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Title:	The Actinides: Magnetism or Bonding?
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The Actinides: Magnetism or Bonding?

(What is a chemical bond?)

Jason C. Lashley

Cavendish Laboratory, University of Cambridge, Cambridge, England

The Physical Review, American Physical Society, APS Physics, Ridge, New York

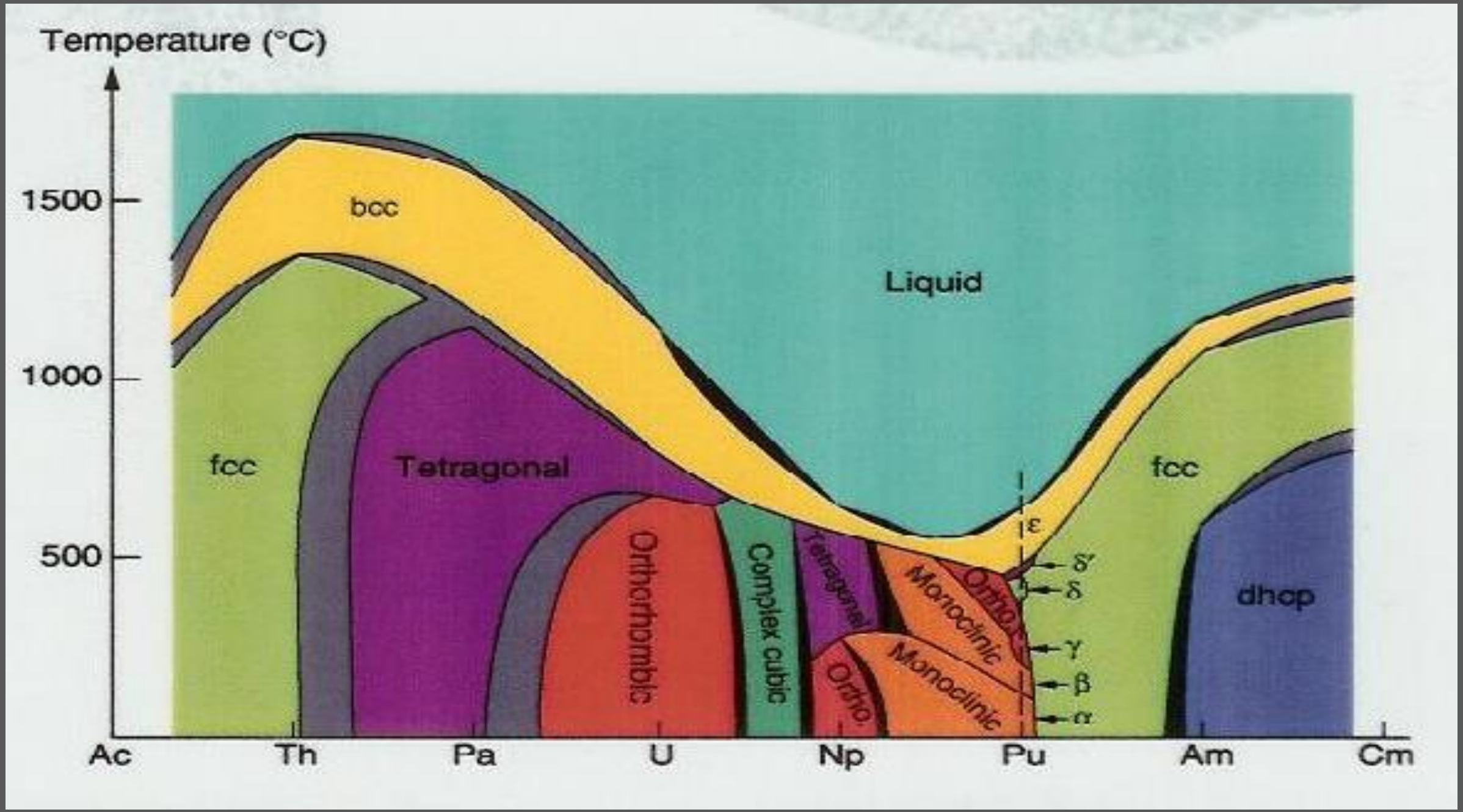
Börje Johansson

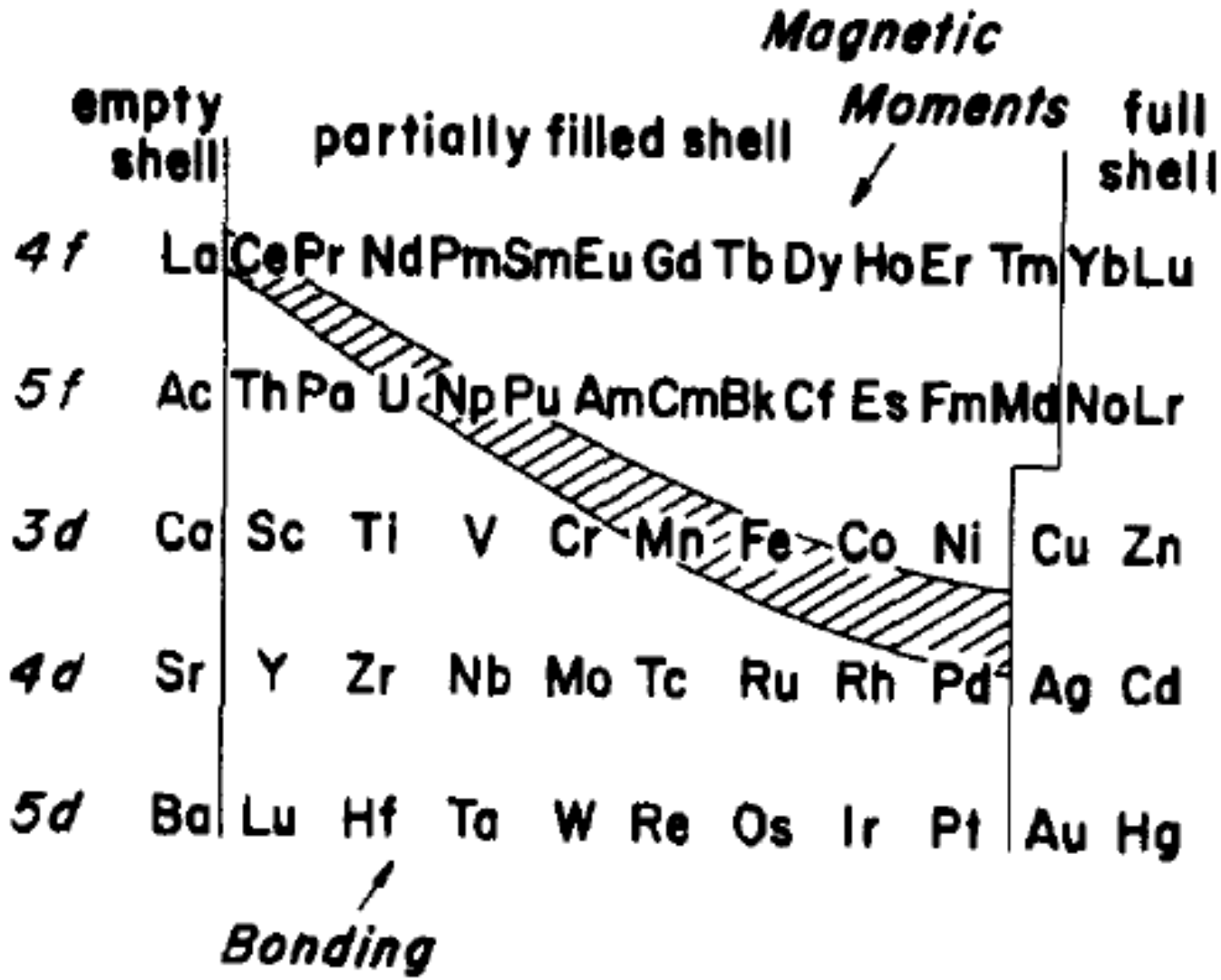
Royal Institute of Technology, KTH, Stockholm, Sweden

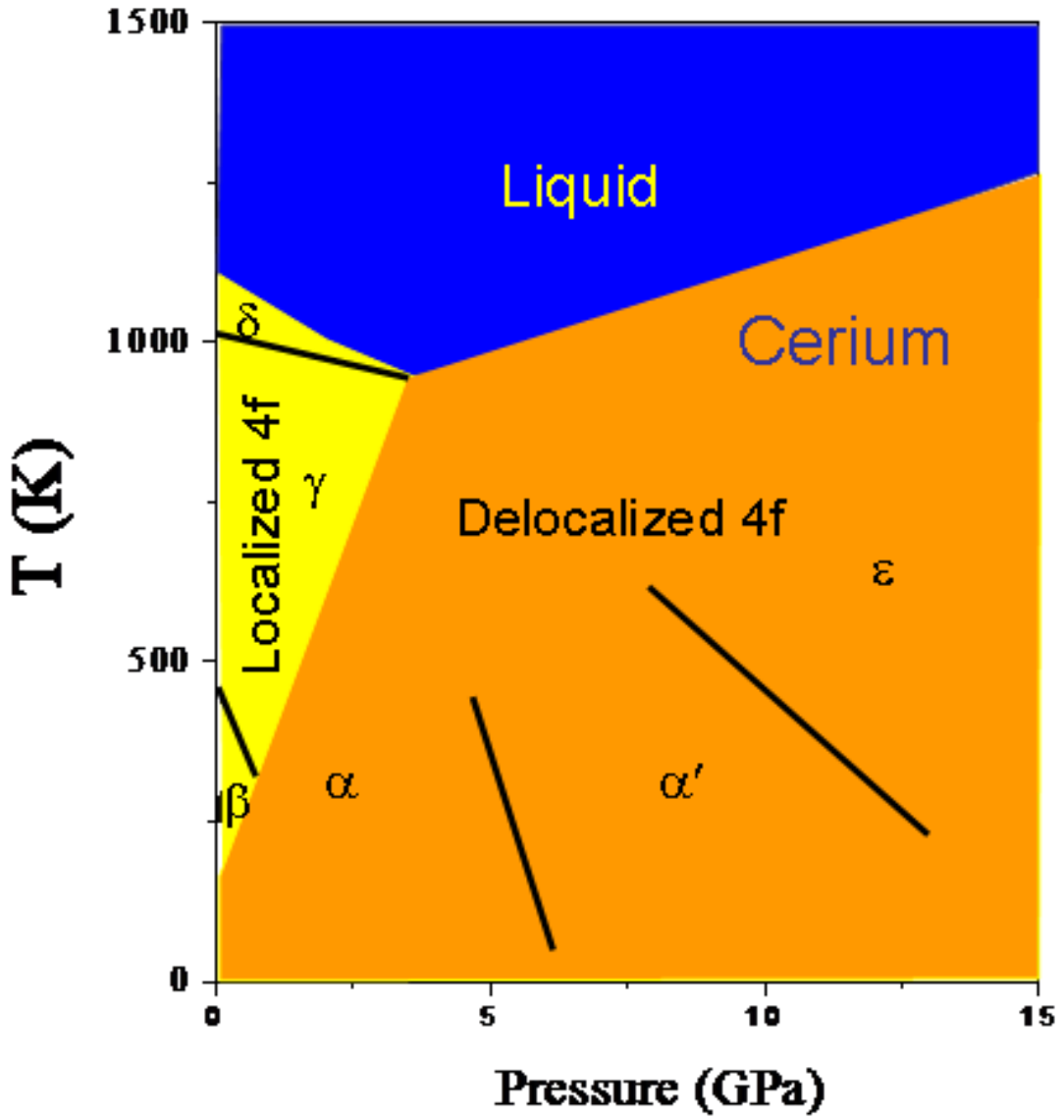
Journal of the Less-Common Metals, *90* (1983) 83–88

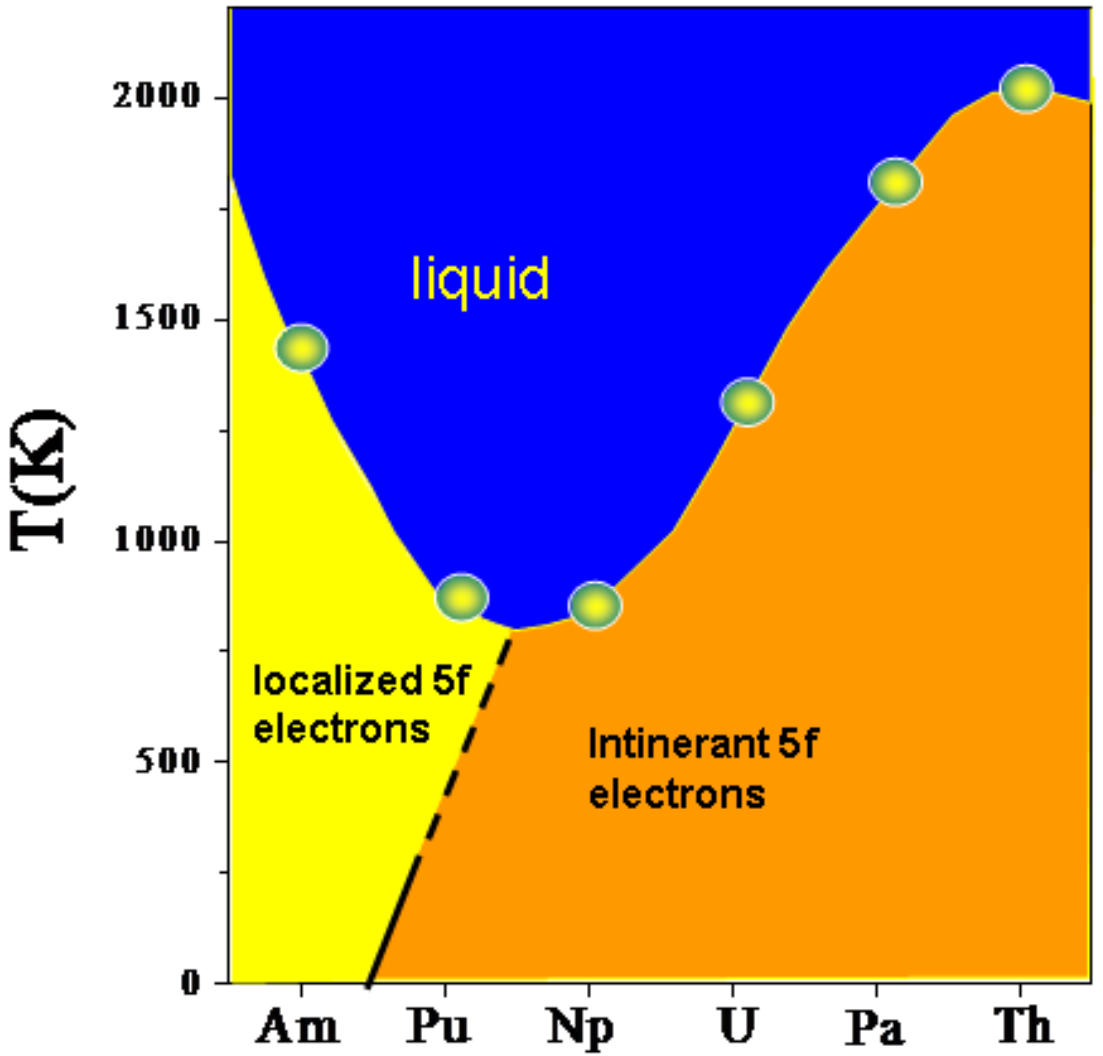
MAGNETISM OR BONDING: A NEARLY PERIODIC TABLE OF TRANSITION ELEMENTS

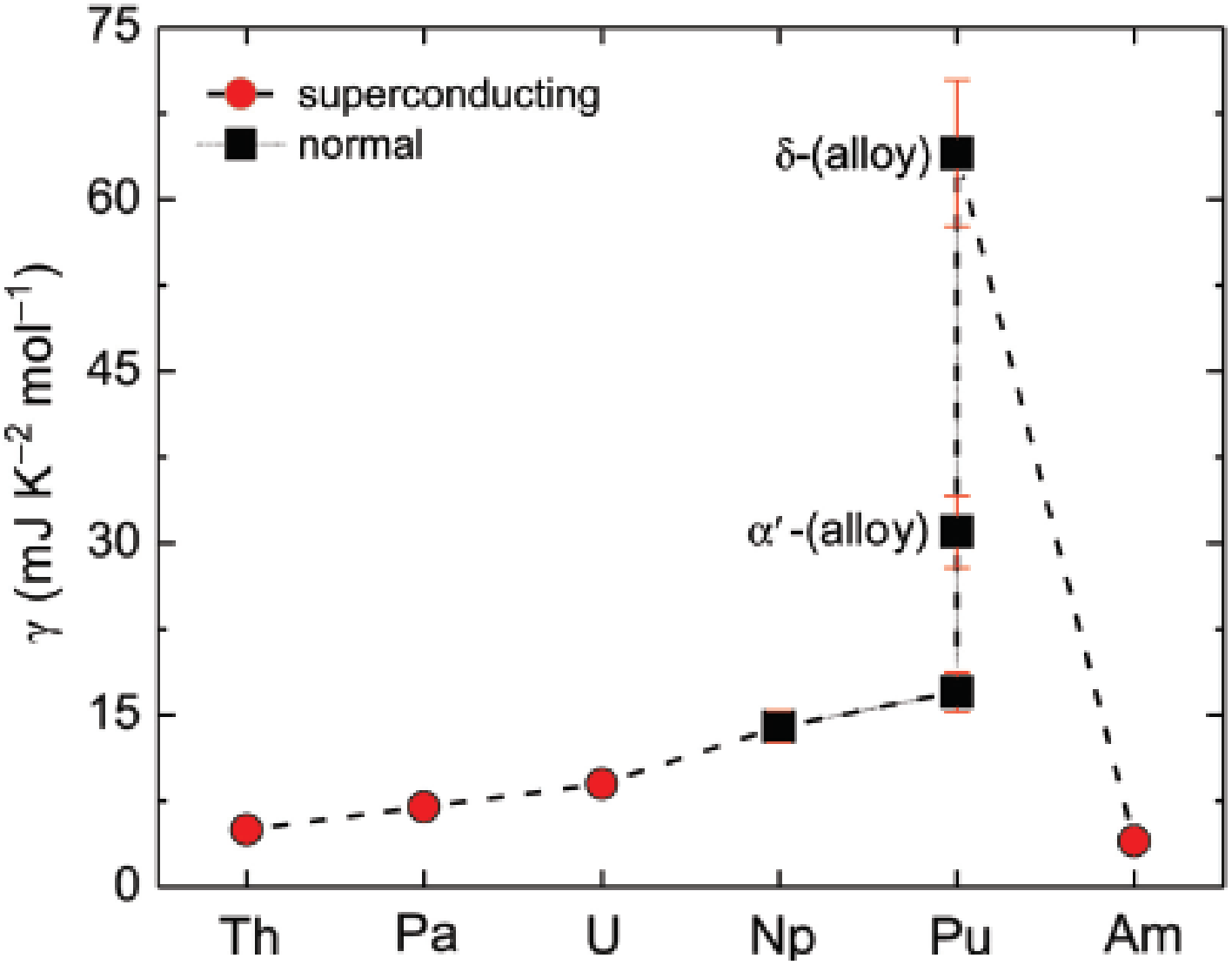
J. L. SMITH and E. A. KMETKO*
Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)
(Received June 26, 1982)


Temperature (°C)
1500
1000
500
bcc
Liquid
fcc
Tetragonal
Orthorhombic
Complex cubic
Tetragonal
Ortho
Monoclinic
Ortho
Monoclinic
ε
δ'
δ
γ
β
α
fcc
dhcp
Ac
Th
Pa
U
Np
Pu
Am
Cm


Magnetic
Moments
empty
shell
partially filled shell
full
shell
4f La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
5f Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
3d Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
4d Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
5d Ba Lu Hf Ta W Re Os Ir Pt Au Hg
Bonding


1500
1000
500
0
T (K)
Liquid
Cerium
δ
Localized 4f
γ
Delocalized 4f
ε
α
α′
β
0
5
10
15
Pressure (GPa)


2000
1500
1000
500
0
T(K)
liquid
localized 5f
electrons
Intinerant 5f
electrons
Am
Pu
Np
U
Pa
Th


75
60
45
30
15
0
γ (mJ K^{-2} mol^{-1})
superconducting
normal
δ-(alloy)
α′-(alloy)
Th
Pa
U
Np
Pu
Am

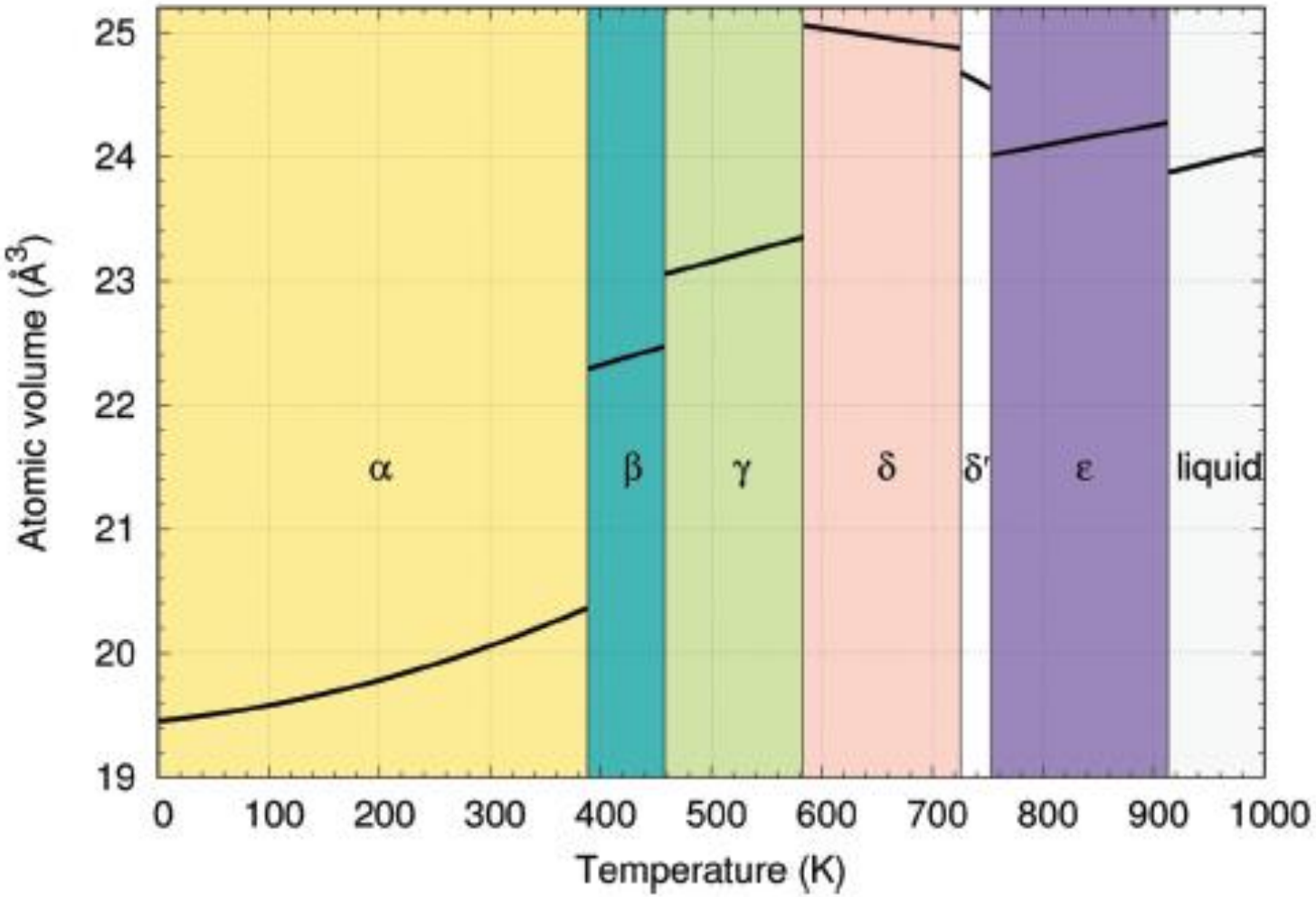
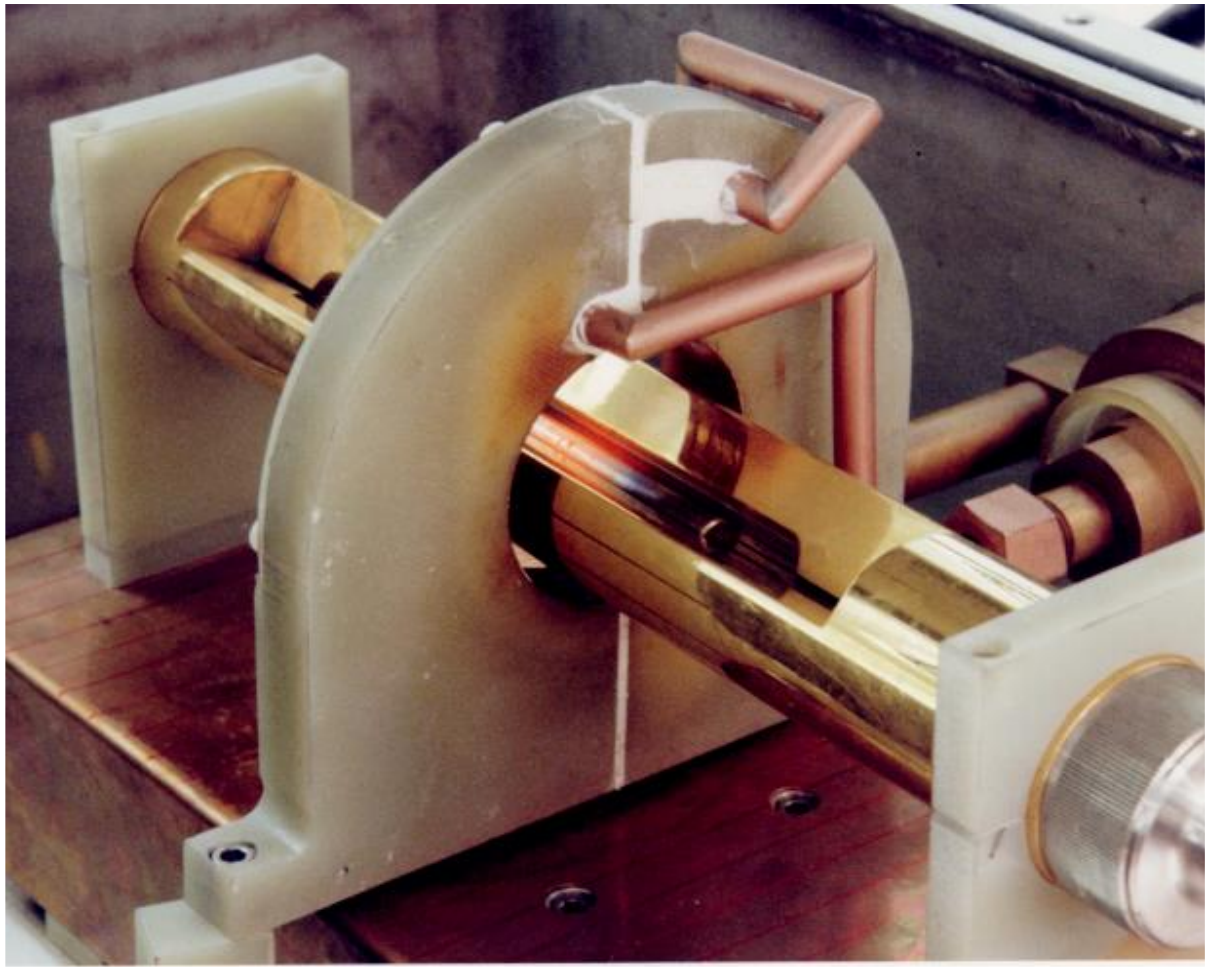


Figure 3. Temperature variation of the atomic volume for the phases of unalloyed plutonium. Generated using data from Ref. 57 with permission of Wiley. Copyright 1974.


14 cm



The α–γ transition in cerium is a Mott transition†

By Börje Johansson
FOA 4, Stockholm 80, Sweden

[Received 18 June 1973 and in final form 17 June 1974]

Abstract

The α–γ transition in cerium is considered as a Mott transition. From spectroscopic data it is concluded that the intra-atomic interaction, U, is considerably smaller than seems to have been believed in the past. Here it is argued that in metallic cerium, U is only of the order of a few electron volts. Current band calculations of the width of a 4f band state are presumably very unreliable, and correlation effects on the crystal potential may be considerable and of considerable importance. Still, some conventional band calculations seem to imply a width of nearly one electron volt for densities appropriate for the dense α phase in cerium.

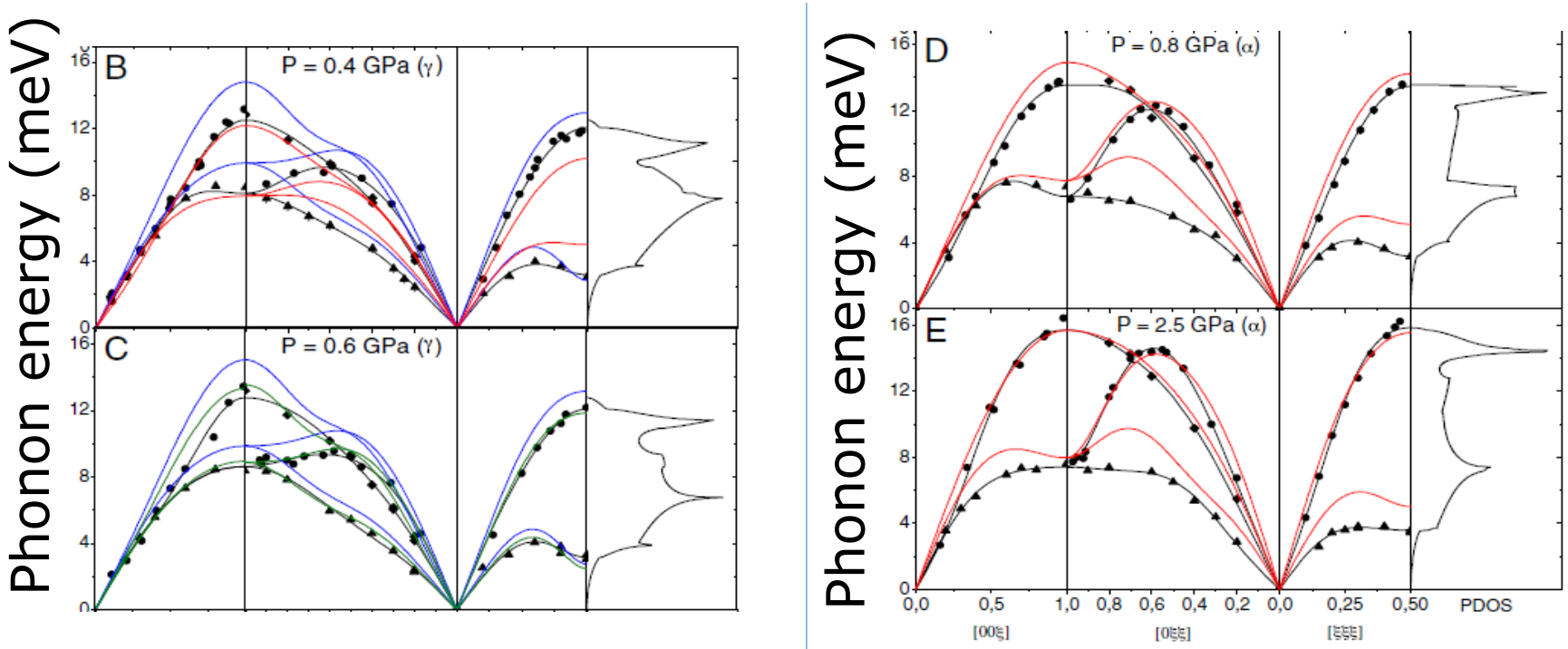
Several experimental facts on the properties of γ and α cerium lead us to assert that metallic cerium cannot promote its f electron into the (sd) configuration. This is most clearly seen from its cohesive energy properties, and it is shown that if cerium were to attain an $(sd)^4$ configuration, say in the α or α′ phase, this would lead to a totally unacceptable behaviour of a tetravalent transition metal. Instead we are led to consider the f electrons as undergoing a Mott transition and in view of our findings within the Hubbard picture this is a most likely occurrence. From this conclusion, the remarkable similarity of the properties of the pressure–temperature phase diagram of cerium and individual elements in the actinide series is pointed out. From this it is concluded that the earlier commonly expressed view that cerium, when compressed, becomes a normal tetravalent transition metal is invalid. Instead, high pressure on light rare earths element rather converts them into actinide type elements.

Phonons of the anomalous element cerium

Michael Krisch[a], D. L. Farber[b,c], R. Xu[d,e], Daniele Antonangeli[b,f], C. M. Aracne[b], Alexandre Beraud[a], Tai-Chang Chiang[d,e], J. Zarestky[g], Duck Young Kim[h,i,j], Eyvaz I. Isaev[h,k], Rajeev Ahuja[h,i,1], and Börje Johansson[h,i]

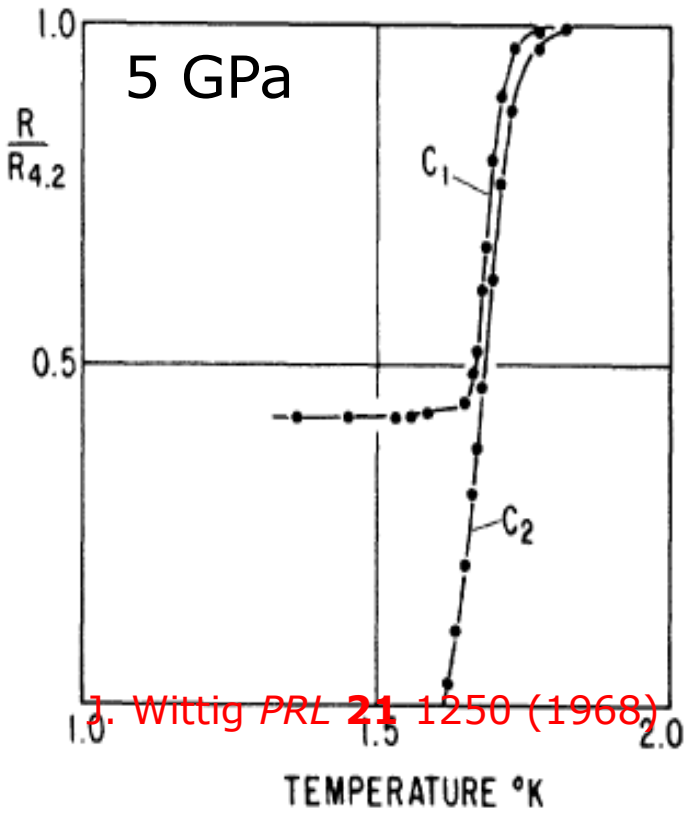
Trivalent (localized f)

Tetravalent (delocalized f)



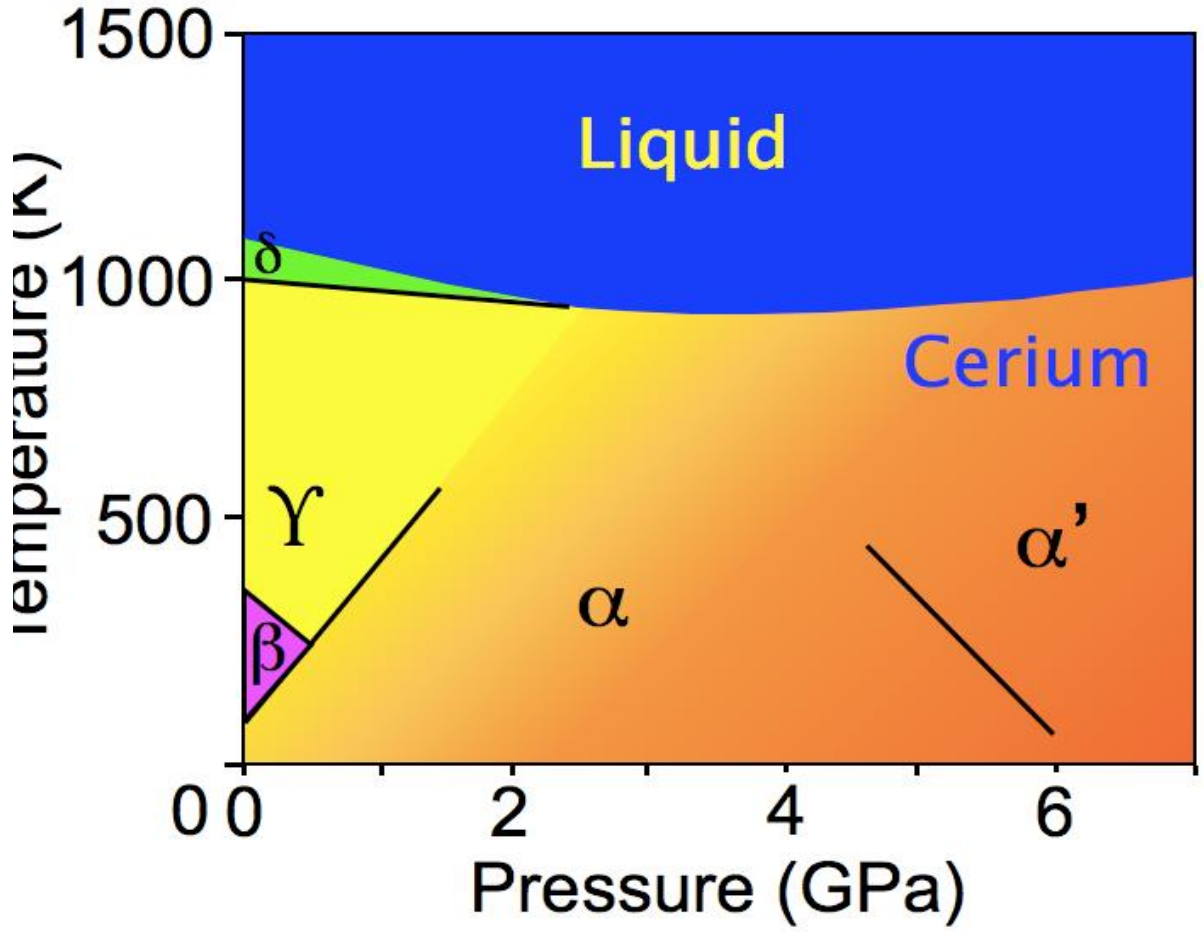
- Trivalent potential gives good agreement with generally accepted picture of localized f electron
- Trivalent potential gives imaginary phonon dispersion at a Ce regime where the tetravalent one gives good agreement with experiments

M. Krisch et al *PNAS* **108** 9342 (2011)



J. Wittig *PRL* **21** 1250 (1968)

FIG. 2. Superconducting transition curves of Ce.



PHYSICAL REVIEW B **72**, 054416 (2005)

Absence of magnetic moments in plutonium

J. C. Lashley,[1] A. Lawson,[1] R. J. McQueeney,[2] and G. H. Lander[3]
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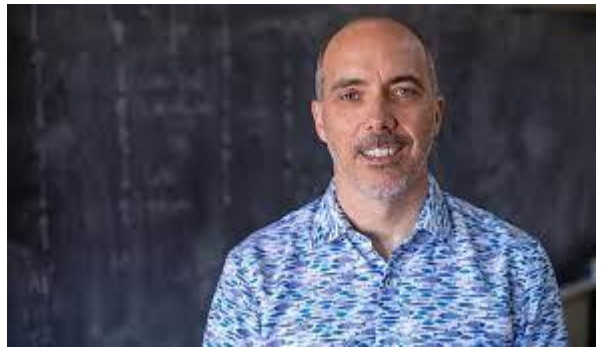
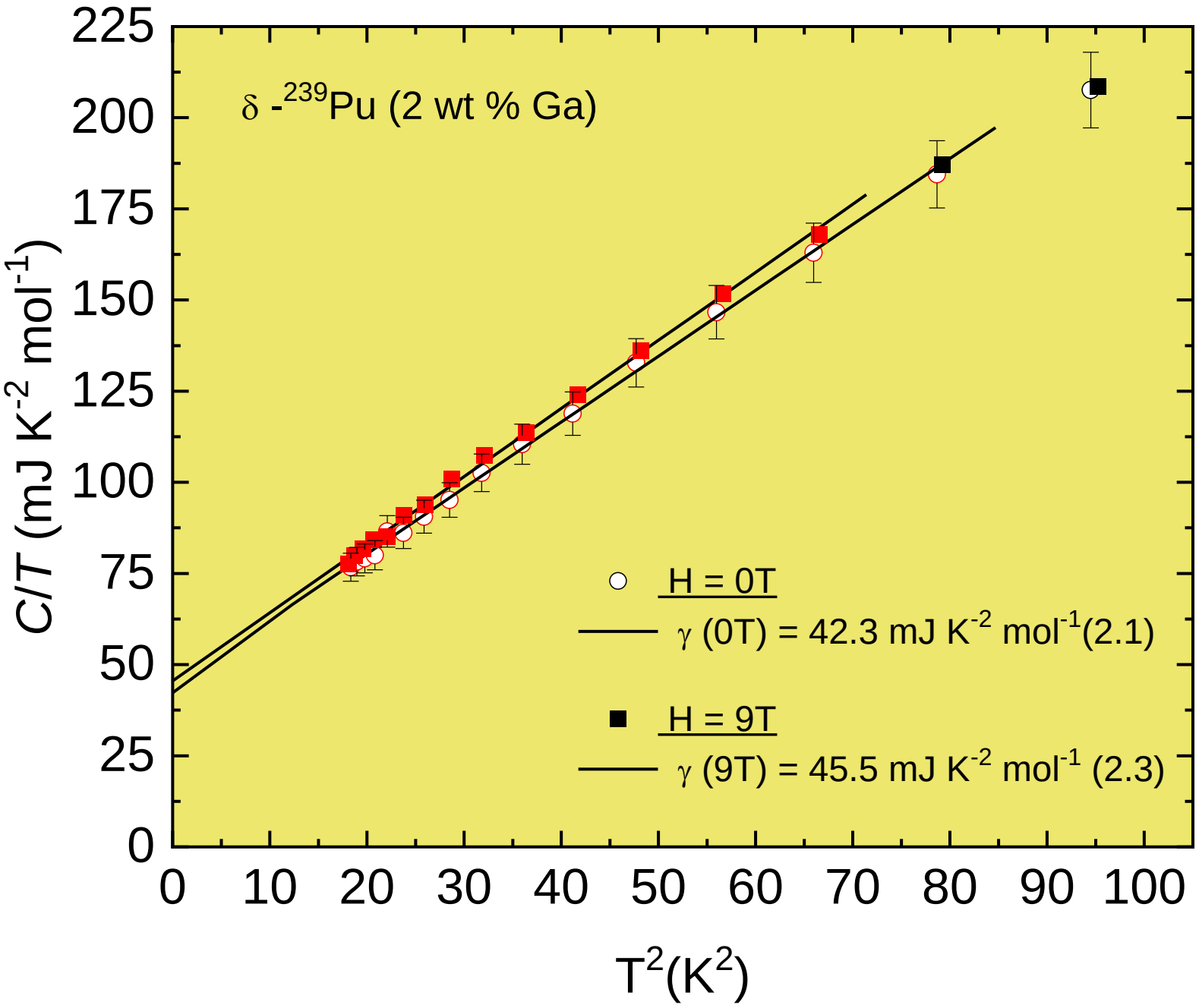
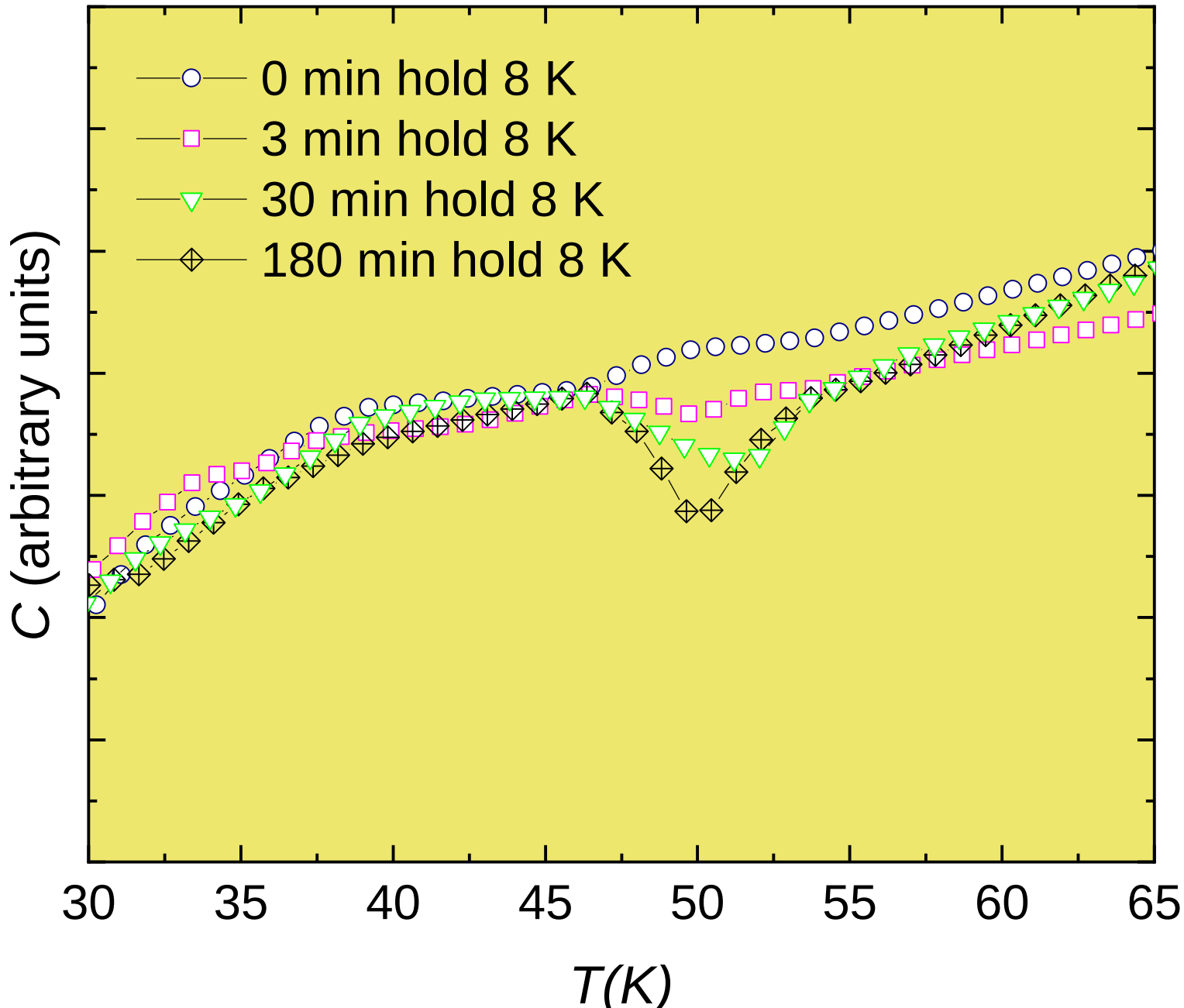
[2]*Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[3]*European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, Karlsruhe, Germany*
(Received 25 June 2004; revised manuscript received 29 November 2004; published 11 August 2005)




δ -239Pu (2 wt % Ga)
H = 0T
γ (0T) = 42.3 mJ K-2 mol-1(2.1)
H = 9T
γ (9T) = 45.5 mJ K-2 mol-1 (2.3)
C/T (mJ K-2 mol-1)
T2(K2)
0
25
50
75
100
125
150
175
200
225
0
10
20
30
40
50
60
70
80
90
100


0 min hold 8 K
3 min hold 8 K
30 min hold 8 K
180 min hold 8 K
C (arbitrary units)
30
35
40
45
50
55
60
65
T(K)

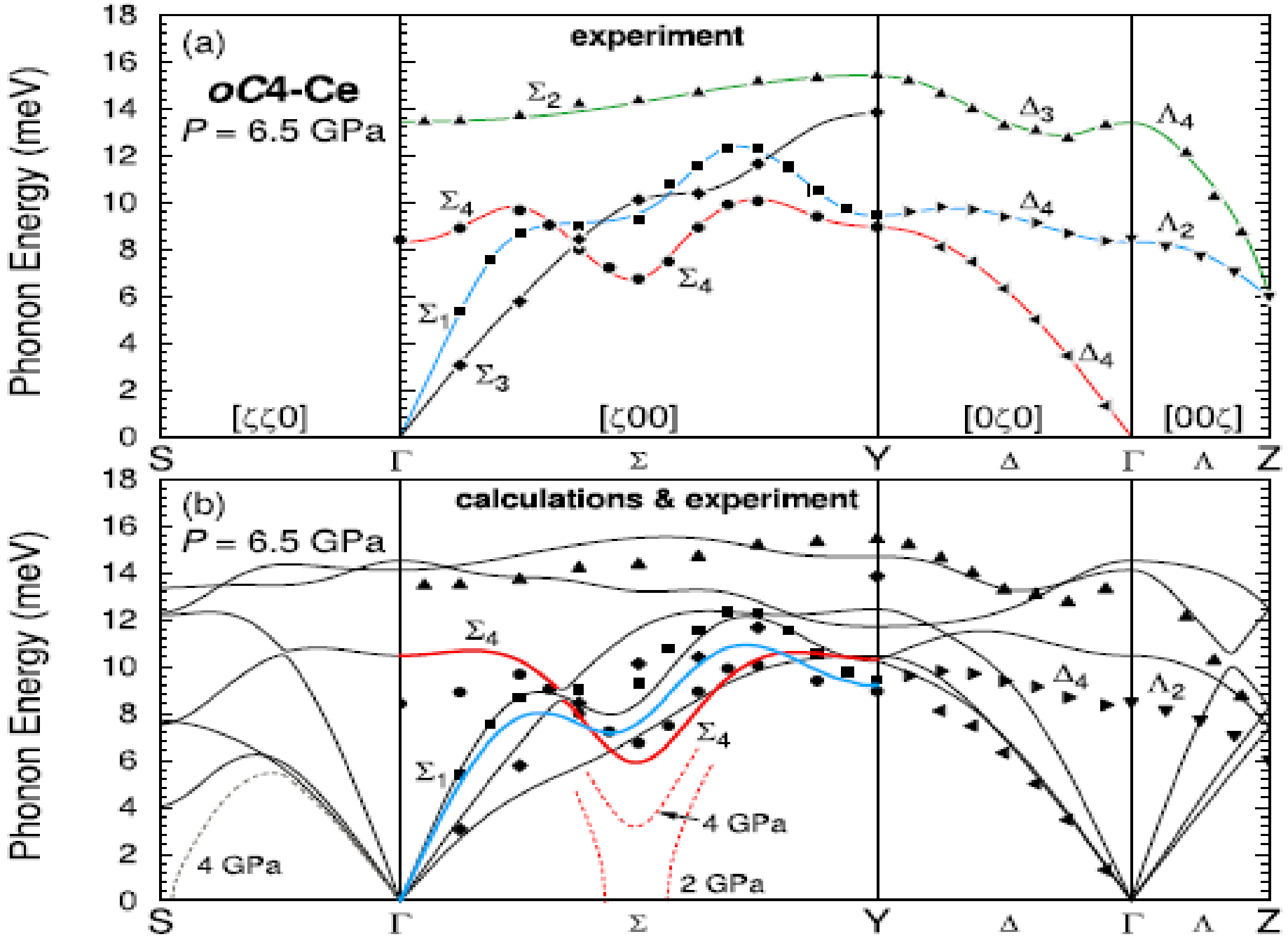
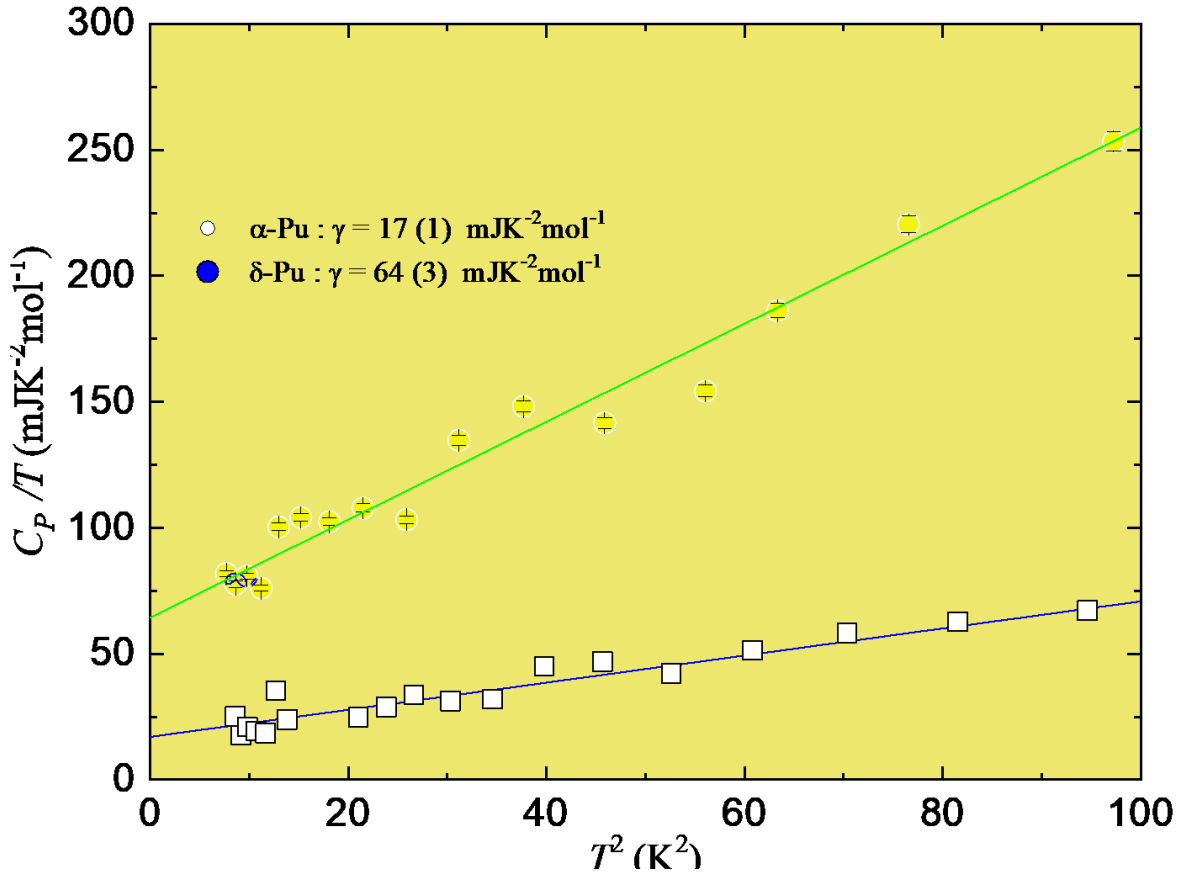
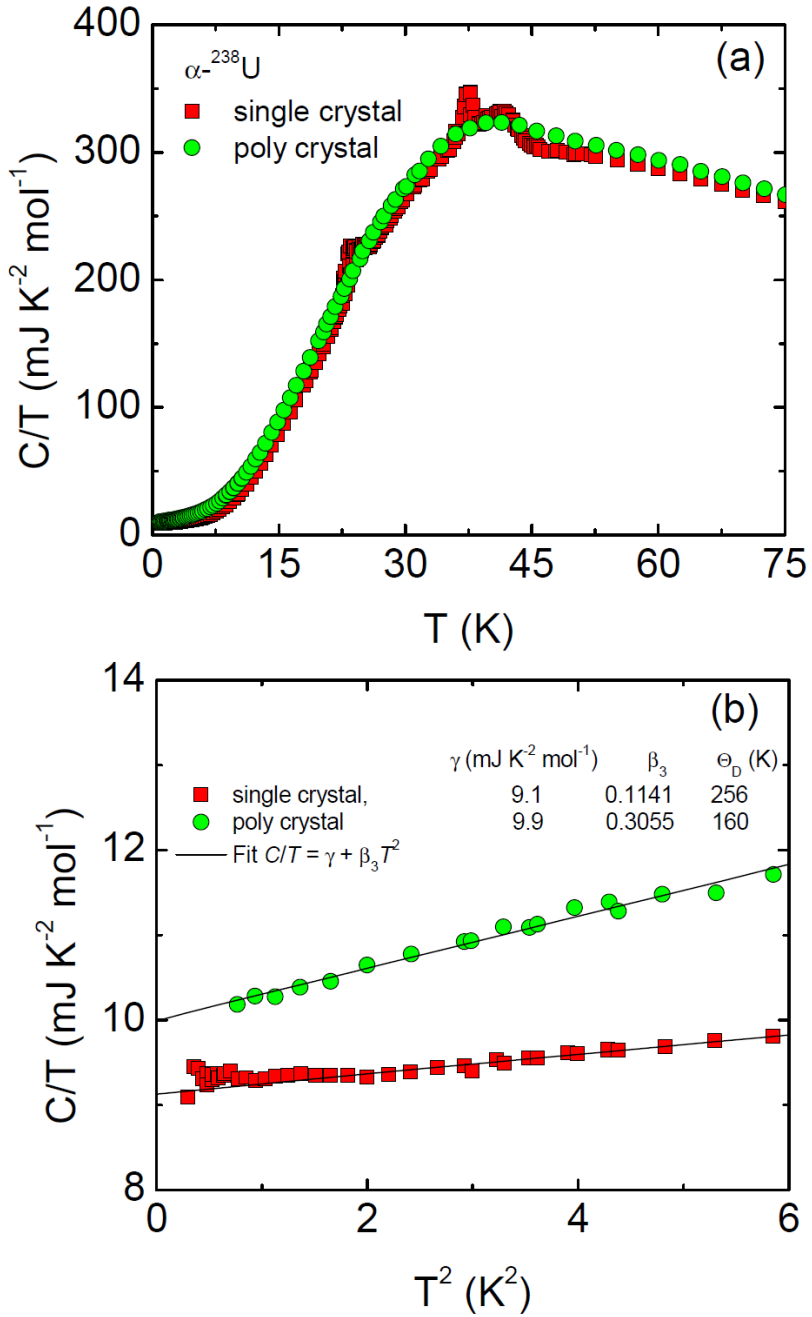

(a)
oC4-Ce
P = 6.5 GPa
experiment
Phonon Energy (meV)
[ζζ0]
[ζ00]
[0ζ0]
[00ζ]
S
Γ
Σ
Y
Δ
Γ
Λ
Z
(b)
P = 6.5 GPa
calculations & experiment
4 GPa
4 GPa
2 GPa

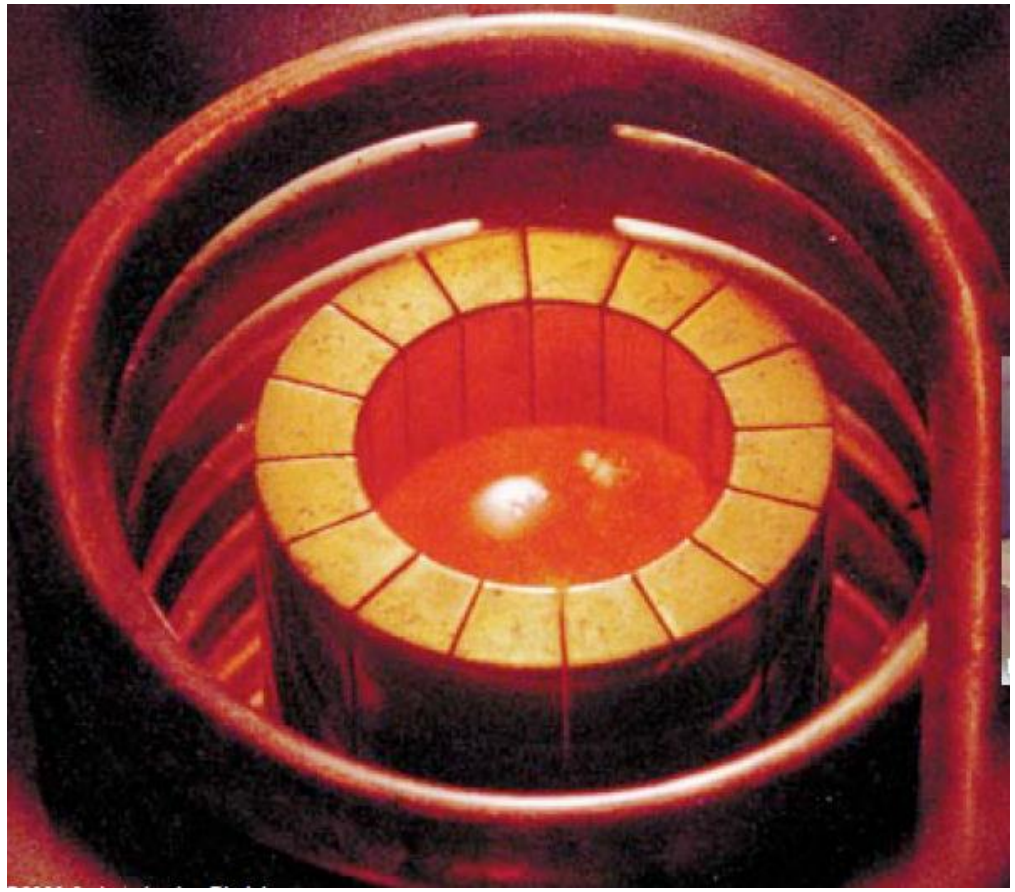
Table 1
Table of Pu impurities[a]

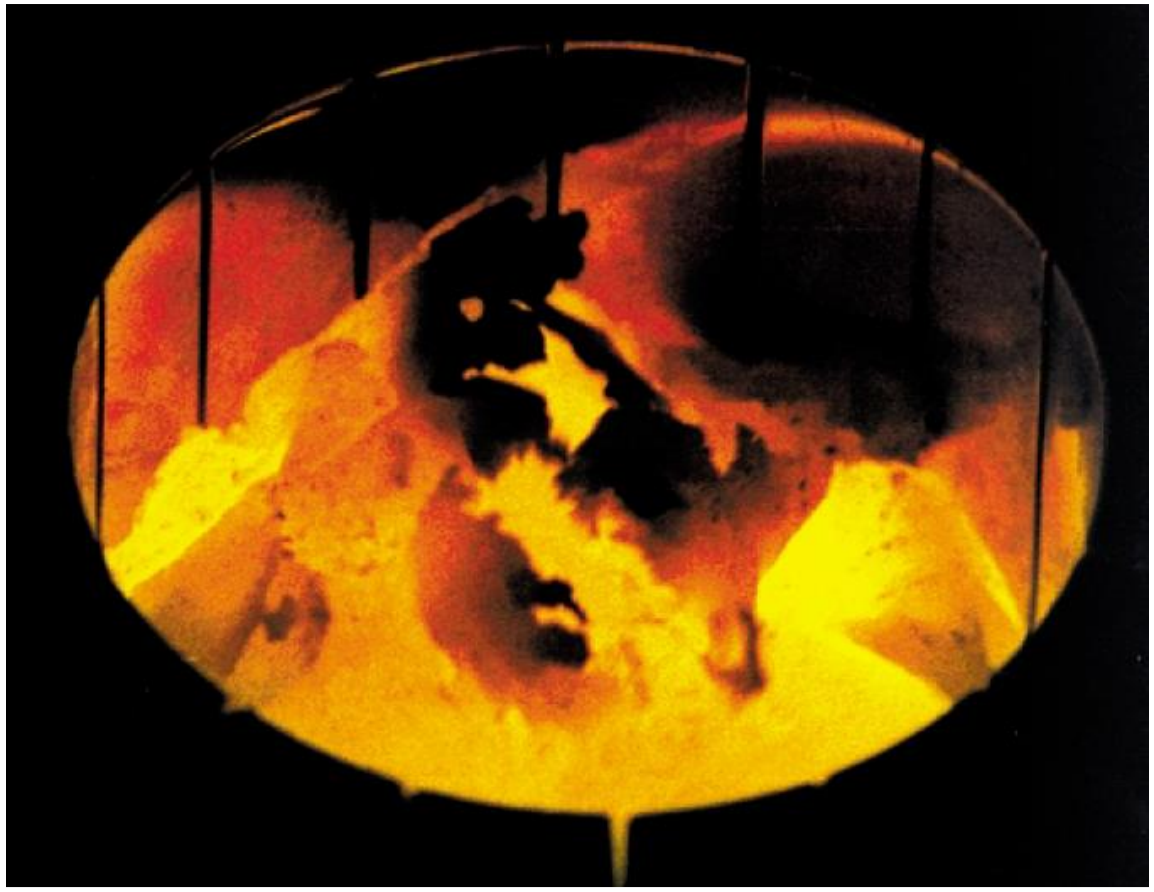
Impurity element	Double electrorefined concentration (ppm)	Zone refined concentration (ppm)	Minimum detection limit (MDL) (ppm)
Lithium	2.70	<0.40	0.40
Beryllium	0.80	<0.18	0.18
Sodium	115.00	<8.80	8.80
Phosphorus	95.00	7.00	5.60
Potassium	95.00	40.00	14.00
Calcium	3.70	<0.50	0.50
Chromium	3.10	4.20	0.13
Manganese	1.00	<0.07	0.07
Iron	61.00	<60.00	60.00
Cobalt	1.00	<0.10	0.10
Nickel	2.10	<0.40	0.40
Copper	1.90	0.80	0.13
Germanium	5.00	<0.32	0.32
Rubidium	1.00	<0.11	0.11
Niobium	1.00	<0.40	0.40
Silver	1.00	<0.13	0.13
Palladium	1.00	<0.07	0.07
Cadmium	1.00	0.05	0.04
Indium	1.00	<0.06	0.06
Tin	1.00	<0.03	0.30
Cesium	1.00	<0.09	0.09
Cerium	1.00	<0.04	0.04
Hafnium	1.00	0.18	0.05
Tantalum	16.00	<2.20	2.20
Tungsten	61.00	10.00	2.20
Rhenium	1.00	0.20	0.14
Gold	1.00	<0.36	0.36
Lead	2.40	1.70	0.08
Uranium	121.00	110.00	0.07
Total	590 (± 88)	174 (± 26)	

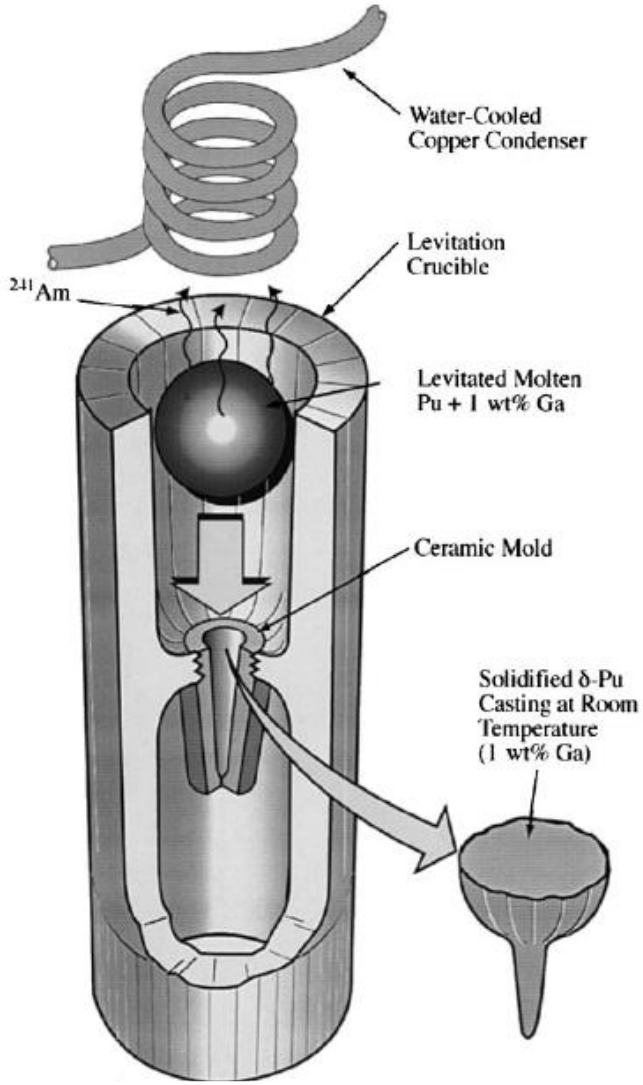
J.C. Lashley et. Al., Journal of Nuclear Materials, 274 (1999) p.315-319

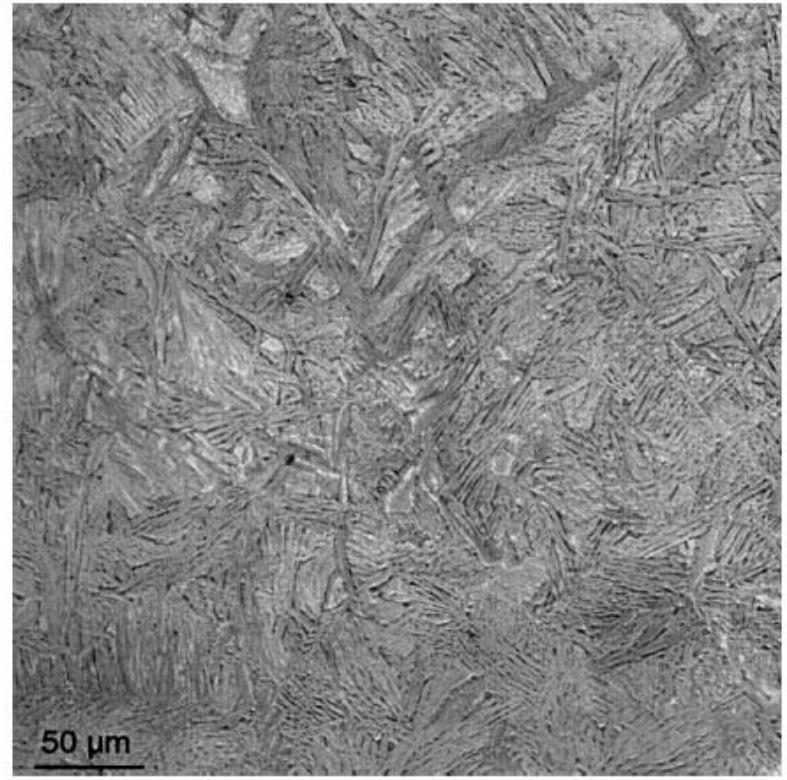

α-Pu : γ = 17 (1) mJK-2mol-1
δ-Pu : γ = 64 (3) mJK-2mol-1
Cp /T (mJK-2mol-1)
T2 (K2)
0
50
100
150
200
250
300
0
20
40
60
80
100

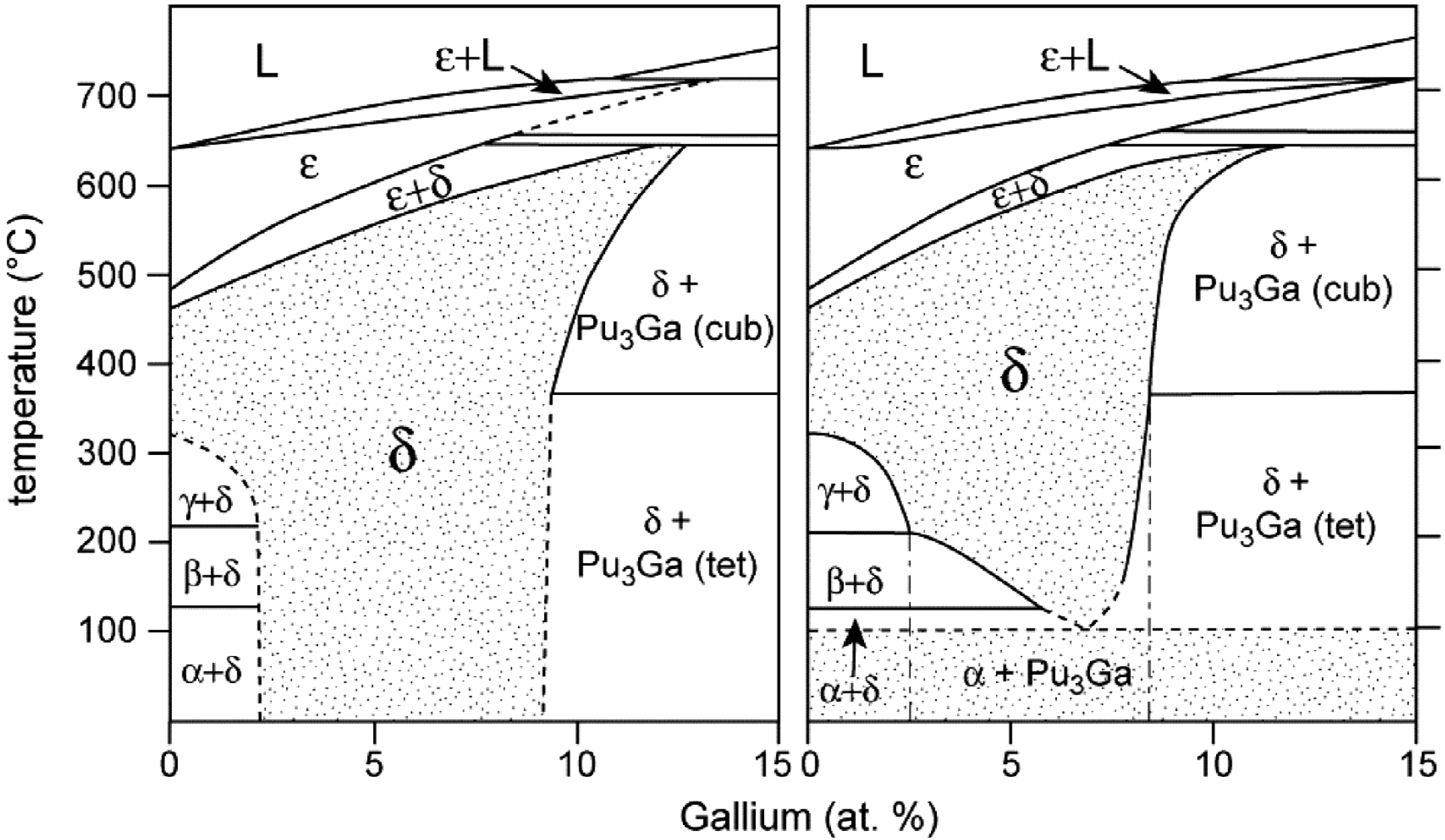

(a)
α-238U
single crystal
poly crystal
C/T (mJ K-2 mol-1)
T (K)
0
100
200
300
400
0
15
30
45
60
75
(b)
γ (mJ K-2 mol-1)
β3
ΘD (K)
single crystal,
9.1
0.1141
256
poly crystal
9.9
0.3055
160
Fit C/T = γ + β3T2
C/T (mJ K-2 mol-1)
T2 (K2)
8
10
12
14
0
2
4
6






Water-Cooled
Copper Condenser
Levitation
Crucible
^{241}Am
Levitated Molten
Pu + 1 wt% Ga
Ceramic Mold
Solidified δ-Pu
Casting at Room
Temperature
(1 wt% Ga)


50 μm



Sig, Met. And Mat. Trans. A, **39A** (2008).

Pergamon

Scripta Materialia, Vol. 34, No. 11, pp. 1717-1722, 1996
Elsevier Science Ltd

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PII S1359-6462(96)00035-8

THE β TO γ TRANSFORMATION IN CERIUM— A TWENTY YEAR STUDY

K.A. Gschneidner, Jr.[+], V.K. Pecharsky, Jaephil Cho[¶] and S.W. Martin
Ames Laboratory and Department of Materials
Science and Engineering
Iowa State University
Ames, IA 50011-3020 USA

(Received November 23, 1995)
(Revised December 18, 1995)

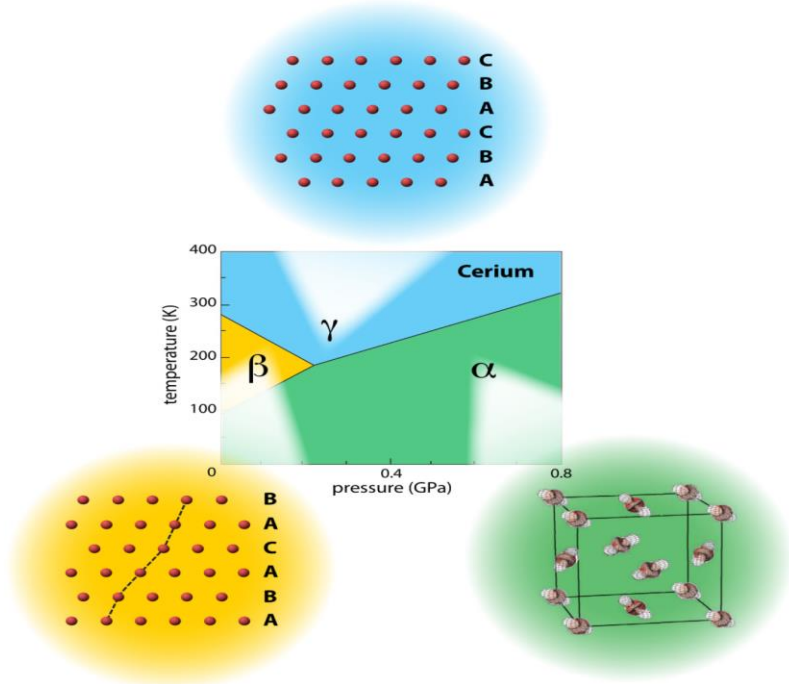
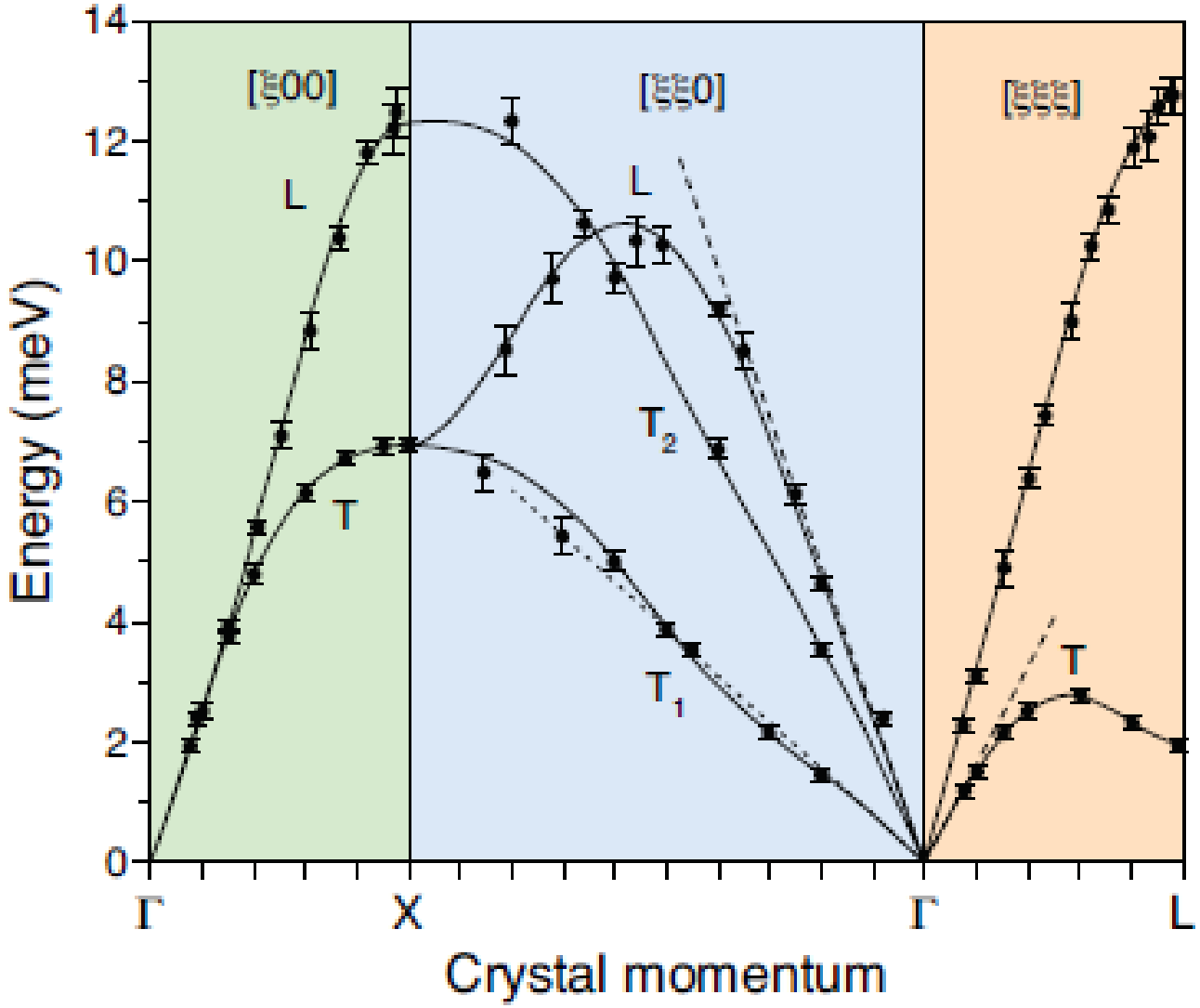
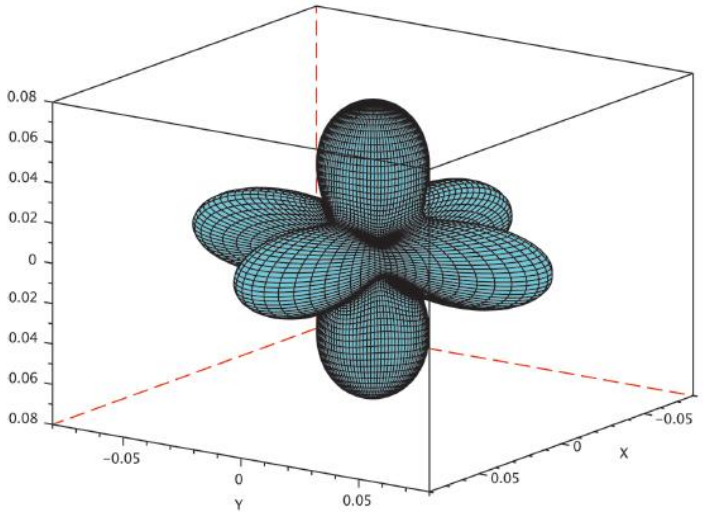
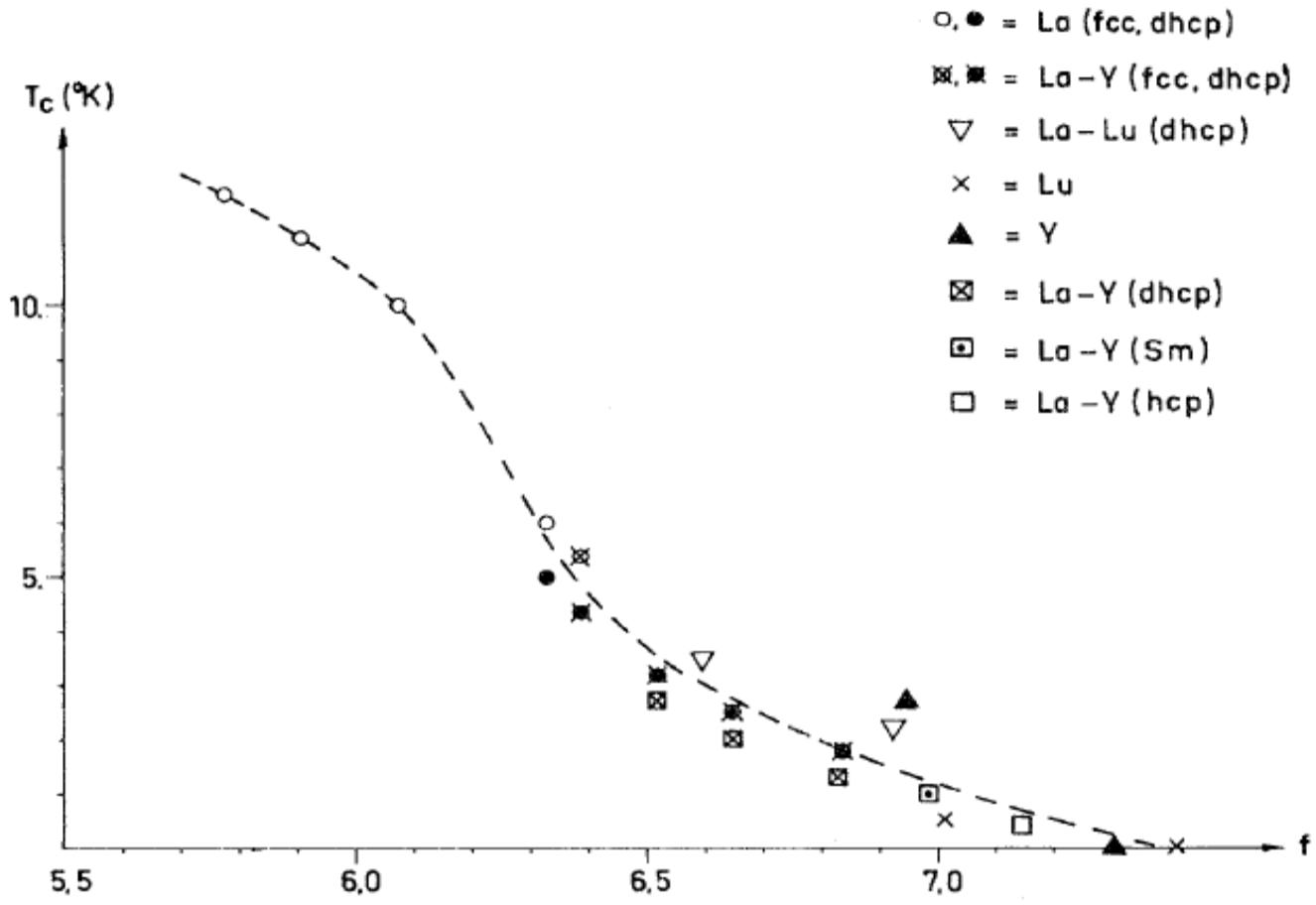


FIG. 1. Cerium phase diagram near ambient temperature and pressure. The crystal structures and stacking arrangements of the γ, β, and α phases are shown. The structure of the γ phase is projected along the close-packed (111) planes (horizontal rows of atoms) in the [110] direction to emphasize the stacking sequences. The structure of the β phase is shown along the close-packed (001) planes in the [100] direction. The possible orbital ordering is shown for the α structure, as determined by nuclear perturbed-angular-correlation spectroscopy [8].

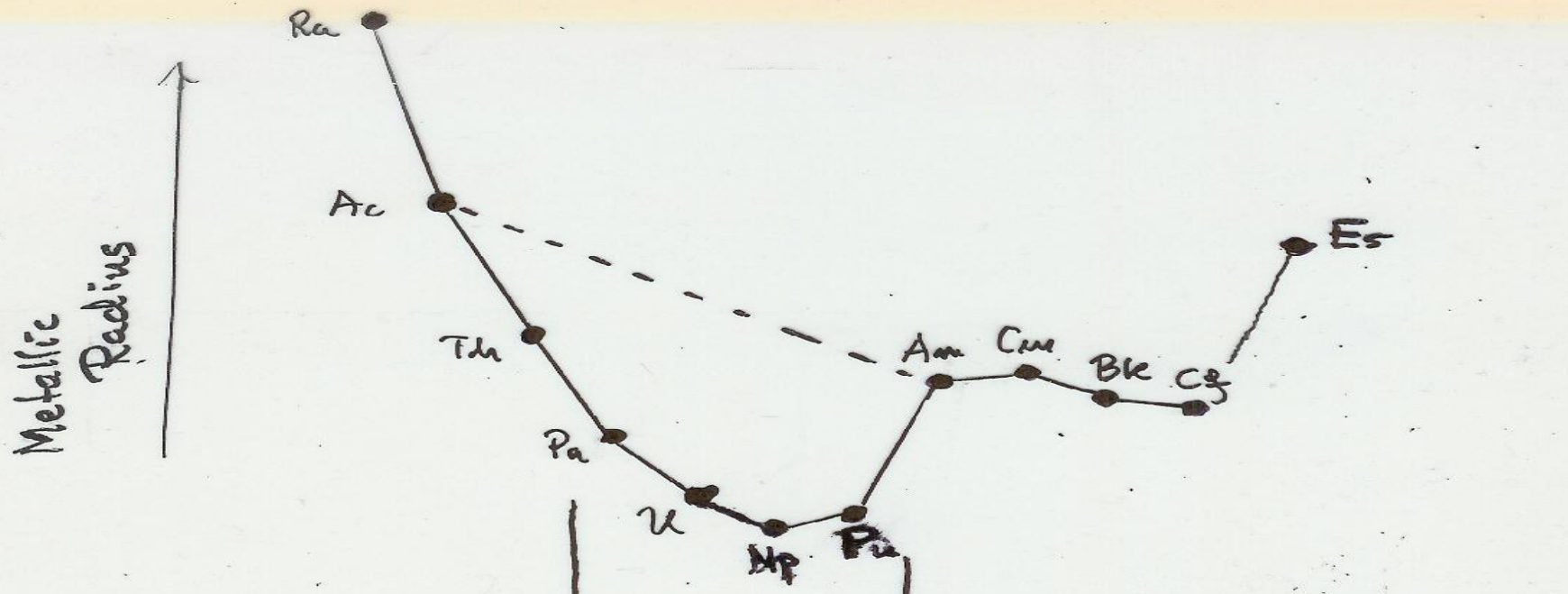

[ξ00]
[ξξ0]
[ξξξ]
L
L
T
T2
T1
T
Energy (meV)
0
2
4
6
8
10
12
14
Γ
X
Γ
L
Crystal momentum


0.08
0.06
0.04
0.02
0
0.02
0.04
0.06
0.08
−0.05
0
0.05
Y
−0.05
0
0.05
X

Generalized superconductivity trend of lanthanides



B. Johansson and A. Rosengren *PRB* **11** 2836 (1975)



Es
fcc
alkaline-earth-like

Ra Ac Th | Pa U Np Pu | Am Cm Bk Cf

bct

bcc fcc fcc
II III IV

dhcp dhcp dhcp dhcp

transition metals

distorted structures

rare-earth-like

Superconductor ($5f^6$, $J=0$)

(Essentially no f-electrons)

Itinerant f-electrons

localized f-electrons

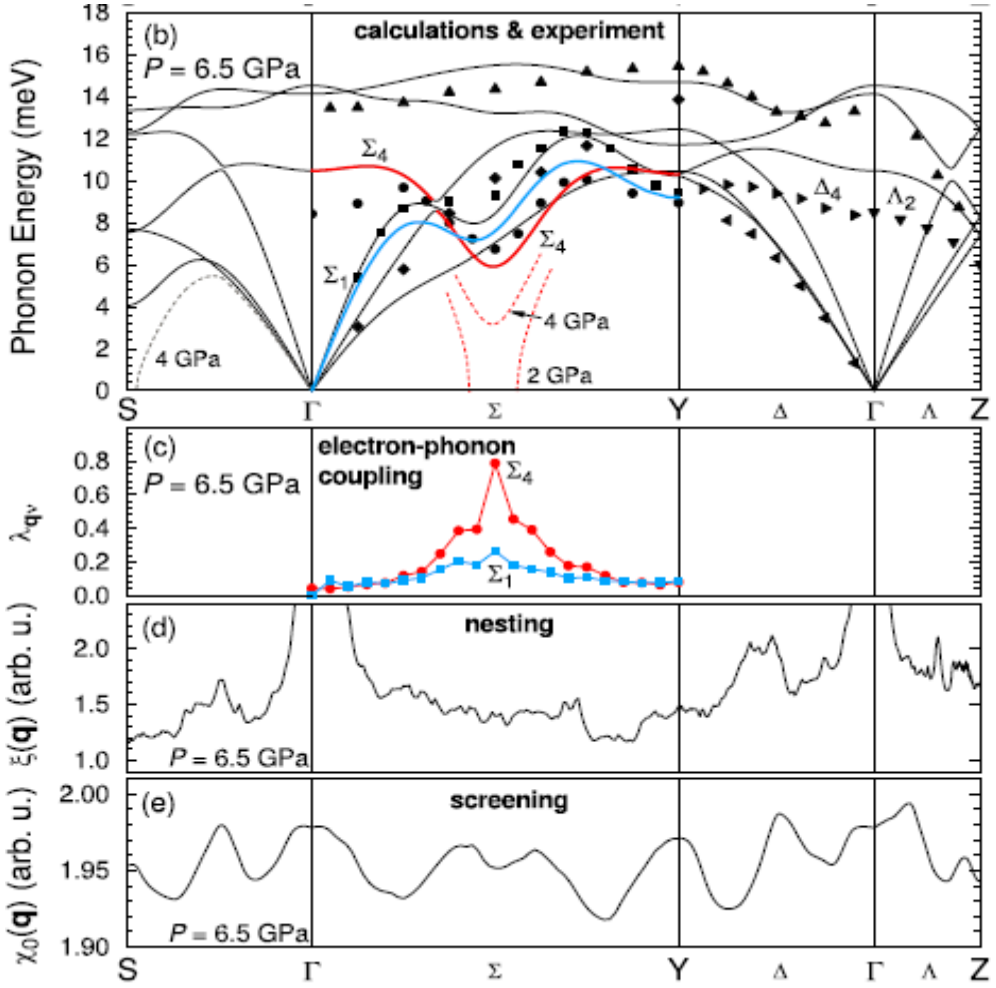
Mott transition

↓

α- Pu monoclinic structure (16 atoms/u.c.)

N.N. distance for certain atoms is small

El-ph coupling and nesting of α-U Ce

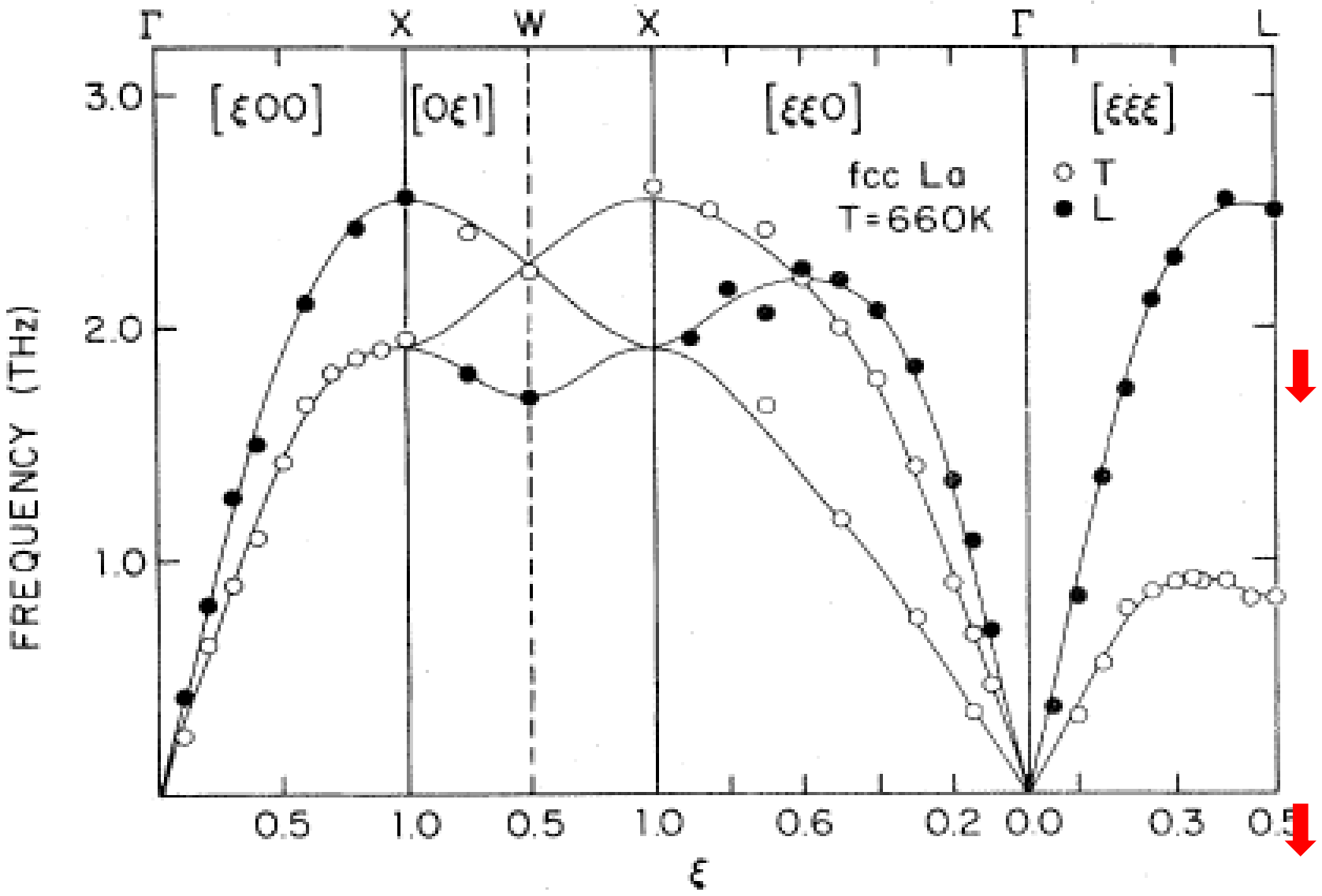


The coupling strength is high at Σ_4 branch
It enhances with lower pressure

With Allen-Dynes equation

$$T_c = \frac{\omega_{\log}}{1.2} f_1 f_2 \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right).$$

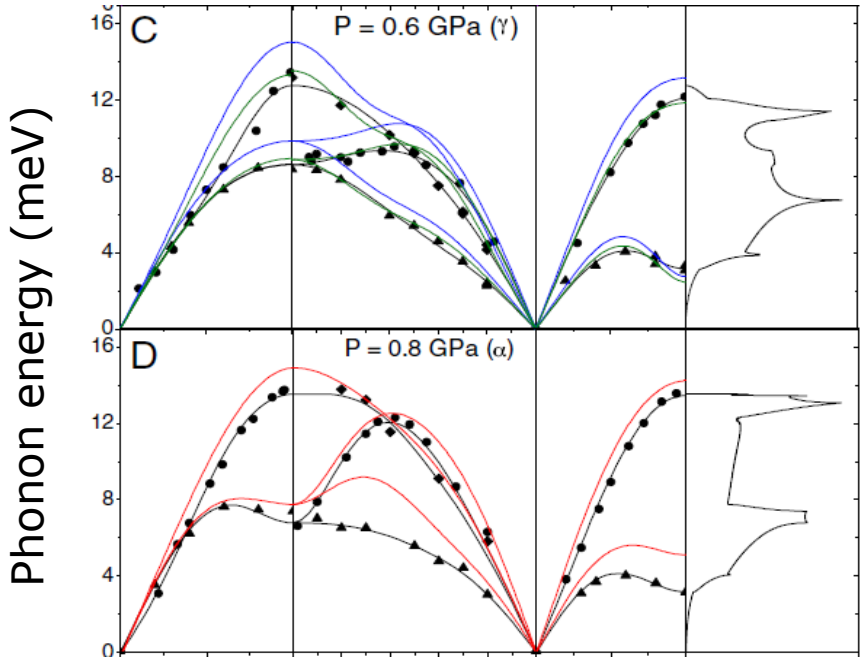
We got Tc = 4.5 K at 6.5 GPa



3 (2003)

C. Stassis *et al PRB* **26** 5426 (1982)

Vibrational entropy contribution to the α-γ phase transition



We calculated the entropy change

$$\Delta S_{\mathrm{vib}}^{\gamma-\alpha} \approx 3\ k_{\mathrm{B}} \ln\left(\frac{138\ \mathrm{K}}{122\ \mathrm{K}}\right) = 0.37\ k_{\mathrm{B}}$$

$$\Delta S_{\mathrm{vib}}^{\gamma-\alpha} \approx (0.75 \pm 0.15) k_{\mathrm{B}}$$

I.-K. Jeong et al PRL 92 105702 (2004)

Ultrasonic measurements

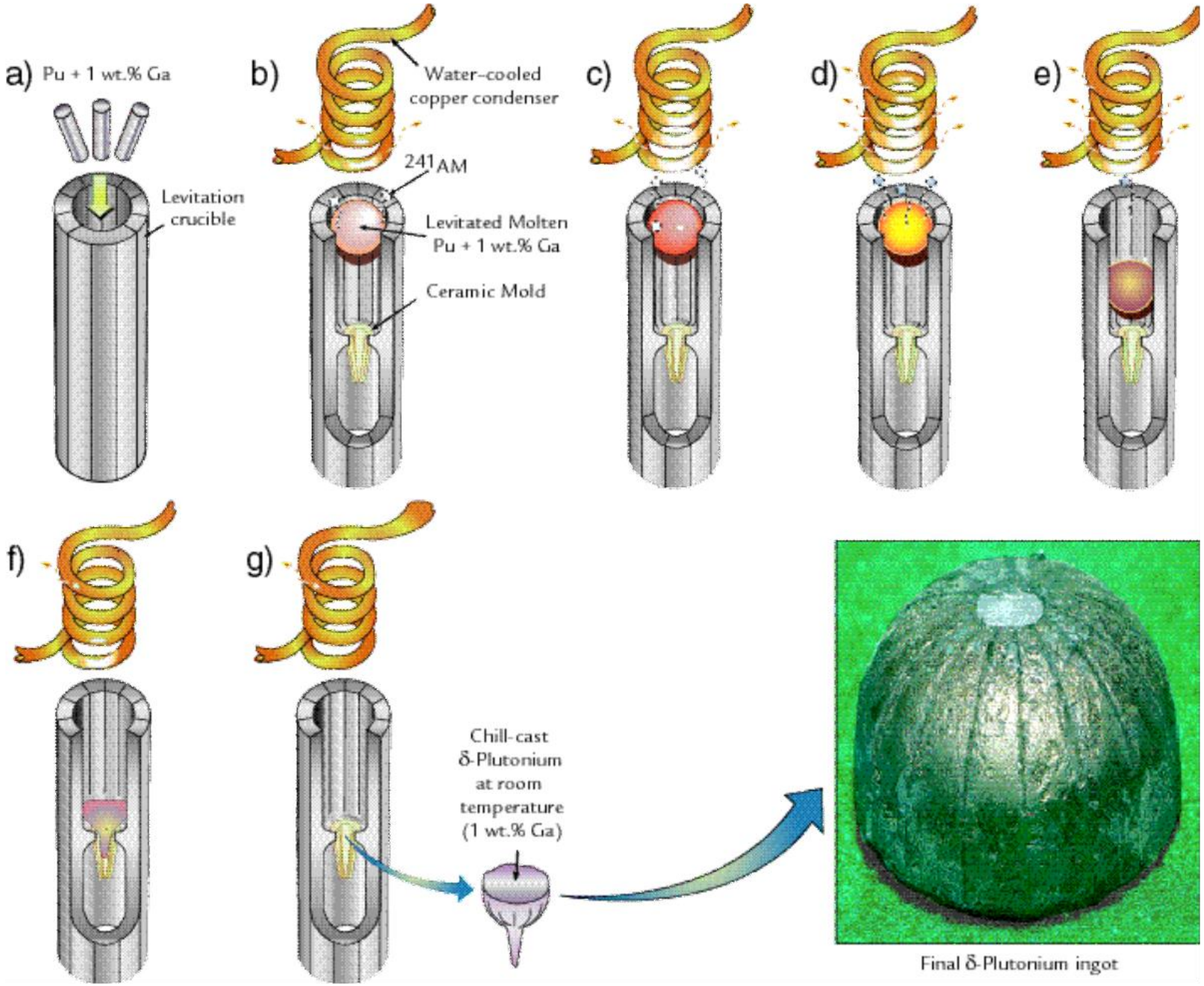
$$\Delta S_{\mathrm{vib}}^{\gamma-\alpha} \approx 0.32\ k_{\mathrm{B}}$$

FF. Voronov *et al* Soviet Physics-Doklady **135**, 1280 (1960)

*Total entropy change across the transition

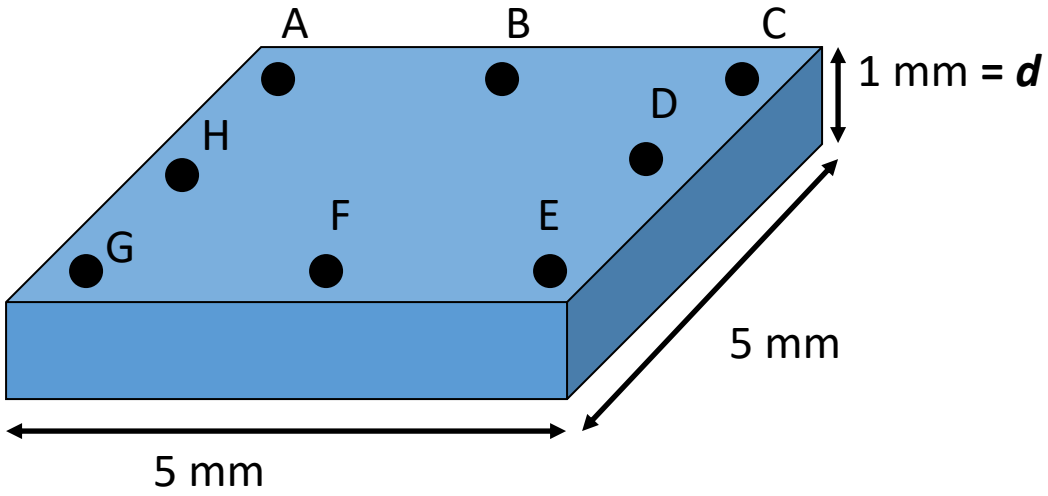
$$dP/dT = \Delta S_{\mathrm{tot}}^{\gamma-\alpha} / \Delta V^{\gamma-\alpha} = 1.5\ k_{\mathrm{B}}$$

Phonon contribution to the phase transition cannot be neglected !


a) Pu + 1 wt.% Ga
Levitation crucible
b)
Water-cooled copper condenser
241AM
Levitated Molten Pu + 1 wt.% Ga
Ceramic Mold
c)
d)
e)
f)
g)
Chill-cast δ-Plutonium at room temperature (1 wt.% Ga)
Final δ-Plutonium ingot

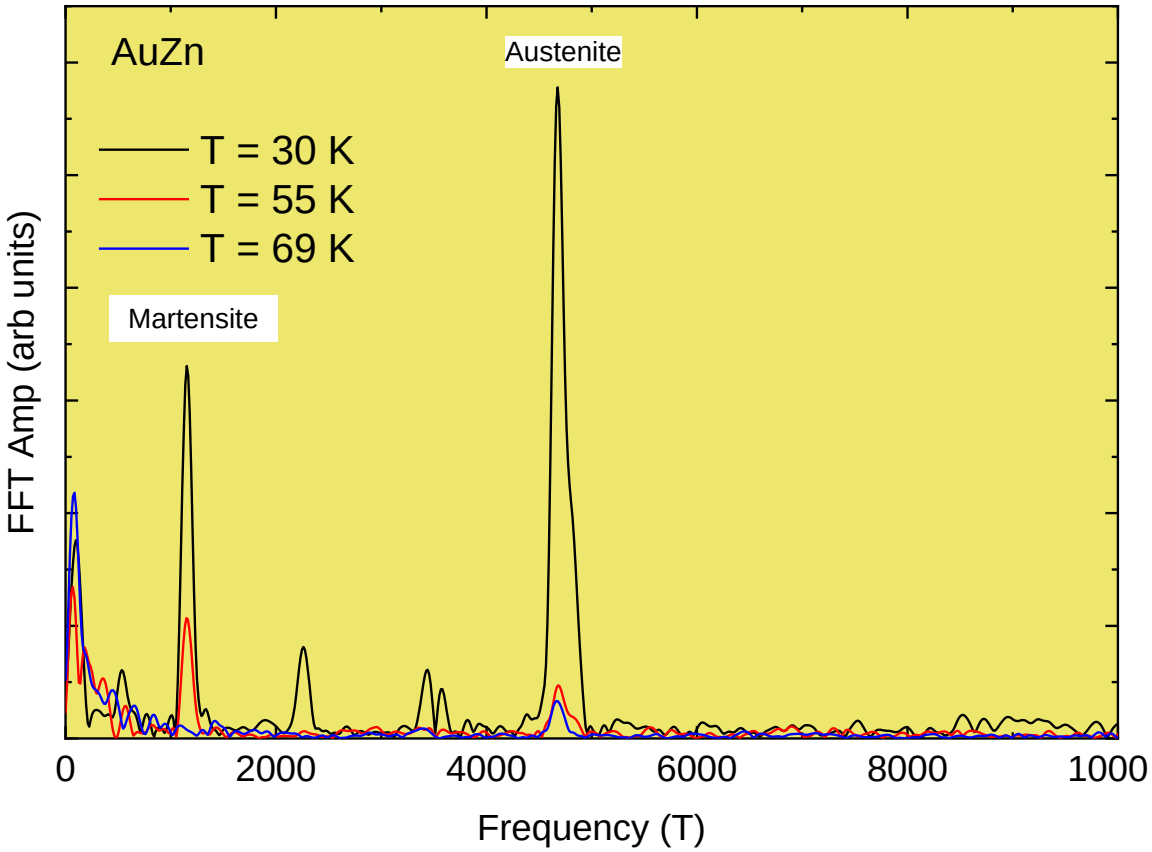
van der Pauw measurement

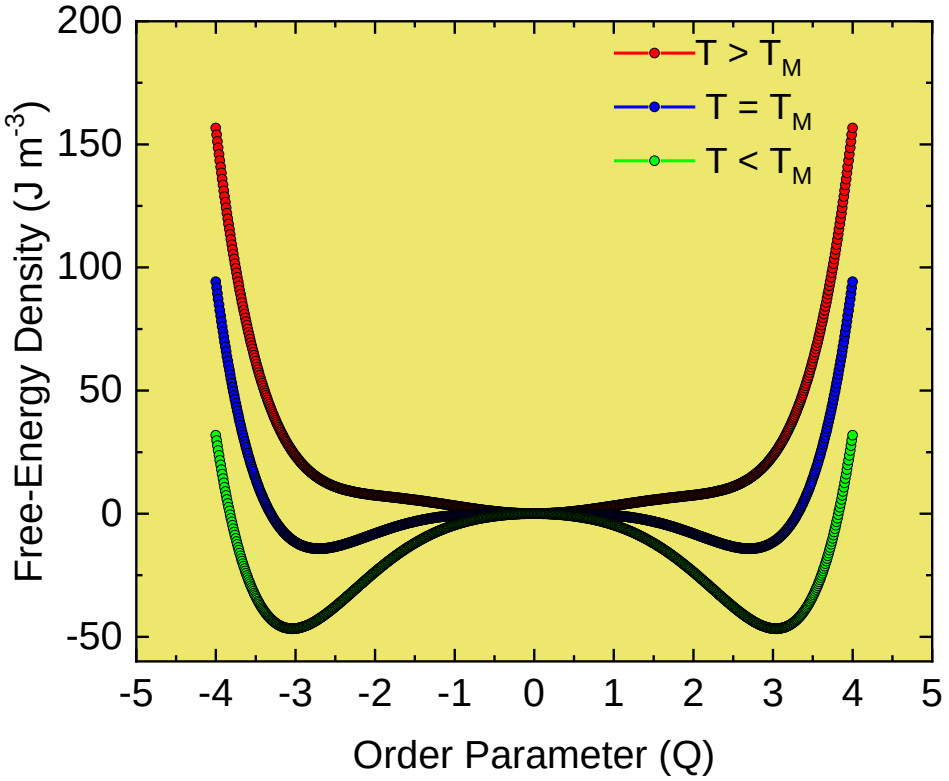
8 contacts, 2 independent van der Pauw configurations

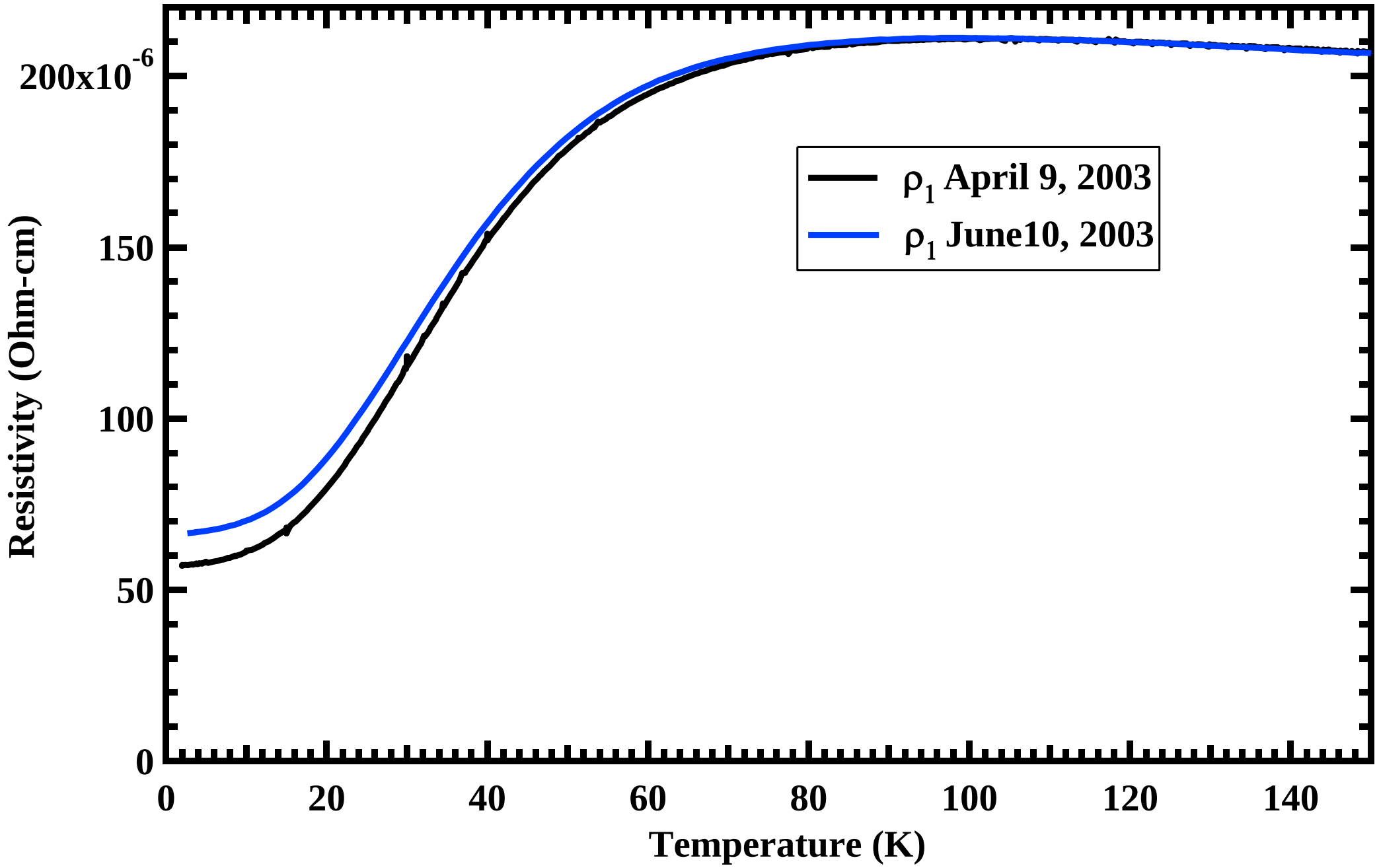


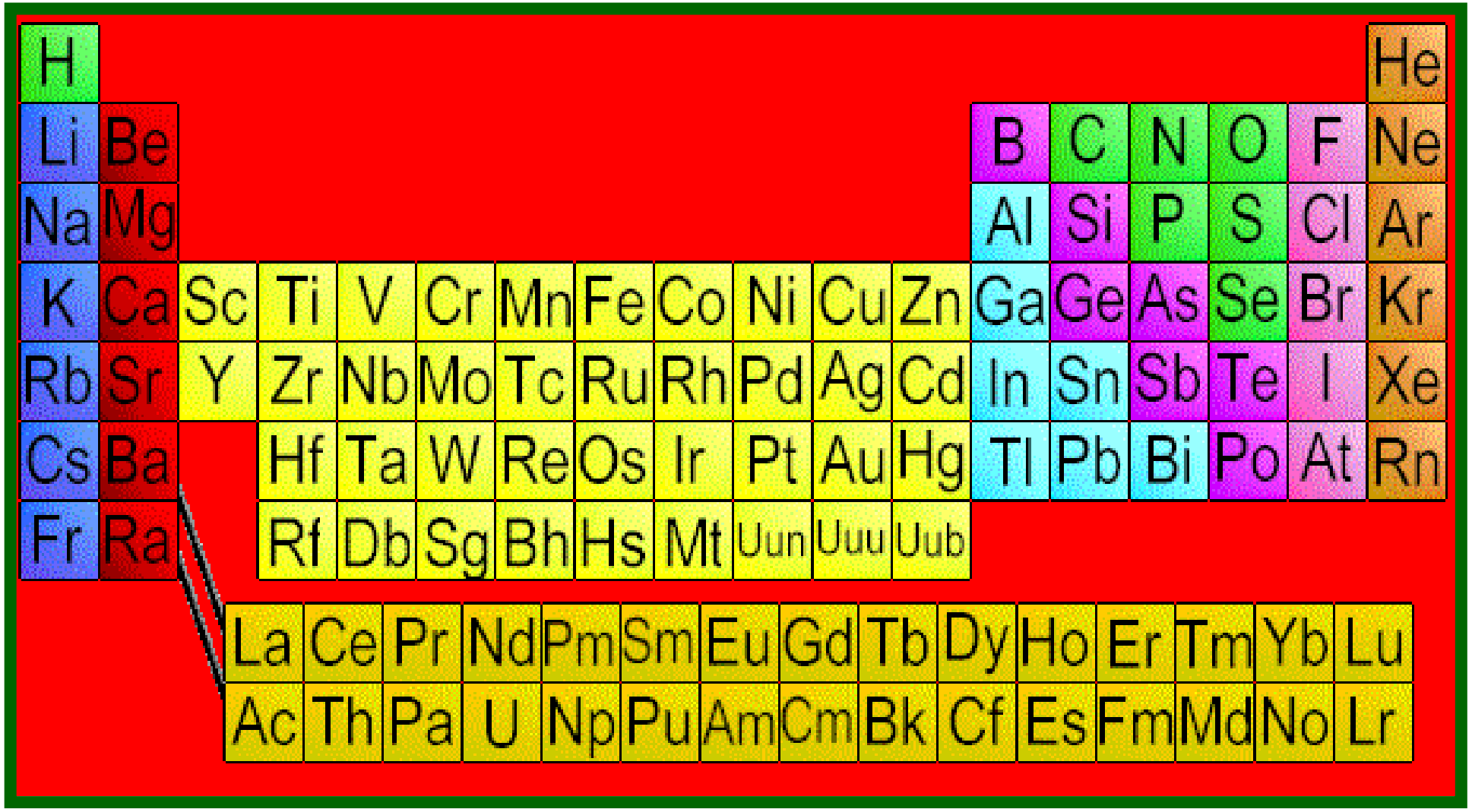
$R_{ACGE} = V_{CE}/I_{AG}$
$R_{CEAG} = V_{CE}/I_{AG}$
$R_{GEAC} = V_{GE}/I_{AC}$
$R_{HFBD} = V_{HF}/I_{BD}$
$R_{FDHB} = V_{FD}/I_{HB}$
$R_{BDHF} = V_{BD}/I_{HF}$

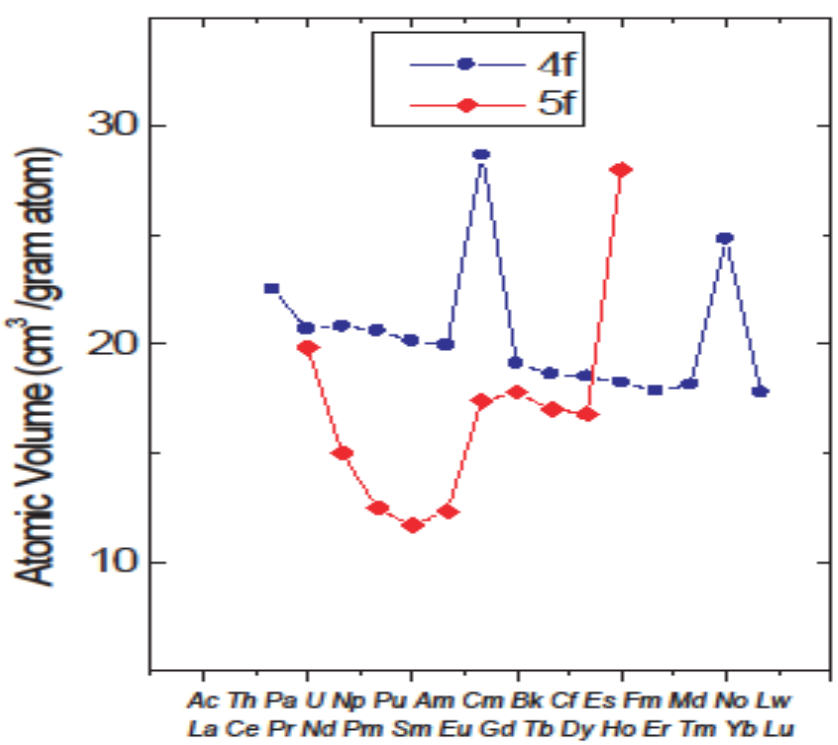
$$\rho_1 = f(R_{ACGE}/R_{CEAG})(\pi d/\ln 2)(R_{ACGE} + R_{CEAG})/2$$
$$\rho_2 = f(R_{GEAC}/R_{CEAG})(\pi d/\ln 2)(R_{GEAC} + R_{CEAG})/2$$
$$\rho_3 = f(R_{HFBD}/R_{FDHB})(\pi d/\ln 2)(R_{HFBD} + R_{FDHB})/2$$
$$\rho_4 = f(R_{BDHF}/R_{FDHB})(\pi d/\ln 2)(R_{BDHF} + R_{FDHB})/2$$

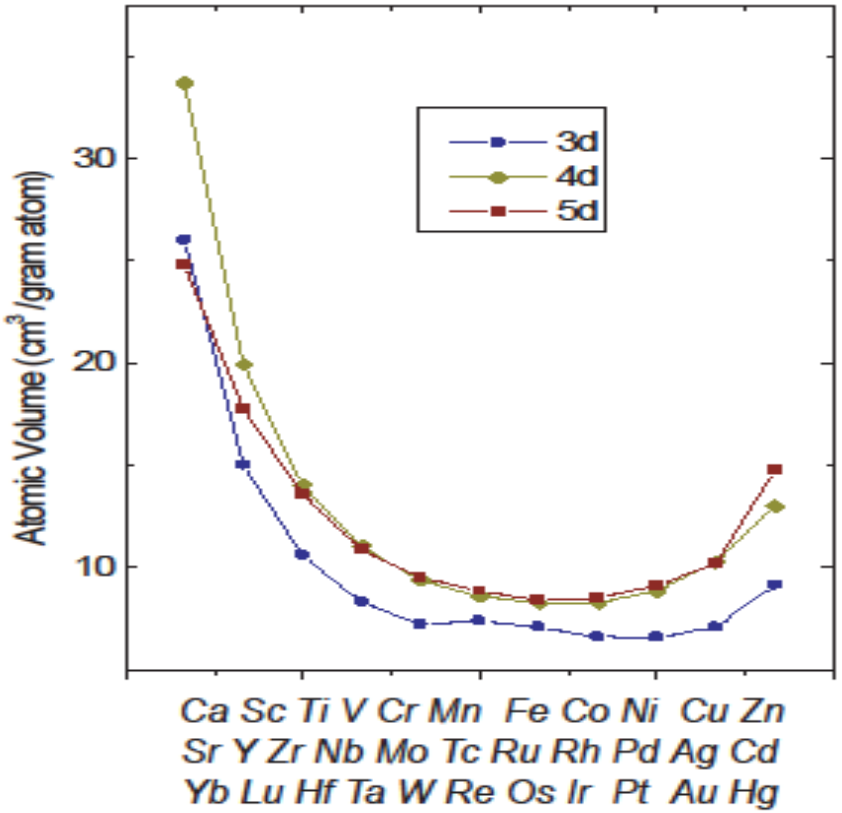

AuZn
Austenite
T = 30 K
T = 55 K
T = 69 K
Martensite
FFT Amp (arb units)
0
2000
4000
6000
8000
1000
Frequency (T)

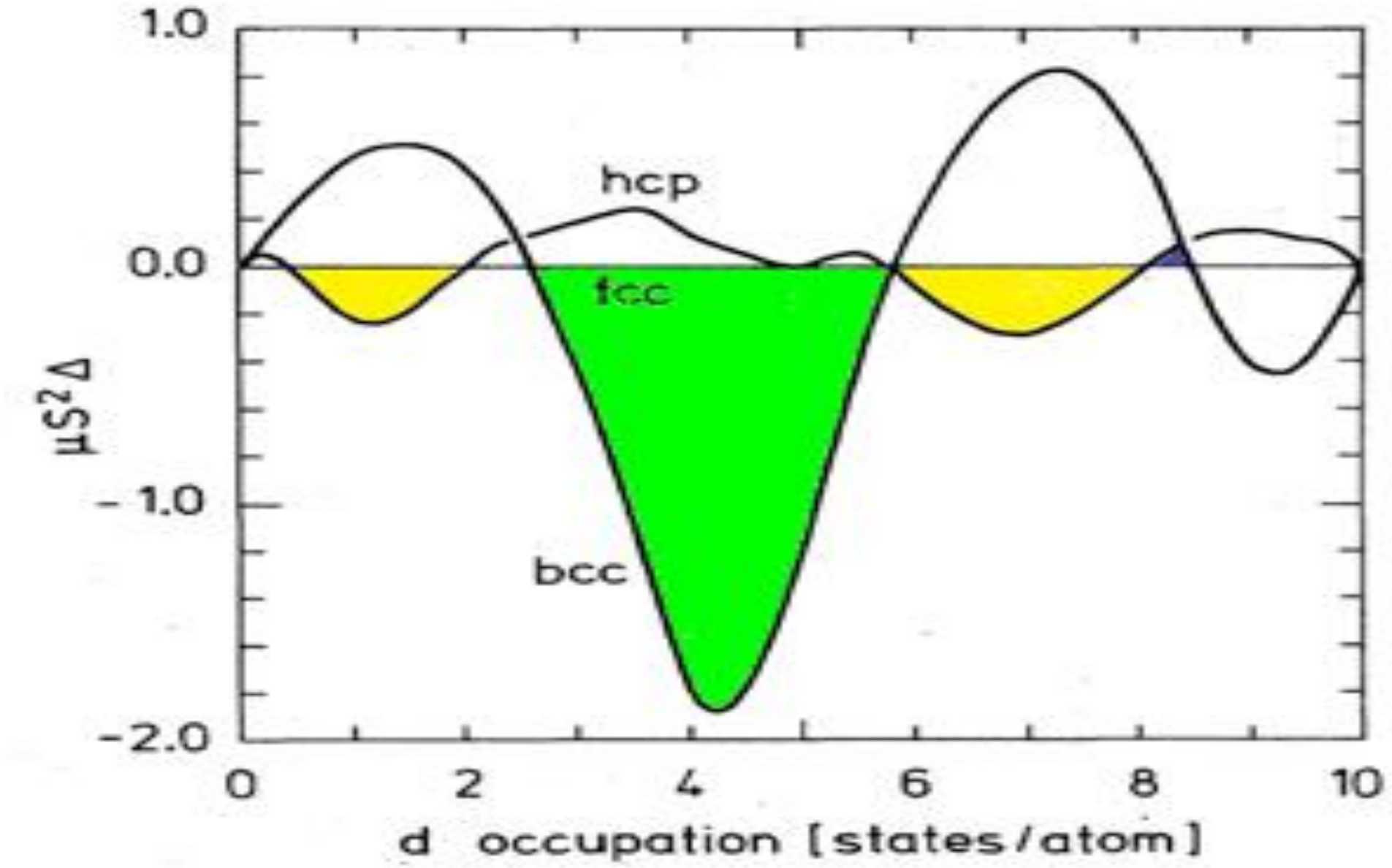

T > T_M
T = T_M
T < T_M
Free-Energy Density (J m^-3)
200
150
100
50
0
-50
-5
-4
-3
-2
-1
0
1
2
3
4
5
Order Parameter (Q)

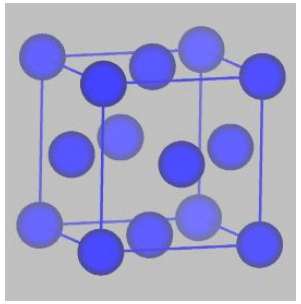

200x10-6
150
100
50
0
Resistivity (Ohm-cm)
0
20
40
60
80
100
120
140
Temperature (K)
ρ1 April 9, 2003
ρ1 June10, 2003


H
He
Li Be
B C N O F Ne
Na Mg
Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Rf Db Sg Bh Hs Mt Uun Uuu Uub
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

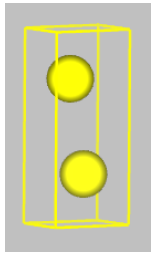

4f
5f
Atomic Volume (cm3 /gram atom)
30
20
10
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu


3d
4d
5d
Atomic Volume (cm3 /gram atom)
30
20
10
Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
Yb Lu Hf Ta W Re Os Ir Pt Au Hg

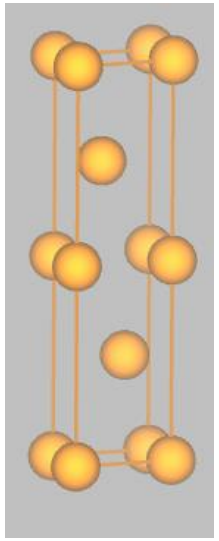

1.0
0.0
-1.0
-2.0
μS²Δ
hcp
fcc
bcc
0
2
4
6
8
10
d occupation [states/atom]



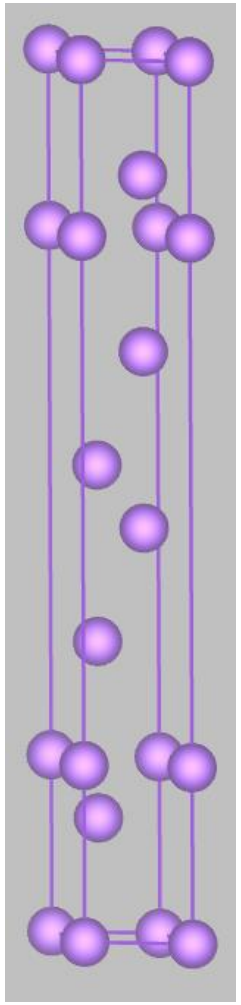
fcc



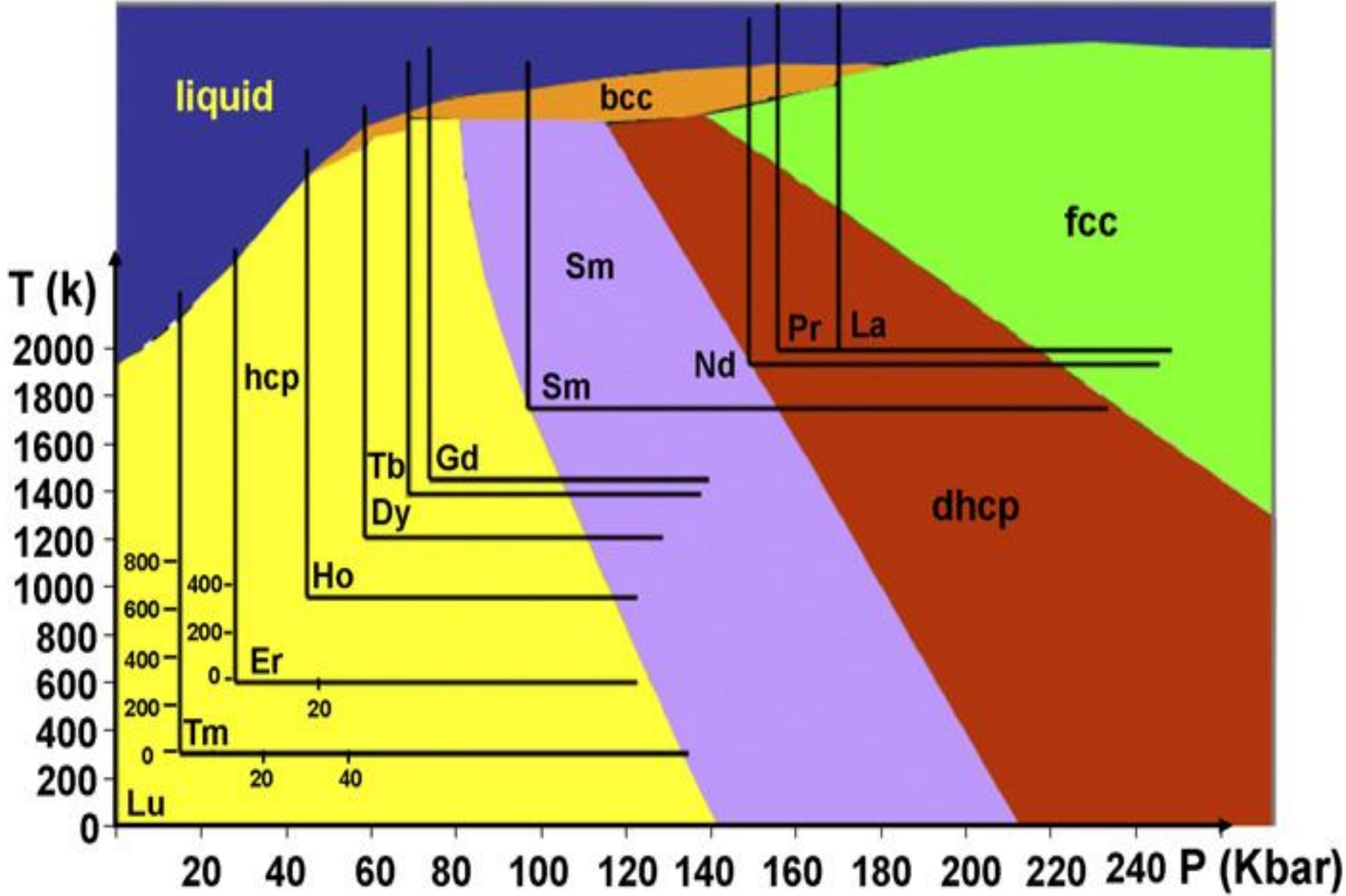
hcp



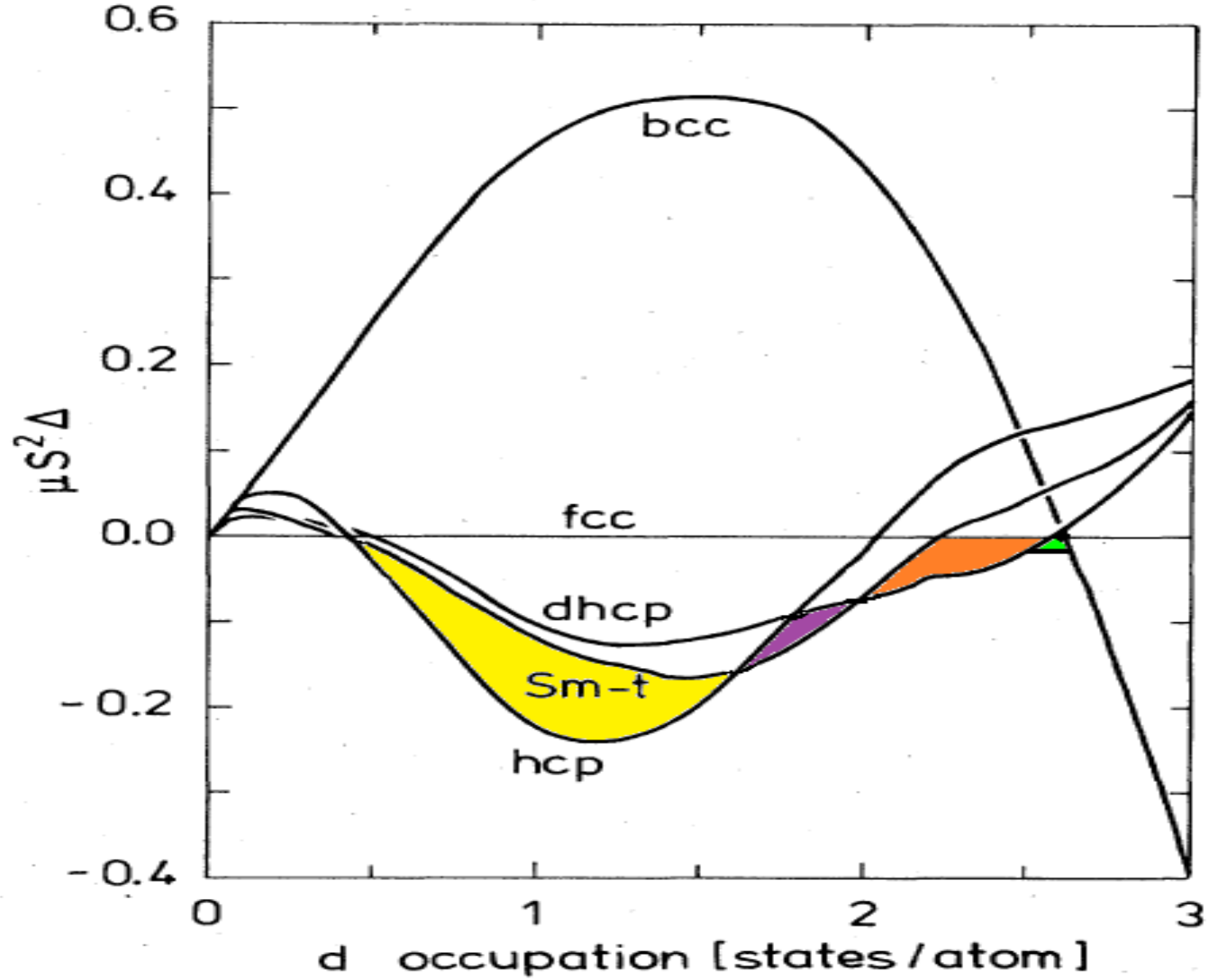
dhcp



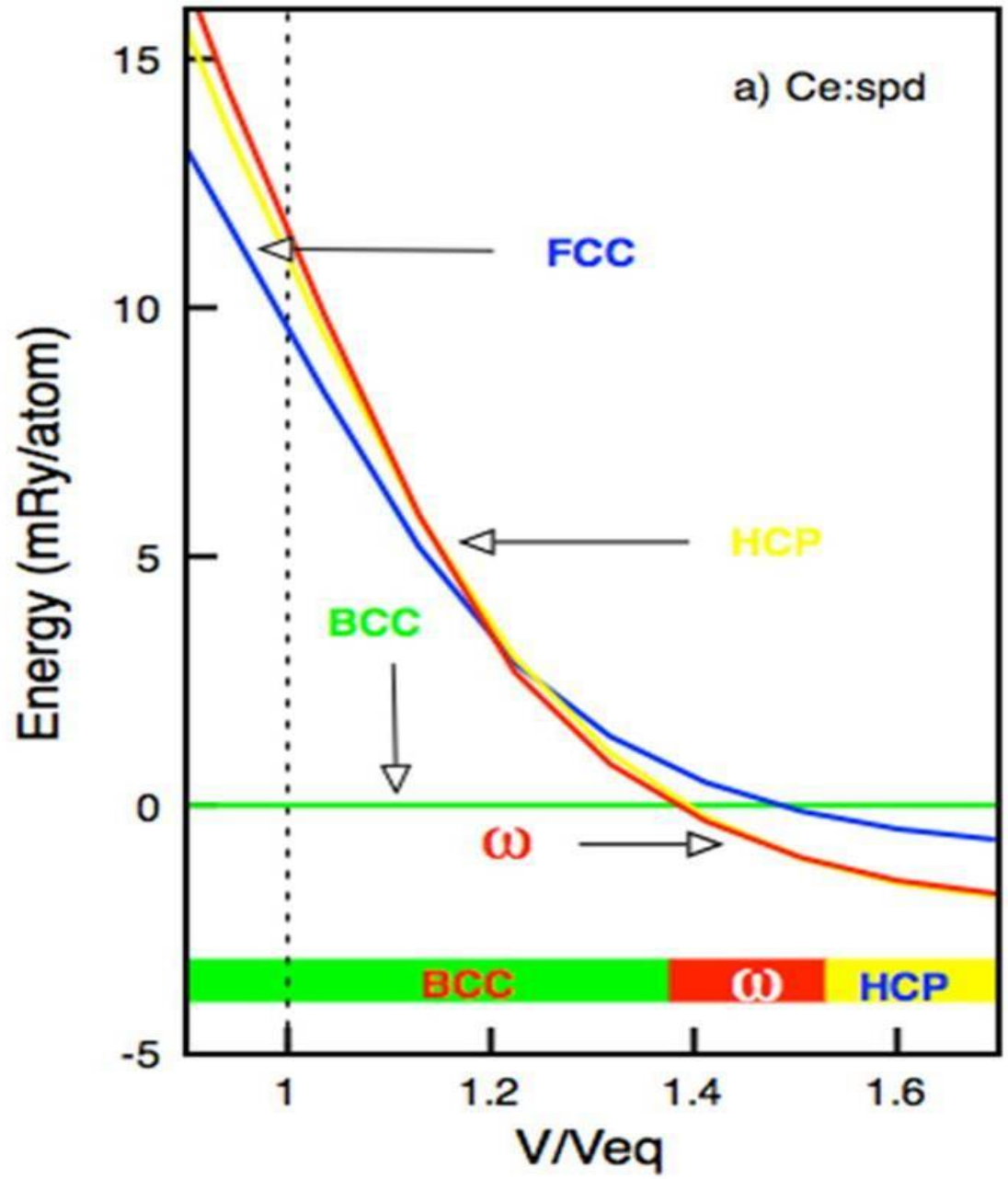
Sm-type

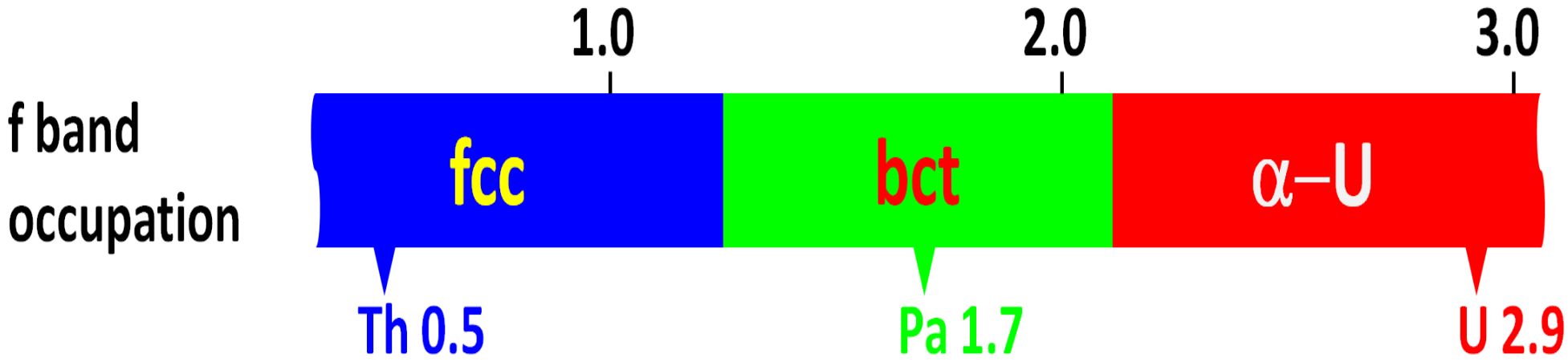


Generalized Phase Diagram for the Lanthanides (Johansson+Rosengren)



CANONICAL D-BANDS

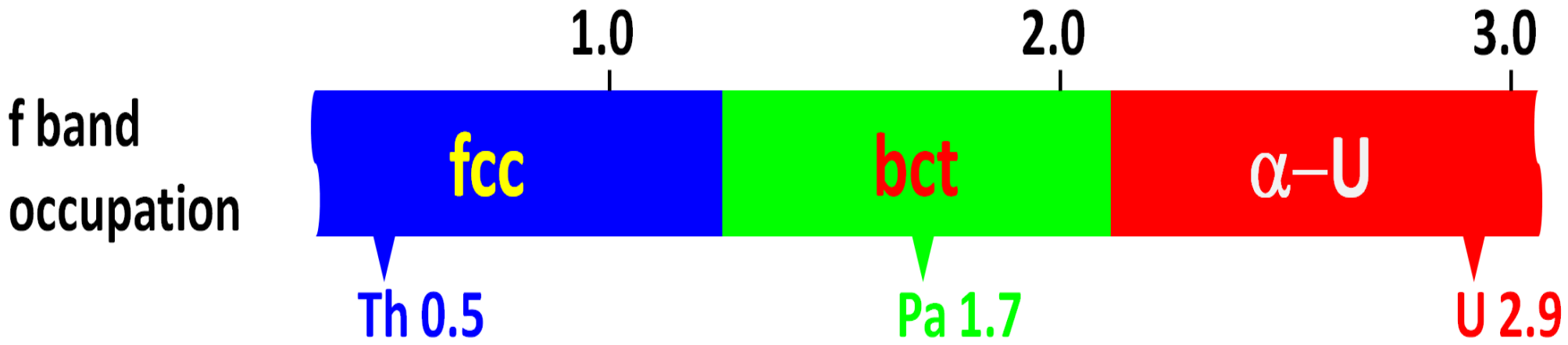

a) Ce:spd
FCC
HCP
BCC
ω
BCC
ω
HCP
Energy (mRy/atom)
15
10
5
0
-5
1
1.2
1.4
1.6
V/Veq



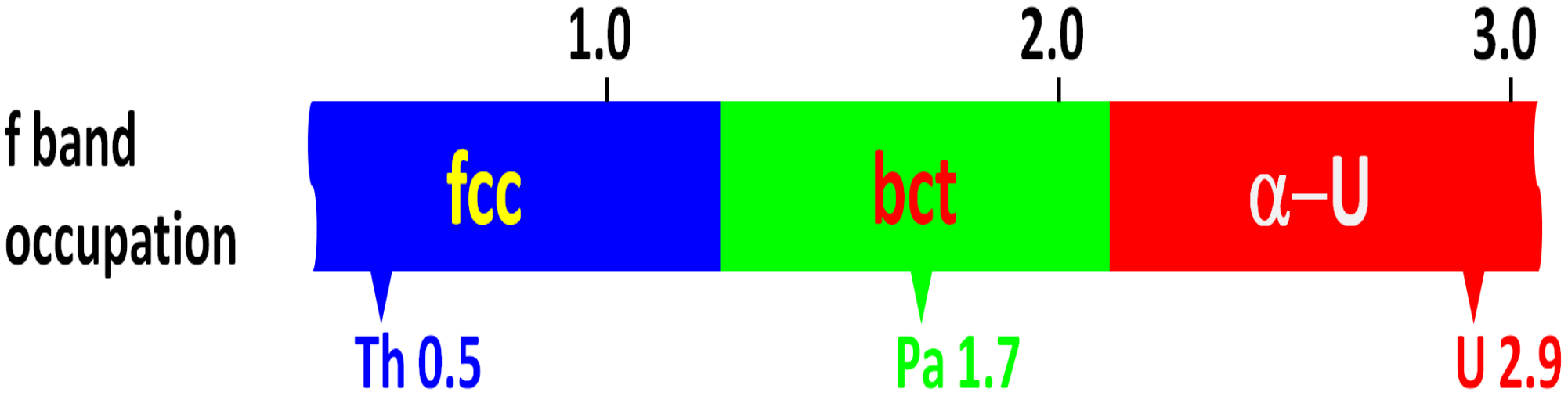
Pressure induced fcc-bct transition in Thorium (Th)

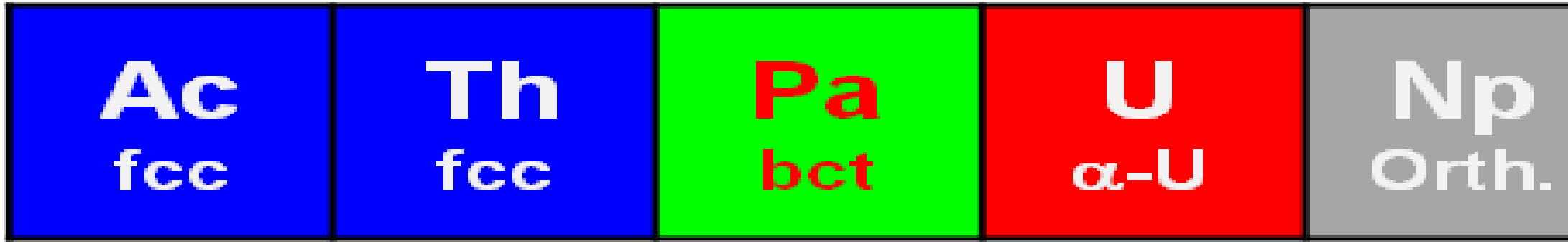
Pressure induced bct – α–uranium structure in Protactinium (Pa)

CANONICAL F-BANDS



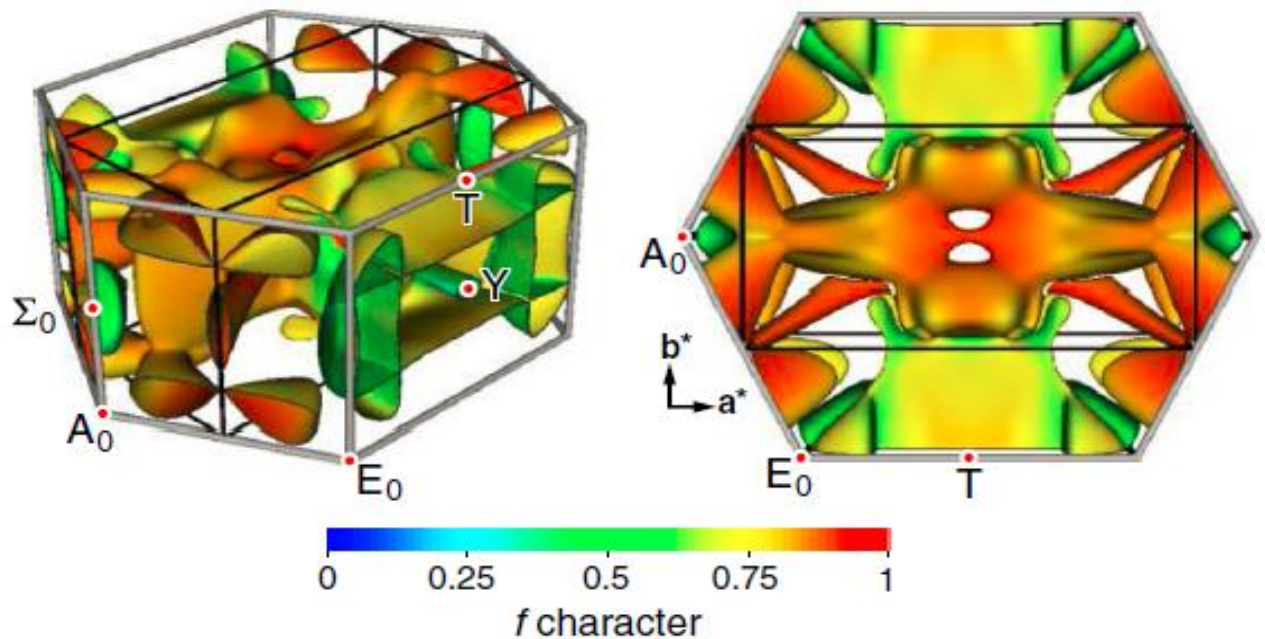
CANONICAL F-BANDS


f band
occupation
1.0
2.0
3.0
fcc
bct
α–U
Th 0.5
Pa 1.7
U 2.9

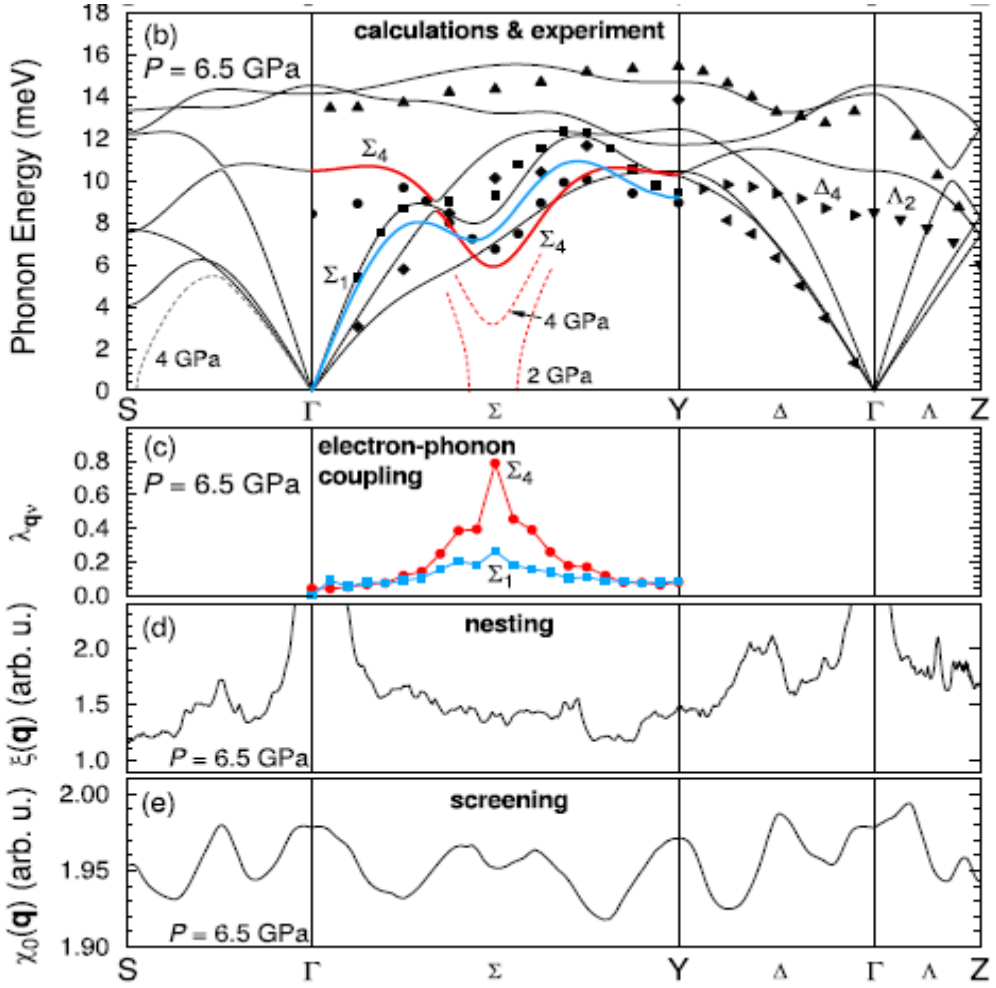

Ac
fcc
Th
fcc
Pa
bct
U
α-U
Np
Orth.

Lattice Dynamics and Superconductivity in Cerium at High Pressure

I. Loa,[1,*] E. I. Isaev,[2,3] M. I. McMahon,[1] D. Y. Kim,[4,†] B. Johansson,[4,5] A. Bosak,[6] and M. Krisch[6]



El-ph coupling and nesting of α-U Ce



The coupling strength is high at Σ_4 branch
It enhances with lower pressure

With Allen-Dynes equation

$$T_c = \frac{\omega_{\log}}{1.2} f_1 f_2 \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right).$$

We got Tc = 4.5 K at 6.5 GPa

The Highest Superconductivity T_C Table of Elements under Pressure

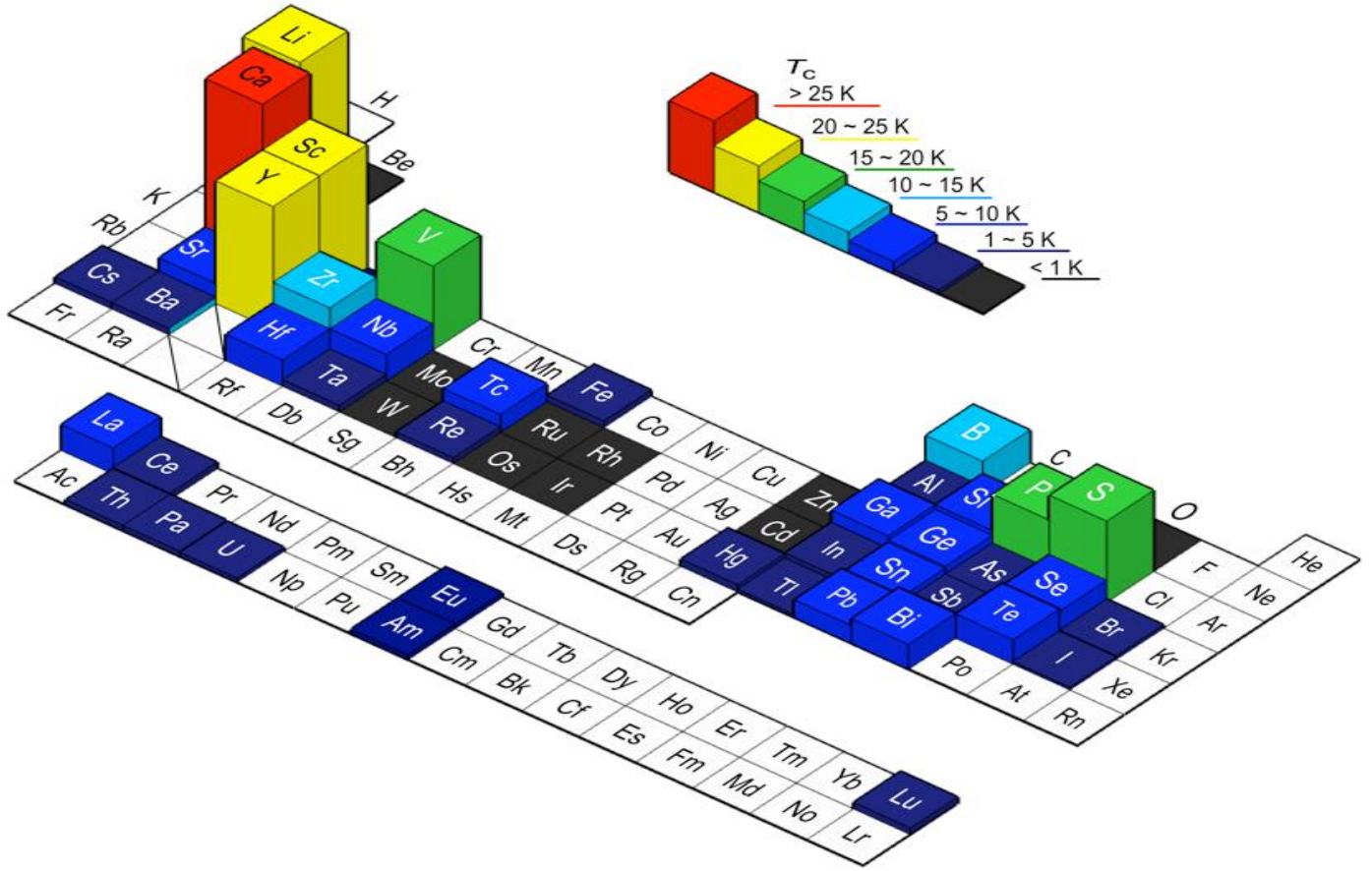


Image courtesy of Dr. Takahiro Matsuoka

- **Allen-Dynes** formula (PR B 12,905 (1975) for Tc
- Calculated Tc for alpha-U Ce 4.5 K
- Calculated Tc for fcc Ce 1.0 K