Complex structures of dense lithium: electronic origin

Valentina F. Degtyareva

ISSP RAS

Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Russia

Outline

- Main factors of crystal structure stability

  Concept of the Fermi Sphere - Brillouin Zone interaction: Cu-Zn alloy system
- Lithium – the simplest metal under pressure: structural complexity
- Core ionization: increase of the valence electron number

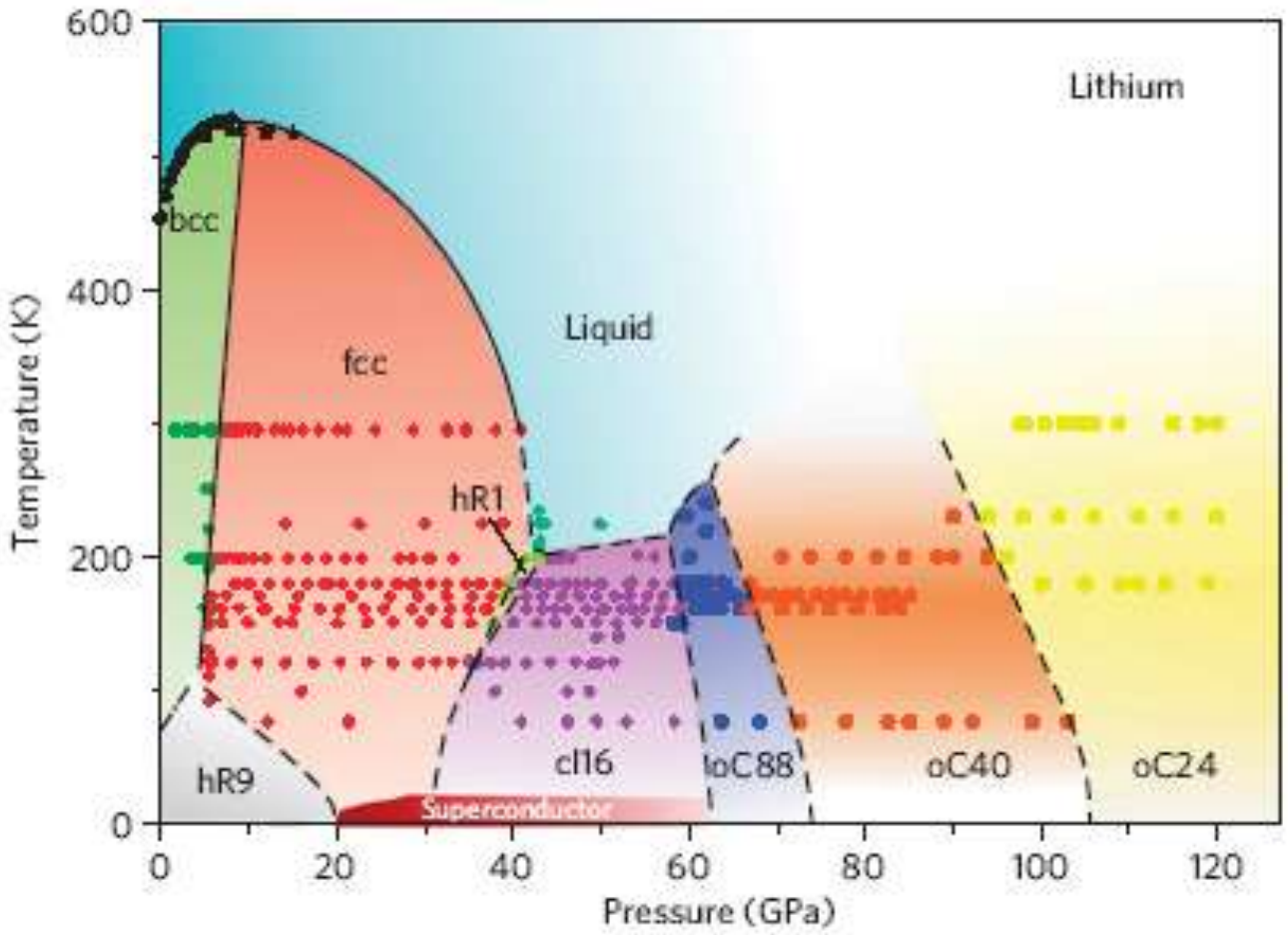
Alkali metals under pressure: structural transformations

Li	bcc (7.5) → fcc (39) → *hR*1 (42) → *cI*16 (60) → *oC*88 (70) → *oC*40 → *oC*24 (95) < 125 GPa
Na	bcc (65) → fcc (104) → *cI*16 (117) → *oP*8 (125) → h-g (*tI*19*) → *hP*4 (180) < 200 GPa
K	bcc (11.6) → fcc (20) → h-g (*tI*19*) (54) → *oP*8 (90) → *tI*4 → *oC*16 (96) < 112 GPa fcc (25) → *hP*4 (35) →
Rb	bcc (7) → fcc (13) → *oC*52 (17) → h-g (*tI*19*) (20) → *tI*4 → *oC*16 (48) < 70 GPa
Cs	bcc (2.4) → fcc (4.2) → *oC*84 (4.3) → *tI*4 (12) → *oC*16 → dhcp (72) < 223 GPa

s-d electron transfer **core ionisation**

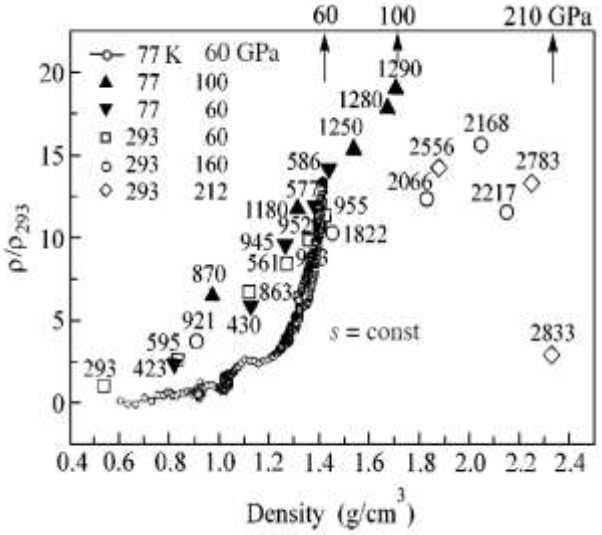
Large arrows indicate supposed core ionization
(at compression V/Vo equal 0.35 for Li, 0.24 for Na, 0.33 for K, 0.31 for Rb and 0.43 for Cs).

Melting curve of the lightest alkali metal: lithium



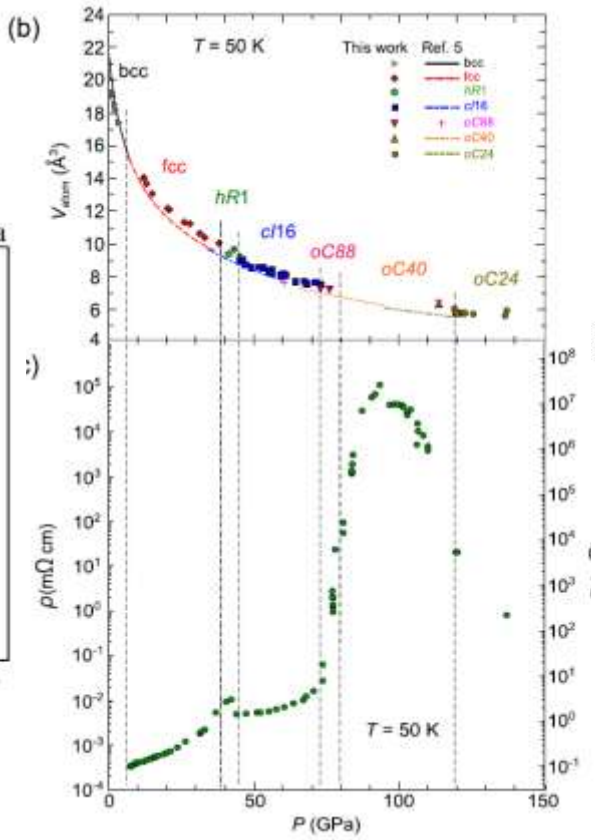
[Guillaume C, Gregoryanz E, Degtyareva O, et al. *Nature Physics* (2011) 7, 211]

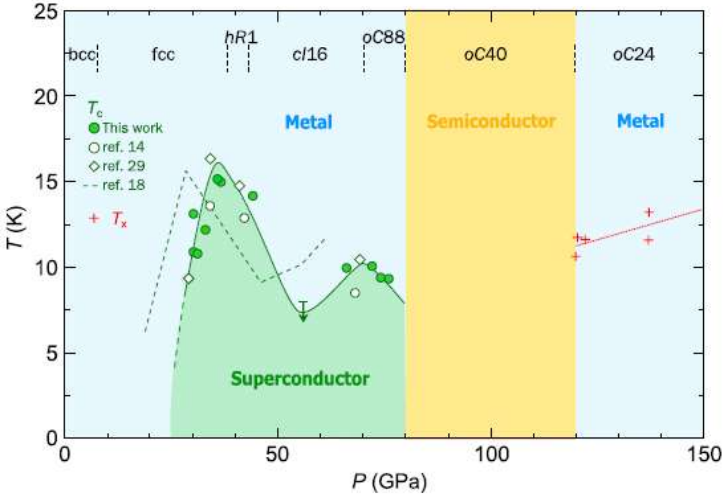
Anomalous Resistivity of Lithium
at High Dynamic Pressure



Resistivity of lithium
as a function of density

Pressure-induced reentrant metallic phase in lithium





The superconducting transition temperature *Tc* as functions of pressure and resistivity drops *Tx*

V.E.Fortov, V.V.Yakushev,
K.L.Kagan, I.V. Lomonosov, et al.
JETP Lett. **74**, 418 (2001)

Matsuoka T, Sakata M, Nakamoto Y, et al.
Phys.Rev.B 89, 144103 (2014)

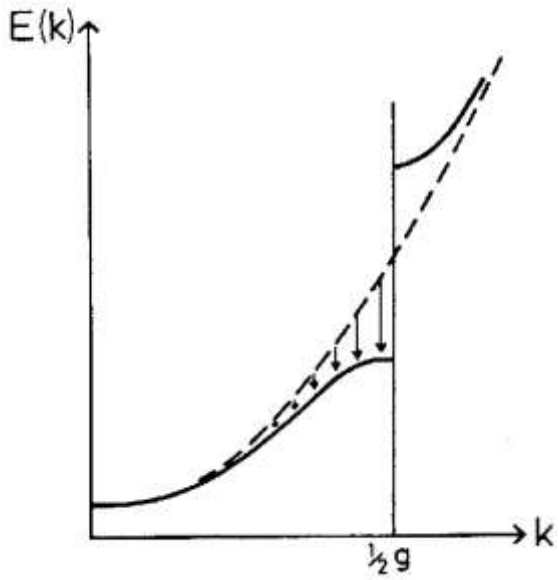
Main factors of phase stability

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

The crystal energy consists of two terms
electrostatic and electronic band structure

$$E_{Ewald} = -\alpha \frac{(Ze)^2}{2r_0}$$

$$E_{BS} = \sum_{q}{}' |S(q)|^2 \Phi(q)$$



Band structure energy E_{BS}

Volume scaling:

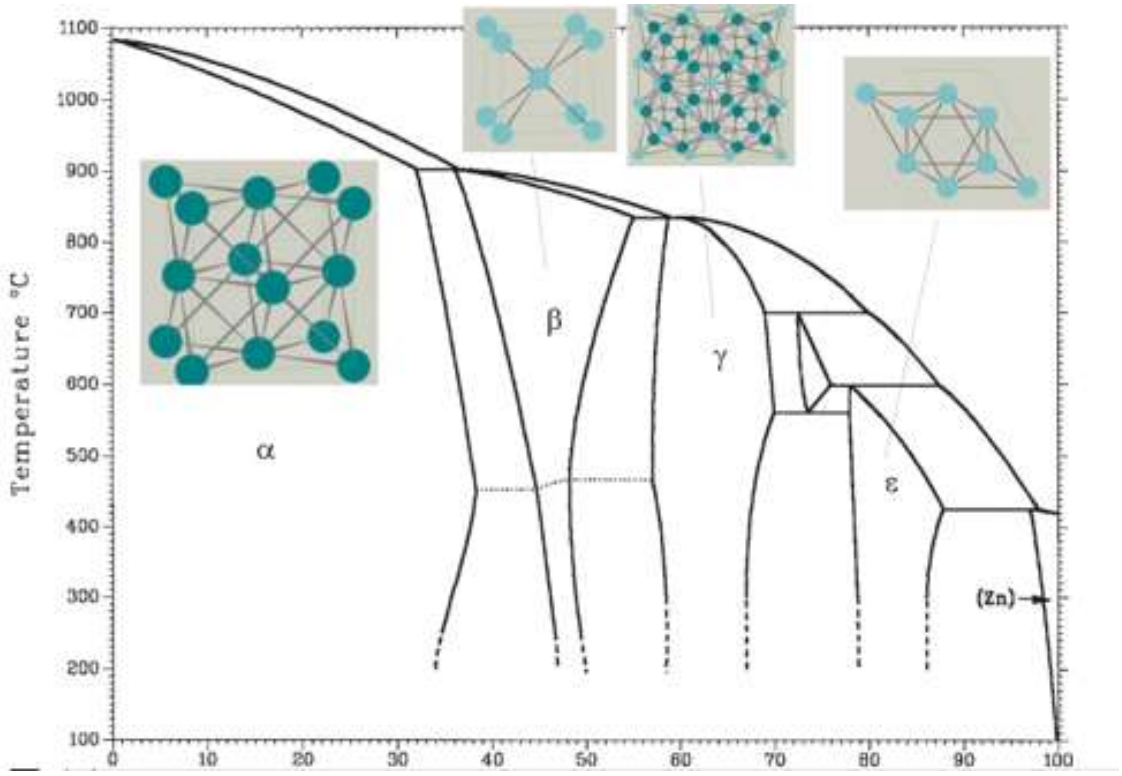
$\sim V^{-1/3}$ $\sim V^{-2/3}$

Enhancement of the Hume-Rothery arguments at compression

The brass alloy Cu-Zn system

The Age of Bronze

A. Rodin

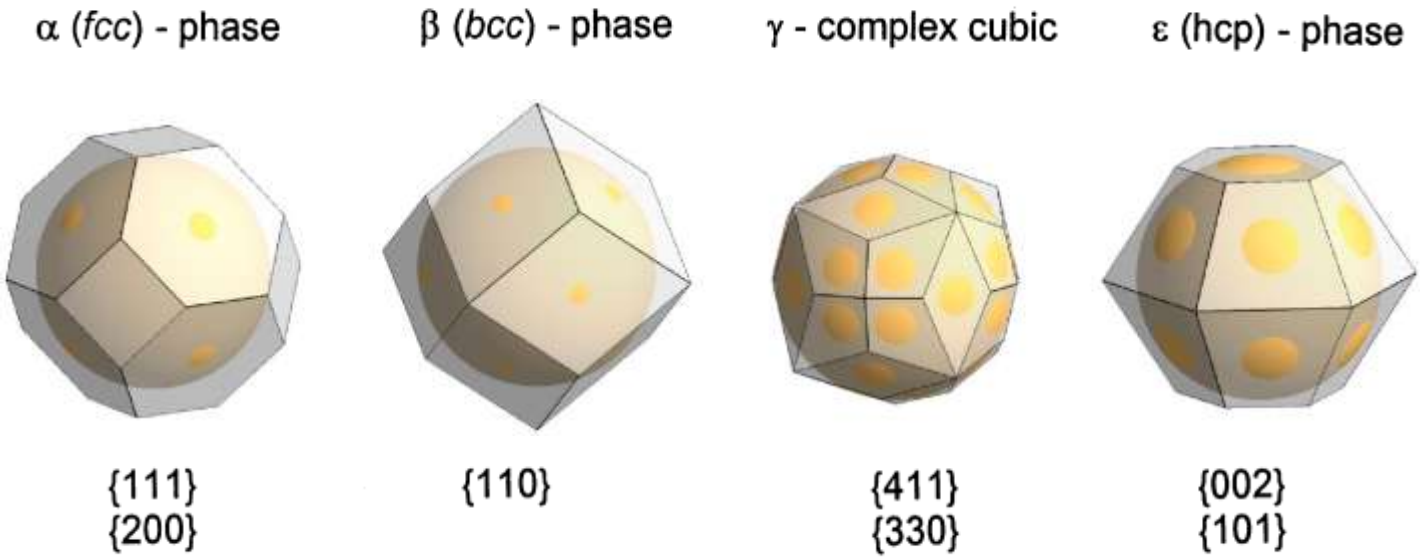


α (fcc) → β (bcc) → γ (complex cubic) → ε (hcp)

1.35 → 1.5 → 1.62 → 1.75 electron/atom

Massalsky (1996)

Hume-Rothery phases: Fermi sphere – Brillouin zone interaction



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

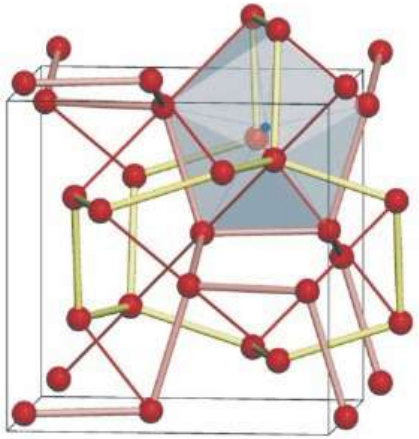
Brillouin zone – planes in reciprocal space with vector $q_{hkl} = \frac{2\pi}{d_{hkl}}$

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

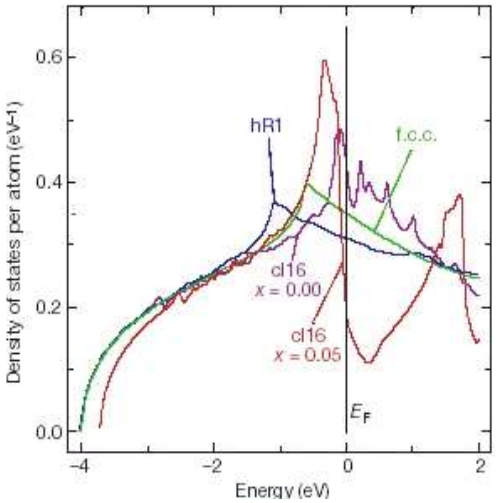
Alkali metals: pressure induced complexity

Li-*cI*16 at 46 GPa

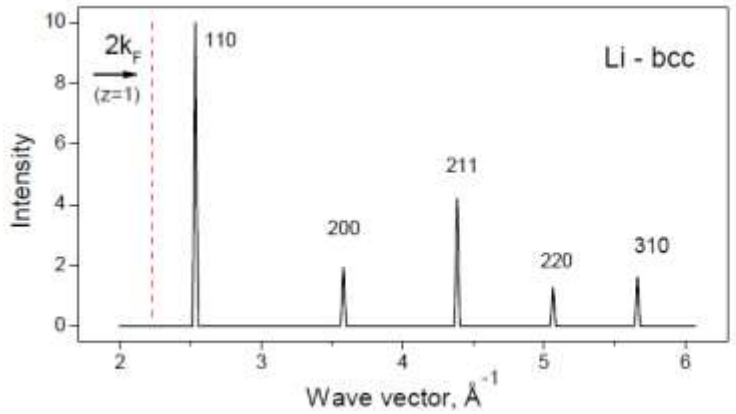
(*Hanfland et al, Nature 2000*)

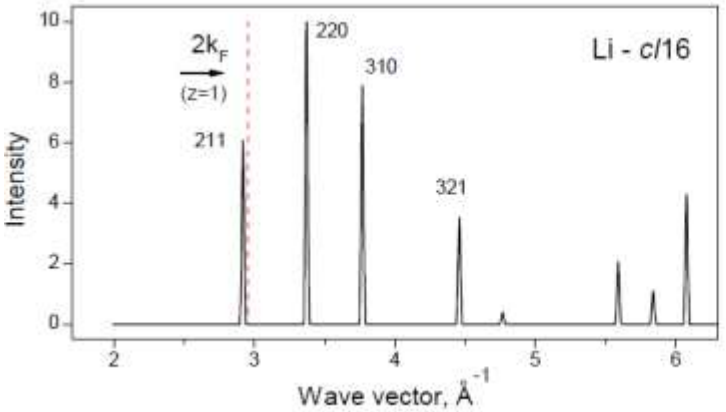


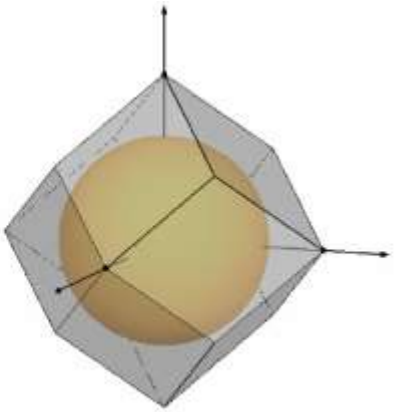
Crystal structure



Electron density of states







V_{FS}/V_{BZ} ~ **0.90**

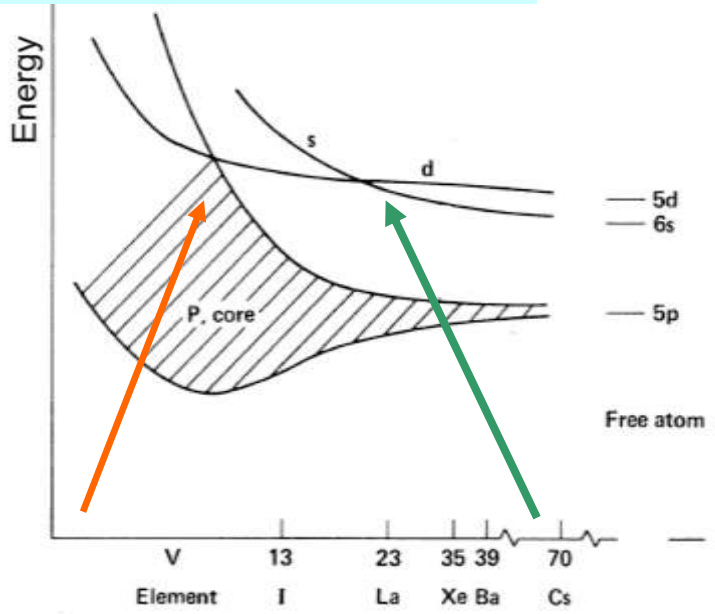
Brillouin zone Li-*cI*16

(*V Degtyareva 2003*)

Electronic energy levels

vs atomic volume

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

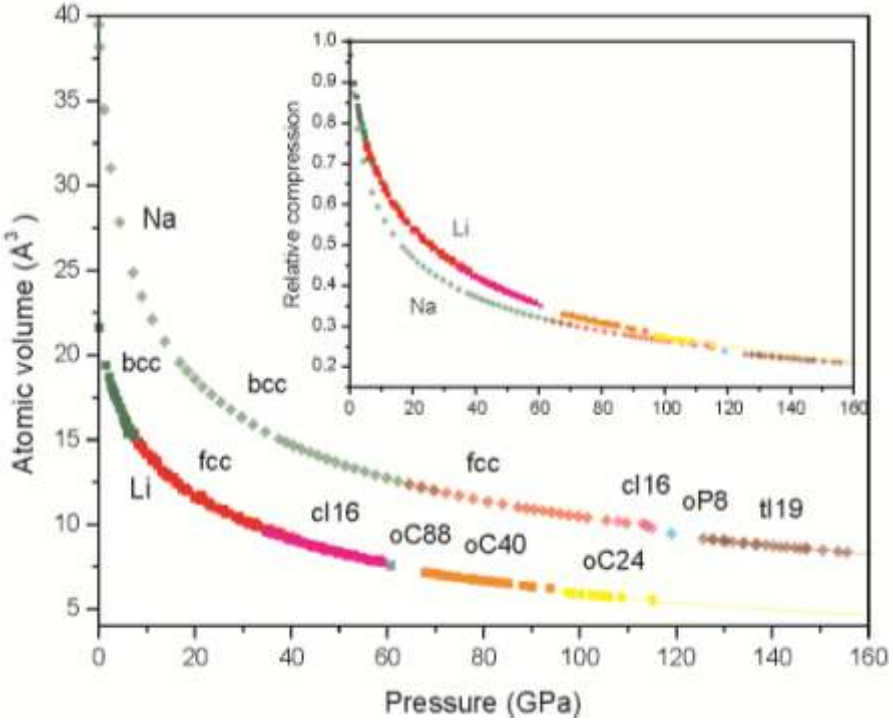


s-d-p(core) hybridization

s-d transfer

Equations of state of Li and Na

Inset: relative compression V/V_0

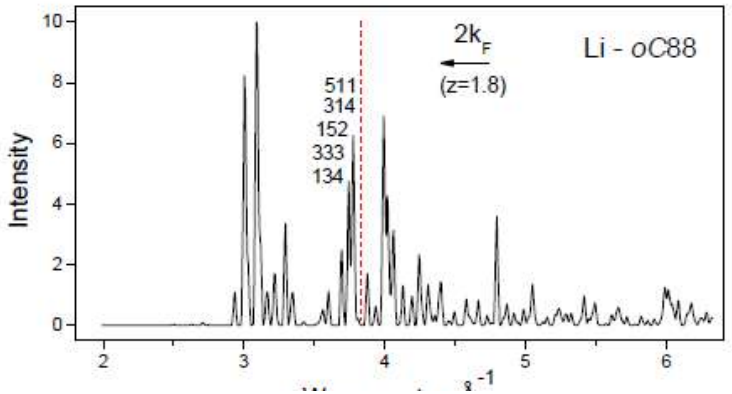


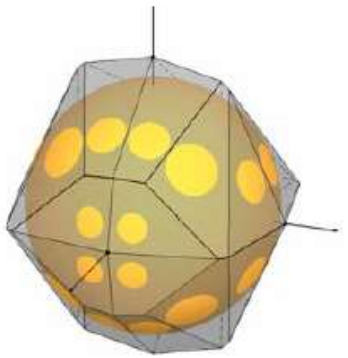
[Guillaume C, Gregoryanz E, Degtyareva O, et al. *Nature Physics* (2011) 7, 211]

Complex semiconducting phases of Lithium above 60 GPa

Li-*oC*88 *C2mb* P= 61 GPa
a=8.569Å, b=9.282Å, c =8.389Å

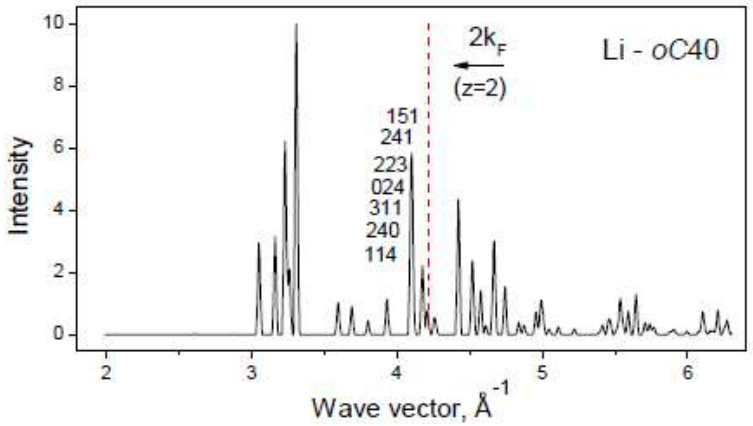
V_{FS}/V_{BZ} = 0.90

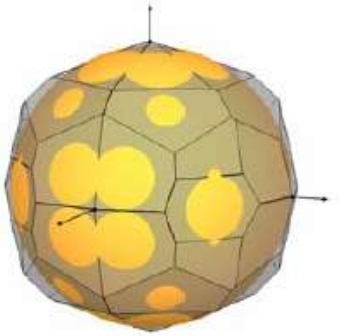




Li-*oC*40 *C2cb* P= 90 GPa
a=4.815Å, b=7.948Å, c =6.613Å

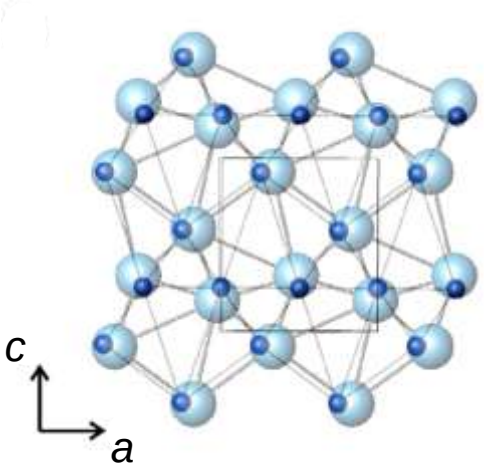
V_{FS}/V_{BZ} = 0.96





For *post–cI*16 phases with compression $V/V_o > 0.35$ we suggest an overlap of valence and core electron levels with increase of effective valence electron numbers. This allows understanding semiconducting properties of *oC*88 and *oC*40 phases as filling of BZ by electron states and returning *oP*24 to metal.

*oP*8 structure in Na and K: 2 valence electrons

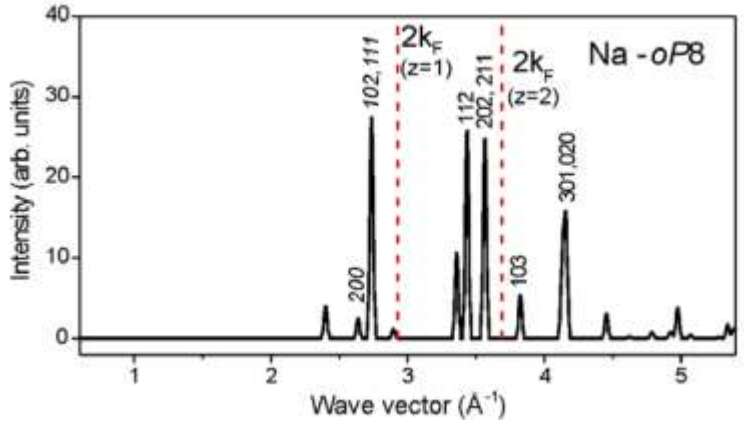


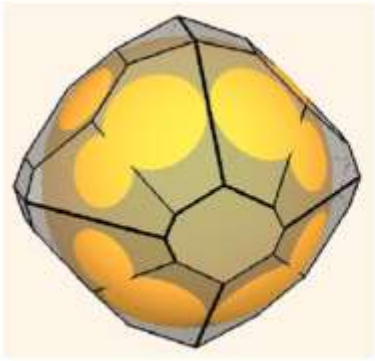
Na-*oP*8 *Pnma*
P = 119 GPa [1]
***a* =4.765 Å, b=3.020 Å,**
c=5.251 Å

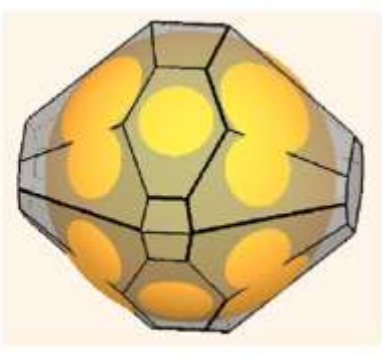
Recently found the *oP*8 structure in Na and K [1,2]
Is considered as a Hume-Rothery phase
assuming alkali elements as divalent metals [3]

[1] Gregoryanz E et al., Science 320, 1054 2008
[2] Lundegaard L F et al., Phys Rev B 80, 020101 2009
[3] Degtyareva V F & Degtyareva O, New J Phys 11, 063037 2009

Brillouin zone of Na – oP8 with the inscribed FS
The position of $2k_F$ for z = 1 and z = 2 for Na, calculated from the free-electron model, is shown [3].
The structure and the form of BZ is similar to AuGa compound (z=2)

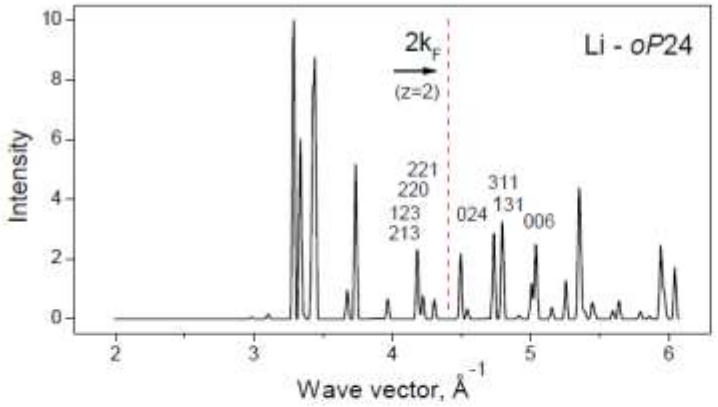


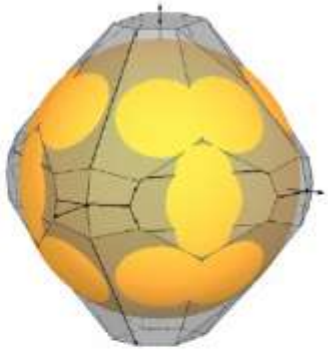




Li-*oP*24 and Na-*oP*8 structural relation

Li-oP24 Pbca P= 115 GPa
a=4.213Å, b=4.205, c =7.482Å

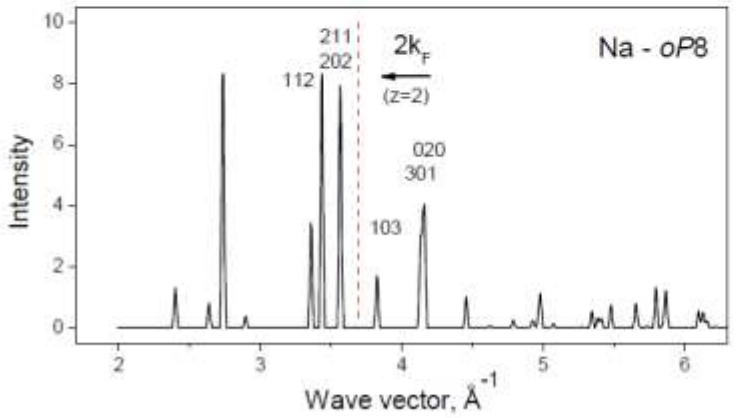


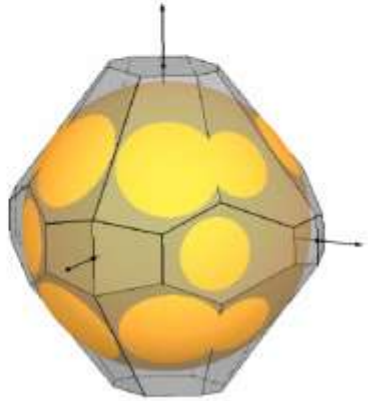


V_{FS}/V_{BZ} = 0.93

Na-*oP*8 *Pnma* P = 119 GPa
a **=4.765 Å, b=3.020 Å, c=5.251 Å**

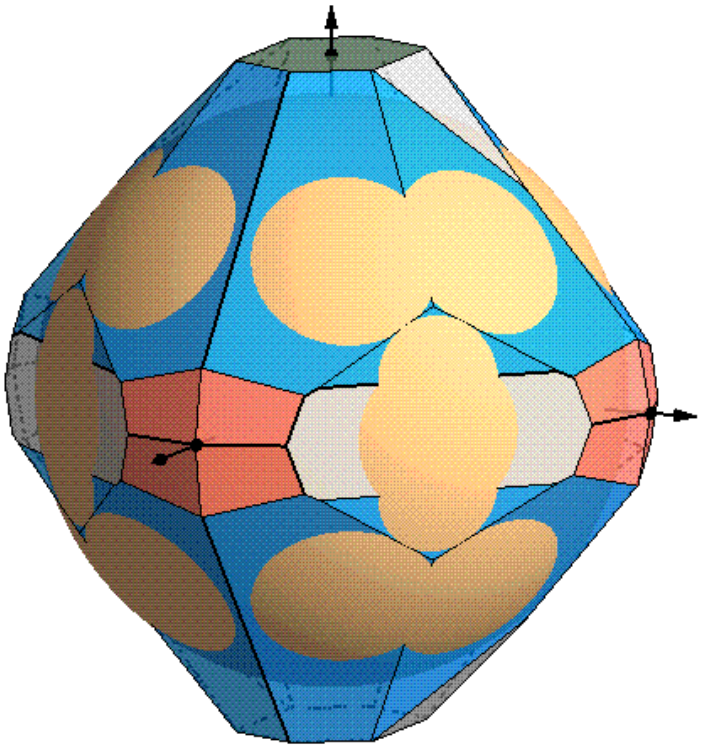
(Gregoryanz et al., Science 320 1054, 2008)
BZ projection is ↑ b* , → a*, down c*





Li-*oP*24 and Na-*oP*8 are related to AuGa-*oP*8 and to hexagonal NiAs-*hP*4.
Cell parameters for Na-*oP*8 are related to c_h, a_h, $a_h\sqrt{3}$,
for Li-*oP*24 are related to $a_h\sqrt{3}$, c_h, $3a_h$.
BZ configurations are similar for both phases.
Valence electron number z =2 is assumed for Li-*oP*24
as in Na-*oP*8 and AuGa-*oP*8 phases.

Li – *oP*24



Conclusions

- Crystal structures of simple metals under pressure are determined by valence electron energy term
- Fermi sphere - Brillouin zone interactions favour the low-symmetry structures with BZ planes close to the FS by the Hume-Rothery mechanism
- Formation of low-packing structures is related to the core ionization
- Melting curve with maximum and negative slope in alkali metals is defined by Hume-Rothery effect

Thanks for attention

Thanks for collaboration to
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