Record volume collapse in valence unstable CeNi

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Kondo volume collapse benchmarks

element or compound	volume change, %	structures
Ce (γ-α)	15	FCC to FCC/P cubic (?)
$Ce_{1-x}(Th,La)_x$	10-12	FCC to FCC
Pu (β-α) (δ-α')	12 26	monocl. to another monocl. cubic to monoclinic
Sm(Y)S	13	cubic to cubic
$YbInCu_4$	0.5	cubic to cubic
CeNi	22	orthorhombic to cubic

s, p, d и f- elements

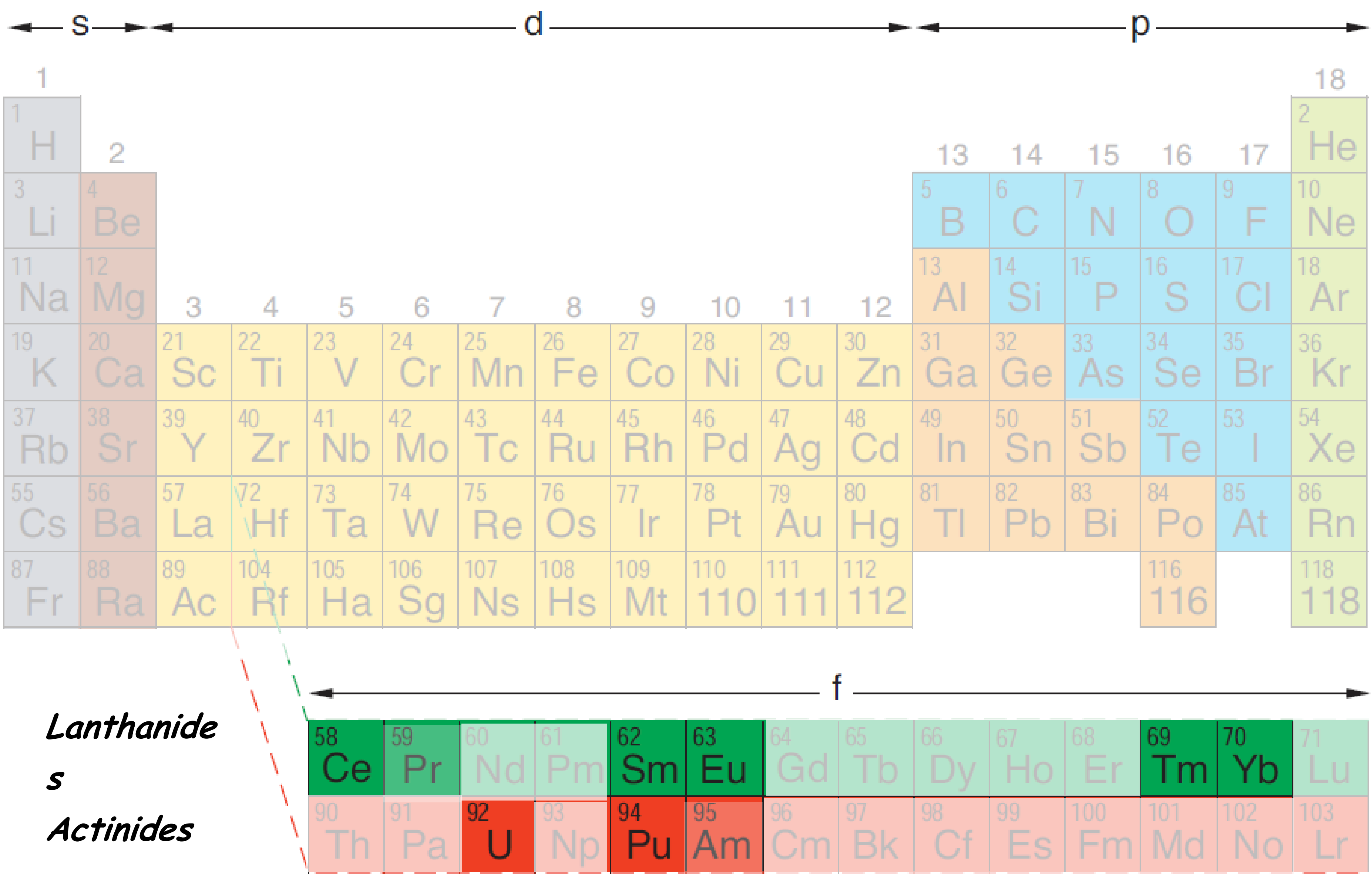
s — d — p

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112				116 116		118 118

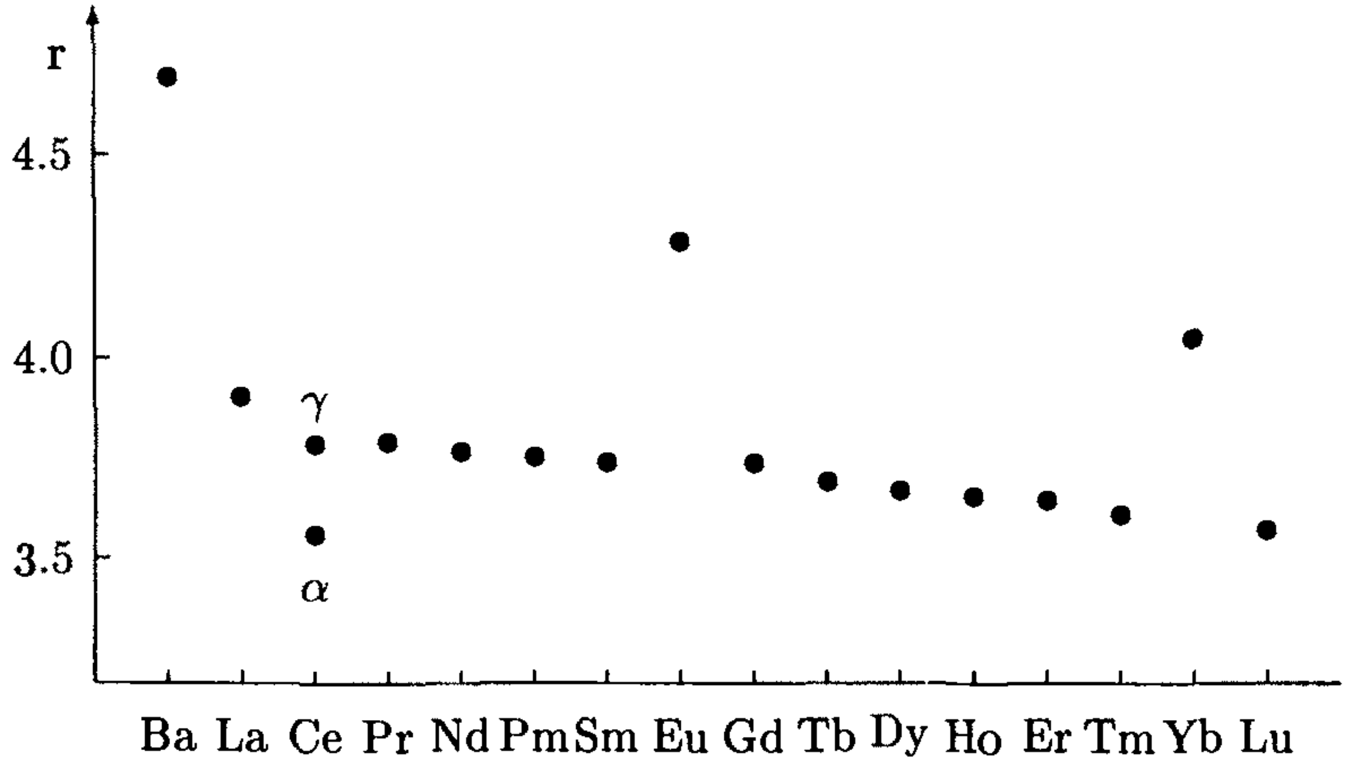
f

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

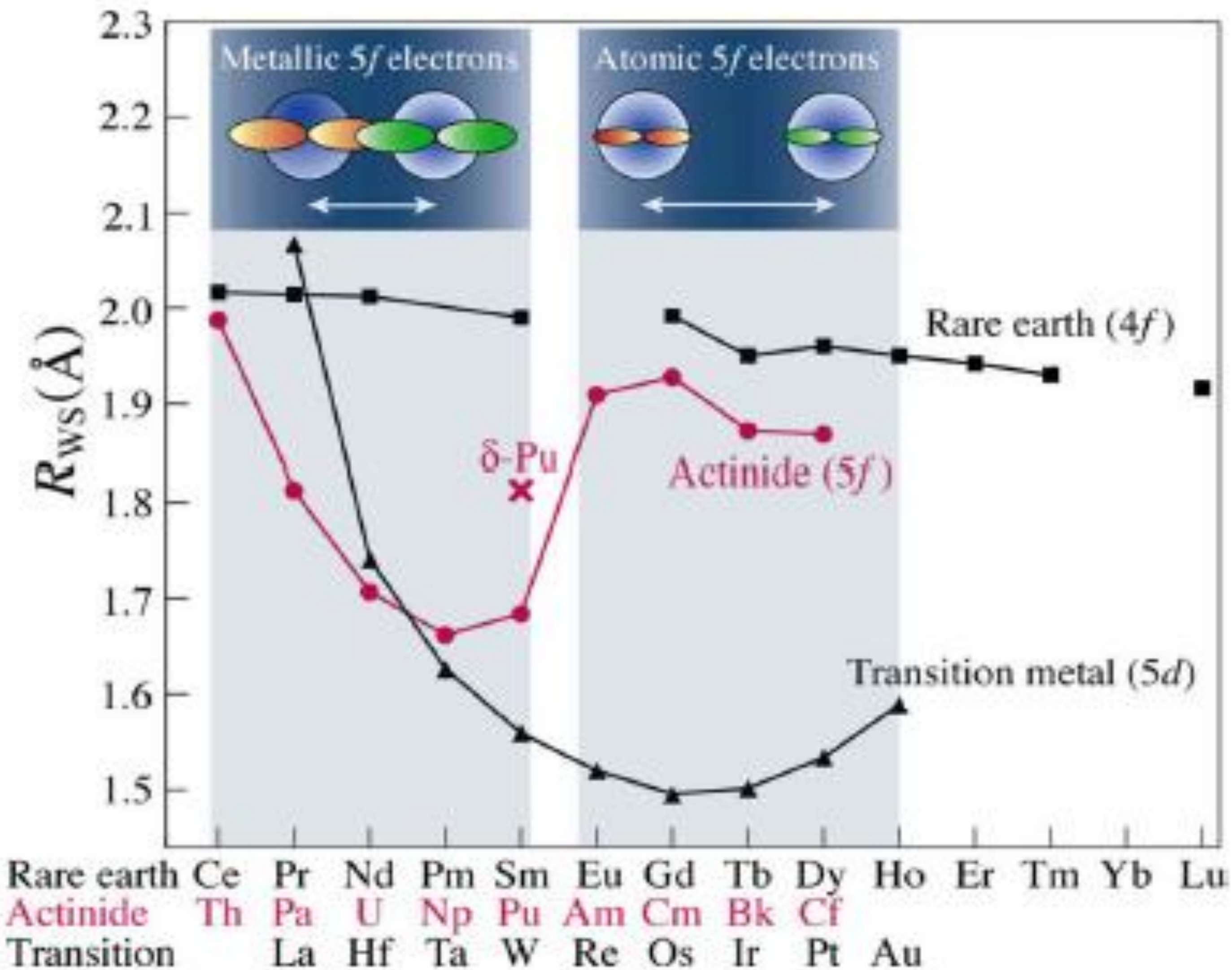
Valence-unstable (anomalous) elements



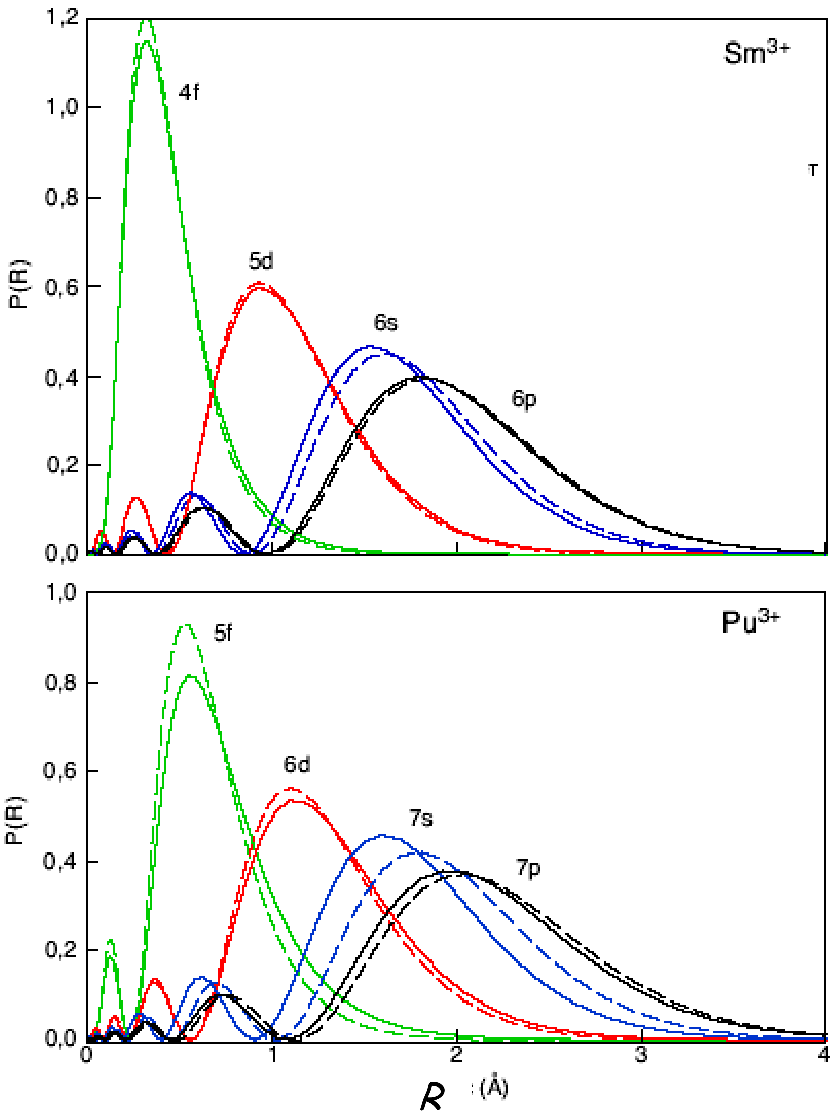
Atomic size along the rare eartn series

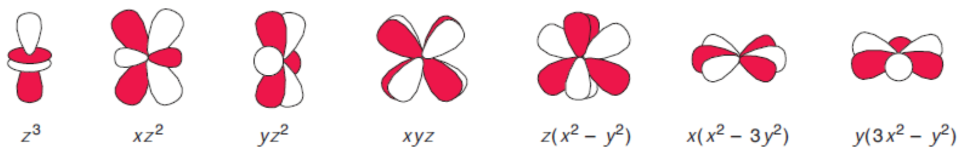


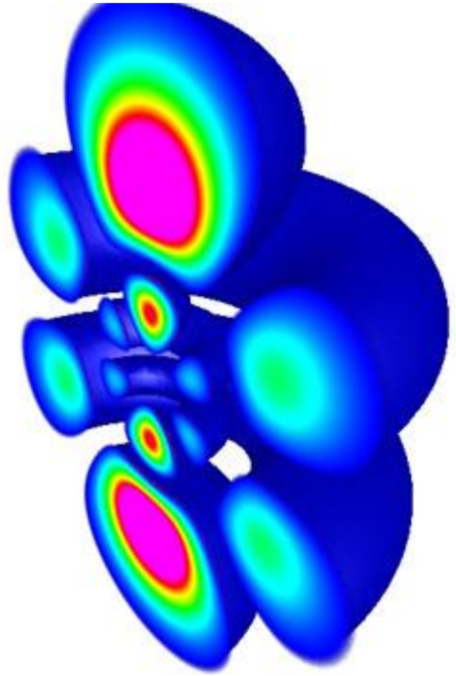
Size of the *d*- and *f*-elements



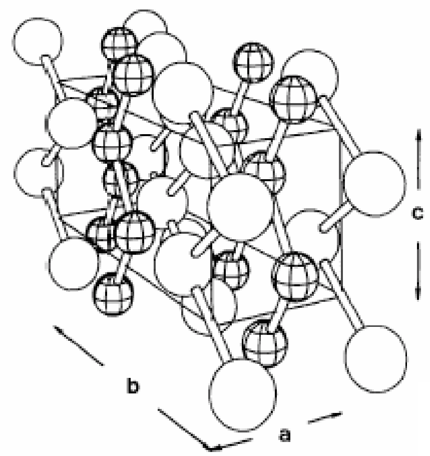
Wavefunctions of the *f*-electrons







The RNi family



LaNi, CeNi, PrNi, NdNi & GdNi are isostructural CrB-type orthorhombic intermetallic compounds, Space group Cmcm

Magnetic properties:

CeNi – intermediate valence regime (E_{KONDO}=26 meV), enhanced Pauli paramagnetism

GdNi – pure spin ferromagnetism (J=S=7/2, T_c=70K)

NdNi – ferromagnetism (Kramers ions, T_c=28K)

PrNi - singlet crystal field ground state ferromagnetism (soft magnetic mode driven ordering, T_c=21K)

LaNi - nonmagnetic reference compound

Ni is nonmagnetic in the RNi series

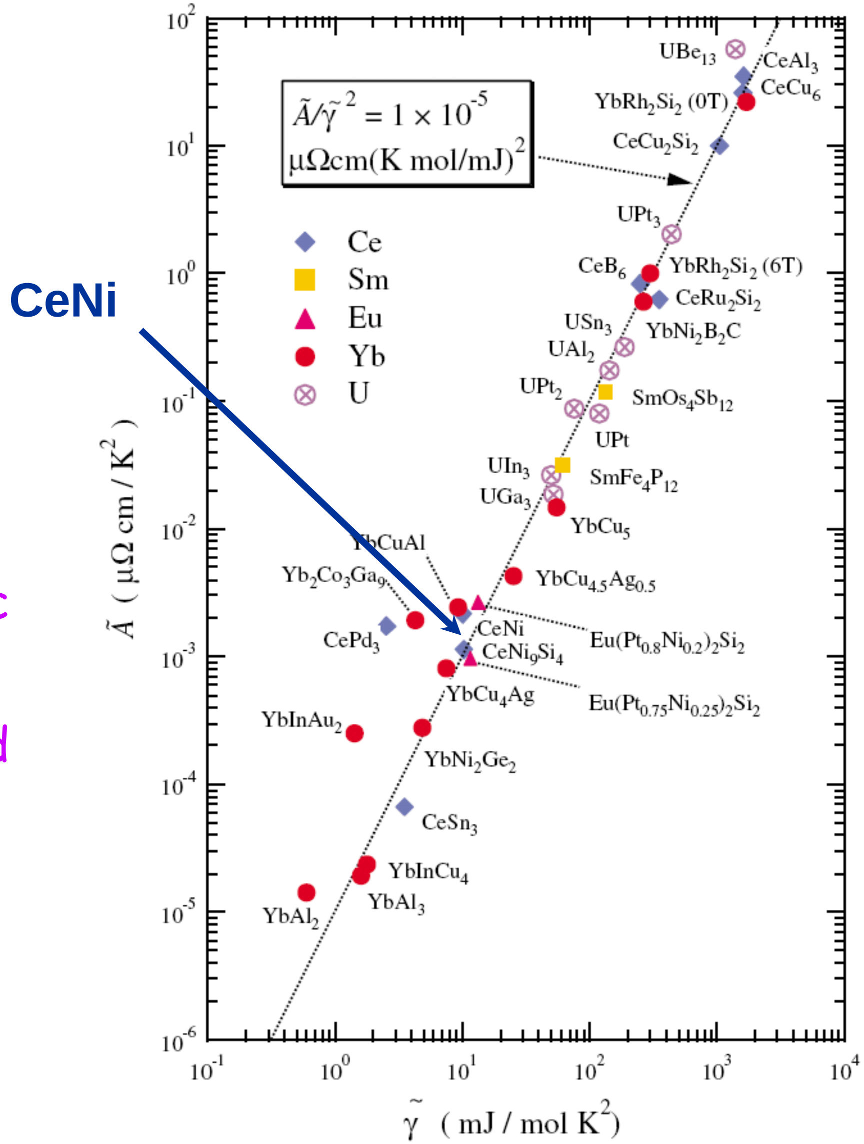
CeNi. The basic facts

usual intermediate valence features:

- many-particle nonmagnetic singlet GS
- Kondo energy 26 meV
- cerium valence 3.14 at T=10K
- γ = 65 mJ/(mol K^2)

specific features:

- valence strongly depends on Temp.
- narrow coherent peaks in the magnetic spectra (neutron scatt. data)
- anomalous phonon softening with T and compared to LaNi (by ~ 30%)
- anomalous thermal expansion
- a good model system for δ-Pu
- volume collapse under low pressure



Volume collapse in CeNi (old data, 1985)

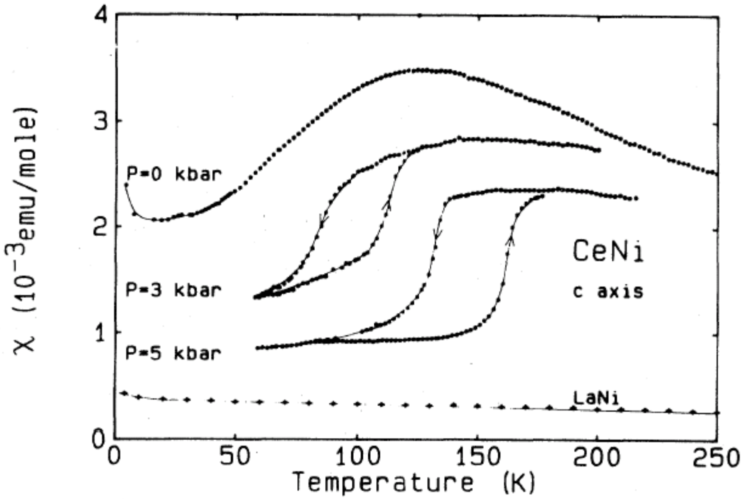
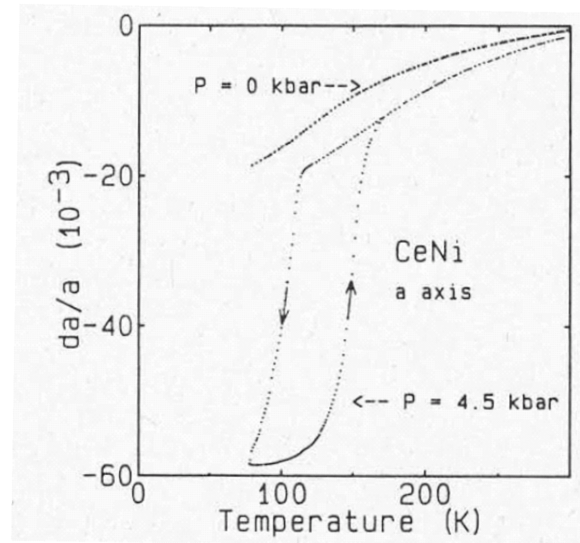


FIG. 1. Thermal variations of the susceptibility of CeNi measured along the **c** axis of the orthorhombic cell at room pressure and under 3 and 5 kbar. Thermal variation of the susceptibility of a polycrystalline sample of LaNi at room pressure.



First order phase transition in CeNi was observed in 1985 by D. Gignoux & G. Voiron PRB 32 (1985) 4822

The structure of the high-pressure CeNi phase remained a puzzle after 27 years and numerous experiments

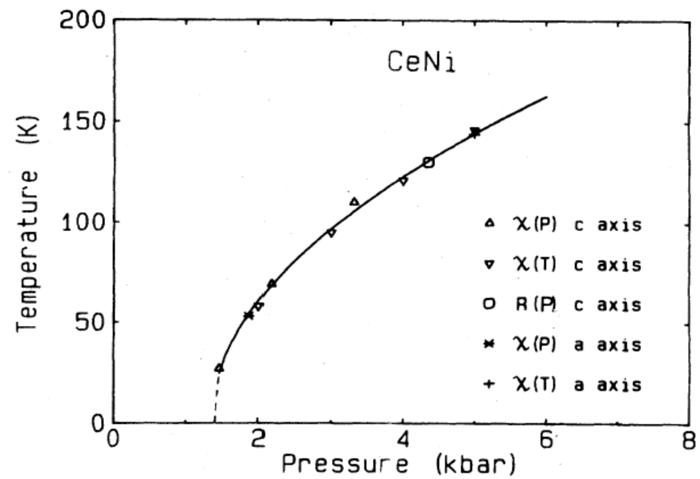


FIG. 5. *T-P* diagram of the low and high magnetic states in CeNi.

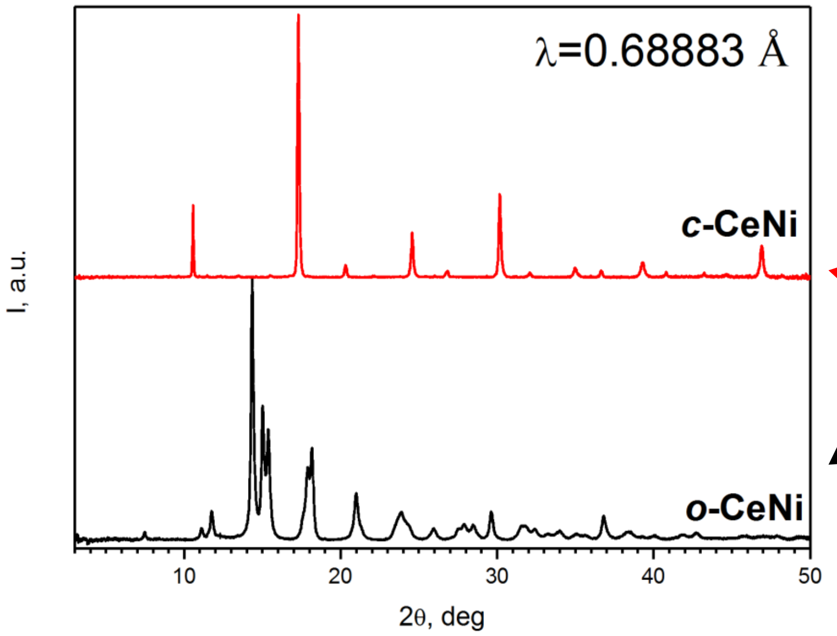
Breakthrough and key factor: metastable CeNi phase

A. Tsvyaschenko and collaborators
Institute for High Pressure Physics, RAS
Troitsk

High temperature synthesis at P ~ 9 Gpa
Sample mass ~ 300 mg

Single phase samples !!!!

Synchrotron XRD on metastable CeNi



XRD was measured on the STM beamline, Sibir-2 synchrotron, Moscow

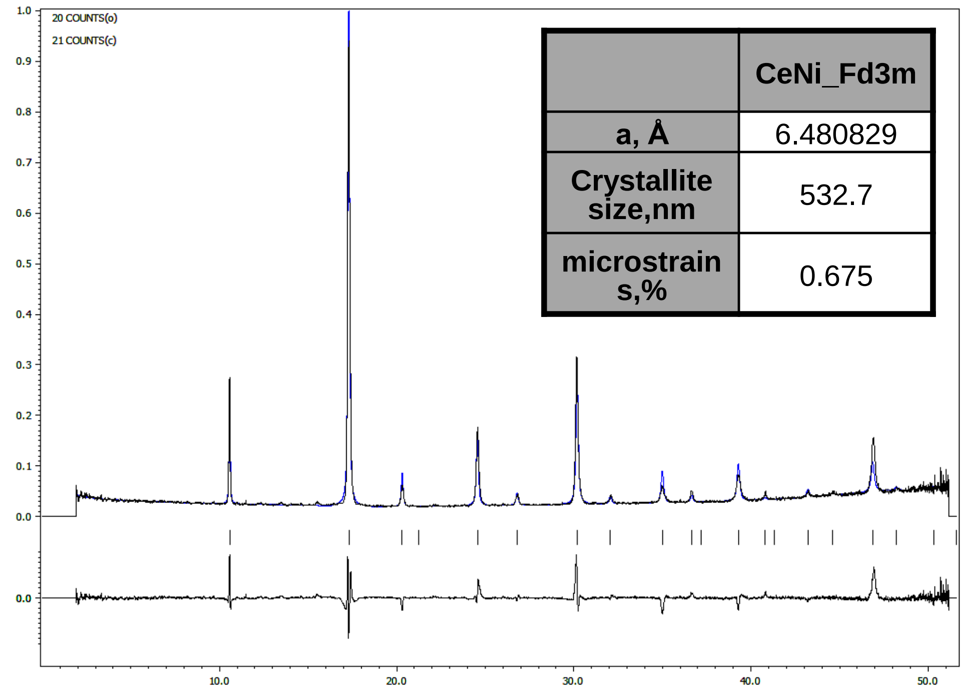
metastable phase

parent orthorhombic phase

The outcome of the full profile structure refinment:

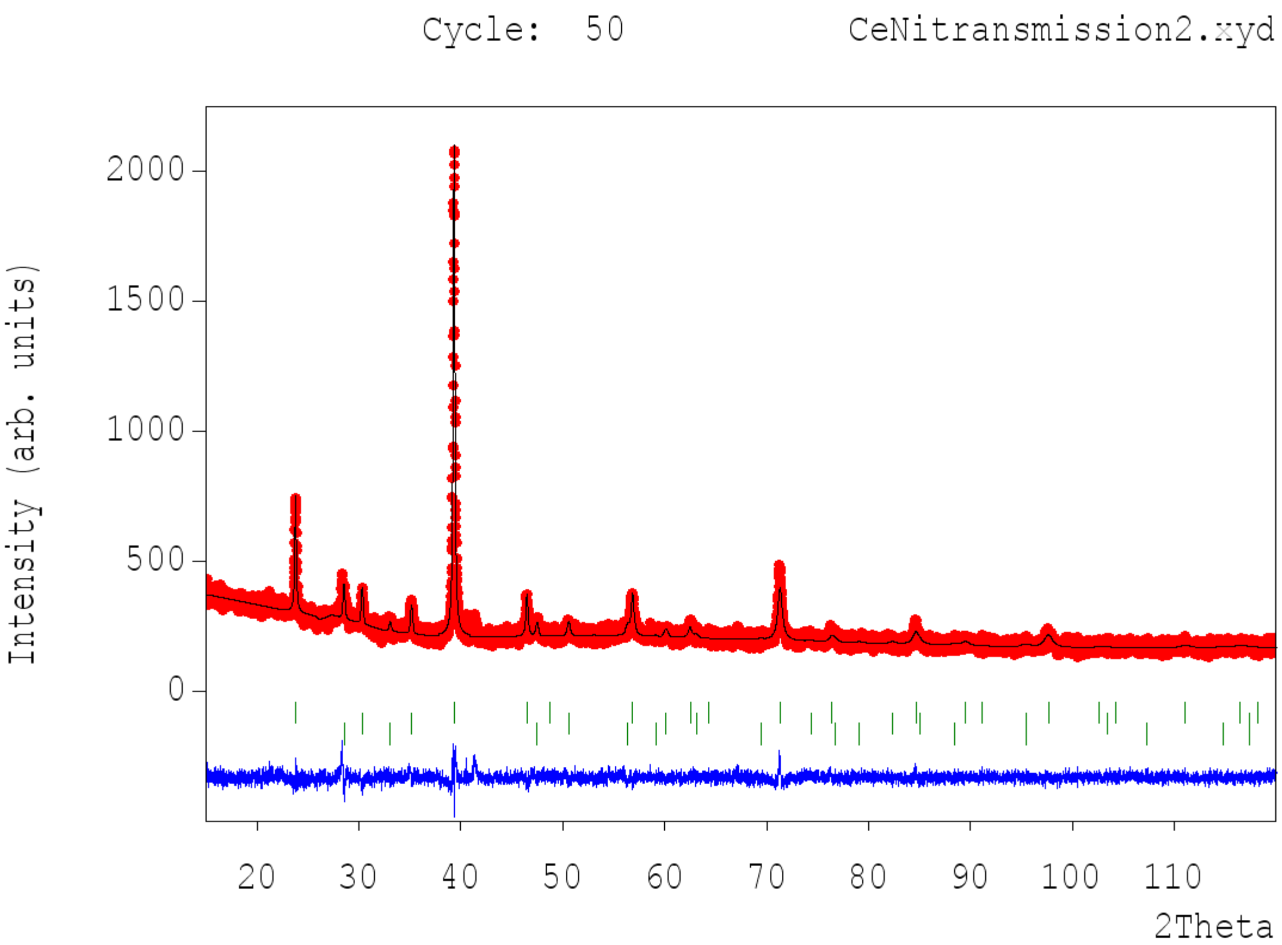
cubic symmetry, space group Fd3m

LiAl structure type

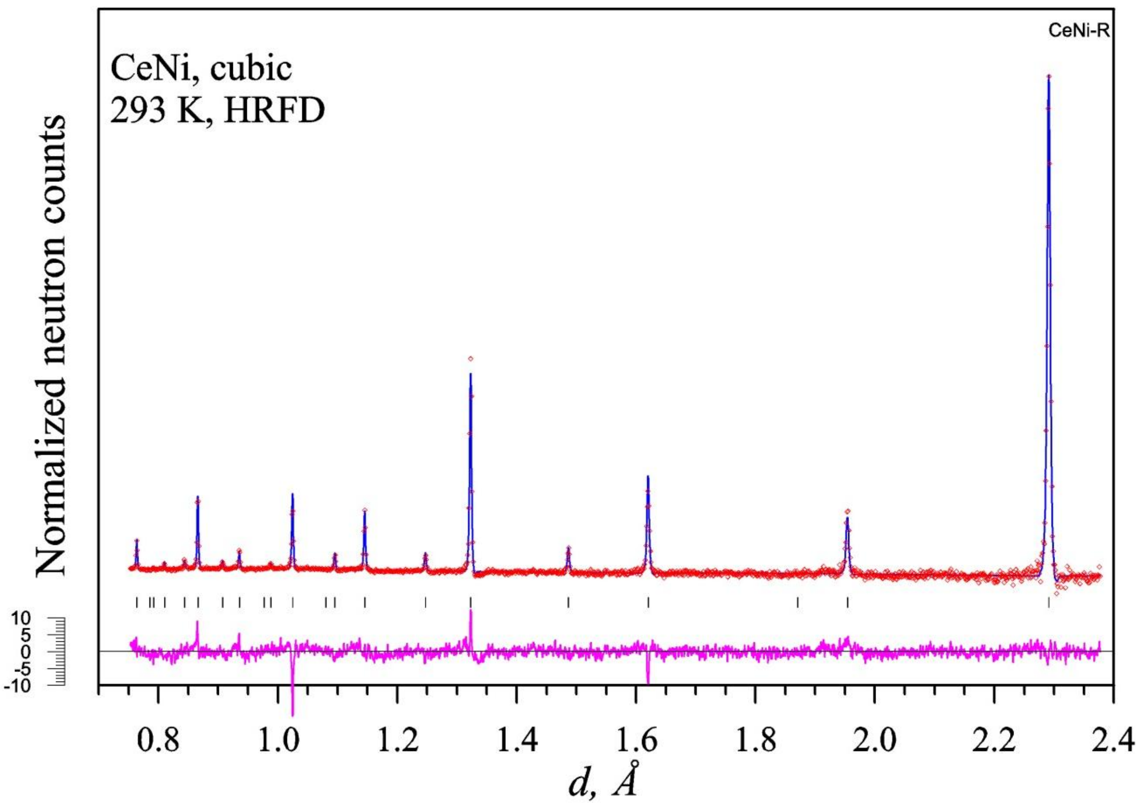


	CeNi_Fd3m
a, Å	6.480829
Crystallite size,nm	532.7
microstrains,%	0.675

CeNi diffraction pattern. Laboratory X-Ray instrument



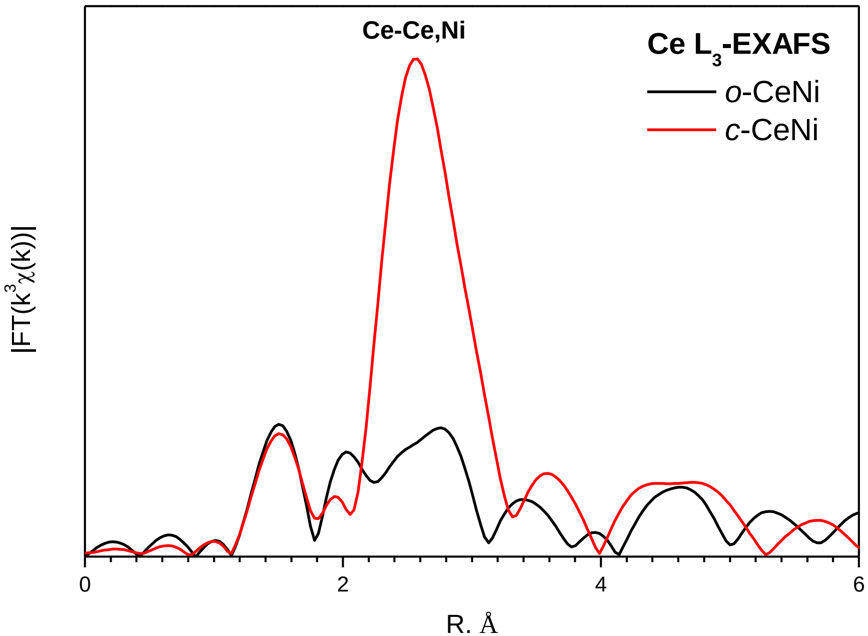
Neutron diffraction on metastable CeNi at T=300K

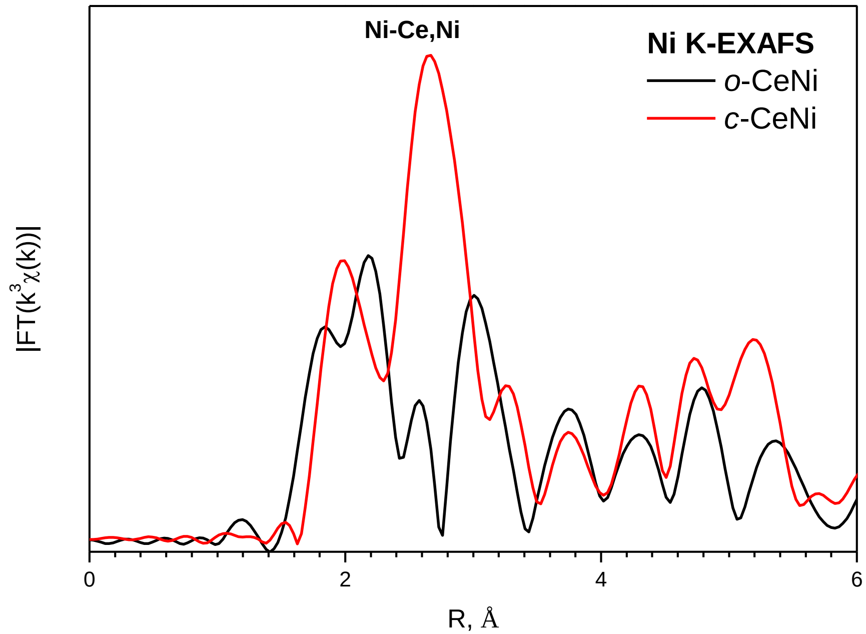


parameter	value
χ^2	1.64
R_w	10.7
R_e	17.4
W0	10.8(1)
W1	4.7(1)
a, Å	6.4796(1)
n(Ce)	0.87(2)
B, Å^2	0.99(5)

High resolution neutron diffraction: HRFD, IBR-2 neutron source

Metastable CeNi. EXAFS data



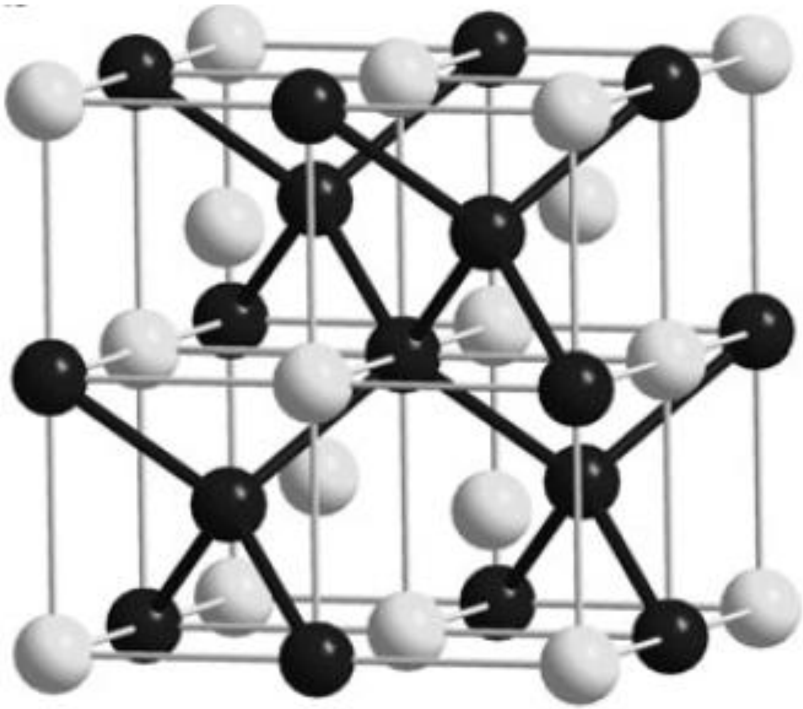


STM beamline, Sibir-2 synchrotron source

EXAFS on Ce L_{III} and Ni K-edges is consistent with the Fd3m space group

LiAl (aka NaTl) crystal structure

Metastable CeNi phase. Crystal structure



CeNi belongs to the Zintl-phase crystal structures with a space group Fd3m (№227),

Ce and Ni positions

(8a): (0 0 0) and

(8b): (½ ½ ½), respectively,

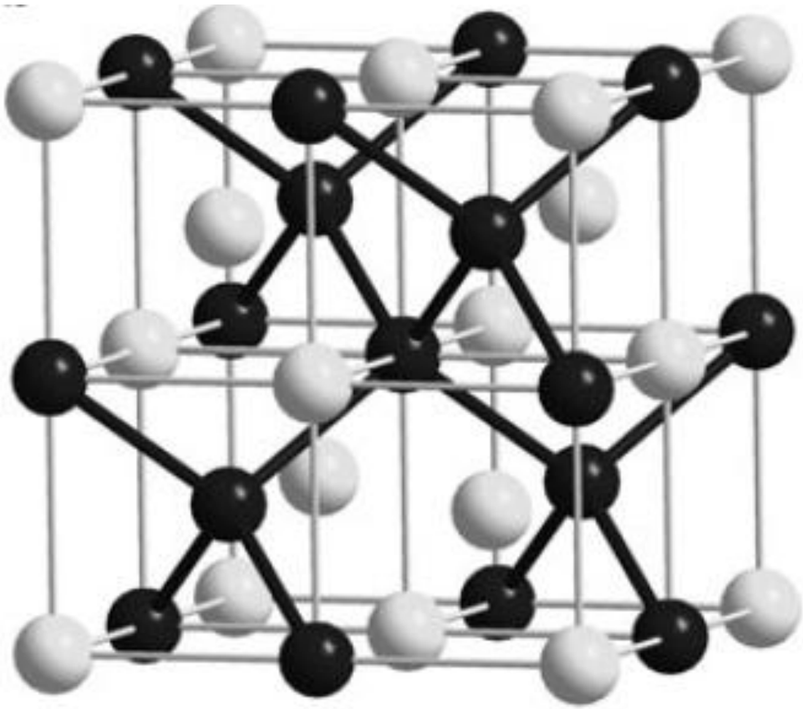
and the lattice spacing

a = 6.4807 Å

LiAl (aka NaTl)

crystal structural type

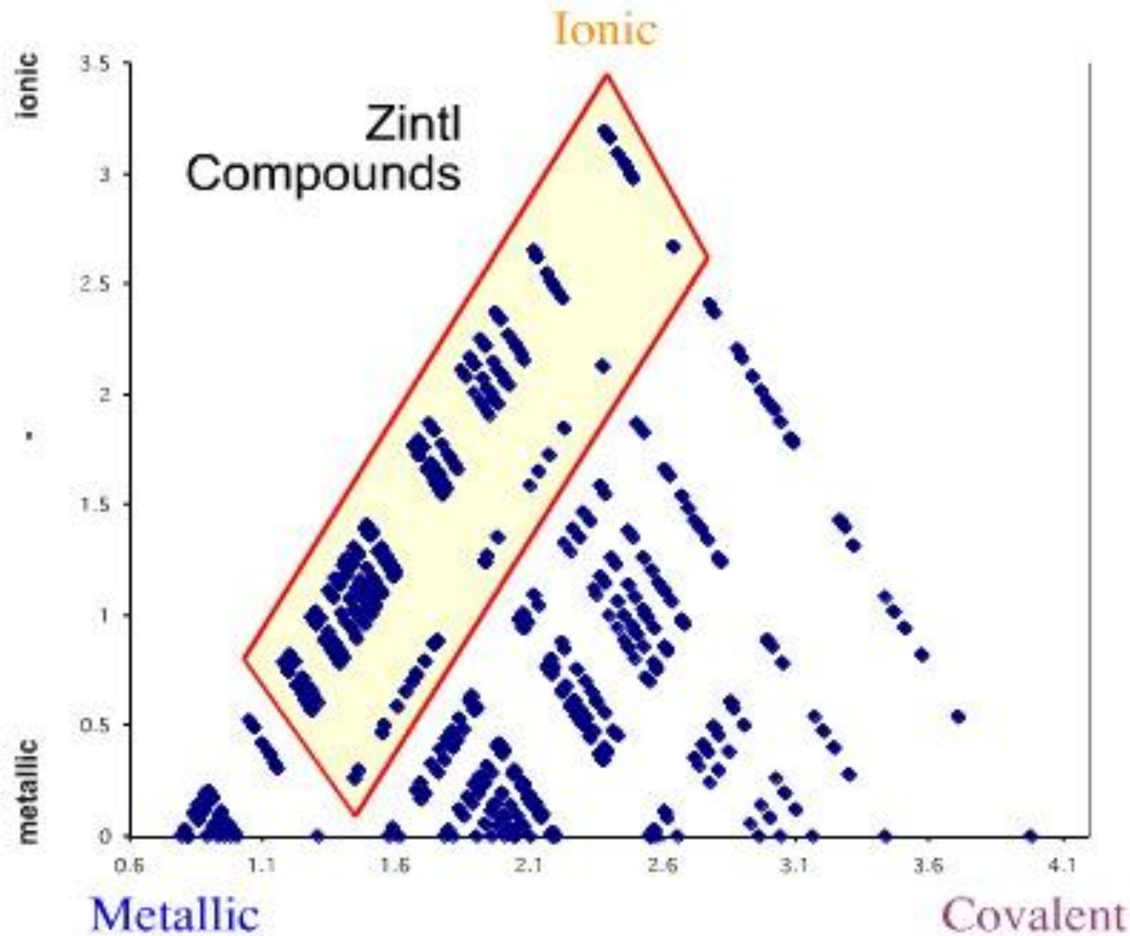
Zintl phase binary systems



Known Zintl binary phases
(since Zintl, 1933)

LiAl
LiCd
LiZn
LiGa
LiIn
NaTl
NaIn

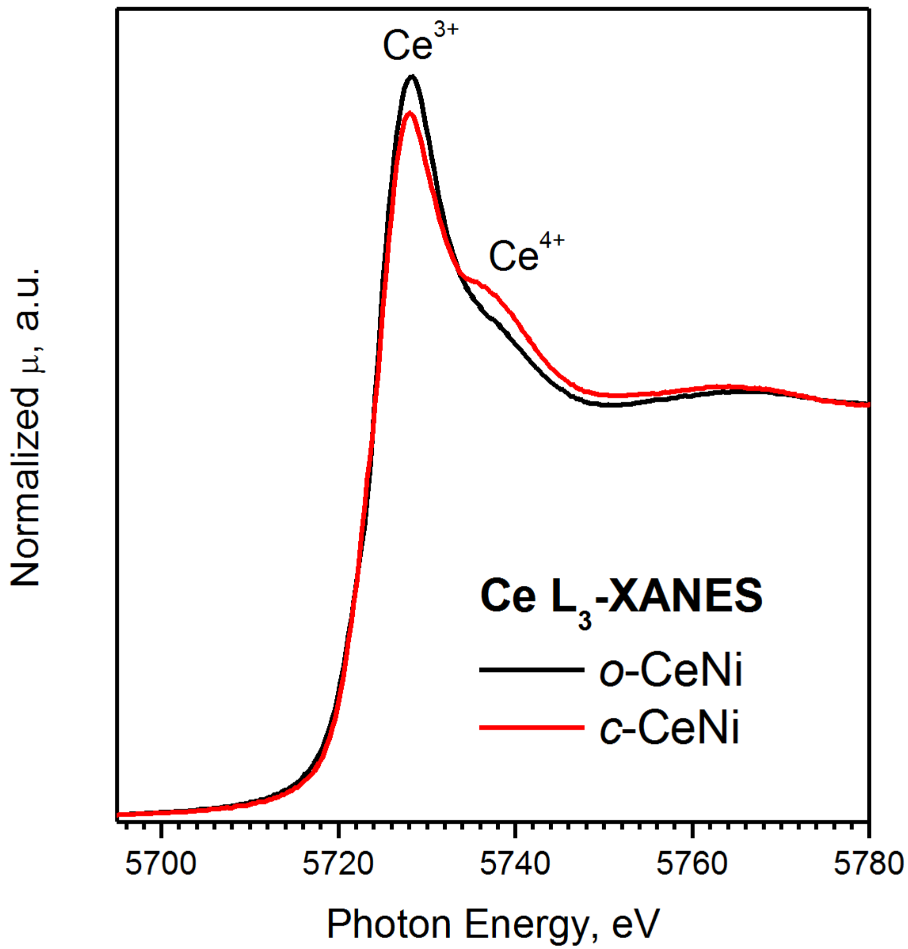
Bonding type & Zintl phases



after W.B. Jensen *J.Chem.Educ.* (1995), **72**, 395)

Metastable and parent phases of CeNi. XANES

STM beamline, Sibir-2 synchrotron source



- effective cerium valence in cubic CeNi is about 3.23 (at room temperature), one of the highest among all intermediate valence cerium-based intermetallics
- the temperature dependence of Ce valence is weak

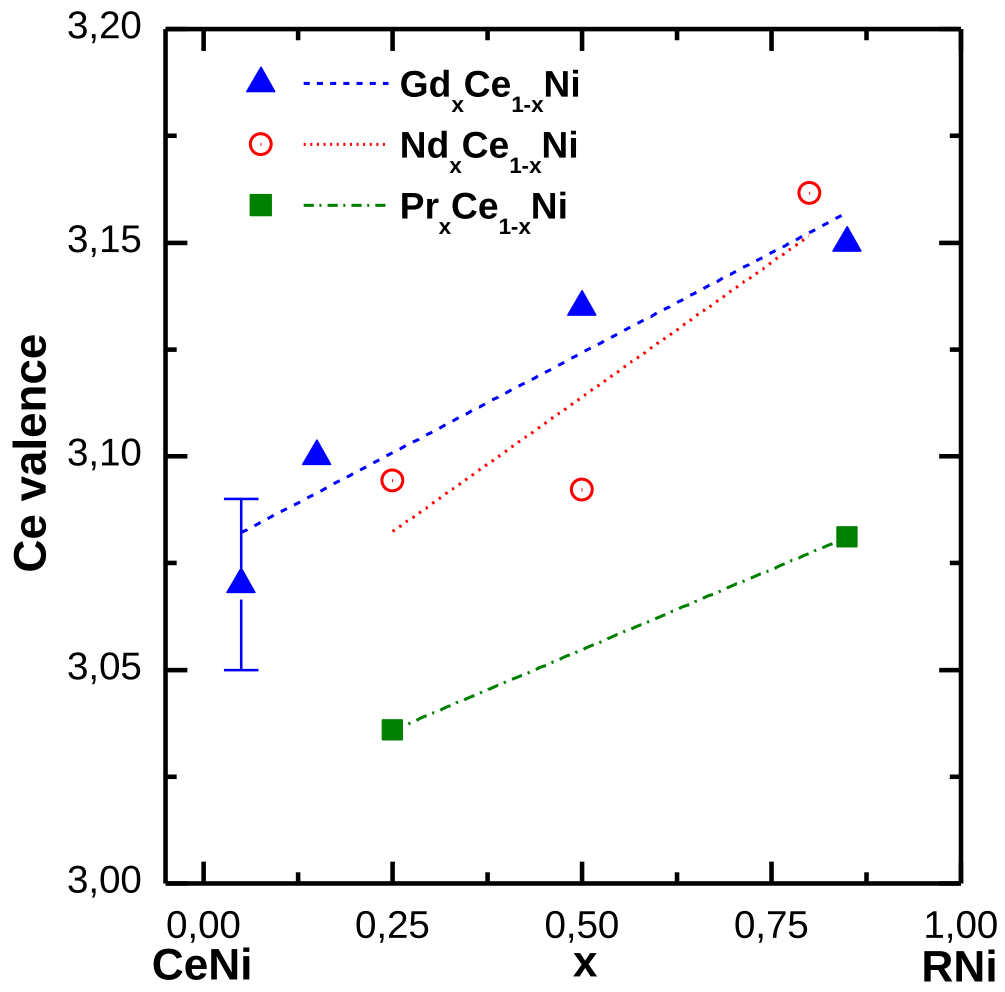
+

- the thermal expansion coefficient is small compared to the parent CeNi phase

Effective cerium valence in $(Gd,Pr,Nd)_xCe_{1-x}Ni$ at T=300K

Synchrotron experiments have been performed at DESY

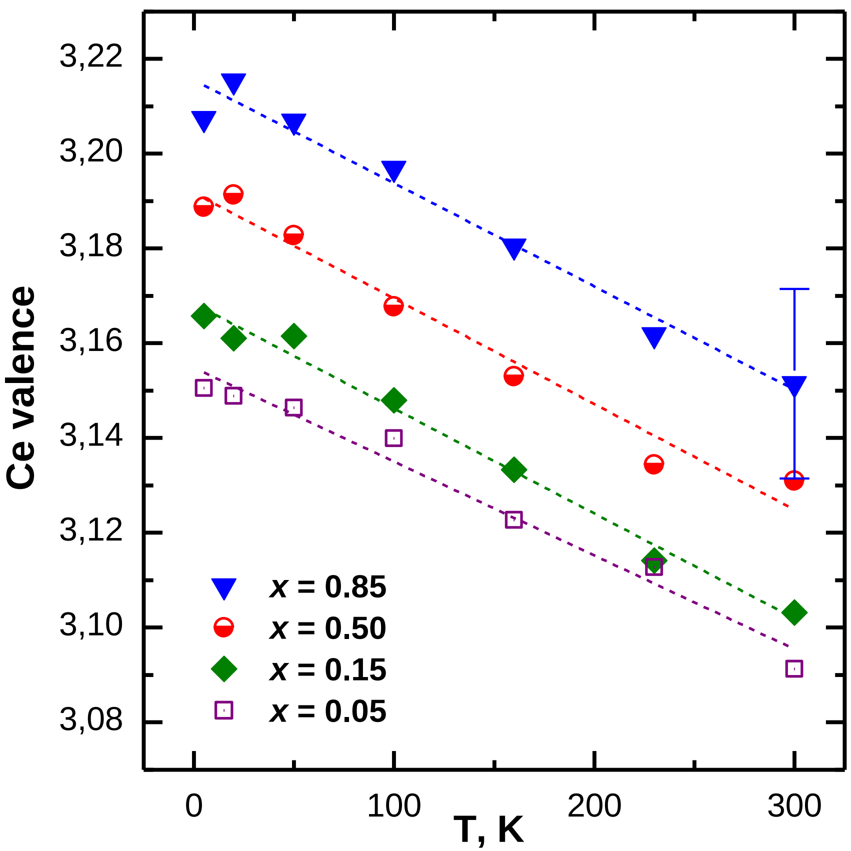
- Ce 4*f* electrons are partialy delocalized in all pseudobinary systems studied by XANES
- the smaller is the dopant the higher is cerium valence (negative chemical pressure effects)



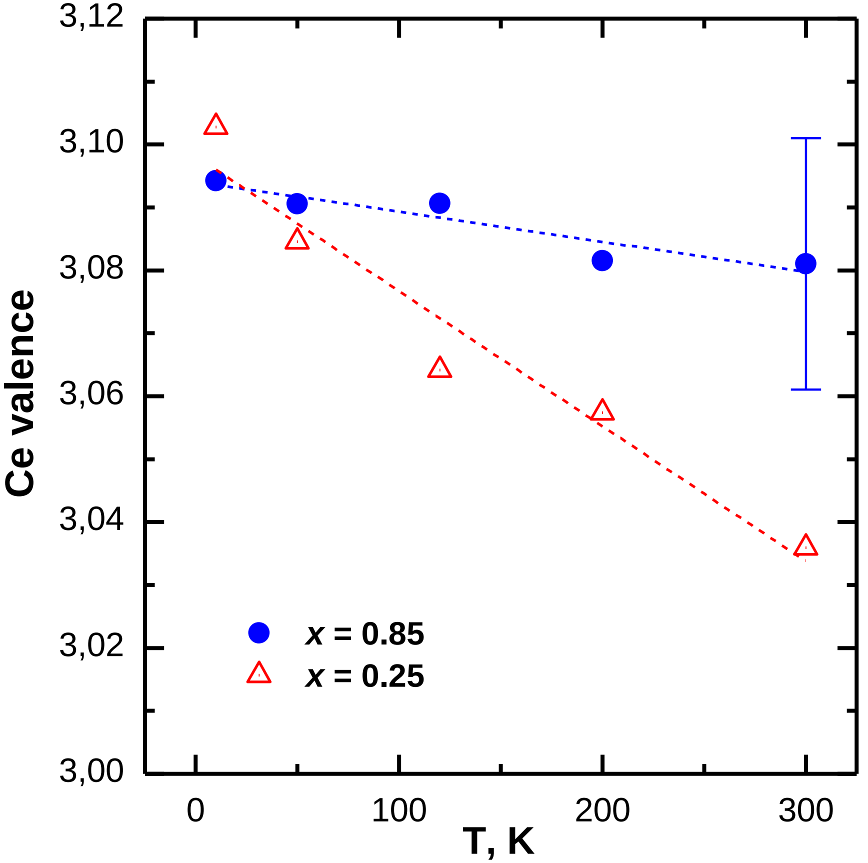
Effective cerium valence in $(Gd,Pr)_xCe_{1-x}Ni$

Synchrotron experiments have been performed at DESY

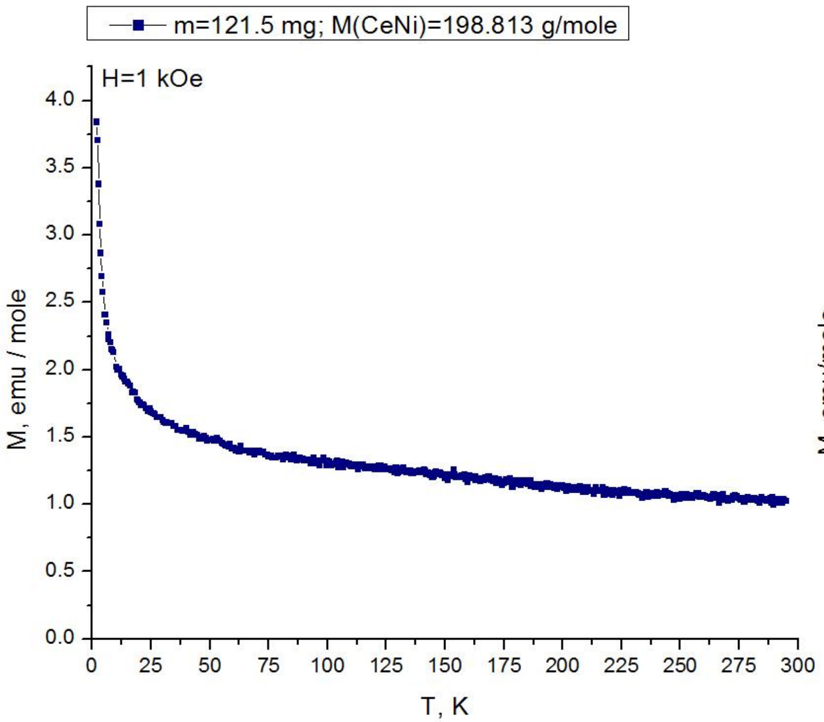
$Gd_xCe_{1-x}Ni$

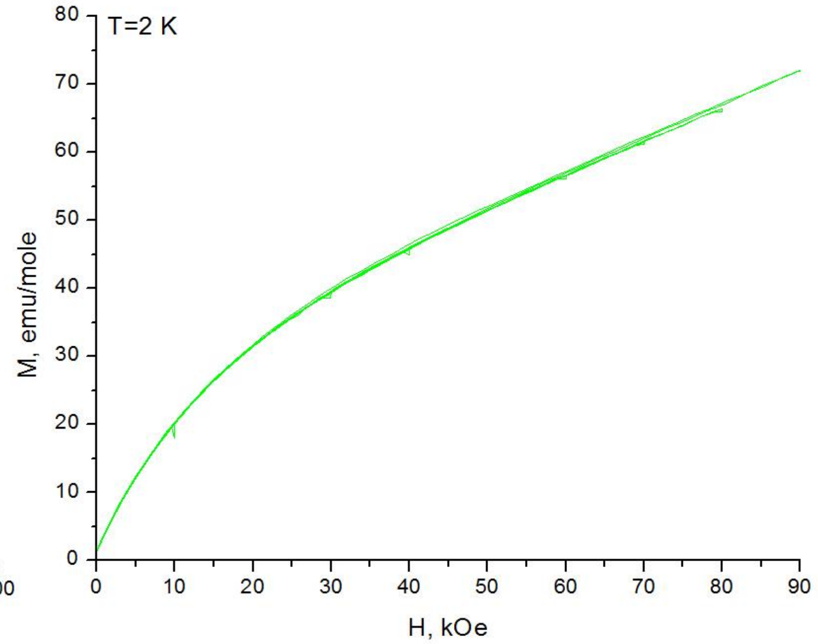


$Pr_xCe_{1-x}Ni$

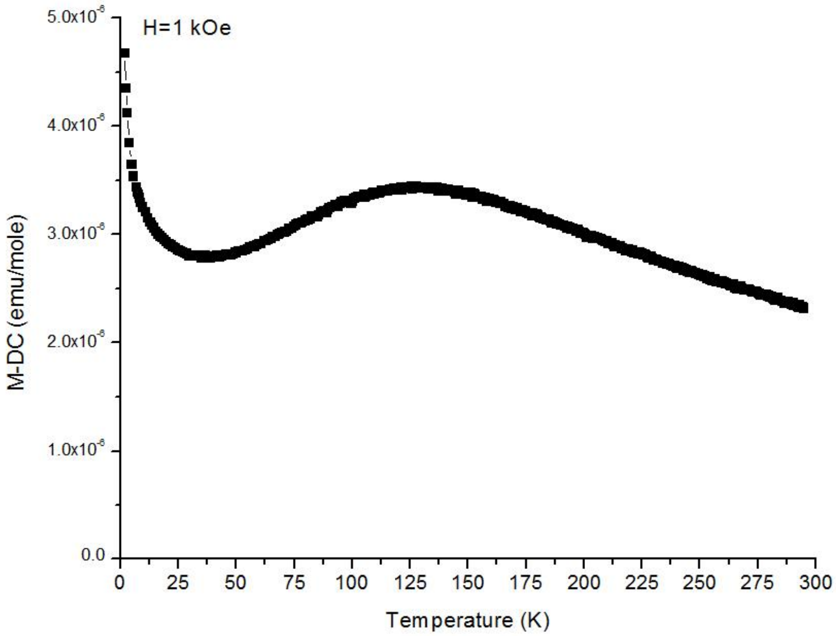


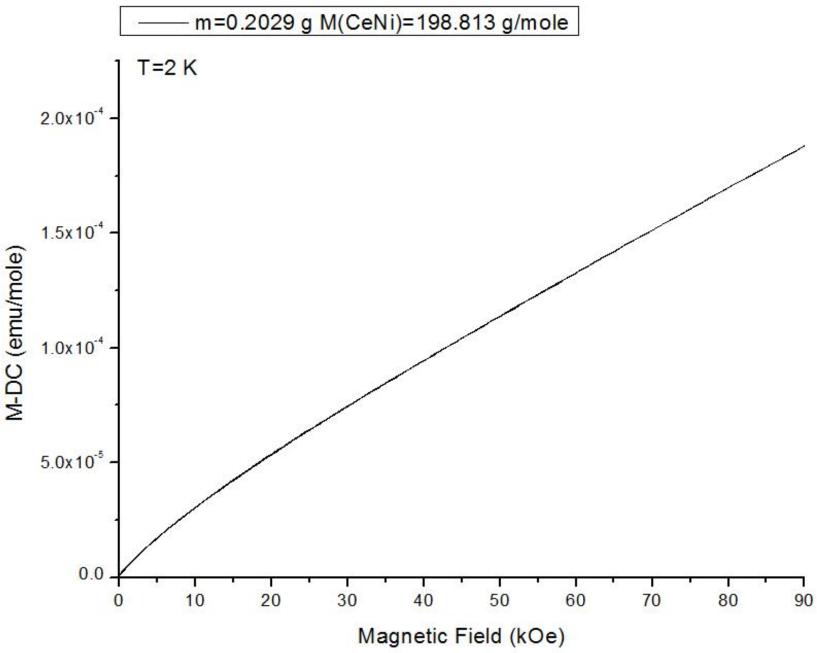
Metastable CeNi. Magnetic properties



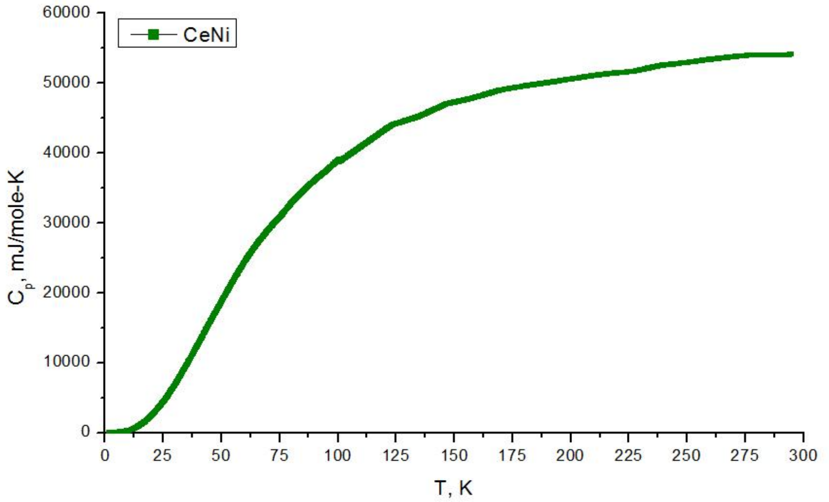


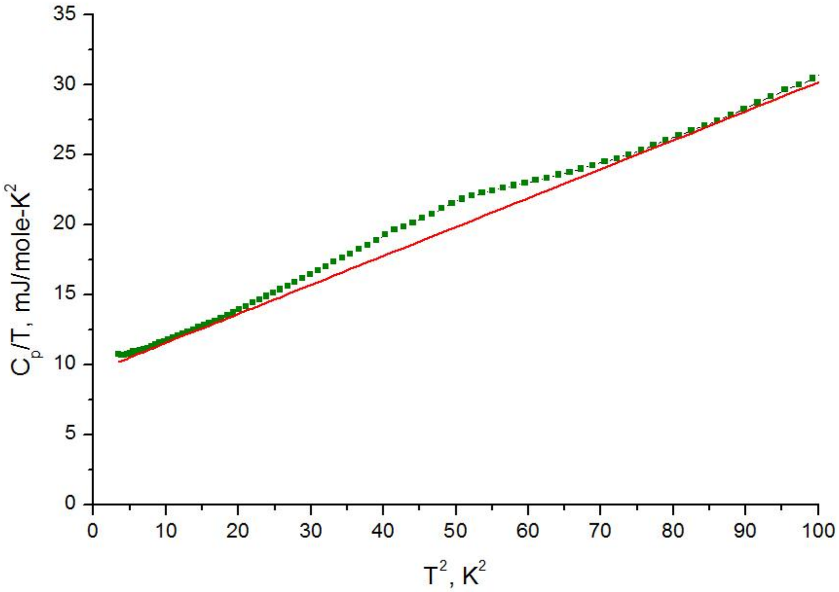
CeNi parent phase. Magnetic properties





Metastable CeNi. Specific heat

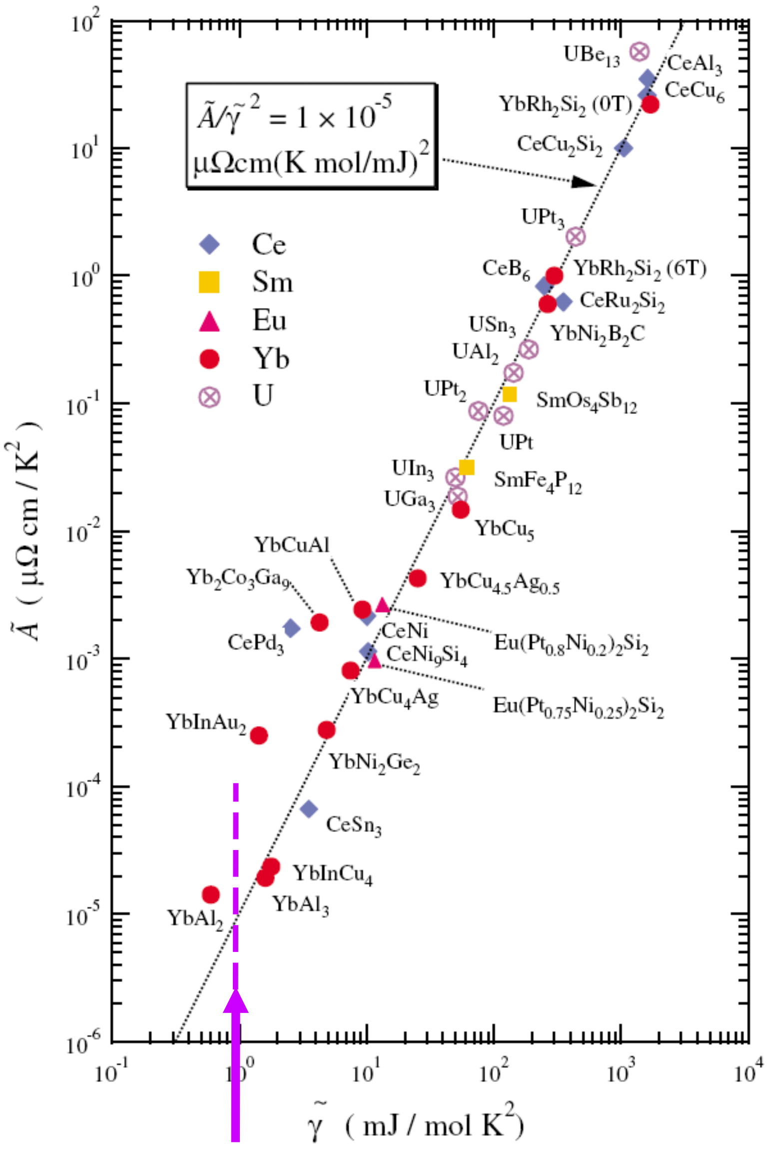




The Sommerfeld coefficient

γ = 9.5 mJ/(mol K^2)

Metastable CeNi on the universal Kadowaki-Woods plot



Conclusion

- a dramatic volume collapse by record high 22% was observed in CeNi
- the structure of the high pressure CeNi phase is cubic, space group Fd3m, LiAl-type (first Zintl phase among the *d*- & *f*-electron-based intermetallics)
- compared to the "parent" orthorhombic phase of CeNi the volume-collapsed phase of CeNi demonstrate much higher degree of the 4*f* electron delocalization and one of the highest deviations of the Ce ions valence from the 3+ state.
- the Sommerfeld coefficient in metastable CeNi is 9.5 mJ/(mol K^2) which is pretty low for an intermediate valence cerium-based compound.