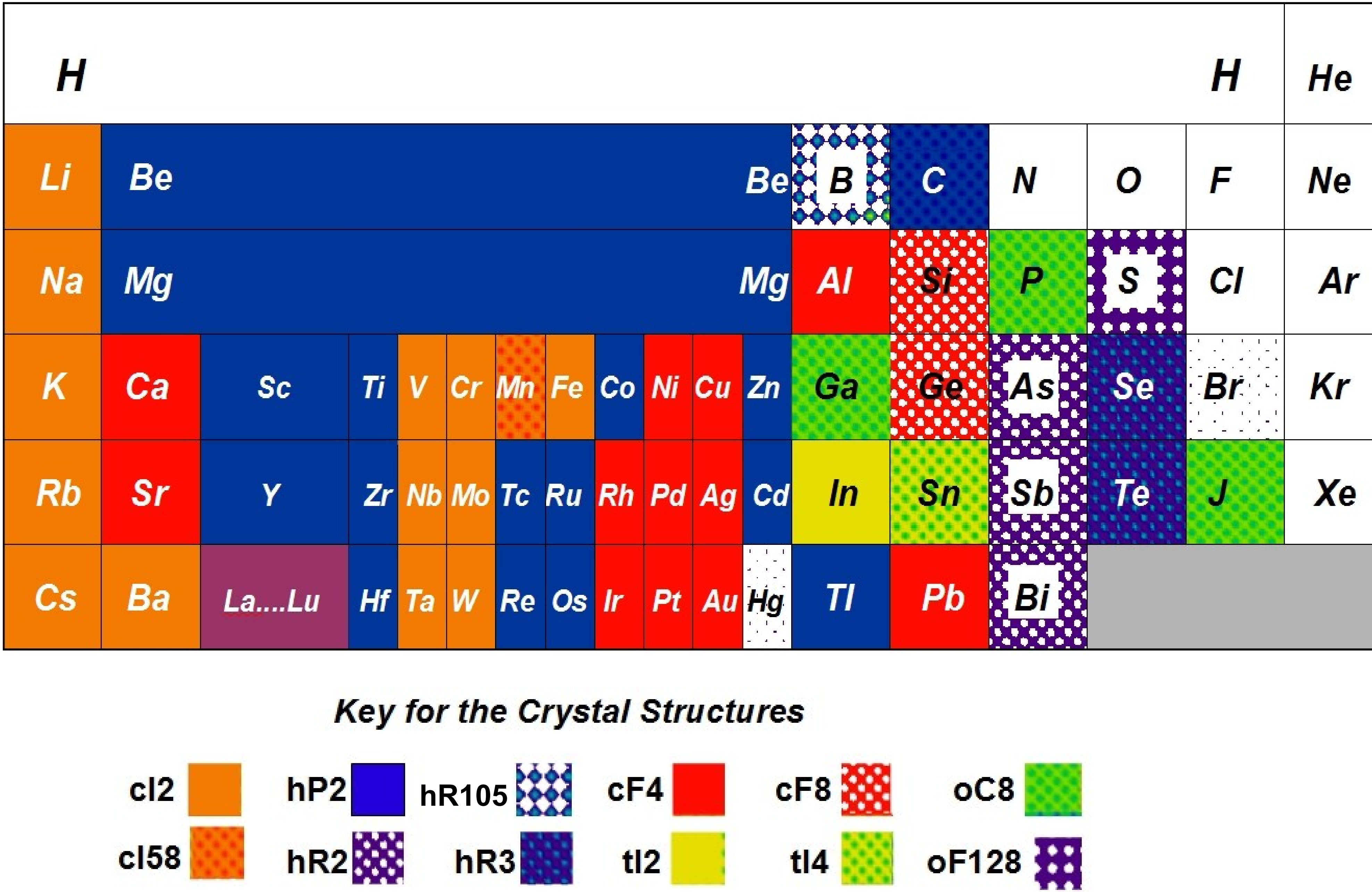
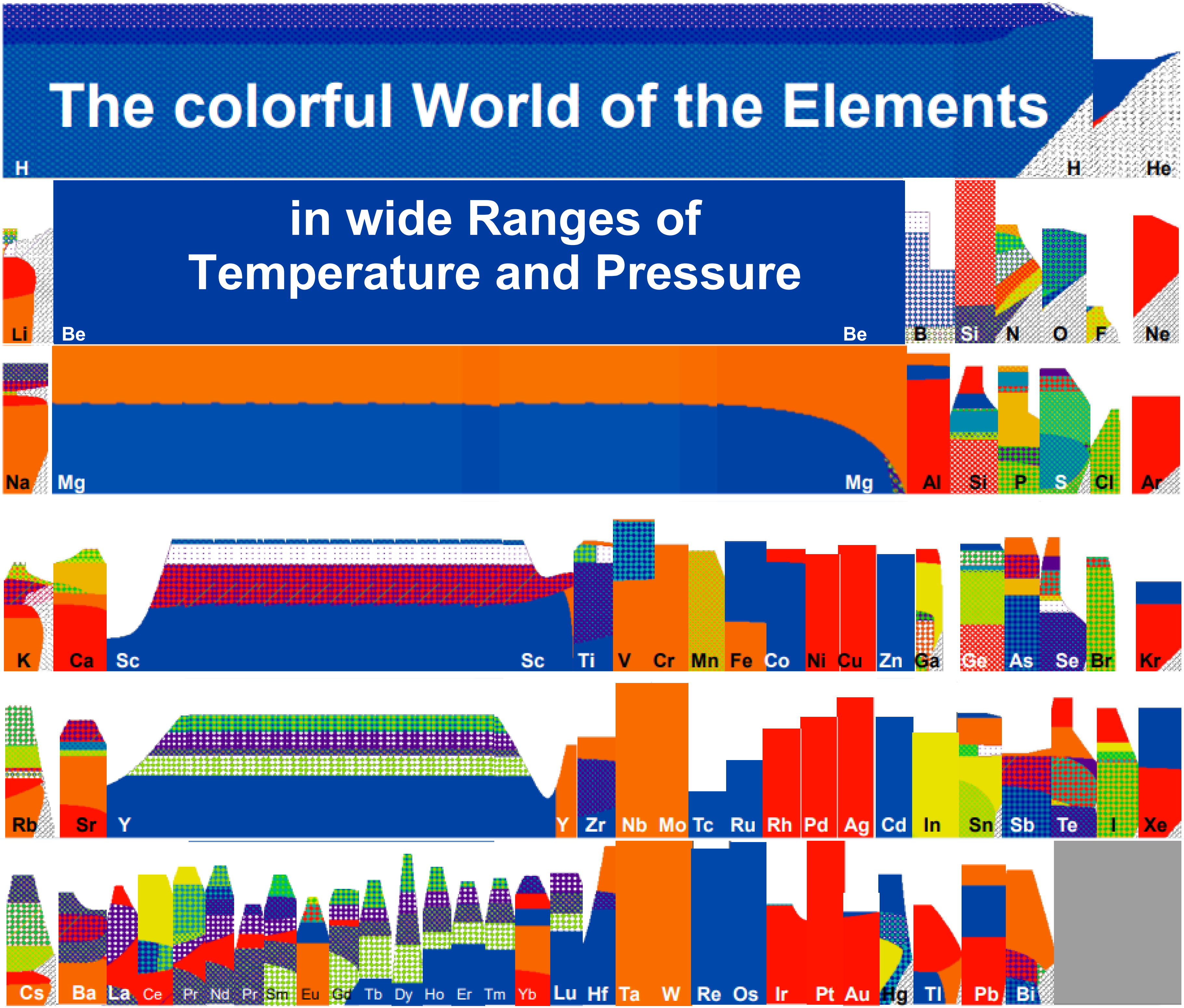
Structural systematic in the phase-diagrams of the elements

A simple guide to the world of high pressure
AIRAPT lecture 2023

Wilfried B. Holzapfel
Emeritus, Department of Physics, University Paderborn, Germany
holzapfel@physik.upb.de

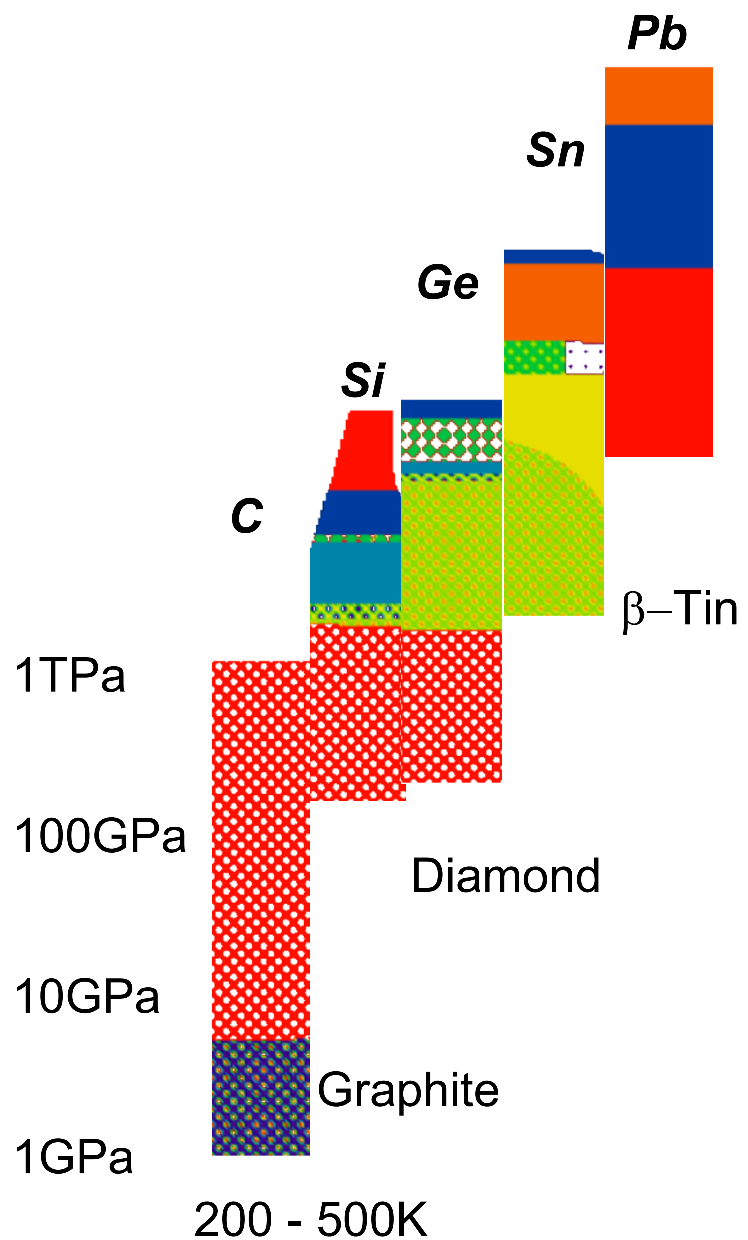
Crystal Structures of the Elements at ambient Pressure



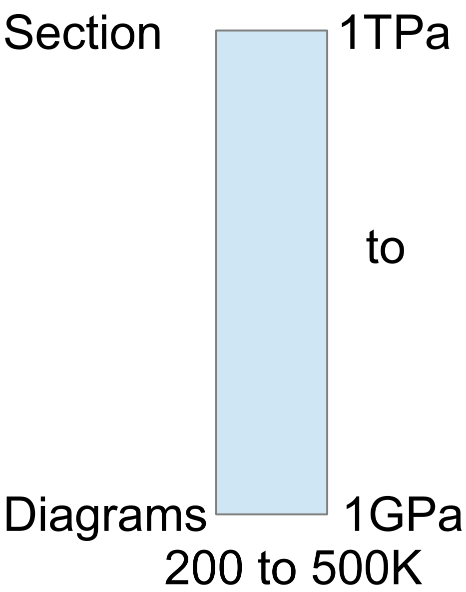

The colorful World of the Elements
in wide Ranges of
Temperature and Pressure
H H He
Li Be Be B Si N O F Ne
Na Mg Mg Al Si P S Cl Ar
K Ca Sc Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Ce Pr Nd Pr Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi

The Carbon Group

Smaller values for the ratio of atomic versus ionic radii result in high pressure structures.
Heavier Elements start with smaller radius ratios.



The Carbon Group



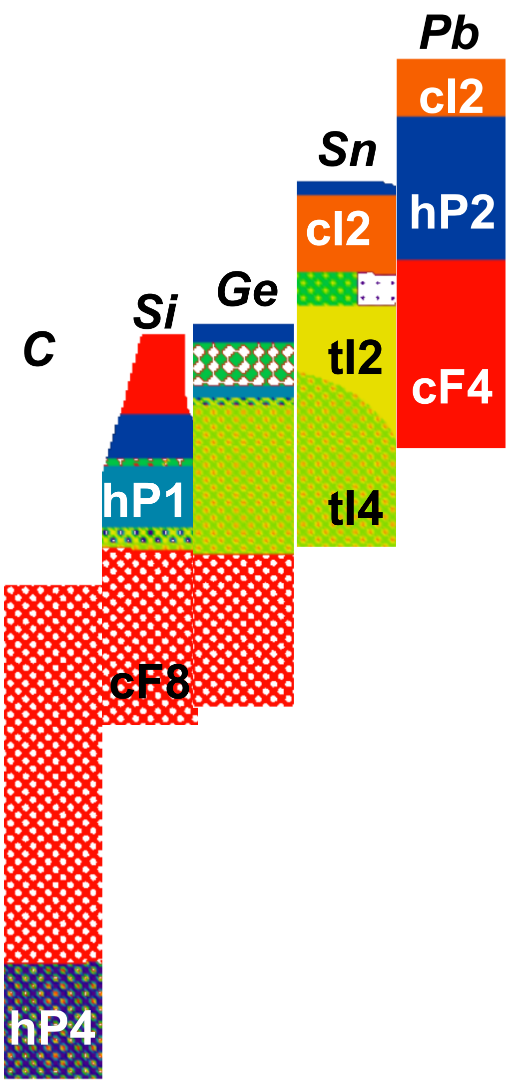
C hP4-----cF8---->275GPa
ptr/GPa 3

Si cF8----tI4-----oI4-----hP1----oC16-----hP2-----cF4---->250GPa
ptr/GPa 12 13 16 38 42 80

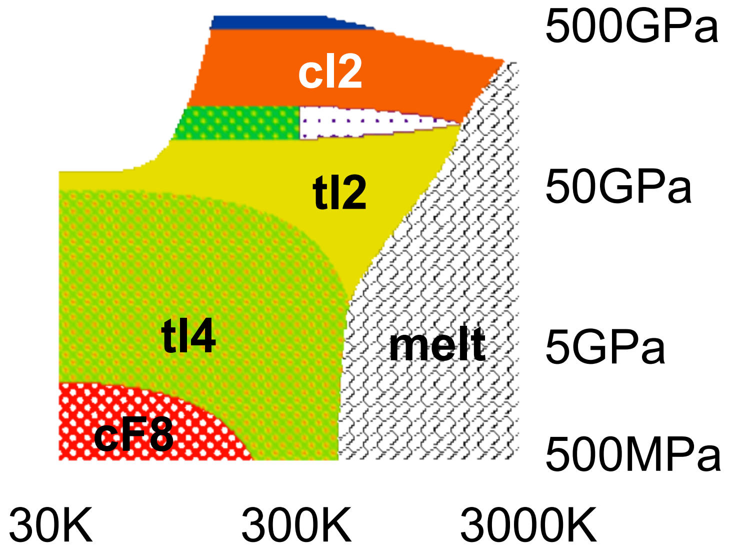
Ge cF8-----tI4-----oI4-----hP1----oC16-----hP2---->180GPa
ptr/GPa 11 75 85 102 160

Sn cF8-----tI4------tI2----oI2----cI2-----hP2---->194GPa
ptr/GPa 0 9.2 32 70 157

Pb cF4-----hP2-----cI2------>272GPa
ptr/GPa 13 127



Sn: 30-3000K, 0.5-500GPa



The Alkaline Metals

Li cI2-----cF4-- liquid --oC40-----oC24--->116GPa

ptr/GPa 7.5 39 75 90

200K: hR1----cI16----oC88-------oC40-------oC24

Na cI2---cF4---cI16--oP8***--HGL--hP4->215GPa

ptr/GPa 65 104 115 125 180 hP2 mP512H

K cI2------cF4------HGL----oP8----tI4----oC16---->112GPa

ptr/GPa 11.6 20 54 90 96

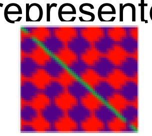
Rb cI2------cF4----oC52----HGL----tI4----oC16---->70GPa

ptr/GPa 7 13 17 20 48

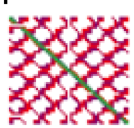
Cs cI2------cF4-------oC84-----------tI4---oC16---hP4-->223GP

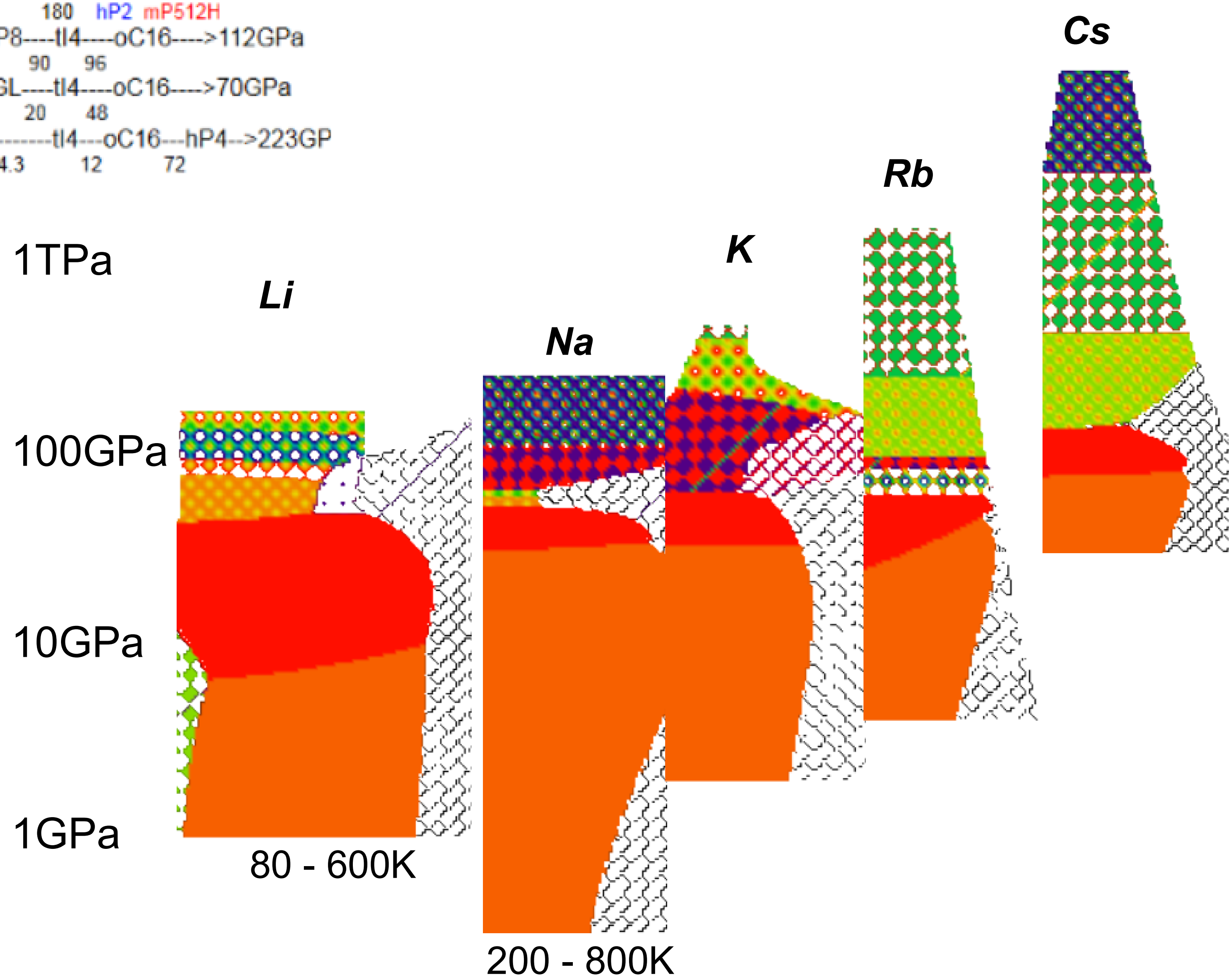
ptr/GPa 2.4 4.2 4.3 12 72

Different types of **ordered HGL** host-guest lattices are represented by



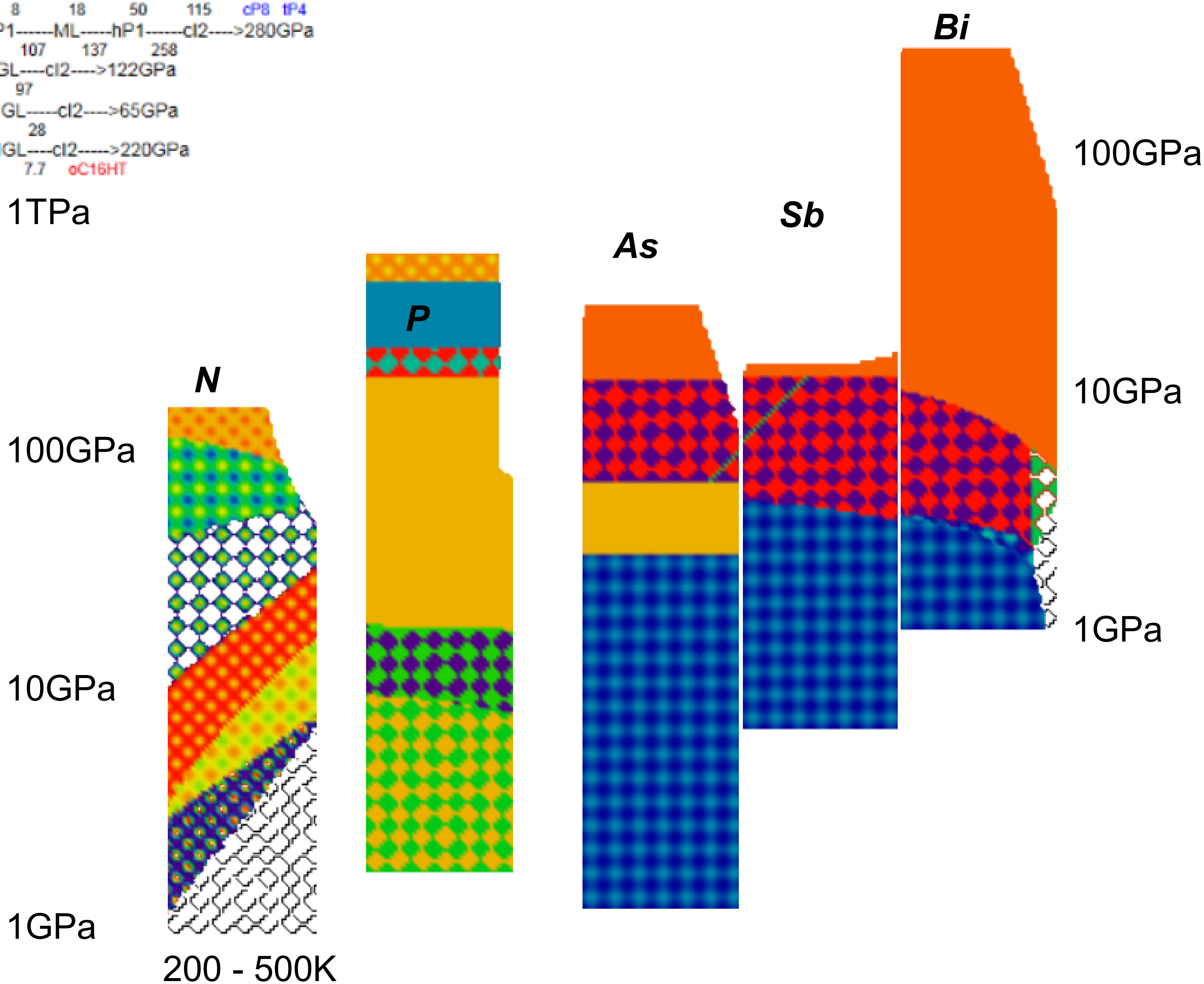
disordered HGD host-guest lattices are represented by





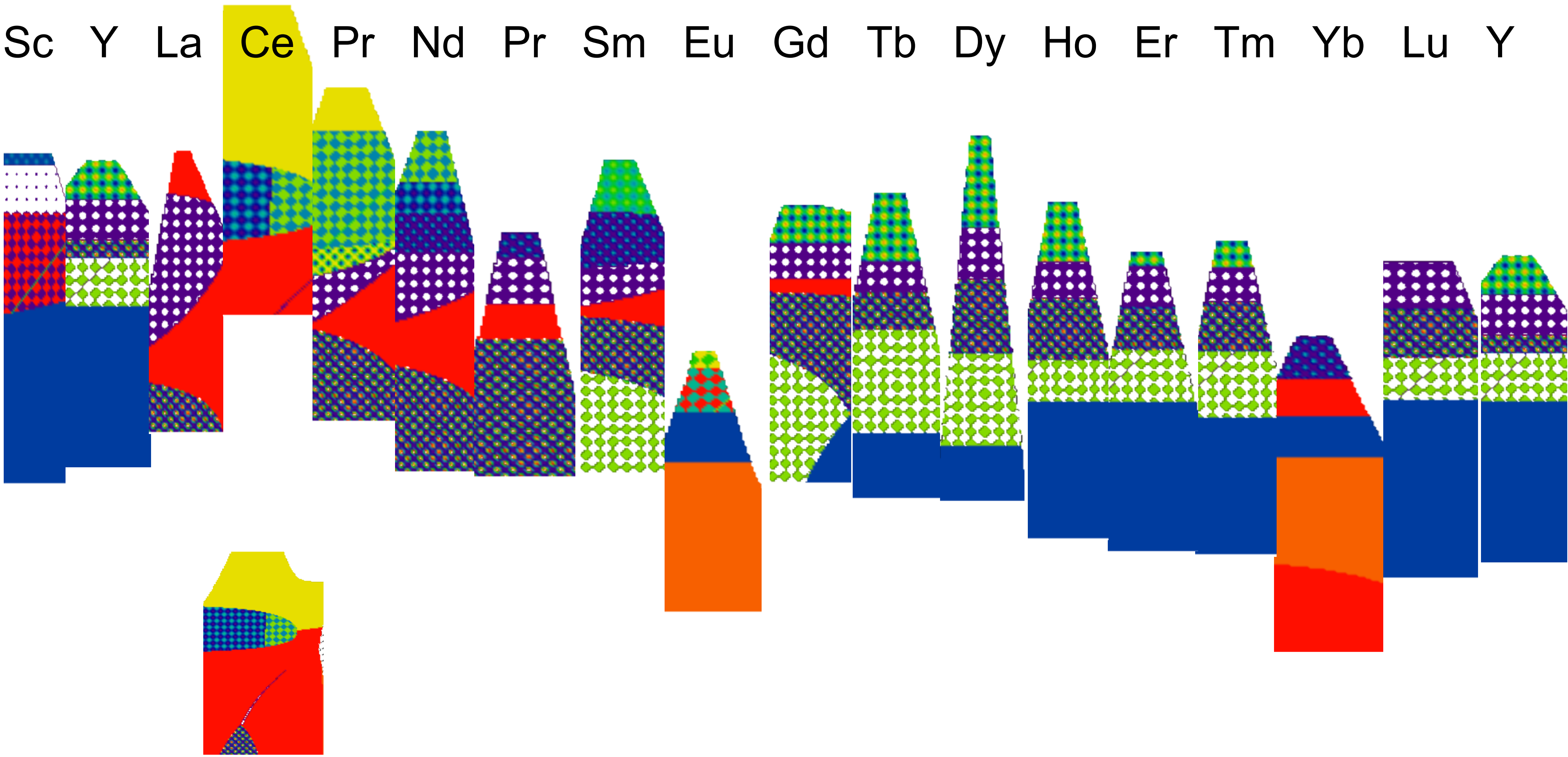
The Nitrogen Group

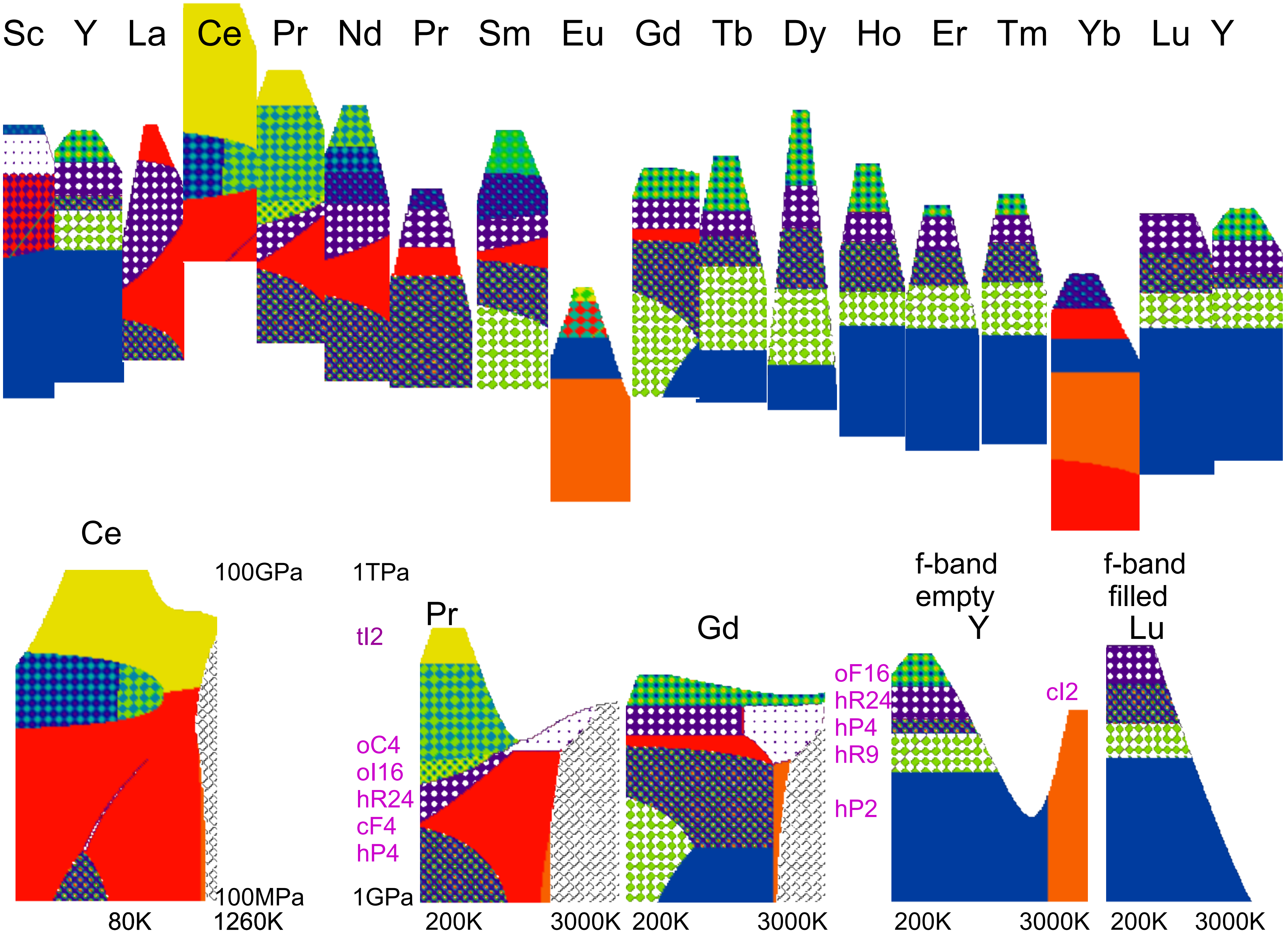
N gas---hP4---cP16----tP32---hR8---oP16---cI8-->120GPa
ptr/GPa 2.6 4.7 8 18 50 115 cP8 tP4
P oC8----hR2----cP1-------ML-----hP1------cI2---->280GPa
ptr/GPa 5 10 107 137 258
As hR2----cP1----HGL----cI2---->122GPa
ptr/GPa 25 48 97
Sb hR2----HGL----HGL-----cI2---->65GPa
ptr/GPa 8.2 9.0 28
Bi hR2----mC4----HGL----cI2----->220GPa
ptr/GPa 2.5 2.7 7.7 oC16HT



La hP4----cF4----hR8----cF4---->70GPa
ptr/GPa 2 7 58 cI2HT
Ce hP4----cF4----cF4-----oC4-----tI2----->20[illegible]Pa
ptr/Ga .2 .67 3.9 13 cI2HT
Pr hP4----cF4----hR8------???-----oC4---->60GPa
ptr/GPa 4 6.2 10 20 cI2HT
Nd hP4----cF4----hR8----hP3----mC4----oC4----->70GPa
ptr/GPa 5 15 40 75 113 cI2HT
Pm hP4----cF4----hR8----hP3----->60GPa
ptr/GPa 10 18 40
Sm hR3----hP4----cF[illegible]----tI2----mC4---->70GPa
ptr/GPa 5 15 75 105 cI2HT
Eu cI2----hP2------ML[illegible]2GPa
ptr/GPa 13 31.5

Gd hP2------hR3-----hP4------cF4-----hR8------mI2----->235GPa
ptr/GPa 3.2 7 26 46 61 cI2HT
Tb hP2------hR3-----hP4------cF4-----hR8----->58GPa
ptr/GPa 3 6 29 32
Dy hP2------hR3-----hP4------cF4-----hR8----->70GPa
ptr/GPa 5 9 38 40
Ho hP2------hR3-----hP4------------------hR8----->70GPa
ptr/GPa 10 25 70
Er hP2------hR3-----hP4------------------hR8----->70GPa
ptr/GPa 12.4 24 67.4
Tm hP2------hR3-----hP4----->42GPa
ptr/GPa 10 30
Yb hP2-----cF4-----cI2-----hP2------cF4------hP3----->202GPa
ptr/GPa 0.1 4 30 53 98
Lu hP2------hR3-----hP4-----cF4------Lu(IV)----->275GPa
ptr/GPa 20 30 88 272





Sc Y La Ce Pr Nd Pr Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y
Ce
100GPa
1TPa
100MPa
1GPa
80K
1260K
Pr
tI2
oC4
oI16
hR24
cF4
hP4
200K
3000K
Gd
200K
3000K
oF16
hR24
hP4
hR9
hP2
f-band
empty
Y
cI2
200K
3000K
f-band
filled
Lu
200K
3000K

IA

H gas----hP4H---->200GPa
ptr/GPa 5.3 hP4B hP4D

Li cI2-----cF4-- liquid --oC40-----oC24--->116GPa [MN06,VD06,OD09,GG11]
ptr/GPa 7.5 39 75 90 hR3
200K: hR1----cI16----oC88-------oC40-------oC24

Na cI2---cF4---cI16--oP8***--HGL--hP4->215GPa [GD05,MN06,VD06,GL08,LG09,ME09,OD09]
ptr/GPa 65 104 115 125 180 hP2 mP512HT oP8*** includes tI50 oC120 aP90

K cI2------cF4------HGL----oP8----tI4----oC16---->112GPa [MN06,VD06,OD09]
ptr/GPa 11.6 20 54 90 96

Rb cI2------cF4----oC52----HGL----tI4----oC16---->70GPa [MN06,VD06,OD09]
ptr/GPa 7 13 17 20 48

Cs cI2------cF4-------oC84-----------tI4---oC16---hP4-->223GPa [MD03,MN06,,VD06,OD09]
ptr/GPa 2.4 4.2 4.3 12 72

IIA

[MN06, VD06, OD09]

Be hP2------->171GPa
ptr/GPa

Mg hP2-------cI2------->58GPa [YK12]
ptr/GPa 50

Ca cF4--cI2--cP1---tP8---oC8---mC6---HGL->216GPa [YN05,VD06,NY07,FN08,MW10,NS10]
ptr/GPa 20 32 113 139 158 210 oC2 tI4 [OM10,SN11,TD12,LD12,FN13,VD14]

Sr cF4 ------cI2------tI4------mI12------HGL---->117GPa [BA05]
ptr/GPa 3.5 27 35 49

Ba cI2-------hP2-------HGL-----hP2----------->105GPa
ptr/GPa 5.5 12 45 cF4HT

IIIA

[MN06,VD06]

B hR106------hR12------oP28----oC8---->250GPa [BT04,OC09,OS11]
ptr/GPa 3 tP192HT 18 89

Al cF4------hP2----> 333GPa [AN06]
ptr/GPa 217

Ga oC8----liquid----tI2----oC104----hR6----tI2----cF4--->150GPa [DM04,MN06]
ptr/GPa 0 2.0 2.8 tI2HT 10.5 14 120

In tI2-----oF4---->93GPa
ptr/GPa 45

Tl hP2-----cF4---->68GPa
ptr/GPa 3.7 cI2HT

IVA

[MN06,VD06,OD09]

C hP4-----cF8---->275GPa
ptr/GPa 3

Si cF8----tI4-----oI4-----hP1----oC16-----hP2-----cF4---->250GPa
ptr/GPa 12 13 16 38 42 80

Ge cF8-----tI4-----oI4-----hP1----oC16-----hP2---->180GPa
ptr/GPa 11 75 85 102 160

Sn cF8-----tI4------tI2----oI2----cI2-----hP2---->194GPa [SG11,SB13]
ptr/GPa 0 9.2 32 70 157

Pb cF4-----hP2-----cI2------>272GPa
ptr/GPa 13 127

VA

N gas---hP4---cP16----tP32---hR8---oP16---cI8-->120GPa [EG04,GG07,SL09, MO09]
ptr/GPa 2.6 4.7 8 18 50 115 cP8 tP4

P oC8----hR2----cP1------ML-----hP1------cI2---->280GPa [VD06,MA08]
ptr/GPa 5 10 107 137 258

As hR2----cP1----HGL----cI2---->122GPa [DM04,VD06,MN06]
ptr/GPa 25 48 97

Sb hR2----HGL----HGL-----cI2---->65GPa [MD07,OD09]
ptr/GPa 8.2 9.0 28

Bi hR2----mC4----HGL----cI2----->220GPa [MD07,OD09]
ptr/GPa 2.5 2.7 7.7 oC16HT

VIA

O gas----hR2----oF8----mC16----mC16---->132GPa [FA06, LW06,WD09,KL10]
ptr/GPa 6 8 9 96 mC4 cP16

S oF128----hP9----tI16----aI6----MG----hR1---->160GPa [DG05abc]
ptr/GPa 1 29 75 90 155 [MN06,HF06,OD10]

Se hP3----???----aI6----ML----hR1----cI2---->150GPa [DG05ab,MN06,HF06,OD10]
ptr/GPa 14 23 35 80 140 tI16HT

Te hP3----???----aI6-----ML----cI2---->75GPa [MH04,DG05,MN06,HF06,OD10]
ptr/GPa 4.0 4.3 4.5 29 hR1HT

Po cP1----->0GPa
ptr/GPa hR1HT

VIIA

F gas----cP16----mC4---->10GPa
ptr/GPa 2.5 ~20

Cl gas----oC8---->45GPa
ptr/GPa 1

Br liquid----oC8-----ML----oI2---->125GPa [KH05]
ptr/GPa 0.2 83 120

I oC8-----ML----oI2----tI2----cF4---->276GPa
ptr/GPa 23 25 43 53

VIIIA

He gas-----hP2----->58GPa [LL93]
ptr/GPa 12 cI2 cF4

Ne gas-----cF4---->110GPa
ptr/GPa 5.1

Ar gas-----cF4---->77GPa
ptr/GPa 1.1

Kr gas-----cF4------hP2---->50GPa
ptr/GPa 0.93 20

Xe gas-----cF4------hP2---->236GPa
ptr/GPa 0.69 20

IB

Cu cF4---->236GPa
ptr/GPa

Ag cF4---->236GPa
ptr/GPa

Au cF4----hP2---->275GPa [DDC07]
ptr/GPa 230

IIB [MN06]

Zn hP2---->126GPa
ptr/GPa

Cd hP2---->75GPa
ptr/GPa

Hg hR1----tI2----oP4----hP2----->67GPa
ptr/GPa 4 12 36

IIIB [MN06]

Sc hP2-----HGL-----Sc(III)-----Sc(IV)-----hP6---->297GPa
ptr/GPa 20 104 140 240

Y hP2-----hR3-----hP4-----cF4---->75GPa
ptr/GPa 13 26 46

IVB [MN06]

Ti hP2----hP3---->oC4?-----oC4?---->220GPa [VS01,AKB01,JJ02]
ptr/GPa 7 116 140 cI2HT

Zr hP2----hP3-----cI2---->75GPa
ptr/GPa 4 32 cI2HT

Hf hP2----hP3-----cI2---->252GPa
ptr/GPa 34 71 cI2HT

VB

V cI2---->160GPa
ptr/GPa

Nb cI2---->150GPa
ptr/GPa

Ta cI2---->174GPa
ptr/GPa

VIB

Cr cI2---->10GPa
ptr/GPa

Mo cI2---->272GPa
ptr/GPa

W cI2---->364GPa
ptr/GPa

VIIB

Mn cI58---->190GPa
ptr/GPa cP20HT

Tc hP2---->10GPa
ptr/GPa

Re hP2---->251GPa
ptr/GPa

VIIIB

[MN06]

[AD13]

Fe cI2------hP2---->305GPa
ptr/GPa 11 cF4HT

Ru hP2---->25GPa
ptr/GPa

Os hP2---->75GPa
ptr/GPa

IXB

[MN06]

Co hP2------cF4---->202GPa
ptr/GPa 120

Rh cI2---->56GPa
ptr/GPa

Ir cF4------hP14---->65GPa
ptr/GPa 59

XB

Ni cF4---->236GPa
ptr/GPa

Pd cF4---->80GPa
ptr/GPa

Pt cF4---->300GPa
ptr/GPa

Ln

La hP4----cF4----hR8----cF4---->70GPa
ptr/GPa 2 7 58 cI2HT

Ce hP4----cF4----cF4-----oC4-----tI2---->208GPa
ptr/Ga .2 .67 3.9 13 cI2HT

Pr hP4----cF4----hR8------???----oC4---->60GPa
ptr/GPa 4 6.2 10 20 cI2HT

Nd hP4----cF4----hR8----hP3----mC4----oC4---->70GPa
ptr/GPa 5 15 40 75 113 cI2HT

Pm hP4----cF4----hR8----hP3---->60GPa
ptr/GPa 10 18 40

Sm hR3----hP4----cF4----hR8----hP3----tI2----mC4---->70GPa
ptr/GPa 5 15 20 37 75 105 cI2HT

Eu cI2----hP2------ML-----???---->92GPa [MK11, HL12]
ptr/GPa 13 31.5 37

Gd hP2-----hR3----hP4-----cF4----hR8-----mI2---->235GPa
ptr/GPa 3.2 7 26 46 61 cI2HT

Tb hP2-----hR3----hP4-----cF4----hR8---->58GPa [TM13]
ptr/GPa 3 6 29 32

Dy hP2-----hR3----hP4-----cF4----hR8---->70GPa
ptr/GPa 5 9 38 40

Ho hP2-----hR3----hP4--------------hR8---->70GPa
ptr/GPa 10 25 70

Er hP2-----hR3----hP4--------------hR8---->70GPa
ptr/GPa 12.4 24 67.4

Tm hP2-----hR3----hP4---->42GPa
ptr/GPa 10 30

Yb hP2----cF4----cI2----hP2-----cF4-----hP3---->202GPa
ptr/GPa 0.1 4 30 53 98

Lu hP2-----hR3----hP4----cF4------Lu(IV)---->275GPa
ptr/GPa 20 30 88 272

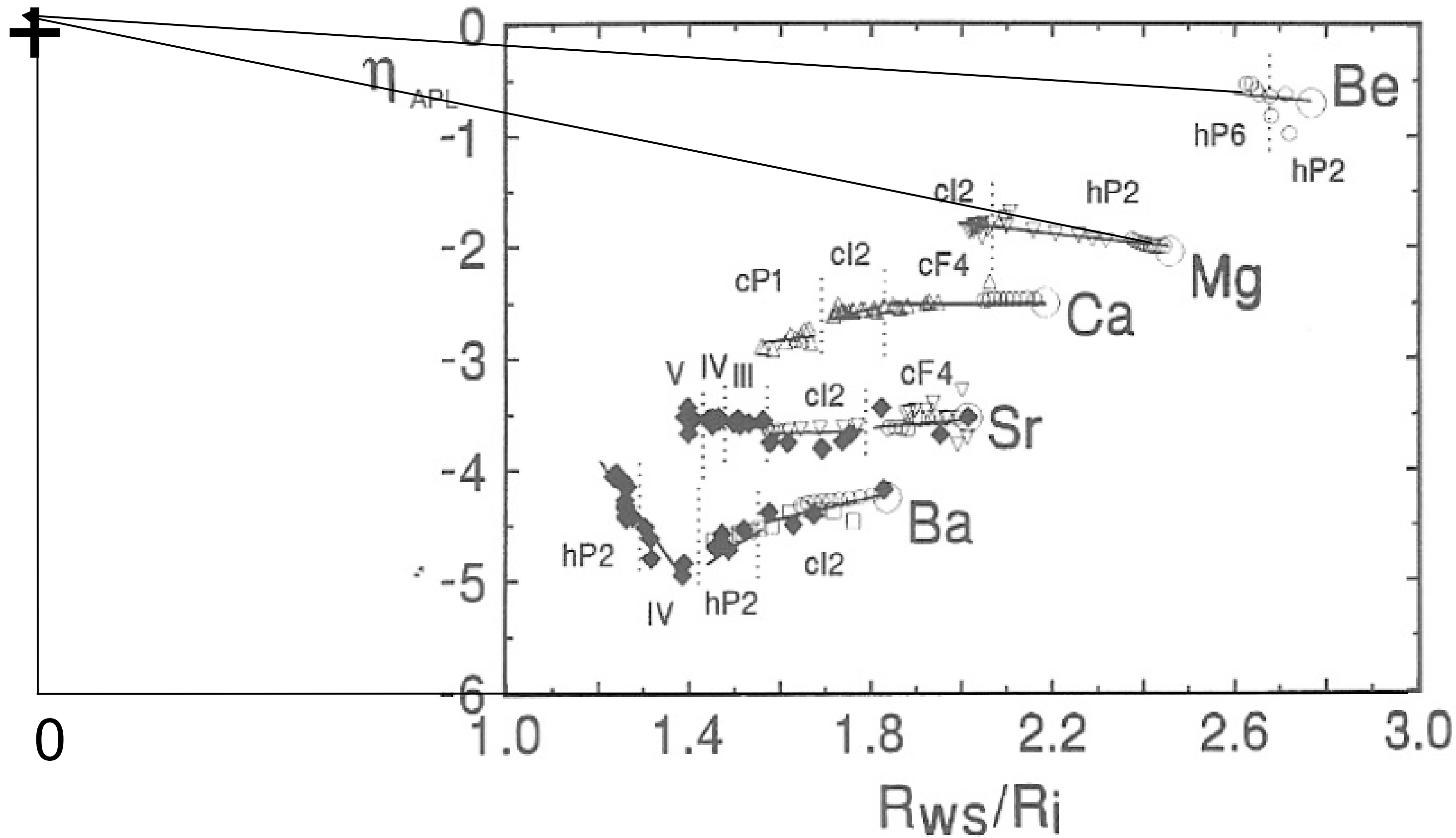


Fig. 17. APL linearization for the EOS data of the alkaline earth metals plotted versus the scale Wigner-Seitz radius ratio R_{WS}/R_i discussed in the text using EOS data from the different sources listed in the original work [7, 37].

"Structural Systematics and Equations of States for the Alkaline Earth Metals under Pressure" M. Winzenick and W.B. Holzapfel, p. 384-386 in "High Pressure Science and Technology" ed. W. Trzeciakowski, World Scientific, Singapore (1996)

"Physics of Solids under Strong Compression"
W.B. Holzapfel, Rep. Prog. Phys. 59, 29-90 (1996)

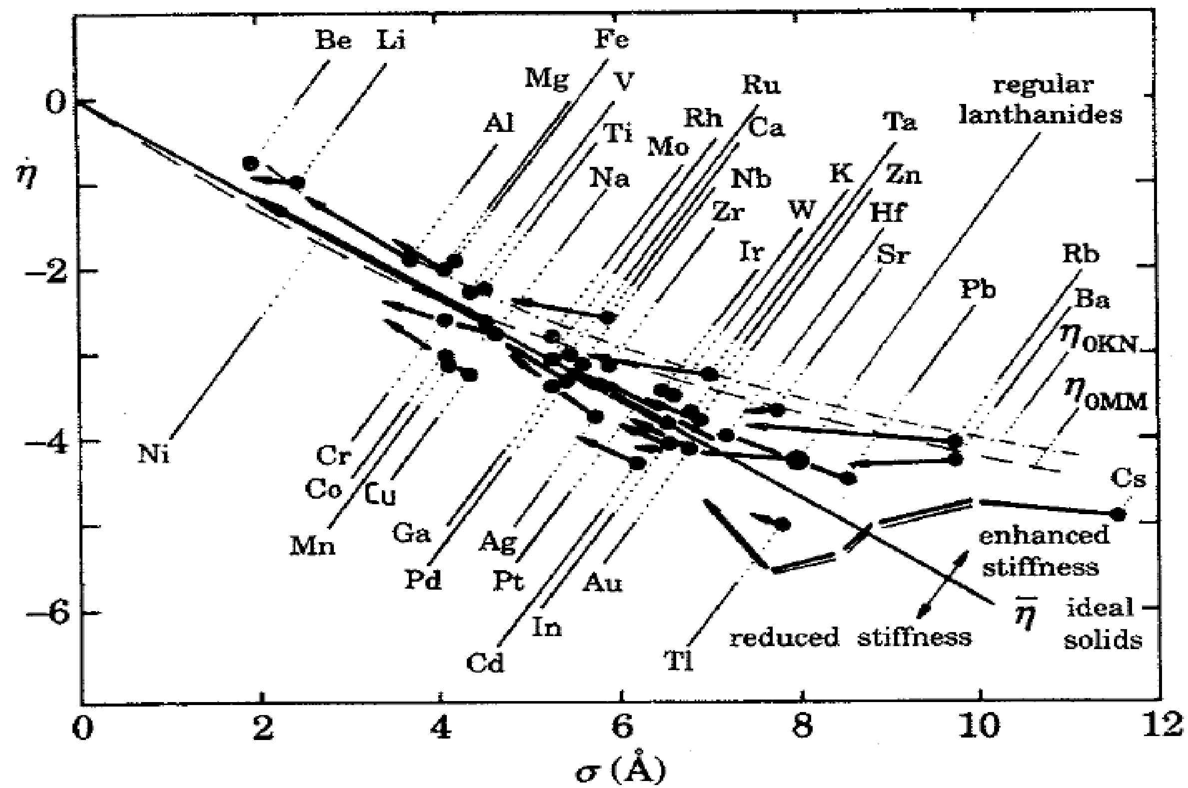


Fig. 1. – EOS data [6, 11-30] for the metallic elements represented in $\eta = \ln(p/p_{FG}) - \ln(1-(\sigma/\sigma_0)$ *vs.* σ plots with $\sigma = (ZV \cdot 3/(4\pi))^{1/3}$. The linear correlation η *vs.* σ, which defines the «ideal» solid behaviour is also compared with earlier correlations between ambient pressure values of K_0 and σ_0 discussed by McMillan [6] and Knopoff [9] and marked with η_{0MM} and η_{0KM}, respectively. Anomalies for the high-pressure phases of Cs are marked by twinned lines.

"Equations of State for Ideal and Real Solids under Strong Compression"
W.B. Holzapfel, Europhys. Lett. 16, 67-72 (1991)

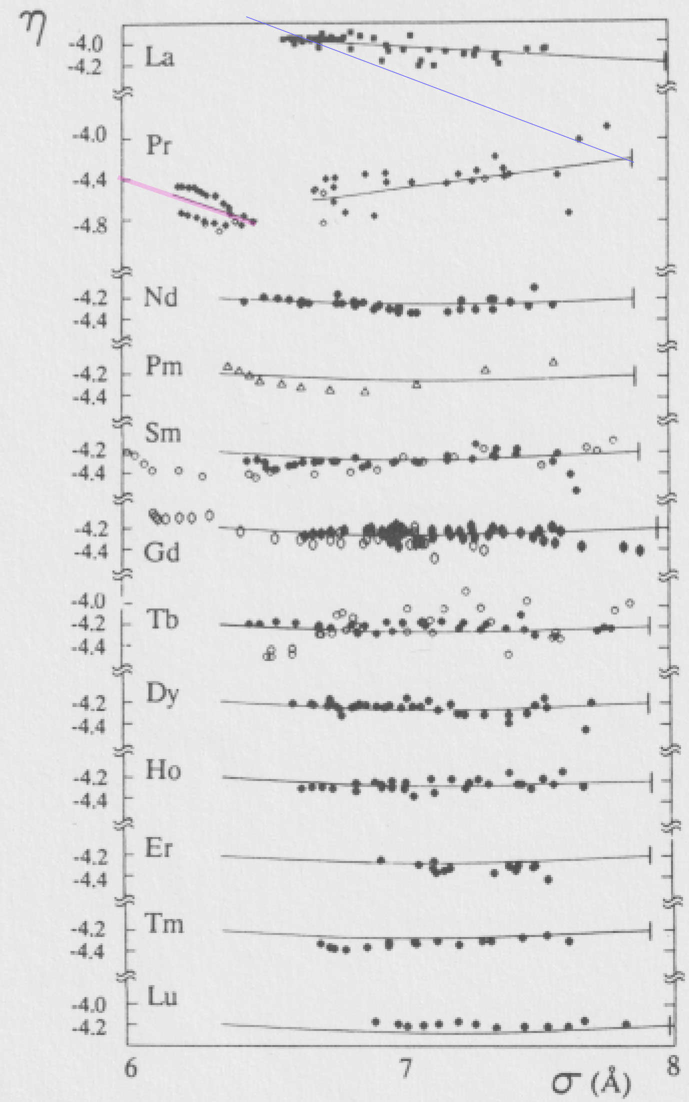


FIG. 16. EOS data for the "regular" lanthanides in η-σ representation with $\eta = \ln(p/p_{FG}) - \ln(1-\sigma/\sigma_0)$ using Thomas-Fermi scaling for the atomic length parameter σ and the Fermi gas pressure p_{FG}. Open symbols refer to recent data from the literature (Refs. 14–23) for this extended pressure range.

"Atomic Volumes for Rare Earth Metals under Pressure to 40 GPa and Above"
W. A. Grosshans and W.B. Holzapfel,
Phys. Rev. B 45, 5171-5178 (1992)

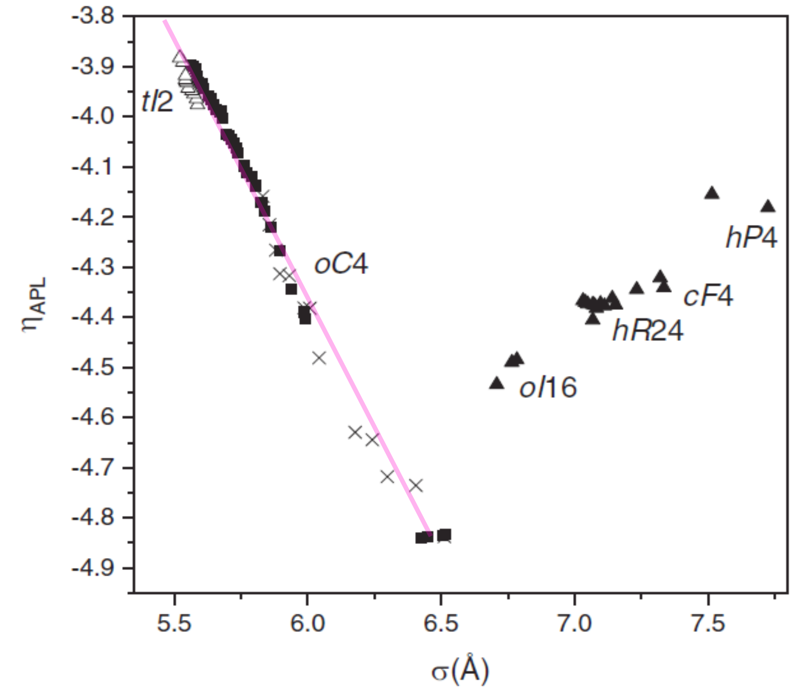


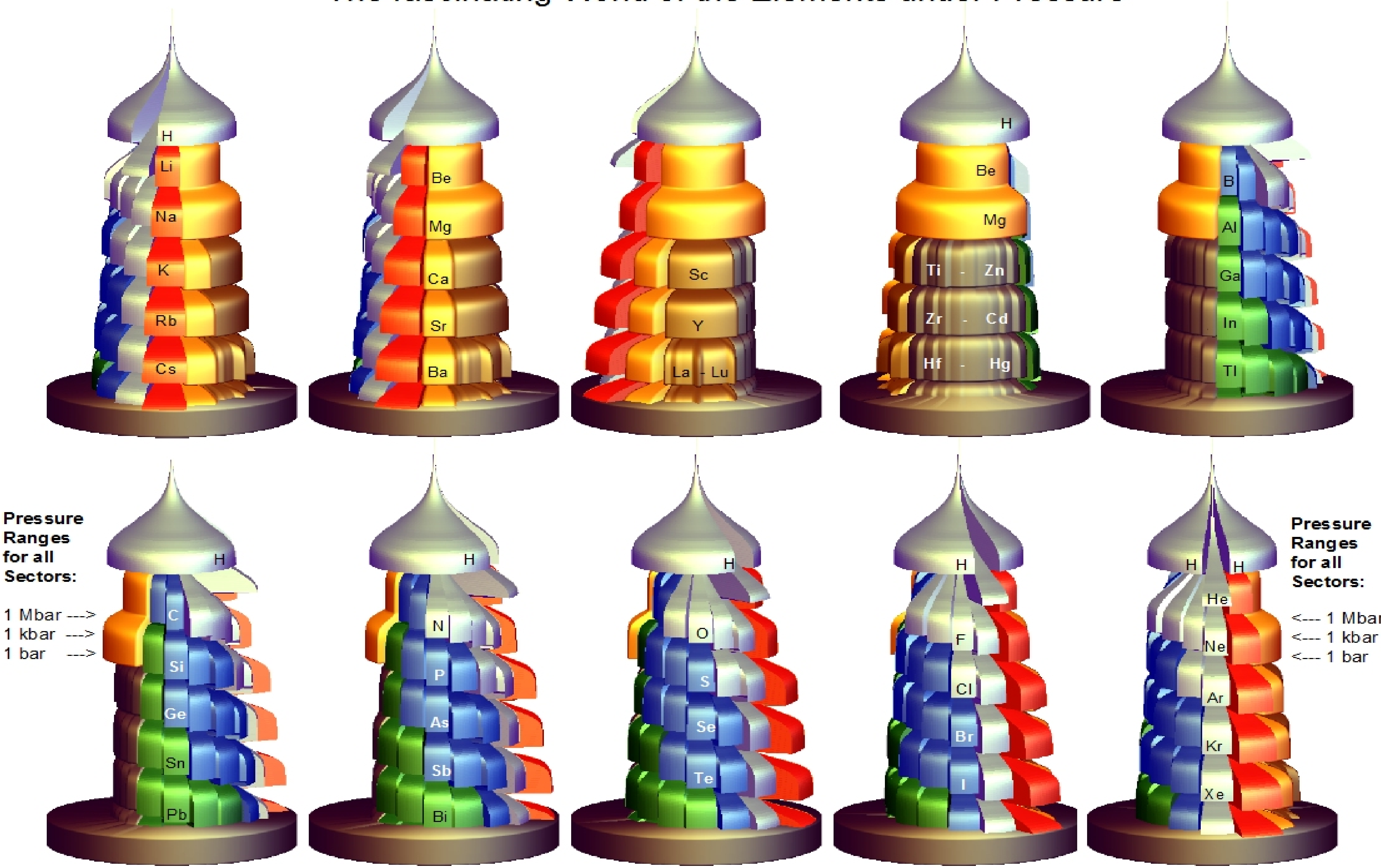
FIG. 7. Linearization of the compression of Pr shown in the form of an η_{APL}-σ plot, where $\sigma = \sigma_0 x$. The data from the lower-pressure phases (*hP*4, *cF*4, *hR*24, and *oI*16) are plotted with filled triangles, while our data from *oC*4-Pr are plotted with filled squares and the *oC*4-Pr data from the study of Chesnut and Vohra [29] are shown as crosses. For clarity, the current data for *tI*2-Pr are plotted with unfilled triangles.

Simple 1. order AP1-EOS

High-pressure structure of praseodymium revisited: In searchot a uniformstructural phase sequence for the lanthanide elements

S.E. Finnegan, M.G. Stevenson, E.J. Pace, C.V. Storm, J.D. McHardy, M.I. McMahon, S.G. MacLeod, E. Plekhanov, N. Bonini, C. Weber,
Phys. Rev. B **105**, 174101 (2022)

The fascinating World of the Elements under Pressure



Model for a sculpture to be decorated with the colouful phase diagrams.
In honour of Aristoteles (†322 B.C.) and Galilei (†1642 A.D.) founders of modern science proclaiming:

Measure all you can measure

and what you can't, make it measurable !

United States of the Elements – USE

At the beginning there was a big bang, which generated the Hydrogen
and little Helium, that is true, was in this early stardust brew.
Some dust condensed by gravity and stars appeared with density
just high enough for the ignition of nuclear fusion with the provision
for many more new elements, but these were not the final ends!
The heavy ones had still to wait for supernovae, which came late
as star explosions, an event, which is considered as the end
of all the element creation, we only miss still the equation
explaining how the numbers came to fit all this! This is the game!
With all the elements now here, some order makes this world more clear.
Wise man produced a Periodic Table with 8 Main Groups which do enable
to show some common properties in 8 columns, but there are these
remaining elements between with 10 at first and then 14,
Transition Metals, 3 rows of 10, and Lanthanoides, with 14 then.
The Actinoides, we will not need, they are unstable, well indeed!-
And still more order is present, if you look carefully at the end!
You can first see right on the top the Hydrogen and if you stop,
you see for Helium a slit just wide enough to give a fit
for the Rare Gases as column on top with our Helium.
The other columns broad and wide include the Main Groups not so tide
as all the lower sections squeezed between for the Transition Metals in this scheme.
And in the column number 3 the Rare Earth Metals you can see.
The chemists now look for reactions. The physicists see other actions!
They change the temperature and pressure and keep in mind, they have to measure
the properties in all these states and some results lead to debates
before one reaches the consensus on these results, which are immense
in these domains, which reach as far, as the interior of some star!
Much more ideas have been cast into this figure, but at last
a book can only give to you for this artwork the final clue!

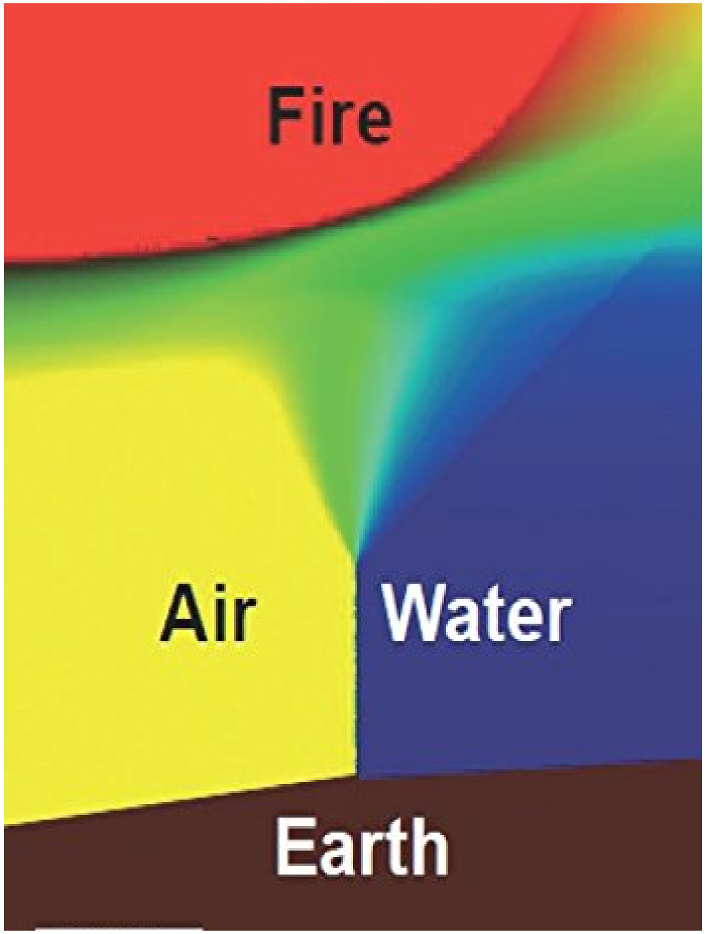
Colorful systematic in the phase-diagrams of the elements

A simple guide to the world of high pressure

Wilfried B. Holzapfel, *Emeritus, Physics Department University Paderborn, Germany,, holzapfel@physik.upb.de*

Intention: stimulate young scientists to look at structural changes in matter
in wide fields of pressure and temperature

4 essentia 4 classical elements 4 forms of being for matter



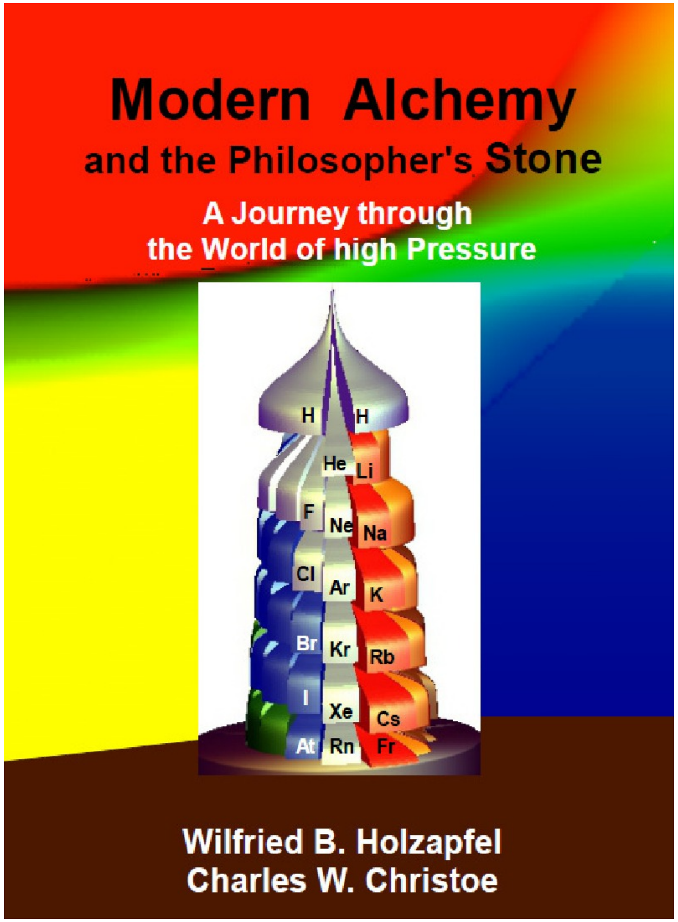
states of matter
in wide ranges
of
temperature
and
pressure

plasma

gas

liquid

solid



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