Post - *simple cubic* structures in compressed phosphorus and calcium: electronic origin

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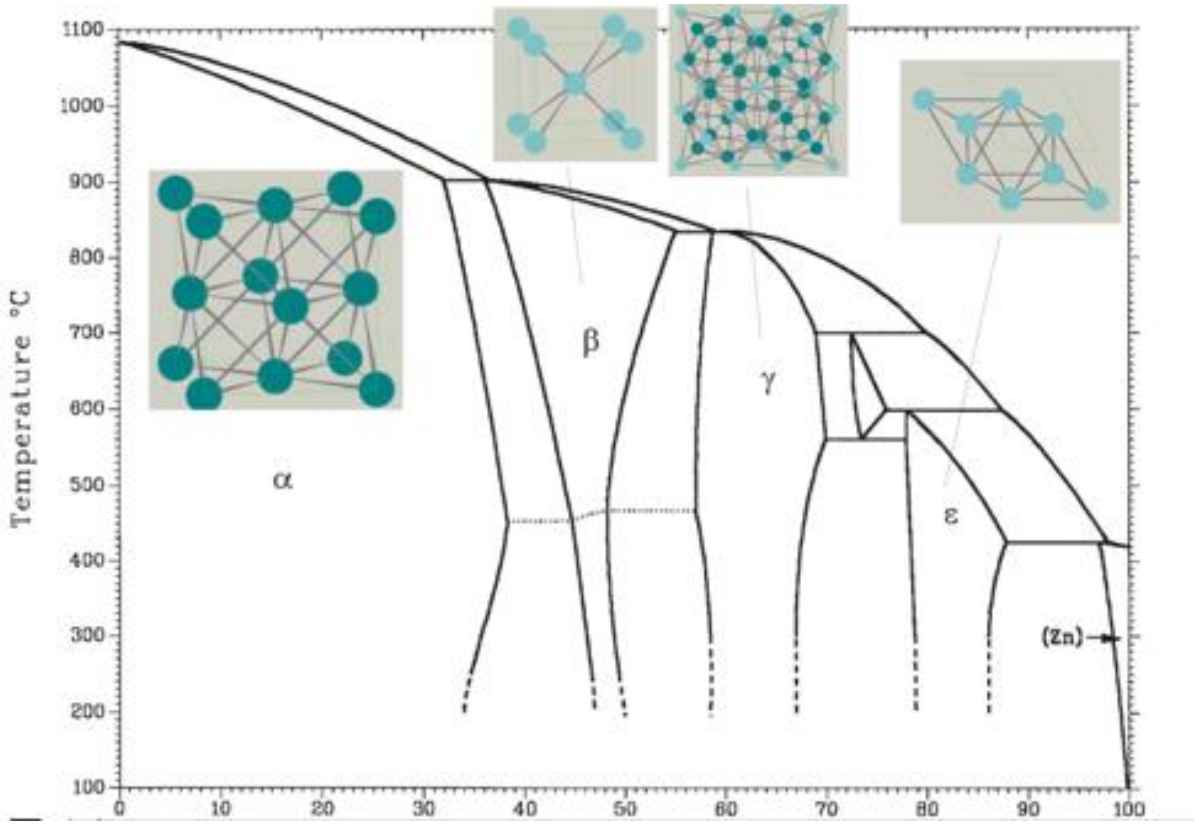
Outline

- Main factors of crystal structure stability
- Concept of the Fermi Sphere - Brillouin Zone interaction: Cu-Zn alloy system
- An incommensurately modulated phase P-IV: consideration with a commensurate approximant
- *Simple cubic* phase in Ca and its distortion on further compression: *pressure ionization* of core electrons

Phase diagram of the Cu-Zn system

The Age of Bronze

A. Rodin



at.% Zn

α (fcc) → β (bcc) → γ (complex cubic) → ε (hcp)

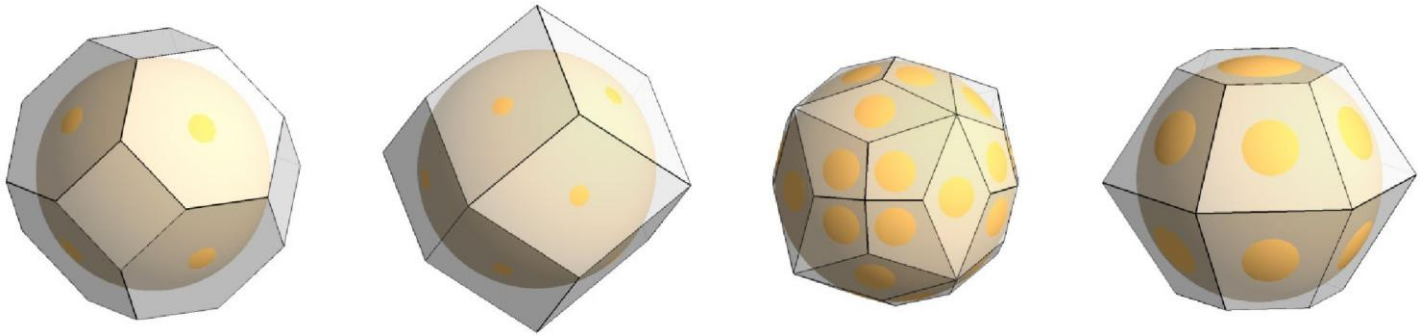
1.35 → 1.5 → 1.62 → 1.75

(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}

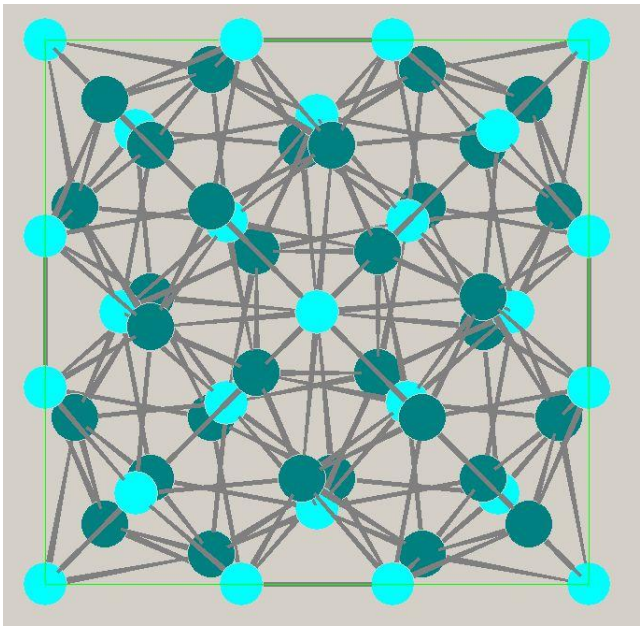
{002}
{101}

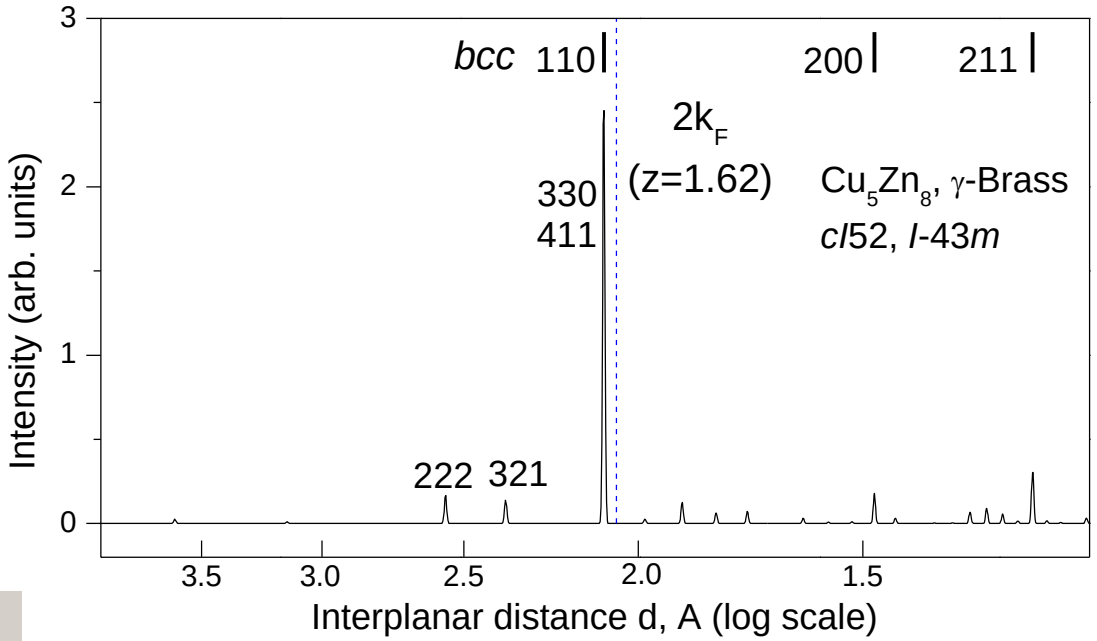
Fermi sphere – energy surface of free valence electrons, radius $k_F = \left(\frac{3\pi^2 z}{V} \right)^{1/3}$

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*].





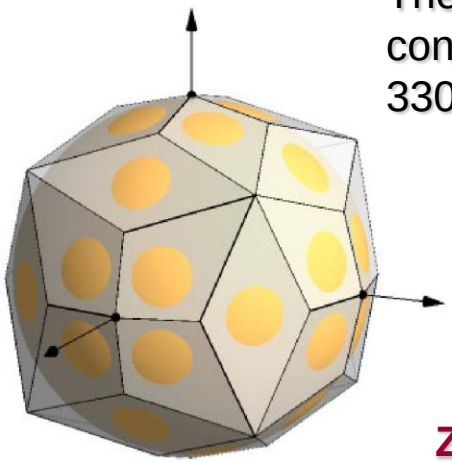
3×3×3 supercell of *bcc*

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

so that an additional reflection {411} appears.

Hume-Rothery effects
stabilize low-symmetry structures

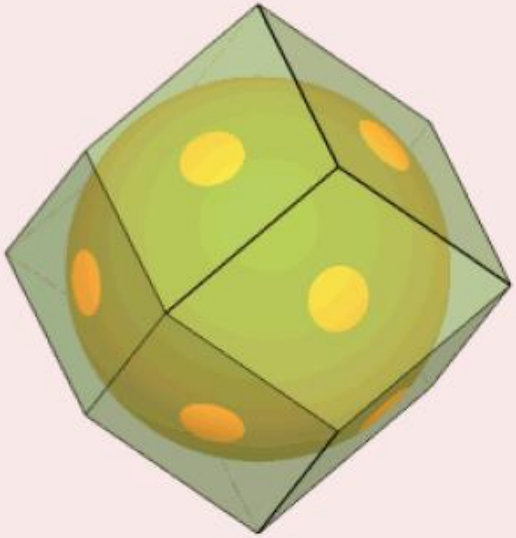
γ - phase Cu_5Zn_8



The Brillouin zone consists of 36 planes 330 and 411 types

Zone filling by valence electrons is ~93%

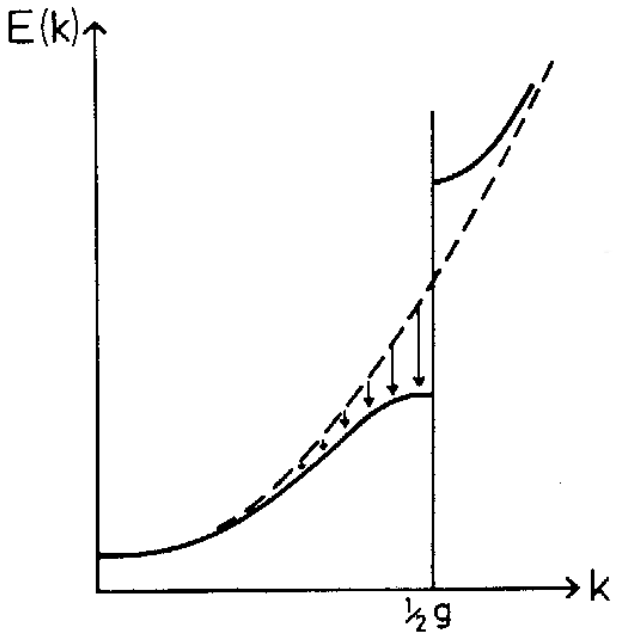
"Jones barrel" is filled



Discussion of stability of the γ-brass

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:

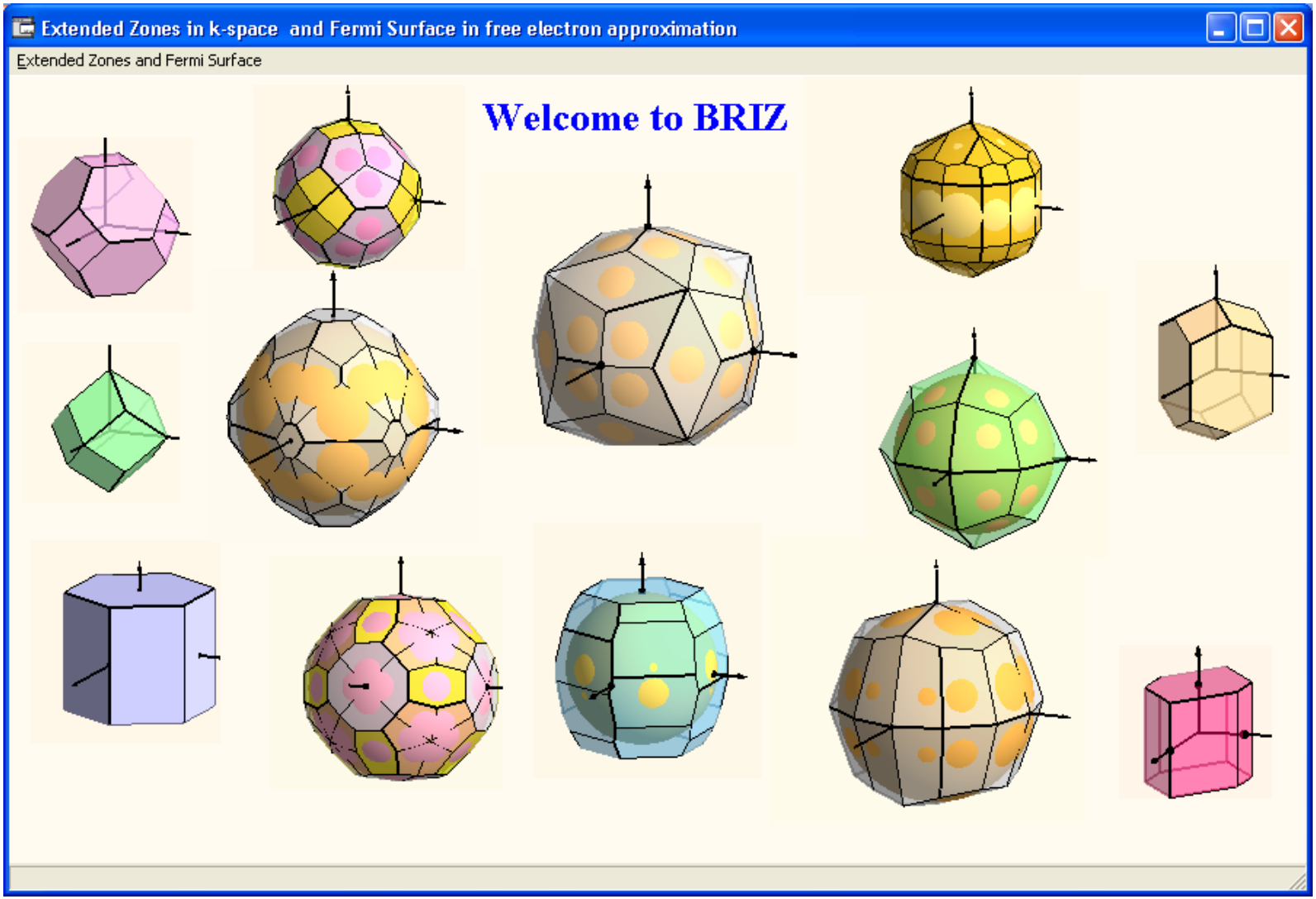
$\sim V^{-1/3}$ $\sim V^{-2/3}$

Enhancement of the Hume-Rothery arguments at compression

BRIZ – a program for the FS-BZ visualization

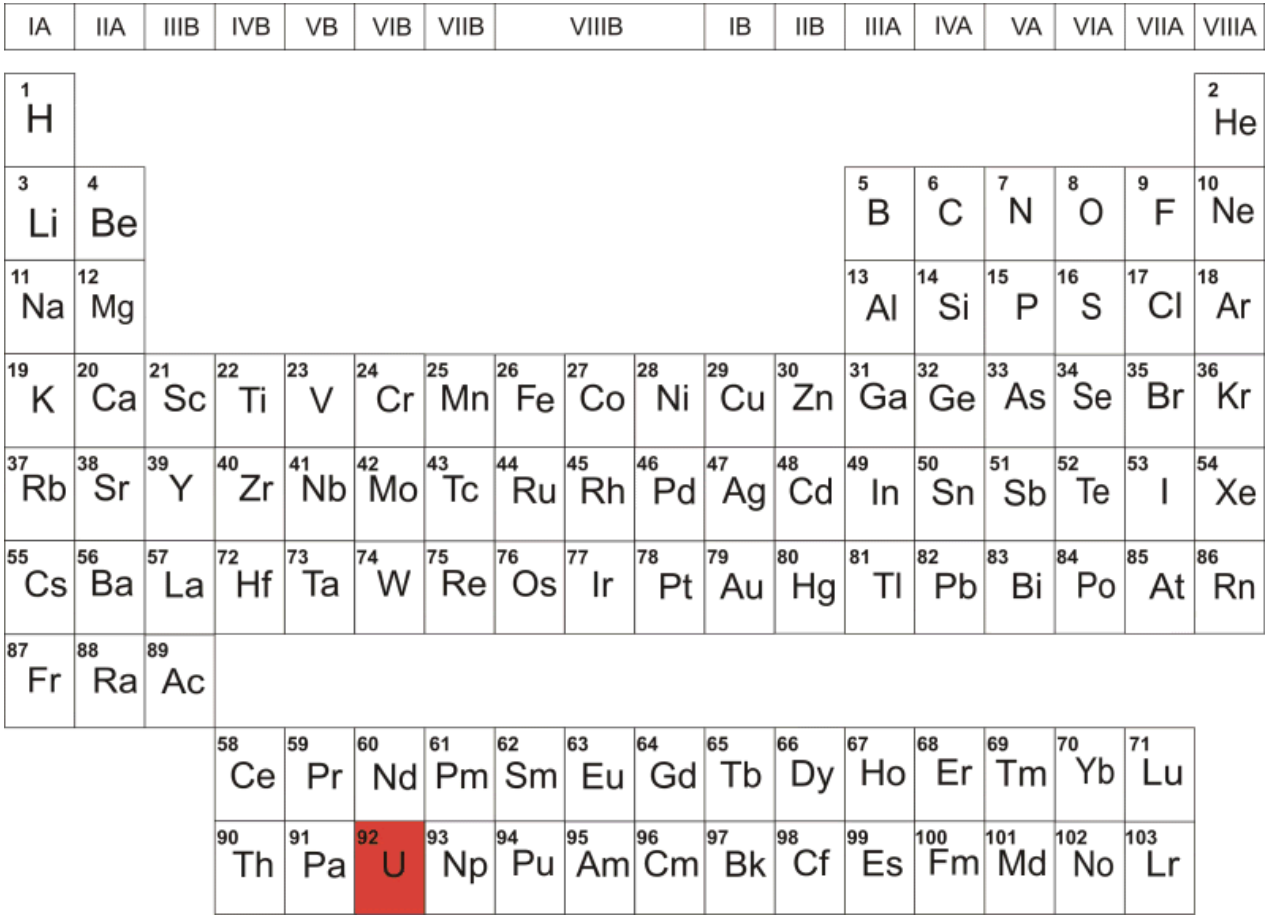
Smirnova I.S. & Degtyareva V.F.

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



Aperiodic structures in elements

1. Incommensurate host-guest structures (1999-2008)
2. Incommensurately modulated structures (2003-2007)
3. Long-period superstructures (2001-2009)



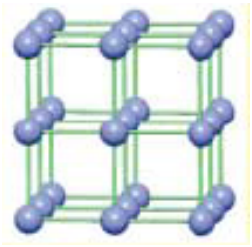
Elemental Complexity ⟺ Elemental Simplisity

Summary of sc – *cP*1

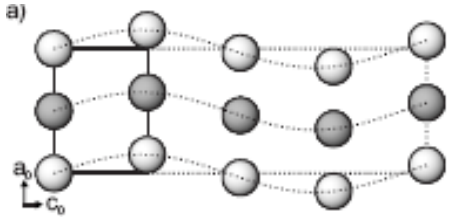
Element (group)	**Conditions**	**Refs**
Po (VI)	Ambient pressure	Pauling File
P (V)	High pressure (10-103 GPa)	J. C. Jamieson, Science **139**, 129 (1963) Y. Akahama, M. Kobayashi and H.Kawamura, *Phys. Rev. B* **59** 8520 (1999)
As (V)	High pressure (25-48 GPa)	T. Kikegawa and H. Iwasaki, J. Phys. Soc. Jpn. **56**, 3417 (1987)
Ca (II)	High pressure (32-113 GPa)	H. Olijnyk and W. B. Holzapfel, Phys. Lett. **100A**, 191 (1984) T. Yabuuchi, Y. Nakamoto, K. Shimizu, and Y. Kikegawa, J. Phys. Soc. Jpn. **74**, 2391 (2005) Q. F. Gu, G. Krauss, Yu.Grin, and W.Steurer, *Phys. Rev. B* **79**, 134121 (2009)
Se (VI)	After shock compression	V. F. Degtyareva, V.N. Sikorov, Solid State Physics 19, 2201 (1977)
Se (VI)	Thin film (sublimation in vacuum)	Andrievskii, I. D. Nabitovich, and P. I. Kripyakevich, Soviet Phys.-Doklady **4**, 16 (1959)

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

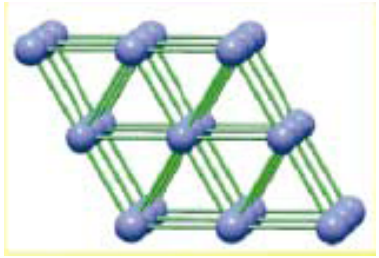
P	**orth** $\xrightarrow{5}$ ***hR2*** $\xrightarrow{10}$ **sc** $\xrightarrow{103}$ **inc.mod.** $\xrightarrow{137}$ **sh** $\xrightarrow{260}$ **bcc** **< 280 GPa**

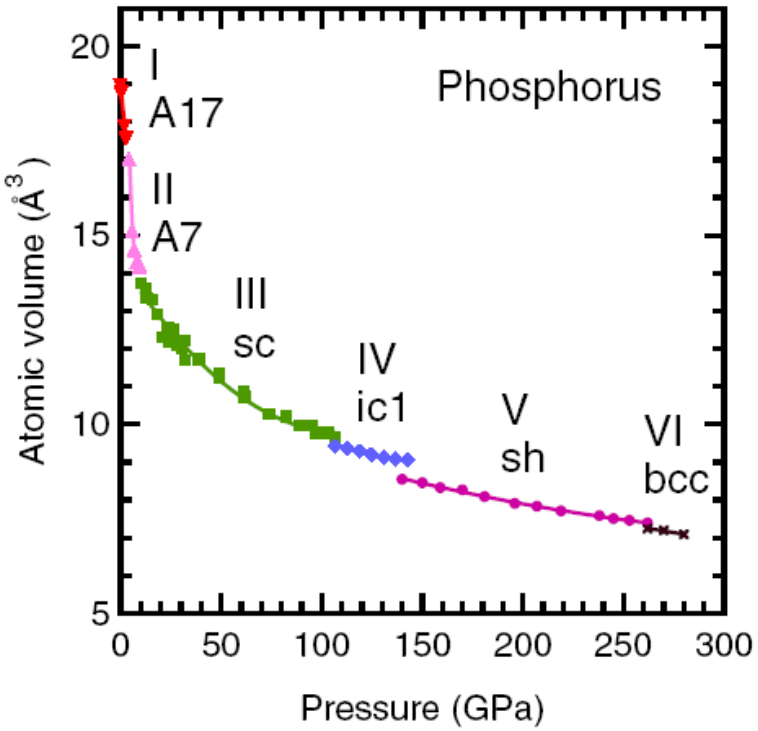


103 GPa



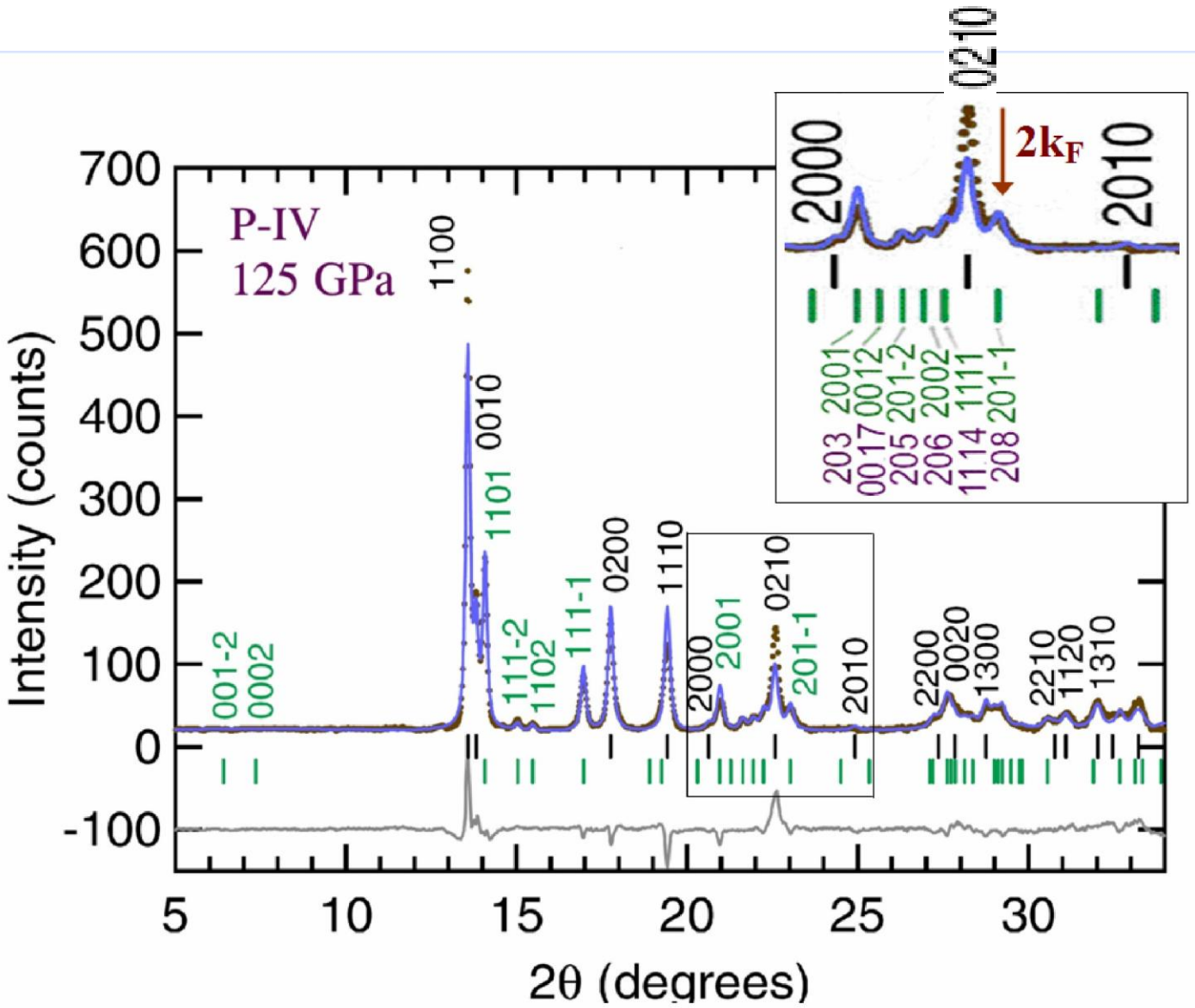
137 GPa



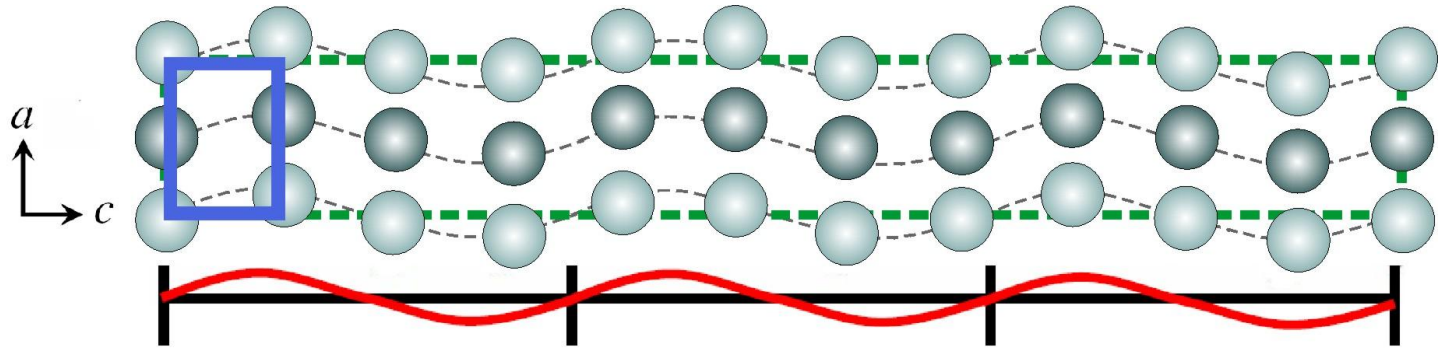


[Fujihisa et al PRL 2007]
[Marques et al PRB 2008]

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



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

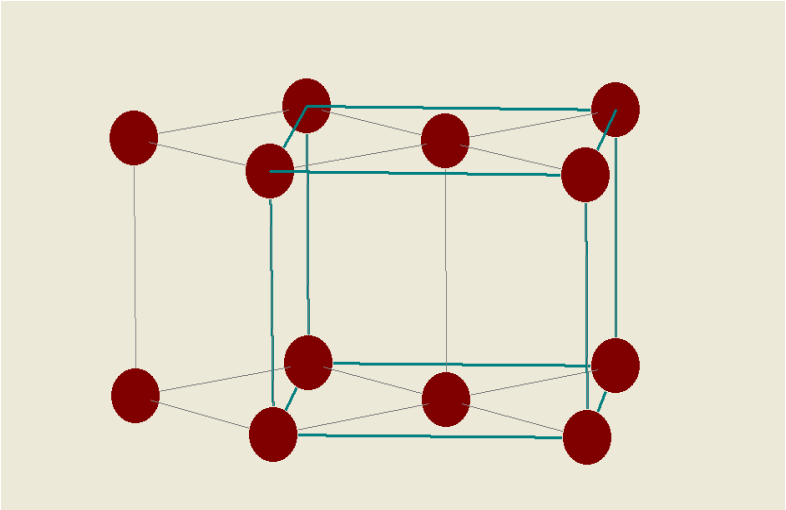
H=*h*a*+*k*b*+*l*c*+*m*γc*

Commensurate approximant

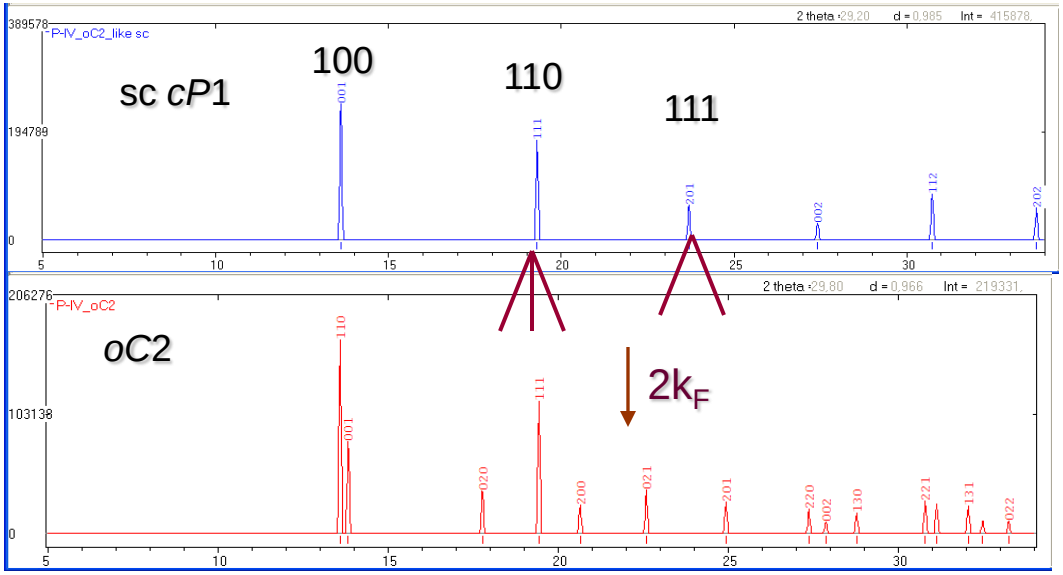
γ = 3/11

(γ = 0.2727)

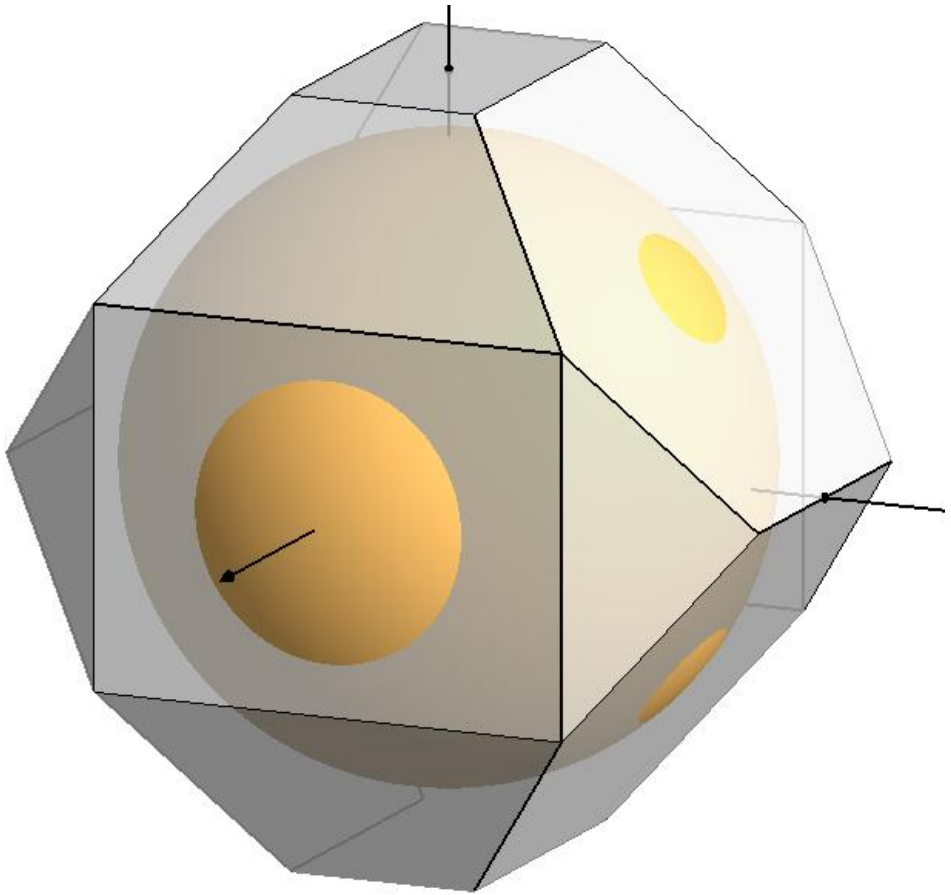
Basic cell of P-IV *oC*2: relation to simple cubic



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



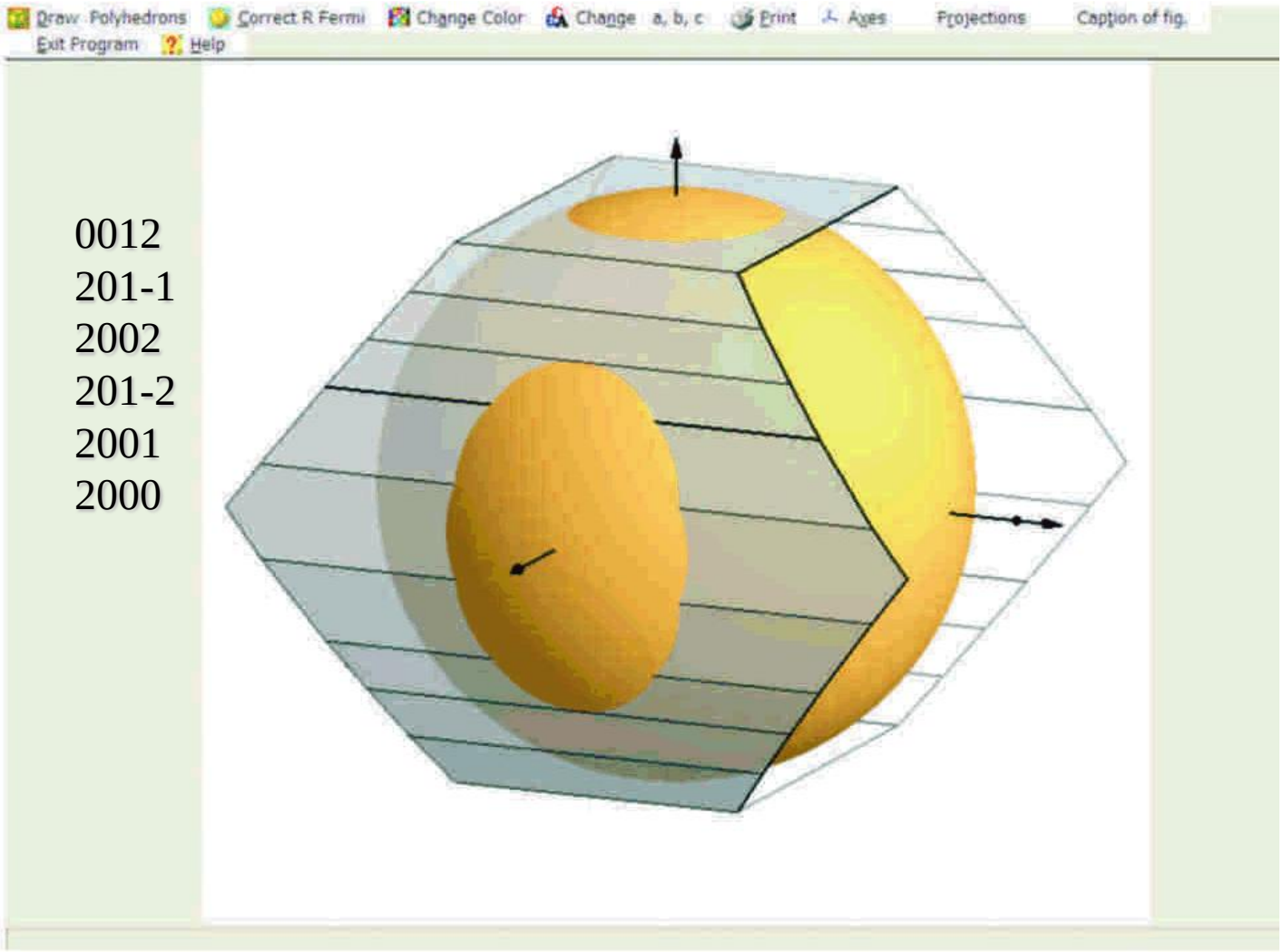
The *oC2* P-IV structure: 5 valence electrons



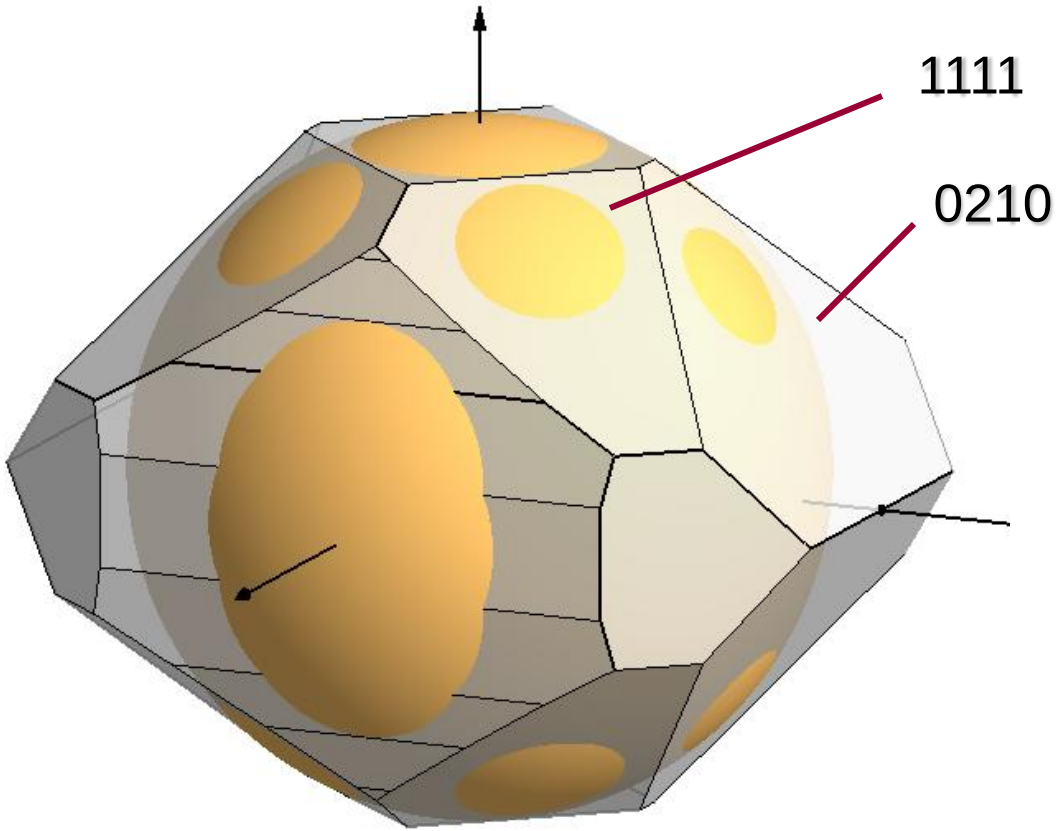
Main reflections:
200
021
220
002
201

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

The *oC2* P-IV structure: 5 valence electrons



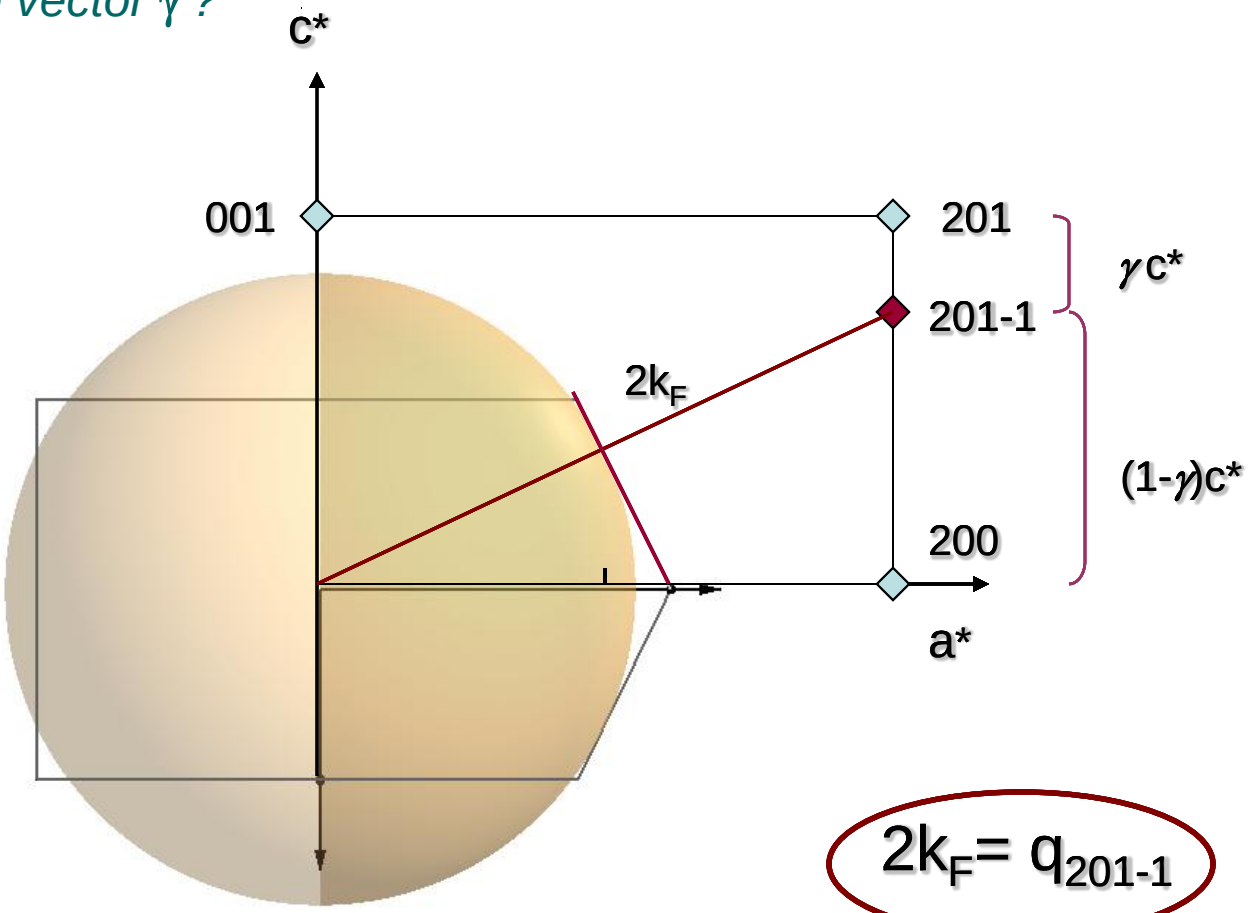
The *oC*2 P-IV structure: 5 valence electrons



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

The *oC2* P-IV structure: 5 valence electrons

How we can define wave vector γ ?



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

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

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

$\gamma = 0.268$

Calcium

*[Olijnyk & Holzapfel, Phys.Lett A **100**, p 191 (1984)]*

$$fcc \xrightarrow{20} bcc \xrightarrow{32} simple\ cubic \xrightarrow{113} complex\ (?) < 120\ GPa$$

$\eta_{bcc}=0.68 \quad \eta_{sc}=0.52 \quad \Delta V(bcc\text{-}sc)= -\ 8\%$ at 32 GPa

$R_{bcc}/R_{sc} = (\eta_{bcc}/0.92\eta_{sc})^{1/3} = 1.12$

$\Delta R(bcc\text{-}sc)= -12\%$

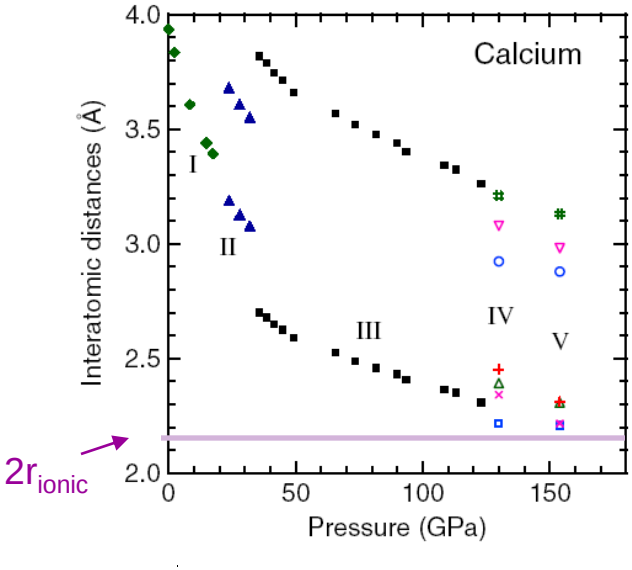
core overlap !?

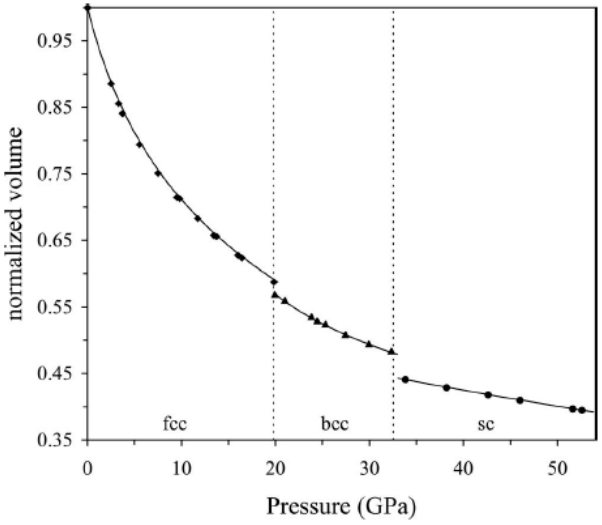
Decrease of atomic radius
at the bcc – sc transition

Structural sequence under pressure in Ca (group-II element)

Ca	**fcc** $\xrightarrow{20}$ **bcc** $\xrightarrow{32}$ **sc** $\xrightarrow{113}$ ***tP8*** $\xrightarrow{139}$ ***oC8*** $\xrightarrow{158}$ ***tP4*** **<** **172 GPa** 10K ***oC2***

[Fujihisa *et al* PRL 2007]
[Marques *et al* PRB 2008]
[Nakamoto *et al* PRB 2010]
[W Mao *et al* PNAS 2010]

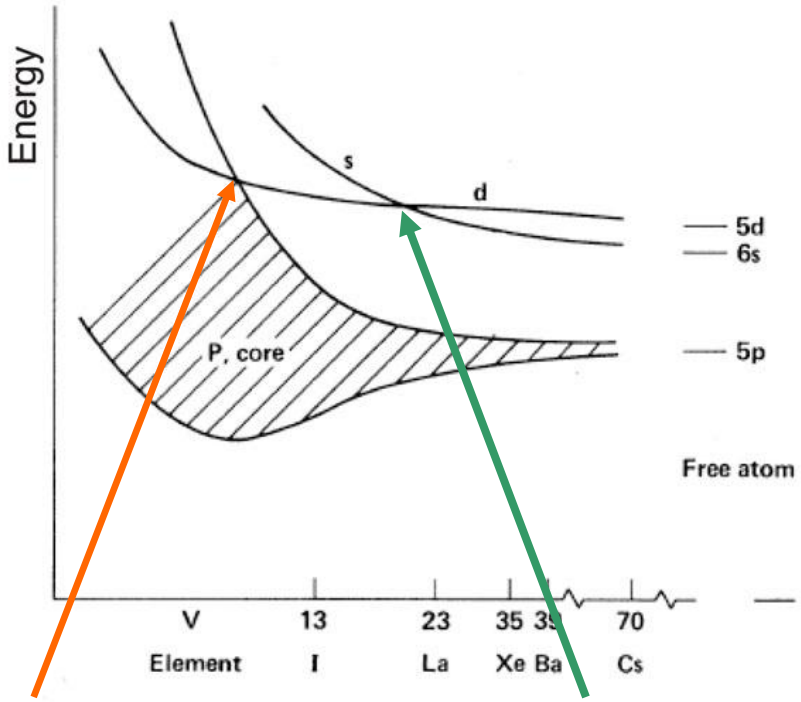




Electronic energy levels

vs atomic volume

Ross & McMahan,*Phys.Rev.B* **26**, 4088 (1982)



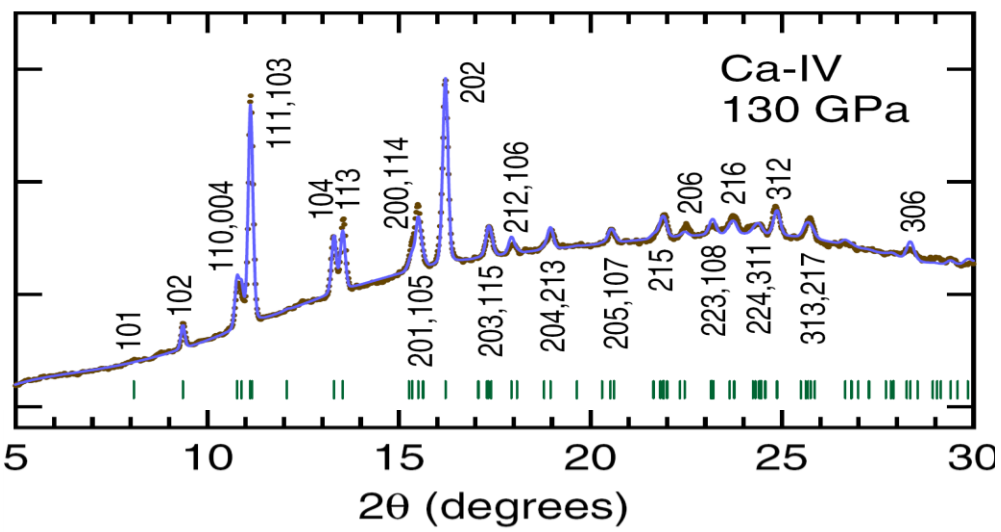
s-d-p(core) hybridization

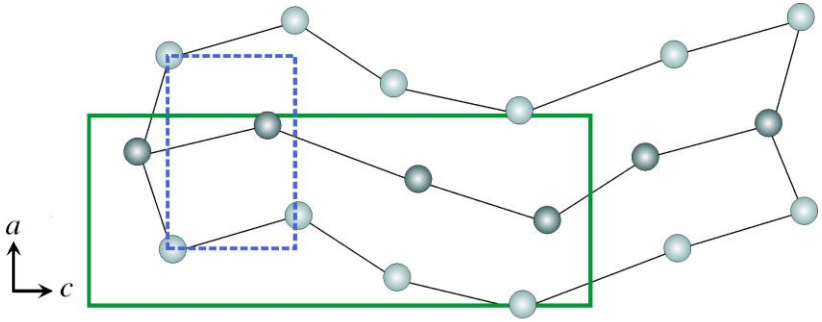
s-d transfer

Ca *post - simple cubic*

$2k_F$

z=3.5 k_F= 2.077 2theta =16.2





Fujihisa PRL 2008

P=130GPa Ca-IV *tP*8 a=3.209 c= 8.97 A (x,y,z)=(0.175; 0.527; 0.096)

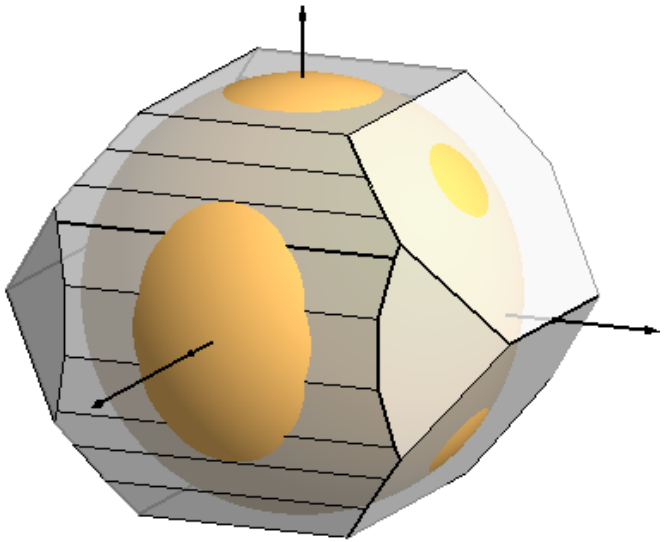
SG $P4_32_12$, 96 Atomic volume 11.553 A^3

Corresponding basic cell *tP*2 a_{basic}=3.209 c_{basic}=2.244 A

=c /4

Common features of BZ formation:

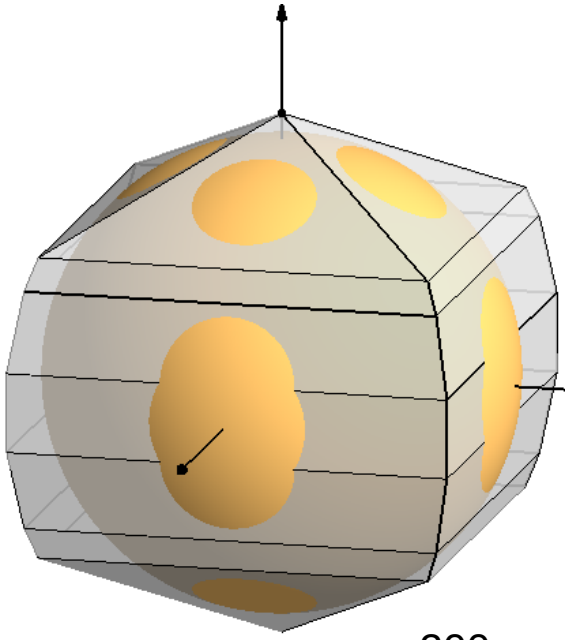
P-IV



FS z=5

h0lm planes

Ca-IV



FS z=3.5

h0l planes

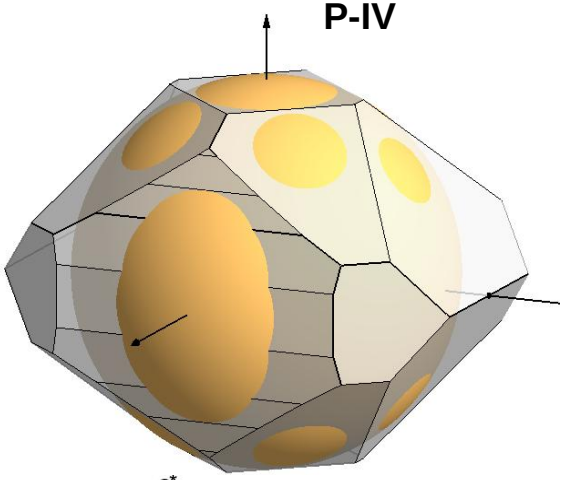
200
201
202
105

Common features of BZ formation:

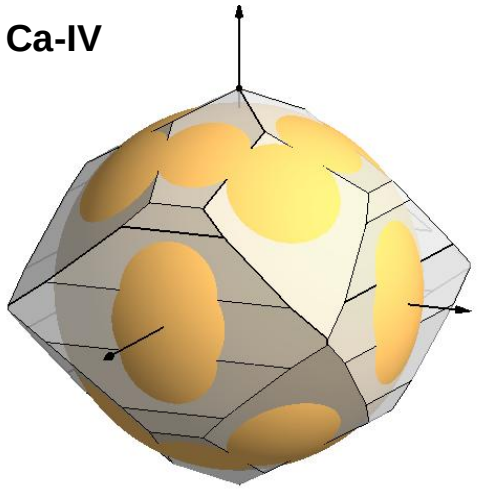
In addition to 200 are formed planes
***201-1* for P-IV or *201-2* (=*2002*) for Ca-IV**

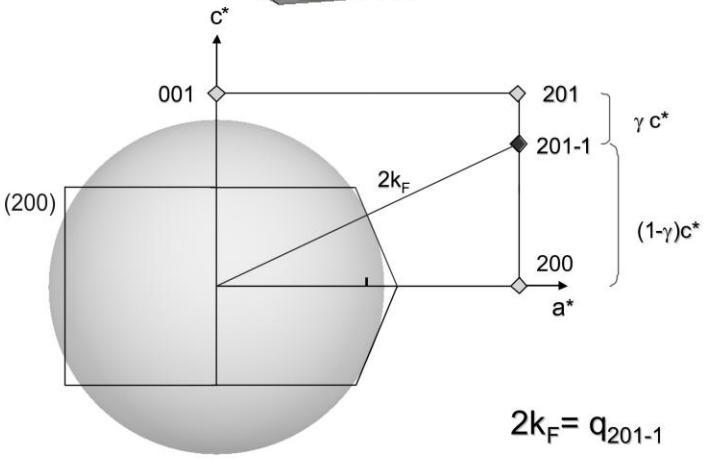
For Ca-IV tP8 basic cell is tP2 (c/4)

P-IV



Ca-IV





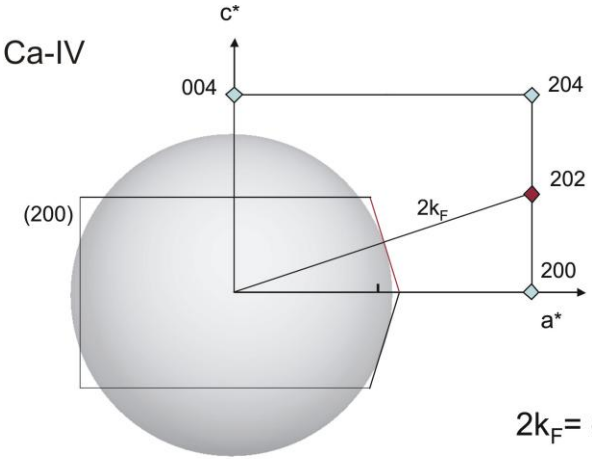
$(2k_F)^2 = (2a^*)^2 + ((1 - \gamma)\, c^*)^2$

$2k_F = q_{201-1}$

$2k_F$=5.05 Å^{-1}

γ = 0.268

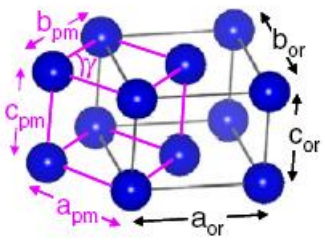
Ca-IV



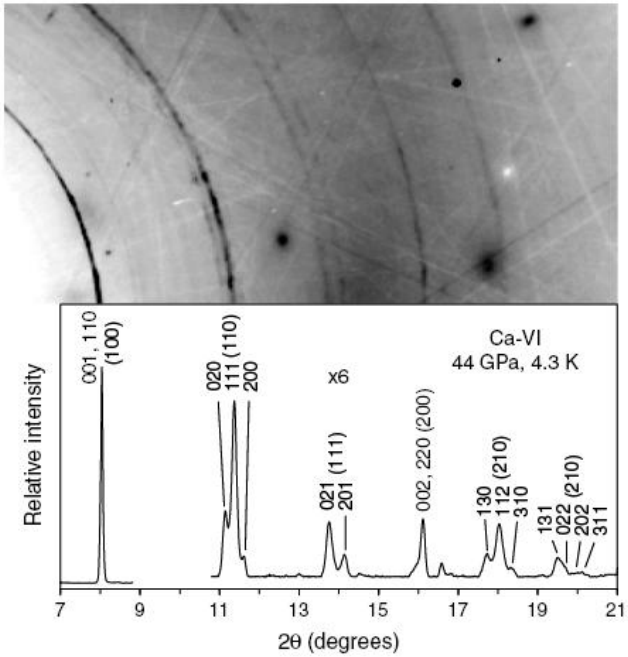
$2k_F = q_{202}$

Low temperature distortion of sc-Ca

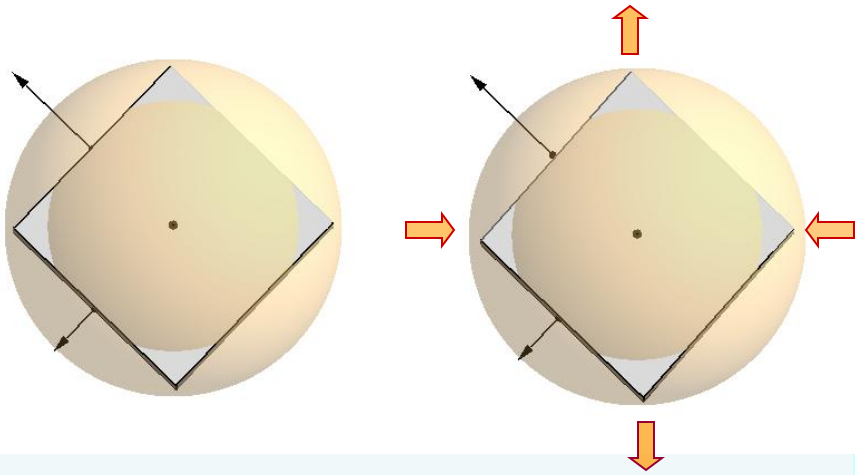
orthorhombic,
C-face-centered unit cell
of *Cmmm* space group with
a =3.6513 Å,
b = 3.8064 Å,
c =2.6350 Å



Ca-VI
Orthorhombic (or), *Cmmm*
Primitive Monoclinic (pm)



Integrated XRD pattern at 44 GPa and 4.3 K (λ = 0.36940 Å) collected at 16-IDB, APS. Peaks are indexed both to the orthorhombic structure and also to sc (in parentheses). The small d spacing (large 2θ) region is magnified ×6

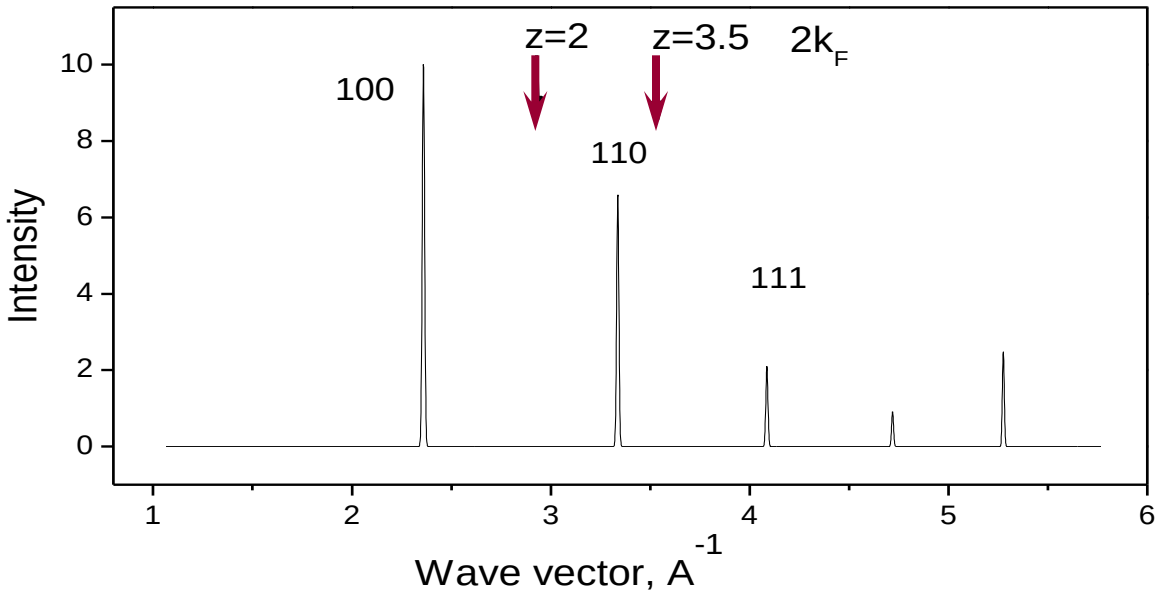


Ca sc LT Ca-oC2

First BZ for sc and LT Ca-oC2:
projection along c*. FS for z=3.5.
Square of sc is distorted with elongation of one diagonal and contraction of another
to contact with FS at least in one direction –
minimization of the band structure energy

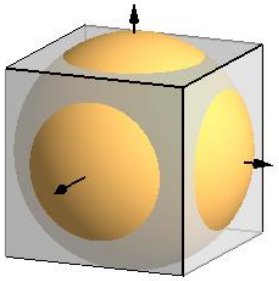
[W Mao *et al* PNAS 2010]

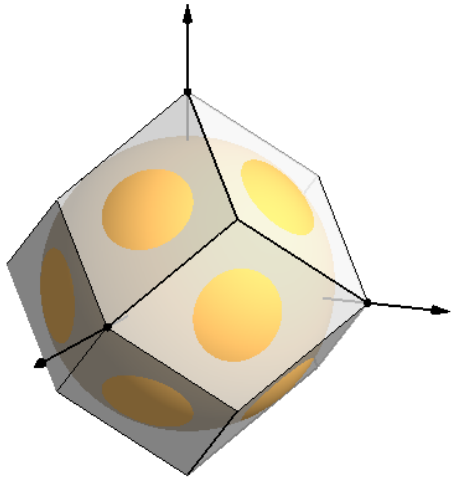
For Ca – sc how many valence electrons?



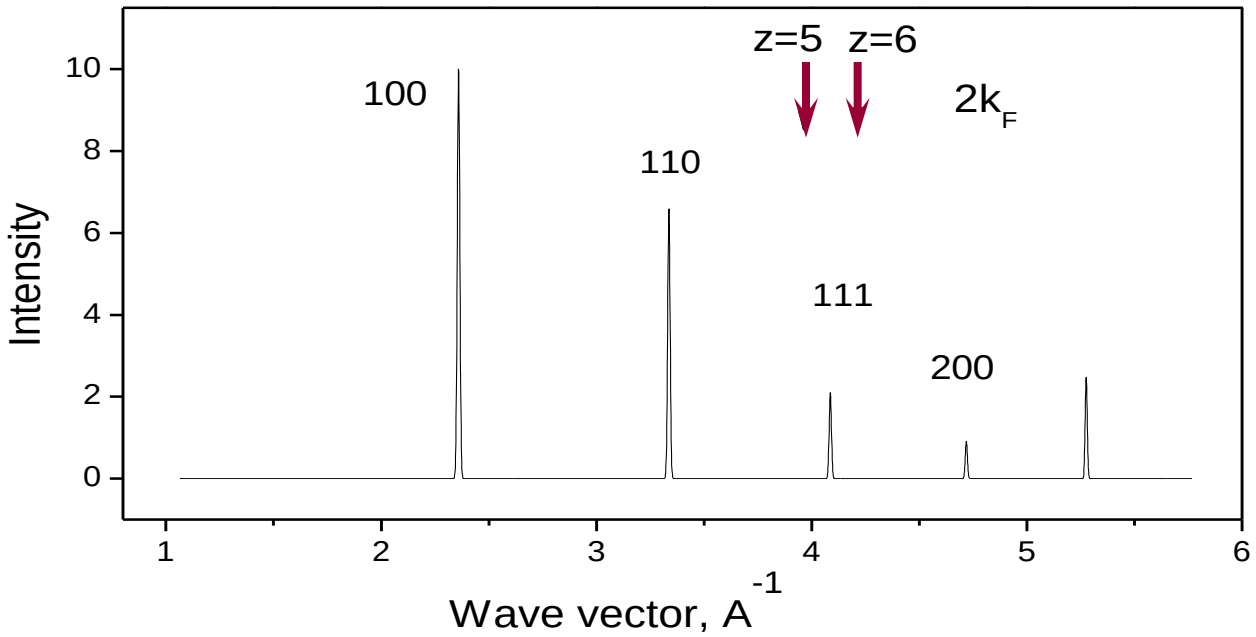
z=2 $2k_F/q_{100} = 1.24$ >> z=3.5 $2k_F/q_{110} = 1.056$

matching Hume-Rothery criteria !



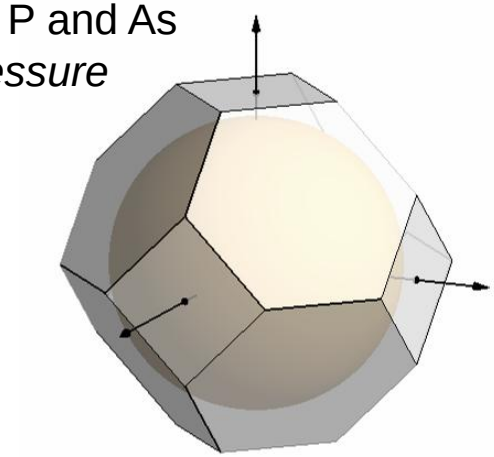


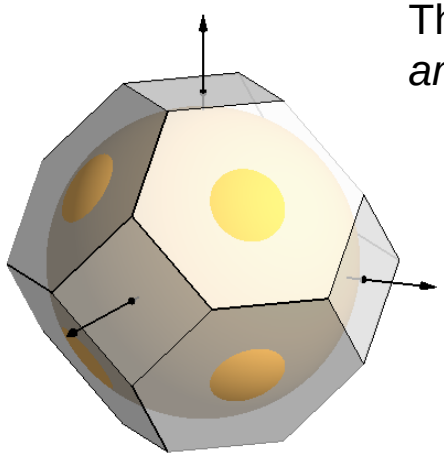
For sc how many valence electrons?



z=5 $2k_F/q_{111} = 0.972$ z=6 $2k_F/q_{111} = 1.033$

The case of sc P and As
under high pressure

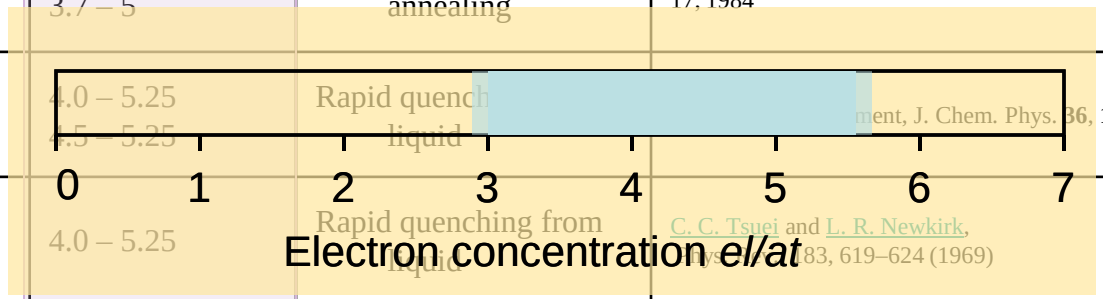




The case of α-Po
ambient pressure

sc metastable phases in alloys

Constituent elements	Number of valence electrons, z	Conditions	Refs
*Au-Bi (60 at.%Bi) *rhombohedral*, 89.1° Au-Bi (70-80 at.%Bi) Au-Sb (80 at.%Sb) Au-Te (60-90 at.% Te)	*3.4 3.8 – 4.2 4.2 4.0 – 5.5	Rapid quenching from liquid	B. C. Giessen, U. Wolff and N. J. Grant, *Trans. met. Soc.AIME*, 242, 597-602 (1968)
Au-Bi (~50-100 at.% Bi) Au-Sb (68-100 at.%Sb)	~3.0 – 5 3.7 – 5	Vapor quenching and annealing	P.Haeussler et.al, Elsevier science publishers B.V, LT-17, 1984
Au-Te (60-85 at.%Te) Ag-Te (70-80 at.%Te)	4.0 – 5.25 4.5 – 5.25	Rapid quench liquid	ment, J. Chem. Phys. **36**, 1870 (1962)
Au-Te (60-85 at.% Te)	4.0 – 5.25	Rapid quenching from liquid	C. C. Tsuei and L. R. Newkirk, 83, 619–624 (1969)
Pb-Sb (50-60 at.%Sb) In-Sb (60-70 at.%Sb)	4.5 – 4.6 4.2 – 4.4	Rapid quenching from liquid	C. Borromee-Gautier, B.C. Giessen, N. J. Grant, J. Chem. Phys. 48, 1905 (1968) C.B. Jordan, J. Chem. Phys., 39, 1613 (1963)
*In-Sb (57.5 at.% Sb) *rhombohedral*, 89.2° In – Sb (60 at.% Sb)	4.15 4.2	High pressure quenching	V.F. Degtyareva, I.T. Belash, G.V. Chipenko, E.G. Ponyatovskii and V. I. Rashchupkin, Soviet Physics Solid State, 25, 1712 (1983), translated from Fiz. Tverd Tela, 25, ,2968 (1983)
Au-Sb (73-84 at.% Sb)	3.9 – 4.4	Thin film, condensed from components	L.S. Palatnik, V.M. Kosevich, L.V. Tyrina, Physics of Metals and Metallography, translated from Fizika Metallov, Metallovedenie 11, 75 (1961)
Au-Te (40-90 at.% Te)	3.0 – 5.5	Ion irradiation	J.D. Meyer and B. Stritzker, Z. Physik B 36, 47 (1979)



SnSb - incommensurately modulated structure

Journal of Solid State Chemistry 179 (2006) 404–412

Old friends in a new light: "SnSb" revisited

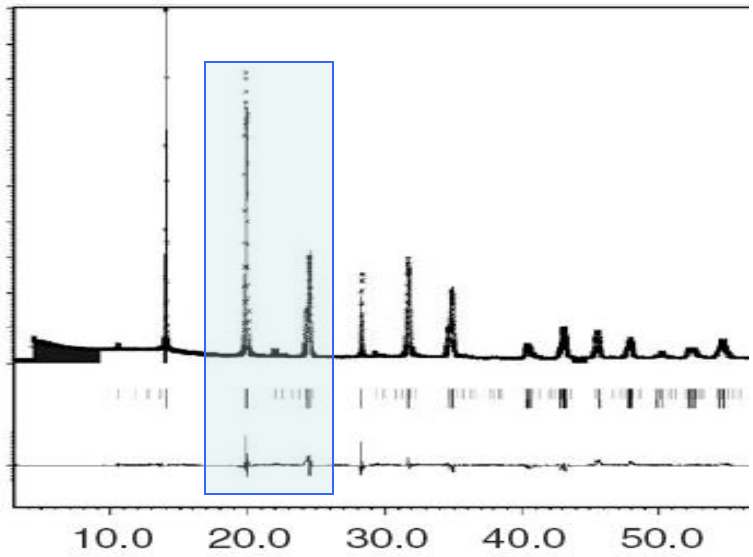
Lasse Norén[a,*], Ray L. Withers[a], Siegbert Schmid[b], Frank J. Brink[a,1], Valeska Ting[a]

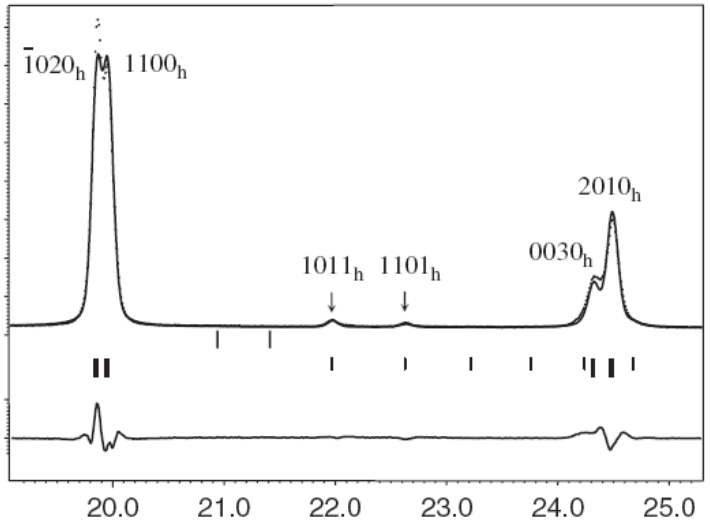
Inorg. Chem. **2009**, *48*, 5497–5503

Incommensurate Stistaite—Order Made to Order

S. Lidin,*,† J. Christensen,† K. Jansson,† D. Fredrickson,† R. Withers,‡ L. Norén,‡ and S. Schmid§

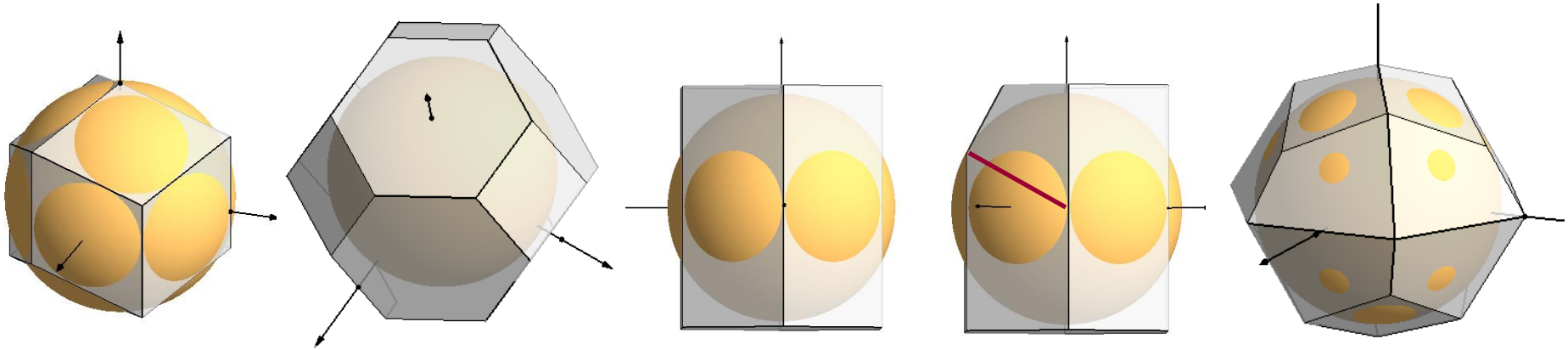
An underlying rhombohedral parent structure of space group symmetry R-3m
unit cell parameters a = 4.3251 A, c = 5.3376 A in the hexagonal setting
a_R = 3.066 A, α_R = 89.7˚ in the rhombohedral setting.
The incommensurate modulation wave vector *q=1.311c**
the superspace group symmetry is R-3m (0, 0, 1.311)





SnSb - incommensurately modulated structure

FS z=4.5



BZ planes

012 110

003 021

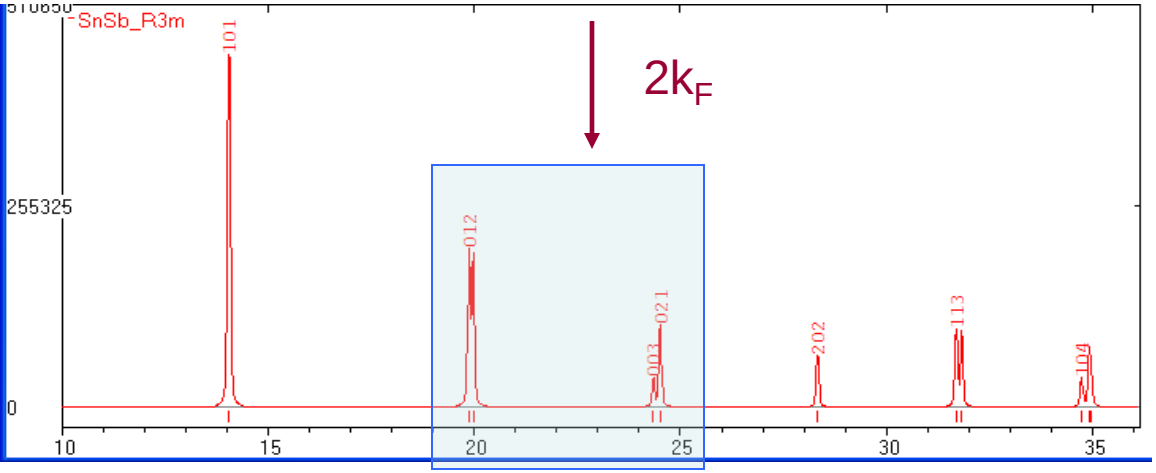
110 003 → add 1101

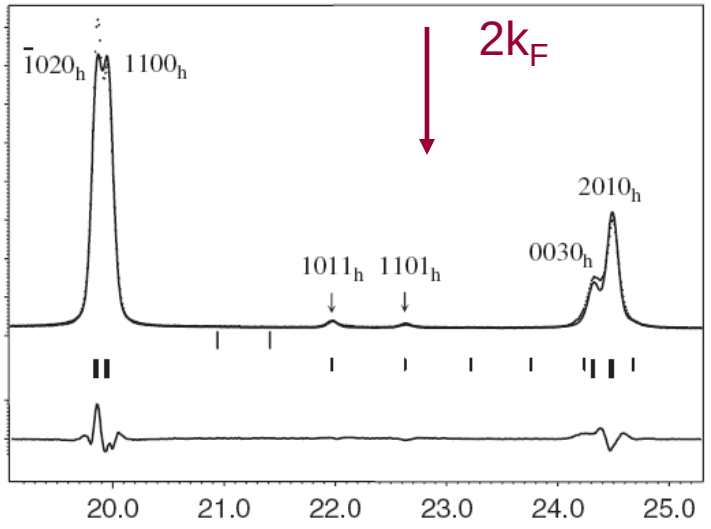
$2k_F/q_{1101} = 1.01$

1101 1011

$2k_F/q_{1011} = 1.035$

V_{FS}/V_{BZ}= 86%

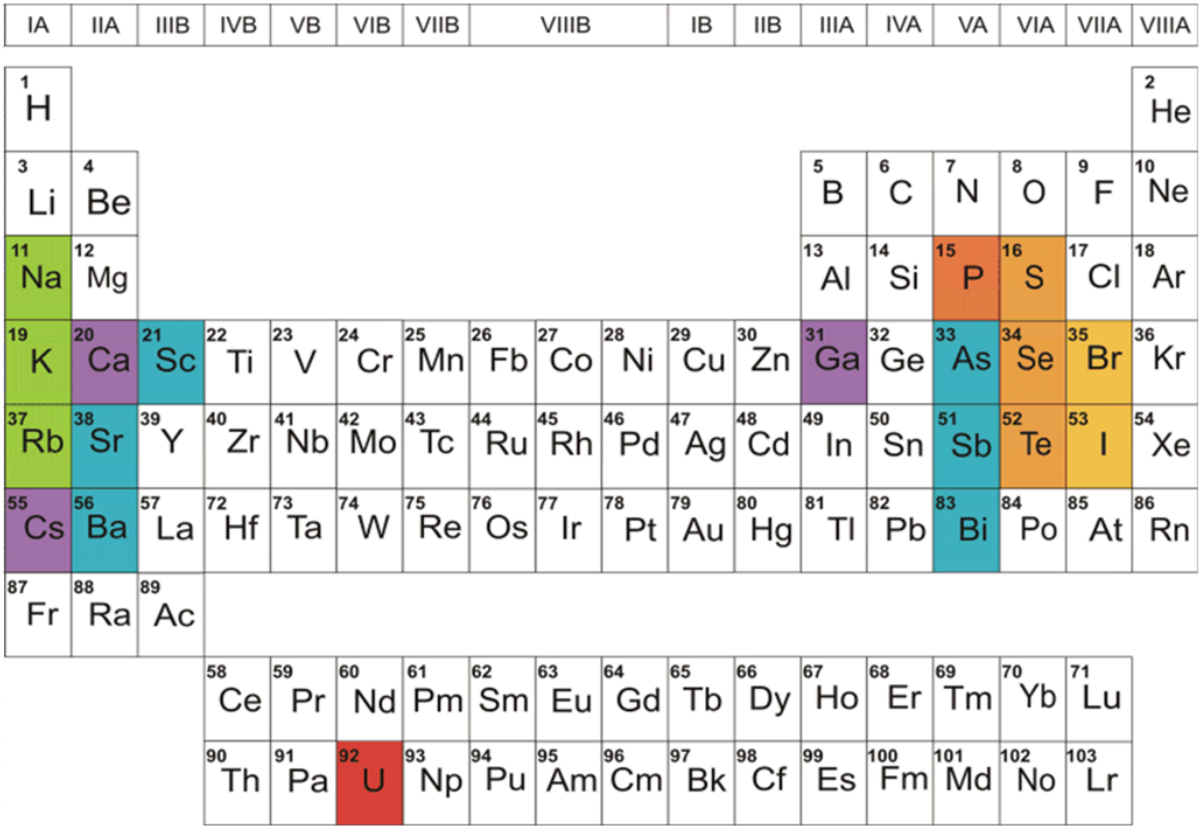




z=4.5 $2k_F$=3.33 2theta=22.95

Aperiodic structures in elements

1. Incommensurate host-guest structures (1999-2008)
2. Incommensurately modulated structures (2003-2007)
3. Long-period superstructures (2001-2009)



Conclusions

- Crystal structures of simple metals under pressure are determined by the valence electron energy term.
- 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.
- Calcium high pressure phases *simple cubic* and *post – simple cubic* stabilized by increase of the number of valence electrons due to the core ionization.

See poster MS18-P01