The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
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International Atomic
Energy Agency

SMR.1824 - 23

**13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

Self-interaction corrections for f-electrons

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These are preliminary lecture notes, intended only for distribution to participants

Self-interaction Corrections for f-electrons

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Trieste, Jan. 13, 2007

Self-interaction Corrections for f-electrons

- Introduction
- 4f: SmX
- 5f: PuSe, Am
- Simplified SIC
- Summary

Self-Interaction Corrected Total Energy Functional

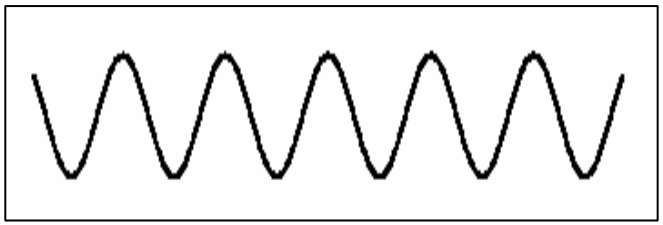
$$E[n] = E^{LSD}[n] - \sum_{\alpha}^{occ.} \delta_{\alpha}$$

$$E^{LSD}[n] = T[n] + U[n] + V_{ext}[n] + E_{xc}[n]$$

$$\delta_{\alpha} = U[n_{\alpha}] + E_{xc}[n_{\alpha}]$$

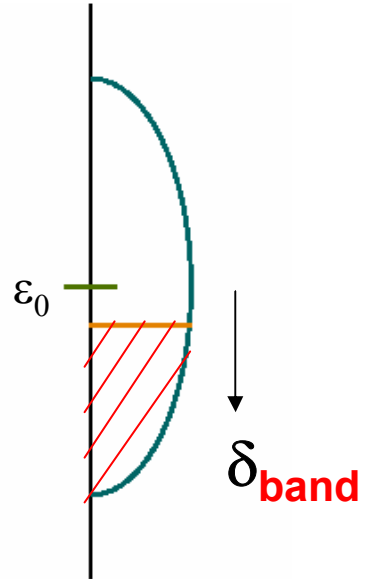
Perdew & Zunger, PRB **23**, 5048 (1981)

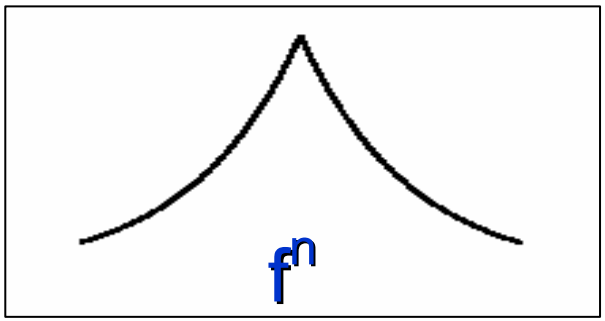
Introduction



Bloch:

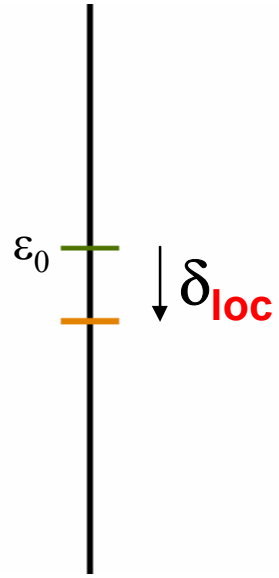
delocalized
band formation





Heitler-London:

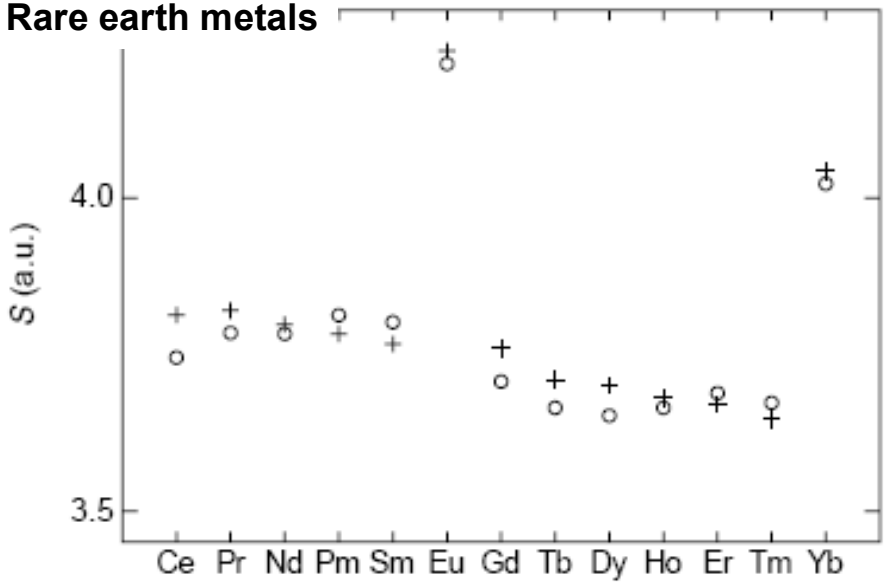
localized
multiplets



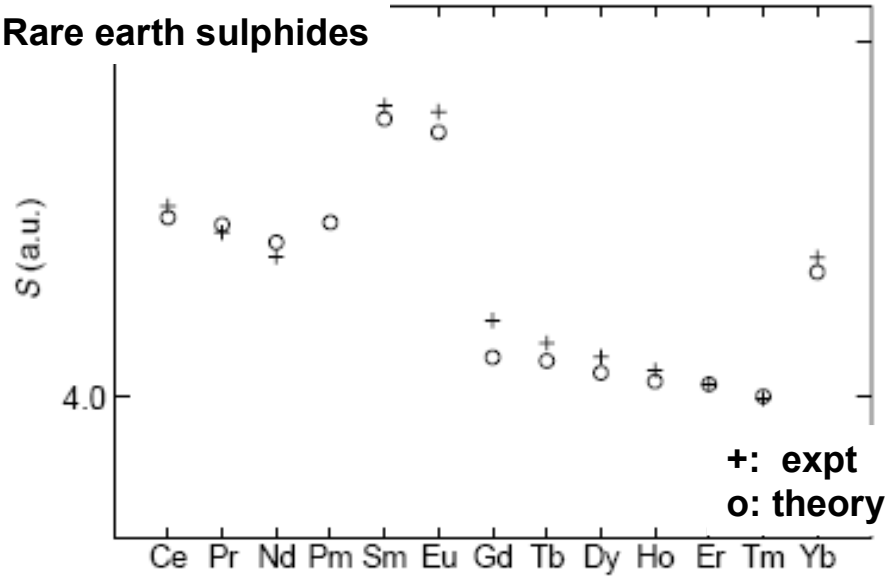
TB-LMTO(ASA)

Lattice constant

Rare earth metals

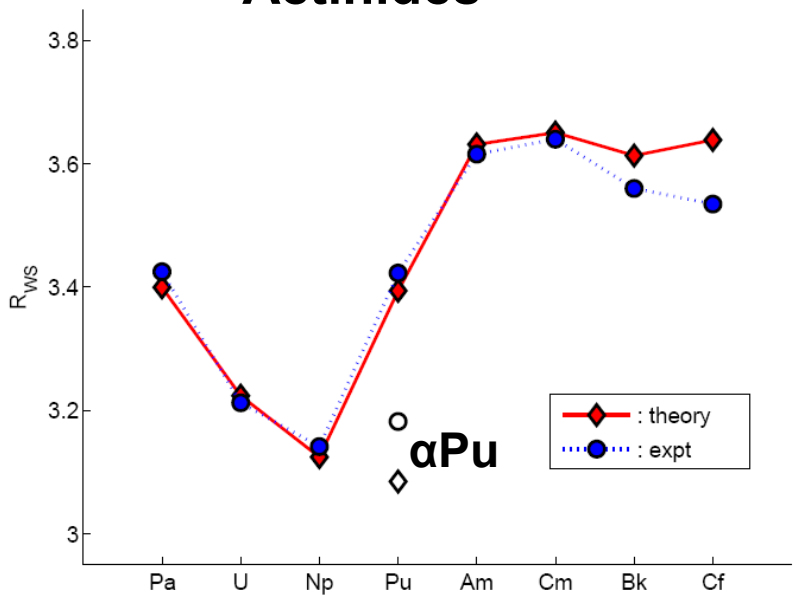


Rare earth sulphides

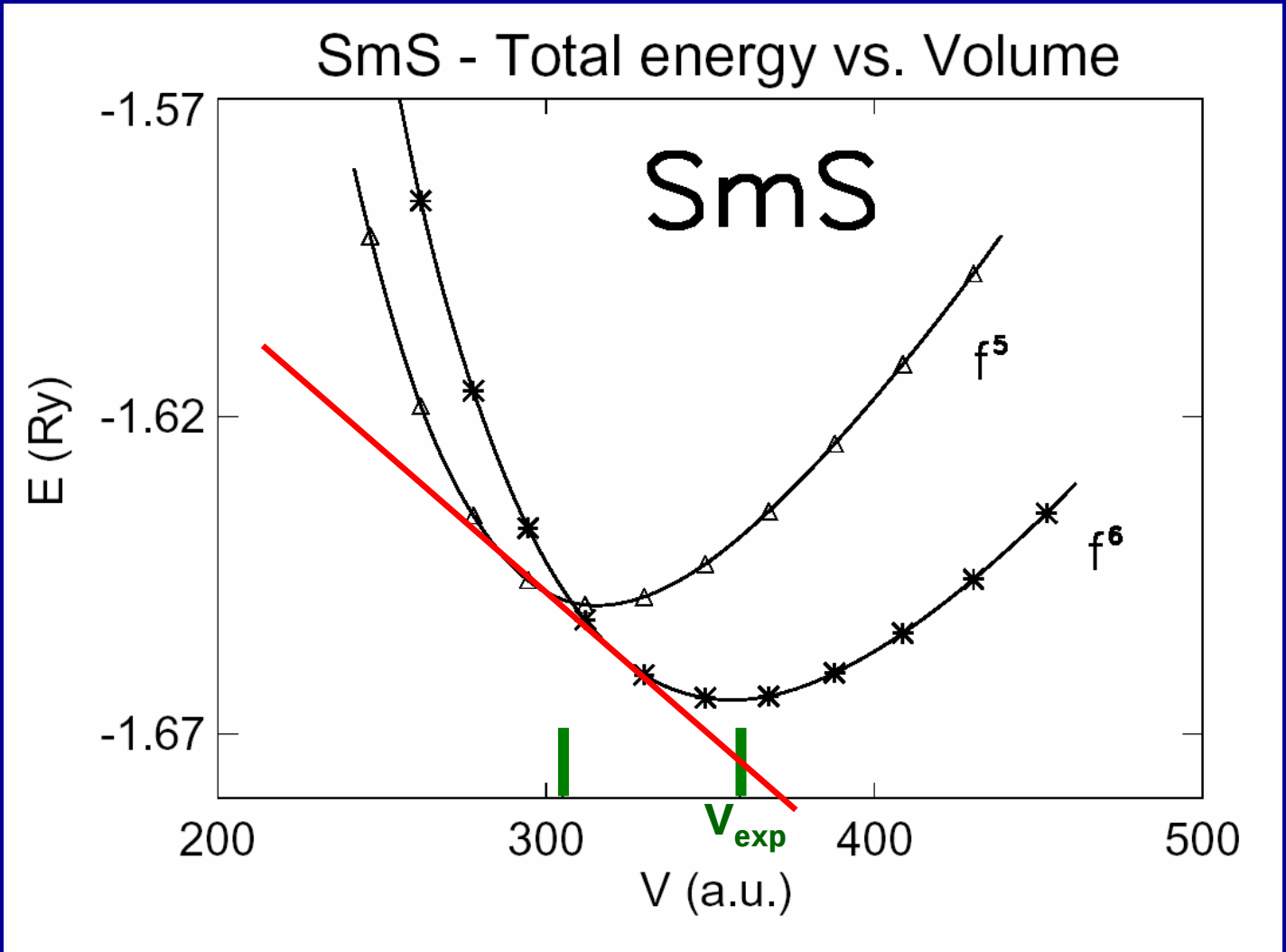


+: expt
o: theory

Actinides

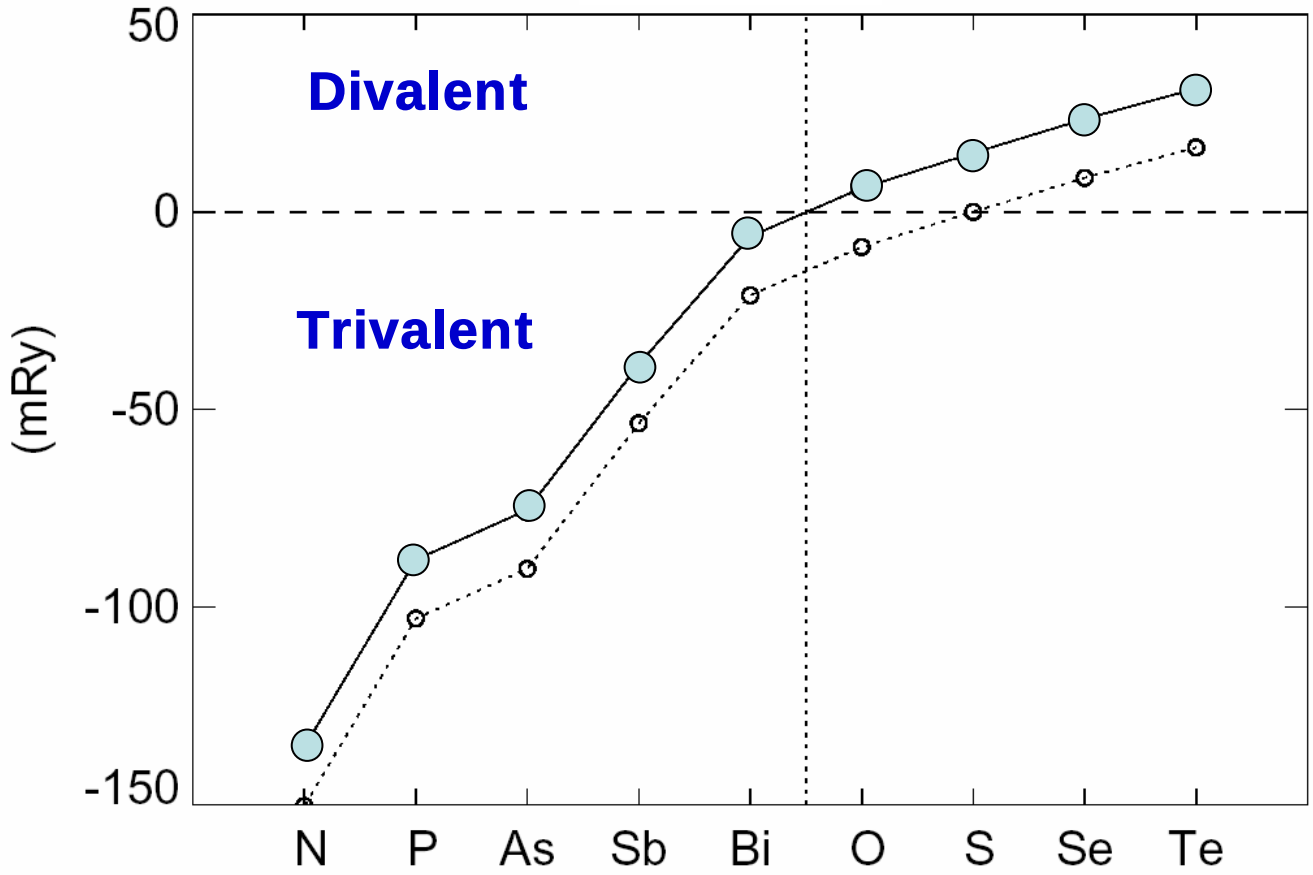


SmS


SmS - Total energy vs. Volume
SmS
-1.57
-1.62
-1.67
E (Ry)
200
300
400
500
V (a.u.)
V_{exp}
f^5
f^6

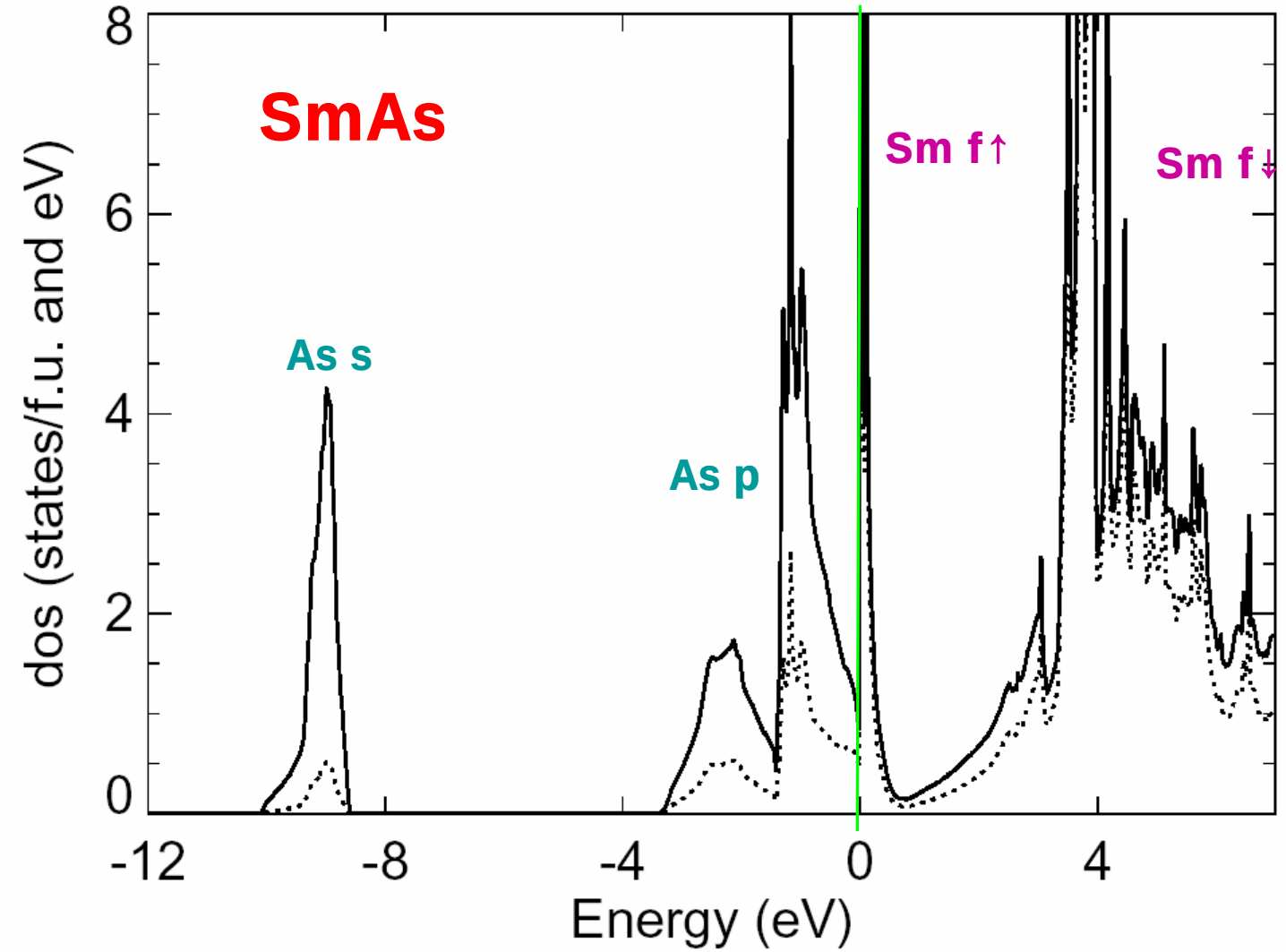
SmX

$$E(f^5) - E(f^6)$$

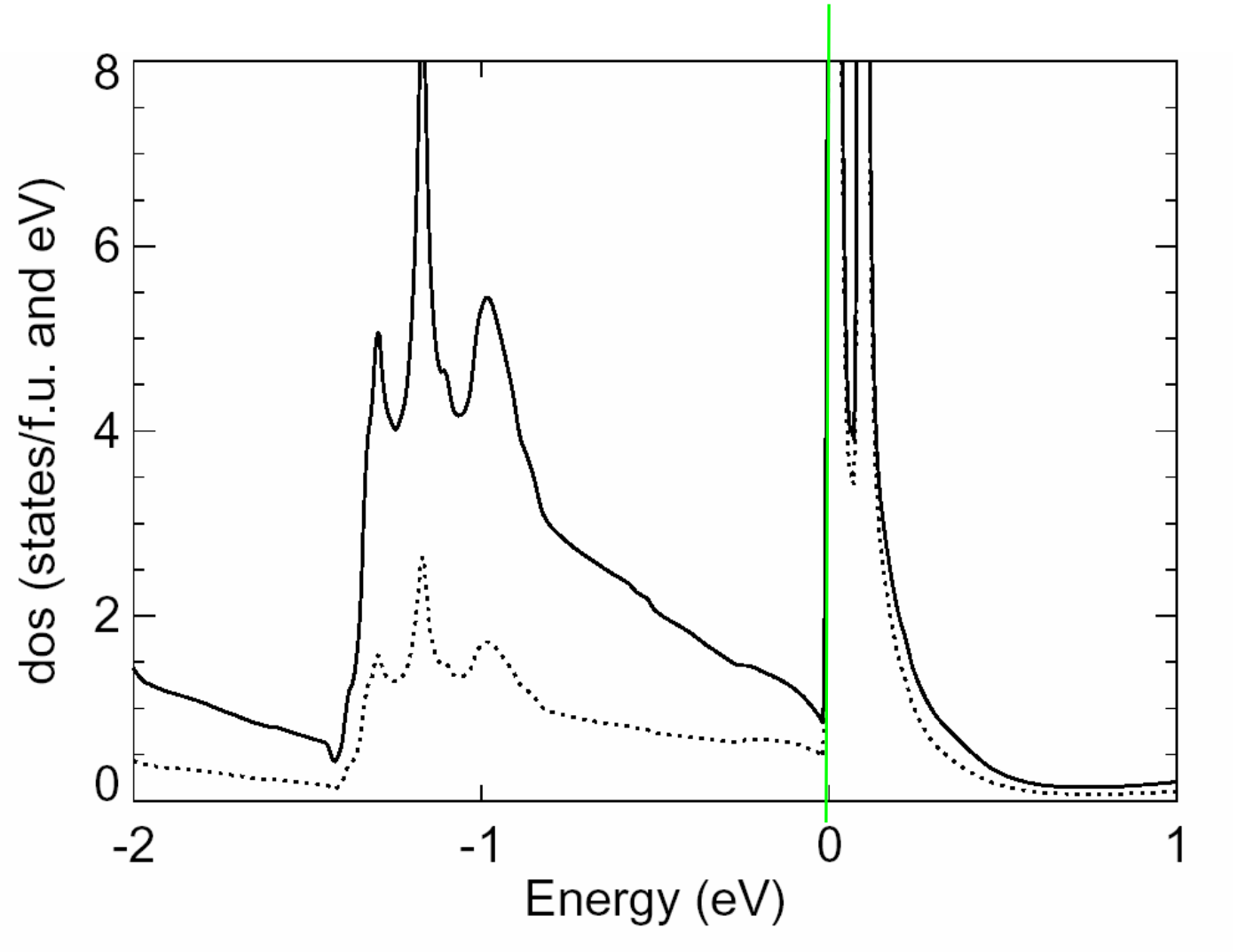


PRB 71, 45119 (2005)

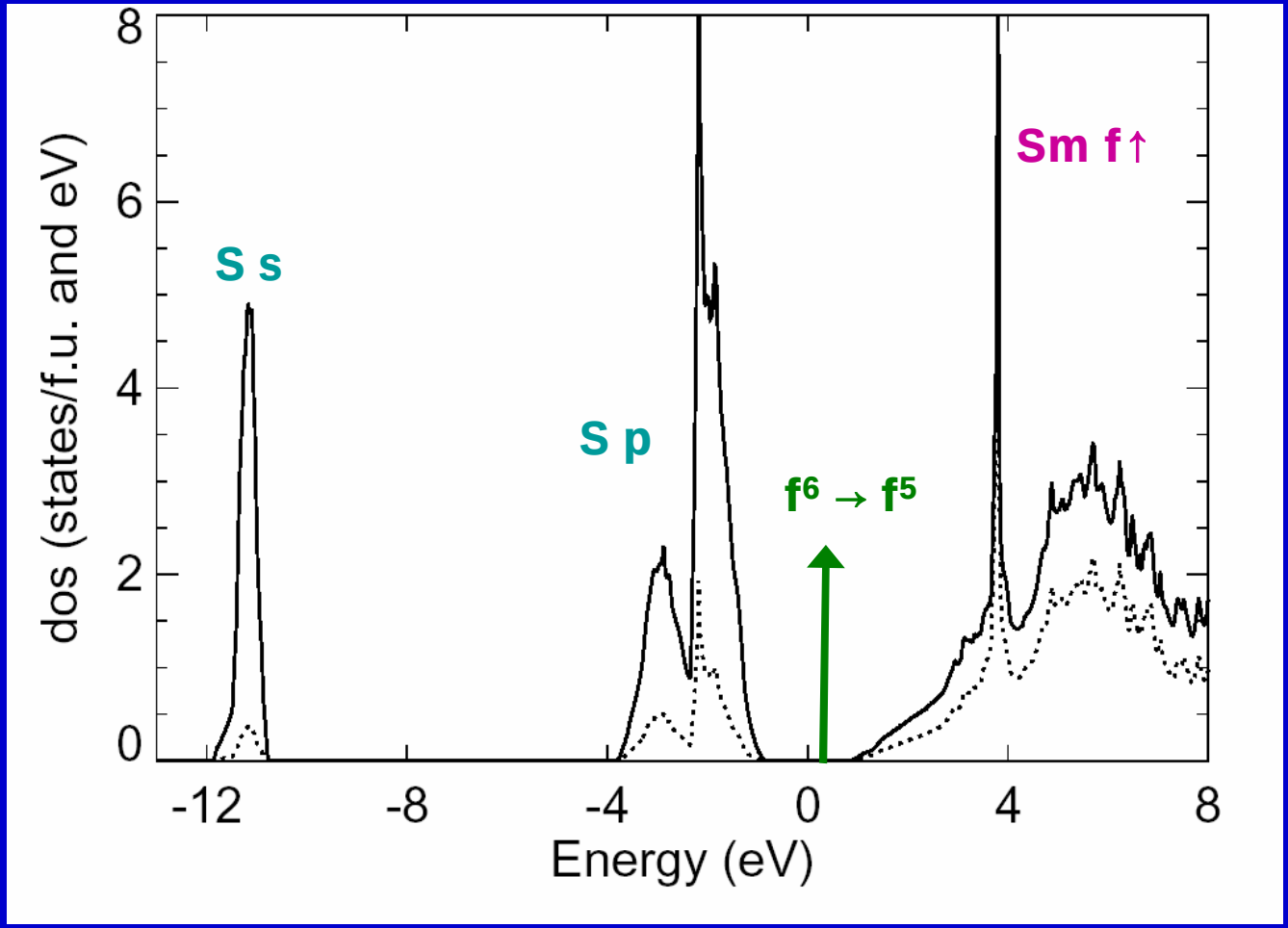
SmAs - density of states



SmAs - density of states

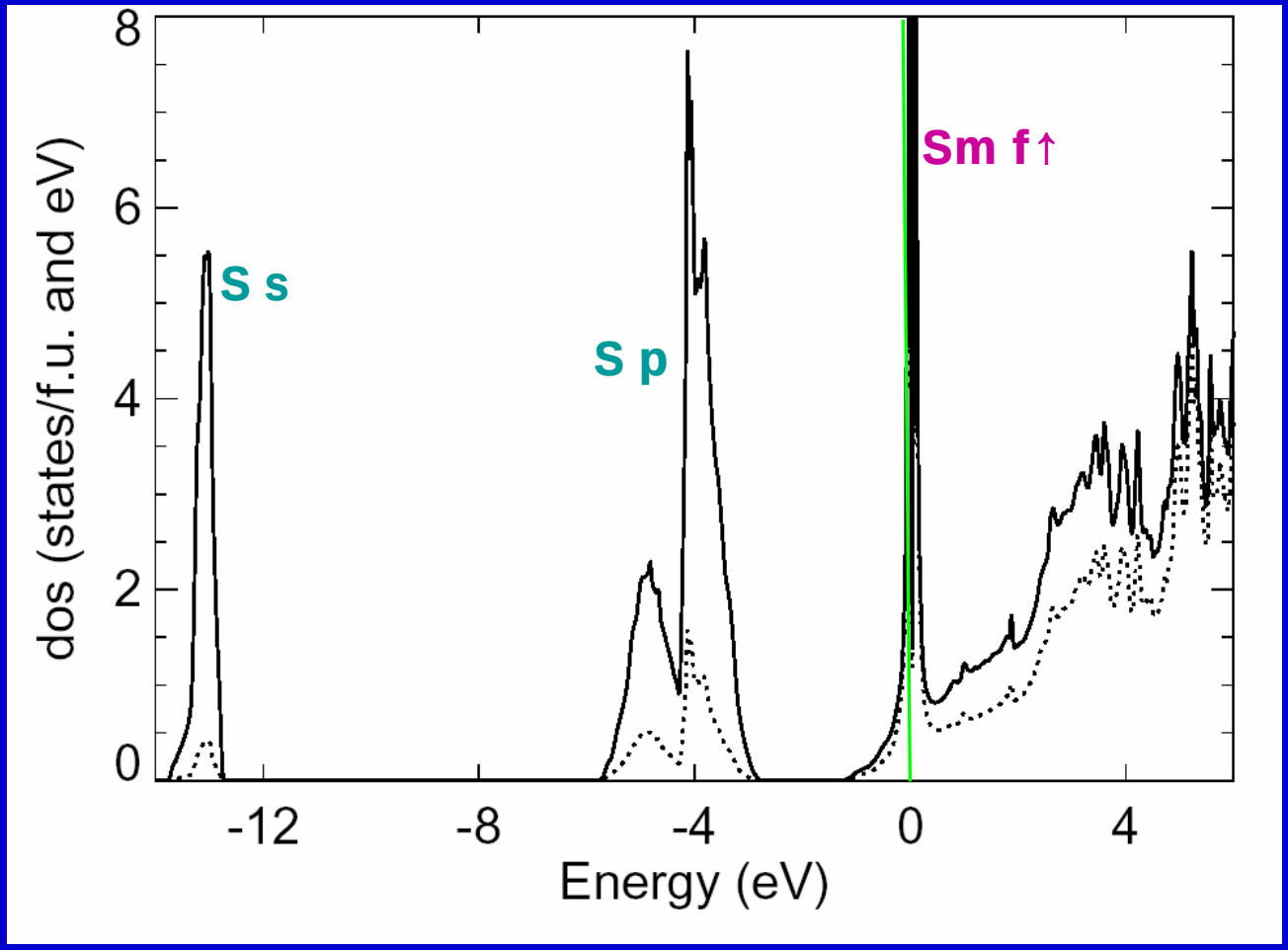


SmS - density of states

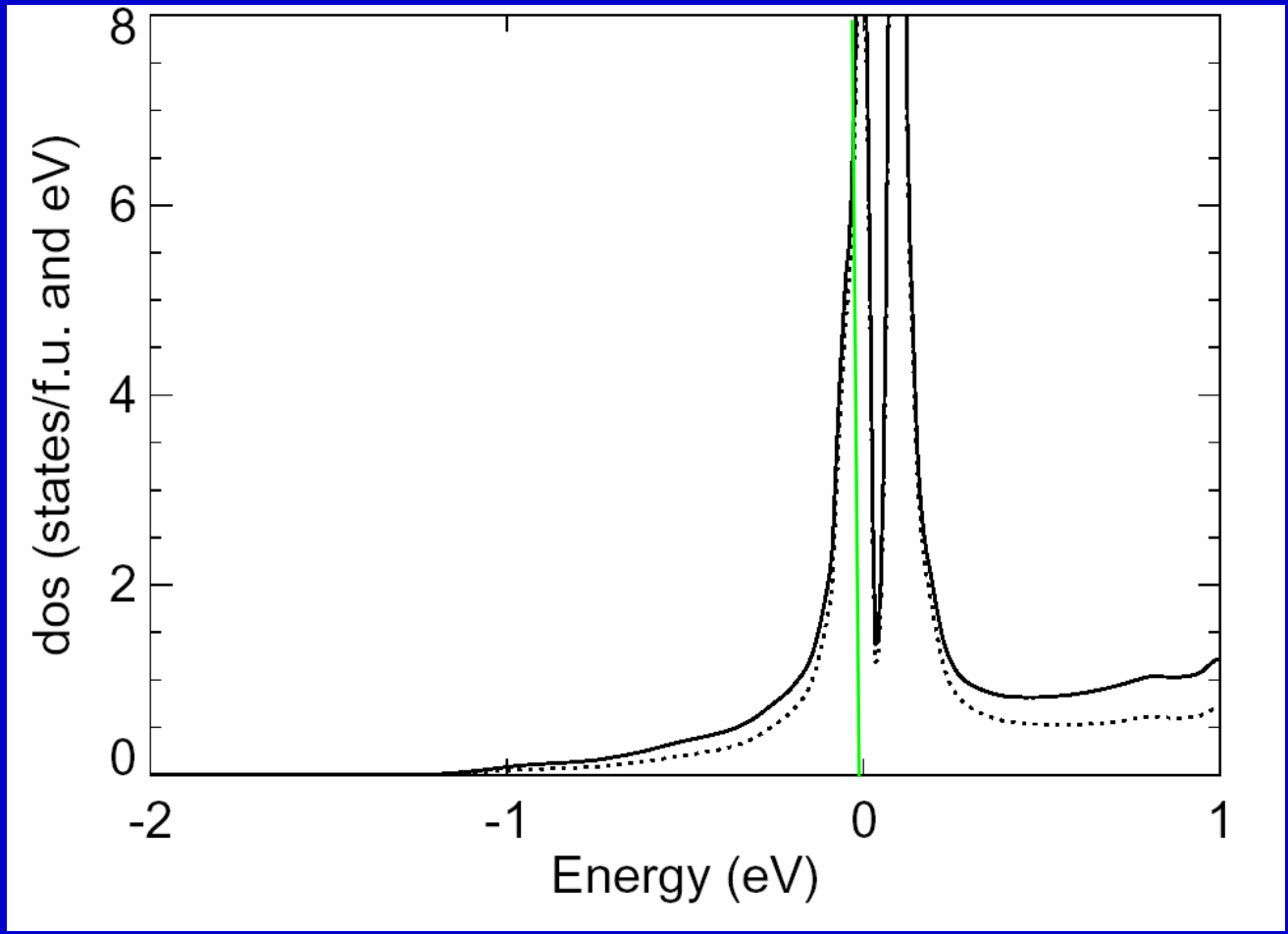


E_g = 0.71 eV

Sm(3+)S - density of states

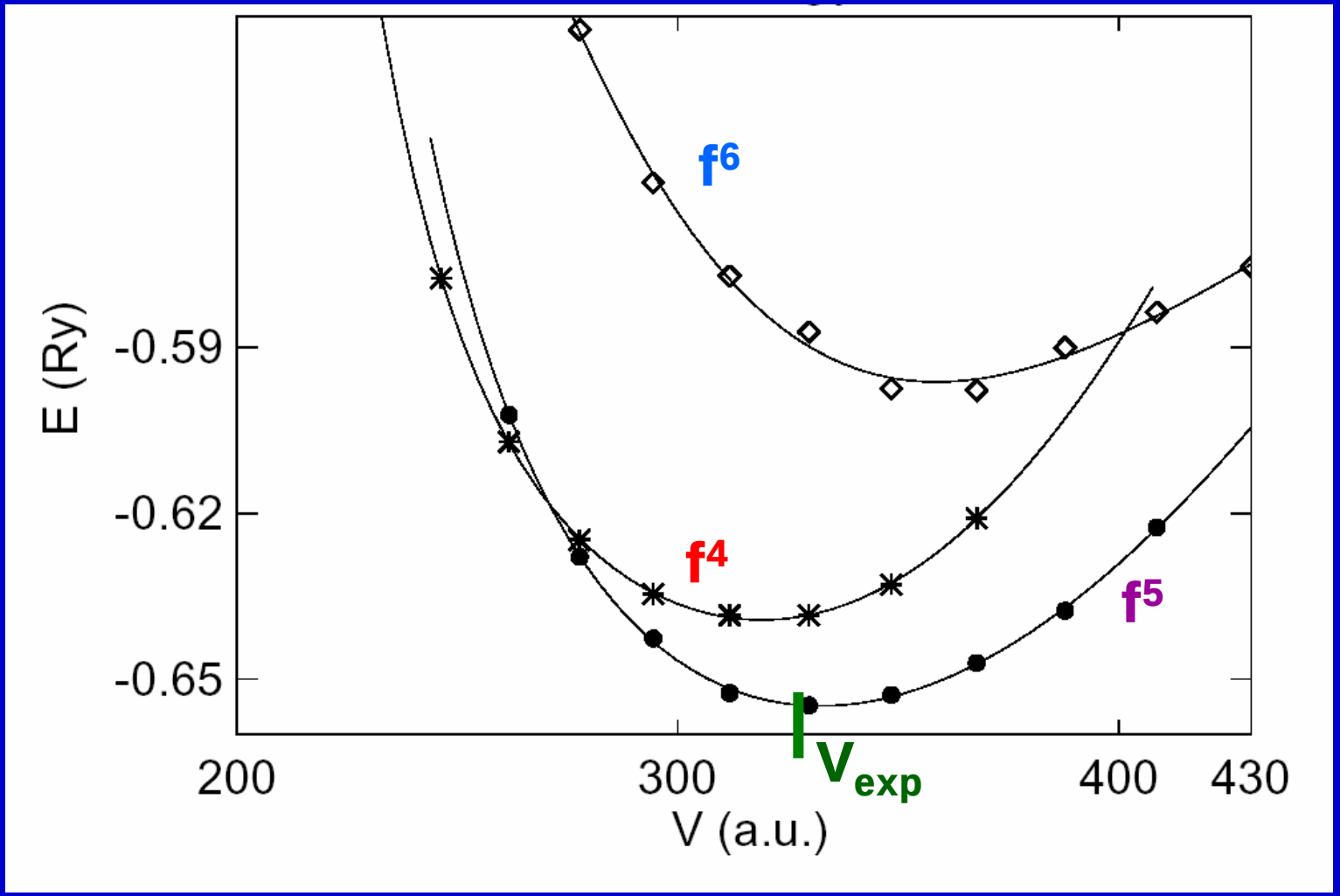


Sm(3+)S - density of states

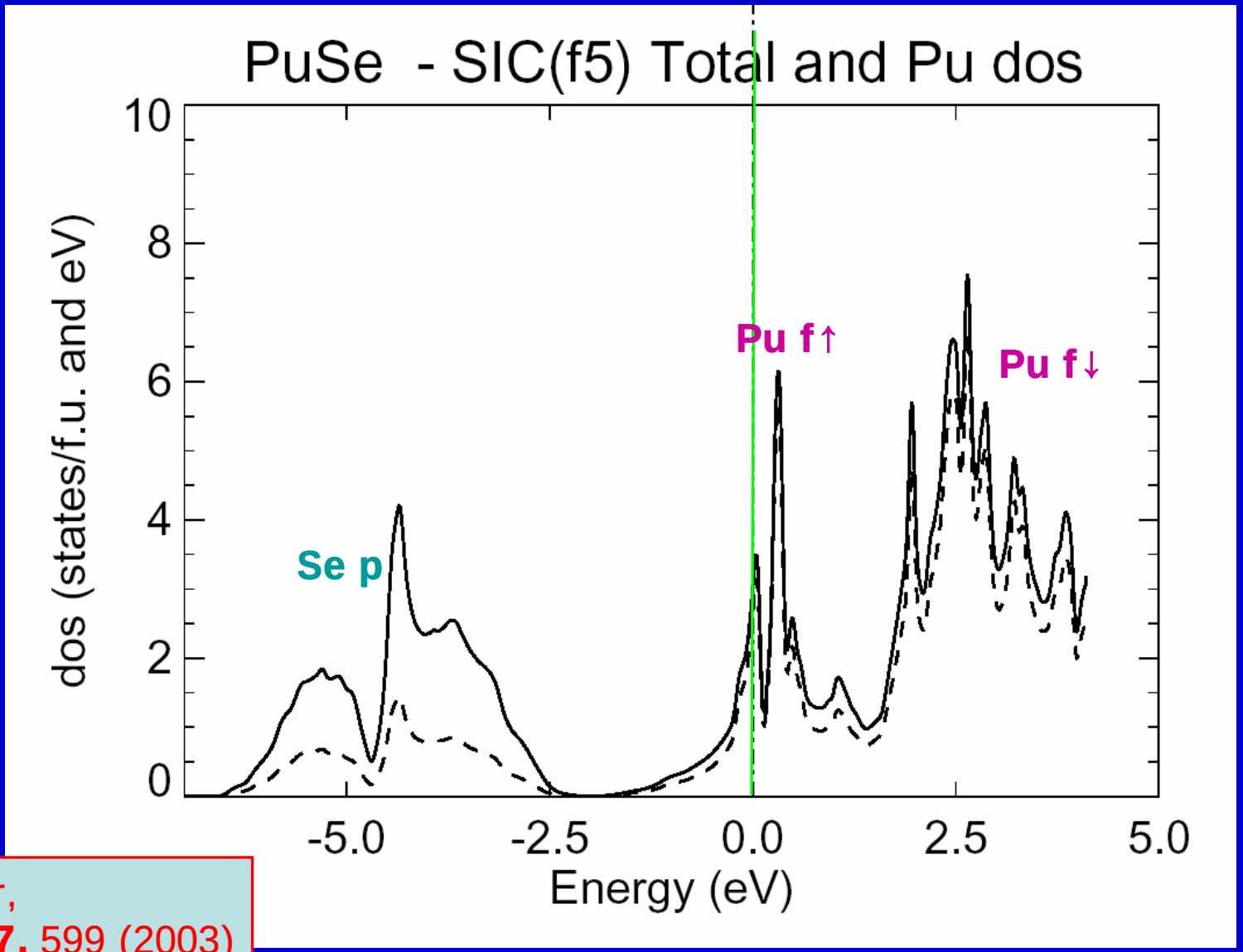


Intermediate Valence

PuSe



Pu(3+)Se - density of states

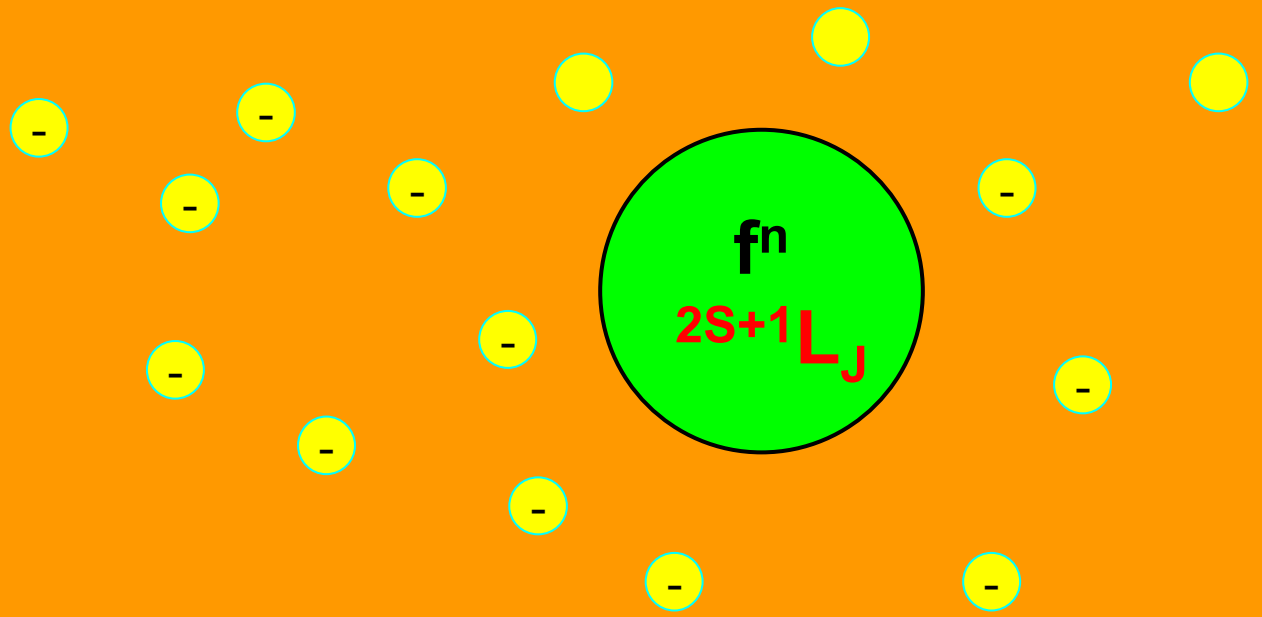


Wachter,
SSC **127,** 599 (2003)

$$< f^n; i | \frac{1}{r_{12}} + \xi \vec{l} \cdot \vec{s} | f^n; j > \rightarrow |\mu>, \; E_\mu$$

$$\sum_{ik} V_{ik} (\hat{c}_k^+ \hat{f}_i + \hat{f}_i^+ \hat{c}_k) = \int V(\varepsilon) \left(\hat{c}^+(\varepsilon) \hat{f}_i + \hat{f}_i^+ \hat{c}(\varepsilon) \right) d\varepsilon$$

$$V \sum_i (c_i f_i^+ + f_i c_i^+) \rightarrow |\tilde{\mu}>, \; \tilde{E}_\mu$$



DMFT implementation

$$G_{ij}^{atom}(\omega) = \sum_{\mu\upsilon} g_{\mu\upsilon} \frac{\langle \tilde{\mu} \mid f_i \mid \tilde{\upsilon} \rangle \langle \tilde{\upsilon} \mid f_j^{+} \mid \tilde{\mu} \rangle}{\omega + \tilde{E}_{\mu} - \tilde{E}_{\upsilon}}$$

$$\Sigma^{atom}(\omega) = G^{bath}(\omega)^{-1} - G^{atom}(\omega)^{-1}$$

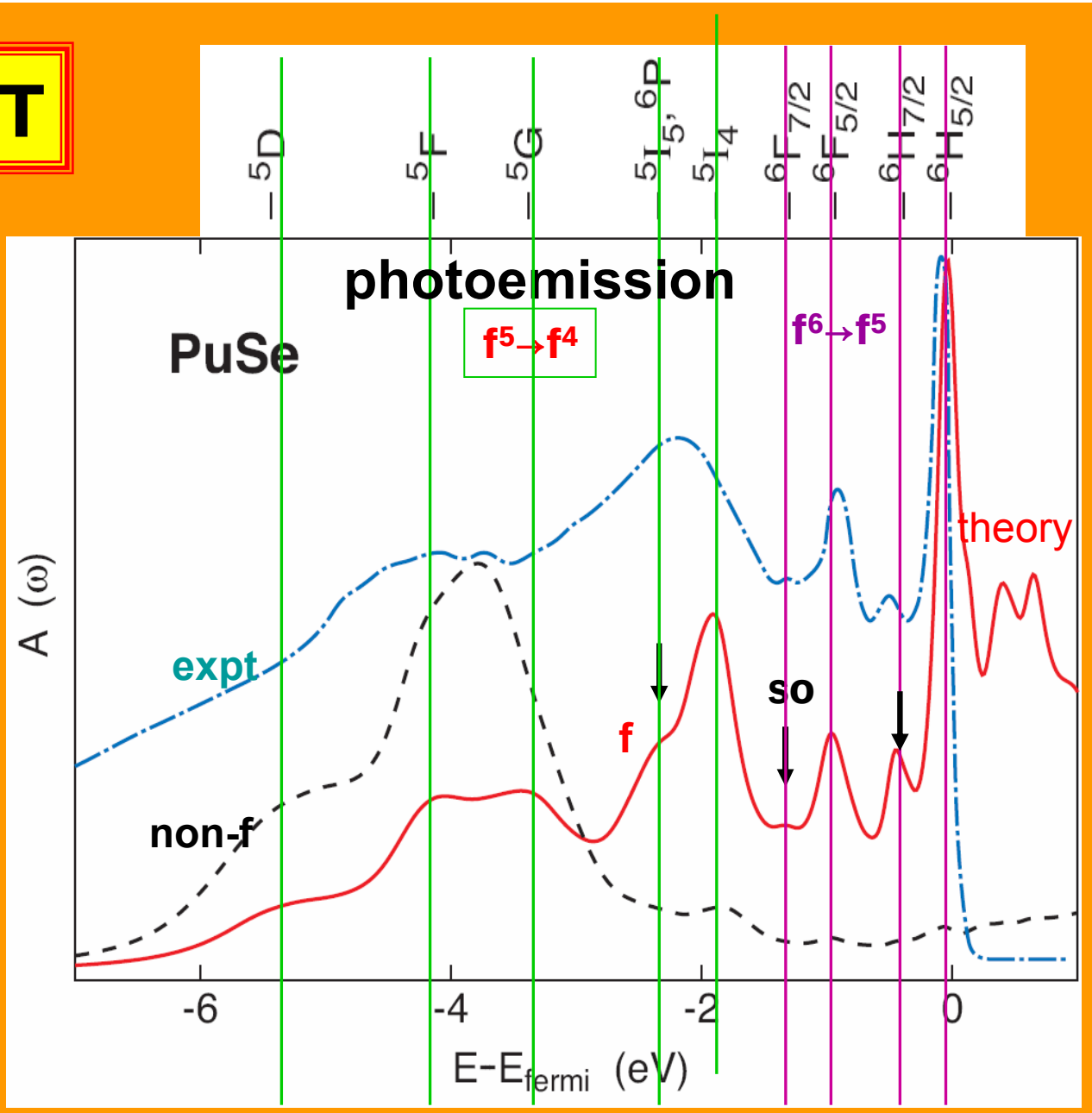
$$G^{solid}(\omega) = \frac{1}{\omega - H_{LDA} - \Sigma^{atom}(\omega)}$$

$$G^{bath}(\omega)^{-1} = \overline{G}^{solid}(\omega)^{-1} + \Sigma^{atom}(\omega)$$

Lichtenstein&Katsnelson, PRB **57,** 6884 (1998)

PuSe - DMFT

$E(f^5)-E(f^6)=-44$ meV
$V = 0.12$ eV
$|\langle\psi_{gs}|f^5\rangle|^2 = 0.70$
$|\langle\psi_{gs}|f^6\rangle|^2 = 0.30$



PES-exp.:
Gouder *et al.*,
PRL **84,** 3378 (2000)

Solid State Commun. 140, 364 (2006)

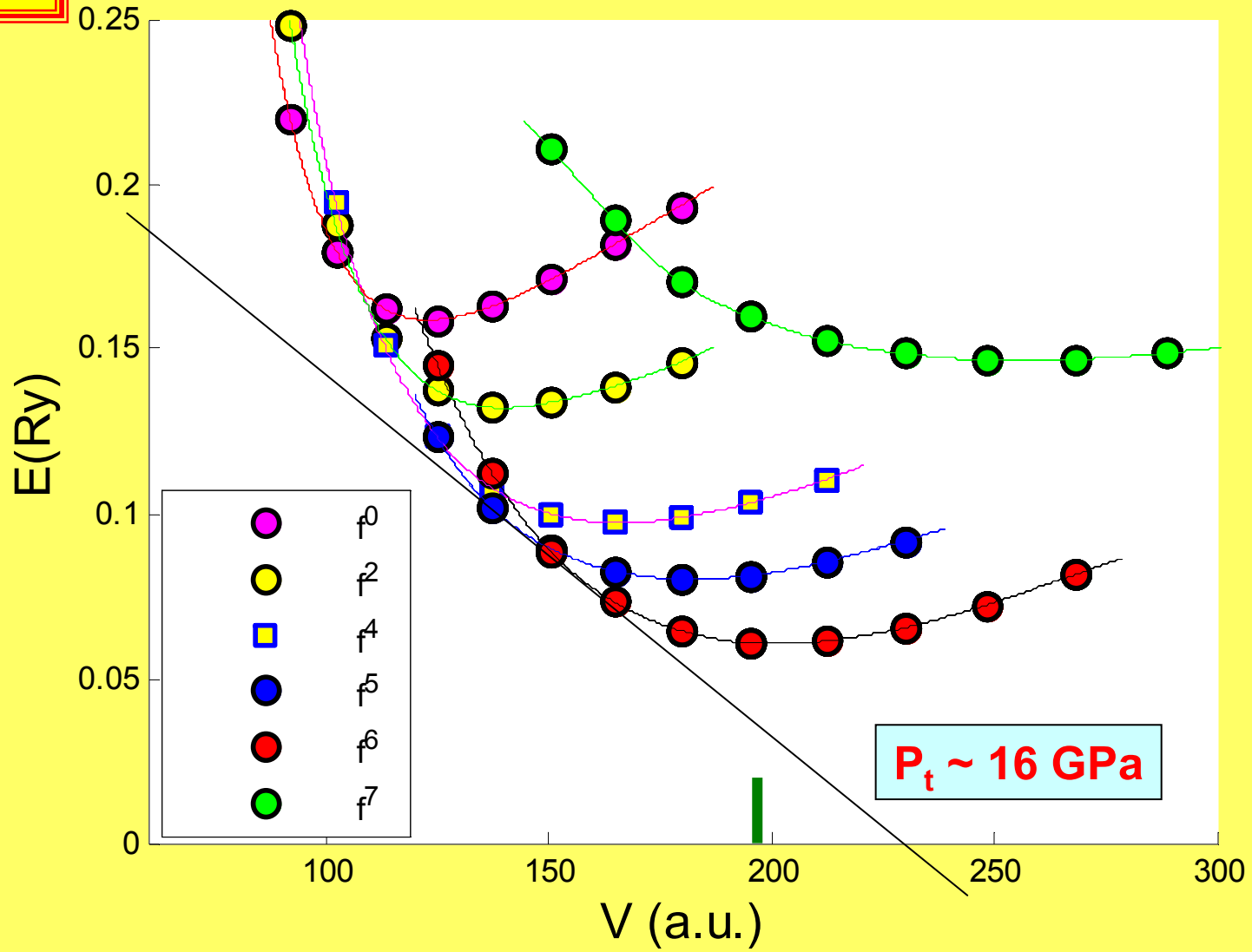
N	O
P	S
As	Se
Sb	Te
Bi	Po

Phase Transitions (2007)

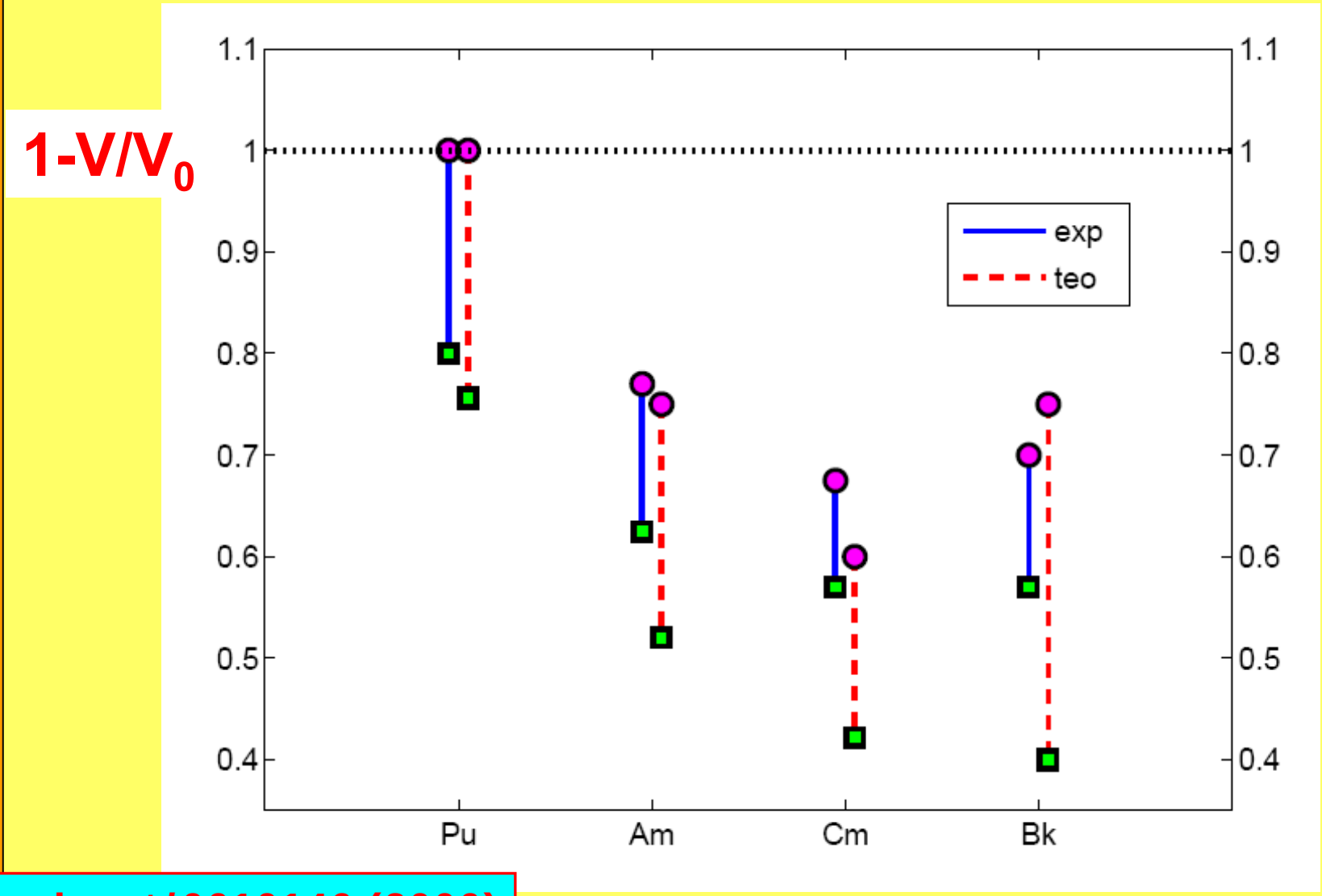
AnX valencies

U		Np		Pu		Am		Cm	
6	5	5	54	54	43	3	3	3	3
5	54	4	4	43	3	3	3	3	3
4	54	4	4	3	3	3	3	3	3
4	4	4	4	3	3	3	3	3	3
3	3	3	3	3	3	3	32	3	3
f^1	f^2	f^3	f^4	f^5		f^6		f^7	

Am


Am SIC (FCC) : E(V)
E(Ry)
V (a.u.)
0.25
0.2
0.15
0.1
0.05
0
100
150
200
250
300
f0
f2
f4
f5
f6
f7
Pt ~ 16 GPa

Actinides - delocalization



cond-mat/0610146 (2006)

Simplified SIC

$$E[n] = E^{LSD}[n] - \sum_{\alpha}^{occ.} \delta_{\alpha}$$

$$E^{LSD}[n] = T[n] + U[n] + V_{ext}[n] + E_{xc}[n]$$

$$\delta_{\alpha} = U[n_{\alpha}] + E_{xc}[n_{\alpha}]$$

Simplified SIC

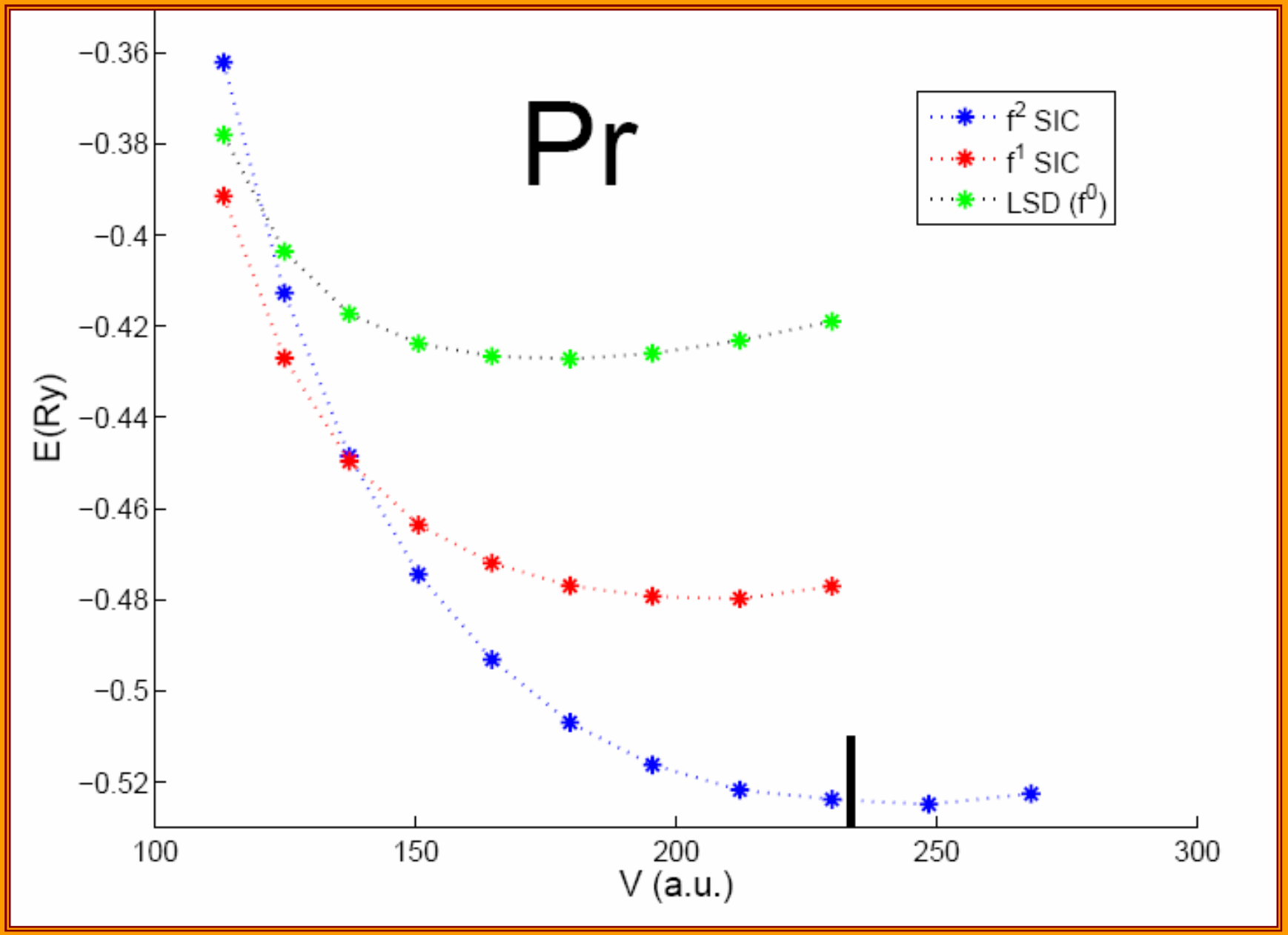
$$E[n] = E^{LSD}[n] - \sum_{i}^{corr.} \delta_i$$

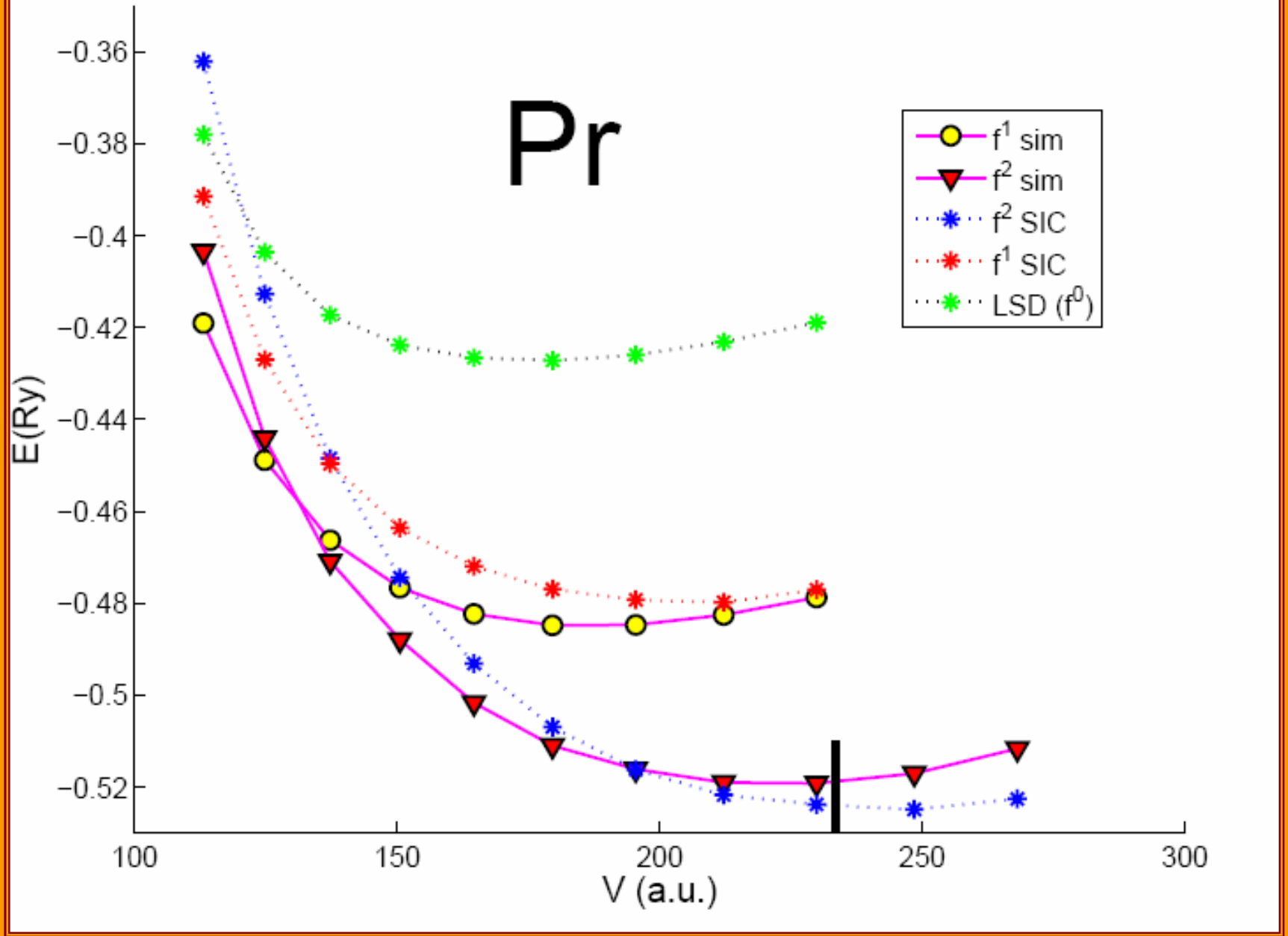
$$\boldsymbol{E^{LSD}[n] = T[n] + U[n] + V_{ext}[n] + E_{xc}[n]}$$

$$\delta_i = U[n_i \mid \varphi(r) \mid^2] + E_{xc}[n_i \mid \varphi(r) \mid^2]$$

$$\rho_{ij} \xrightarrow{diag} n_i$$

$$\Delta V_i = -V_H[n_i \mid \varphi(r) \mid^2] - V_{xc}[n_i \mid \varphi(r) \mid^2]$$


Pr
f2 SIC
f1 SIC
LSD (f0)
E(Ry)
V (a.u.)
−0.36
−0.38
−0.4
−0.42
−0.44
−0.46
−0.48
−0.5
−0.52
100
150
200
250
300


Pr
E(Ry)
−0.36
−0.38
−0.4
−0.42
−0.44
−0.46
−0.48
−0.5
−0.52
100
150
200
250
300
V (a.u.)
f1 sim
f2 sim
f2 SIC
f1 SIC
LSD (f0)

Summary

- SIC-LSD:
  - f^n localized states
  - valency (ground state)

SSC 116, 399 (2000)
Science 301, 498 (2003)
Phase Transit. (2007)

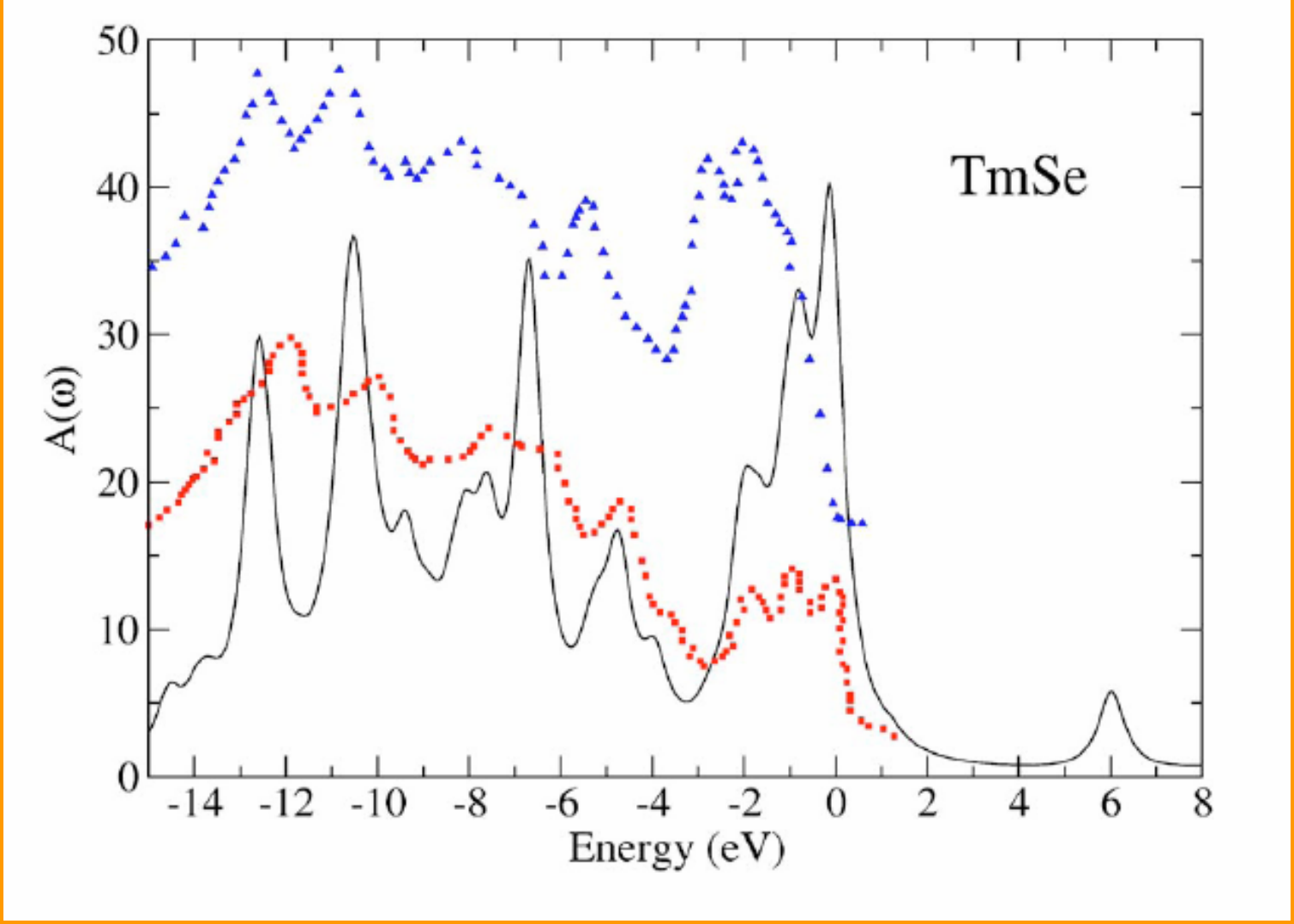
- Excit's.: LDA++Hubbard-I:
  - multiplets
  - Sm and Tm: pure atomic
  - PuSe and Am: complex gr.states

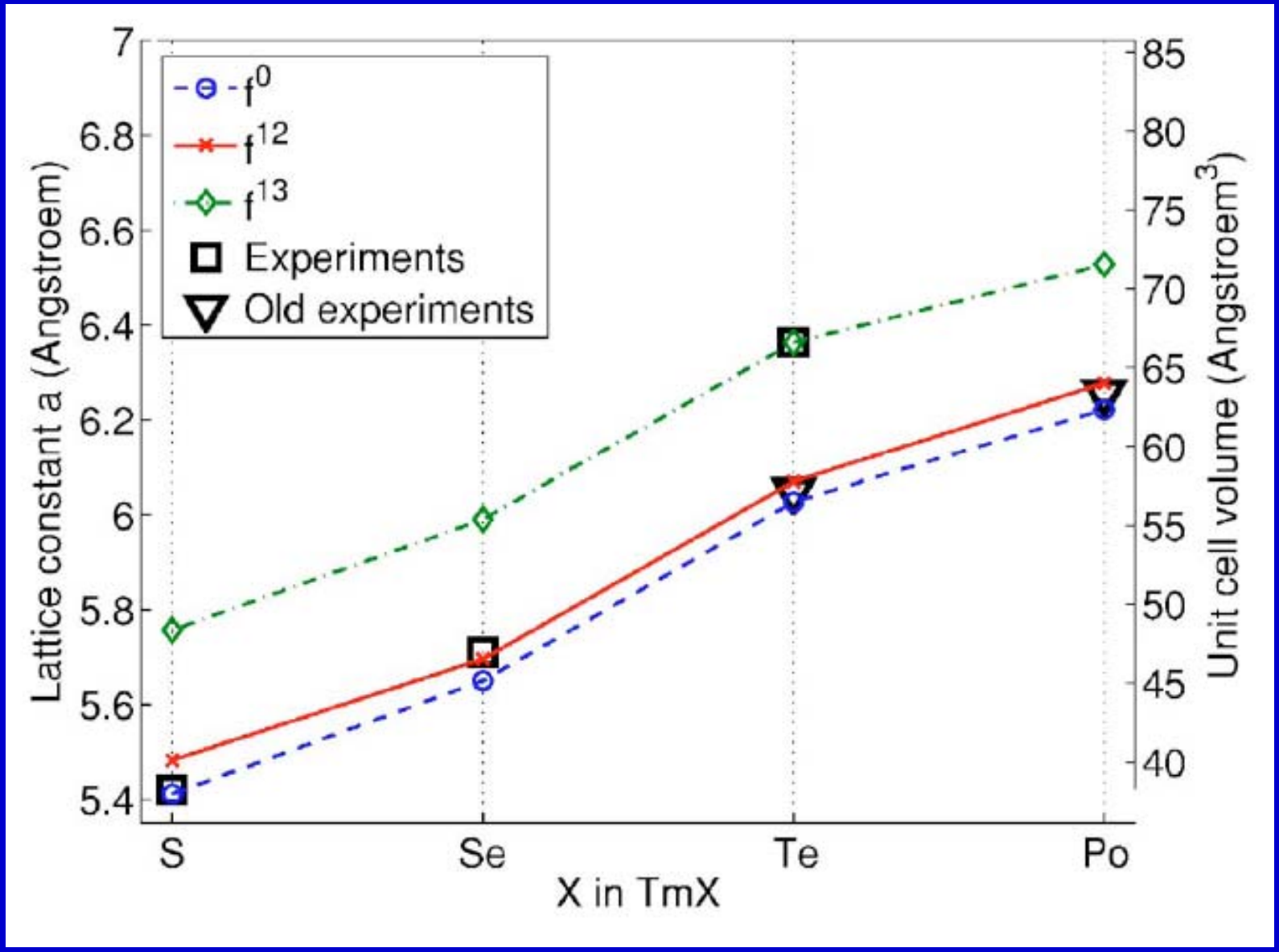
PRB 71, 45119 (2005)
PRB 72, 245102 (2005)

SSC 140, 364 (2006)

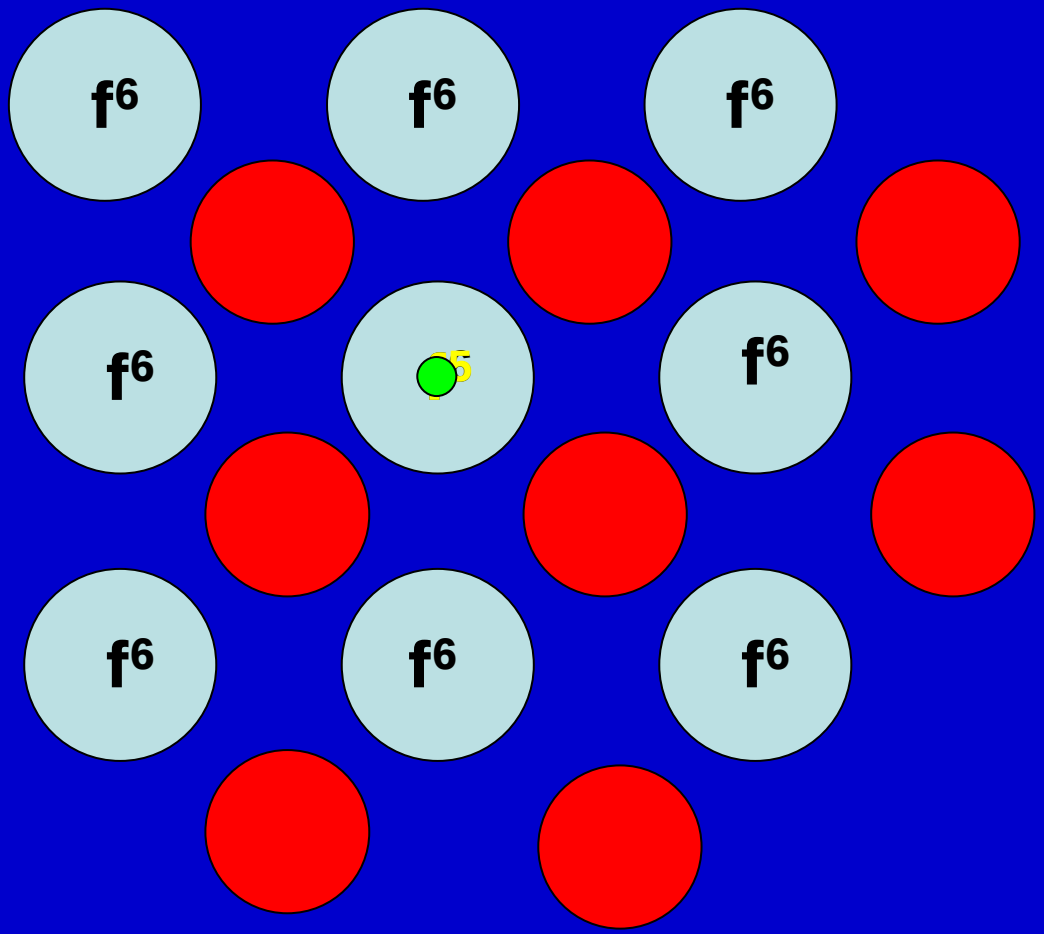
- Simplified SIC:
  - LDA+U like ...maybe...

TmSe




Lattice constant a (Angstroem)
Unit cell volume (Angstroem^3)
X in TmX
S
Se
Te
Po
7
6.8
6.6
6.4
6.2
6
5.8
5.6
5.4
85
80
75
70
65
60
55
50
45
40
f^0
f^{12}
f^{13}
Experiments
Old experiments

$$E(f^6) \leftrightarrow E(f^5) + \varepsilon_{Fermi}$$

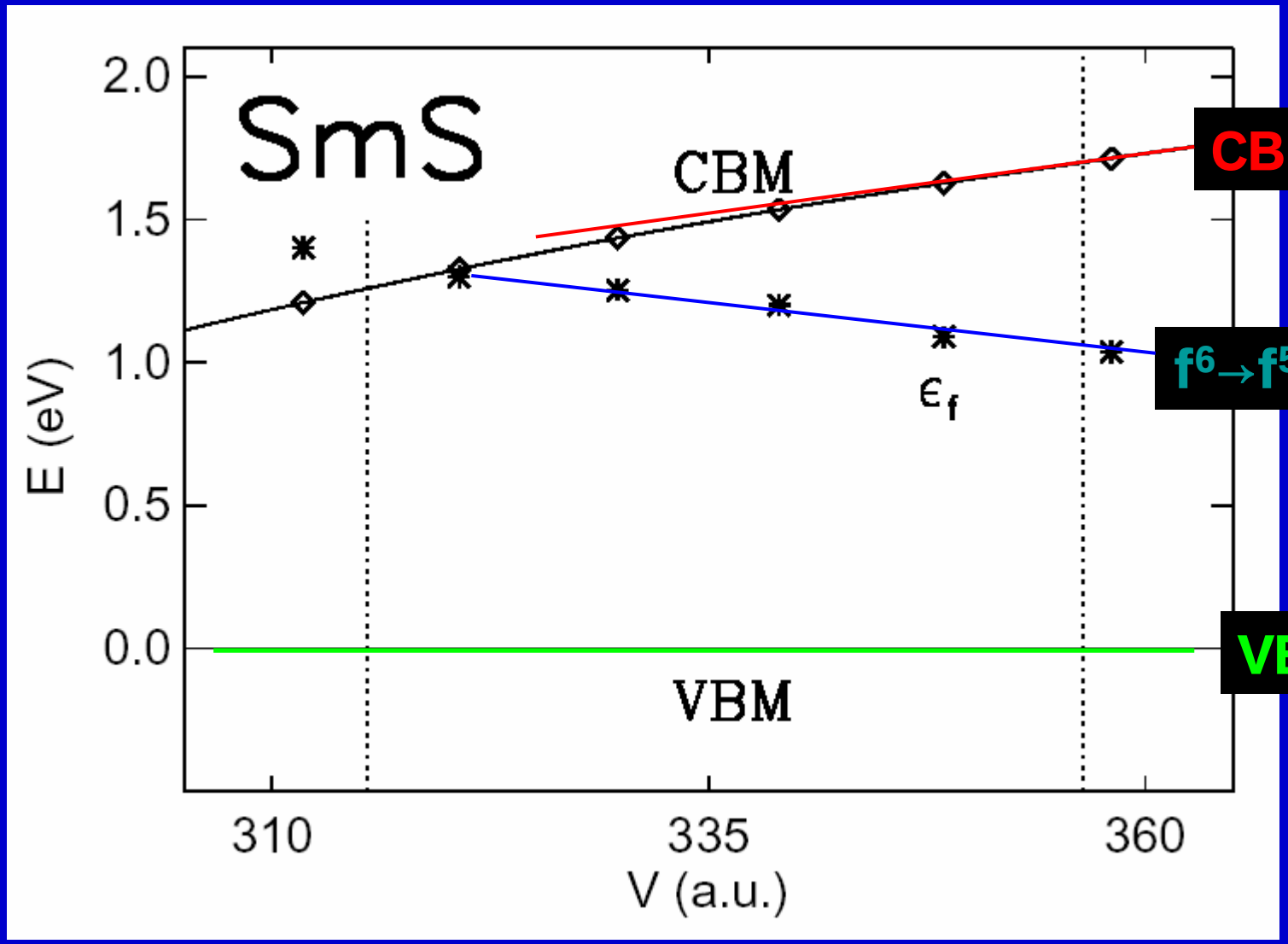


CB

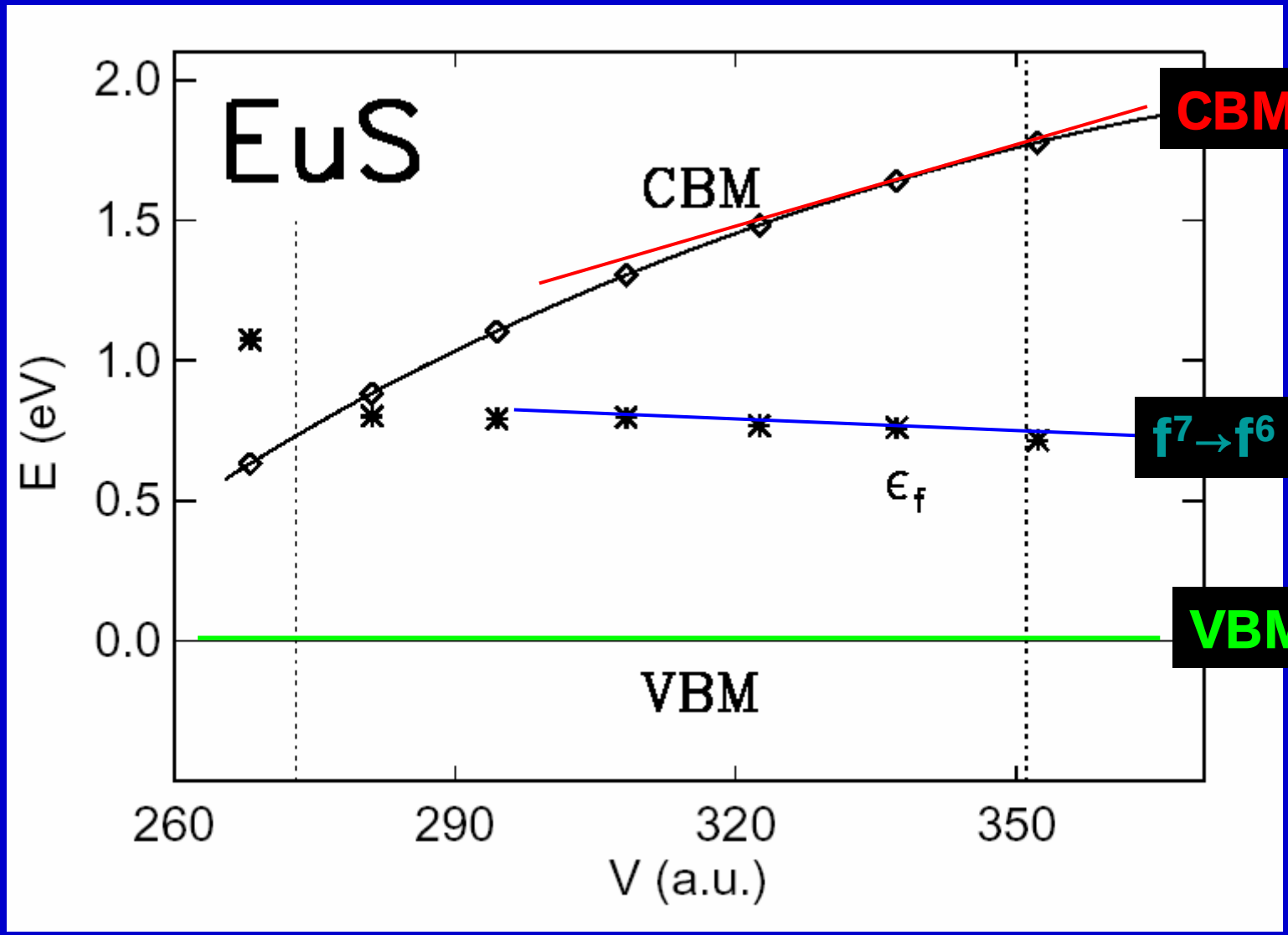
ε_{Fermi}

VB

SmS - band gap


SmS
CBM
VBM
ϵ_f
2.0
1.5
1.0
0.5
0.0
E (eV)
310
335
360
V (a.u.)
CBM
$f^6 \rightarrow f^5$
VBM

EuS - band gap


EuS
CBM
VBM
ϵ_f
E (eV)
V (a.u.)
2.0
1.5
1.0
0.5
0.0
260
290
320
350
CBM
$f^7 \rightarrow f^6$
VBM

gap	E_{gap}		$-dE_{gap}/dp$	
	theory	expt.	theory	expt.
EuS	1.10	1.7	7.8	7.9, 11
SmS	0.71	0.15	11.5	10
SmSe	0.63	0.45	10.0	11

Syassen (1986);
Jayaraman *et al.*, (1974)

eV

meV/kbar

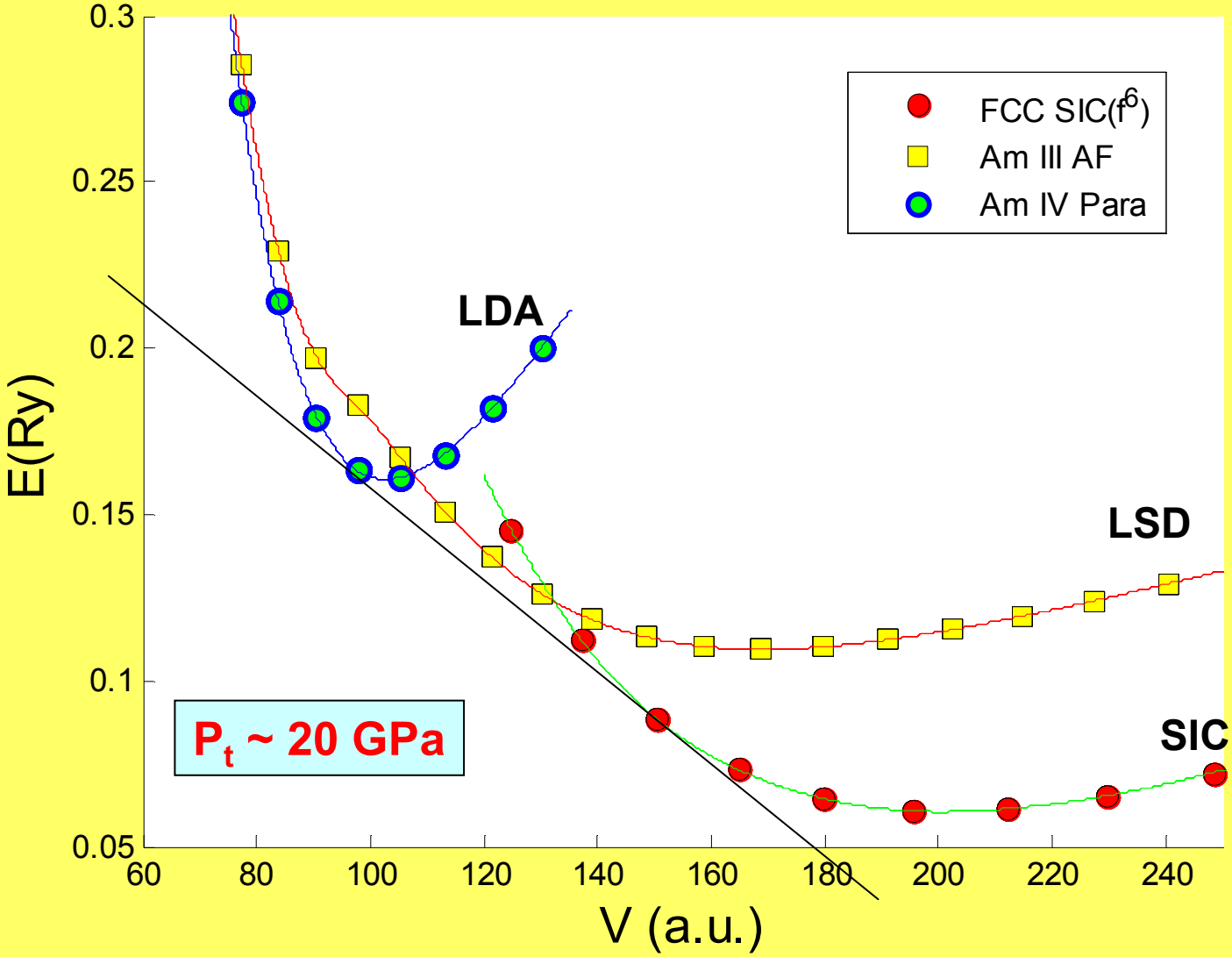
isostructutal transition pressures

GPa	theory	Expt.
SmS	0.1	0.65
SmSe	3.3	3-8
SmTe	6.2	6-8
EuS	11.6 (B1→B1)	16-20 (I→M) 20 (B1→B2)

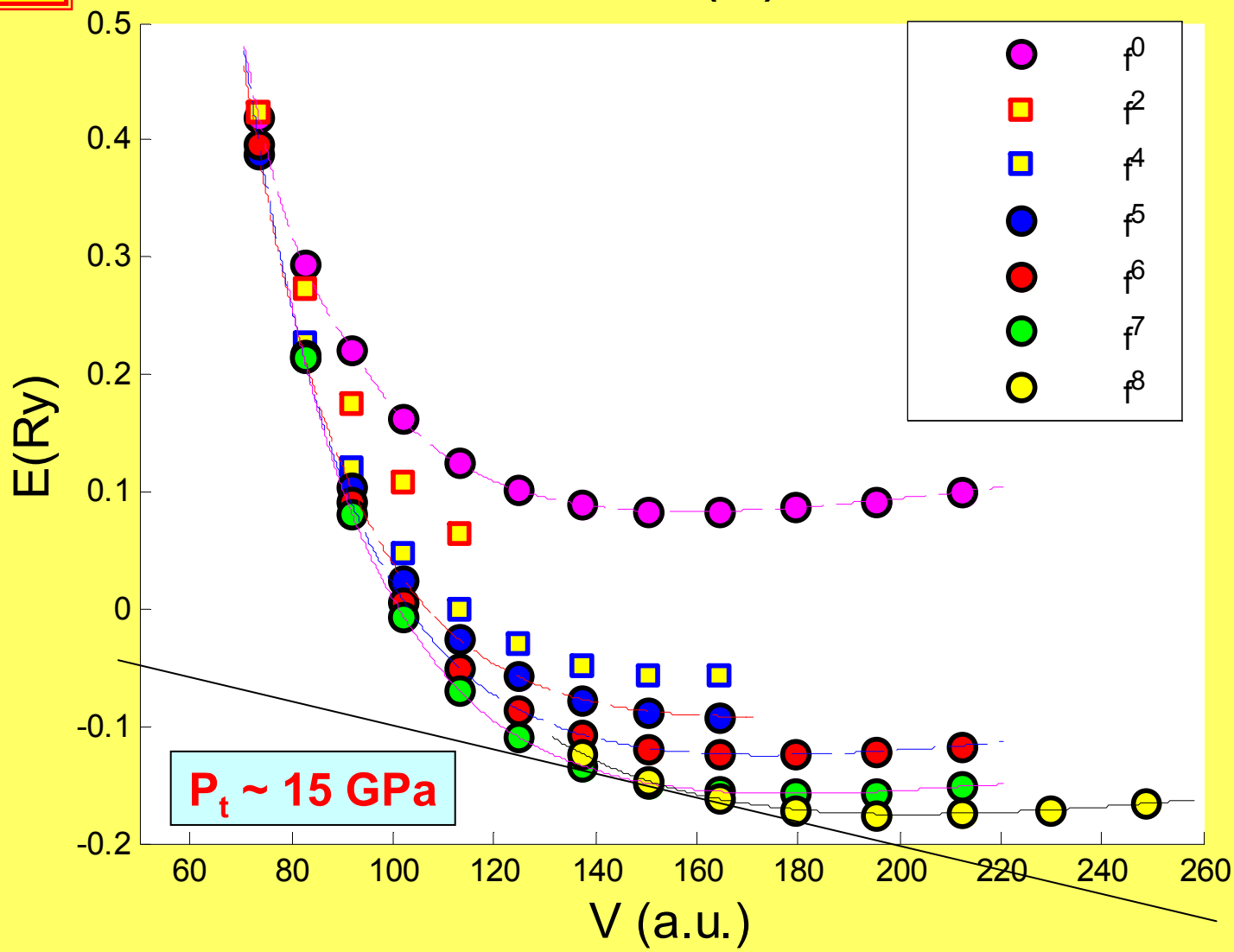
Syassen (1986)

Am

Americium E(V)

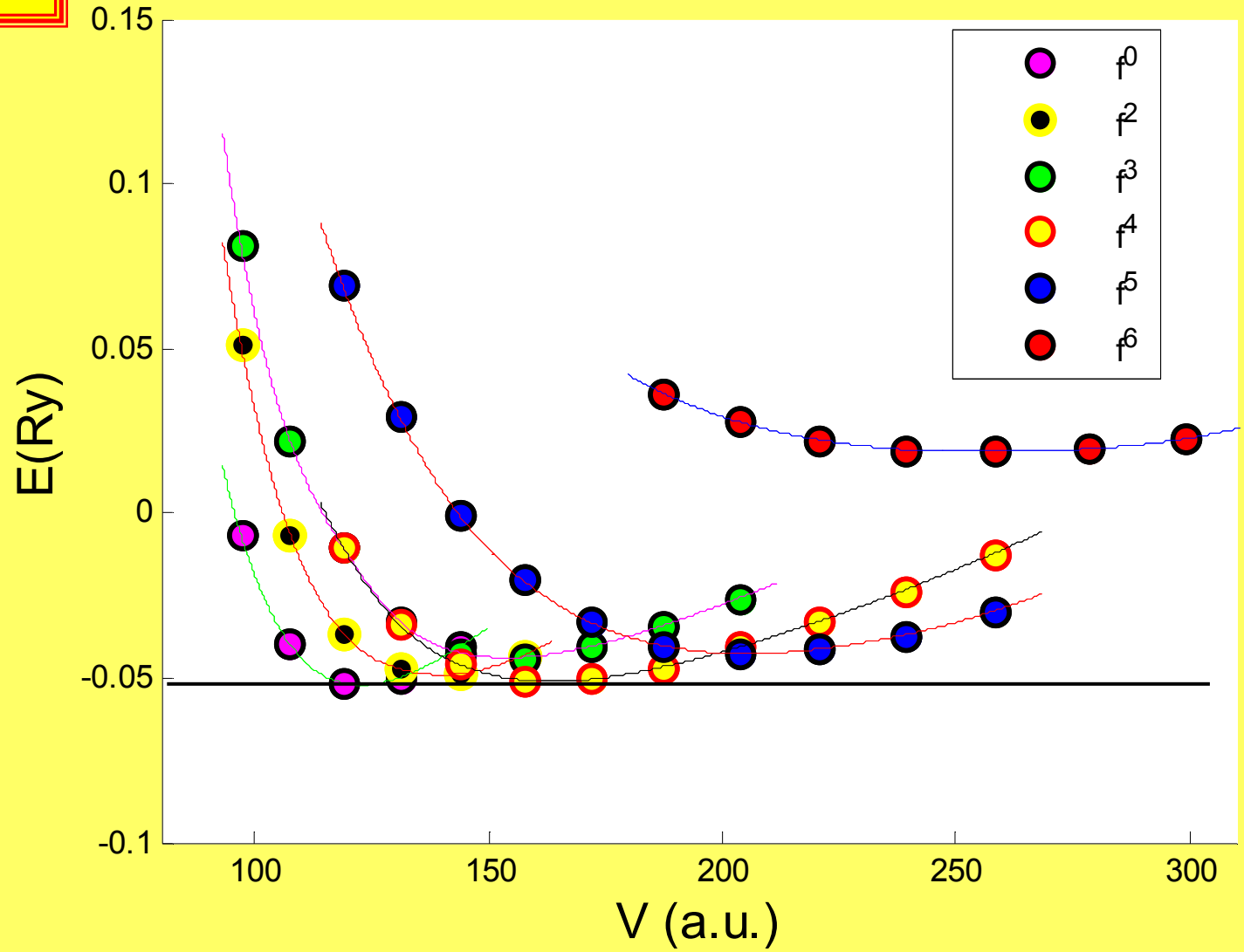


Bk


Bk E(V)
E(Ry)
V (a.u.)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
60
80
100
120
140
160
180
200
220
240
260
f0
f2
f4
f5
f6
f7
f8
Pt ~ 15 GPa

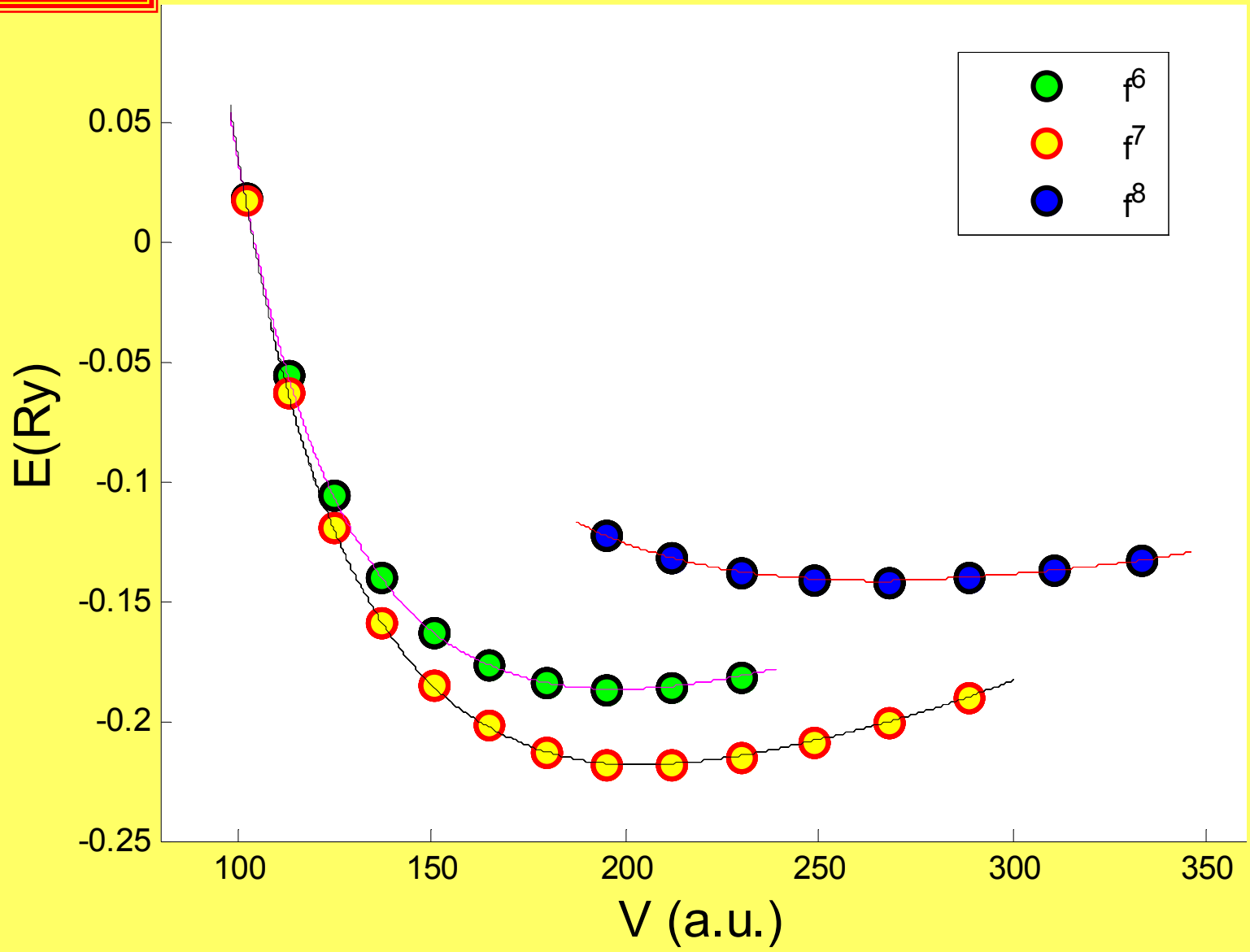
Pu

δ-Pu jj coupling: E(V)



Cm

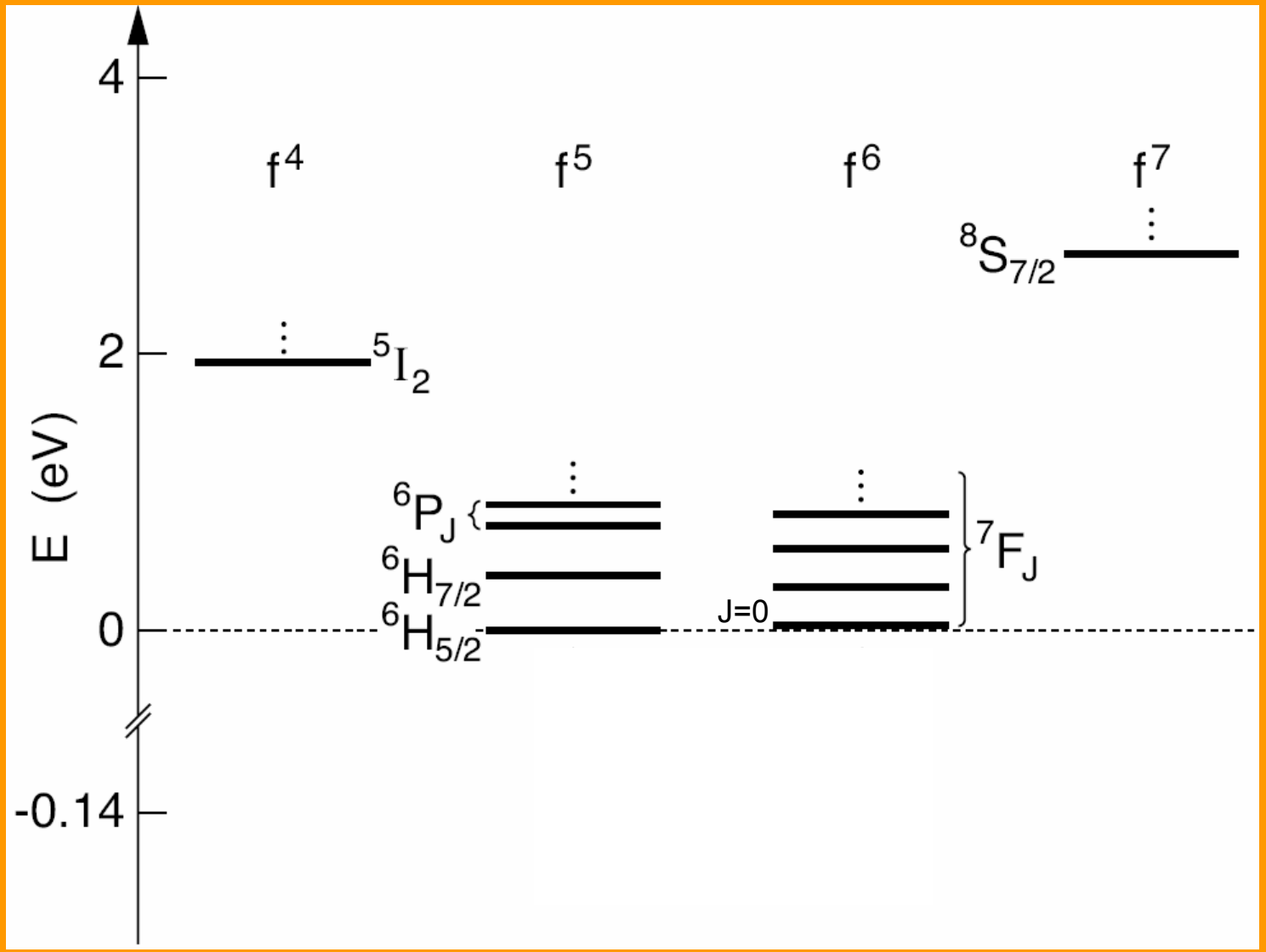
Cm SIC-LSD: E(V)



Actinides: equilibrium volume

a.u.	V_0(theo)	V_0(expt)	
δPu	**163.8**	**168**	**jj**
Am	**196.7**	**198**	**jj**
Cm	**203.5**	**202**	**LS**
Bk	**201.4**	**189**	**LS**

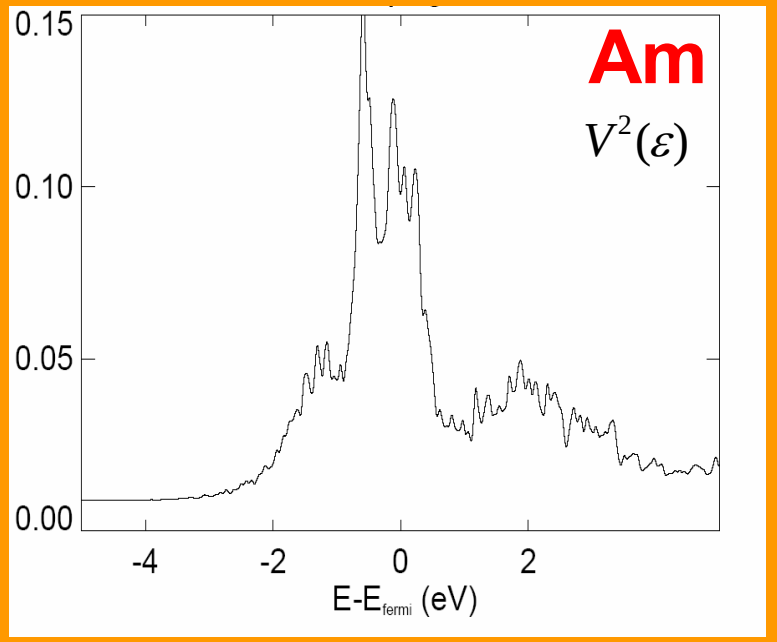
PuSe



$$< f^n; i \left| \frac{1}{r_{12}} + \xi \vec{l} \cdot \vec{s} \right| f^n; j > \rightarrow |\mu>,\ E_\mu$$

$$\sum_{ik} V_{ik} (\hat{c}_k^+ \hat{f}_i + \hat{f}_i^+ \hat{c}_k) = \int V(\varepsilon) \left(\hat{c}^+(\varepsilon) \hat{f}_i + \hat{f}_i^+ \hat{c}(\varepsilon) \right) d\varepsilon$$

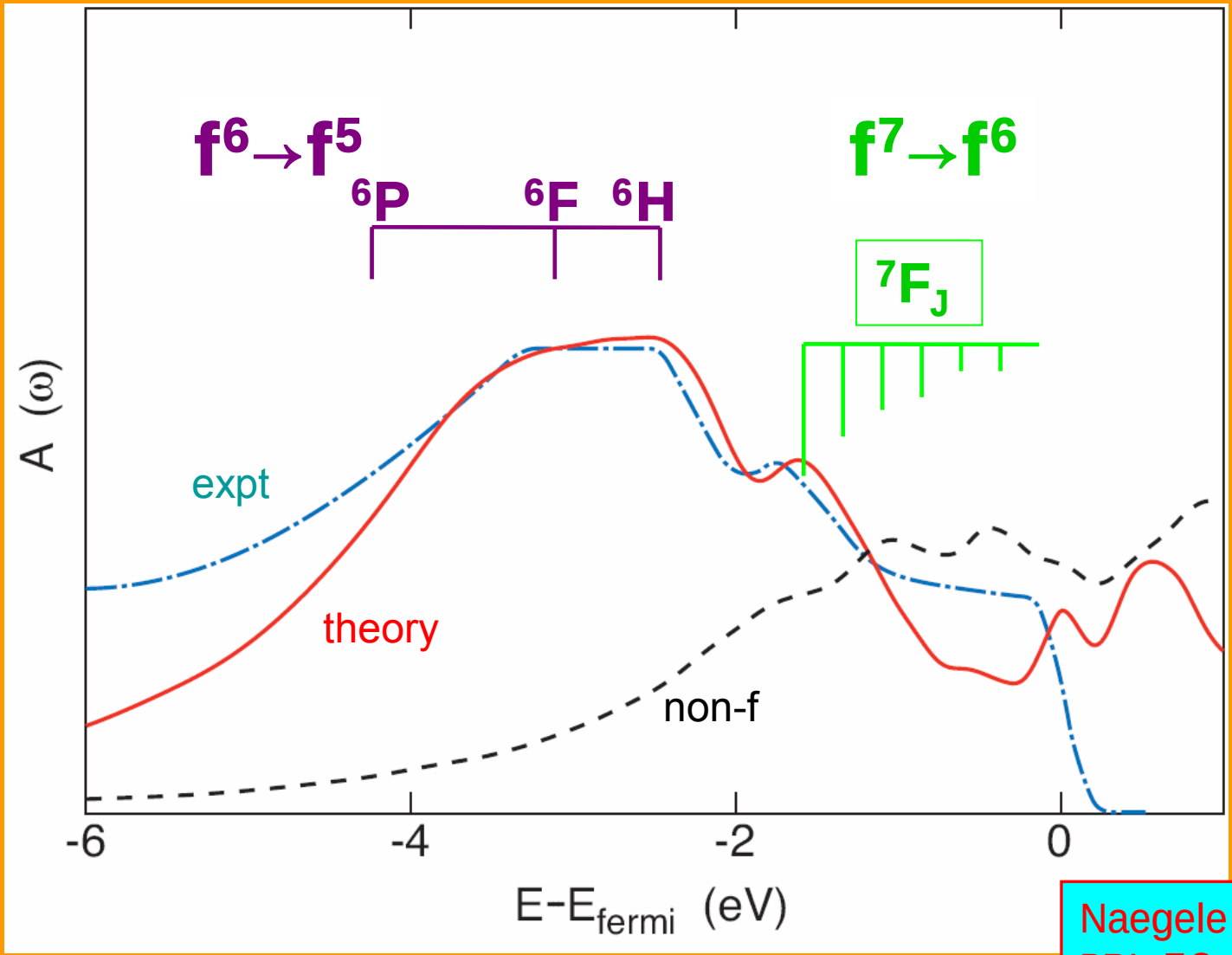
$$V \sum_i (c_i f_i^+ + f_i c_i^+) \rightarrow |\tilde{\mu}>,\ \tilde{E}_\mu$$



Am

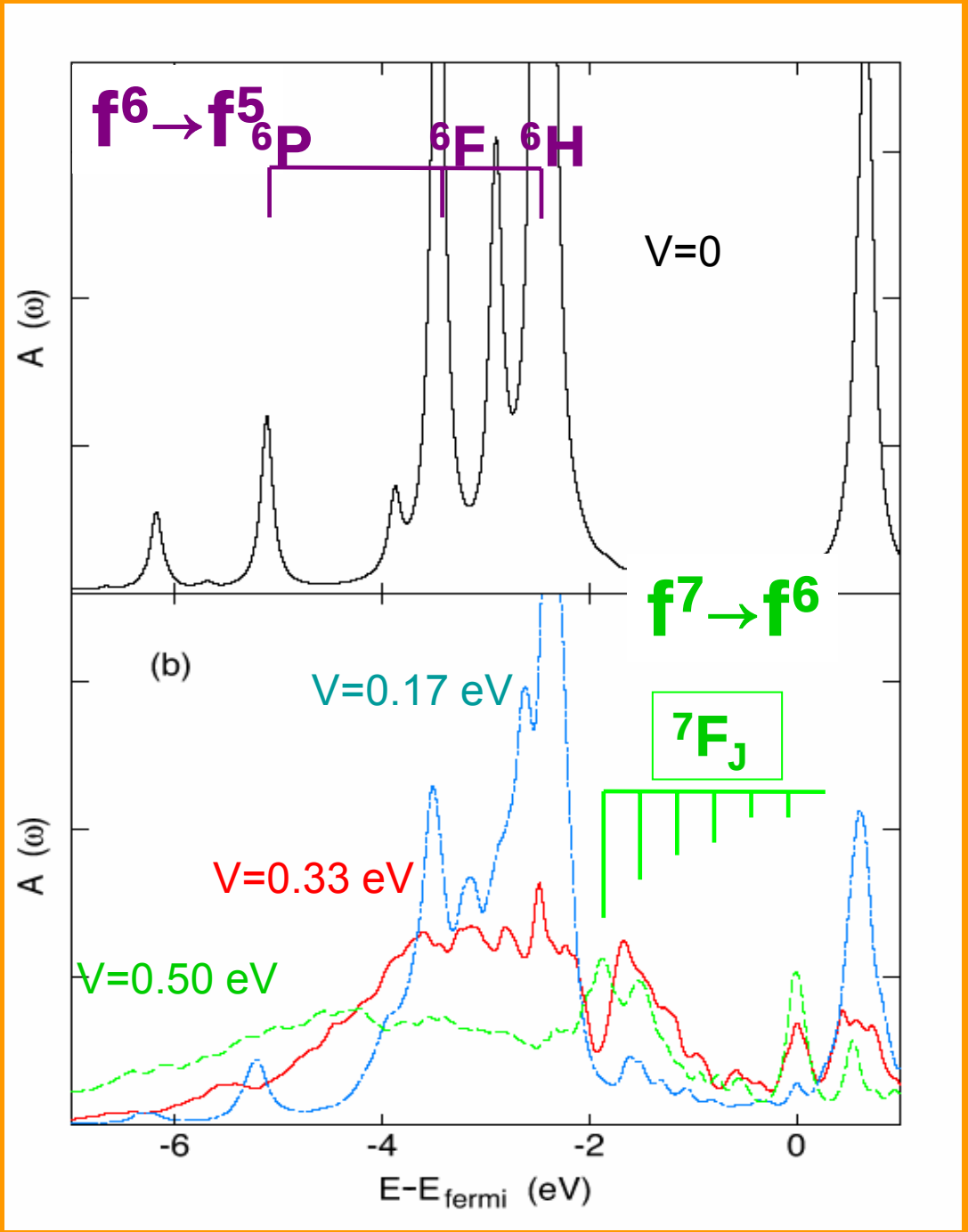
$E(f^7)-E(f^6)= +0.7$ eV

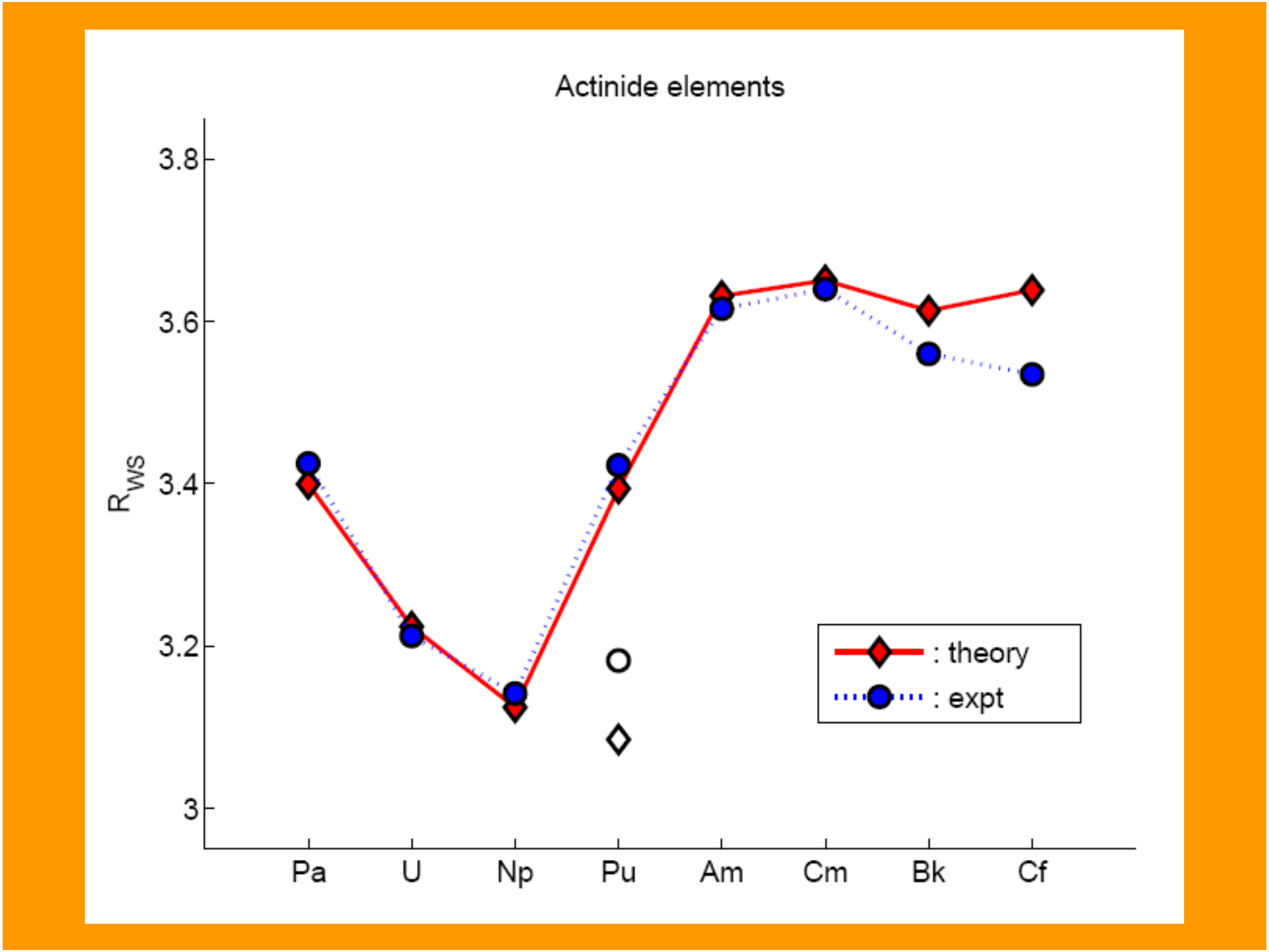
$V=0.33$ eV



Naegele *et al.*,
PRL **52,** 1834 (1984)

Am


f6→f5 6P
6F 6H
V=0
A (ω)
f7→f6
(b)
V=0.17 eV
7FJ
V=0.33 eV
V=0.50 eV
A (ω)
-6
-4
-2
0
E-Efermi (eV)


Actinide elements
3.8
3.6
3.4
3.2
3
R_{WS}
Pa
U
Np
Pu
Am
Cm
Bk
Cf
: theory
: expt