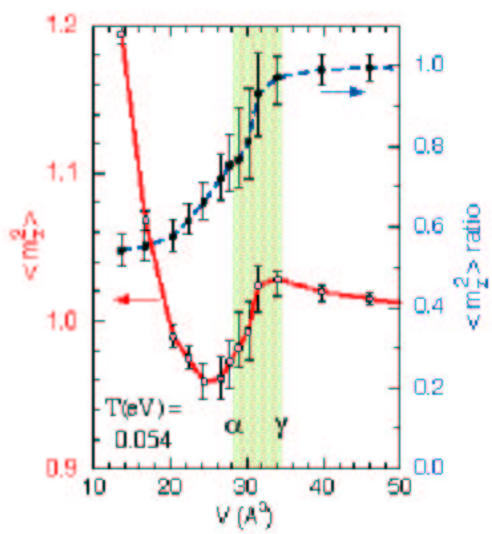
- Repulsive Coulomb energy = Ud

  $$d \equiv \frac{1}{2N}\sum_i \sum'_{m\sigma,m'\sigma'} \langle \hat{n}_{ifm\sigma} \hat{n}_{ifm'\sigma'} \rangle$$

  Uncorrelated limit (d_{max}) from $V \to 0$, where $\langle \hat{n}_1 \rangle \langle \hat{n}_2 \rangle \sim (n_f/14)^2$; fully correlated limit (d_{min}) from $V \to \infty$ at $T=0$.

- Ratio $(d_{max}-d)/(d_{max}-d_{min})$ = *1* (strong), *0* (weak) correlation
- Hartree-Fock (HF) transition is from strong to weak, but in wrong place
- DMFT(QMC) has rapid decrease in corre- lation over γ–α transition, but still signif- icantly correlated at smallest volumes
- Consistent with persistence of residual Hubbard sidebands to these volumes

Ce moment



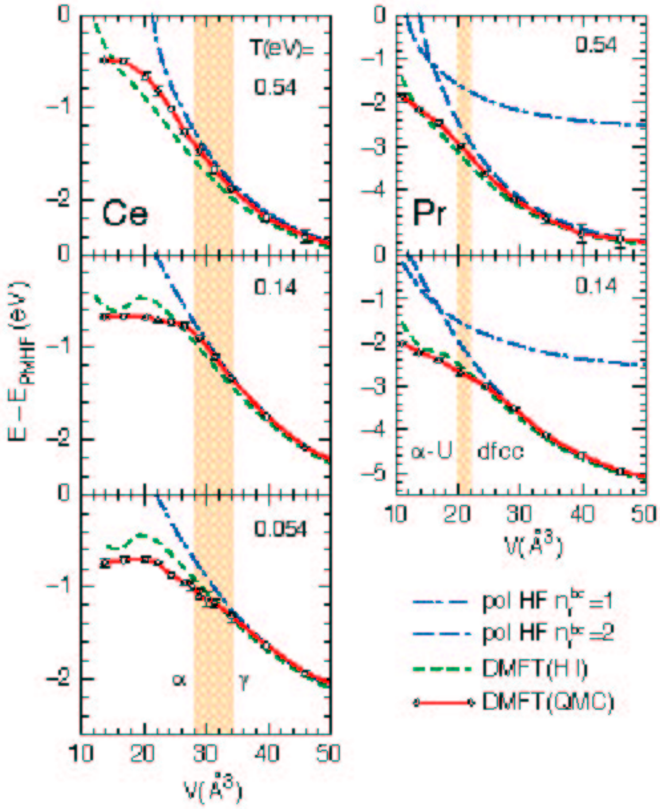
$$\langle \hat{S}_{if}^2 \rangle = \tfrac{3}{4}\langle m_z^2 \rangle, \quad \langle \hat{L}_{if}^2 \rangle = 12\langle m_z^2 \rangle$$

$$\langle m_z^2 \rangle \equiv \sum_m \langle (\hat{n}_{ifm\uparrow} - \hat{n}_{ifm\downarrow})^2 \rangle = n_f - \tfrac{2}{13} d$$

$$\text{if } \langle \hat{n}_{ifm\sigma} \hat{n}_{ifm'\sigma'} \rangle = \begin{cases} n_f/14 & \text{if } m\sigma = m'\sigma' \\ d/91 & \text{if } m\sigma \neq m'\sigma' \end{cases}$$

- Rare earth collapse transitions are about "local moment" $<m_z^2>$ (changes in size, screening), *not* magnetic order
- Static mean field measures analog of $<m_z>$ (polarization, magnetic order) not $<m_z^2>$
- Present $<m_z^2>$ drops only 5% across γ–α transition, overall V-dependence like n_f
- Hard to get rid of moment, e.g., fully uncorrelated limit $\langle m_z^2 \rangle_{min} = n_f - \tfrac{2}{13} d_{max} = n_f(14-n_f)/14$
- Can still have T-independent paramag- netism (Kondo screening or Pauli free electron argument), and reduced entropy
- Where does $<m_z^2>$ lie between fully correlated $<m_z^2>_{max}$ and uncorrelated $<m_z^2>_{min}$ – identical to d ratio. Again note that α-Ce is still strongly correlated

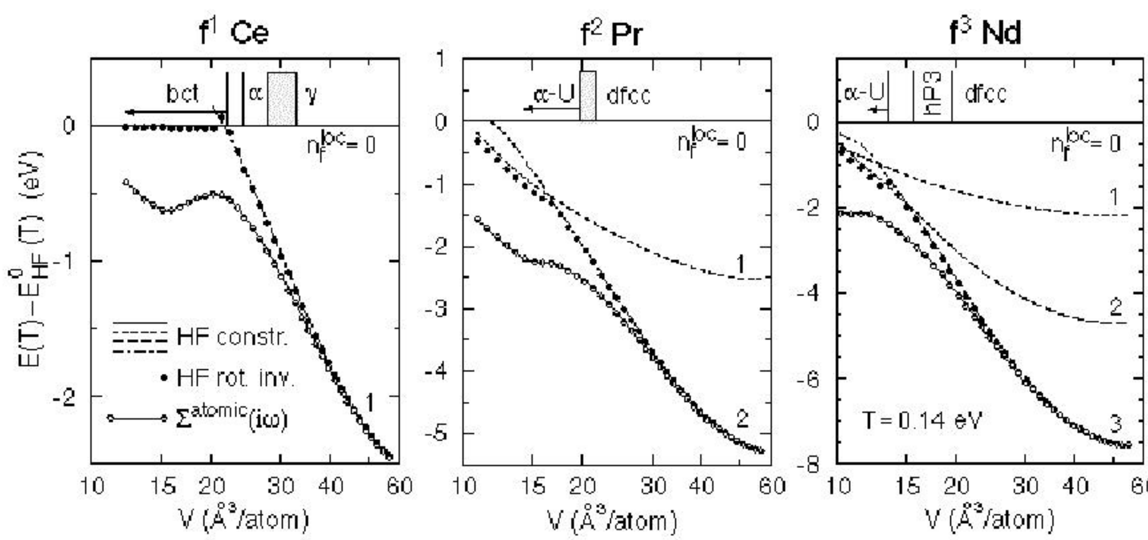
Correlation energy of Ce f^1 and Pr f^2



- Energy relative to paramagnetic Hartree Fock (PMHF), i.e., $n_f^{loc} = 0$.
- Polarized HF has one transition in Ce (n_f^{loc}=1→ 0), and two in Pr (n_f^{loc}=2→ 1→ 0), all at too small V. n_f^{loc}=1 correlation energies comparable
- Pr is more strongly correlated (larger U_f and smaller W_f)
  - Bends away from pol HF at smaller V.
  - Closer agreement DMFT QMC and atomic-like H-I
  - Suggests higher low-T limit

Note: no spin orbit or intraatomic exchange

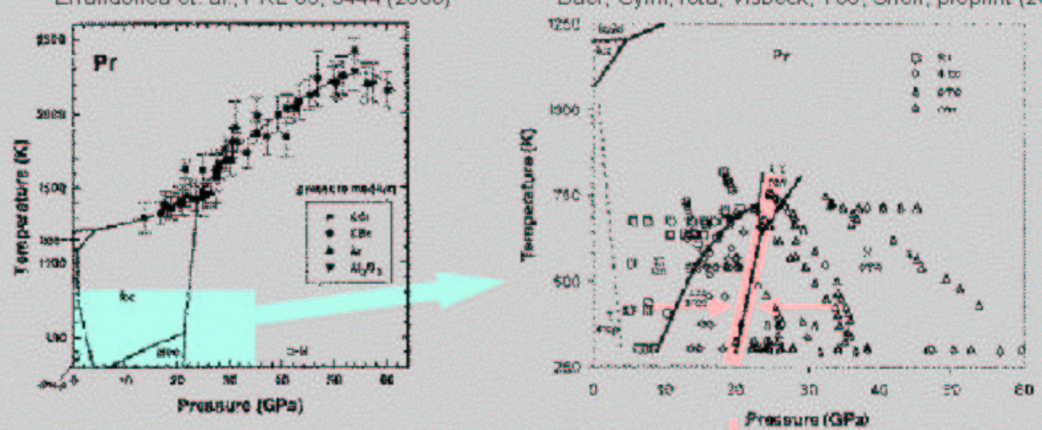
HF and DMFT-Σ^{atomic} energies — Ce, Pr, Nd



- Suggests cascade of HF transitions $n_f^{loc} = n \rightarrow n-1 \rightarrow n-2$ ..., ***not*** just $n \rightarrow 0$ (except Ce). No experimental evidence for this. Transitions at *too* small V for constrained occupation U_f's
- DMFT with Σ^{atomic} (Hubbard I; large V approximation)
  - Agrees with polarized HF at large V, then breaks away ~ $exp(-cV)$
  - Always Hubbard split, unphysical at small V, no transitions

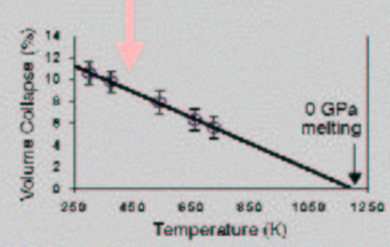
The Praseodymium volume collapse

Errandonea et. al., PRL 85, 3444 (2000) Baer, Cynn, Iota, Visbeck, Yoo, Shen, preprint (2001)

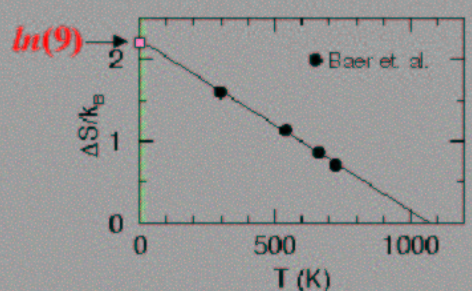


Baer et. al. find the collapse ΔV decreases linearly with T, → 0 near melt line.

Clausius-Clapeyron: $\frac{dT_{tr}}{dP} = \frac{\Delta V(T)}{\Delta S(T)}$
ΔS also decreases linearly with T.



Loss of Hund's rules moment in Pr entropy

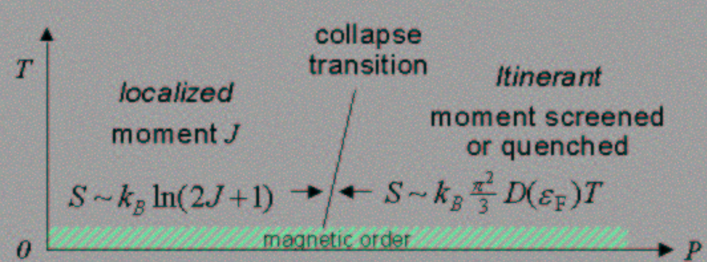


Clausius-Clapeyron

$$\Delta S(T) = \frac{dT_{tr}}{dP}\,\Delta V(T)$$

data

$T=0$ ΔS intercept for Ce ***also*** $\sim k_B \ln(2J+1)$! (Johansson et. al. 1995)



Hund's rules ground states		$2J+1$
Ce	f^1 $^2F_{5/2}$	6
Pr	f^2 $^3H_4$	9

S. Weir (LLNL) & Y. Vohra (U. Ala) are about to measure the moments (from $\chi(T)$) under pressure using designer diamond anvil cells

Summary/conclusions

300-K properties	static MF (HF, ..?)	correlated (DMFT)	exp't
γ-Ce			
magnetic order	yes	no	no
magnetic moment	yes	yes	yes
mag. susceptibility			$C/(T \pm \theta)$ [2]
entropy	~0	$k_B \ln(2J+1)$	$k_B \ln(2J+1)$ [2]
4f spectra	LH+UH	LH+C+UH	LH+C+UH [3]
correlation	strong	strong	strong
α-Ce			
magnetic order	no	no	no
magnetic moment	no	yes	yes [4]
mag. susceptibility			T-indep. [2]
entropy	~0	~0	~0 [2]
4f spectra	C (1)	LH+C+UH	LH+C+UH [3]
correlation	weak	strong	strong

(1) Outstanding puzzle is why LDA (believe ~ static mean field) does so well for volume and structural dependence of E_{tot} in α-Ce like phases. Possibly gets quasiparticle interactions right but not binding energy

[2] Gschneidner et al., 62; Manley et al. (preprint), 02 [3] Liu et al., 92 [4] Murani et al., 93