Transformations of Phosphorus under pressure from *simple cubic* to *simple hexagonal* structures via *incommensurately* modulations: electronic origin

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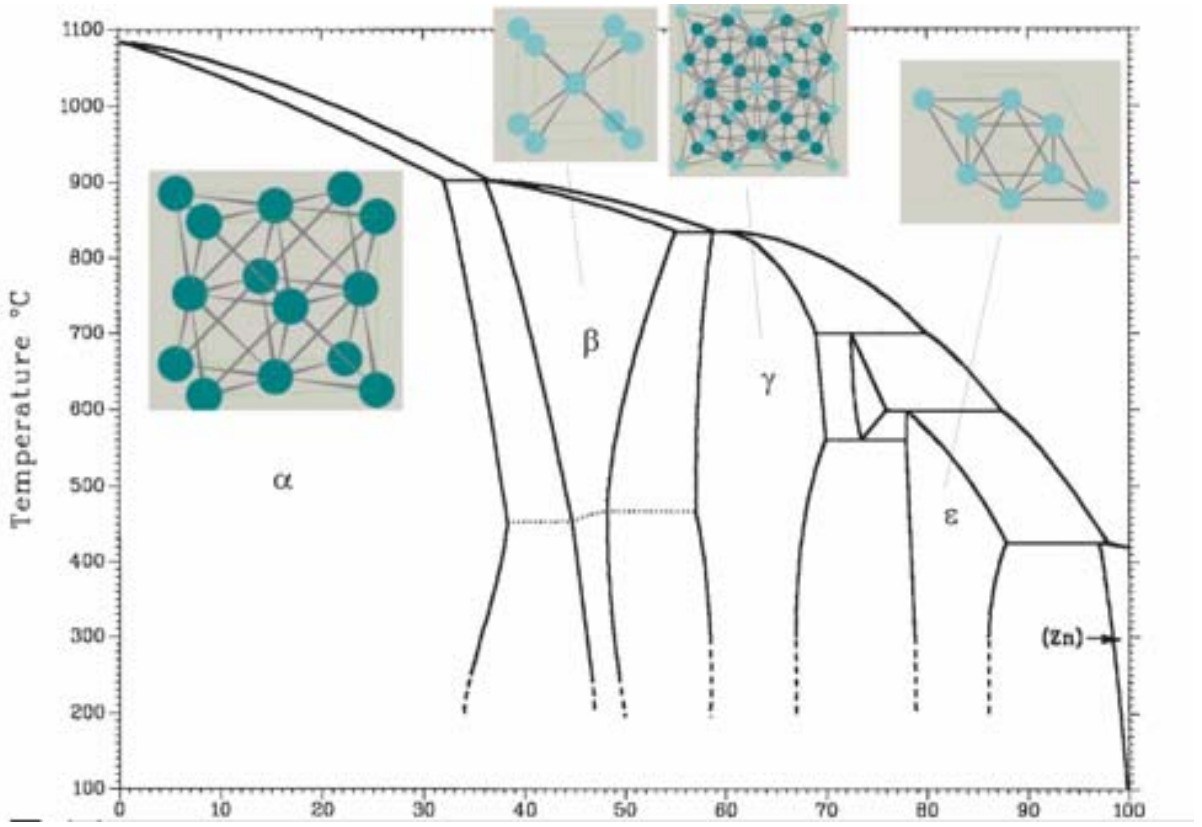
Outline

- Main factors of crystal structure stability
- Concept of the Fermi Sphere - Brillouin Zone interaction: Cu-Zn alloy system
- *Simple cubic* phase in P-III at pressures 10 – 100 GPa and its distortion on further compression
- An incommensurately modulated phase P-IV: consideration with a commensurate approximant
- *Simple hexagonal* phase in P-V up to 260 GPa

Phase diagram of the Cu-Zn system

The Age of Bronze
A. Rodin

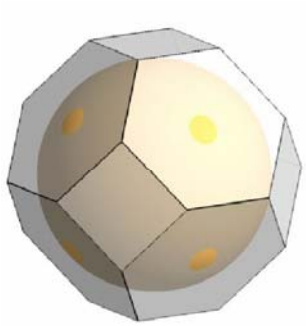
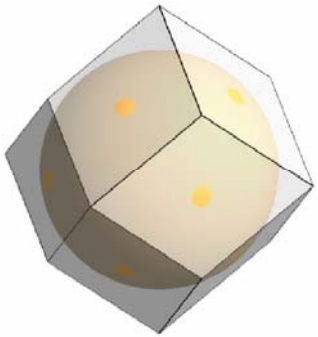
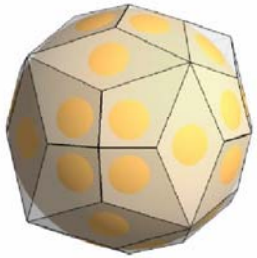
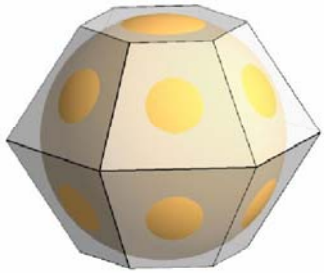


at.% Zn

α (fcc) → β (bcc) → γ (complex cubic) → ε (hcp)
1.35 → 1.5 → 1.62 → 1.75
(electron / atom)

after Massalsky (1996)

Hume-Rothery phases: Fermi sphere – Brillouin zone interaction

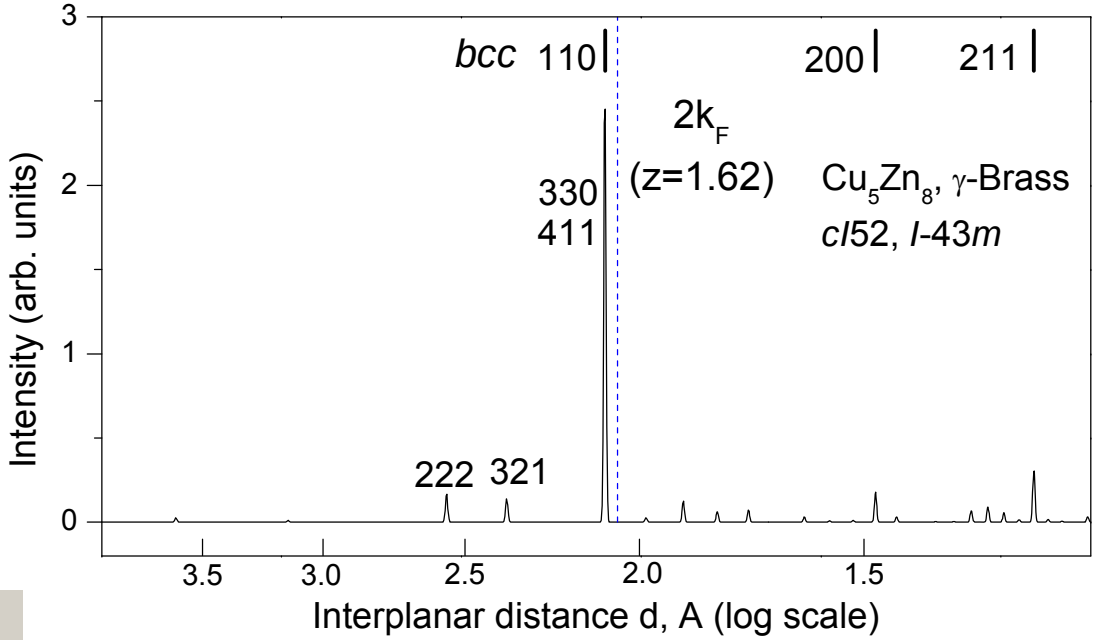
α (*fcc*) - phase	β (*bcc*) - phase	γ - complex cubic	ε (hcp) - phase
			
{111} {200}	{110}	{411} {330}	{002} {101}

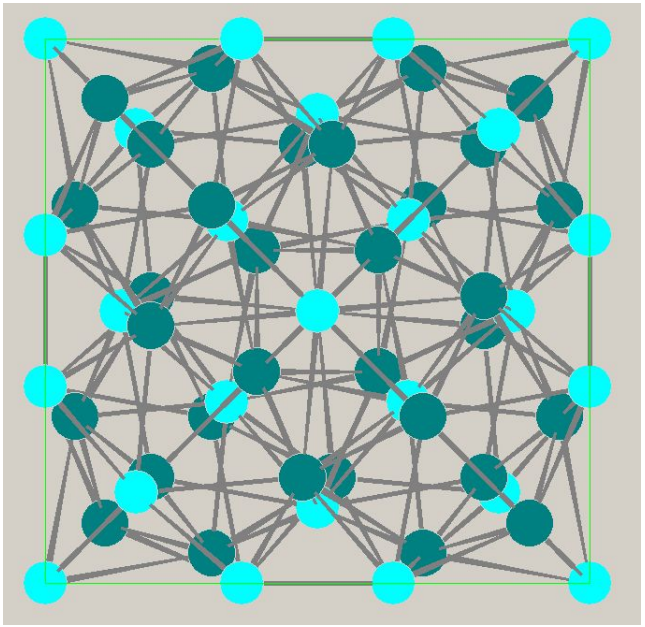
Fermi sphere – energy surface of free valence electrons, radius $k_F = \left(\frac{3\pi^2 z}{V} \right)^{1/3}$

Brillouin zone – planes in reciprocal space with vector $q_{hkl} = \frac{2\pi}{d_{hkl}}$

Interaction (condition of phase stability): $k_F \approx \frac{1}{2} q_{hkl}$

The γ-phase Cu_5Zn_8: complex cubic structure 52 atoms per unit cell, space group *I*-43*m*, lattice parameter *a* = 8.86 Å
[*Pearson 1976*].





3×3×3 supercell of *bcc*

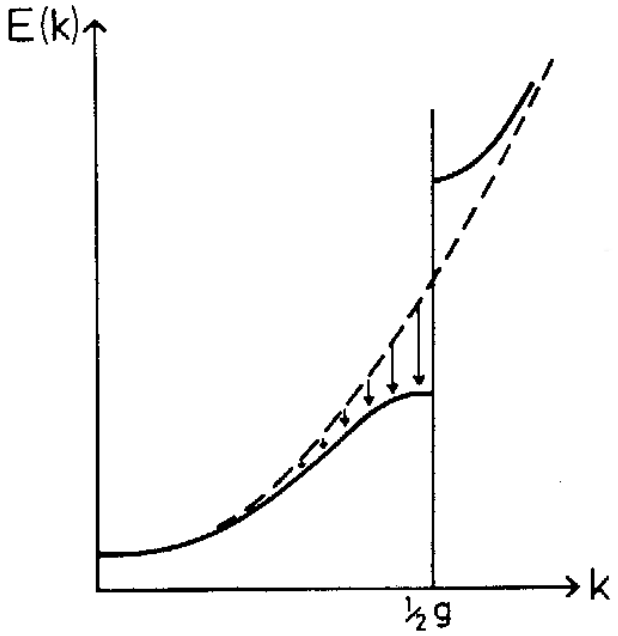
2 out of 54 atoms are removed the remaining 52 atoms are slightly displaced

so that an additional reflection {411} appears.

Discussion of stability of the Hume-Rothery phases

The criterion of stability for the crystal structure of Hume-Rothery phases is a contact of Brillouin zone planes to the Fermi sphere.

Formation of an energy gap at the Brillouin zone boundary lowers the kinetic energy of the free electrons and accounts for the stability of the crystal structure.



Band structure energy E_{BS}

$$E = E_o + E_{Ewald} + E_{BS}$$

$$E_{Ewald} = -\alpha \frac{(Ze)^2}{2r_0} \qquad E_{BS} = \sum_{q}{}' |S(q)|^2 \Phi(q)$$

Volume scaling:

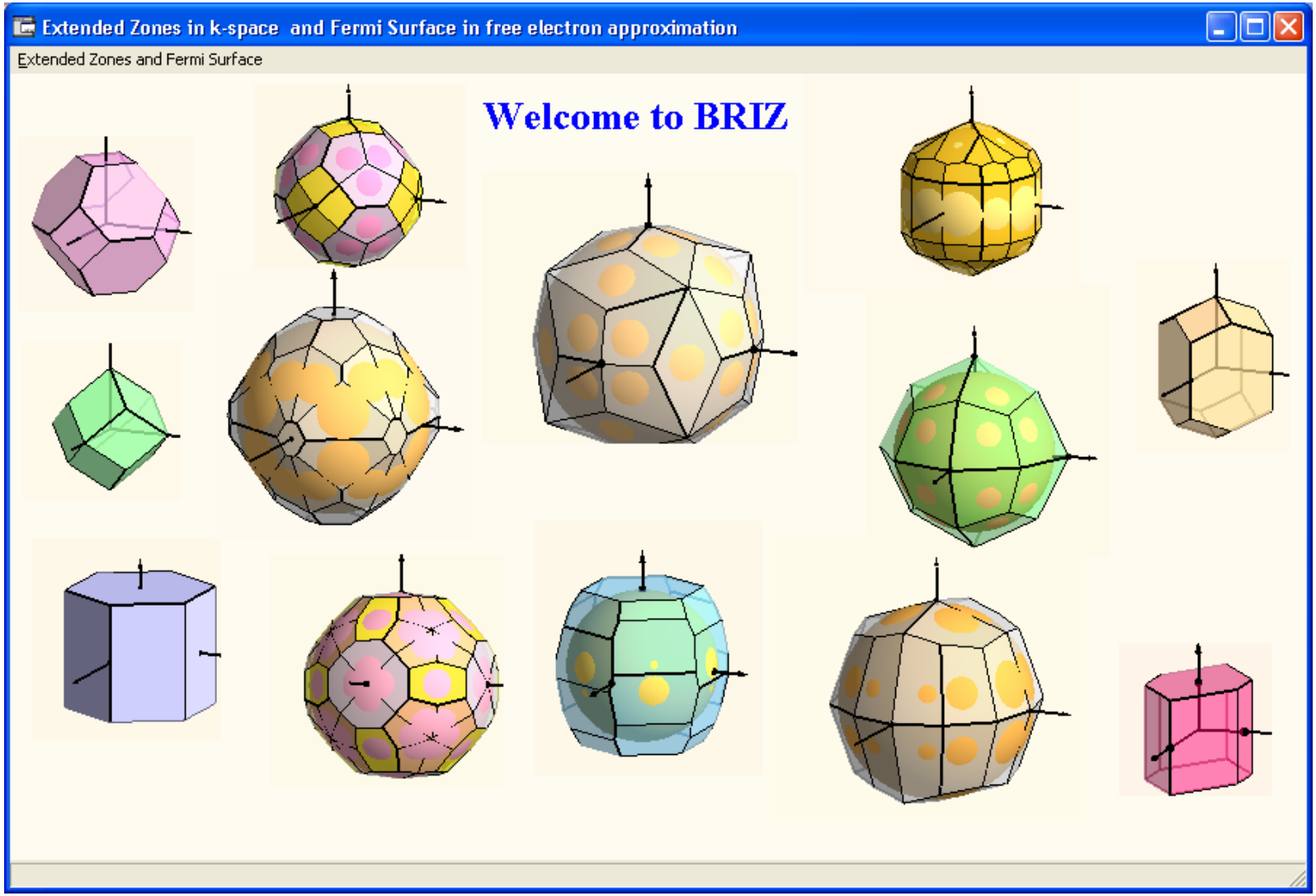
$\sim V^{-1/3}$ $\sim V^{-2/3}$

Enhancement of the Hume-Rothery arguments at compression

BRIZ – a program for the FS-BZ visualization

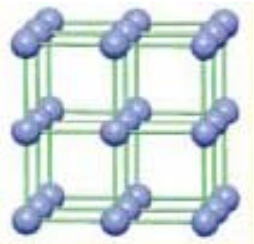
Degtyareva V.F. and Smirnova I.S.

Z.Kristallog. ***222****, 718. 2007*

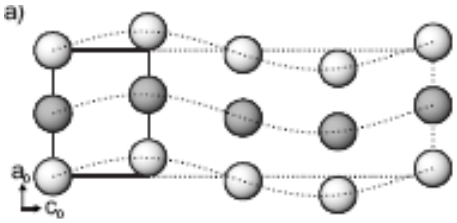


Structural sequence under pressure in P (group-V element)

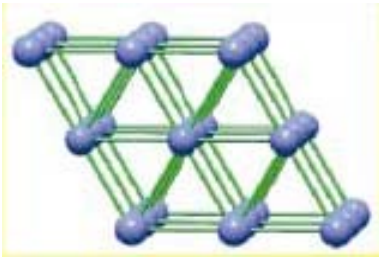
P	GPa 5 10 103 137 260 **orth** → ***hR2*** → **sc** → **inc.mod.** → **sh** → **bcc/ *cI*16 < 280**

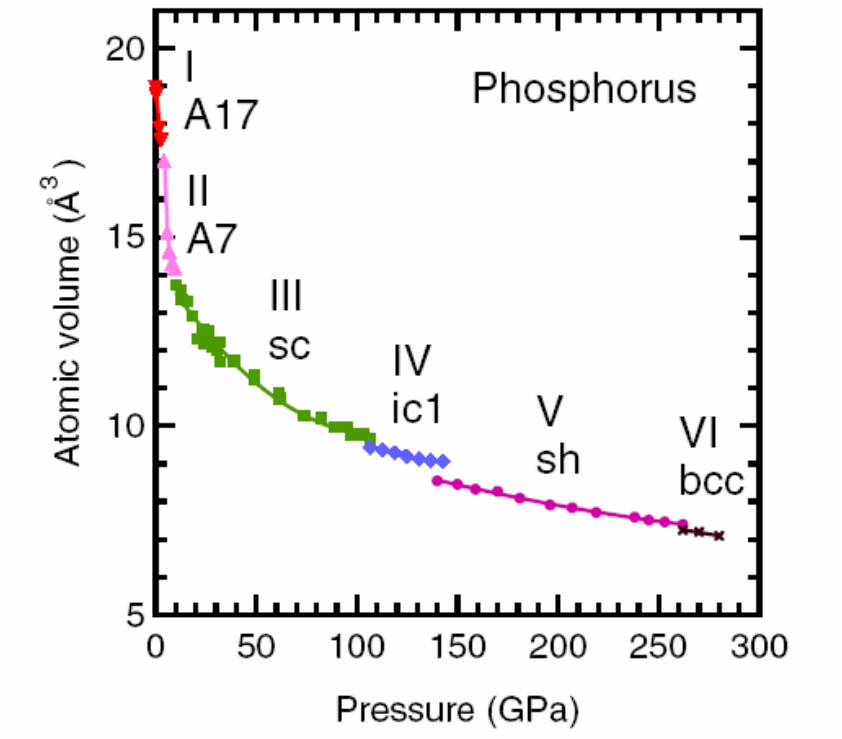


103 GPa →



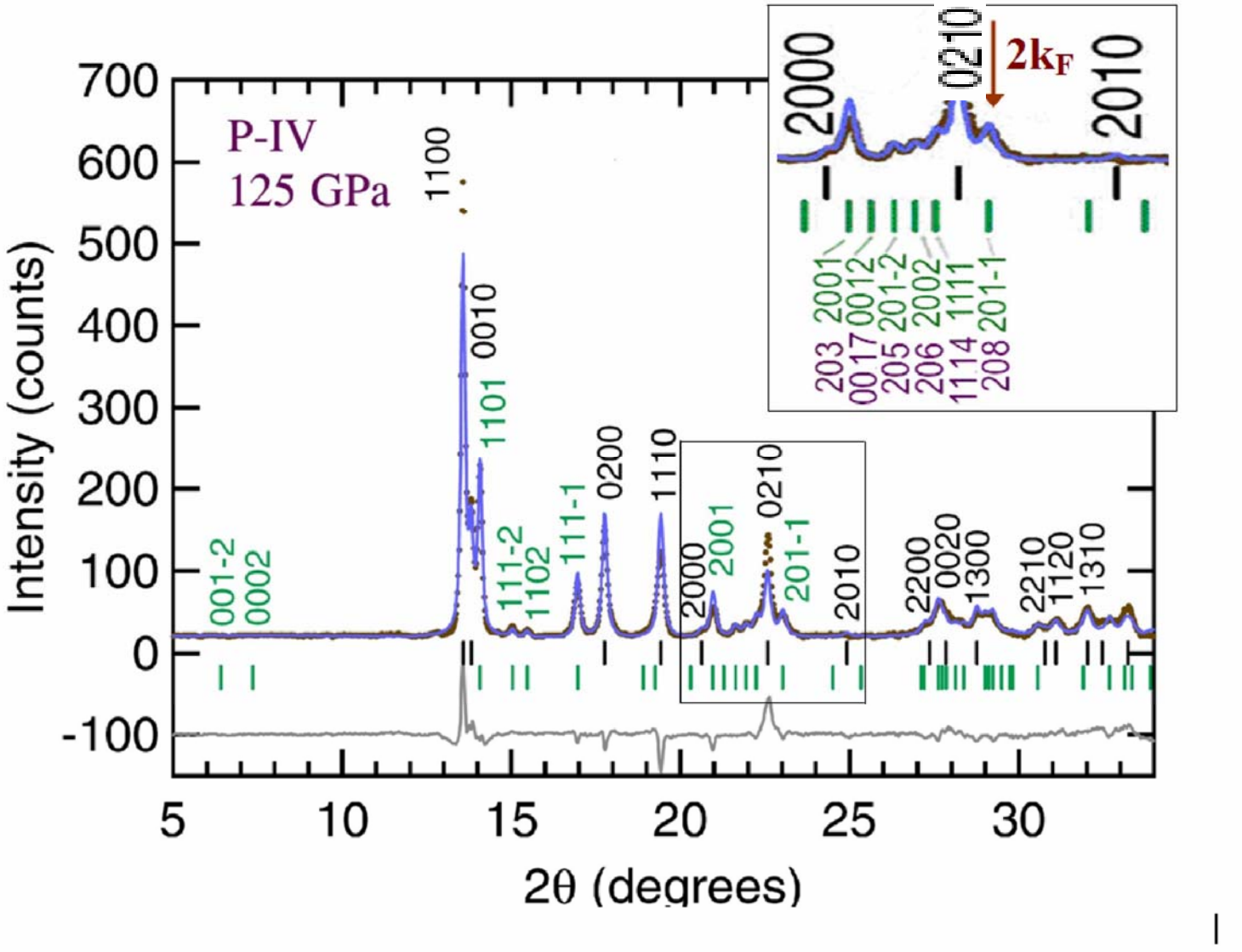
137 GPa →





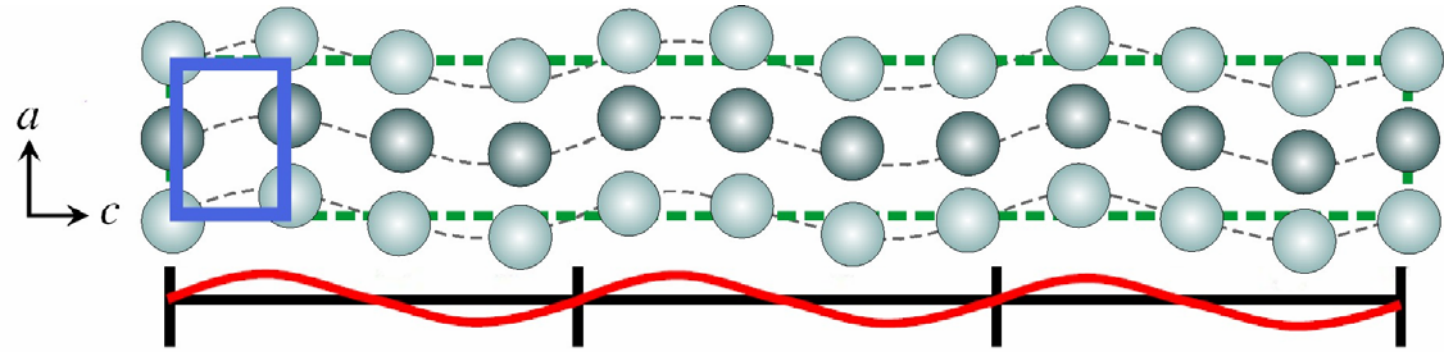
[Fujihisa et al PRL 2007]
[Marques et al PRB 2008]

The *oC*2 P-IV structure: 5 valence electrons



Fujihisa et al, PRL **98,** 175501 (2007)

The *oC*2 P-IV structure



Fujihisa et al, PRL **98,** 175501 (2007)

a=2.772 A, *b*=3.215 A, *c*=2.063 A

Cmmm (00γ) *s*00

125 GPa atomic volume of 9.19 A^3

The modulation wave number

γ = 0.2673, 1/γ =3.741

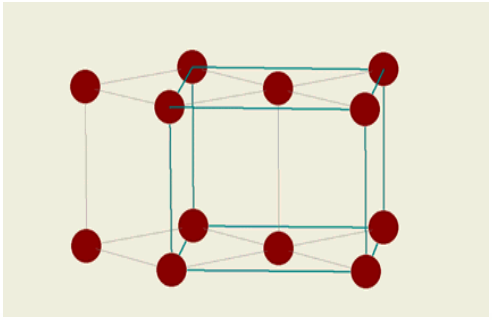
H=*h*a*+*k*b*+*l*c*+*m*γc*

Commensurate approximant

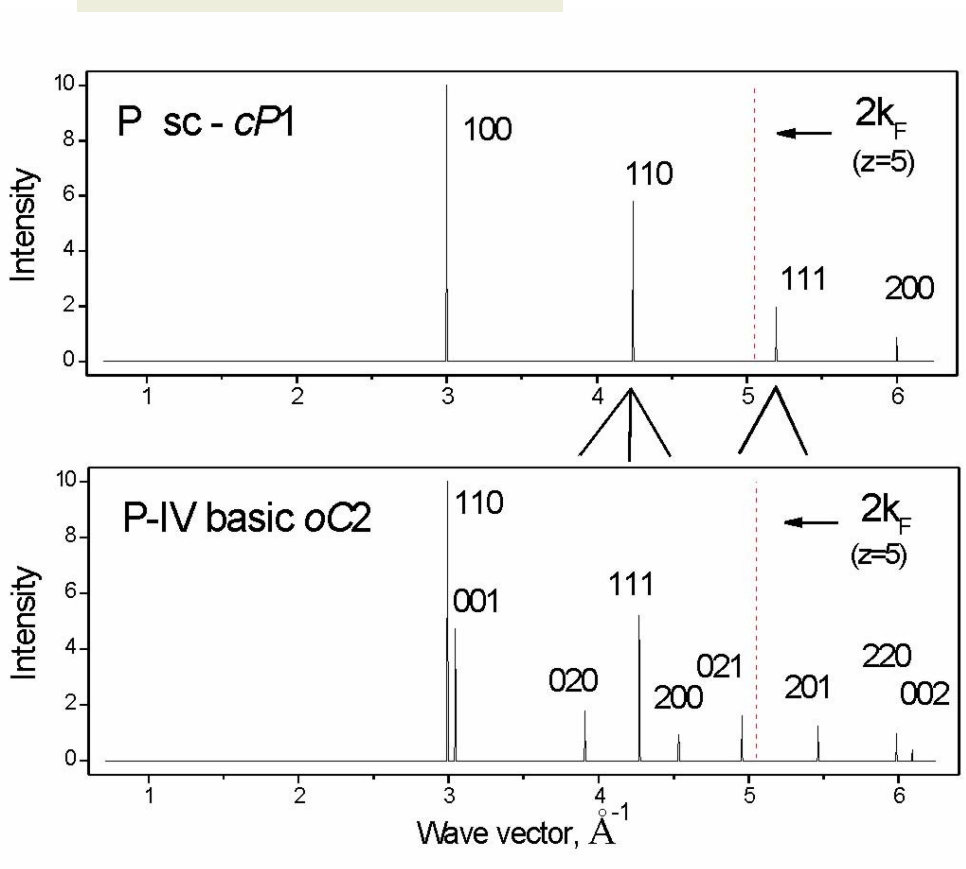
γ = 3/11

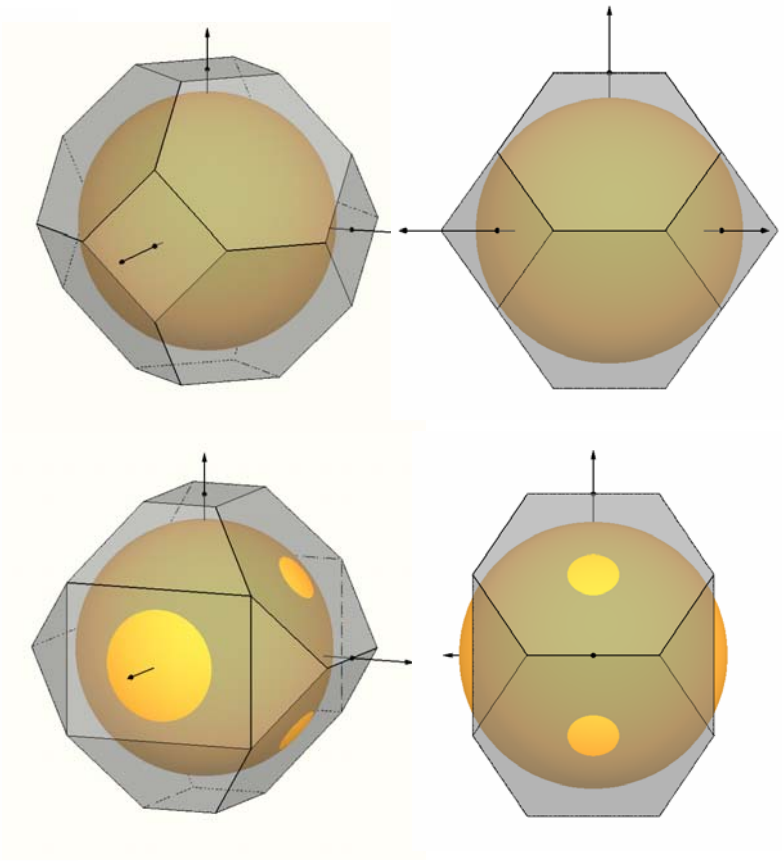
(γ = 0.2727)

Basic cell of P-IV *oC*2: relation to simple cubic

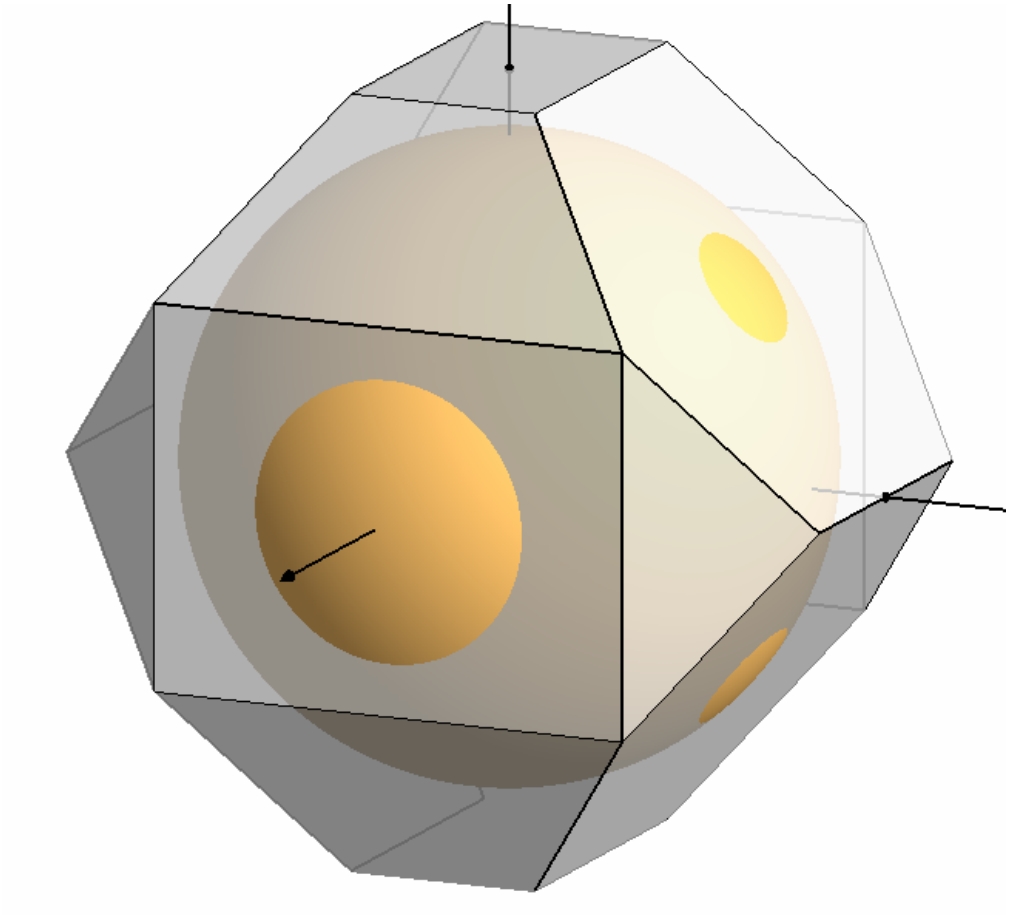


$$c_{ort} \approx a_{cub}$$
$$a_{ort} \approx a_{cub}\sqrt{2}$$
$$b_{ort} \approx a_{cub}\sqrt{2}$$





The *oC*2 P-IV structure: 5 valence electrons *(basic cell)*

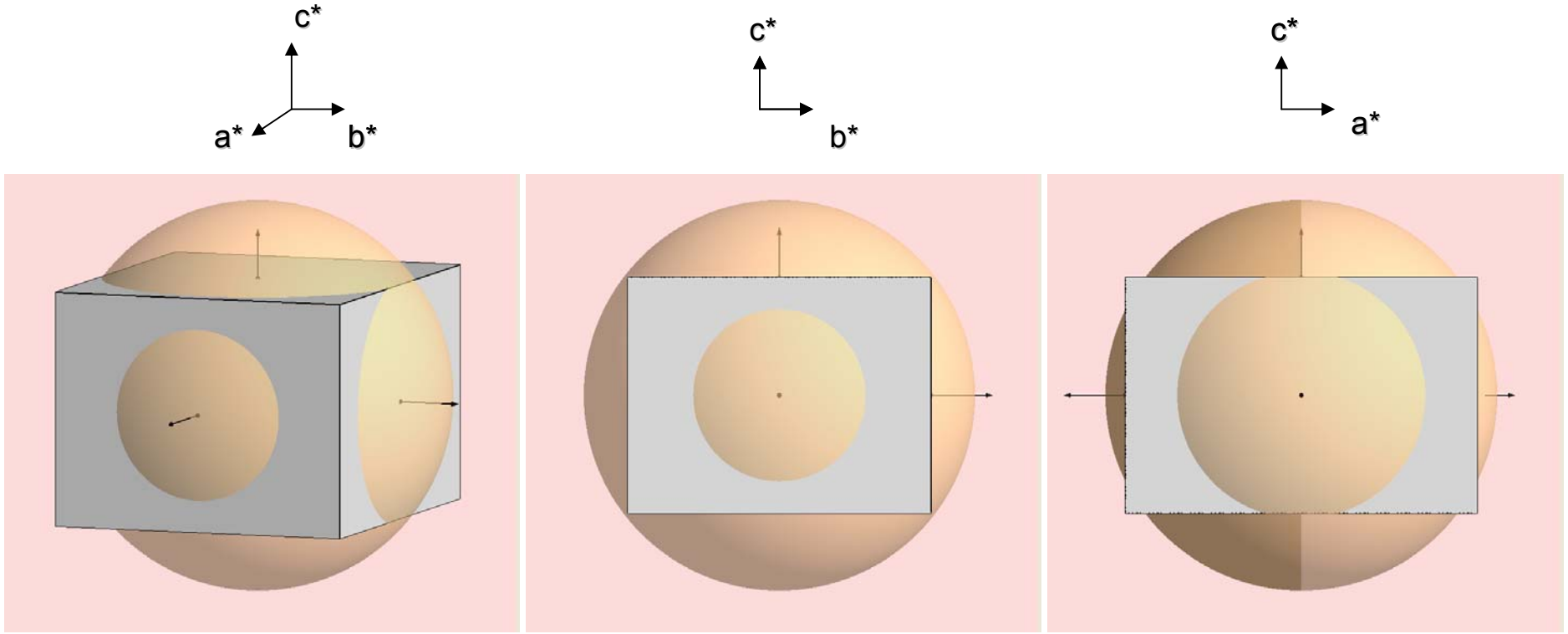


Main reflections:
200
021
220
002
201

V(FS) / V(BZ) = 69%

The *oC*2 P-IV structure: 5 valence electrons

The Brillouin zone with planes 200, 020 , 001

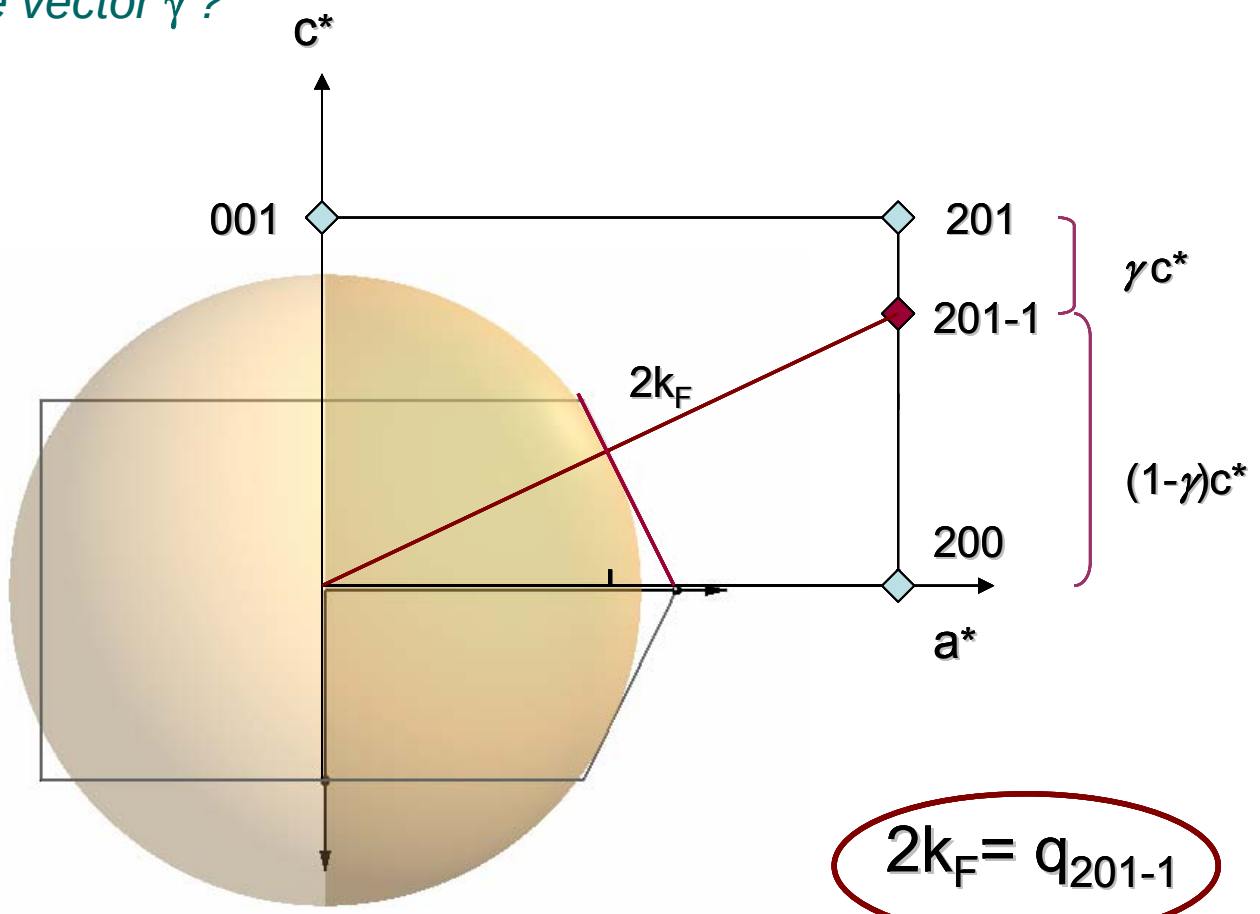


$q_{021} \approx 2k_F$ $\quad a_{ort} < a_{cub}\sqrt{2} \quad b_{ort} > a_{cub}\sqrt{2}$

basic cell *a*=2.772 A, *b*=3.215 A, *c*=2.063 A

The *oC*2 P-IV structure: 5 valence electrons

How we can define wave vector γ ?



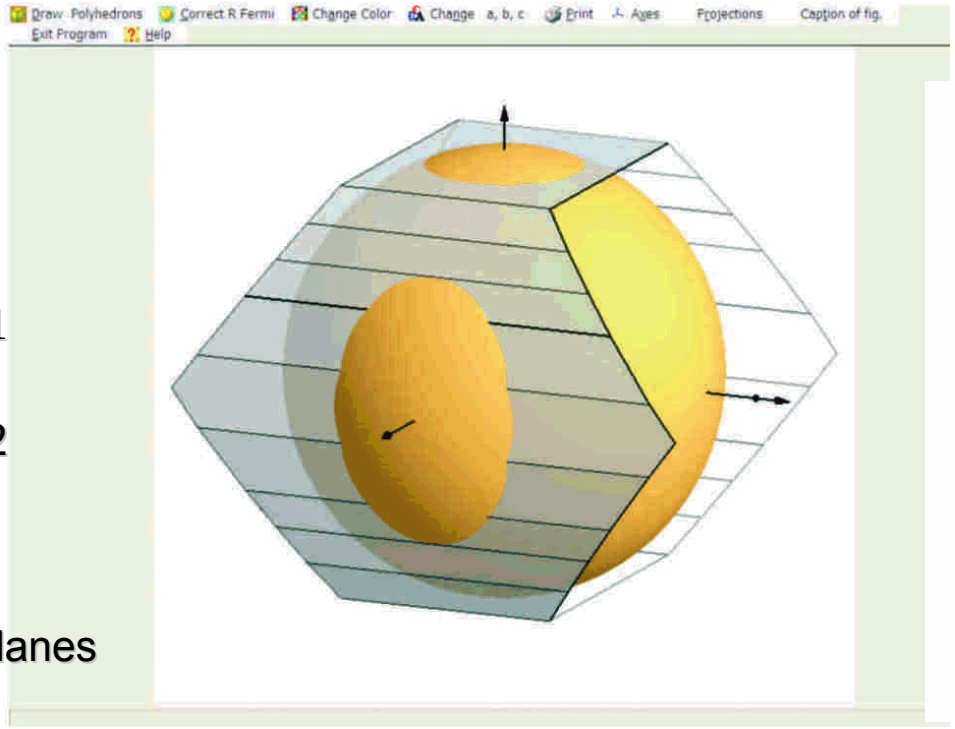
$(2k_F)^2 = (2a^*)^2 + ((1 - \gamma)\, c^*)^2$

$2k_F = q_{201\text{-}1}$

$2k_F = 5.05\ A^{-1}$

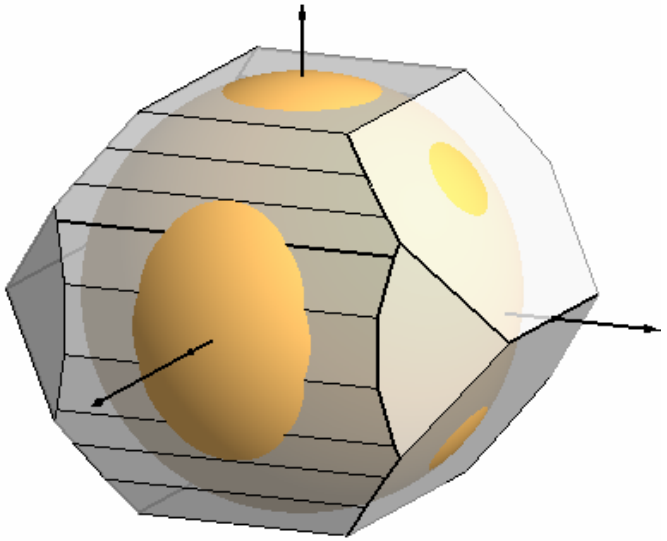
$\gamma = 0.268$

The *oC*2 P-IV structure: 5 valence electrons
(incommensurate cell)

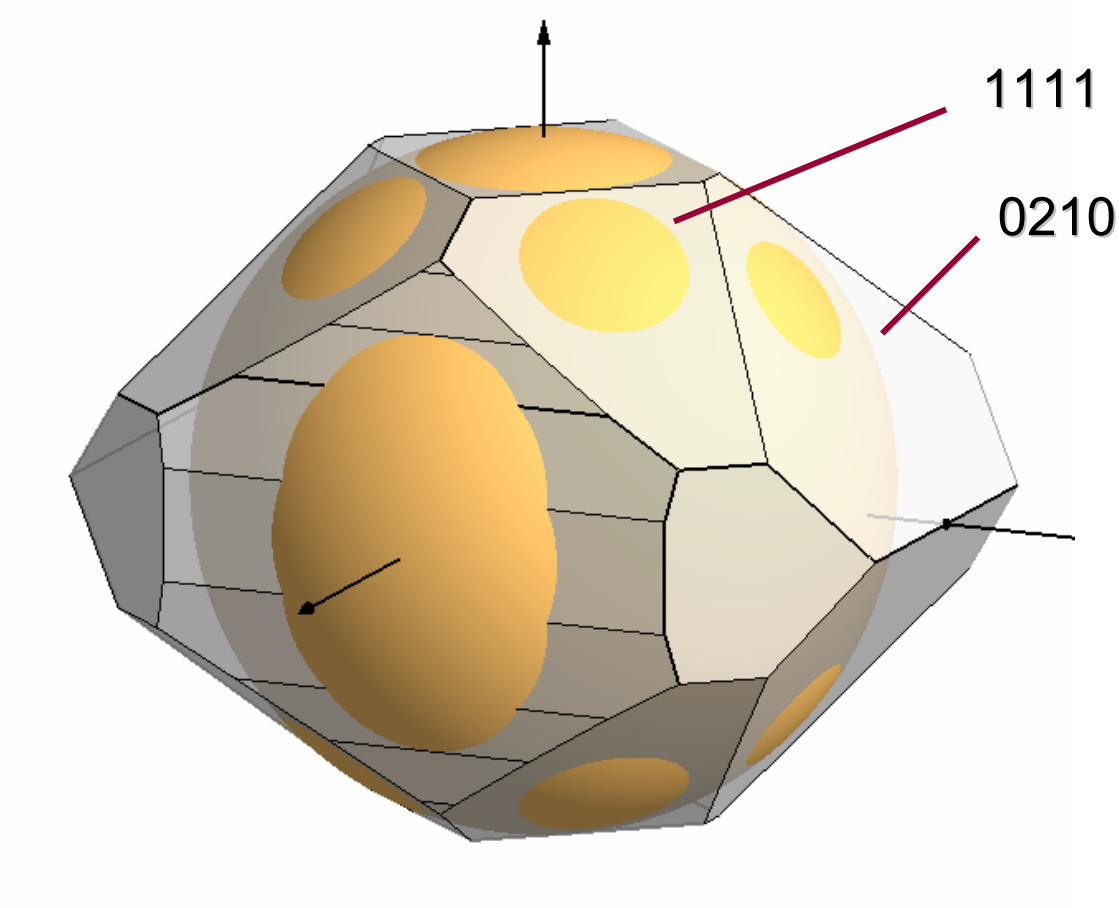


0012
201-1
2002
201-2
2001
2000

h0lm planes

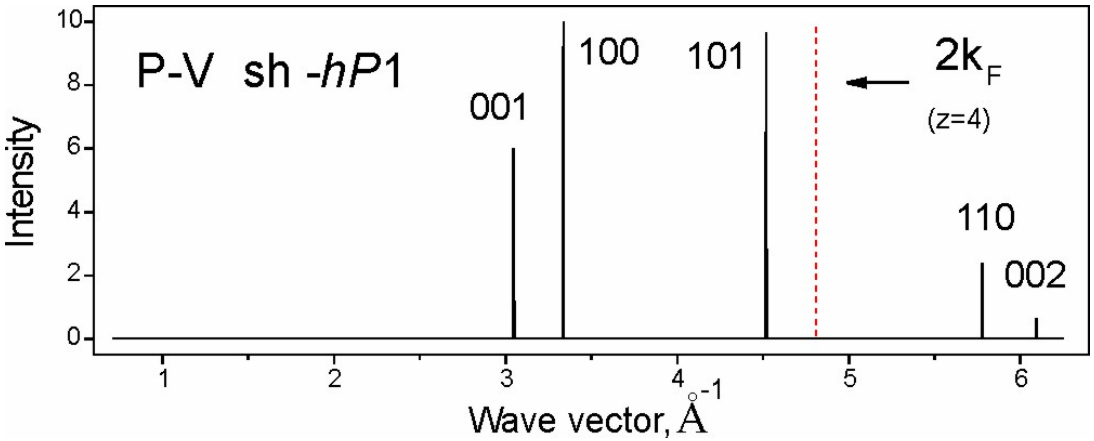


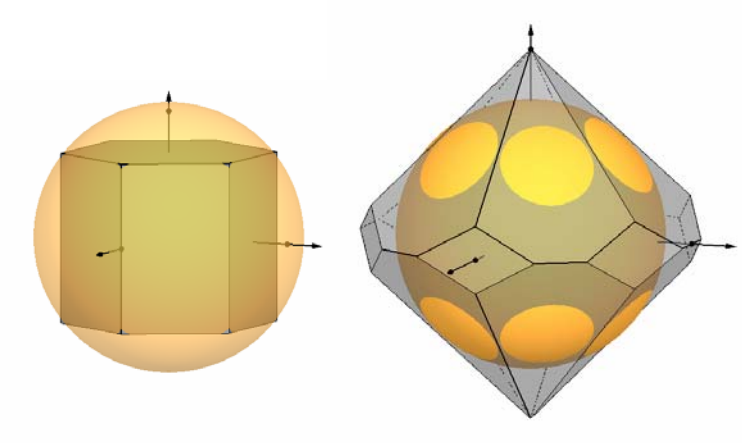
The *oC*2 P-IV structure: 5 valence electrons



V(FS) / V(BZ) = 85%

The *hP1* P-V structure: 4 valence electrons
(electron 3p – 3d transfer)





P = 151 GPa
/Akahama prb 1999/
P-sh, hP1, SG P6/mmm
a=2.175 c= 2.0628 A
z=4.0

Conclusions

- Crystal structures of simple metals under pressure are determined by the valence electron energy term.
- Open-packed structures *sc* and *sh* satisfy Hume-Rothery effects
- Fermi sphere - Brillouin zone interactions favor the low-symmetry structures with BZ boundaries close to the Fermi sphere.
- Phosphorous-IV phase is incommensurately modulated structure due to the FS nesting effect and stabilized by the Hume-Rothery mechanism.