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Working Party on
PHYSICS OF CONDENSED MATTER AT HIGH PRESSURES
(11 - 29 August 1986)

HIGH PRESSURE TRENDS IN ELECTRONIC STRUCTURE

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High Pressure Trends in Electronic Structure

Many diverse phenomena including
- metal, semimetal, insulator tran's
- structural phase transitions
- pressure-volume anomalies

Due to simple changes in electronic structure with P
- s,p → d transition
- loss covalency
- f-shell delocalization

Often trends with P (fixed Z) ⇔ Z (P=0)

P changes R_{ws} (Wigner-Seitz)

Z changes ionic (i.e. core) radius R_I

Talk reviews electron band theory interpretation of expt. to illustrate trends

Brief Review of Electron Band Theory

- The whole story for T~298 K

$$P(V,T) = P(V,0) + \underset{\sim 0}{\Delta P_e(V,T)} + \underset{\Theta(0.01\,\text{Mbar})}{\Delta P_n(V,T)}$$

- T=0 band theory (e.g. APW, LMTO)

self-consistent

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{\vec{R}} \frac{-Ze^2}{|\vec{r}-\vec{R}|} + \int d\vec{r}\,' \frac{\rho(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|} + v_{xc}(\rho)\right]\psi_i = \varepsilon_i \psi_i$$

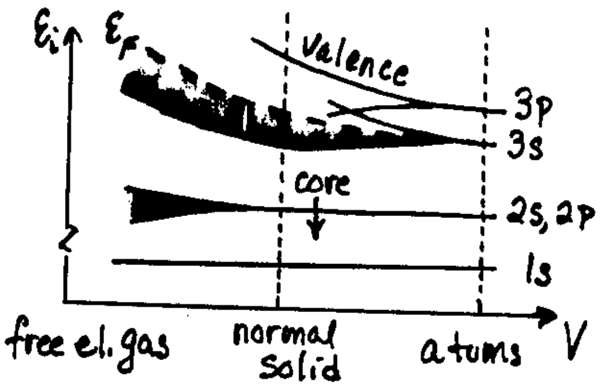
$$E(V,0) = \sum_i^{occ.} \varepsilon_i - \text{overcounting P.E.} + \sum_{\vec{R}<\vec{R}'} \frac{Z^2e^2}{|\vec{R}-\vec{R}'|}$$

$$P(V,0) = \frac{-dE(V,0)}{dV} = \sum_i^{occ} P_i \quad \text{(Liberman)}$$

- atoms → free el. gas

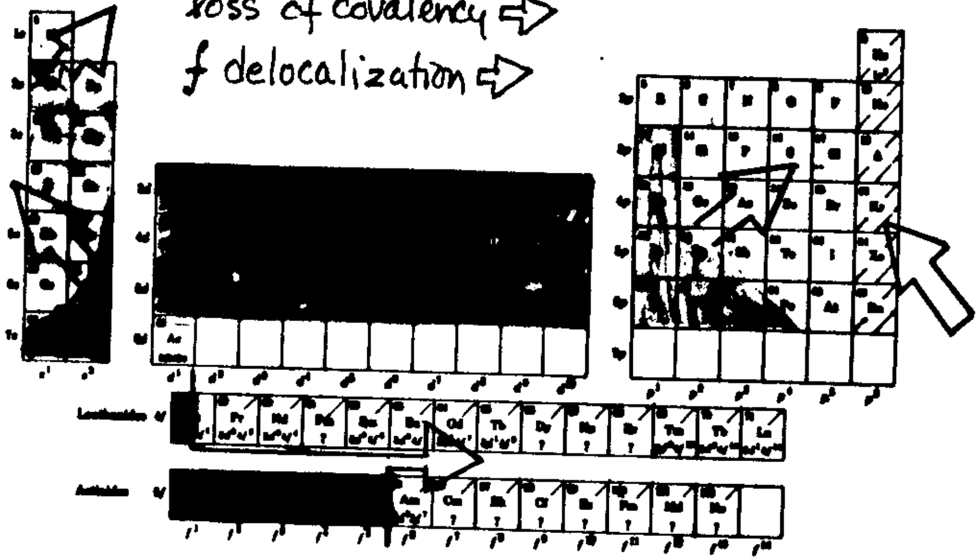
K.E. ~ $V^{-2/3}$ (wins out)

P.E. ~ $V^{-1/3}$



Trends with increasing pressure

sp → d transition ⇨
loss of covalency ⇨
f delocalization ⇨

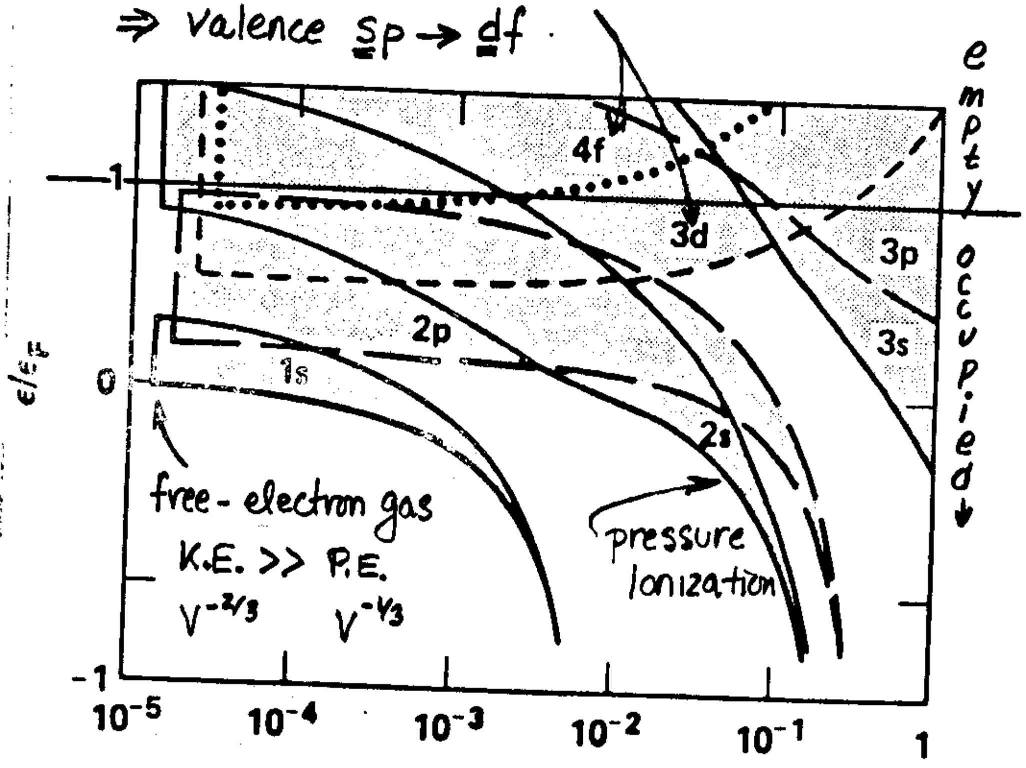


- ◪ filled shell (sp)
- ☐ covalent (sp)
- ■ simple metal (sp)
- ■ transition metal (d)
- ☐ rare earth / late actinide (f)
- ■ early actinide (f)

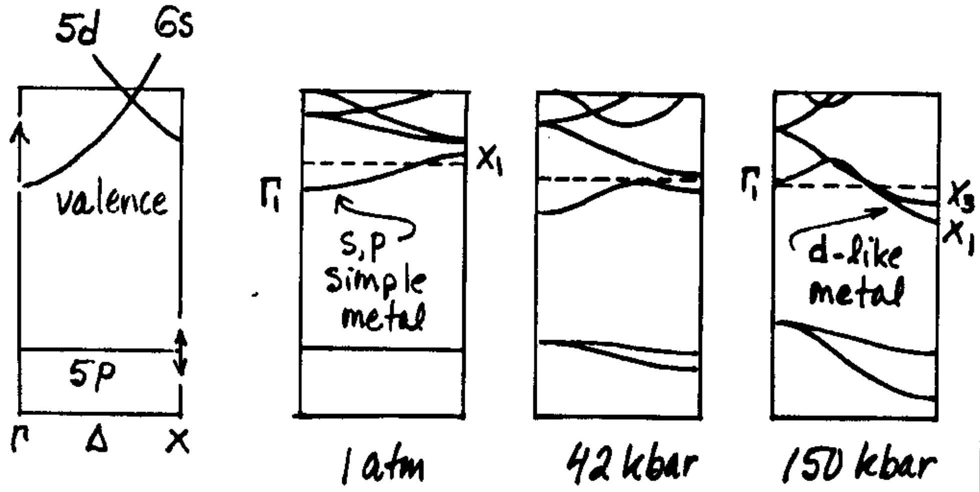
I: Electronic s→d transition ... e.g. Al

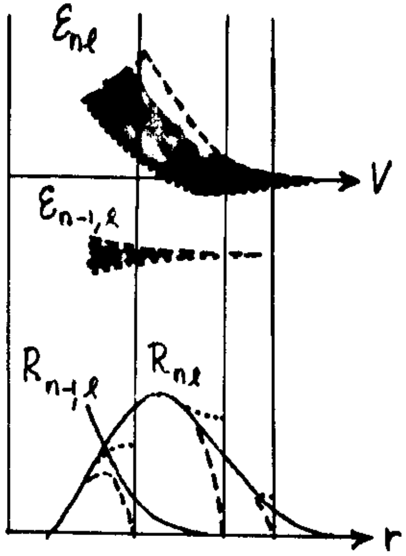
Higher ℓ bands with fewer radial nodes drop relative to other levels

⇒ valence sp → df.



Electronic s → d transition ... e.g. Cs





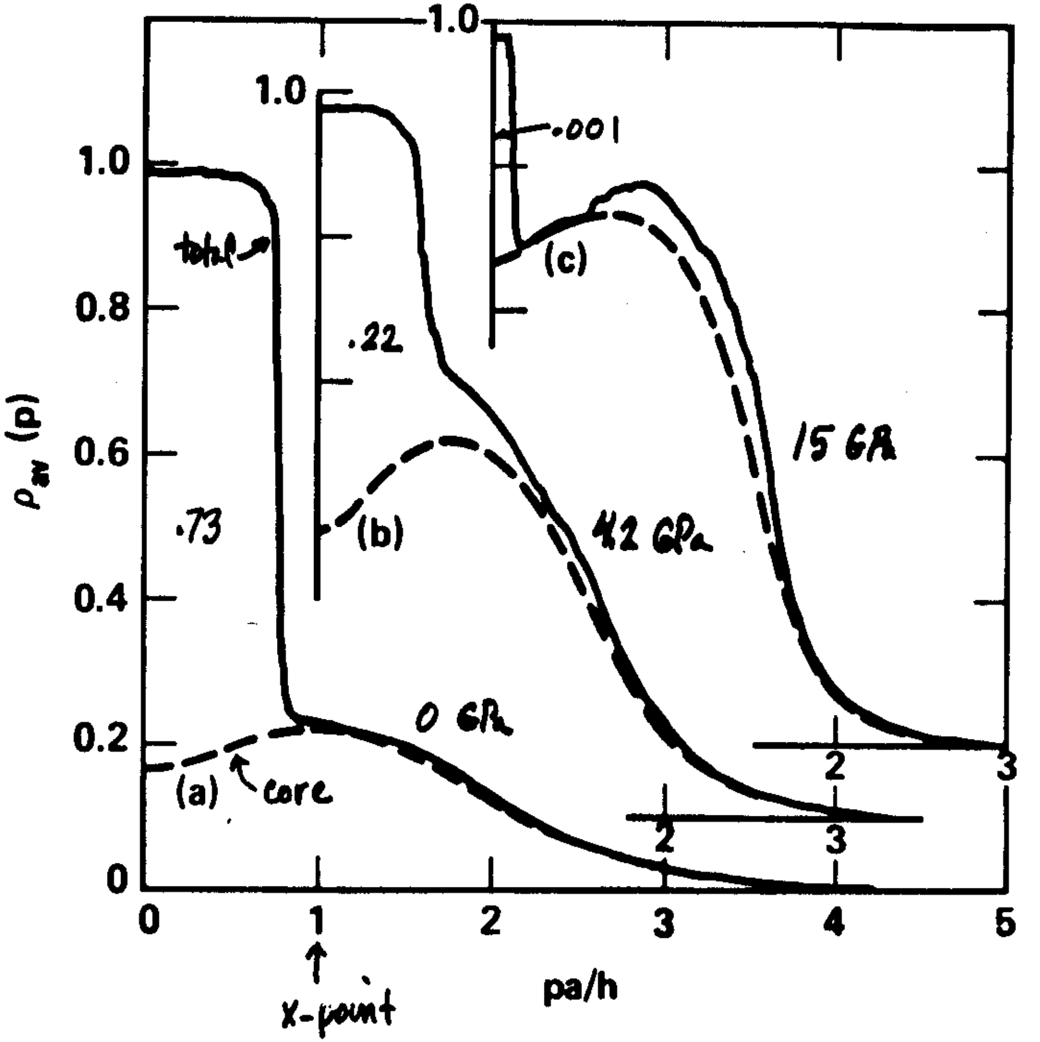
Why?

- KE ($V^{-2/3}$) vs. PE ($V^{-1/3}$)
  6s (5 nodes) 5d (2 nodes)
- more localized 5d orbital

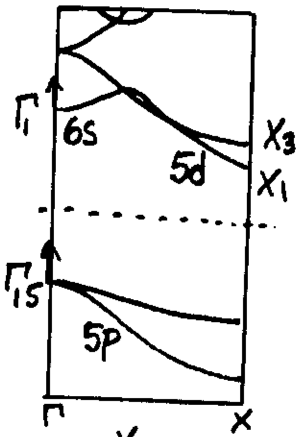
Note

- pressure ionization (5p core)
  ⇔ elect. trans. (s → d val)

Cs electron momentum density $\bar{\rho}(p)$

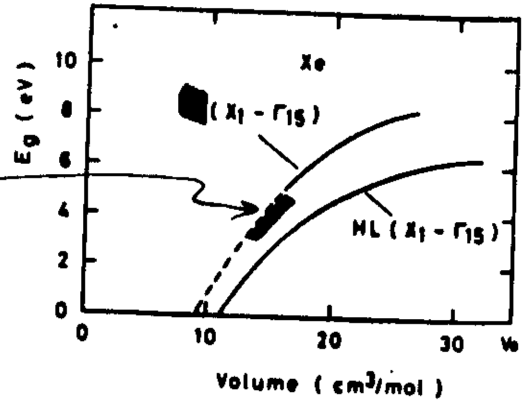


Closed-Shell Metallization

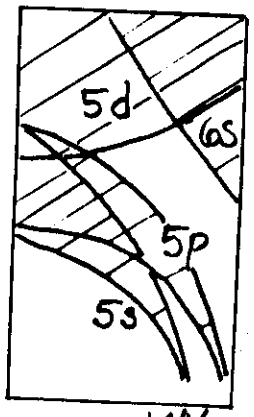


Xe

SLATER EXCH. CORR. IS BEST



Asuami et. al.



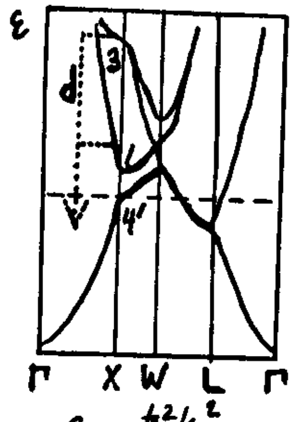
V/V₀

	ℓ	$\ell+1$	P_{Th}^{HL}	P_{Th}^{S}	$P_{expt.}$
He	1s	2p	112		
Ne	2p	3d	1,580[a]		(Mbar)
Ar	3p	3d	6.9		
Kr	4p	4d			
Xe	5p	5d	1.3[b]	2[b]	~2 (extra.)[c]
CsI	"	"	0.56[d]		1.1±0.1[e]
BaTe	"	"			0.20[f]

[a] Hama [b] Ross-McM [c] Asuami et. al., Syassen
[d] Satpathy et. al. [e] Reichlin et. al. [f] Grzybowski-Ruoff

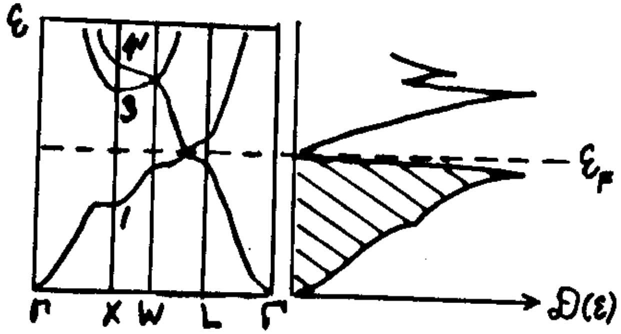
Metal → semimetal → metal transitions

- Divalent, fcc, nearly-free-el. metal



$\varepsilon \sim \frac{\hbar^2 k^2}{2m}$

- d band comes down with P
  ⇒ semimetal range



- Predictions semimetal range
  *Skriver (many earlier, incl. Vasvari et. al., Mickish et. al.)

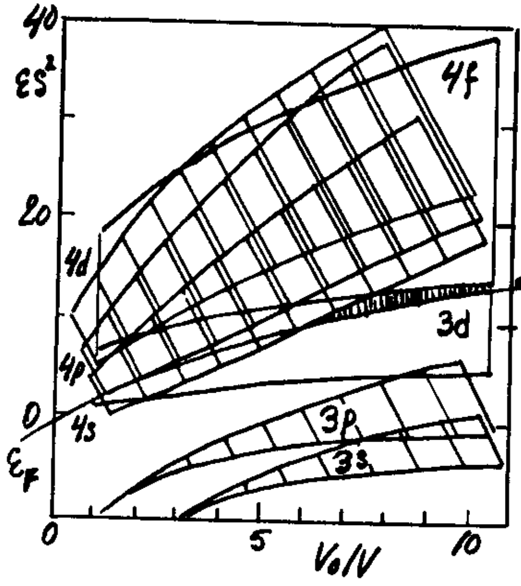
Mg	24-62 Mbar !		
Ca	70-210 kbar*		
Sr	3-40*		0-60*
~~Ba~~		~~Eu~~	Yb

(Ba, Eu: bcc)

- Resistivity expt. (eg., Ca, Dunn-Bundy)

  ρ increas. with P — consistent with semimetal
  $\partial\rho/\partial T < 0$ — they suggest 180 kbar →

Metal-insulator-metal trans. in high P nickel



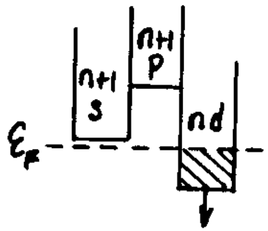
- 10 3d,4s valence el's
- gap opens when 3d drops below 4s (34 TPa)
- back to metal when 4f overlaps 3d (51 TPa)

Gandel'man et al.
McMahan & Albers

end s-d transition, P(GPa)

	50	260		34,000	
d	K	Ca	Sc		Ni
	Rb	Sr	Y	. . .	Pd
	Cs	Ba	La		Pt
	10	60			

s	Cu	Zn
	Ag	Cd
	Au	Hg

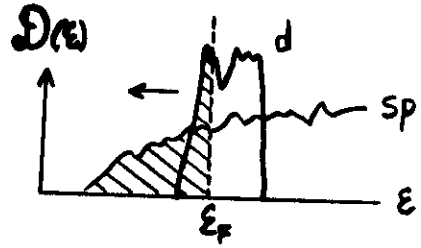


Structural Phase Transitions and sp-d transition

- Seq's of structures with P or Z ← delicate energy diff's

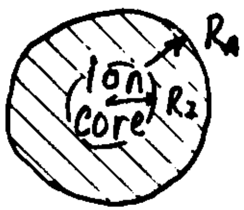
$$E_{bcc} - E_{fcc} \sim \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon \left[\mathcal{D}_{bcc}(\varepsilon) - \mathcal{D}_{fcc}(\varepsilon) \right]$$

- But driving force – change in el. structure – clear:



change in relative sp-d position

- Due to compression of valence electrons



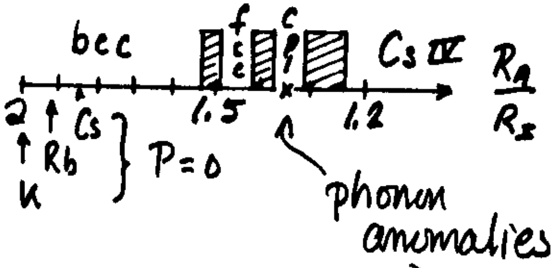
R_A/R_I decreases due to P or Z

∴ structures ⇔ R_A/R_I or N_d (no. of d electrons, another measure of sp-d separation).

s-d driven structural sequences

K	Ca		Sc														
Rb	Sr		Y														
Cs	Ba		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

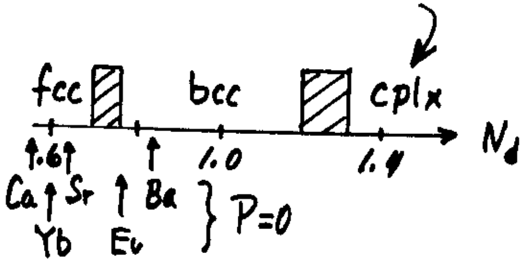
mono-valent



Takemura - Syassen

Olynyk - Holzapfel

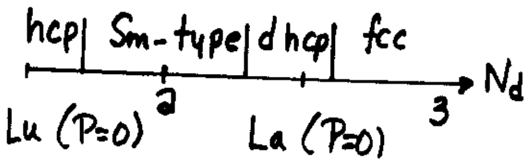
di-valent



Olynyk - Holzapfel

Skriver

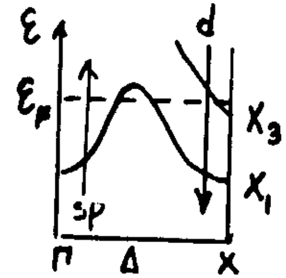
tri-valent



Jayaraman

Duthie - Pettifor

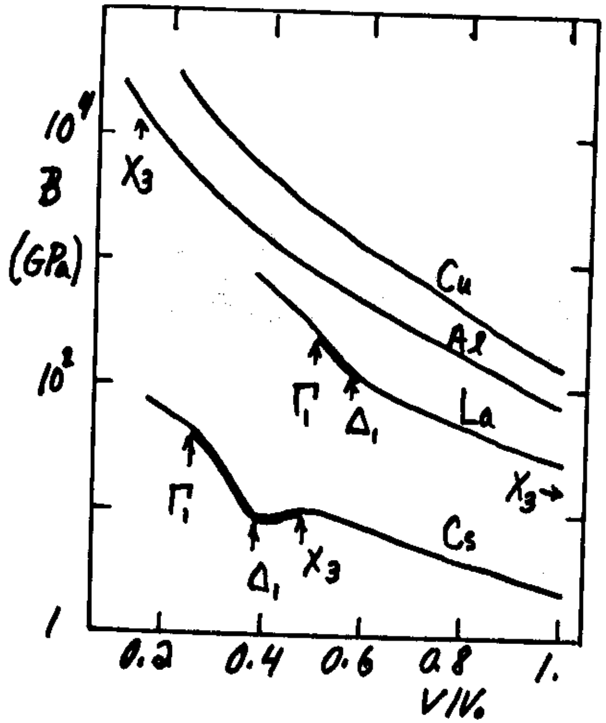
Equation of state & Phonon anomalies



$$P \sim \sum_i^{occ} \left(\frac{-d\varepsilon_i}{dV} \right)$$

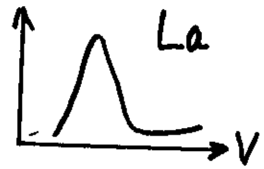
$$B = - \frac{dP}{d\ln V}$$

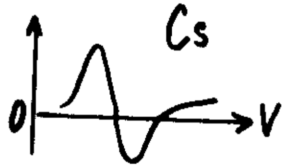
$$\gamma = -\frac{d\ln\omega_D}{d\ln V} \leftarrow k_D \sqrt{B/\rho}$$



(Slater) Grüneisen γ

$$\gamma \sim -\frac{1}{6} - \frac{1}{2} \frac{d\ln B}{d\ln V}$$

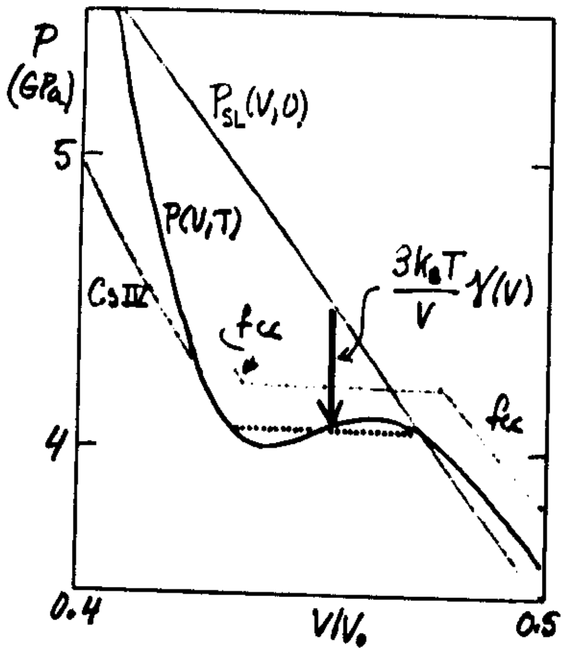




Phonon induced fcc - fcc transition in Cs

$$P(V, 298\,K) = P_{SL}(V,0) + \frac{3k_BT}{V}\gamma(V)$$

static lattice — Phonon



negative $\gamma(V)$

↓

van der Waals loop in $P(V, 298\,K)$

=

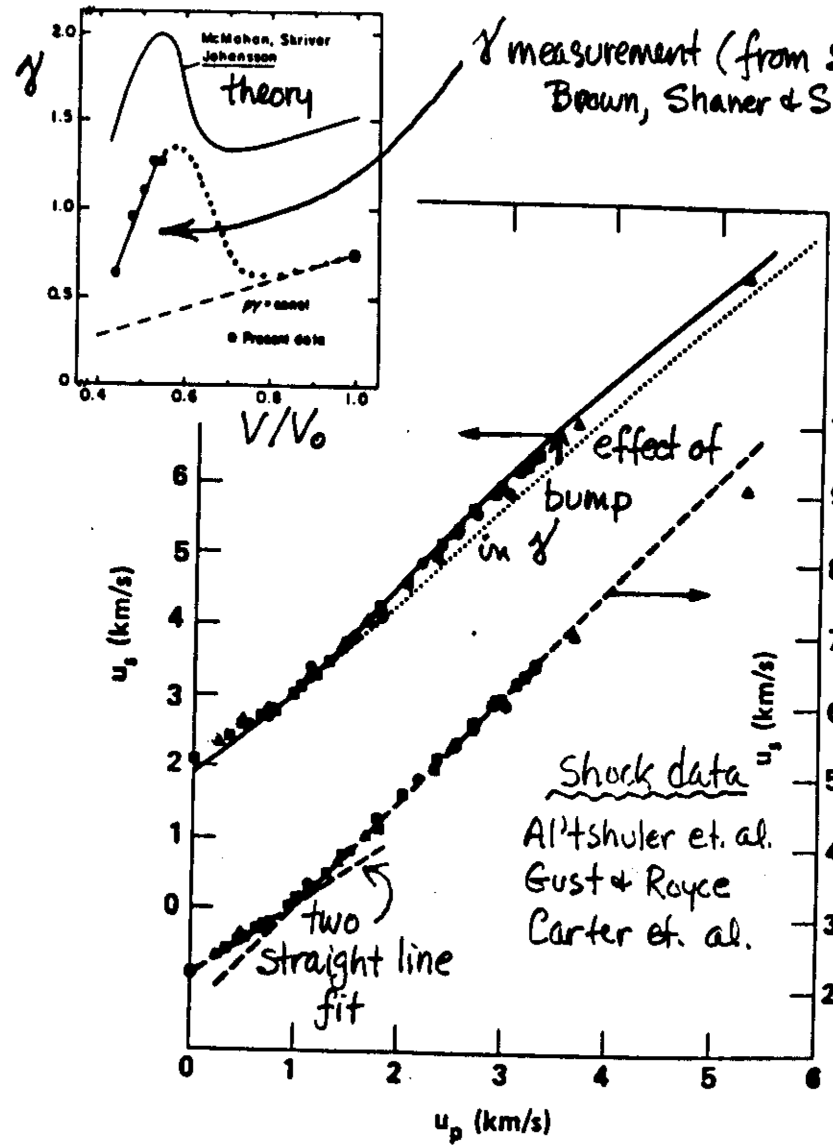
1st order fcc → fcc transition

phonon anomalies ⟷ "complex" regions of alkali, alkaline earth sequences

Boehler - Ross

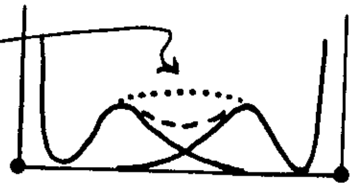
Anomaly in La shock data

γ measurement (from sound speed) Brown, Shaner & Swenson

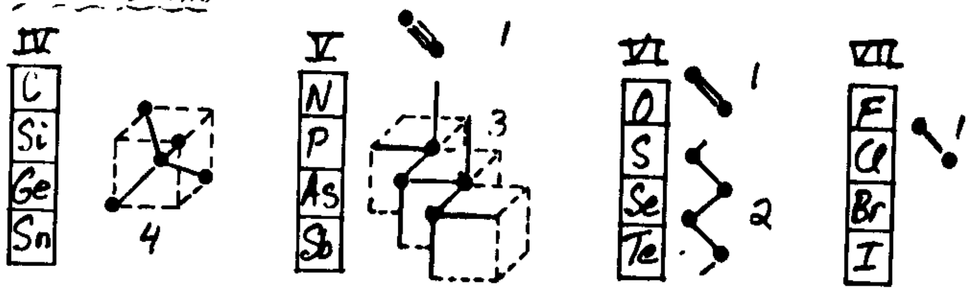


II. Loss of covalency: bonding (PE) vs. delocalized (KE)

bond charge exceeds superposed atoms



coordination



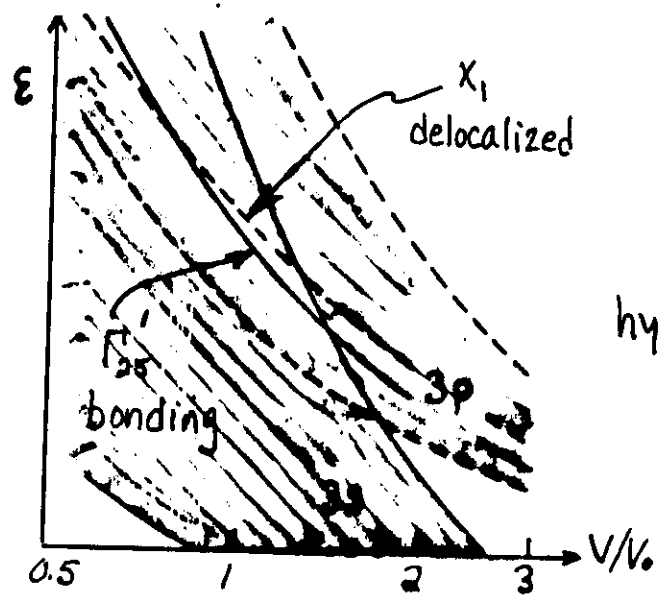
trends

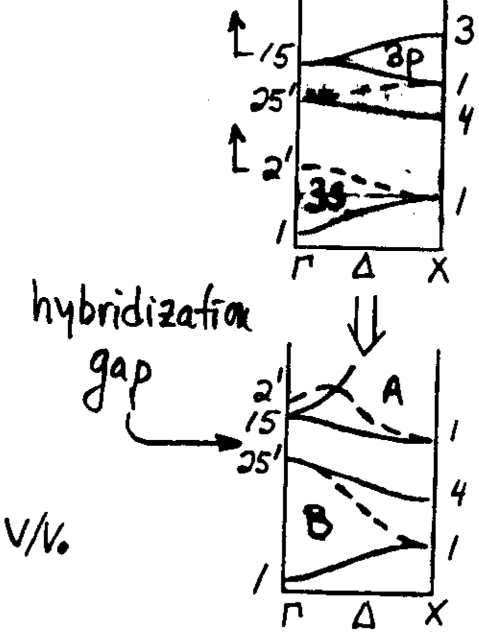
- decreasing bond charge
- tran's to higher coordination 1-4 → 6-12
- insulator → semicond./semimetal → metal

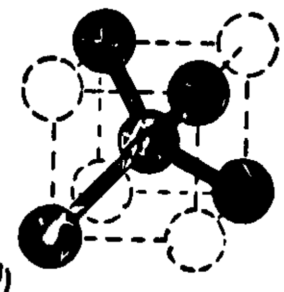
why

- advantage localized bond charge mostly PE ($V^{-1/3}$)
- KE ($V^{-2/3}$) favors delocalized charge & wins out

Loss of hybridization gap in diamond phase Si







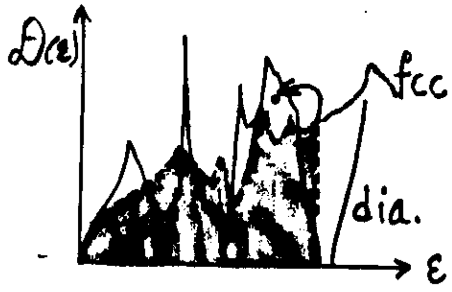
% of $|\psi|^2$ in*

	●	○
Γ_{25}'	93	7
X_1	51	49

*space filling spheres

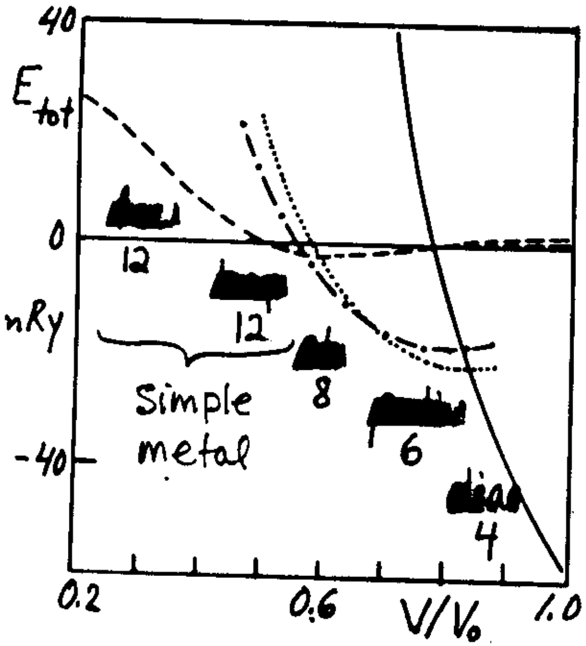
KE favors more delocalized Δ_1 & X_1. They drop relative to bonding Γ_{25}' ... closing gap.

Even at $V/V_0 = 1$ fcc Si ~ simple metal ($\mathcal{D}(\varepsilon) \sim \varepsilon^{1/2}$)



hybridization gap gives covalent diamond structure lower E_{tot}

with loss of gap ($V/V_0 \sim 0.78$) diamond str. less competitive.



Covalent → simple metal evolution completed by hcp, coordination 12

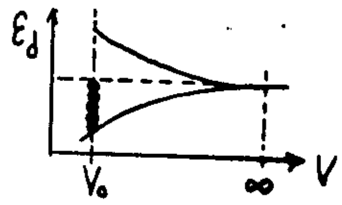
sequence observed through hcp (Olijnyk et al, Hu & Spain)

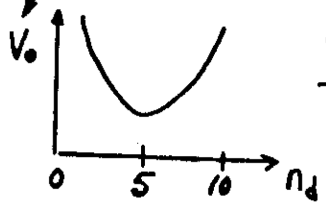
theory: Needs & Martin, Chang & Cohen, McM & Moriarty

III. f-shell delocalization

□ parabolic $V_0(n_f)$ complex structures ■ flat $V_0(n_f)$ rare earth structures

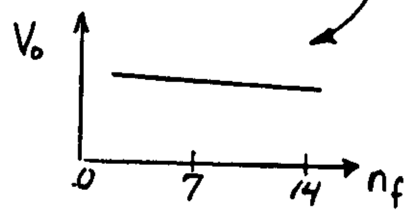
• Simple tight binding ⇒ parabolic $V(P=0)$ with no. d el's, n_d

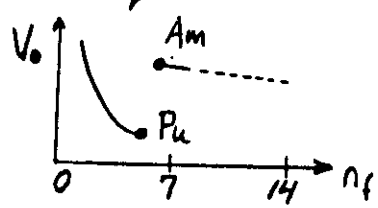




seen for trans. metals

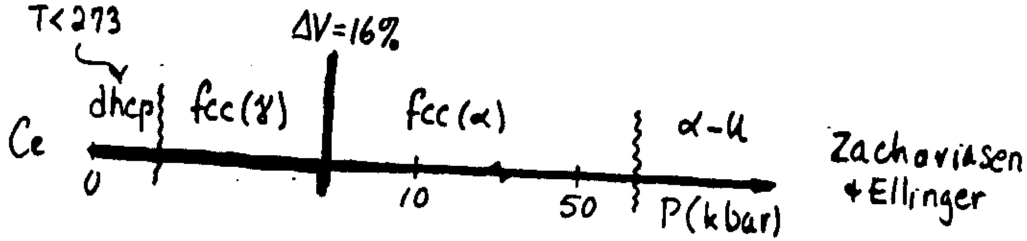
• But for f bands, rare earths (+3) and actinides, see

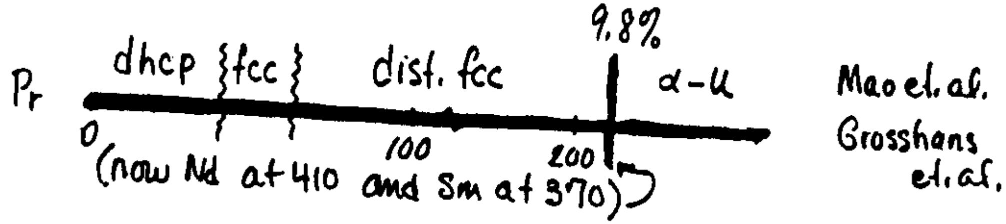


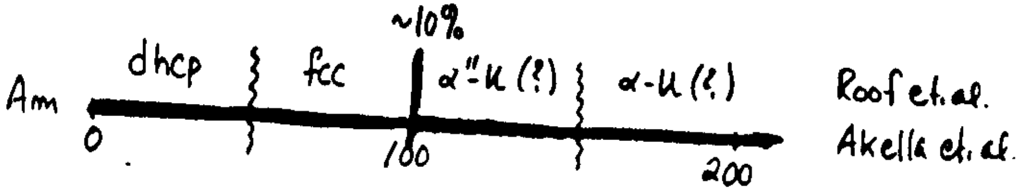


• As if f's atomic-like, "localized" in RE's + late actinides
" band-like, "delocalized" in early actinides

Localization → delocalization trans. seen under P







Note: Grosshans et. al. suggest "localized" RE^{+3} seq.
is hcp → Sm → dhcp → fcc → dist. fcc ← Seen Y, La, Pr