Propriétés thermophysiques des métaux à très hautes températures par chauffage résistif impulsionnel : état de l'art

<u>M. Boivineau</u>
Commissariat à l'énergie atomique et aux énergies alternatives (CEA)
Centre DAM Île-de-France, Bruyères-le-Châtel

G. Pottlacher
Institut für Experimentalphysik, Technische Universität
Graz, Austria

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"Thermophysical properties of metals at very high temperatures obtained by dynamic heating techniques: recent advances"

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from multispectral pyrometry to laser polarimetry

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Millisecond resolution systems

First developed at the end of the 60's by A. Cezairliyan *et al.* at NIST (NBS), Gaithersburg (MD, USA)

- European laboratories : IMGC (F. Righini *et al.* Torino, Italy), INSV (Maglic *et al*., Belgrade, Serbia), ÖGI (Kaschnitz *et al*., Leoben, Austria)
- Asian laboratories : NRLM (Matsumoto *et al*., Ibaraki, Japan), HIT (Fan *et al*., Harbin, China)
- heating rates ~10^4 $K.s^{-1}$

➢ Goals

- thermophysical properties measurements of solid metals (ρ_{el} , C_P, etc.) up to the melting point (~3000 K)
- metrology : determination of melting points (combination of radiance temperature and spectral emissivity measurements)

Microsecond resolution systems

First developed in the early 70's in Russia (Lebedev et al. : Institute of High Temperature) and Martynyuk *et al.* : Patrice Lumumba University in Moscow)

- later on in the 70's by LLNL (Henry *et al.* + Gathers + Shaner + etc., *Livermore, USA), University of Kiel* (Seydel et al., Kiel, Germany)

- 80s : TUG (Jäger + Pottlacher, Graz, Austria) and CEA (Berthault *et al.* + Boivineau *et al.*, France)

- heating rates ~ 10^6 K.s^{-1} to 10^8 K.s^{-1}

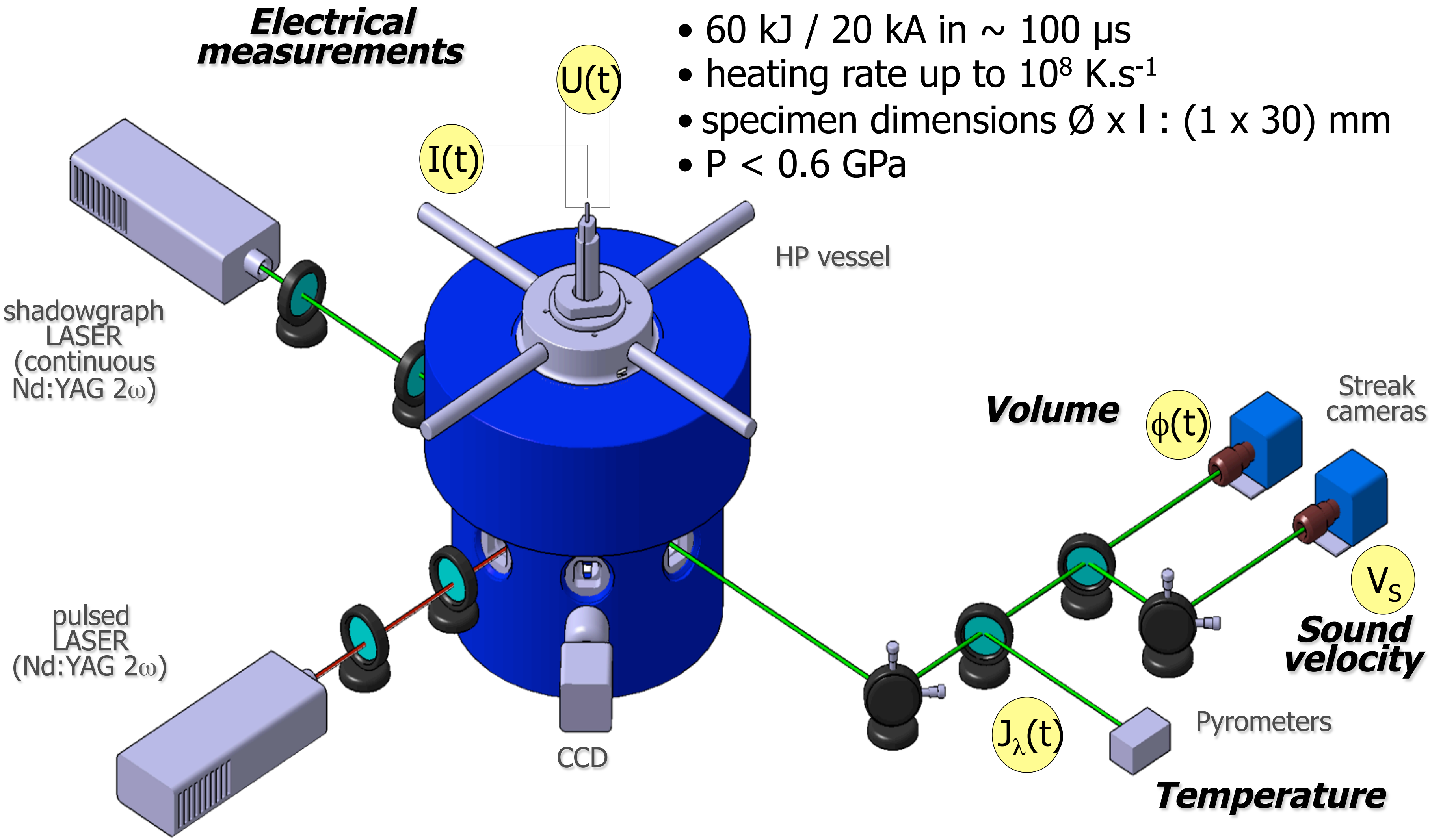
➢Goals

- thermophysical data measurements of solid and liquid metals in the 2000 – 8000 K temperature range (attention onto refractory liquid metals: Nb, Mo, Re, Ta, W, etc.)
- determination of critical points (pressure vessels)

II. CEA experimental device and available data

CEA device

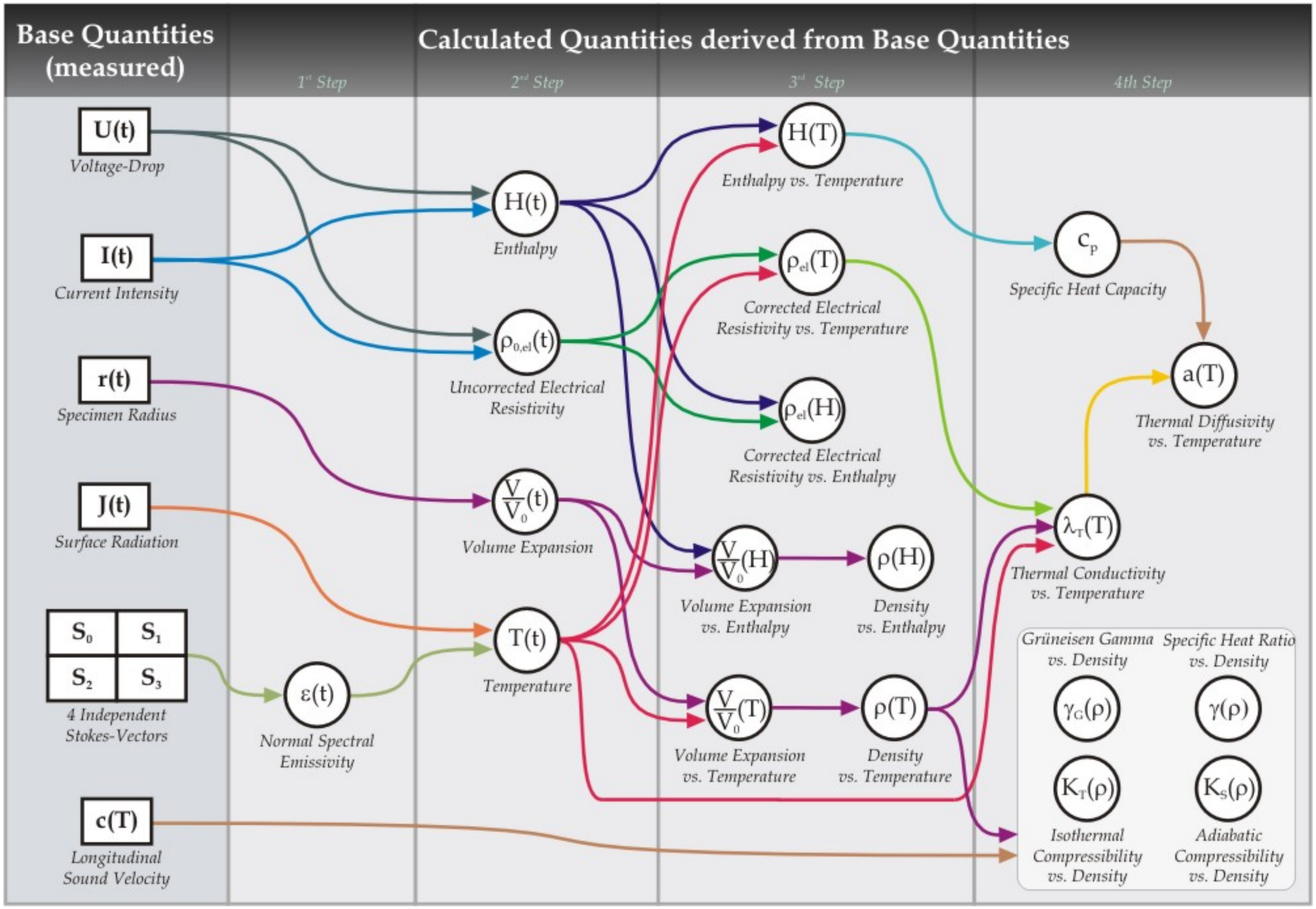
- 60 kJ / 20 kA in ~ 100 µs
- heating rate up to 10^8 K.s^{-1}
- specimen dimensions Ø x l : (1 x 30) mm
- P < 0.6 GPa



λ = 450, 600, 750, 900 nm

NB : high-speed measurements before sample's collapse

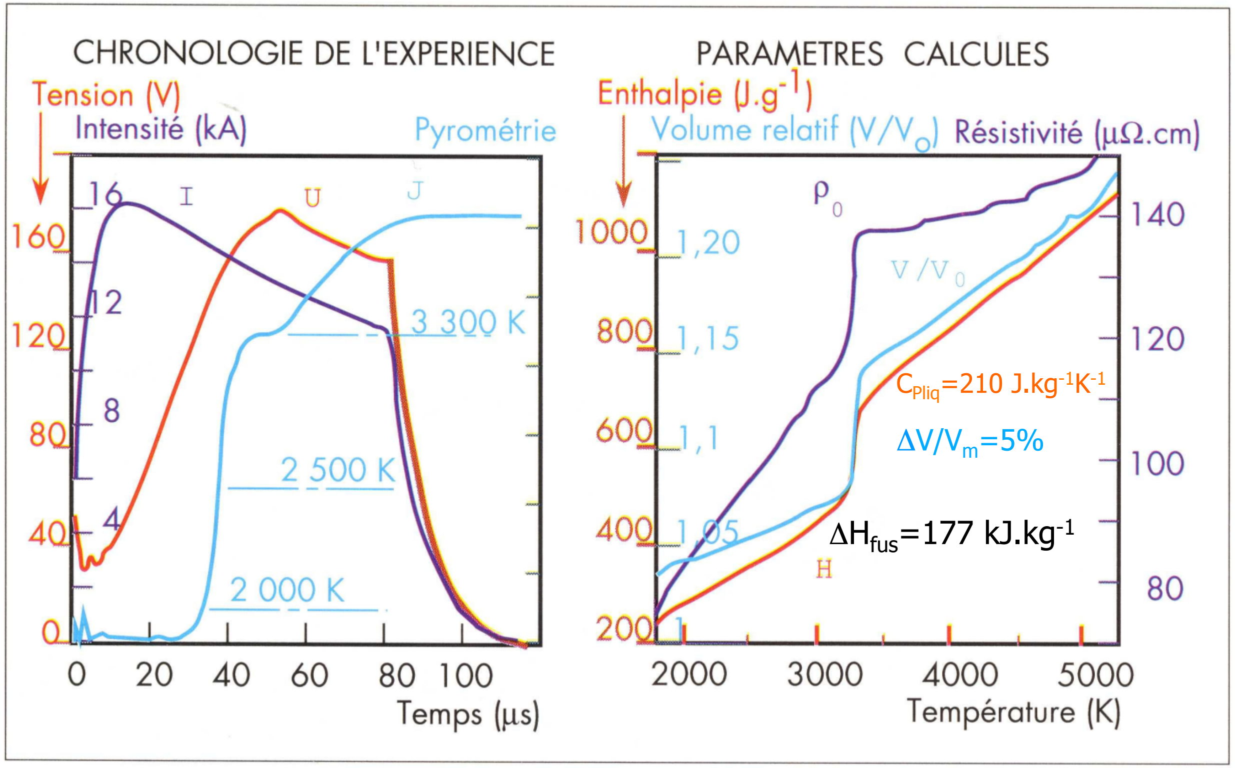
Updated table of measured quantities and calculated parameters

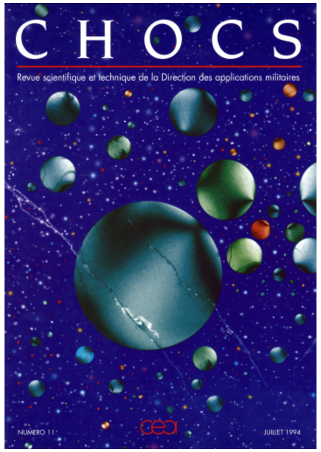


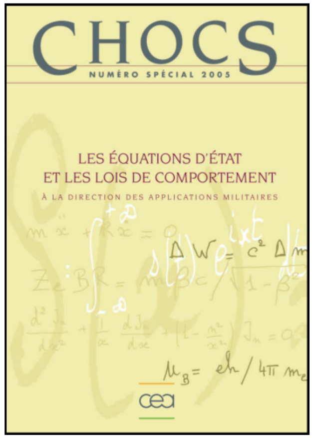
III. Thermophysical properties : A few examples

III.1 Pure metals

Example of a refractory material : Ta







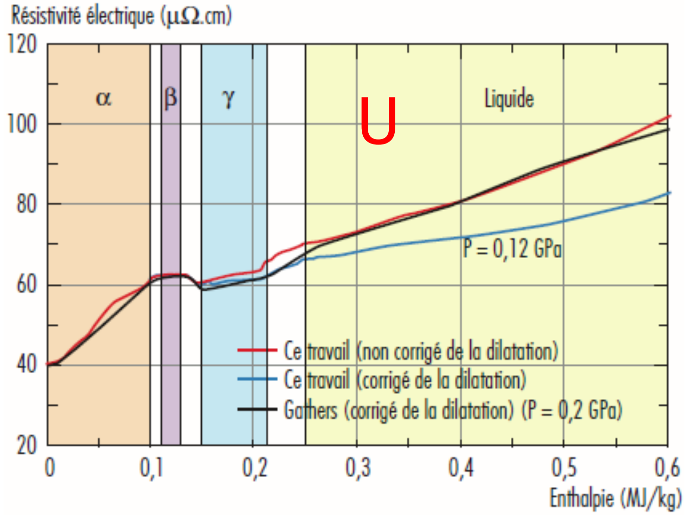
NB : pas de transition solide-solide pour Ta

Thévenin *et al.*, *chocs*, <u>11</u> (3), 65-74 (1994) – “Caractérisation des matériaux”

M. Boivineau, *chocs*, n° spécial « Equations d’état et lois de comportement » (2005)

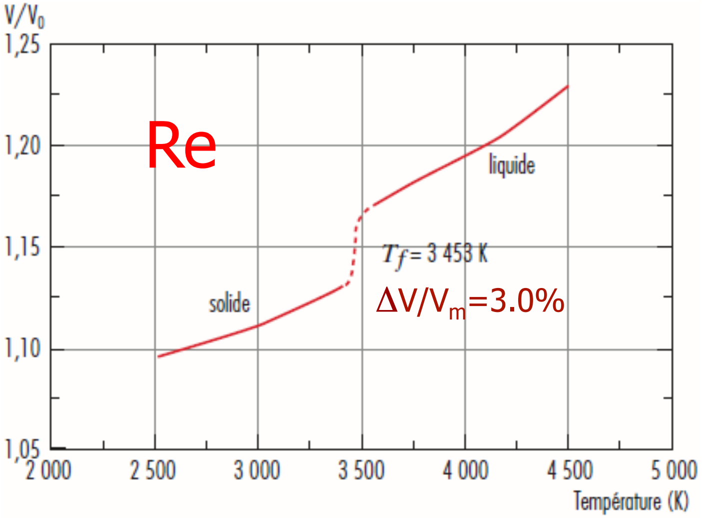
III. Thermophysical properties : pure metals

U, Th, Re examples



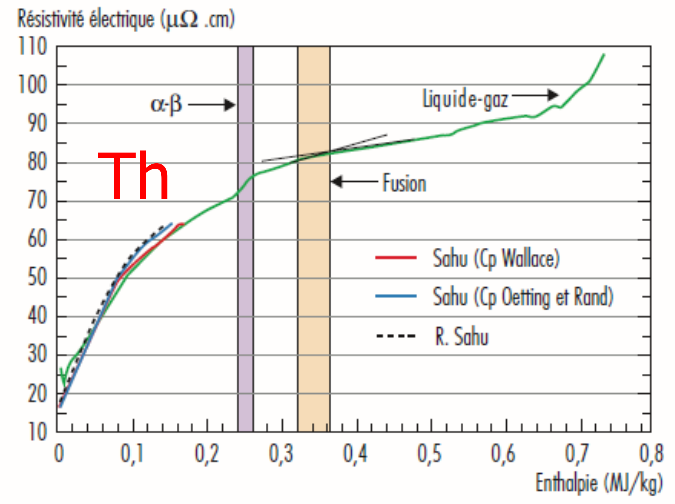
Boivineau *et al.*, Physica B, 190, 31-39 (1993)

Boivineau, *chocs*, n° spécial EE et LdC (2005)

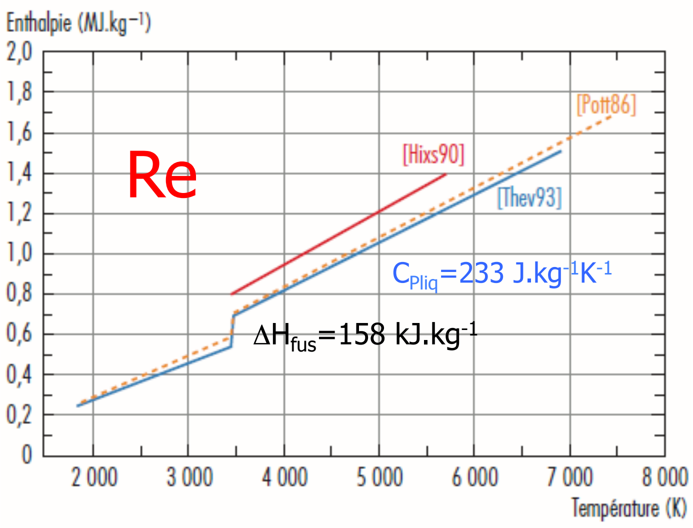


Thévenin *et al.*, IJT, 14 (3), 427-440 (1993)

Boivineau, *chocs*, n° spécial EE et LdC (2005)



Boivineau *et al.*, IJT, 17 (5), 1001-1011 (1996)



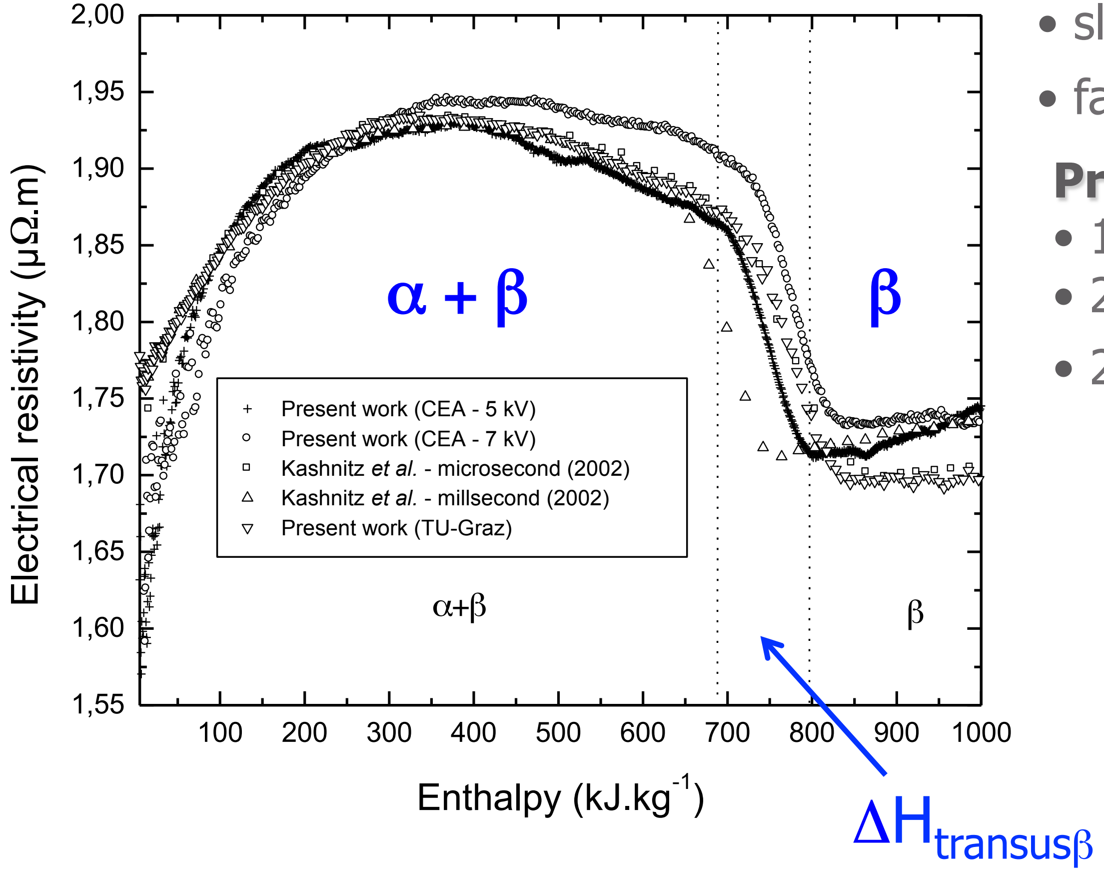
III. Thermophysical properties : A few examples

III.2 Alloys (e.g. TA6V : Ti90%-Al6%-V4%)

Boivineau et al., Int. J. Thermophys., 27(2), pp 507-529 (2006)

Boivineau et al., Proc. Matériaux 2006, Dijon (2006)

Electrical resistivity (β-transus)

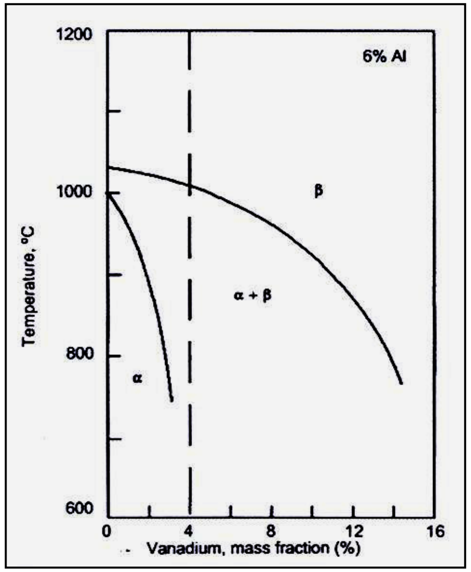


Kaschnitz et al. (2002)

- slow system : 10^3 K.s^{-1}
- fast system : 10^7 K.s^{-1}

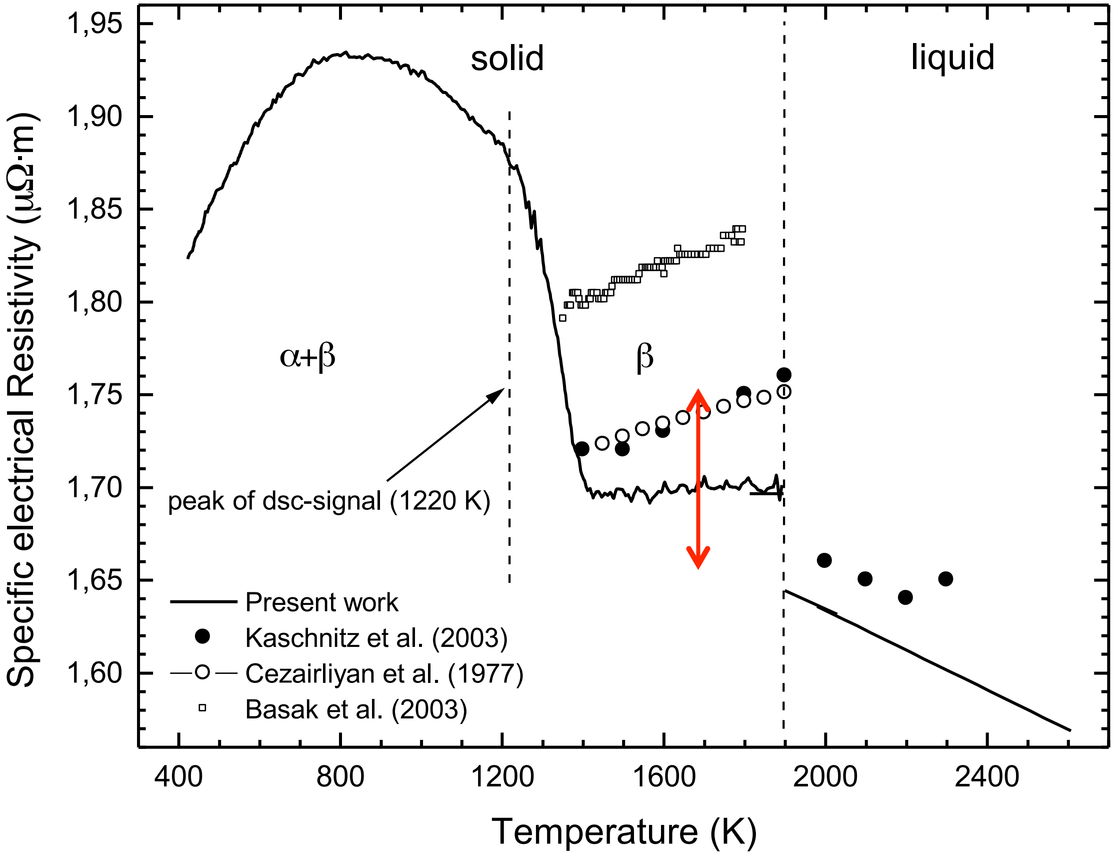
Present work

- 1.3×10^7 K.s^{-1},
- 2.3×10^7 K.s^{-1}
- 2.6×10^7 K.s^{-1}



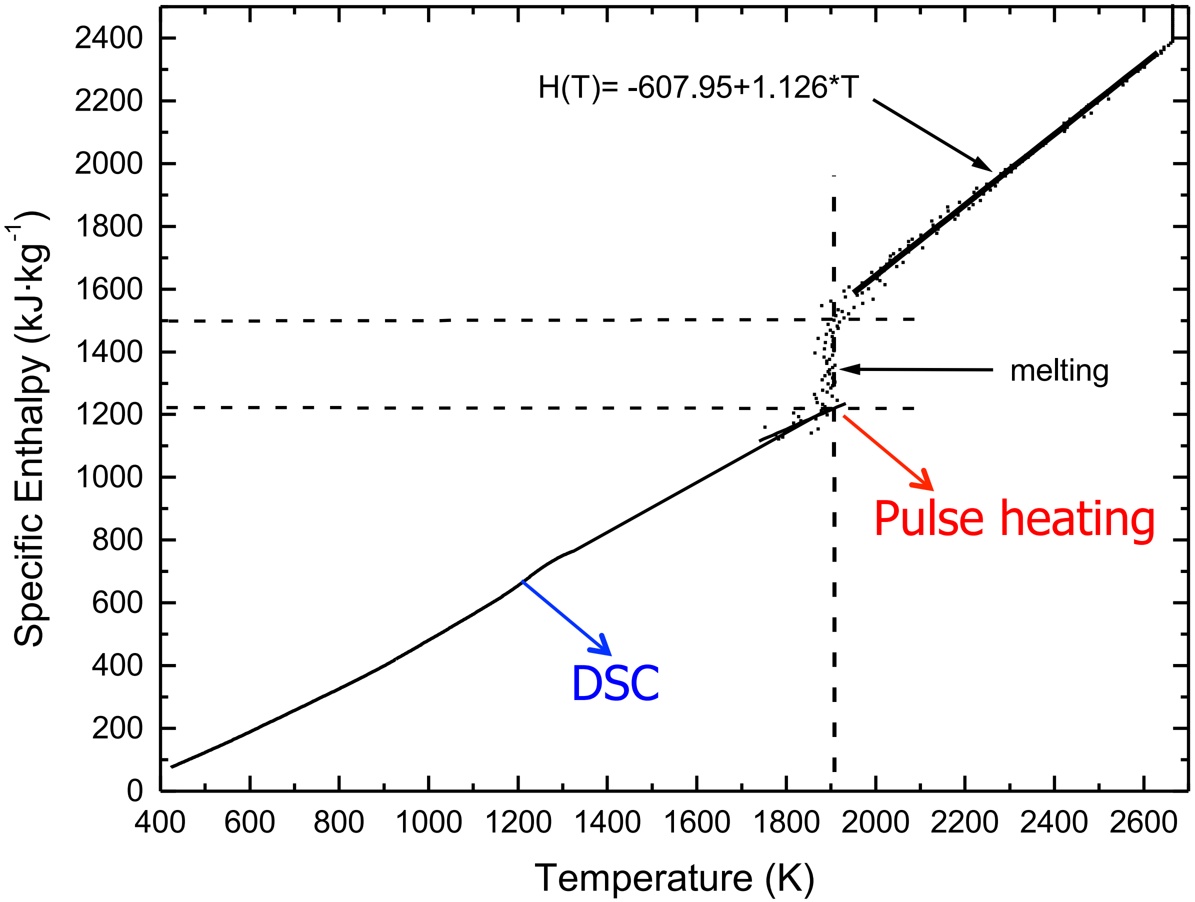
➔ **Strong influence of heating rate**

Electrical resistivity (2)



$\rho_{el0}(T) = 1.85 - 1.07\text{x}10^{-4}.T$ for $Tm < T < 2600$ K

Heat capacity of solid and liquid Ti-6Al-4V



ΔH_m = 290 ± 5 $kJ.kg^{-1}$ present work
ΔH_m = 286 ± 3 $kJ.kg^{-1}$ (McClure, 1992)

IV. Temperature measurements and experimental developments for µs systems :

from multispectral pyrometry to laser polarimetry

The major difficult task for dynamic heating techniques

→ **non-contact techniques (high-speed optical pyrometry)**

⬇

Measurements of surface temperature by using the Wien's law:

$$\frac{1}{T} - \frac{1}{T_R} = \frac{\lambda}{c_2} \log \cdot \varepsilon_{n,\lambda}$$

valid for : $\lambda.\mathrm{T} \leq \frac{\mathrm{C}_2}{4.965} \approx 2900 \mu m.K$

$C_2 = 14388\ \mu m.K$

→ strong need of normal spectral emissivity data

⬇

Large improvement during decades for $\varepsilon_{n,\lambda}$ measurements for millisecond devices : blackbody configuration (NIST, USA), integrating sphere reflectometer (IMGC, Italy)

Millisecond devices concepts **not suited** for faster systems (sample collapse in the liquid phase, obstruction of the blackbody hole) → **multispectral pyrometry**

$$T = \frac{c_2}{\lambda \ln\left\{1 + \boxed{\frac{J_m(T_m)}{J(T)}}\left[\exp\left(\frac{c_2}{\lambda T_m}\right) - 1\right]\right\}}$$

NB : requires the <u>melting plateau</u> observation (reference point)
→ limited to high T_m (> ~ 1500 K)

Difficulties :

- Care of calibration
- very large ΔJ(T) due to the wide ΔT (2000-8000 K) → ~ eight orders of magnitude → logarithmic amplifiers (problems of calibration procedure)
- **unknown emissivity**

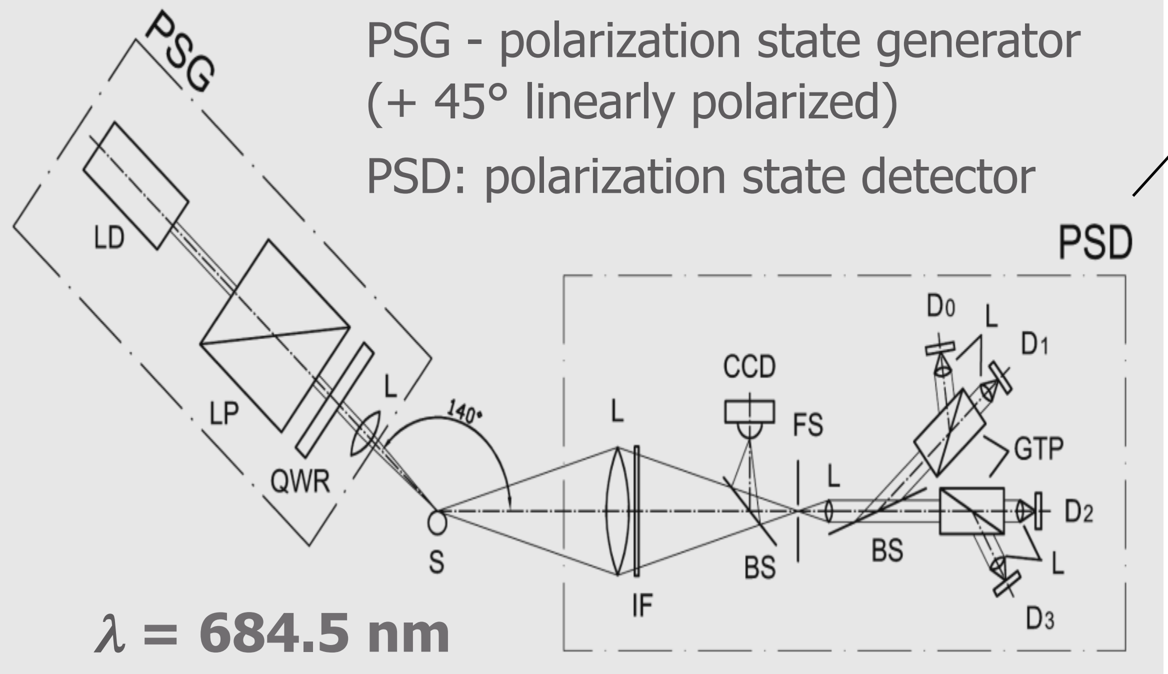
Main assumption $\varepsilon(\lambda,T)/\varepsilon(\lambda,T_M) = 1$ → possible large uncertainties in T measurements at elevated T (> ±10%)

⬇

new concept for ms and μs systems (S. Krishnan) : **laser polarimetry**

TUG laser polarimeter

Basic concept = analysis of the polarization change of the light upon reflection from the wire



PSG - polarization state generator (+ 45° linearly polarized)

PSD: polarization state detector

λ = 684.5 nm

S_i = Stokes vectors

$$\mathbf{I_i \rightarrow S_i\ (i=1,2,3,4)}$$

$\downarrow$

Ellipsometric parameters ψ, Δ

$\downarrow$

Optical constants:
n = refractive index
k = extinction coefficient

$\downarrow$

$$R_\lambda = \frac{(n-n_0)^2+k^2}{(n+n_0)^2+k^2}$$

(normal spectral reflectivity)

$$\varepsilon_\lambda = 1 - R_\lambda \quad \Rightarrow \quad \frac{1}{T}-\frac{1}{T_R}=\frac{\lambda}{c_2}\log\varepsilon_\lambda$$

(T_R determined by visible pyrometry)

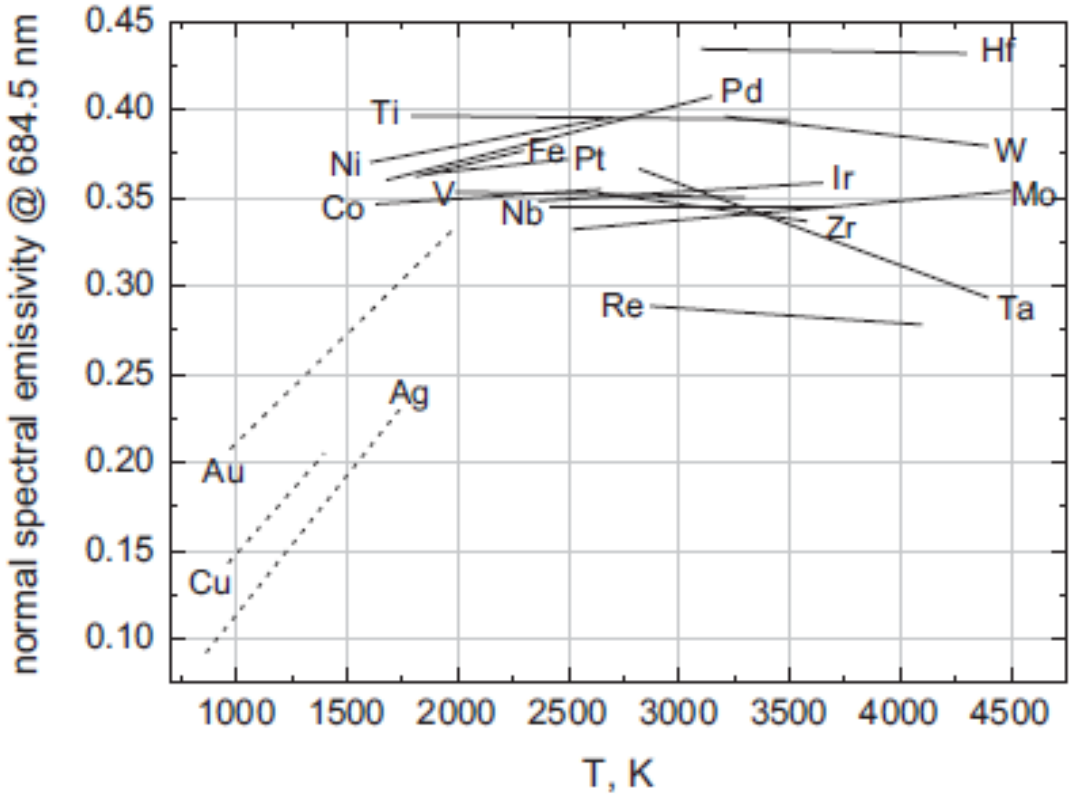
Kirchhoff's law for opaque materials

Seifter *et al.*, IJT, 22, pp. 1537-1547 (2001)

V. Recent experimental data

- Normal spectral emissivity of liquid metals
- Thermal conductivity and thermal diffusivity

Different kinds of behavior…



G. Pottlacher et al., Temperature: its measurement and control in Science and Industry, AIP Conf. Proc., 2013

3 different types of liquid metals at <u>λ=684.5 nm</u> :

- Increase of ε : Au, Ag, Cu, Co, Fe, Ir, Mo, Ni, Pd and Pt.
- Constant ε : Nb.
- Decrease of ε : Ta, Hf, Re, Ti, V, W and Zr.

Thermal conductivity and diffusivity of liquid metals

with the help of the old Wiedemann-Franz law which is known to work well for liquid metals (Cf. Mills et al., Int. Mat. Rev., 41(6), 209-242 (1996))

$T \sim T_m$ ➔ electronic conduction = predominant mechanism for thermal conduction (pure metals)

$$\lambda_T(T) = \frac{L \cdot T}{\rho_{el}(T)}$$

($L = 2{,}45.10^{-8}$ V^2/K^2)

ρ_{el} = electrical resistivity

$$a(T) = \frac{\lambda_T(T)}{c_P(T) \cdot \rho}$$

C_P = heat capacity

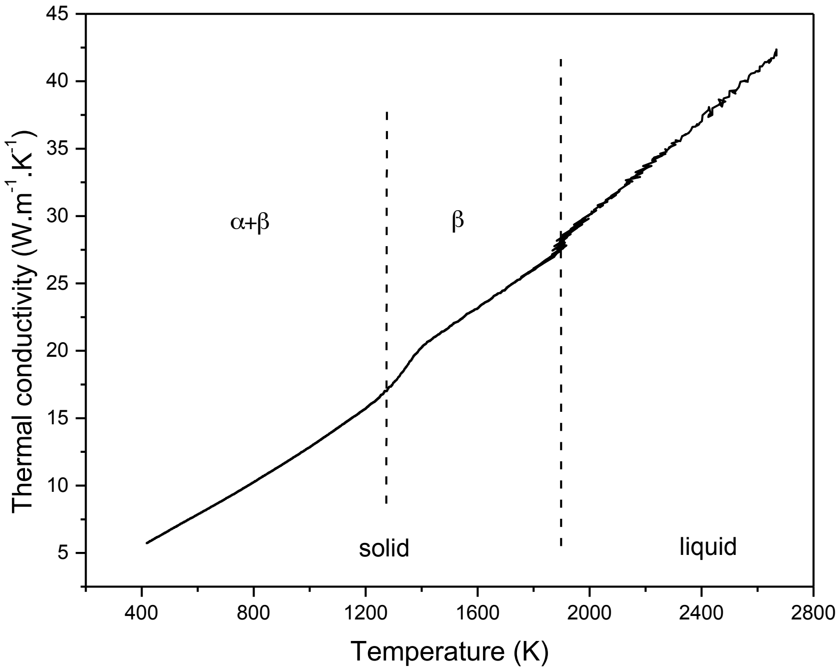
ρ = density

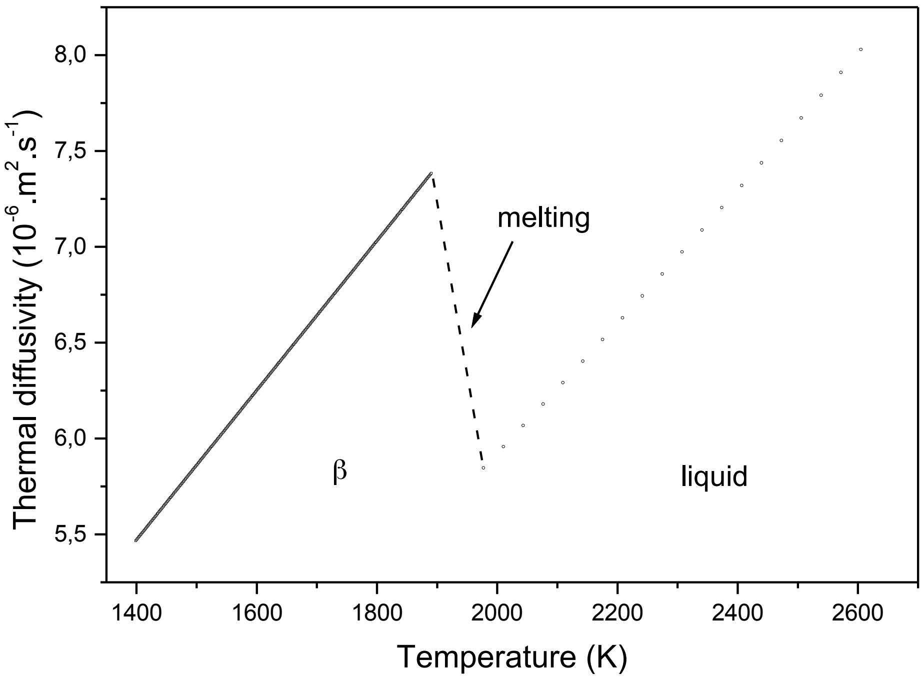
→ Numerous data on pure metals : W, Re, Ta, Mo, Nb, Fe, Co, Ni, Au, Cu, etc.
(Cf. Pottlacher, J. Non-Cryst. Solids, 250-252, 177-18 (1999))

→ Alloys : Inconel 718, Ti-6Al-4V, CF8M stainless steel, Ti-Nb alloys, Fe-Al alloys, Fe-Ni alloys, Ni- or Co-based alloys, We-Re refractory alloys, W-2%ThO_2, etc.

V. Recent experimental data

Thermal conductivity and thermal diffusivity of solid and liquid TA6V





Boivineau et al., IJT, 27(2), pp 507-529 (2006)

Conclusion

- **Microsecond** resistive dynamic heating techniques are well suited for investigating the thermophysical properties of **liquid pure metals** as well as **liquid alloys**
- Temperature measurements : a difficult task

  Need of **normal spectral emissivity** data → laser polarimetry
- From "classical" data, determination of thermal conductivity and thermal diffusivity using the Wiedemann-Franz law
- In addition to **new experimental data** (normal spectral emissivity, sound velocity) the last major advances concern the investigation of **liquid alloys** (NB : strong effect of heating rate for the solid phase)

Acknowlegments

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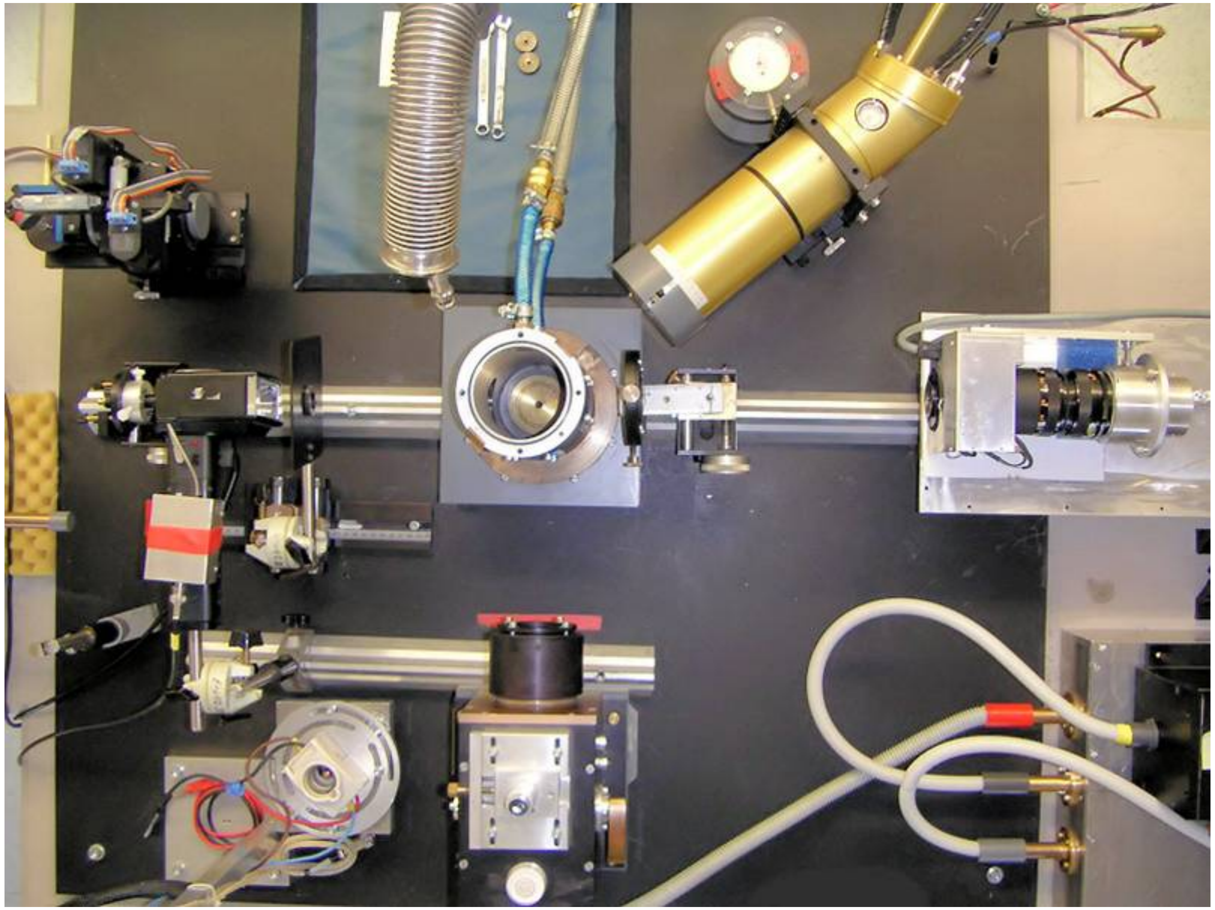
Institut für Experimentalphysik, Technische Universität Graz, Austria

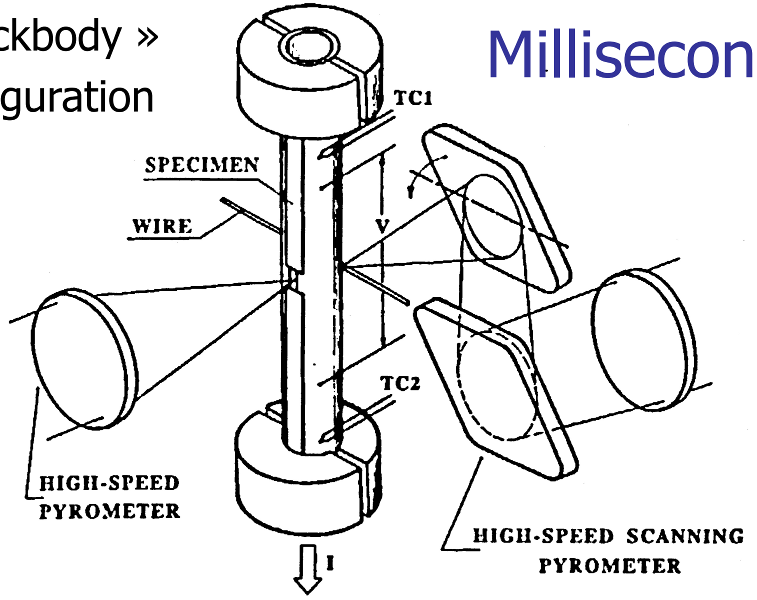
TUG laser polarimeter



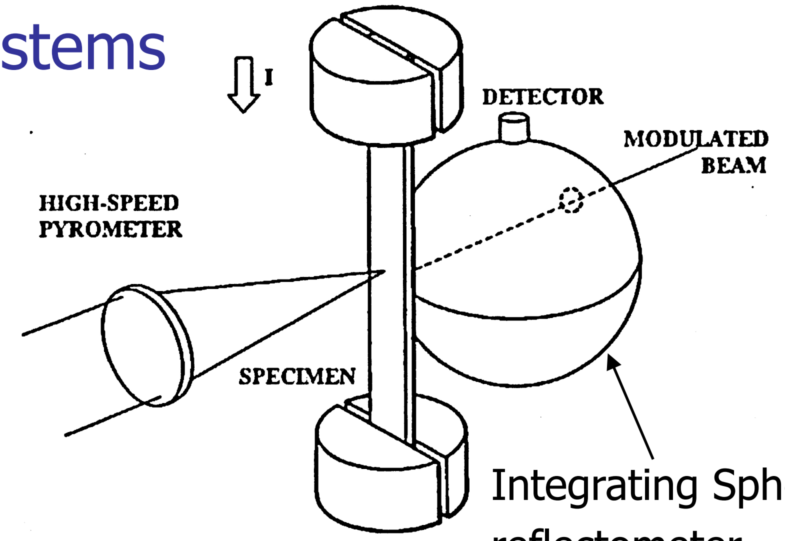
High-speed pyrometry developments

Millisecond systems

« blackbody » configuration



NIST



Integrating Sphere reflectometer

IMGC

Cezairlyian A. and Righini F. "Issues in high-speed pyrometry" *Metrologia*, 33(4), 299-306 (1996)

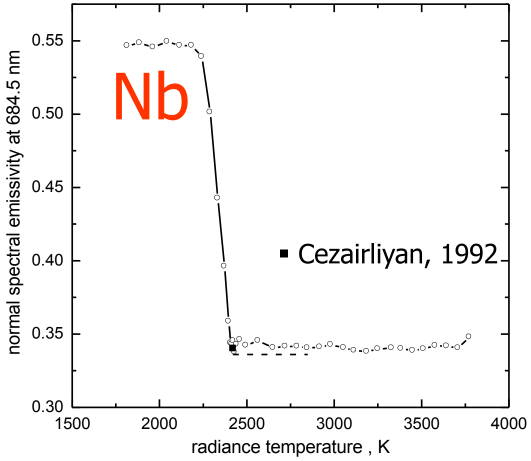
$$\varepsilon_{n,\lambda} = \frac{L_{\lambda,S}(T)}{L_{\lambda,b}(T)} = \frac{e^{C_2/\lambda T} - 1}{e^{C_2/\lambda T_R} - 1}$$

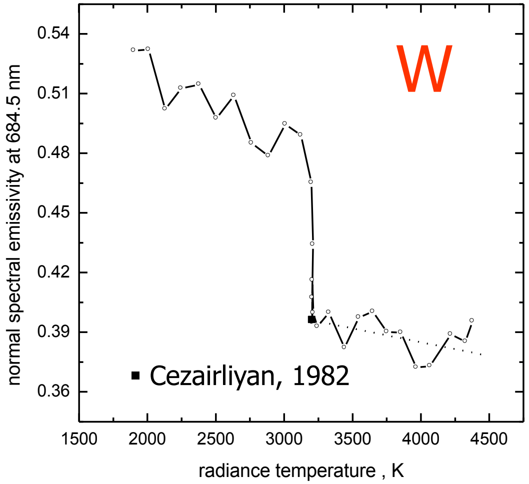
$L_{\lambda,S}$ = sample spectral radiance

$L_{\lambda,b}$ = blackbody spectral radiance (Cf. Planck's law)

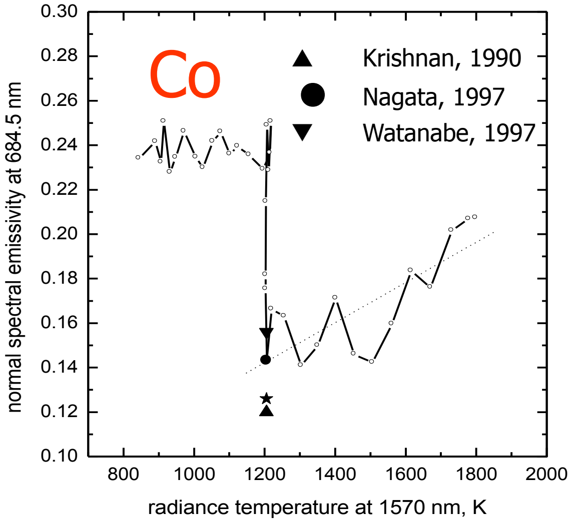
→ numerous $\varepsilon_{n,\lambda}$ data of solid pure metals for $1800 < T < 3500$ K up to T_M ($0.2 < \varepsilon_{n,\lambda} < 0.6$ for metals)

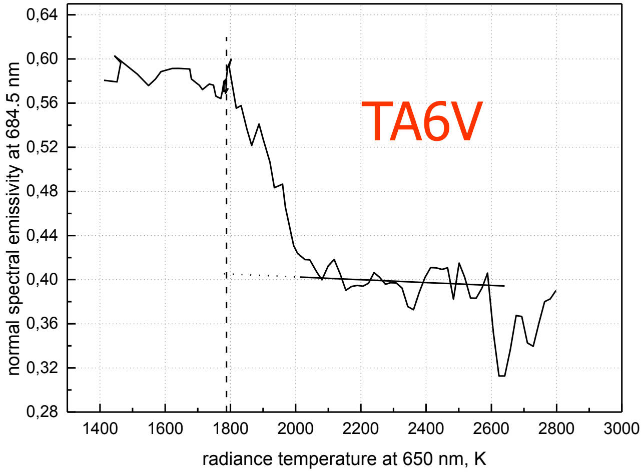
Normal spectral emissivity (λ = 684,5 nm) of liquid metals versus radiance temperature : examples





Cagran et al., HT-HP; 34(6): 669-79 (2002)





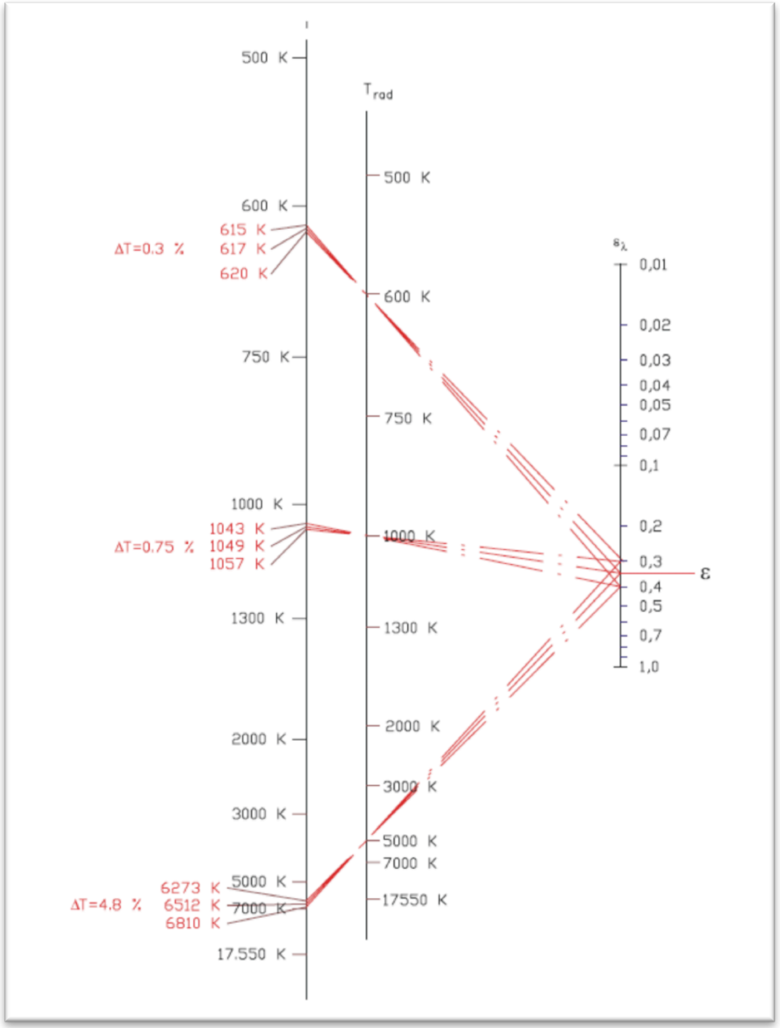
Boivineau et al., IJT, 27(2), pp 507-529 (2006)

$\varepsilon = \pm 0.05$

$T = 600K \rightarrow \Delta T = 0.3\%$

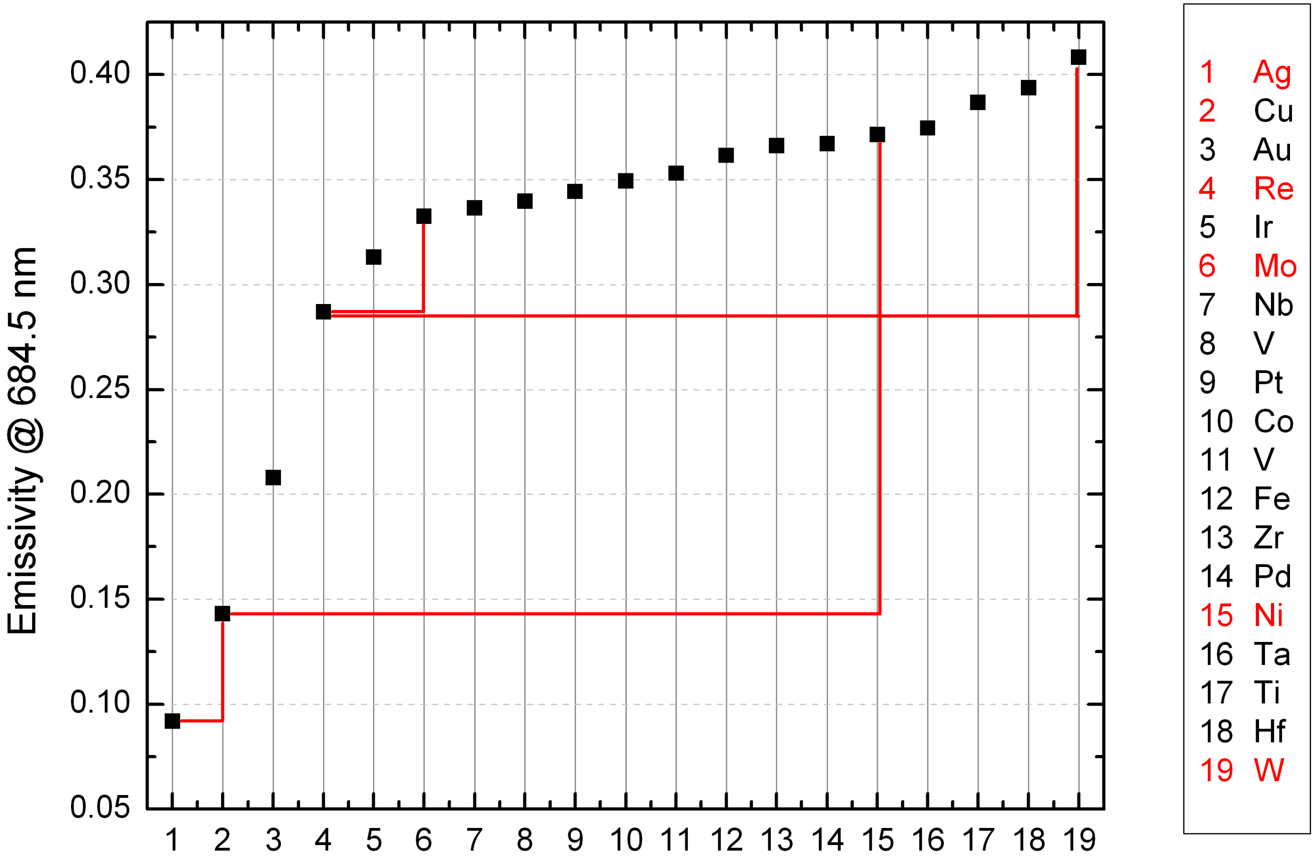
$T = 1050K \rightarrow \Delta T = 0.75\%$

$T = 6500K \rightarrow \Delta T = 4.8\%$



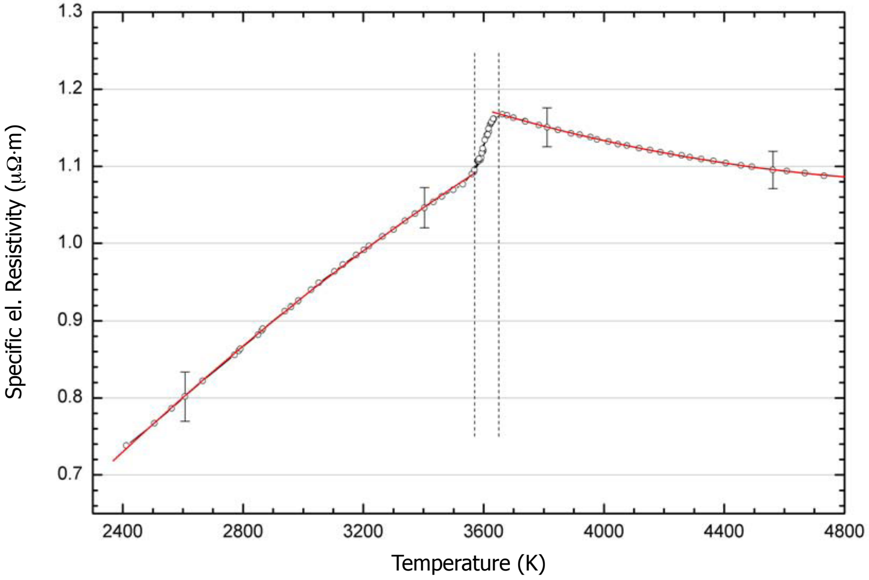
Alloys under investigation

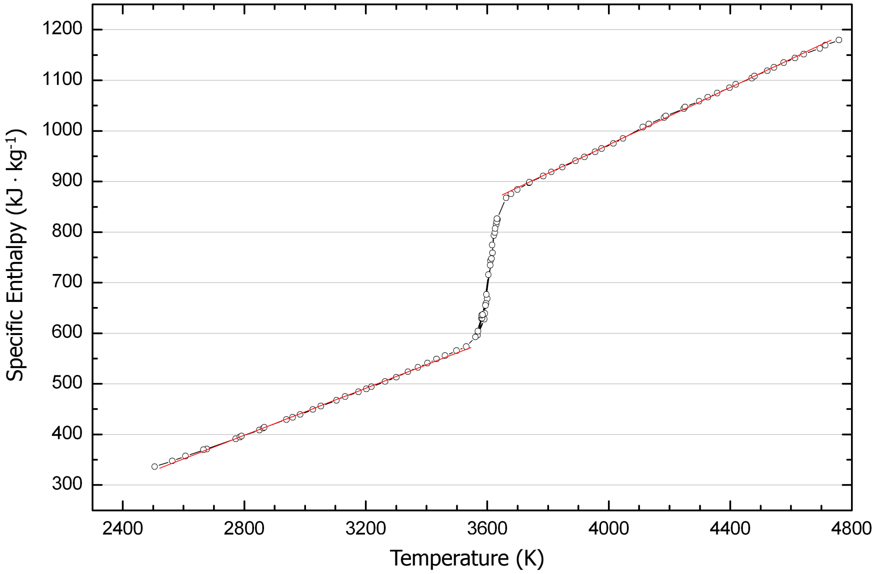
- Ag72Cu28
- Cu55Ni45
- Mo52Re47
- W95Re5
- W74Re26



Cu-Ag, Cu-Ni, Re–Mo, and Re–W.

W95Re5

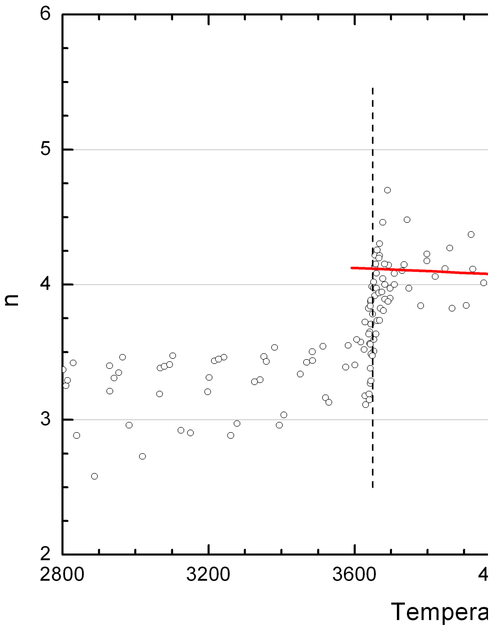


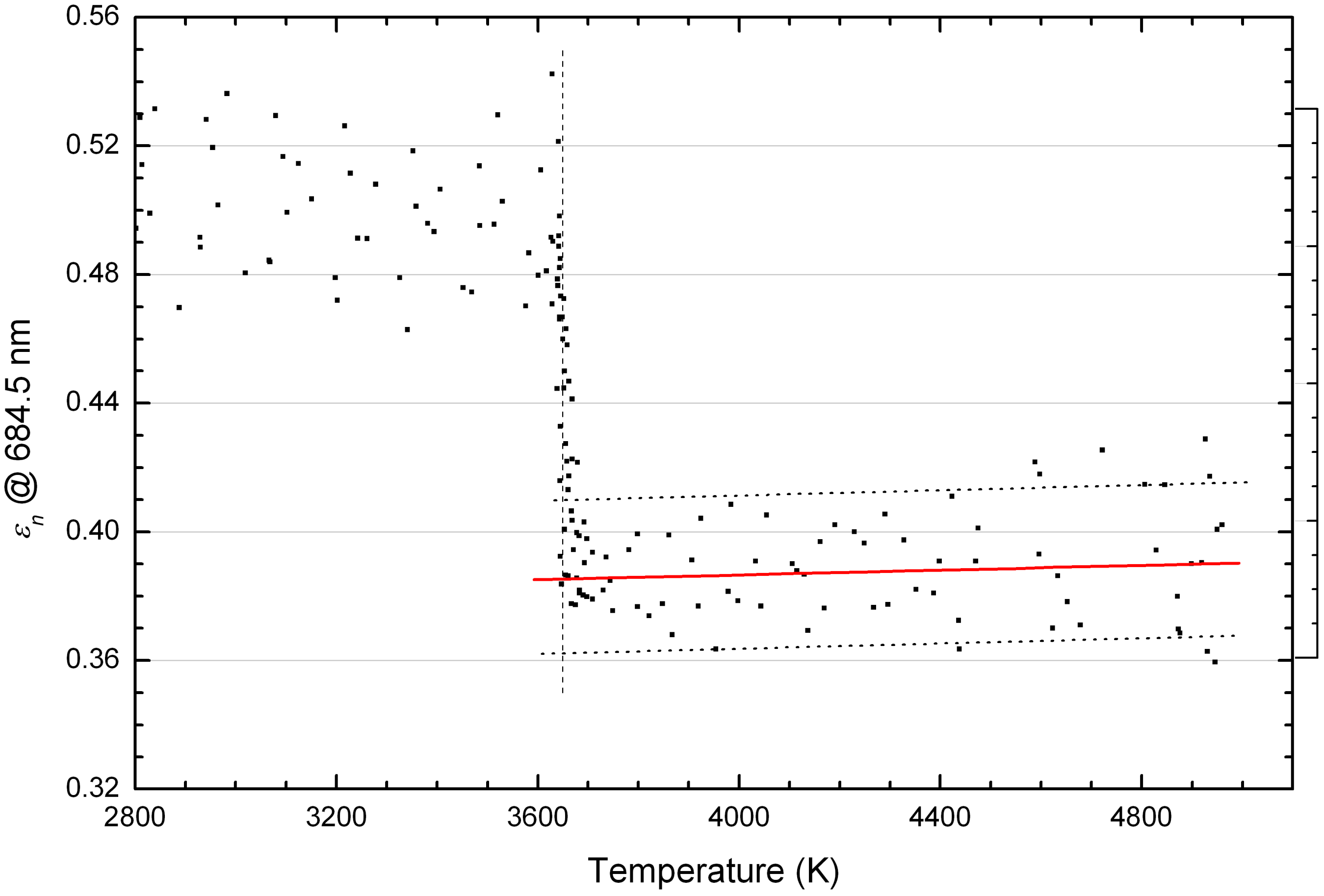


$c_{p,\,s} = 233$ kJ/kg $T_s = 3570$K

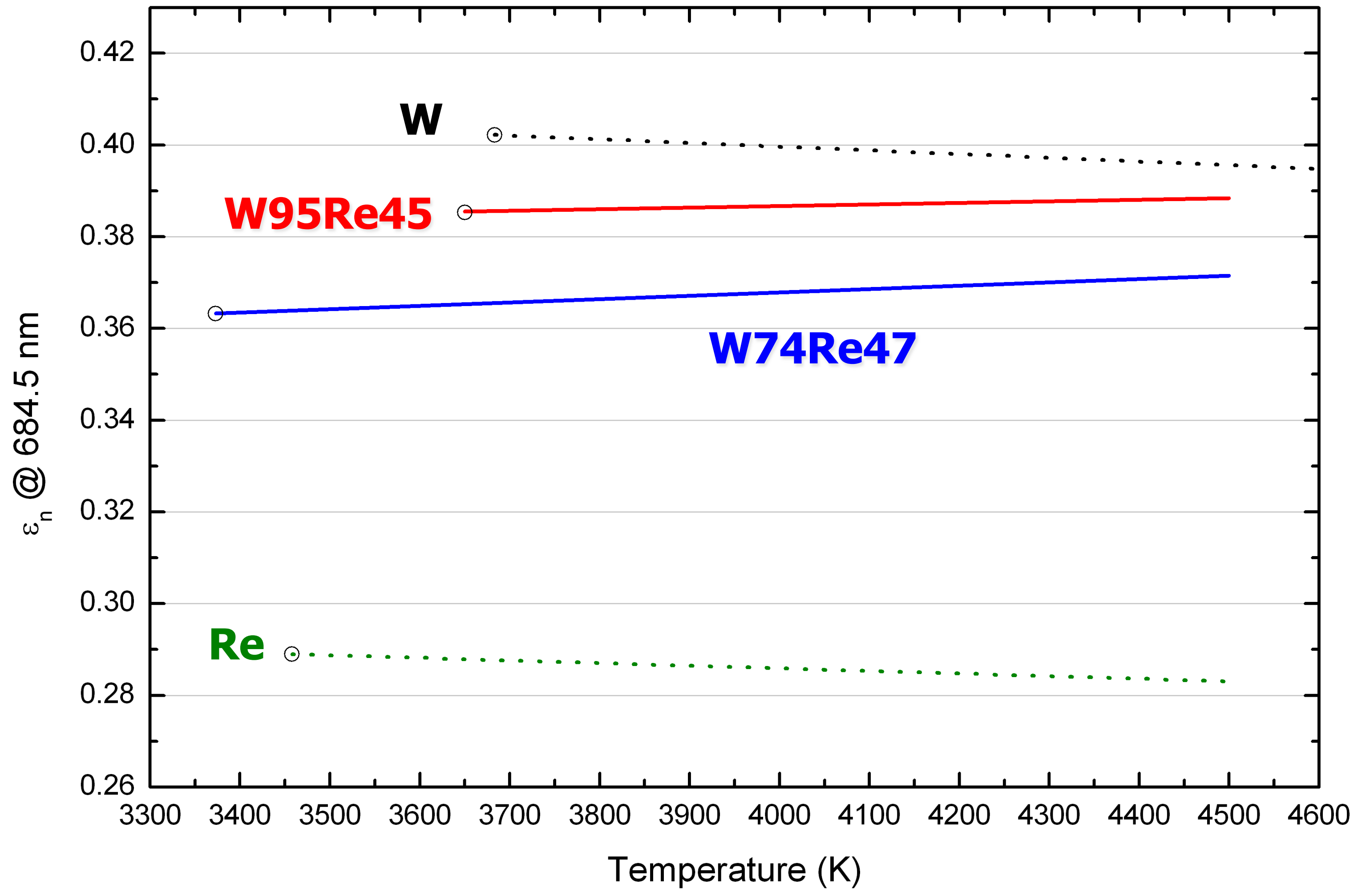
$c_{p,\,l} = 283$ kJ/kg $T_l = 3650$K

W95Re5


6
5
4
3
2
n
2800
3200
3600
4
Tempera

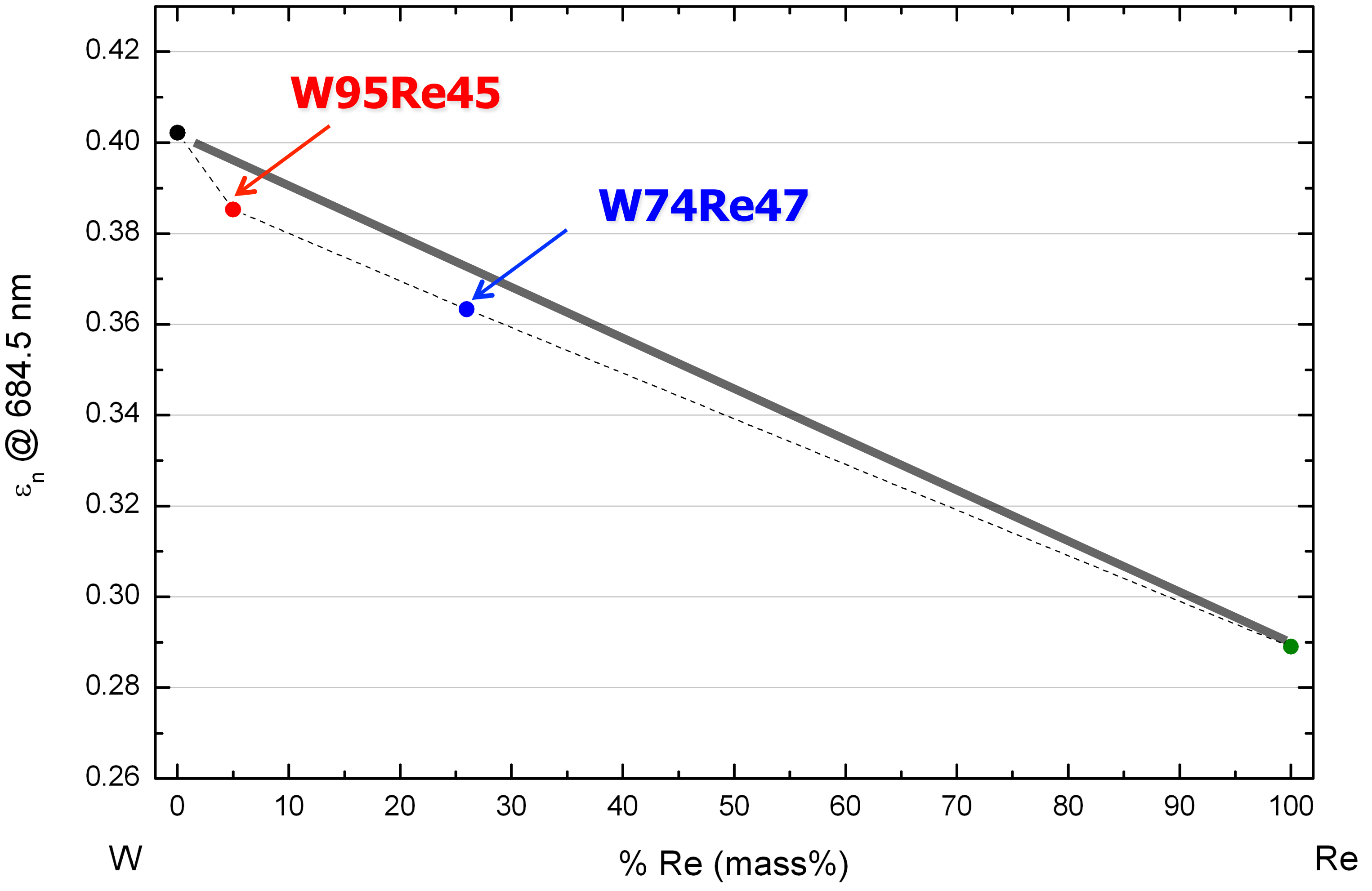

0.56
0.52
0.48
0.44
0.40
0.36
0.32
ε_n @ 684.5 nm
2800
3200
3600
4000
4400
4800
Temperature (K)

W-Re



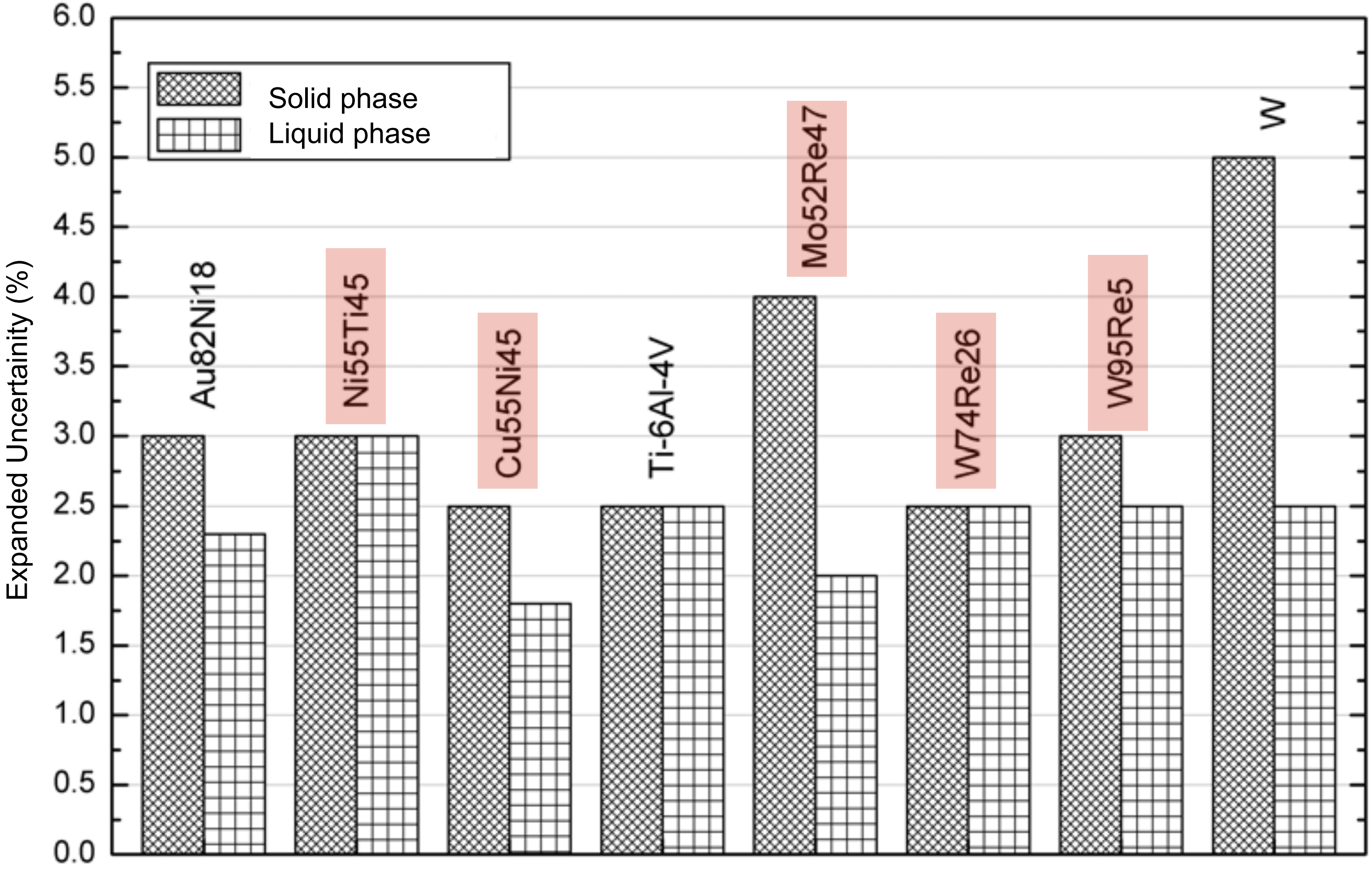
W
W95Re45
W74Re47
Re
ε_n @ 684.5 nm
Temperature (K)
0.42
0.40
0.38
0.36
0.34
0.32
0.30
0.28
0.26
3300
3400
3500
3600
3700
3800
3900
4000
4100
4200
4300
4400
4500
4600

W-Re



W95Re45
W74Re47
ε_n @ 684.5 nm
0.42
0.40
0.38
0.36
0.34
0.32
0.30
0.28
0.26
0
10
20
30
40
50
60
70
80
90
100
W
% Re (mass%)
Re

Uncertainties for electrical resistivity



Uncertainties for specific Enthalpy

Material	Solid (%)	Liquid (%)
Ag72Cu28	2.2	2.0
Cu55Ni45	4.2	3.9
Mo52Re47	4.6	3.0
W95Re5	3.9	2.5
W74Re26	3.5	3.0

II. Experimental device and available data

Calculated parameters

- $\Delta H = \mathbf{H(T) - H(298)} = \frac{\mathbf{1}}{\mathbf{m}} \int_{t0}^{t} I(t).U(t).dt$
- $C_p = \left[\frac{\partial H(T)}{\partial T} \right]_{P=cte}$
- $\frac{V(t)}{V_0} = \frac{\phi(t)^2}{\phi_0^2}$ and $\rho = \rho_0 \frac{V_0}{V(t)}$
- $\rho_{el0}(t) = \frac{U_c(t)}{I(t)} \frac{\pi\phi_0^2}{4l}$ and $\rho_{el}(t) = \frac{U_c(t)}{I(t)} \frac{\pi\phi(t)^2}{4l} = \rho_{el0}(t) \frac{\phi(t)^2}{\phi_0^2}$
- $\lambda = \frac{L.T}{\rho_{el}}$ and $a = \frac{\lambda}{C_P.\rho}$ $(L = 2{,}45.10^{-8} V^2 K^{-2})$

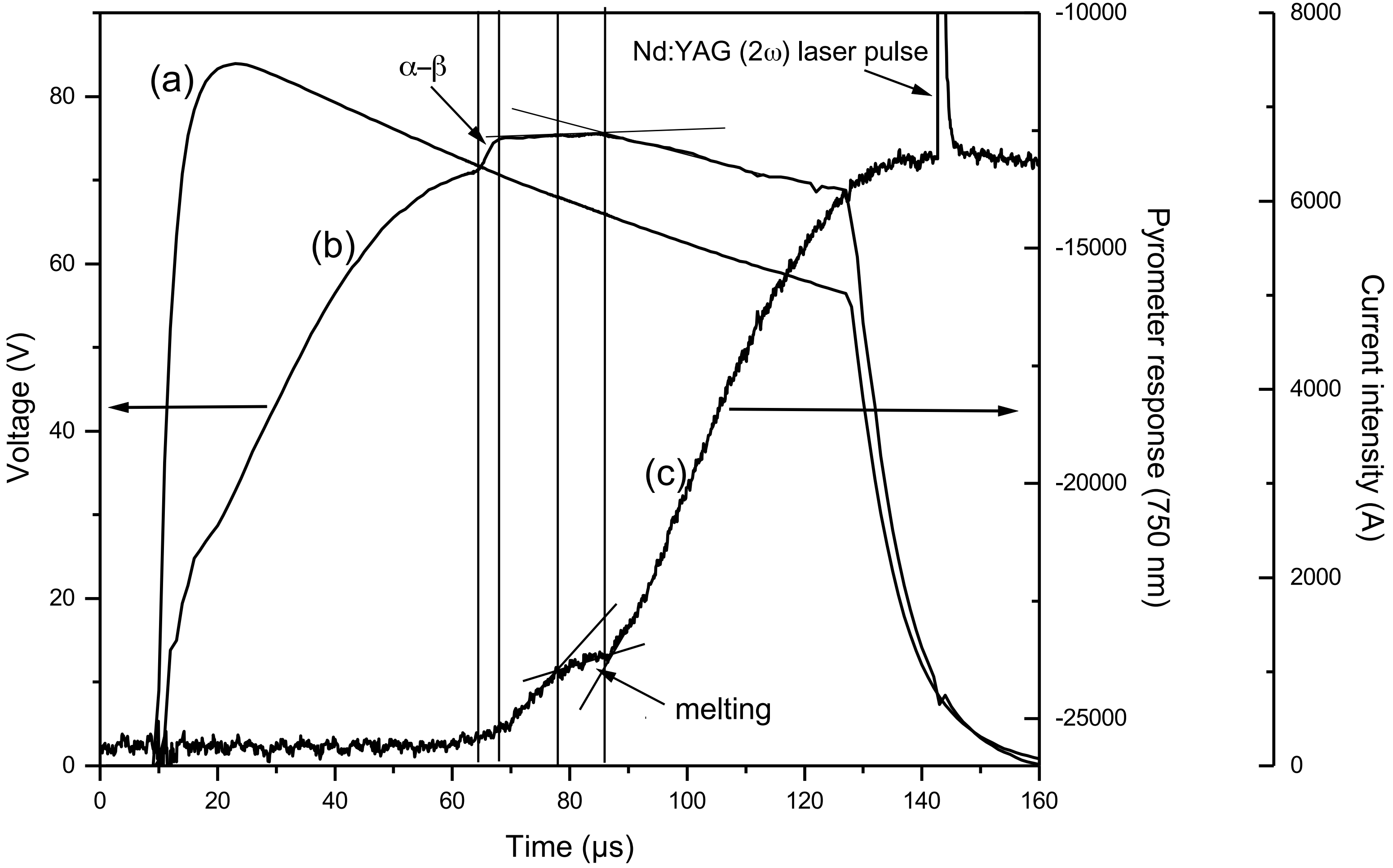
Parameter	Uncertainty
ΔH	±1.5%
ρ_{el0}	±4%
ϕ/ϕ_0	±1%
V/V_0	±2%
T	5-10%
C_P	±10%
λ	±10%
a	±20%
c	±5-10%

+ sound velocity measurements → EOS parameters

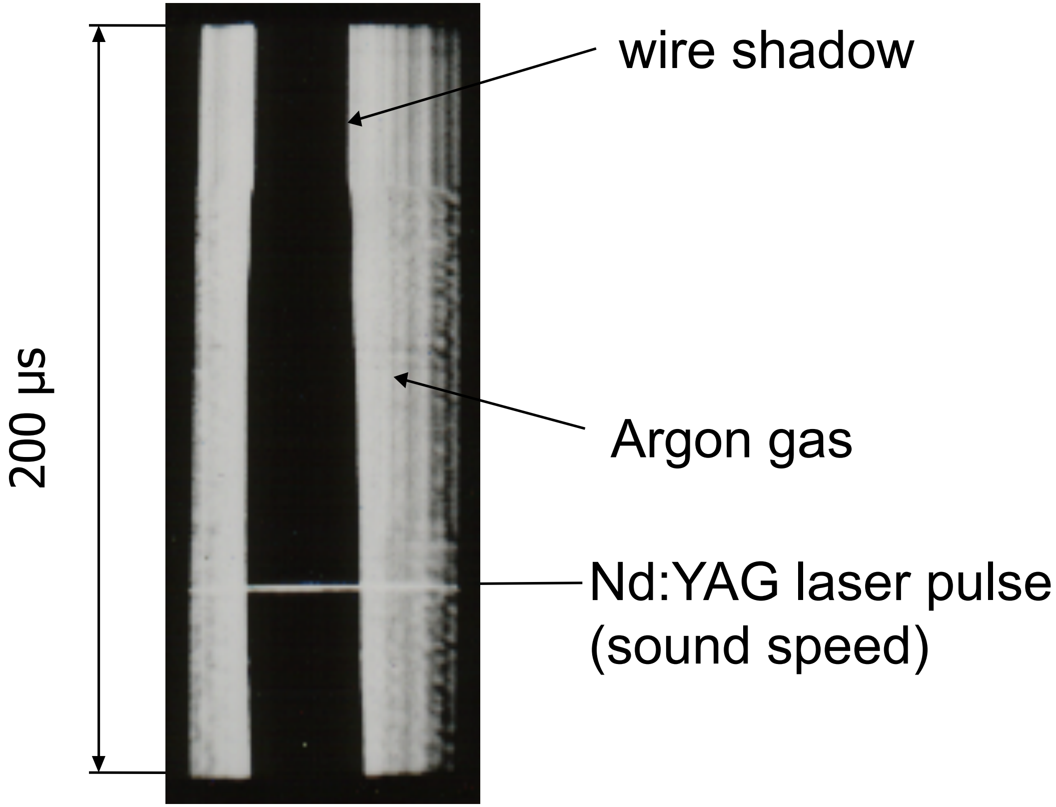
Basic measurements : electrical and pyrometry data

All of them are recorded as a function of time

Example : Thorium

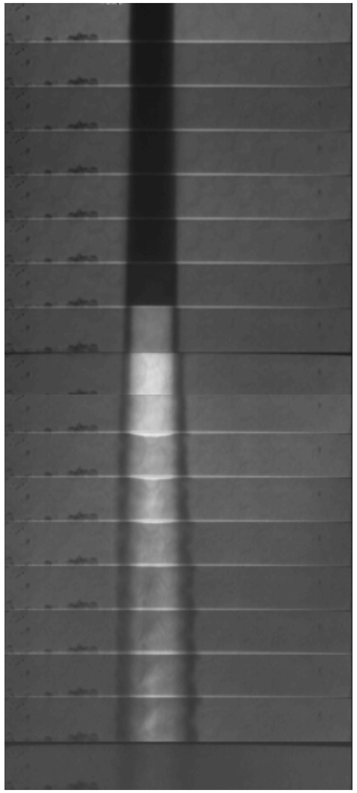


Basic measurements : radial expansion



CEA

(streak camera)



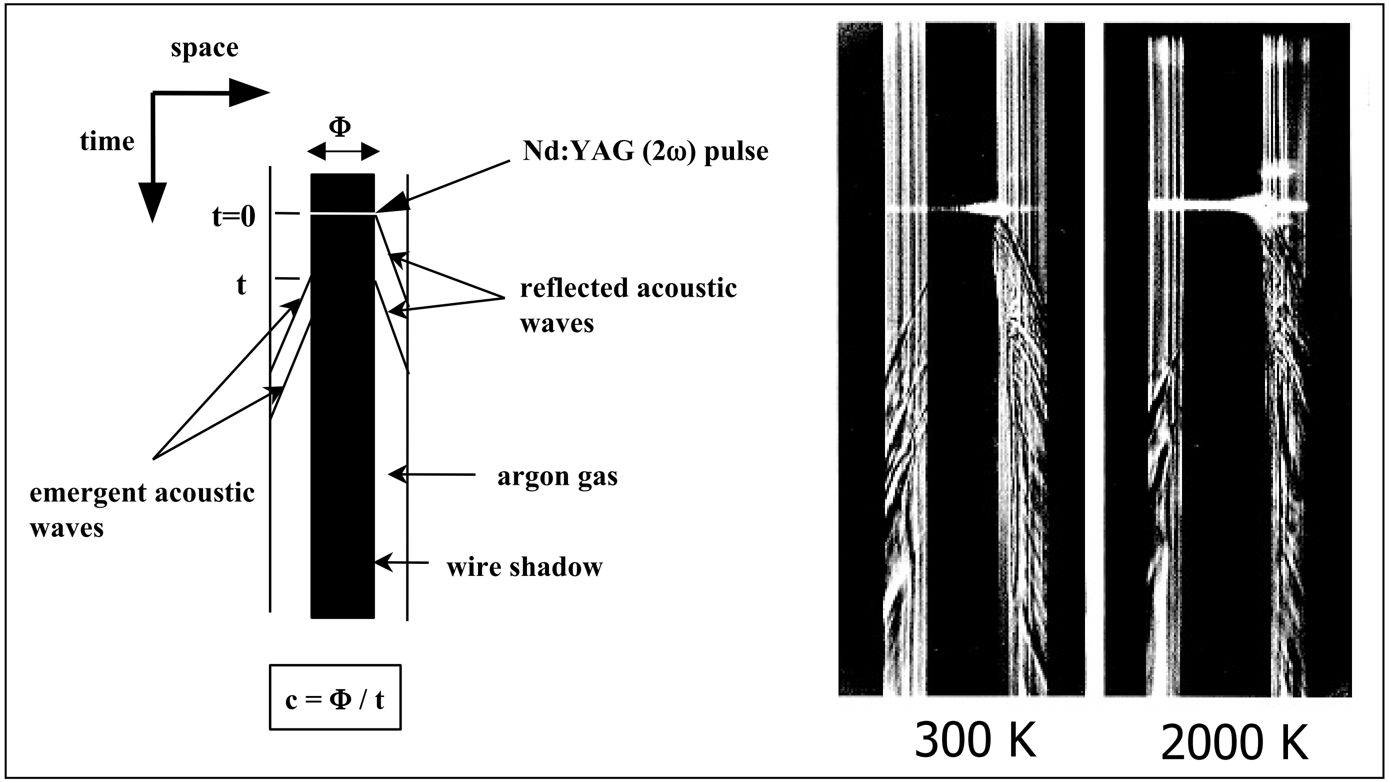
TUG

(fast framing
CCD camera)

+ traitement d’image associé

Sound velocity measurements

→ New method developed in 80’s-90’s at LLNL (Hixson et al.) and CEA → use of a streak camera



NB : the interferometric method is very sensitive to the sample motion (liquid state) → abandoned technique

Sound velocity : a useful and powerful tool…

sound velocity measurements provide EOS parameters

- Sound velocity : c = c_L (liquid state)
- Adiabatic bulk modulus : $$B_S = \frac{1}{K_S} = -V\left(\frac{\partial P}{\partial V}\right)_{S=const} = \rho\left(\frac{\partial P}{\partial \rho}\right)_{S=const} = \rho c^2$$
- Isothermal compressibility : $$K_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T=cte} = \frac{1}{B_T}$$
- Grüneisen parameter : $$\gamma_G = V\left(\frac{\partial P}{\partial E}\right)_V = \alpha\frac{c^2}{C_p}$$
- Specific heats ratio : $$\gamma = \frac{C_p}{C_v} = 1 + \alpha T \gamma_G$$ or $$\frac{K_T}{K_S} = \frac{B_S}{B_T} = \gamma$$

with $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Temperature measurement procedure

- Analysis of the thermal emission of a rectangular portion of the wire (0.3 x 3 mm)
- 4 λ : 450, 600, 750, 900 nm with Δλ(IF) ~100 nm
- $$I_i = G_i \int F_i(\lambda).D_i(\lambda).\varepsilon(\lambda,T)\frac{C}{\lambda^5 \exp(c/\lambda T - 1)}d\lambda$$

G_i = instrument factor including losses of optics and spectral response of the photodiode

$F_i(\lambda)$ = spectral response of the filter F_i

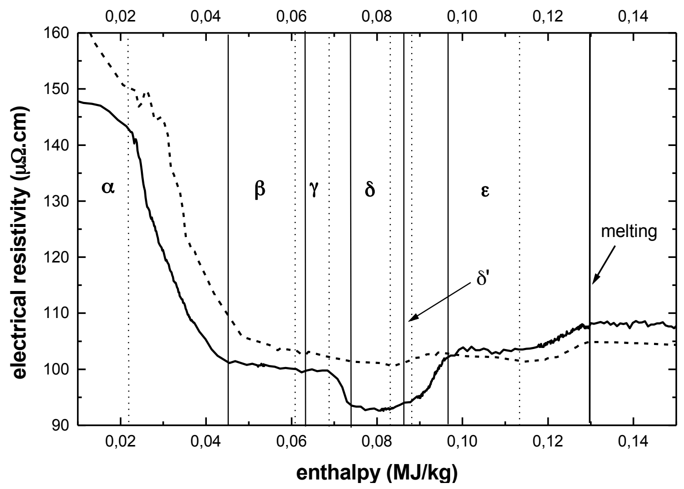
$D_i(\lambda)$ = spectral response of the photodiode D_i

Calibration of the logarithmic amplifiers: simulation of the entire temperature range by illuminating the photodiodes with an attenuated laser beam with calibrated neutral density filters

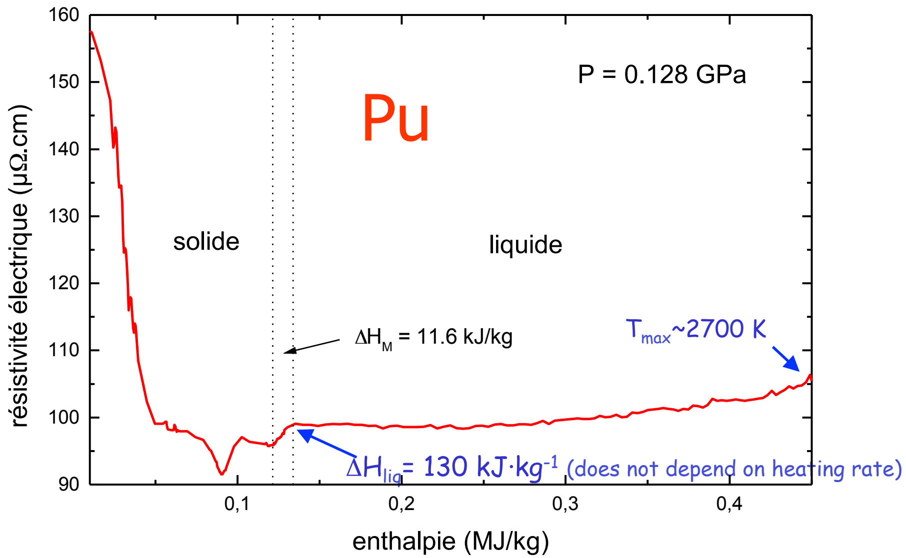
Another example: Pu

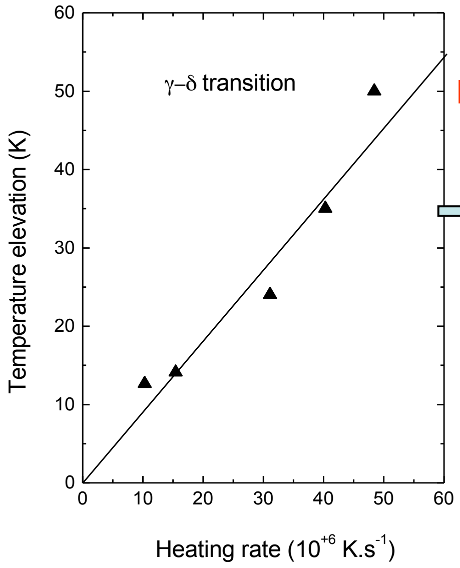
Boivineau M., J. Nucl. Mat., 297(1), 97-106 (2001)

Boivineau M., J. Nucl. Mat., 392, 568-577 (2009)



Pu: highest number (6) of solid phases of the periodic table elements at amb. cond.



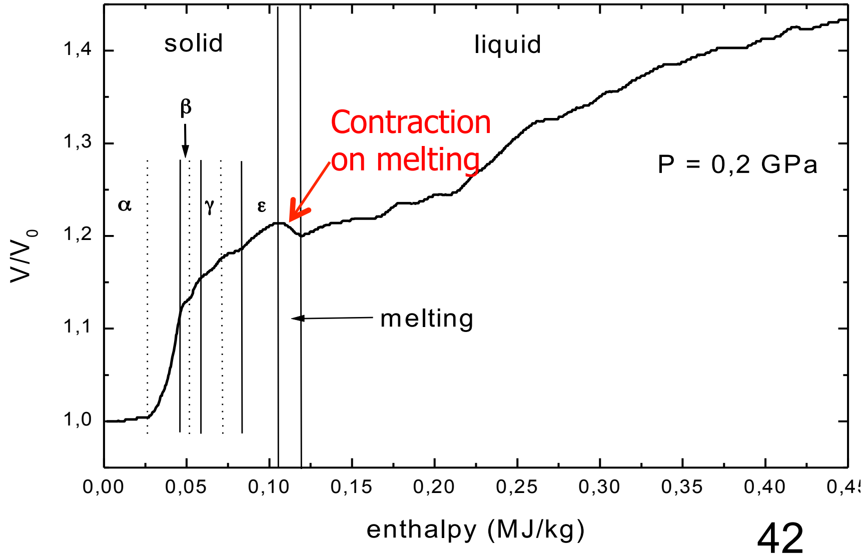


Heating rate: $8.10^6 – 6.10^7$ K.s^{-1}

- Linear fit: $\Delta T(K) = 0.9.10^{-6}.a$

where *a* is the heating rate (in K.s^{-1})

NB: intersection at the zero point → isothermal conditions at very low heating rates

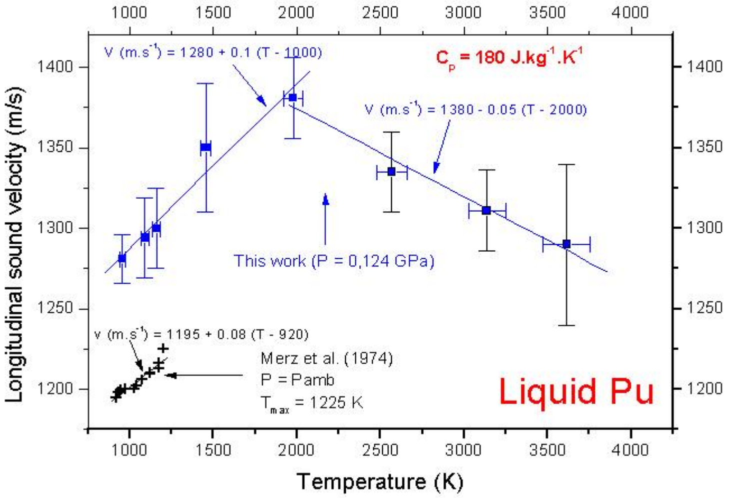


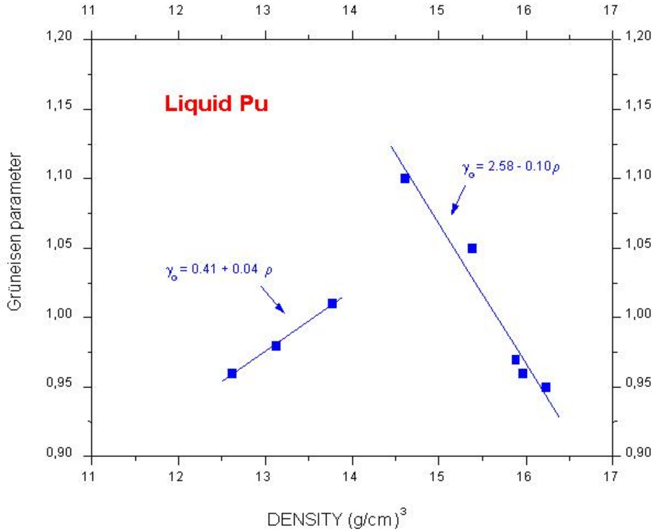
Contraction on melting

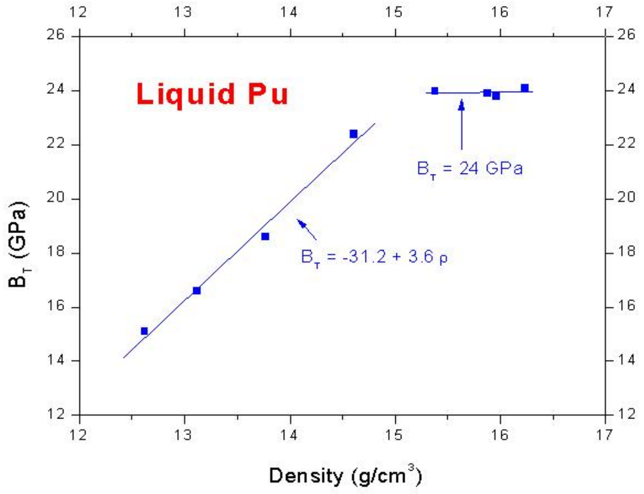
III. Thermophysical properties : pure metals

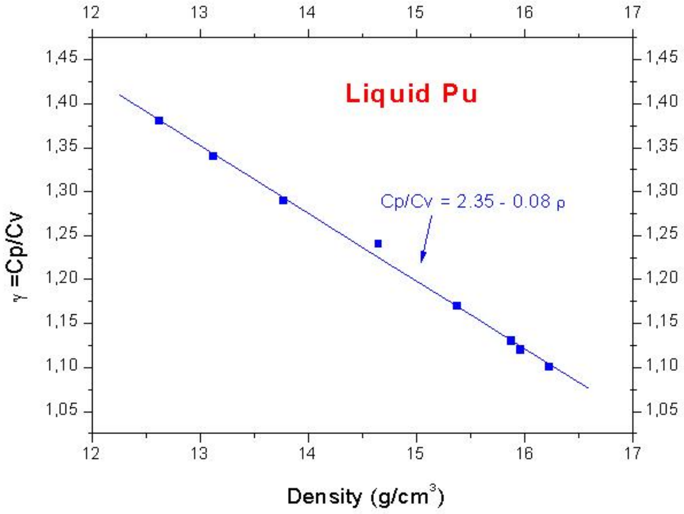
Sound velocity and EOS parameters of liquid metals : Pu exemple

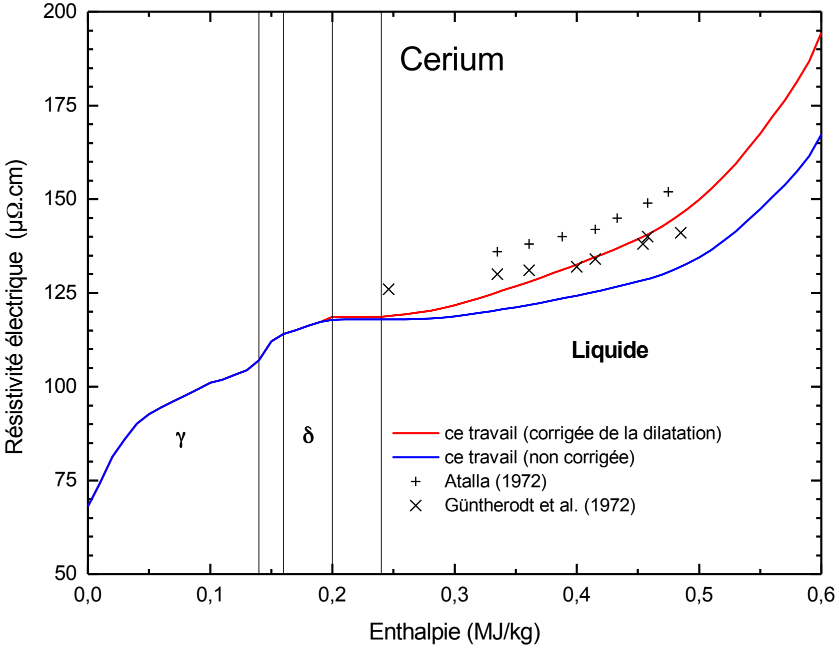
Boivineau M., J. Nucl. Mat., 297(1), 97-106 (2001)
Boivineau M., J. Nucl. Mat., 392, 568-577 (2009)

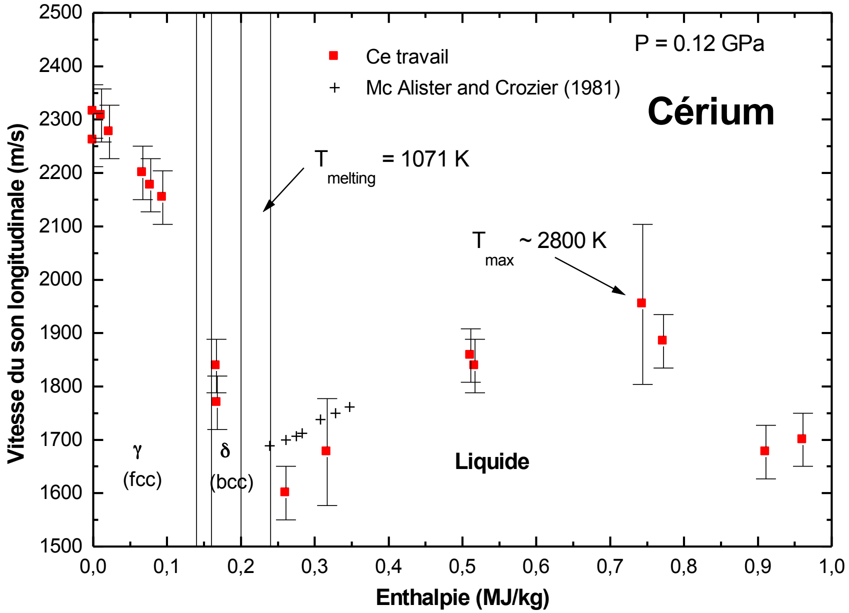









Cerium
Résistivité électrique (µΩ.cm)
200
175
150
125
100
75
50
0,0
0,1
0,2
0,3
0,4
0,5
0,6
Enthalpie (MJ/kg)
γ
δ
Liquide
ce travail (corrigée de la dilatation)
ce travail (non corrigée)
+ Atalla (1972)
× Güntherodt et al. (1972)


P = 0.12 GPa
Cérium
■ Ce travail
+ Mc Alister and Crozier (1981)
T melting = 1071 K
T max ~ 2800 K
Vitesse du son longitudinale (m/s)
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
Enthalpie (MJ/kg)
γ
(fcc)
δ
(bcc)
Liquide

Stoke’s formalism

The Stoke‘s vector:

The Stoke‘s parameters:

$$\vec{S} = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix} \longrightarrow$$

$$S_0 = I_0$$

$$S_1 = I_x - I_y$$

$$S_2 = I_{+\pi/4} - I_{-\pi/4}$$

$$S_3 = I_r - I_l$$

Ellipsometric parameters

Specular reflection off the sample: $N_1 \cdot \sin(\Theta_i) = N_2 \cdot \sin(\Theta_t)$

With the complex index of refraction: $N = n - i \cdot k$

Fresnel equation relates s and p via amplitude and phase to the reflection coefficients r_p and r_s:

$$r_{s,p} = \frac{R_{s,p}}{A_{s.p}} = \left| r_{s,p} \right| \cdot e^{i \cdot \delta_{s,p}}$$

n, k - ε

The ellipsometric parameters:

$$q = \frac{r_p}{r_s} = \tan(\Psi)\cdot e^{i\Delta}$$

$$\Delta = \delta_p - \delta_s$$

$$\tan\Delta = \frac{-S_3}{S_2}$$

$$\tan 2\Psi = \frac{\left(S_2^2 + S_3^2\right)^{1/2}}{-S_1}$$

↓

With known angle of incidence the complex index of refraction N$_2$ can be determined:

$$\boxed{n_2 - i\cdot k_2 = n_i\cdot\tan(\Theta)\cdot\left(1 - \frac{4\cdot q}{(1-q)^2}\cdot\sin^2(\Theta)\right)^{\frac{1}{2}}}$$

n, k - ε

$$\boxed{\varepsilon = 1 - \Re = \frac{(n_2 - n_1)^2 + k_2^2}{(n_2 + n_1)^2 + k_2^2}}$$

Normal spectral emissivity at a given wavelength