Jülich Centre for Neutron Science

JÜLICH FORSCHUNGSZENTRUM

Université de Liège

Thermoelectric materials

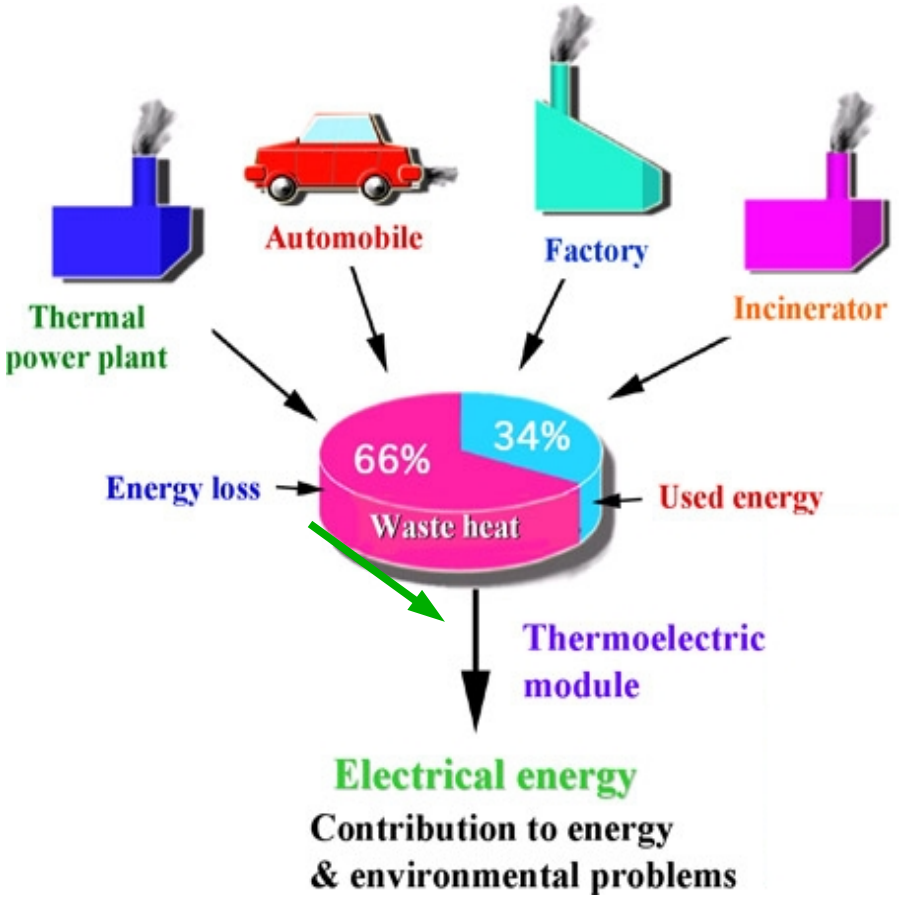
Raphaël Hermann

Jülich Centre for Neutron Science and Peter Grünberg Institut, Forschungszentrum Jülich GmbH, Germany

Université de Liège, Faculté des Sciences, Belgium

German-Georgian Science Bridge ,Tbilisi, Juli 8th 2014

Efficient Thermal Management



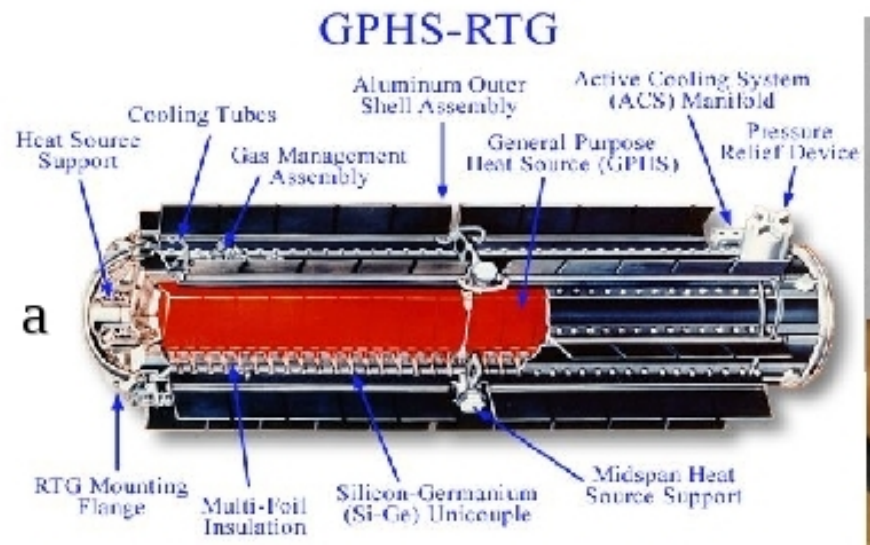
http://www.aist.go.jp/

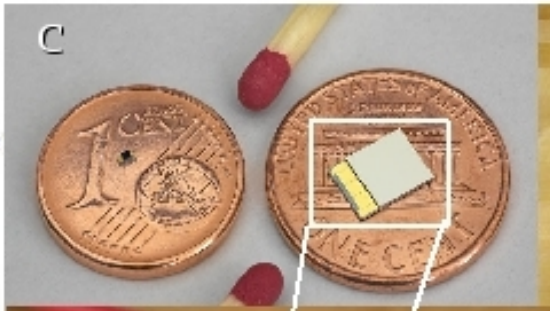
Efficiency of waste heat: 0%

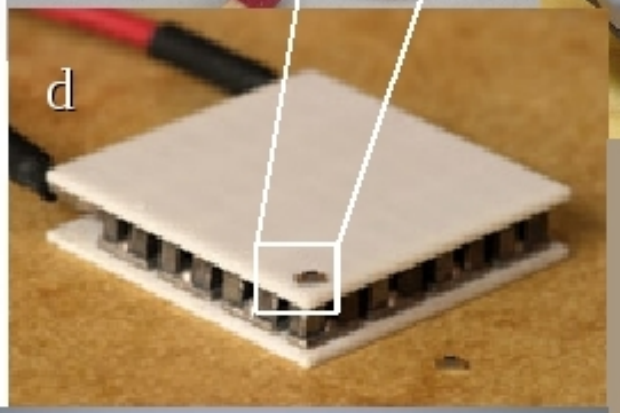
Efficiency of thermoelectric converters: >7-8%

~10% fuel economy for the automotive industry.

Applications





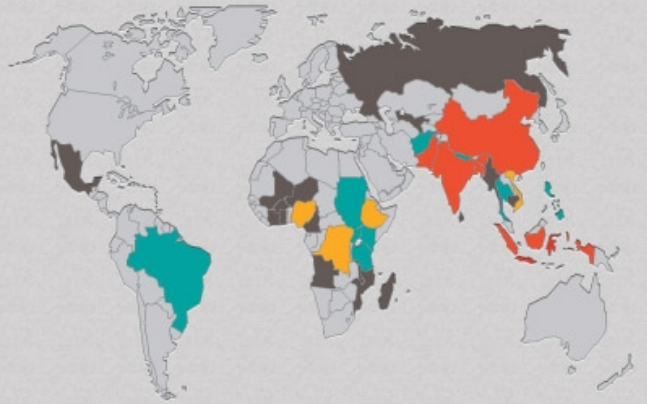


Sources: a,b WikiMedia (NASA, JPL); c,d MicroPelt; e BMW; f,g: Commercials

Worldwide number of people cooking on open fires

3 billion people worldwide cook on open fires

1.3 billion of these lack access to electricity



Over 100 million · Over 50 million · Over 20 million · Over 10 million

1 billion metric tons of CO_2 from cooking fires are released into the atmosphere each year

2 million people die each year from indoor smoke from inefficient cooking fires (more than twice as many as malaria)

Many hours spent per week collecting fuel.

Health effects from indoor smoke are equivalent to smoking *two packs of cigarettes daily.*

www.biolitestove.com

CO_2e emissions per year (metric tons)

Average car	5.1
Three-stone fire	5.3

Cost to reduce CO_2e emission by 1 metric ton

$787.03 Toyota Prius

$6.66 HomeStove

Average amount of income spent on energy

20-30% *of income* — Average amount the world's poor spend on fuel alone

4% *of income* — Average amount Americans spend on energy

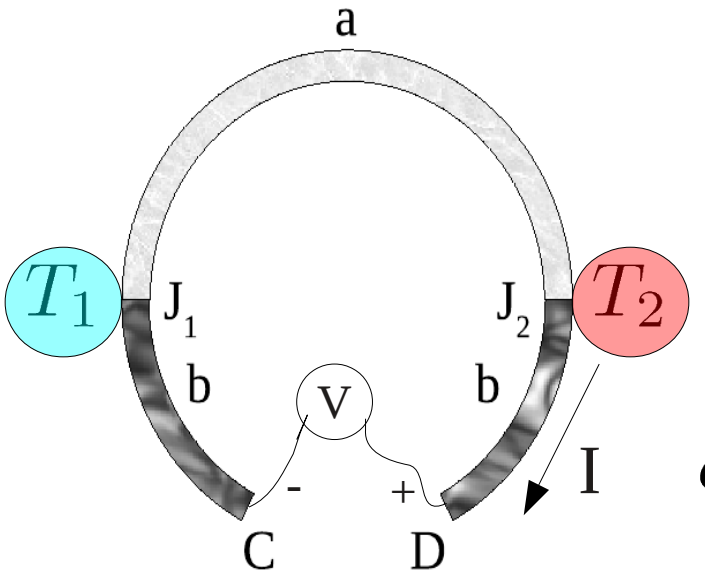
Annual savings by an average family in India using the HomeStove

$72

- Electricity savings (cell phone charging, switching from kerosene to LED lighting)
- Fuel savings from more efficient burning

Introduction: A brief history – Seebeck effect

T. Seebeck
(1770-1831)



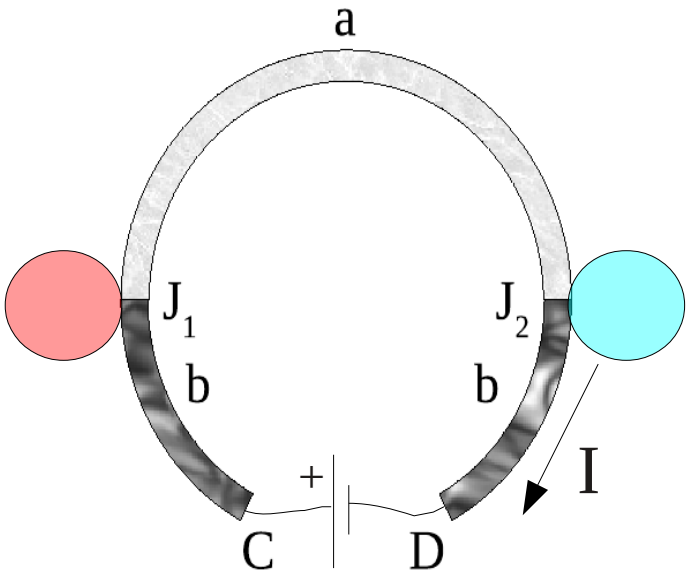
$\alpha_{ab} > 0$

$$V = (\alpha_b - \alpha_a)(T_2 - T_1) = \alpha_{ab}\Delta T$$

- Depends on the temperature difference and not on the specific geometry!
- Original mistake by Seebeck: „Magnetic polarization … by temperature difference“
- Clarified by Oersted: thermo-electric effect

Introduction: A brief history – Peltier effect

J.-C. Peltier
(1785-1845)



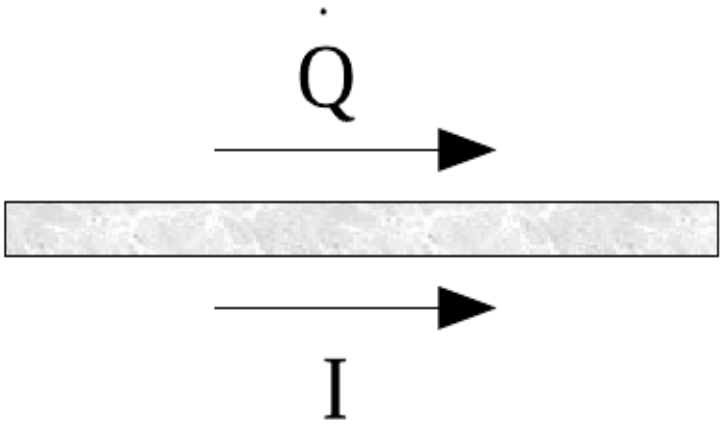
$$\Pi_{ab} > 0$$

$$\dot{Q} = (\Pi_b - \Pi_a) \cdot I = \Pi_{ab} \cdot I$$

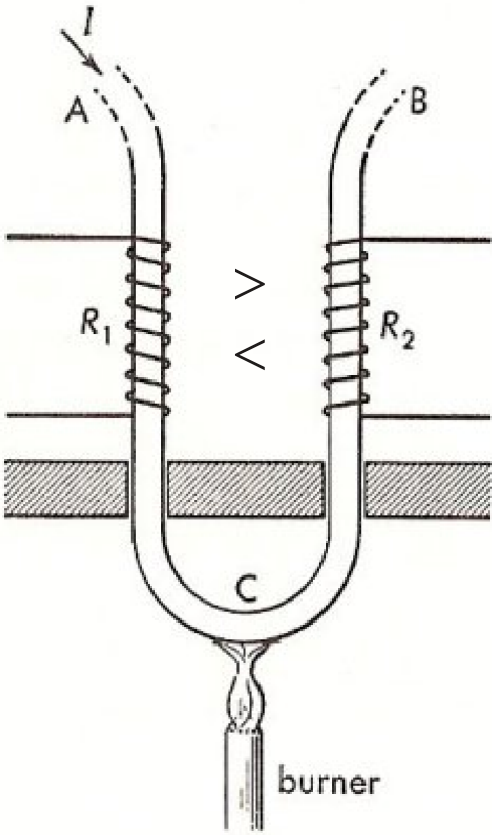
- Heating or cooling of the junctions is reversible with the current sign

Introduction: A brief history – Thomson effect

W. Thomson
(1824-1907)



$$\dot{Q} = RI^2 - \mu_T I \Delta T$$



Duckworth, Electricity and magnetism

- Heating of R_1 and cooling of R_2 or conversely depending on the sign of I and μ
- Predicted effect, then verified experimentally
- μ <0 in Bi, Fe, Pt, … and >0 in Sb, Cu, Ag, … . μ is f(*T*) and can reverse sign.

Introduction: Unifying thermoelectricity

W. Thomson
Lord Kelvin
(1824-1907)

Kelvin relations

Consequences of
non-equilibrium thermodynamics

J.-C. Peltier
(1785-1845)

$$\mu_T = T\frac{d\alpha}{dT}$$

$$\Pi = \alpha T$$

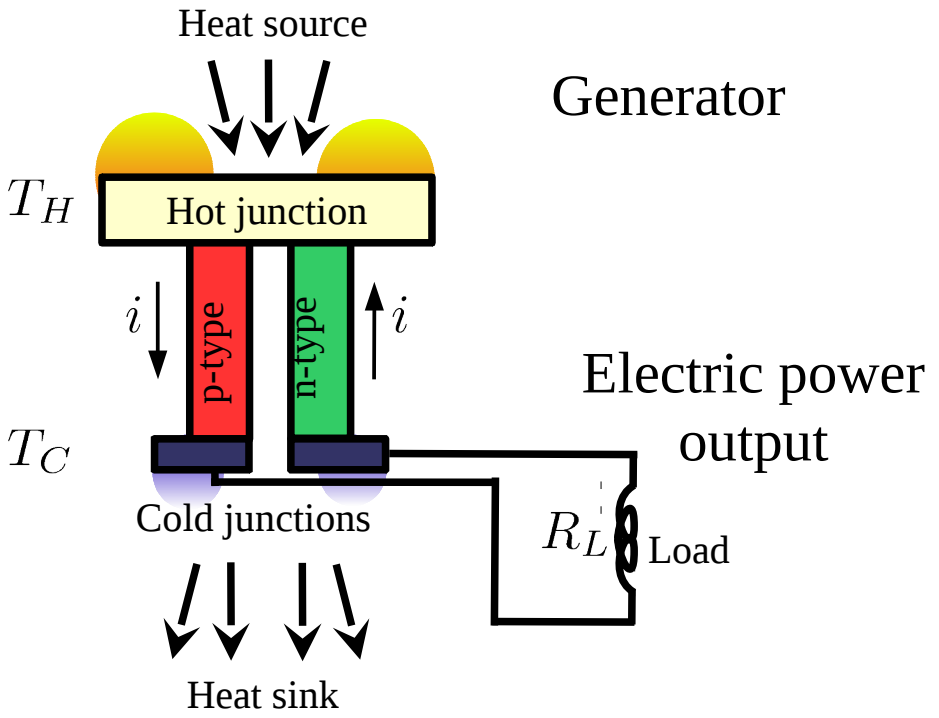
T. Seebeck
(1770-1831)

- For a superconductor, $\alpha = 0$ (*e.g.* Pb for $T < 7$ K)
- The Peltier and Seebeck coefficients can be defined for a single material

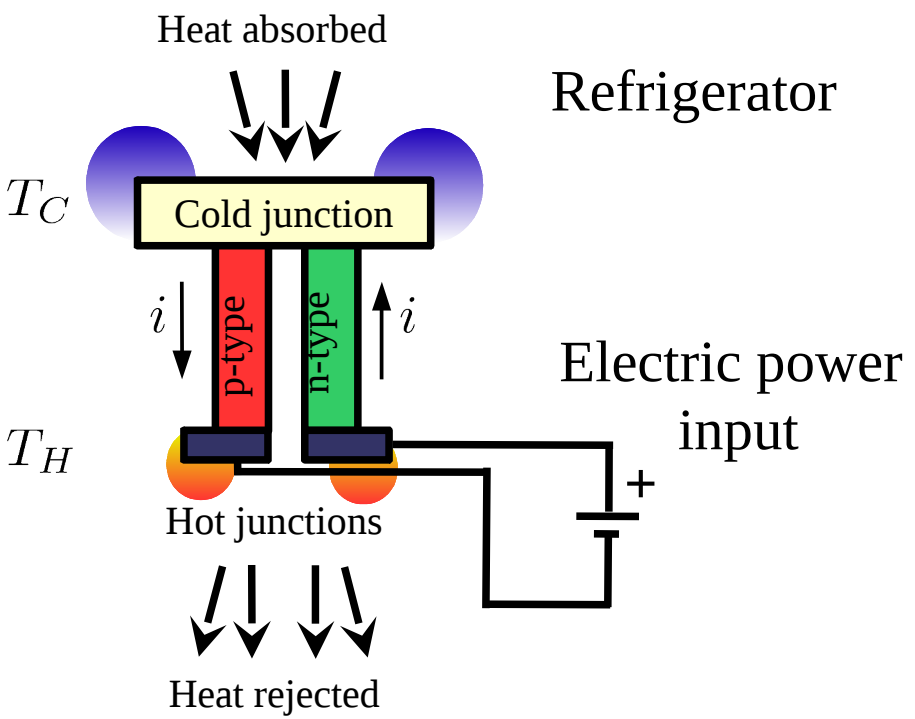
$$\alpha = \int d\alpha = \int \mu(T) \cdot dT/T$$

Thermoelectric conversion

Seebeck effect

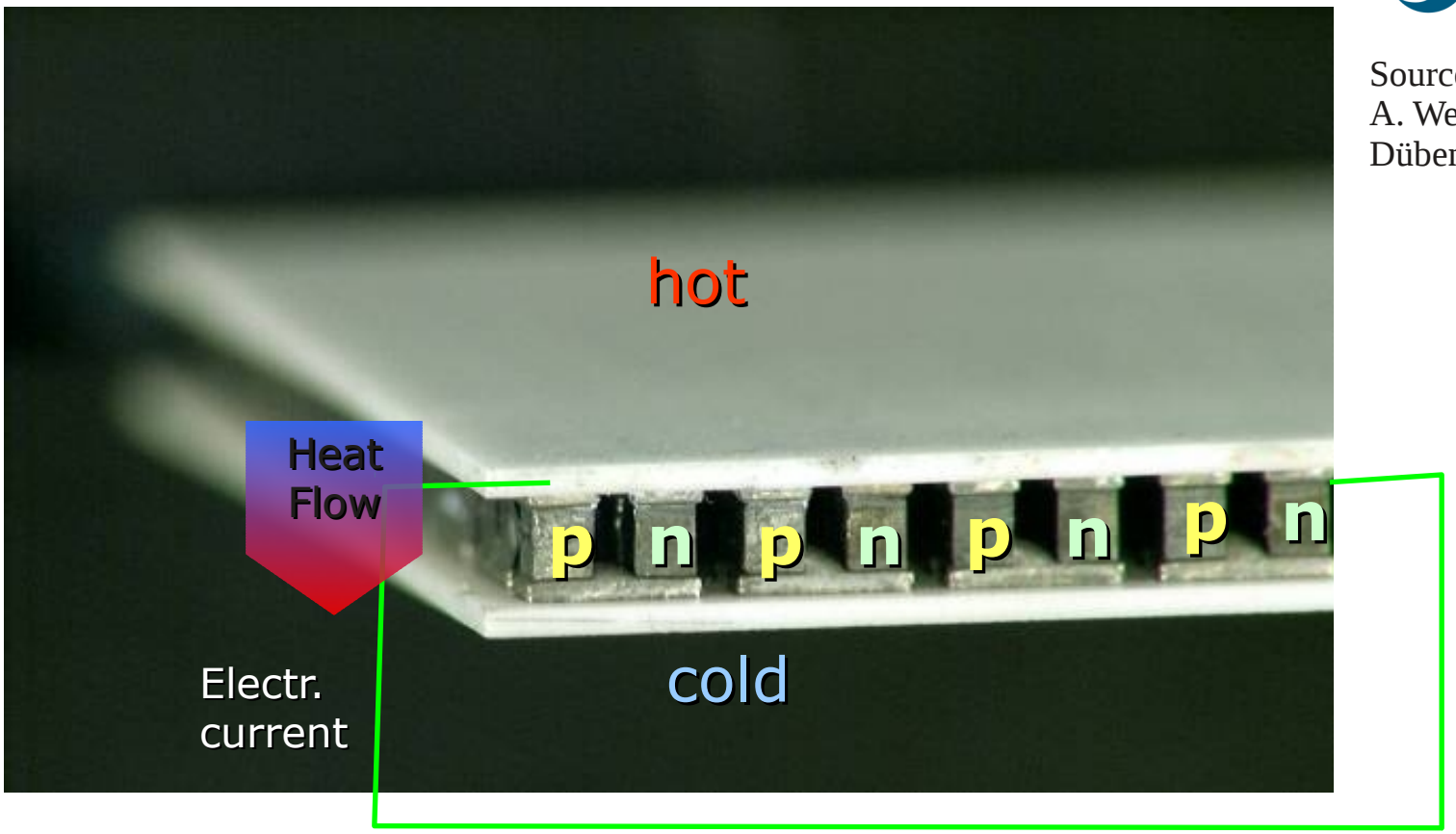


Peltier effect



- No moving parts
- Direct conversion: clean and silent
- High power density: small size
- No scale merit, small ΔT

Thermoelectric conversion



Source:
A. Weidenkaff, EMPA Dübendorf

- Device: junctions thermally in parallel, electrically in series
- Efficiency?
- Upper limit: Carnot efficiency $\eta < \eta_C = \frac{T_H - T_C}{T_C}$

$$\eta = \eta_C \frac{\sqrt{1 + Z_{ab} T_{av}} - 1}{\sqrt{1 + Z_{ab} T_{av}} + T_C / T_H}$$

Thermoelectricity: finding a compromise

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

Electric conductivity

$$\sigma = ne\mu$$

Thermopower

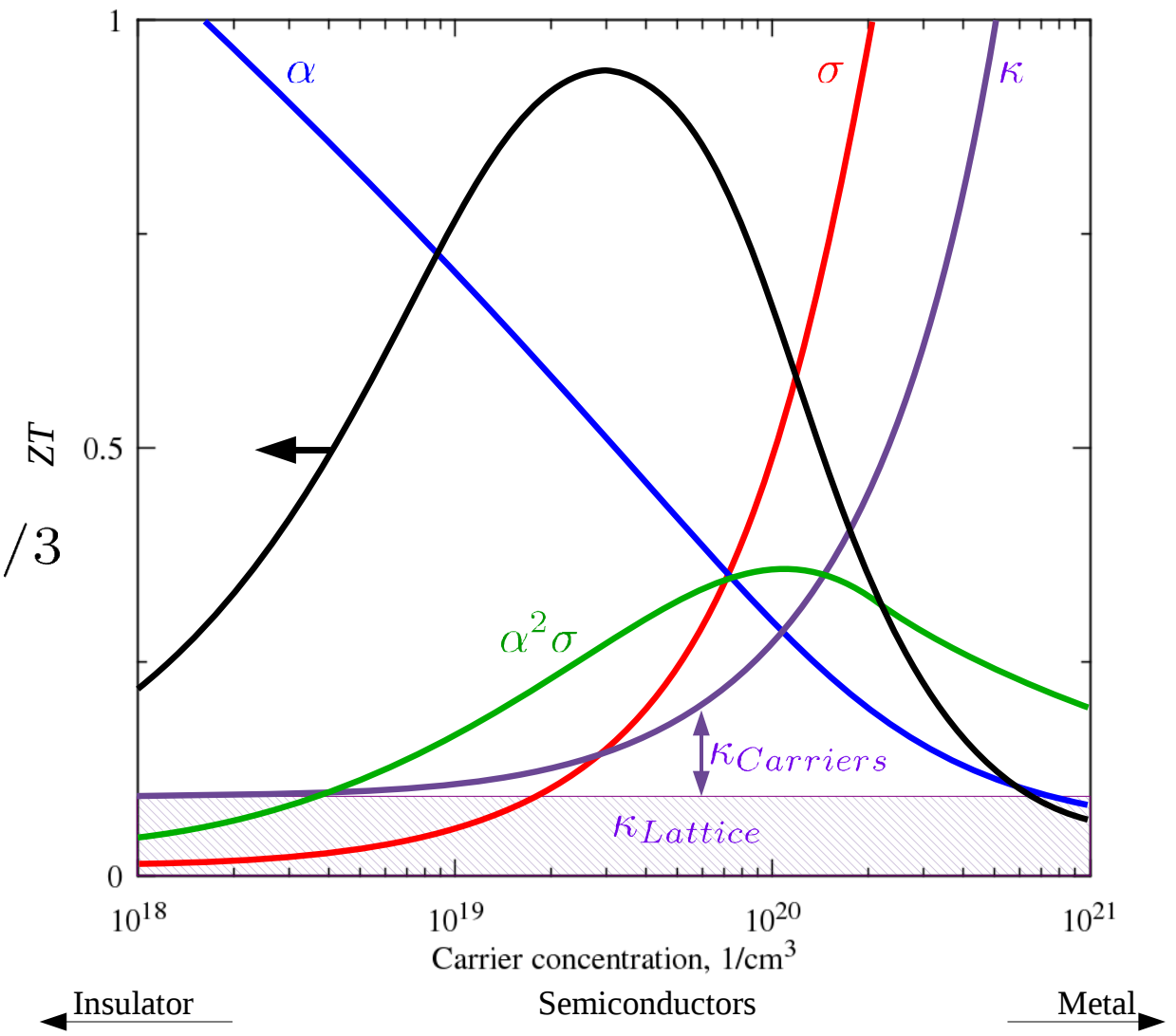
$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

Charge carrier thermal conductivity

$$\kappa_e / \sigma \approx L \cdot T$$

Total thermal conductivity

$$\kappa = \kappa_e + \kappa_l$$



Debye model: $\kappa_l \approx \frac{1}{3} c_v v_s \lambda_{ph} = \frac{1}{3} c_v v_s^2 \tau_{ph}$

Thermal conductivity

$$\kappa_L = 1/V \sum_{i,k} v_{i,x}^2(k)\tau_i(k)C_i(k)$$

Low mean phonon velocity

- → guest host interaction
- → soft materials

Low phonon mean free path

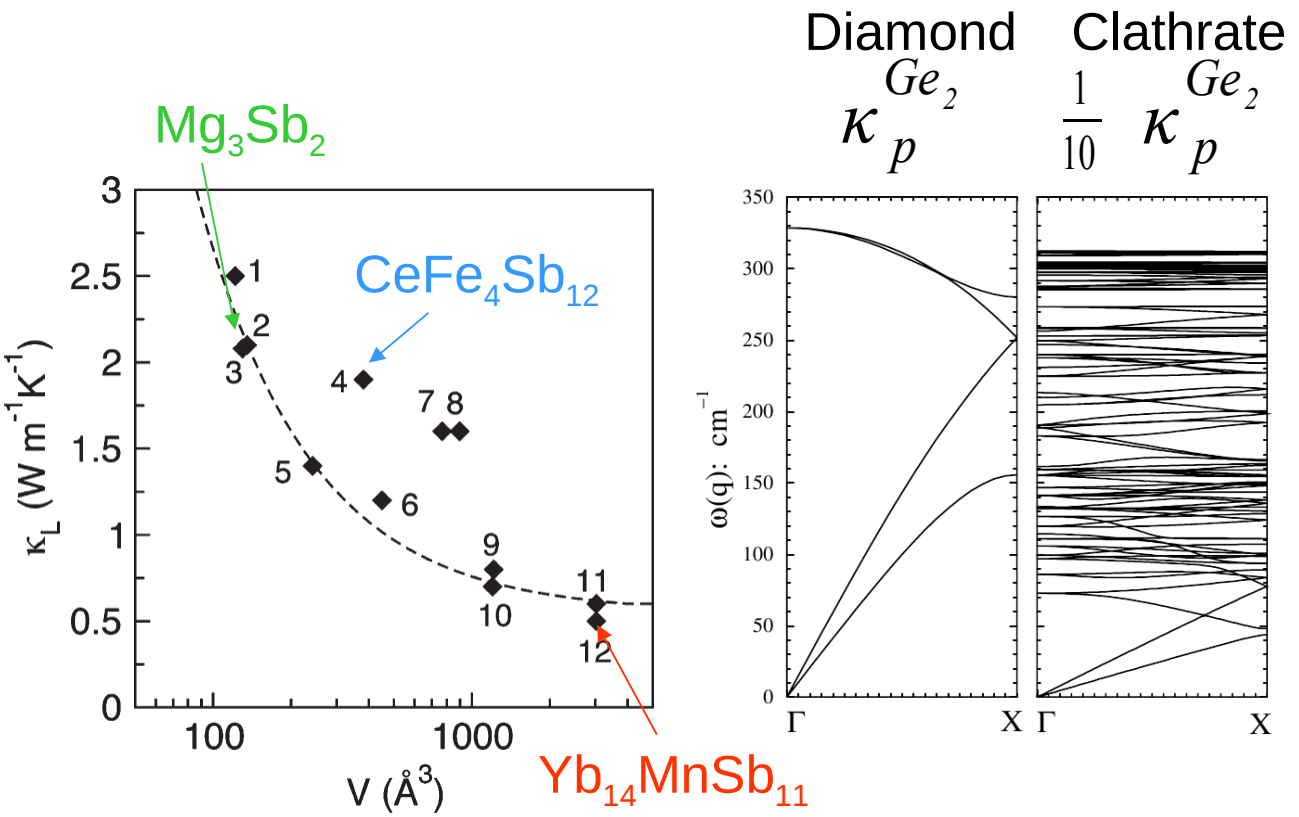
- → guest and host interaction
- → nanostructuring
- → anharmonicity

Low 'specific heat' contribution

- → large unit cell

Effective Heat Capacity

$$\kappa_p = \frac{1}{3} C_V v_s \lambda$$



Large unit cell → small ratio of the number of acoustic to optical modes

→ small contribution of the heat capacity to the thermal conductivity

$$C_V \rightarrow C_V^{eff}$$

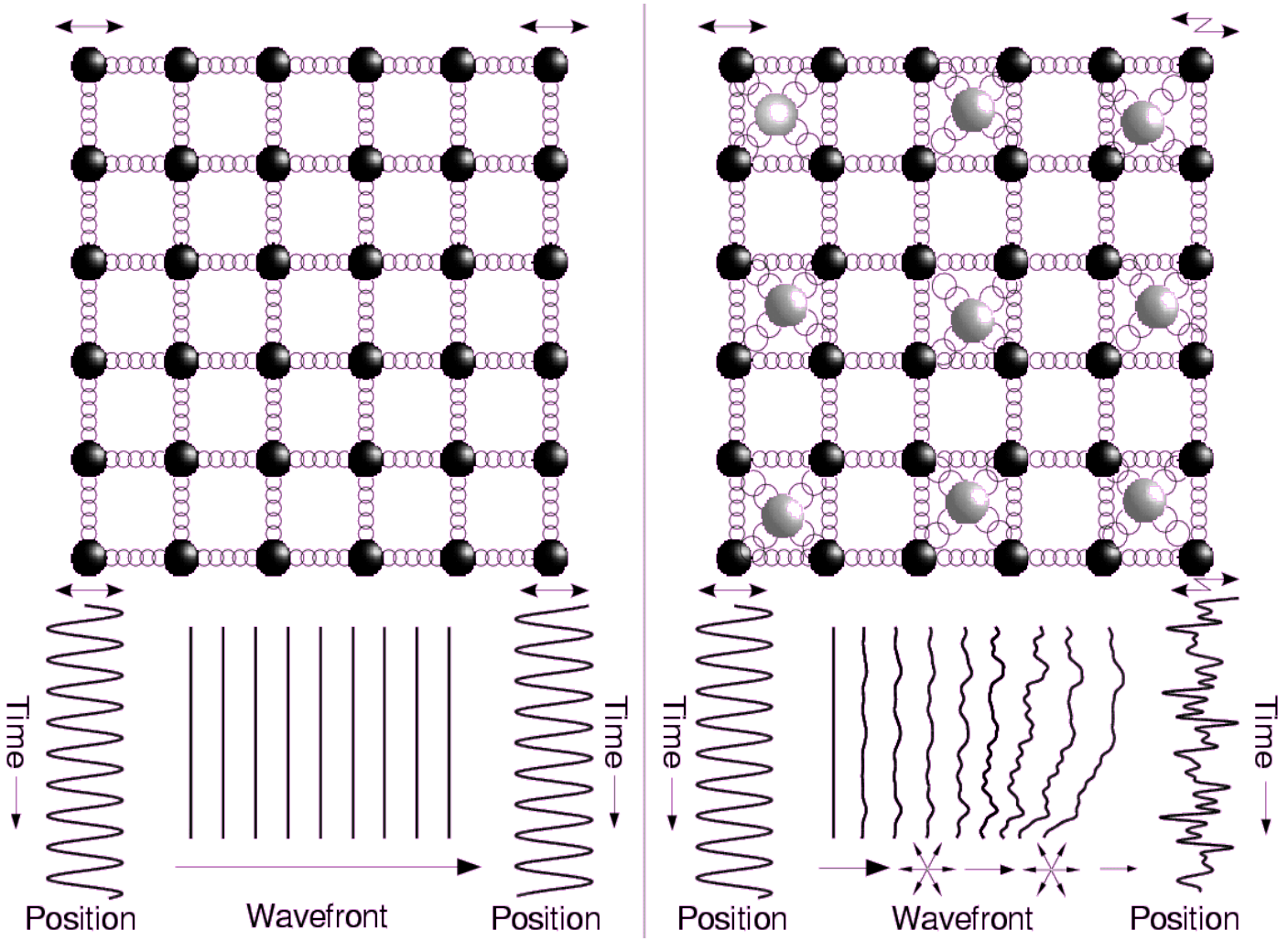
Toberer *et al. Chem. Mater.* **22** (2010)

Dong *et al. Phys. Rev. Lett.* **86** (2001)

Phonon mean free path

$$\kappa_p = \frac{1}{3} C_V v_s \lambda$$

→ interaction of guest and cage atom



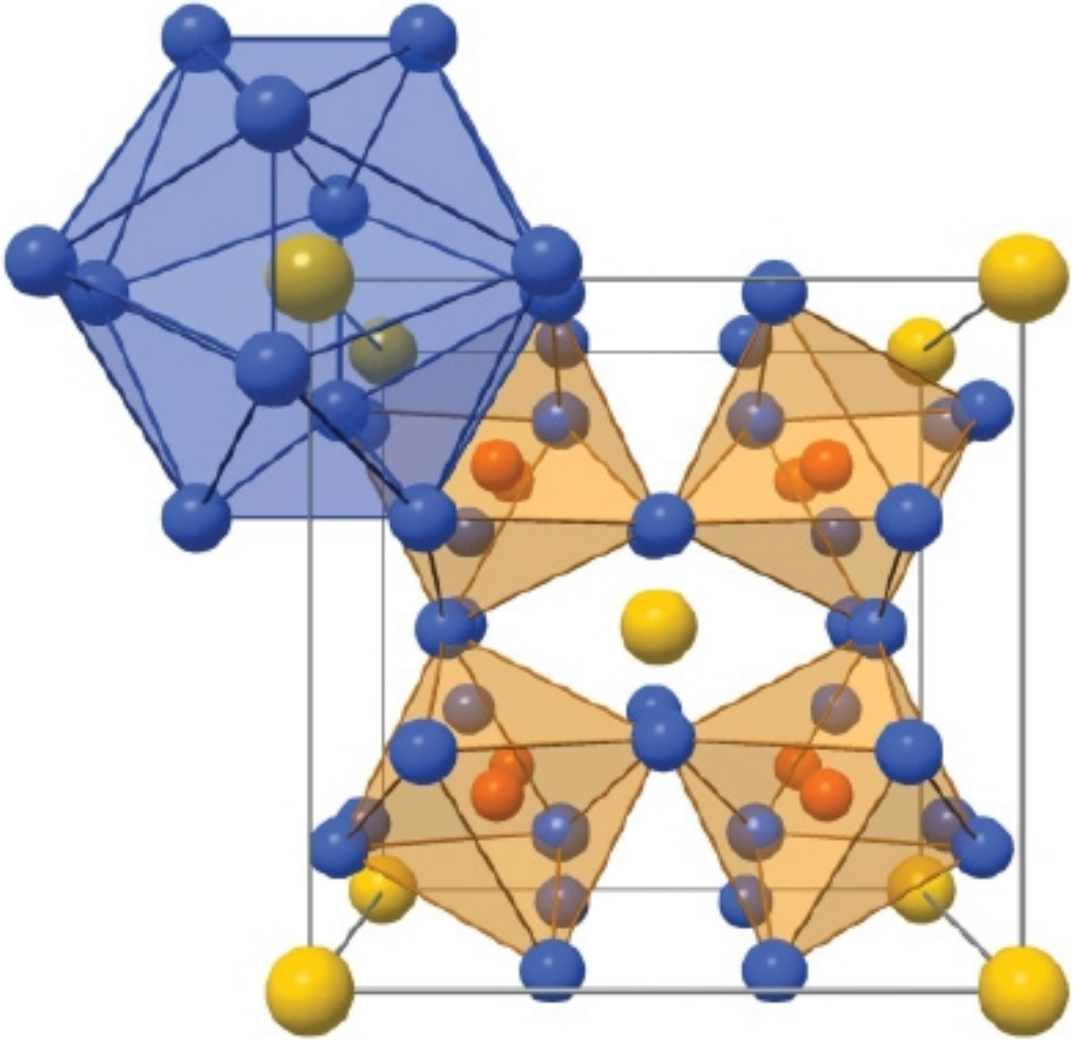
Hermann *et al.*, *Am. J. Phys.* **73** (2005)

$YbFe_4Sb_{12}$

PHYSICAL REVIEW B **84**, 184306 (2011)

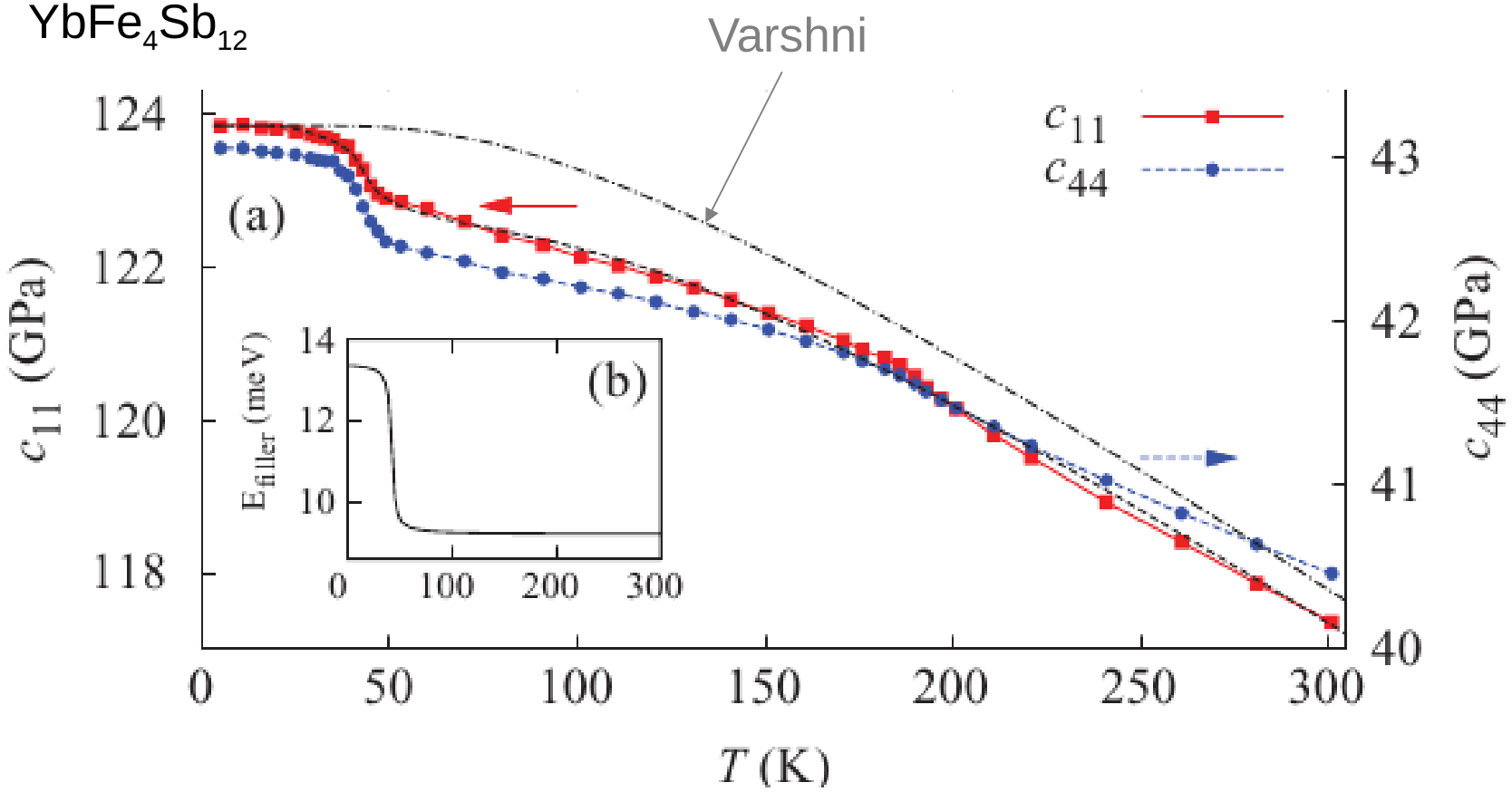
Lattice dynamics and anomalous softening in the $YbFe_4Sb_{12}$ skutterudite

A. Möchel,[1,2] I. Sergueev,[3] H.-C. Wille,[4] J. Voigt,[1] M. Prager,[1,*] M. B. Stone,[5] B. C. Sales,[6] Z. Guguchia,[7] A. Shengelaya,[7] V. Keppens,[8] and R. P. Hermann[1,2,†]



Resonant ultrasound spectroscopy

$YbFe_4Sb_{12}$



V. Keppens, University of Tennessee

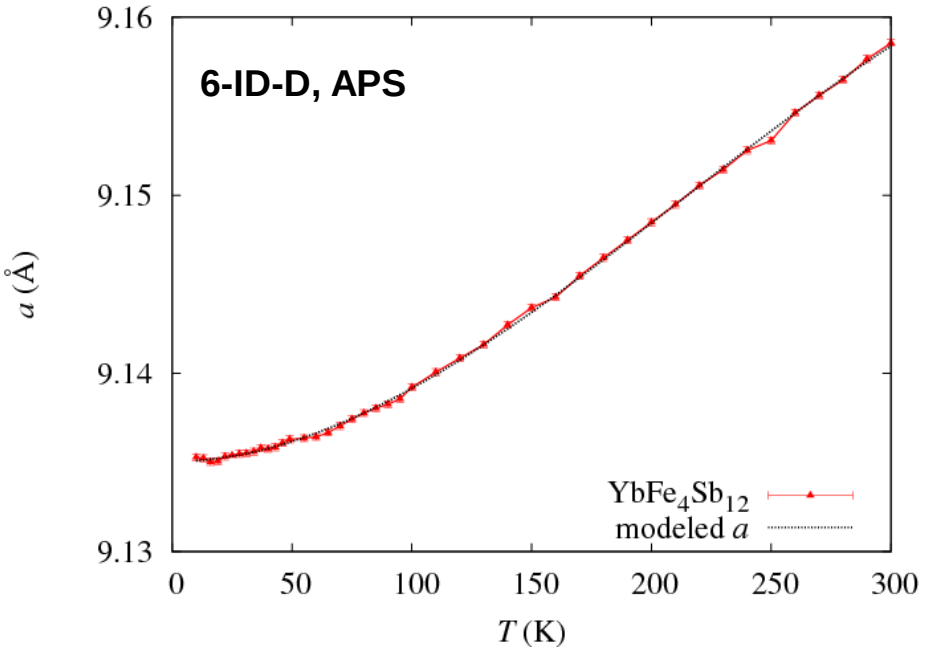
Possible explanations:

- structural phase transition
- magnetic phase transition
- shift of the guest mode energy
- Yb valence change

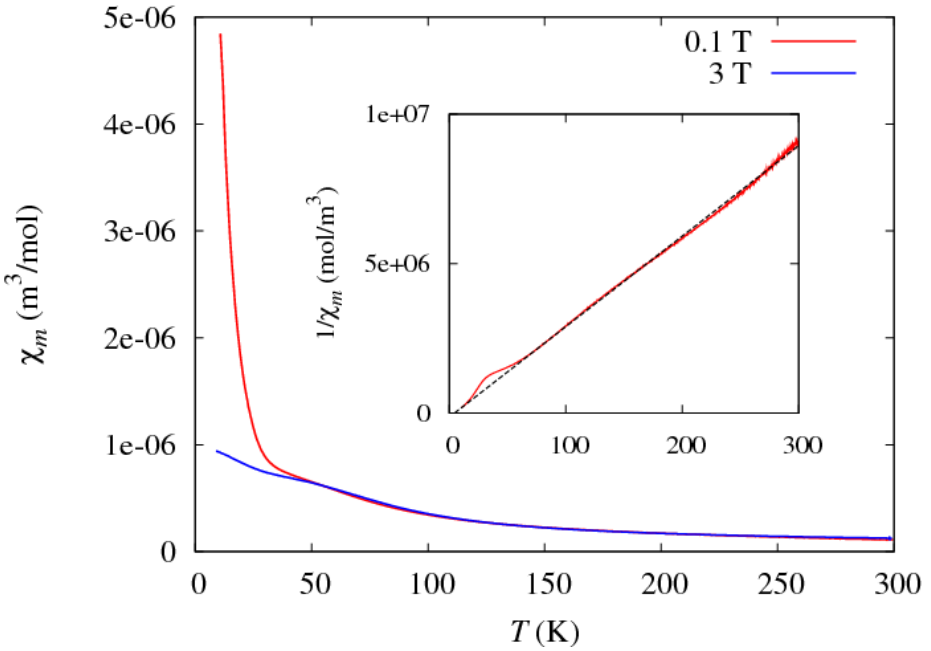
Phase transition

$YbFe_4Sb_{12}$

Diffraction



Magnetometry (VSM, PPMS)

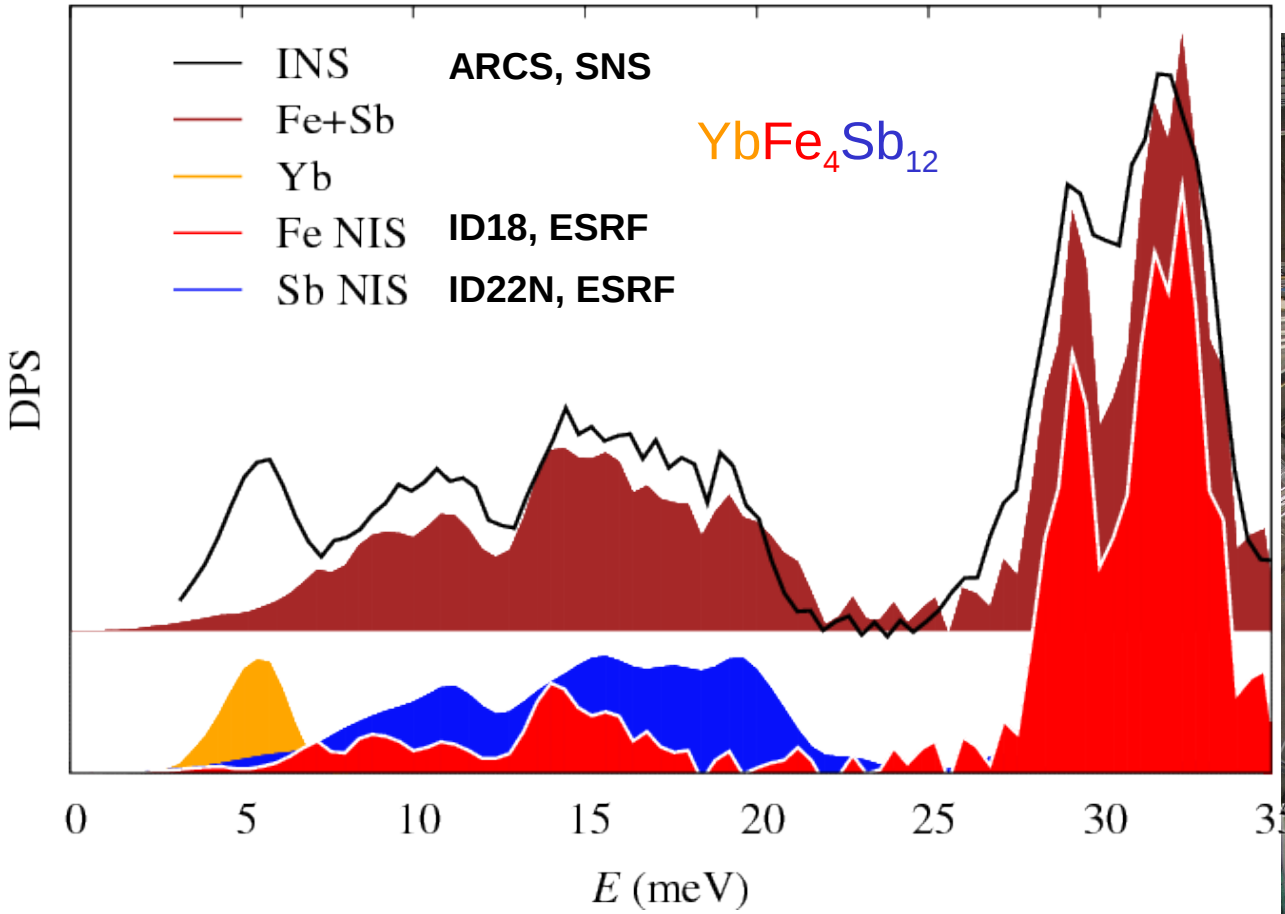


→ **no** structural or magnetic **phase transition**

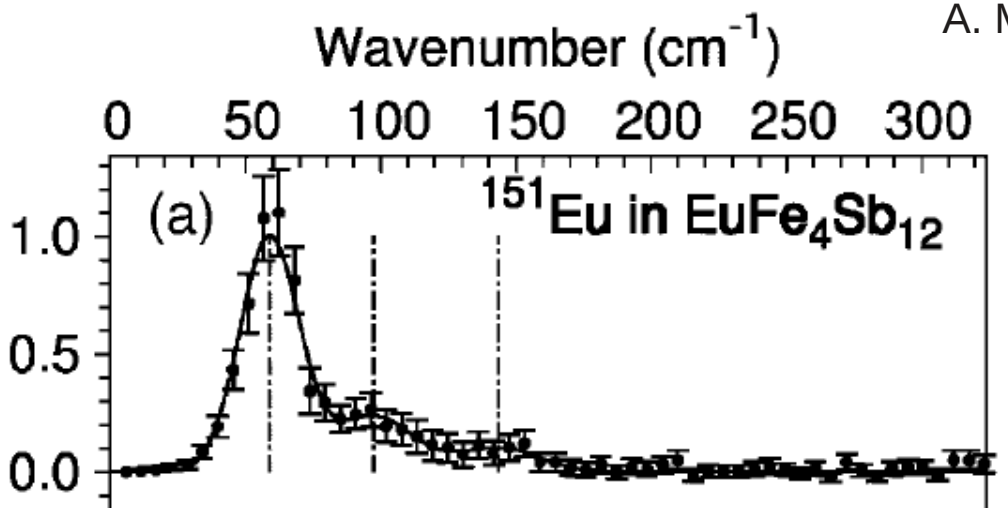
Alleno *et al.*, *Physica B: Condensed Matter* **77** (2008)

Ikeno *et al.*, *JPSJ* **76** (2007)

Density of phonon states

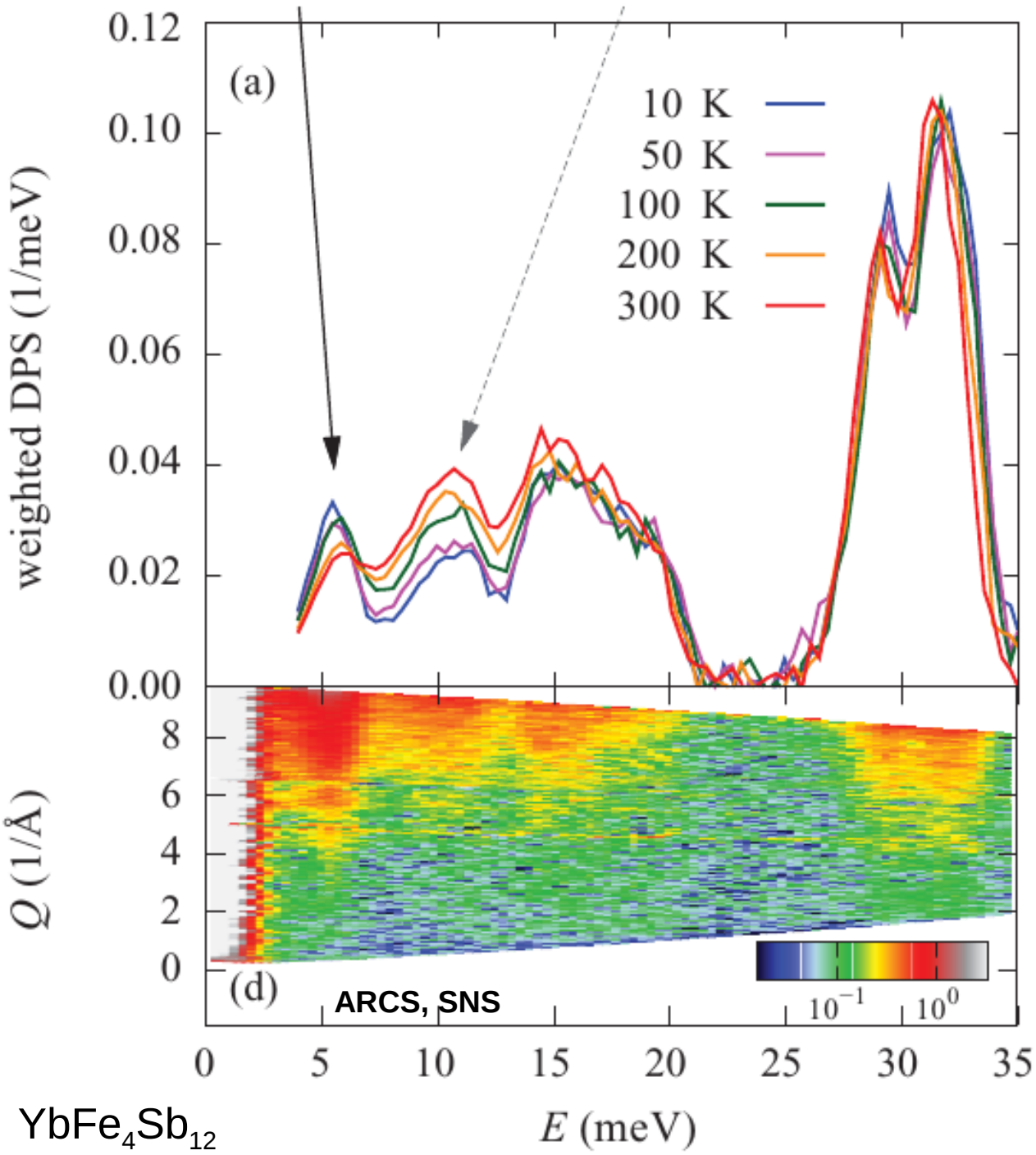


A. Möchel et al. Phys. Rev. B **84**, 184306 (2011)



G. Long et al. Phys. Rev. B **71**, 140302R (2005)

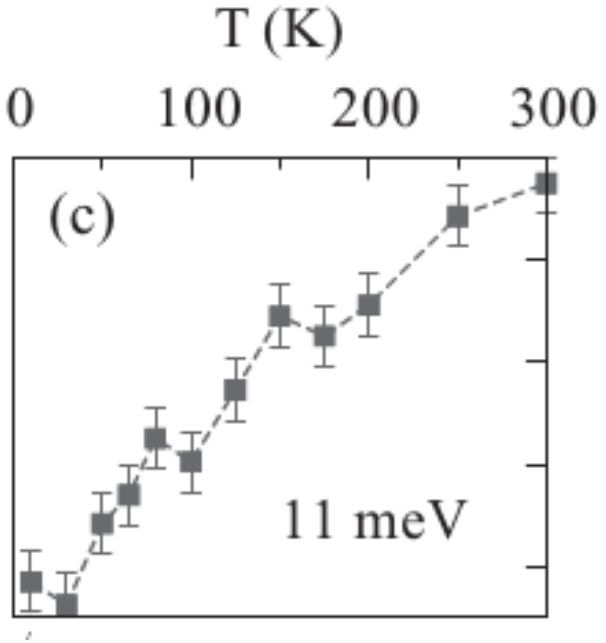
Frequency shift?



$YbFe_4Sb_{12}$

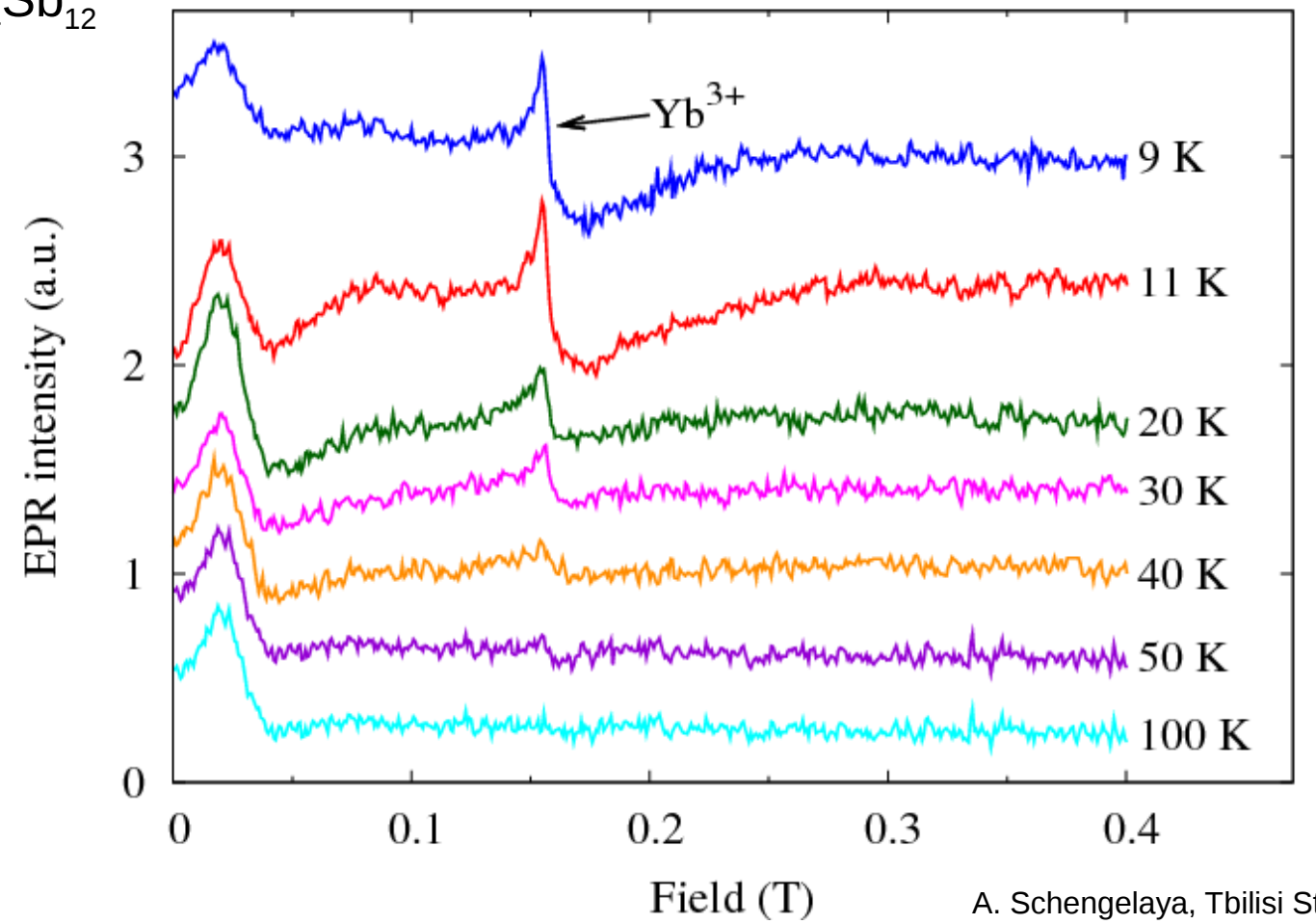
→ **no shift** of the guest energy

→ rearrangement of the spectral weight



Valence change

$YbFe_4Sb_{12}$



A. Schengelaya, Tbilisi State University

→ partial change of the Yb valence (?)

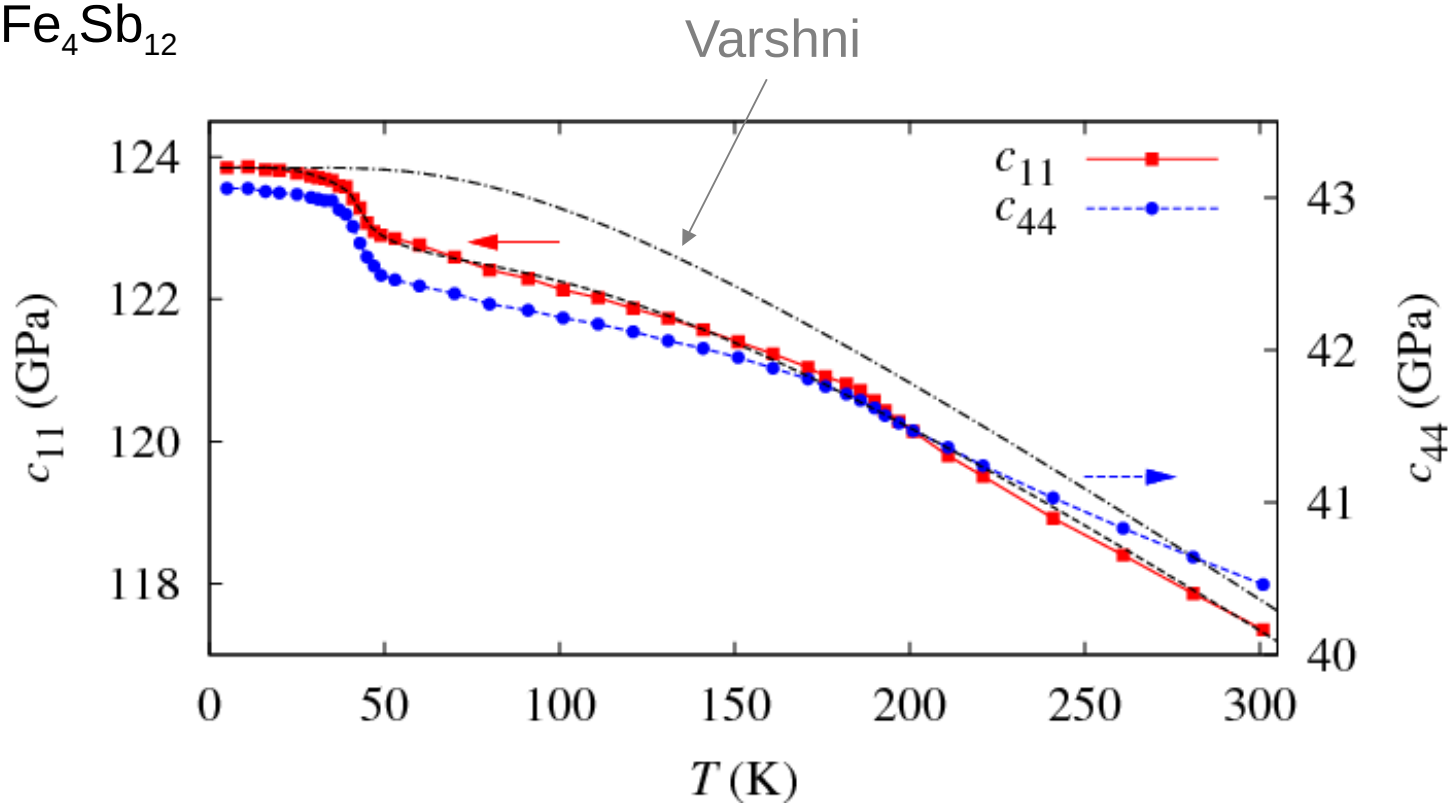
Dilley *et al.*, *Phys. Rev. B* **61** (2000)

Schnelle *et al.*, *Phys. Rev. B* **71** (2005)

Dedkov *et al.*, *Physica C* **460-462** (2007)

Resonant ultrasound spectroscopy

$YbFe_4Sb_{12}$



V. Keppens, University of Tennessee

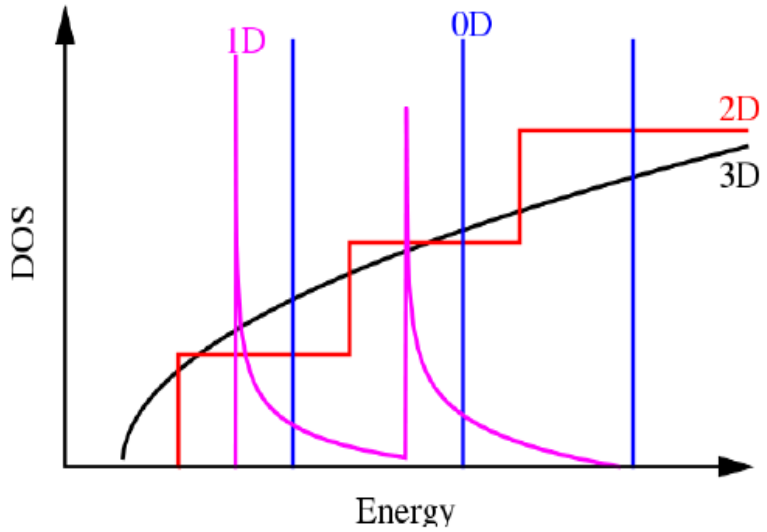
- ✘ structural phase transition
- ✘ magnetic phase transition
- ✘ shift of the guest atom frequency
- ✓ Yb valence change → has to be confirmed (e.g. by XPS)

Nanostructured thermoelectrics

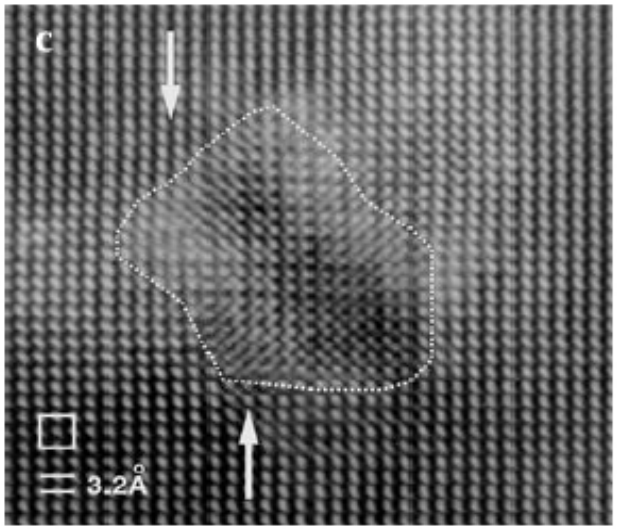
Key idea (Hicks, Dresselhaus,1992):

Electronic band engineering

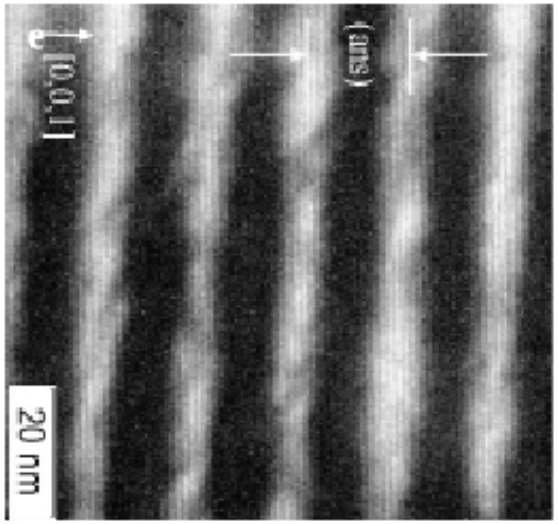
and phonon blocking

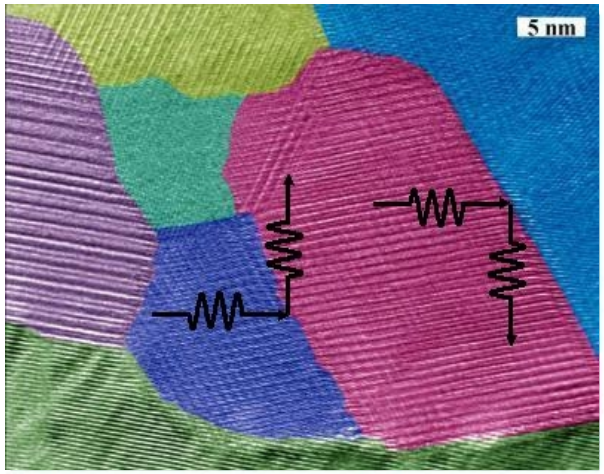


Embedded nanodots
(Kanatzidis group)

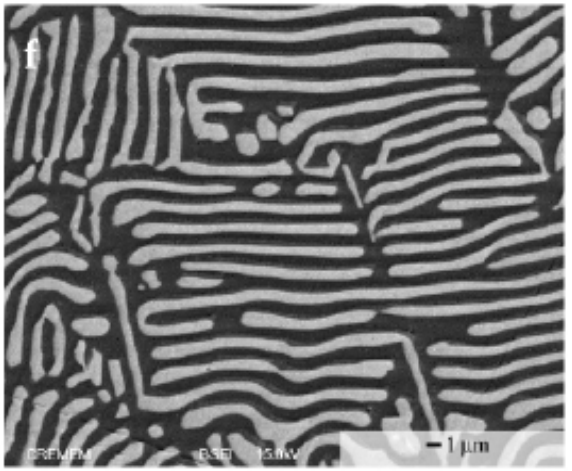


Artificial nanostructures
(N. Peranio, PhD diss., U. Tübingen)





Nanocomposites
(Poudel et al., Science 2008)

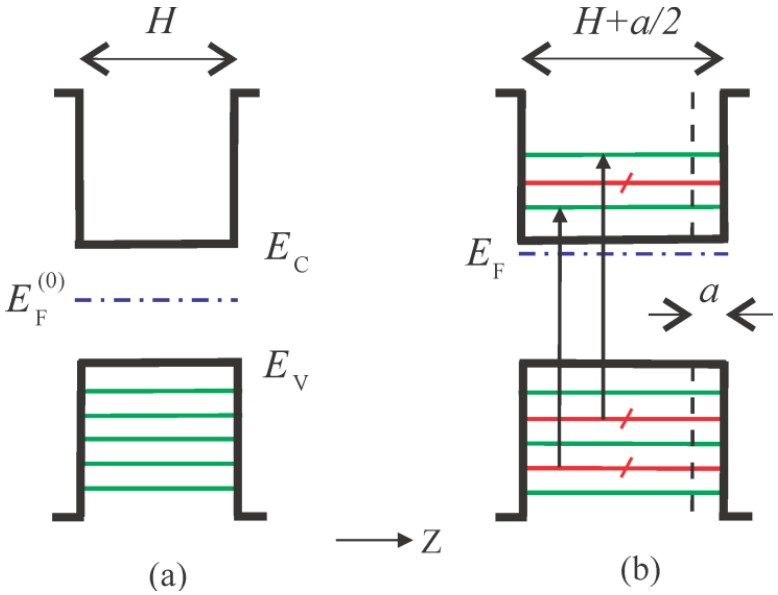


Self organization
(Gorsse et al., Chem. Mater 2009)

Thermoelectric properties of nanogratings

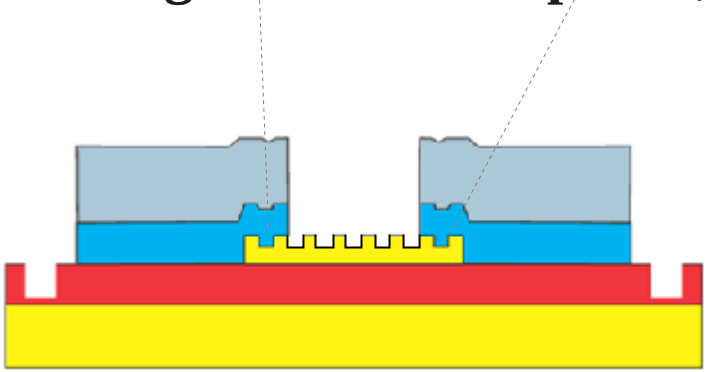
Key idea: geometrically modulated
density of electronic states (DOS)

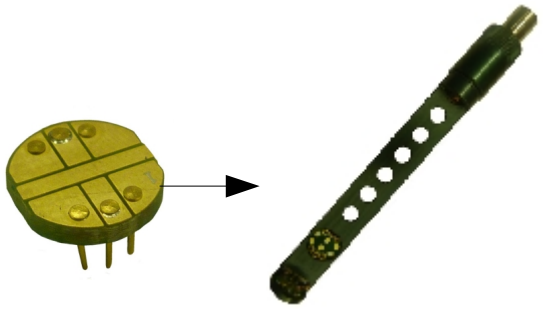
Nanoscale patterning that matches the
electron De Broglie wavelength

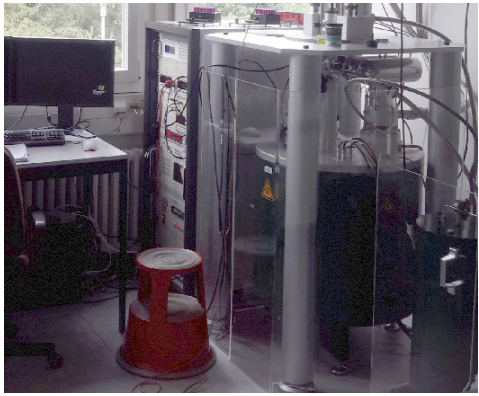


Prof. Avtandil Tavkhelidze, ISU
M. Sc. Michael Mebonia ISU and FZJ

→ **Tuning of the thermopower, the derivative of the DOS at the Fermi level**







Fabrication with Extreme UV Lithography
and in the future at the Helmholtz Nano Facility

Prof. Larissa Jushkin, RWTH and FZJ

Structure and transport characterization:
Scattering (JCNS, GALAXI) and cryomagnet

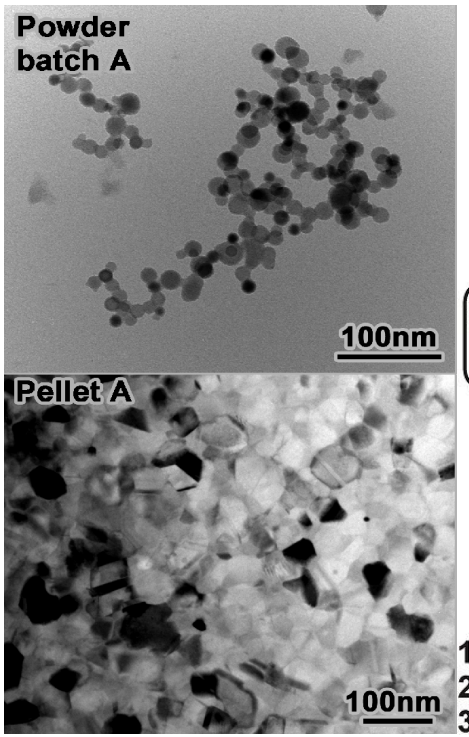
Prof. Raphaël Hermann, FZJ and Liège

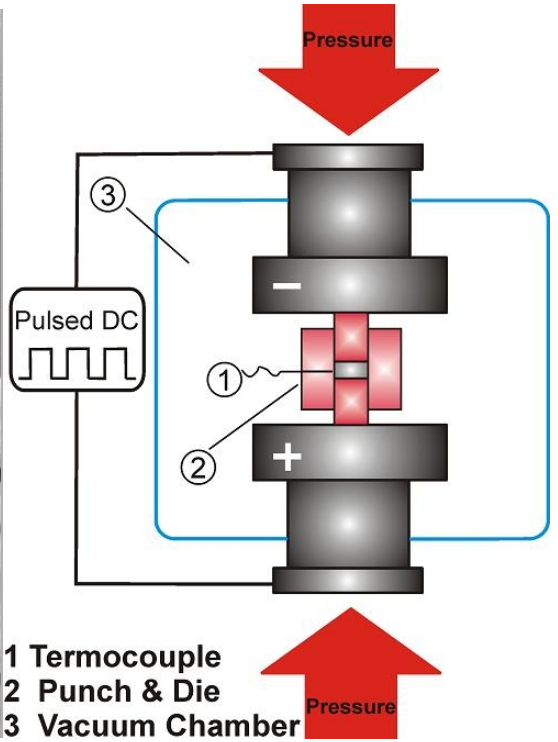
Nano Si (P-doped) preparation

- Gas phase synthesis with hot wall reactor and plasma-assisted microwave reactor

Source: cpfs.mpg.de

- Variables:
  - *microwave power*
  - *chamber pressure*
  - *concentration of precursor gases* (SiH_4,GeH_4) + PH_3 *and plasma gases* Ar *and* H_2





AG Schierning, U. Duisburg-Essen

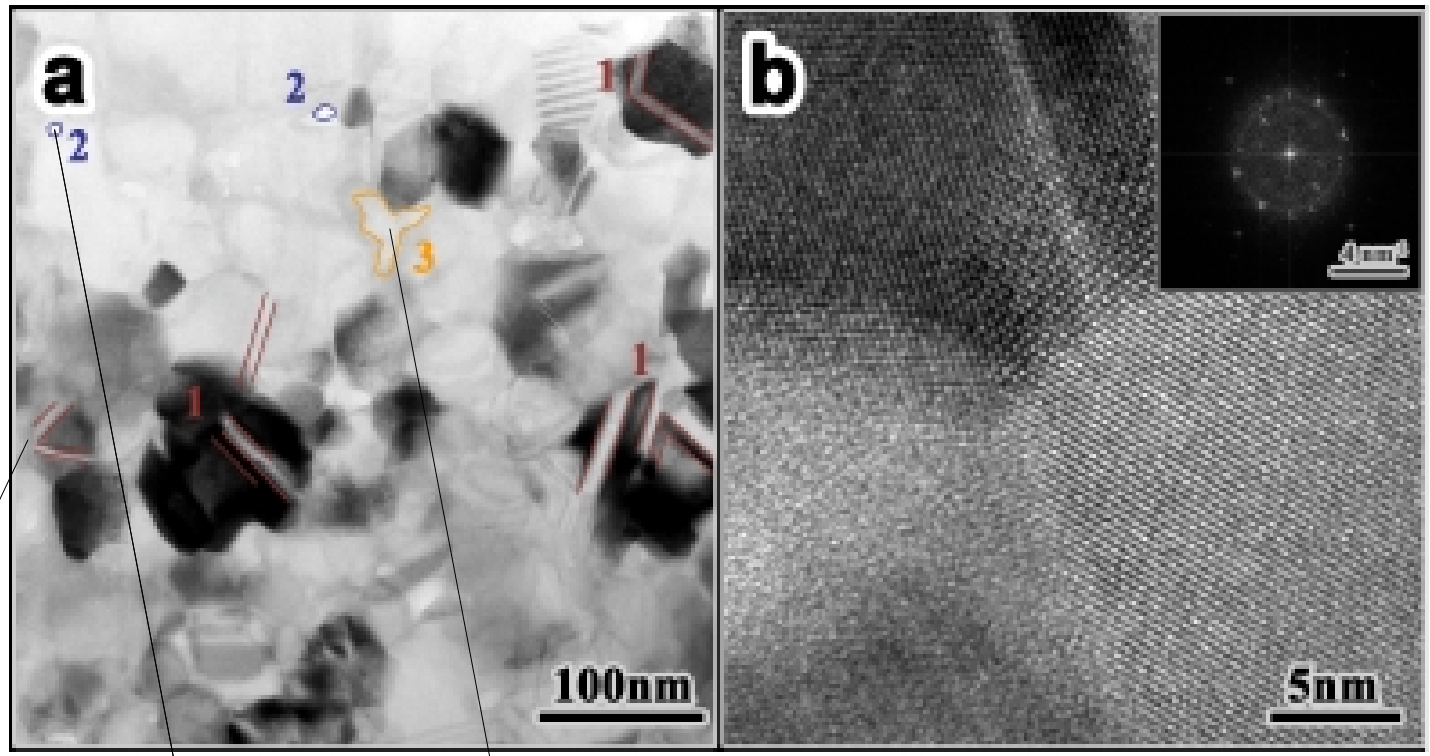
- Pellets: Spark Plasma Sintering

  aka
  Current And Pressure Assisted Sintering

Nanocrystalline silicon: impurities

First attempts: contains SiO_2

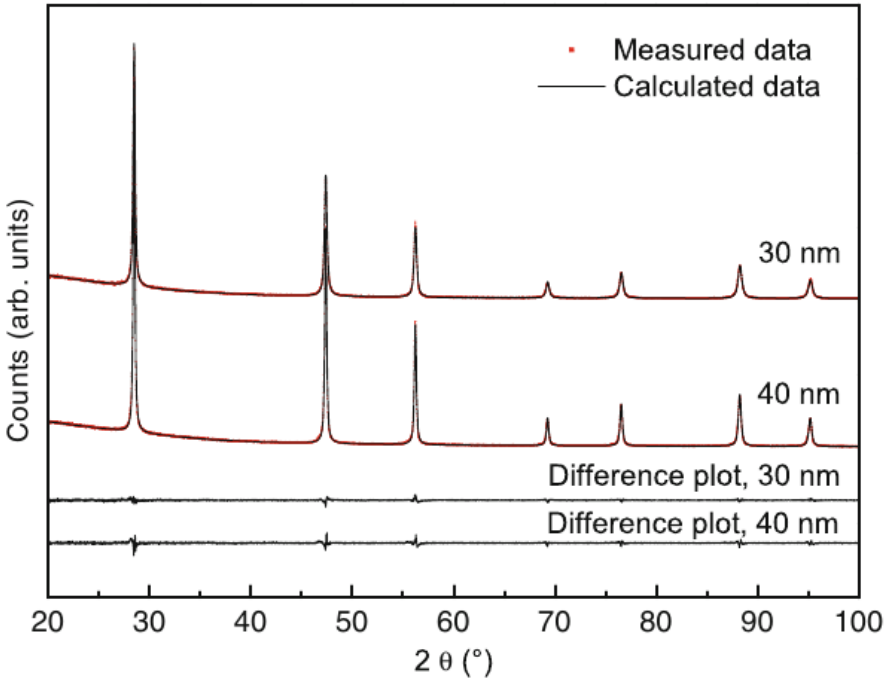
Briefest exposure to air between production and sintering → oxidation



Twins Pores Oxidic precipitates

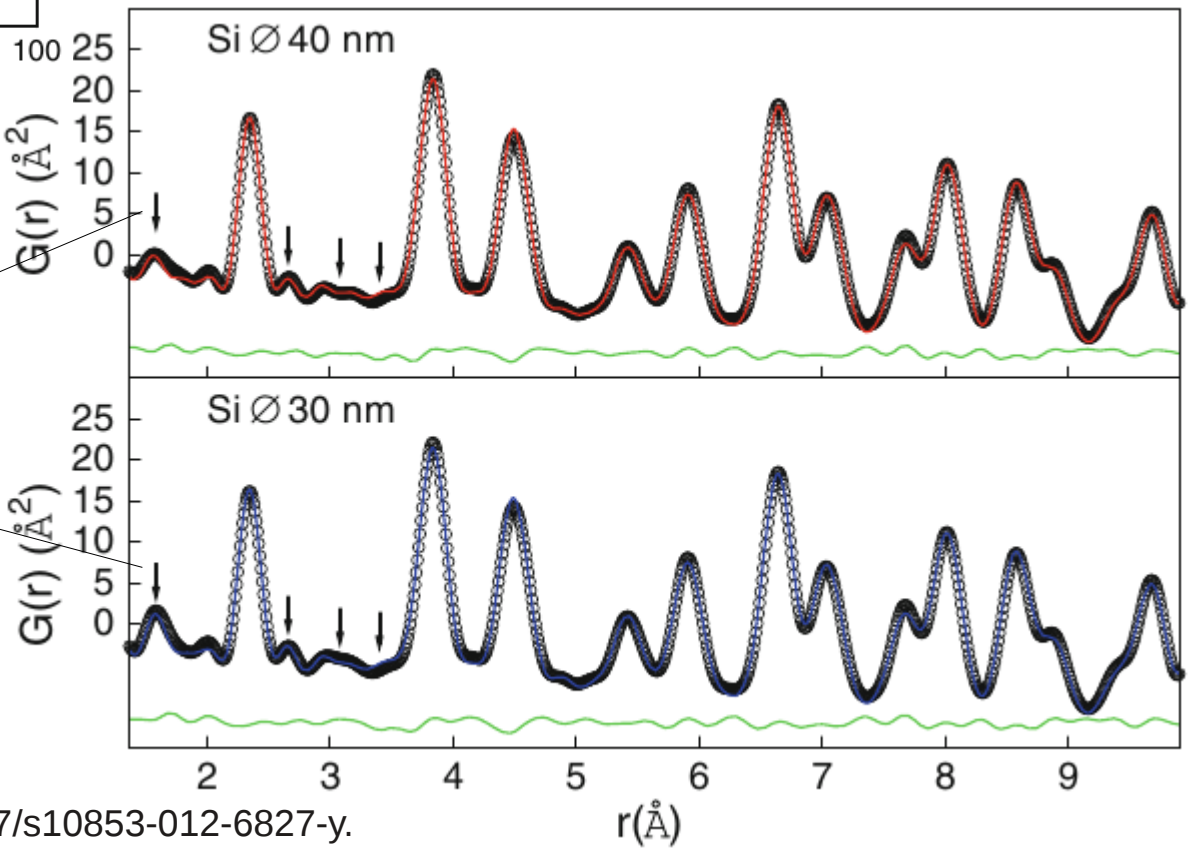
T. Claudio *et al.*, J. Mater. Sci. (2012) DOI 10.1007/s10853-012-6827-y

Diffraction and pair distribution function



→ Phase pure ?

PDF, JCNS 6-ID-D, APS



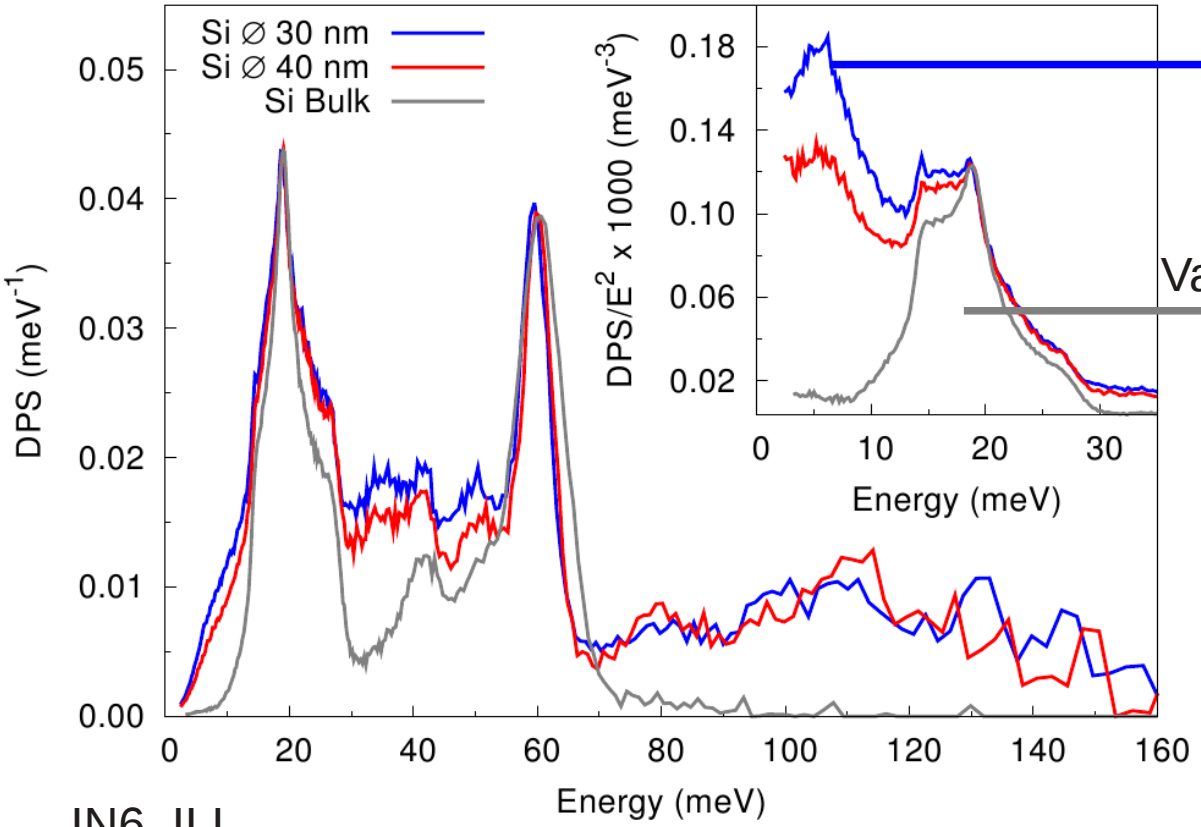
10%

SiO_2

15%

T. Claudio *et al.*, J. Mater. Sci. (2012) DOI 10.1007/s10853-012-6827-y.

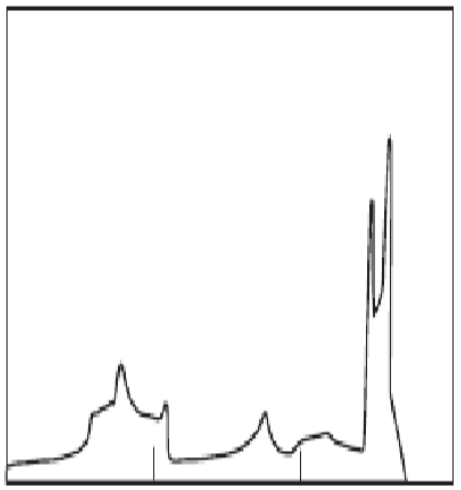
Nano-Si Inelastic neutron scattering and specific heat



„Boson peak“

Van Hove singularity

IN6, ILL

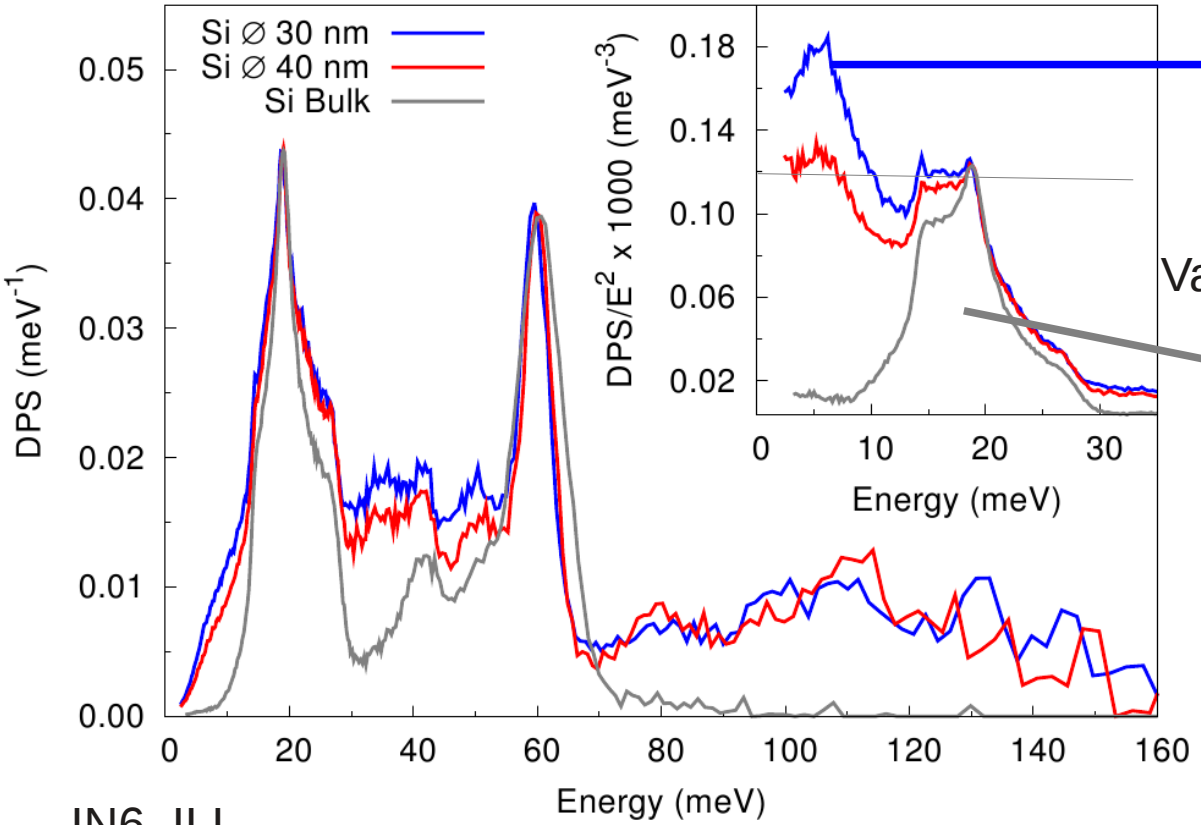


- No obvious peak broadening

- **Impurity signatures:** SiO_2 + Si-H stretching

T. Claudio *et al.,* J. Mater. Sci. (2012) DOI 10.1007/s10853-012-6827-y.

Nano-Si Inelastic neutron scattering and specific heat



„Boson peak“

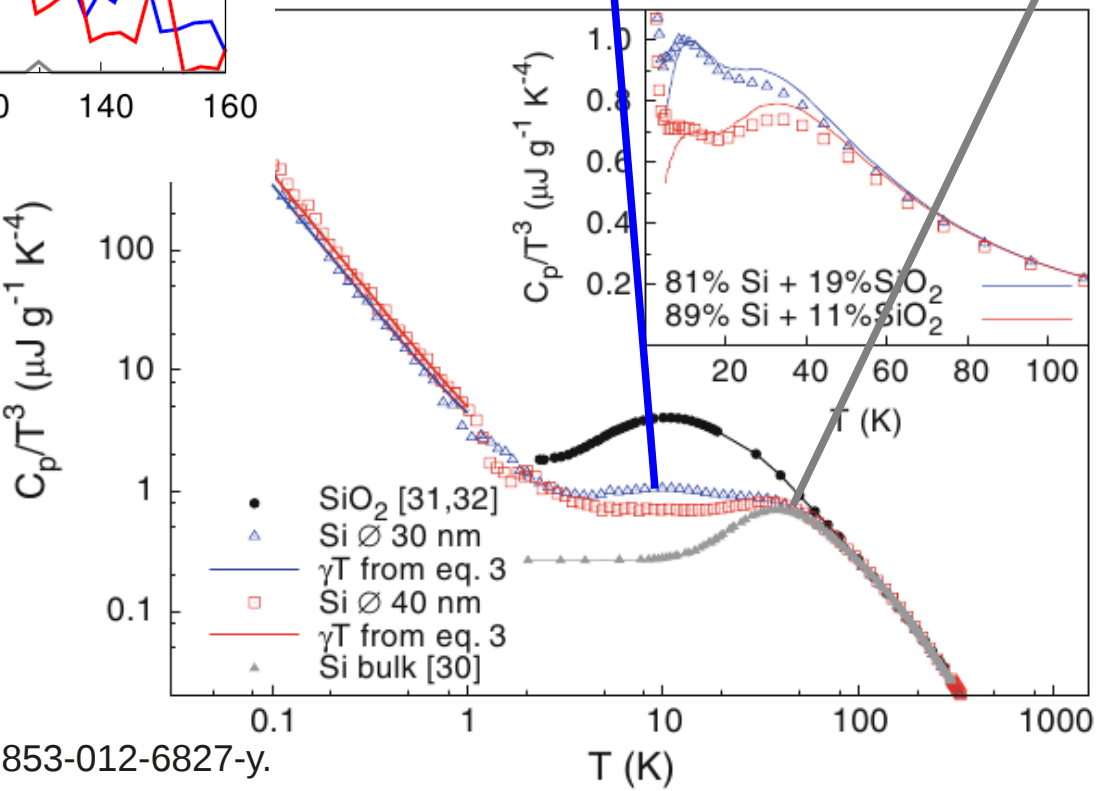
Van Hove singularity

IN6, ILL

Highly doped: no charge freeze out:

$\gamma = 0.120(2)$ mJ/mol/K^2

$\gamma = 0.097(2)$ mJ/mol/K^2



T. Claudio *et al.*, J. Mater. Sci. (2012) DOI 10.1007/s10853-012-6827-y.

Nanocrystalline silicon – controlling purity

Functionalisation by hydrogen to avoid oxidation

Inert conditions at all steps

Sintering immediately after synthesis:

Heating/cooling 100 K/min

T = 1150 °C, *P* = 35 Mpa

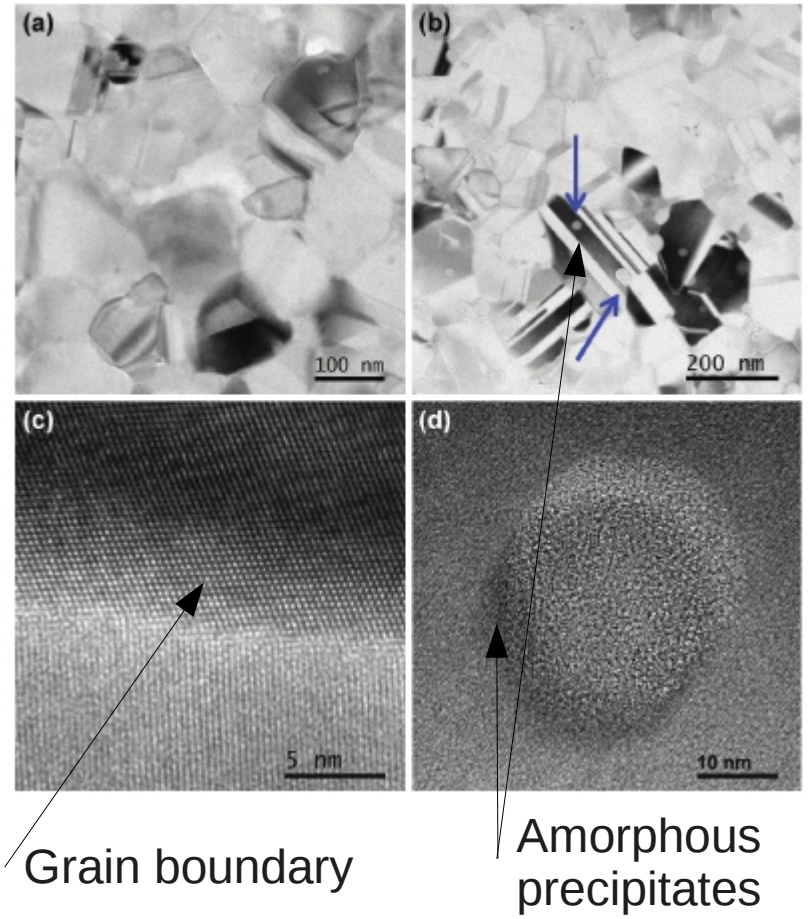
Sample A: 14 nm initial, 3 minutes

Sample B: 52 nm initial, 30 minutes

Sample C: 52 nm initial, 3 minutes

Elemental analysis at PGAA, MLZ:

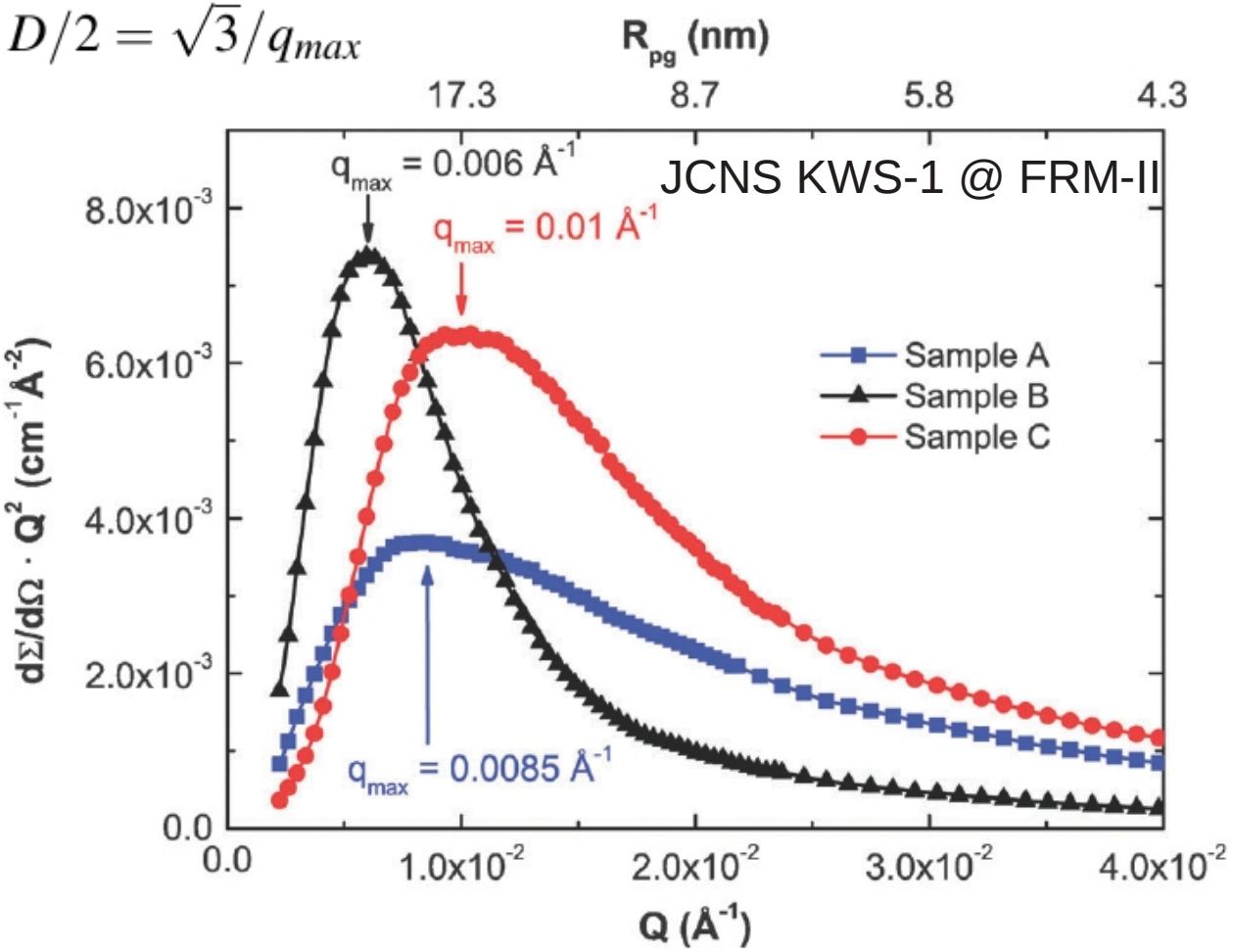
99.0(1)% Si, 1.0(7)% of P dopant
H ~ 0.20(1)% in sample A
ppm B (diborane in silane precursor)

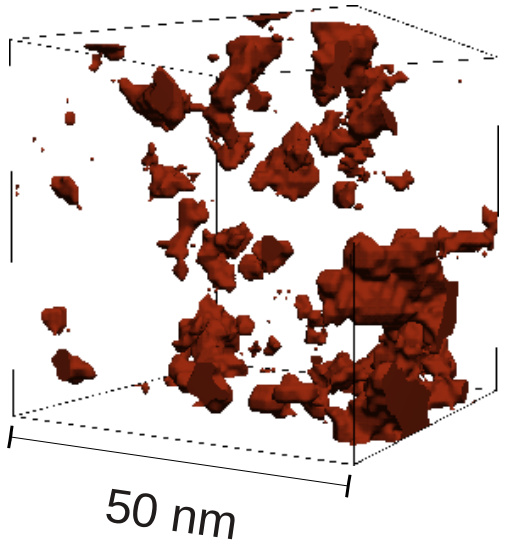


T. Claudio *et al.,* PCCP, DOI 10.1039/c3cp53749h, (2014).

Microstructure: SANS

$D/2 = \sqrt{3}/q_{max}$





Representative morphology

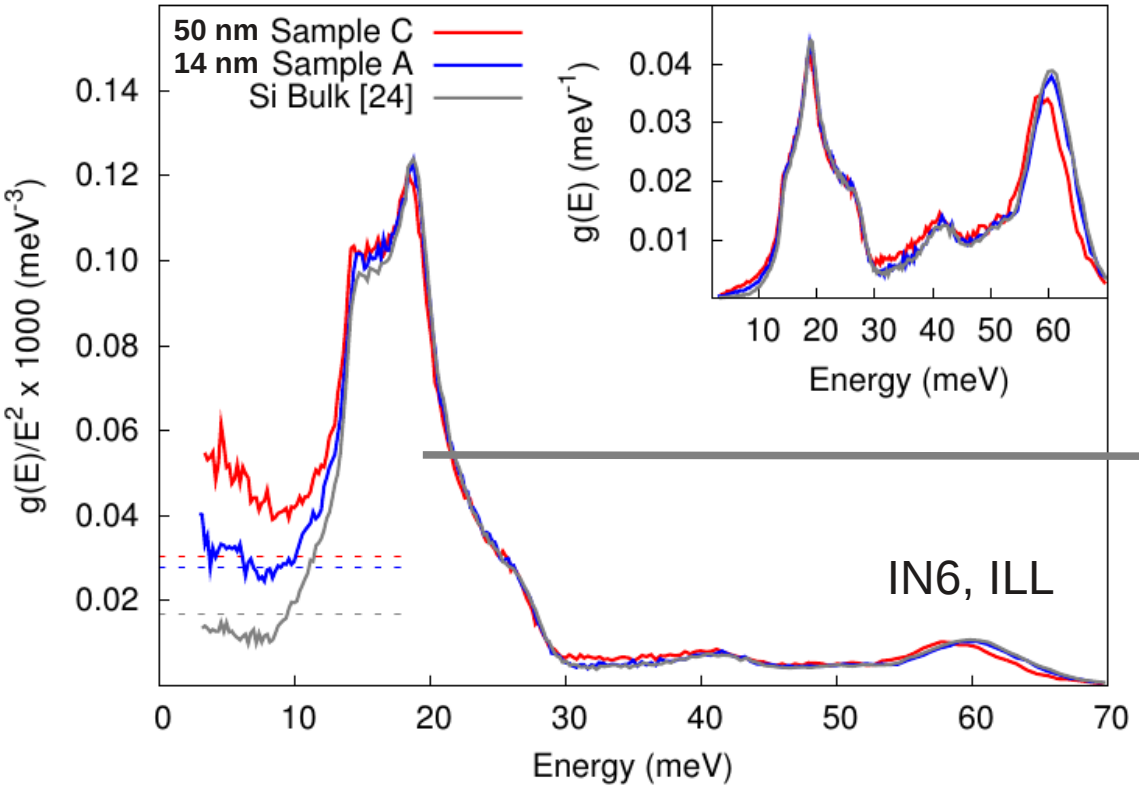
(SAXSmorph)

„pores“ depicted in brown

	TEM			XRD		SANS
	D_{min} (nm)	D_{max} (nm)	D_{av} (nm)	D (nm)	ε (%)	D (nm)
Sample A	48	264	114	40(2)	0.00138	42
Sample B	—	—	—	42(2)	0.00133	58
Sample C	47	246	112	33(1)	0.00150	34

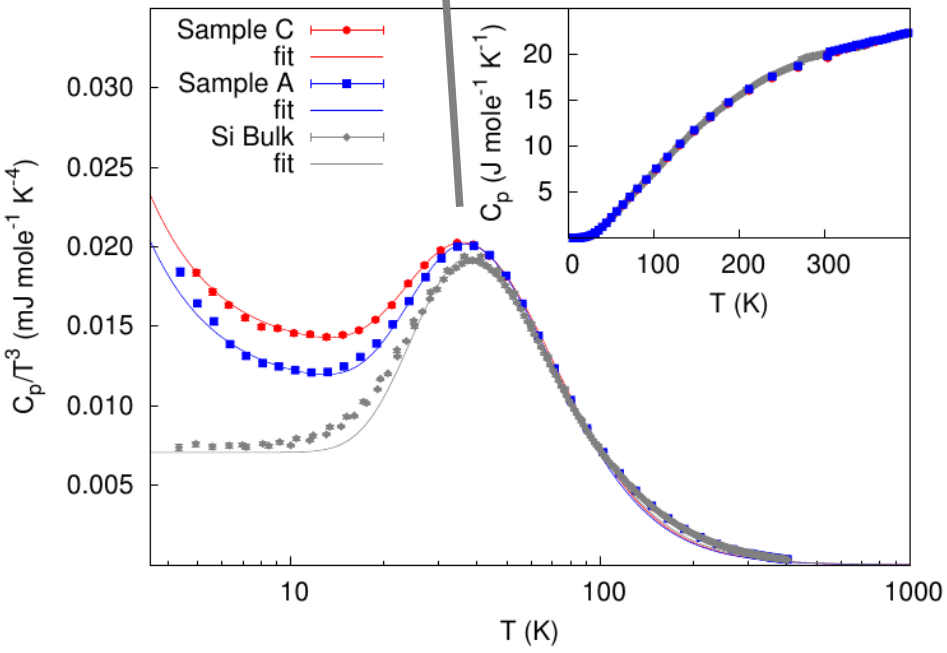
T. Claudio *et al.,* PCCP, DOI 10.1039/c3cp53749h, (2014).

Clean samples: inelastic scattering and specific heat



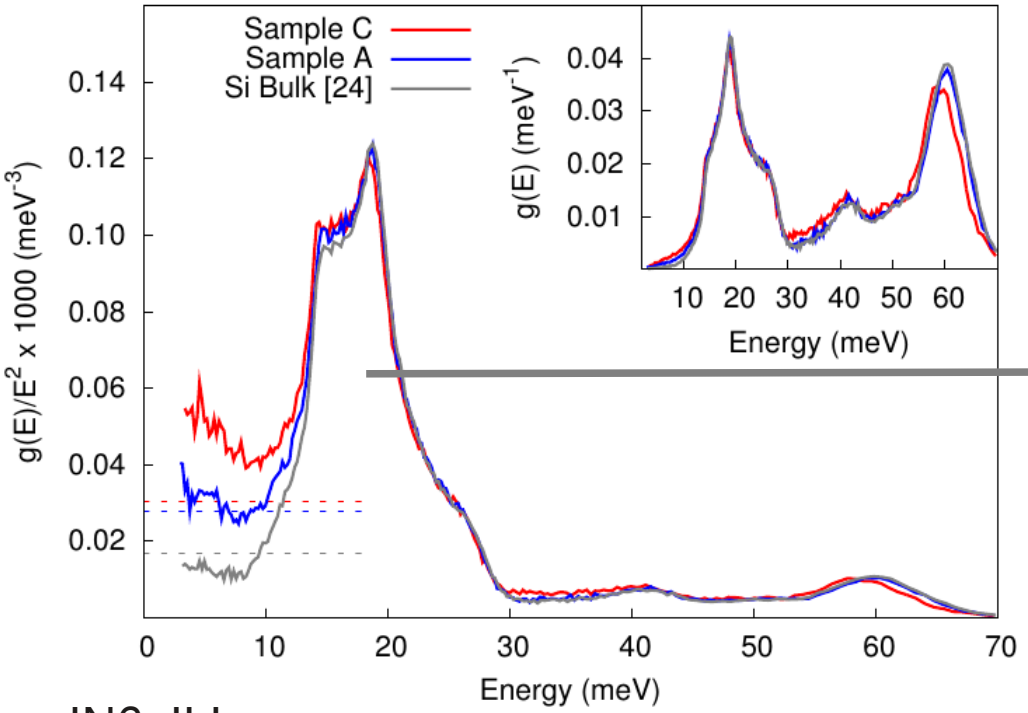
SiO_2 strongly reduced

Van Hove singularity



T. Claudio *et al.*, PCCP, DOI 10.1039/c3cp53749h, (2014).

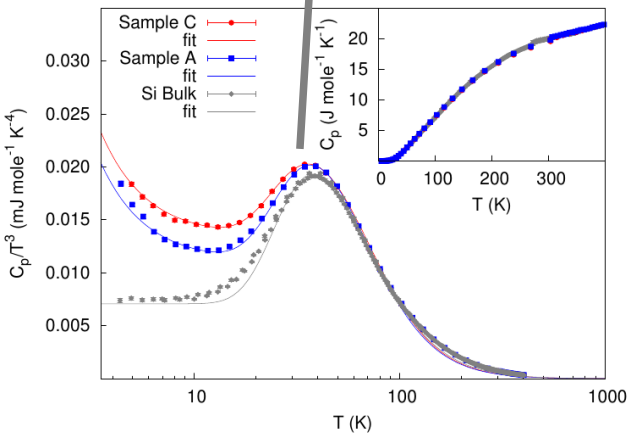
Clean samples: inelastic scattering and specific heat



IN6, ILL

SiO_2 strongly reduced

Van Hove singularity

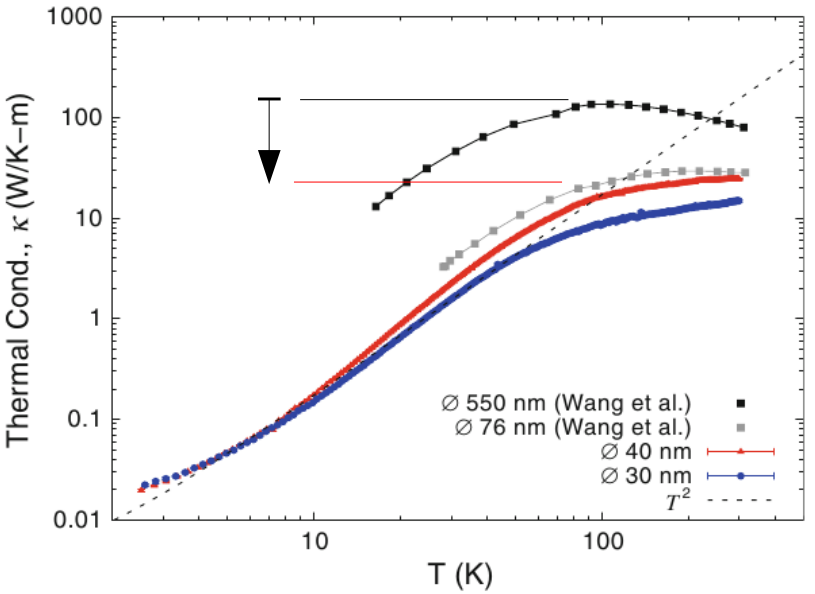


Reduced speed of sound, reduced shear modulus

	C_{11} (GPa)	C_{44} (GPa)	v_s (km/s) RUS	DPS	C_p, Θ_D^{LT}
Bulk	160.1 [32]	80.0 [32]	5.94	6.73(5)	5.70(5)
Sample A	173(3)	59.0(8)	5.0(1)	5.0(3)	4.44(9)
Sample C	172(3)	58.2(7)	4.9(1)	4.3(3)	4.2(1)

T. Claudio *et al.,* PCCP, DOI 10.1039/c3cp53749h, (2014).

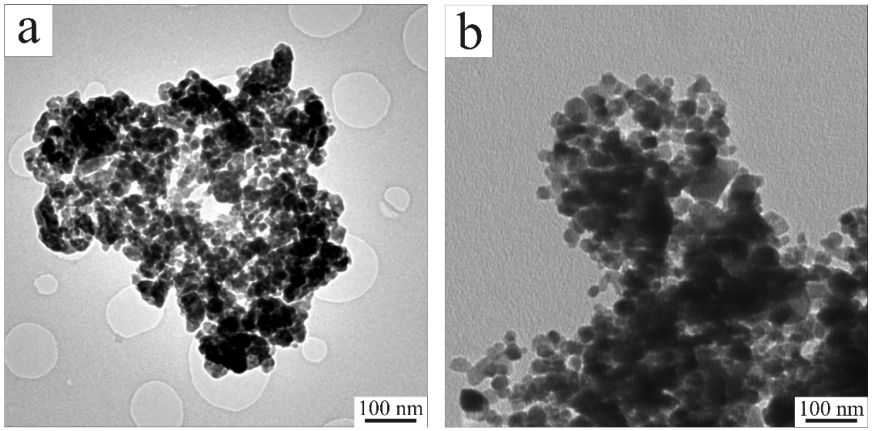
Thermoelectric properties

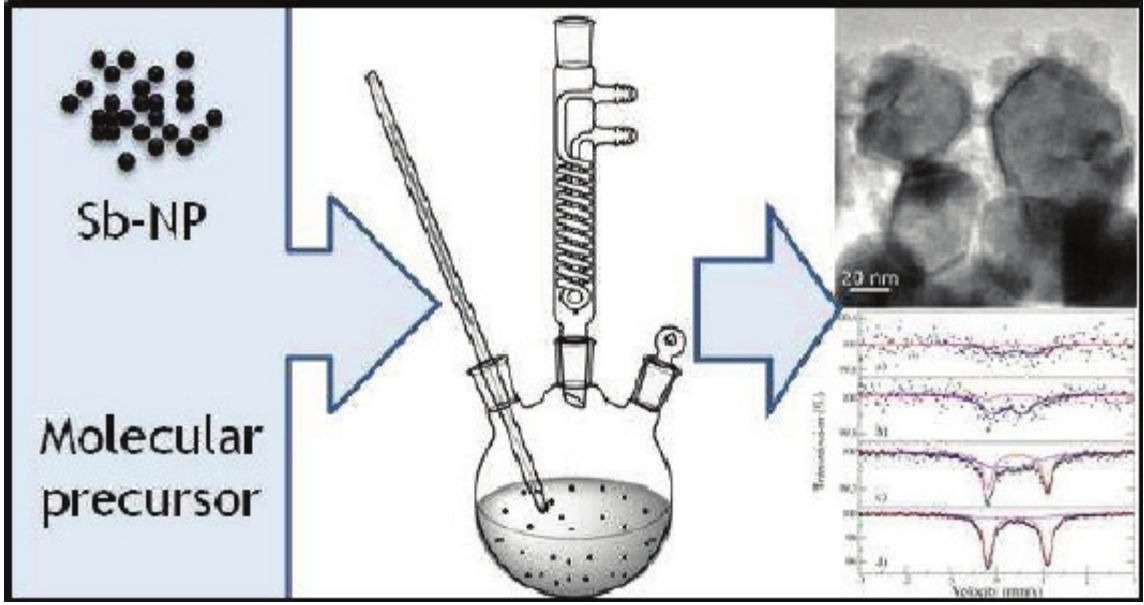


	Single-cryst.	Nanocryst.[37]	Nanocryst.[24]	Sample A	Sample B	Sample C
Nanoparticles production	-	Ball-milling	Gas phase synthesis		Gas phase synthesis	
SPS temperature (°C)	-	-	1050	1150	1150	1150
SPS hold time (min)	-	-	3	3	30	3
Additives / Impurities	-	(from ball-mill)	P, SiO_2, H	P	P	P
Av. nanocryst. size (nm)	-	50-100	30	42	58	33
S (μV/K)	-86	-70	-81.2	-94.3	-116	-114
ρ (μΩ-m)	27.3	9.1	23.7	9.3	11.0	13.2
κ (W/K-m)	101.6	7.0	14.8	25.0	27.2	21.9
$S^2\sigma$ (mW/K^2-m)	0.3	0.5	0.2	1.4	0.8	1.0
ZT at RT	0.008	0.023	0.0055	0.017	0.009	0.014
ZT_{max} at 980°C	-	0.68	-	0.57	0.43	0.52

Wang XW et al. (2008) Appl Phys Lett 93(19):193121.
[37] Bux S et al. (2009) Adv Funct Mater 19(15):2445.
[24] T. Claudio *et al.*, J. Mater. Sci. (2012) DOI 10.1007/s10853-012-6827-y.

Nano M_xSb_y: preparation





1. Fe, Ni, Zn precursor + Sb nanoparticles
   - *dispersion of metal precursor (Fe: cyclopentadienyl iron(II) dicarbonyl dimer; Ni, Zn: chloride) in tetraethylenglycol added to mixture*
2. Solutions were cooled down to RT
3. Reaction products collected by centrifugation
4. Washed with ethanol and dried

Coll. W. Tremel, U Mainz

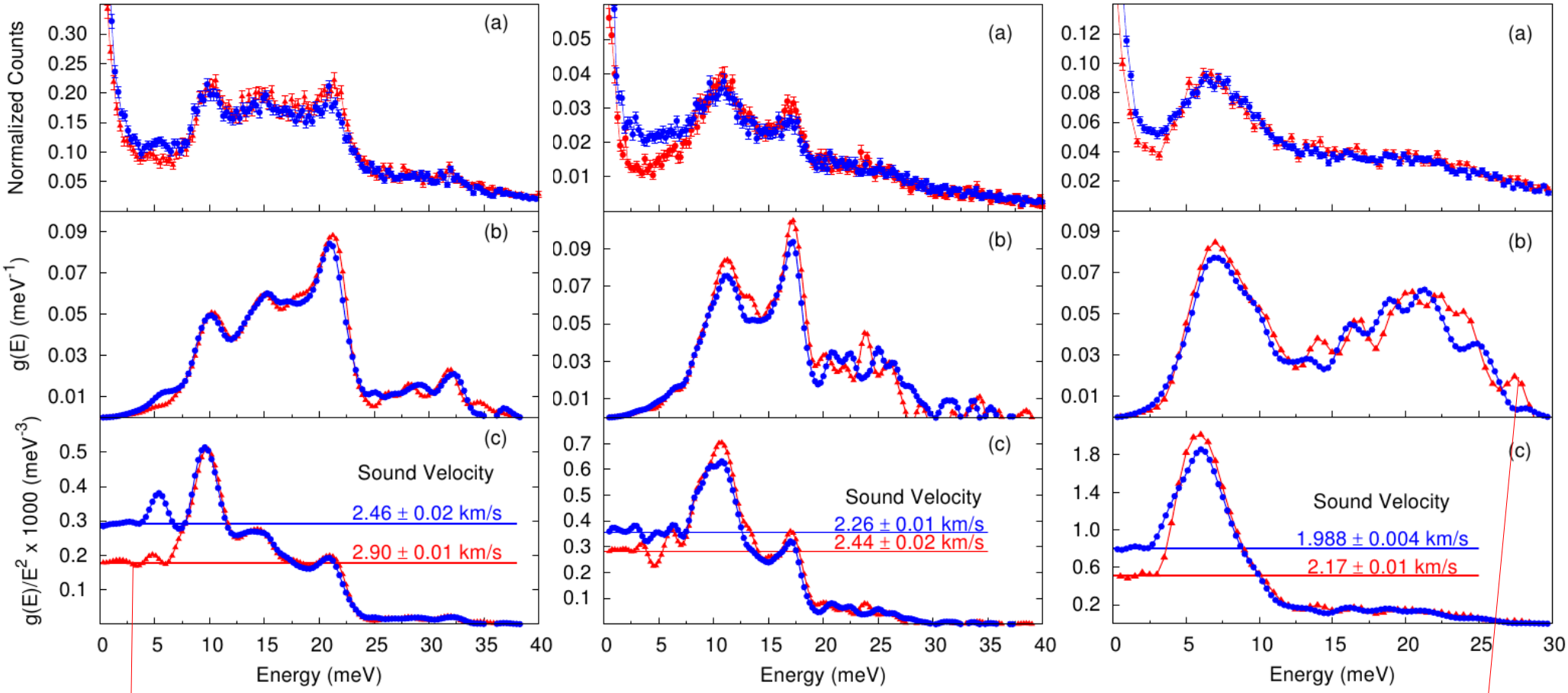
Kieslich G. *et al.*, ChemInform, 42(39), (2011).
Birkel C. S. *et al.*, Inorg. Chem., 50(22):11807–11812 (2011).
Birkel C. S. *et al.*, J. Am. Chem. Soc., 132(28):9881–9889 (2010).

^{121}Sb phonons in bulk and nano metal antimonides

T. Claudio, PSS-B, May 8 (2014), DOI: 10.1002/pssb.201470128.

Bulk Nano

$FeSb_2$ **NiSb** **„Zn_4Sb_3“**



Systematic reduction of the speed of sound in the nano phases

Diakhate M. S., *Phys. Rev. B* **84**, 125210 (2011).

Moechel A., *Phys. Rev B* **84**,184303 (2011).

ISSN 0370-1972
Phys. Status Solidi B
251 · No. 5 May
913–1104 (2014)

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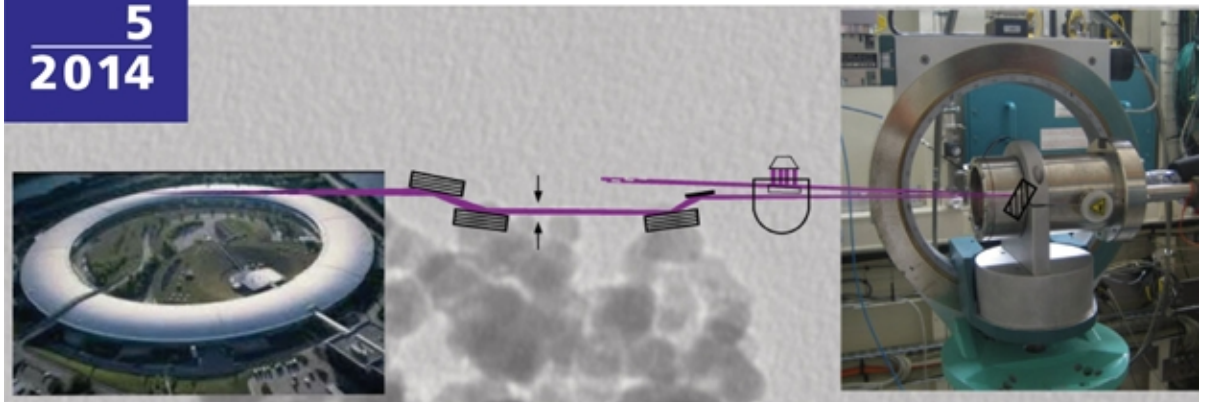
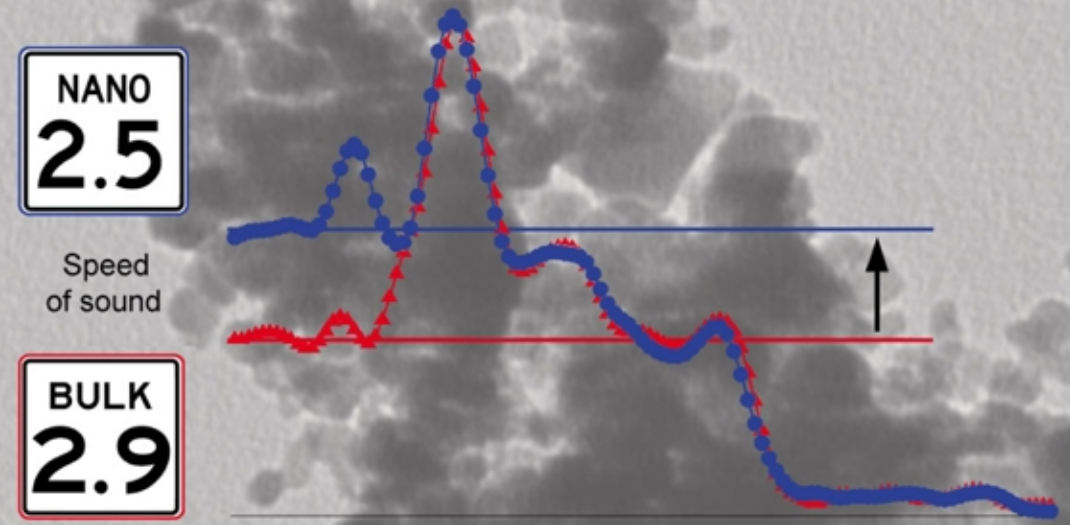
2014





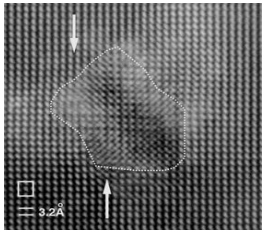
Editor's Choice

Enhanced Debye level in nano $Zn_{1+x}Sb$, $FeSb_2$ and NiSb: Nuclear inelastic spectroscopy on ^{121}Sb

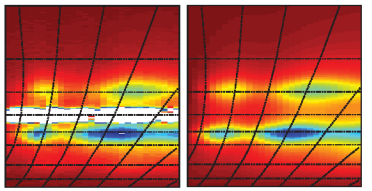
Tania Claudio, Dimitrios Bessas, Christina S. Birkel, Gregor Kieslich, Martin Panthöfer, Ilya Sergueev, Wolfgang Tremel, and Raphaël P. Hermann

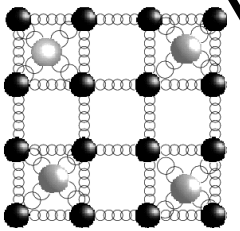
WILEY-VCH

Scattering methods


Kanatzidis et al.
JACS 2005

Materials





Understanding

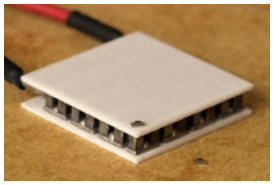
Where are the atoms?
How do they move?

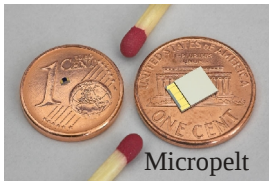
How does structure and dynamics affect the functionality?

Optimization

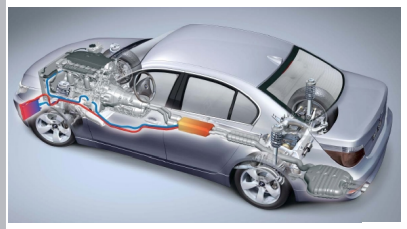

Poudel et al. Science
2008

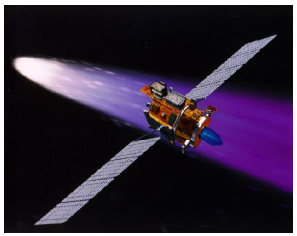
Devices




Micropelt

Applications





Collaborative setting and outreach

JÜLICH FORSCHUNGSZENTRUM

Priority program: "*Nanostructured thermoelectrics*" DFG SPP1386
(German Universities, FhF, MPI, **DLR, GSI, KIT, FZJ**)

BMBF WING: "*Nanostrukturierte Komplexe Chalkogenide*"
(**DLR, FZJ,** IOM, FhF IWM)

German-Georgian Science Bridge "*Geometric effects in TE nanostructures*"

WE Heraeus Seminars (collab. FZJ, U Hamburg, U Duisburg-Essen, DLR, Fraunhofer IPM, U Göttingen)

- "*Nanostructured Thermoelectrics*", 2010

"*Thermal Transport at the Nanoscale*", 2013

"*Electrons and Phonons: Interactions and Interfaces*", April 2016

Acknowledgments

The Helmholtz Association for funding group VH-NG 407

DFG SPP1386 „Nanostrukturierte Thermoelektrika“

BMBF WInG Initiative, Projekt 03X3540B „NanoKoCh“

DFG SFB 917 „Nanoswitches“ → **Phase change materials**

Large scale facilities for access: ESRF, APS, Hasylab, SOLEIL, FRM II, ILL, SNS, SINQ

Prof. K. Nielsch, U. Hamburg
Prof. O. Eibl, U. Tübingen
Dr. H. Böttner, Fraunhofer IPM
Dr. E. Müller, DLR
Prof. Th. Höche, Fraunhofer IWM
Dr. A. Neubrand, Fraunhofer IWM
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Prof. M. Albrecht, TU Chemnitz
Dr. V. Pacheco, Fraunhofer IFAM
Prof. W. Tremel, U. Mainz
Prof. M. Wuttig, RWTH Aachen
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Lattice Dynamics in Emerging Functional Materials Group

Raphaël Hermann
Group Leader

B. Klobes
Post Doc

V. Potapkin
Post Doc

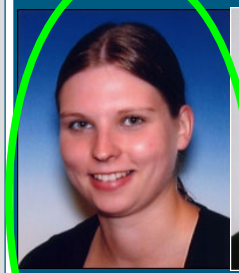
A. Mahmoud
Post Doc

M. Herlitschke
PhD student

R. Simon
PhD student

M. Mebonia
PhD student

Former members



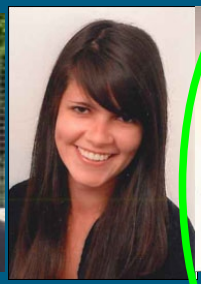
A. Houben
(Möchel)

J. Gallus

T. Rademacher

I. Sergeev

D. Bessas



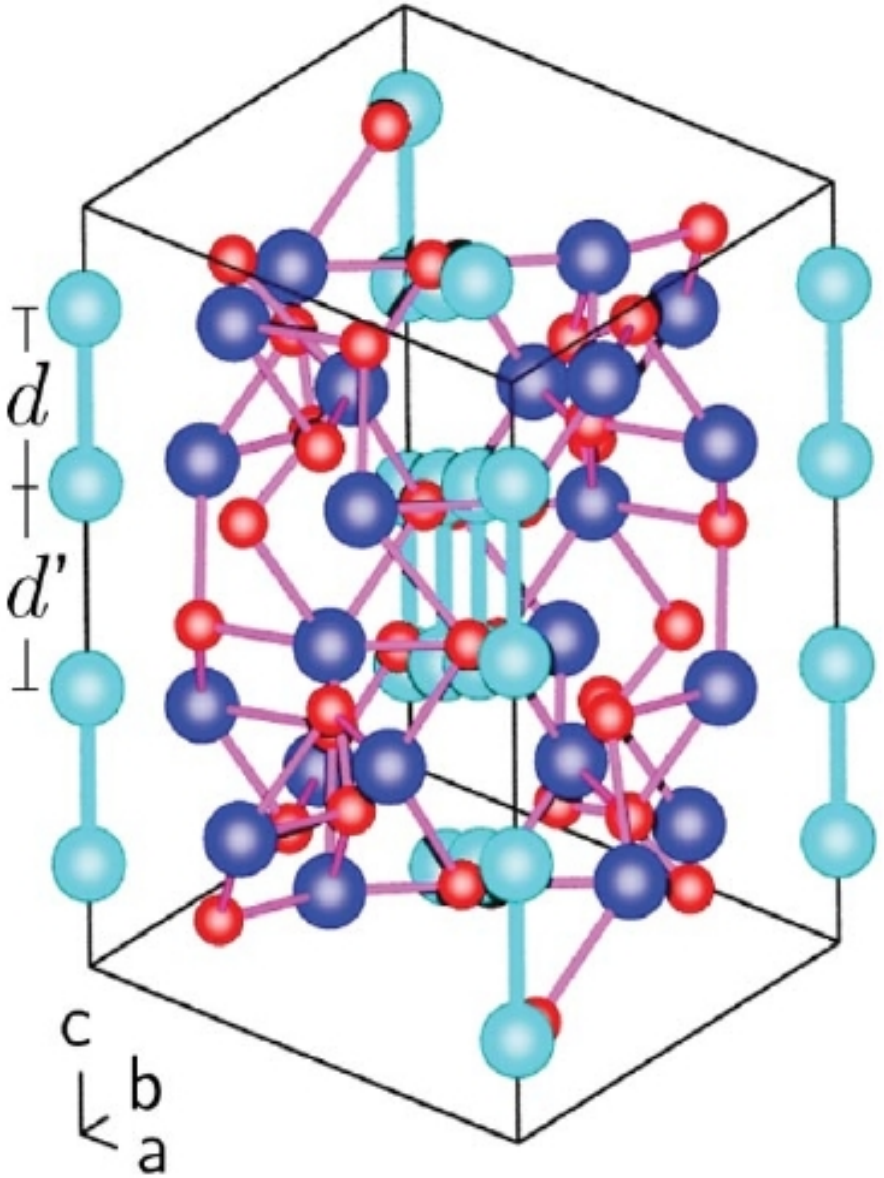
P. Bauer Pereira

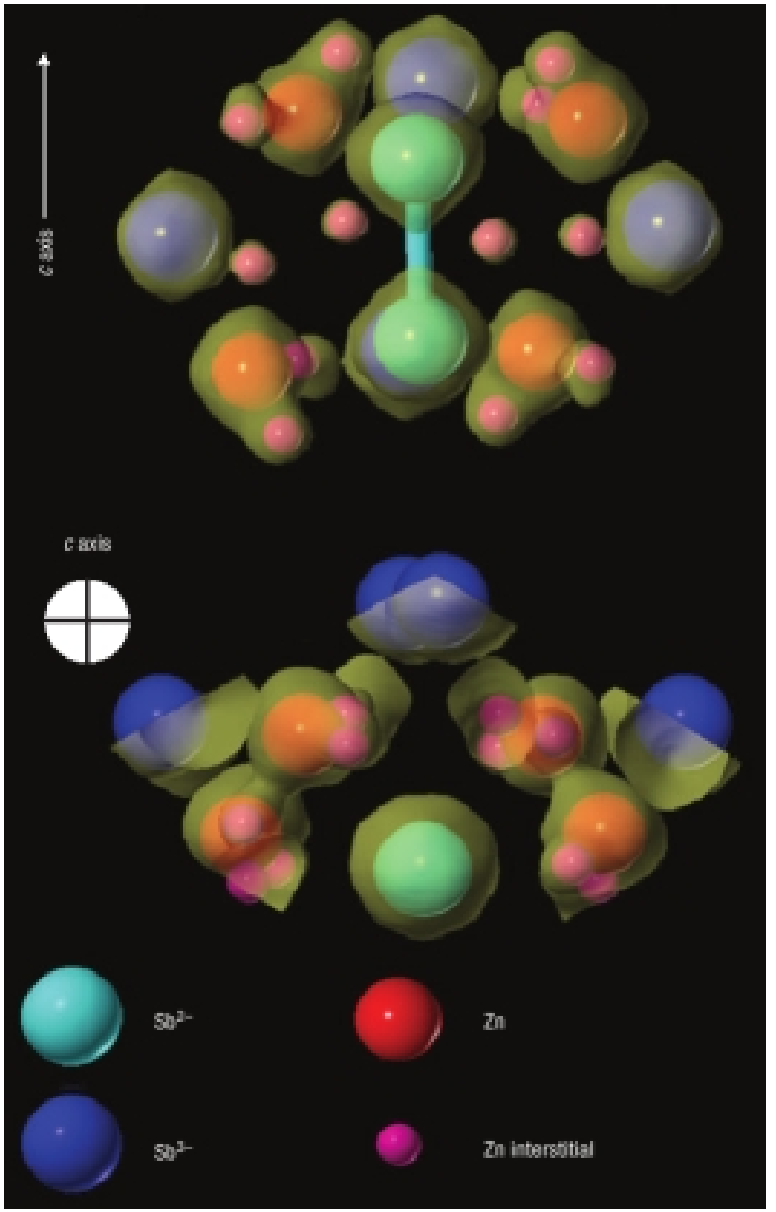
T. Claudio

A. Jafari
PhD student

P. Alexeev
PhD student
(DESY Hamburg)

“Zn_4Sb_3” - Structure and Zn interstitials

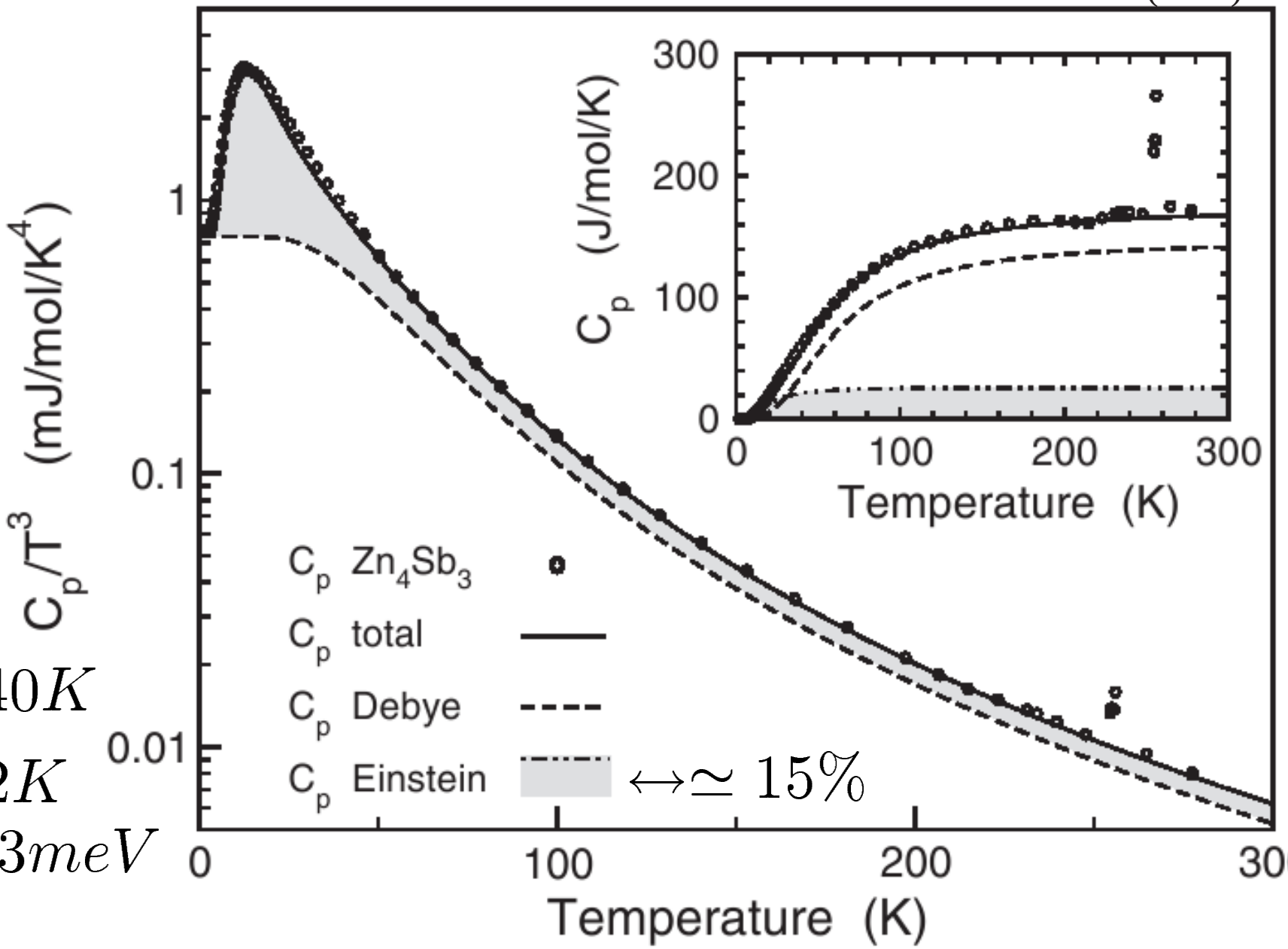




Snyder *et al., Nat. Mat.* **3**, 458–463 (2004)

Zn_4Sb_3 - Heat capacity

Schweika *et al.* PRL **99** 125501 (2007)

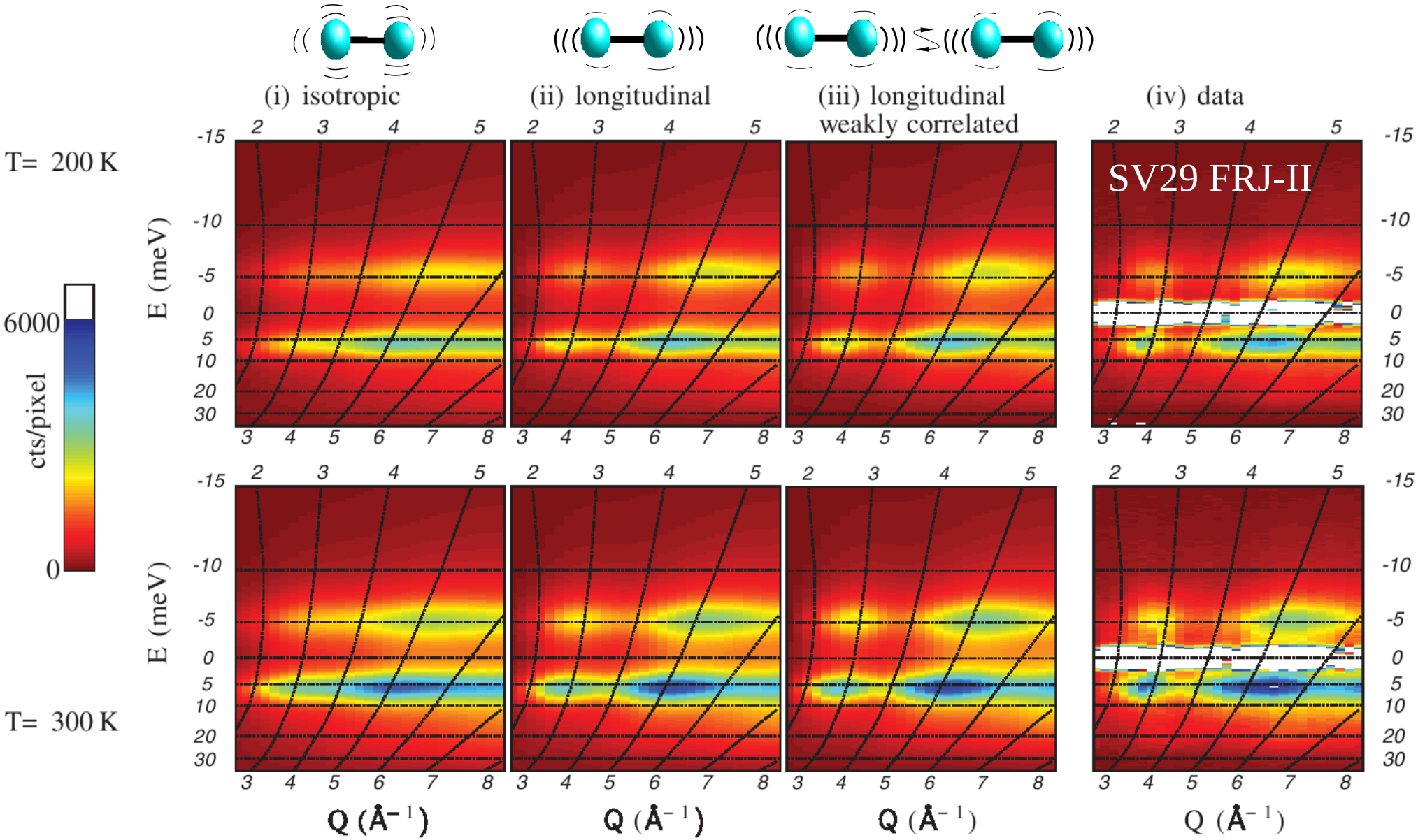


$$\Theta_D = 240K$$

$$\Theta_E = 62K \simeq 5.3meV$$

Zn_4Sb_3 - Inelastic neutron scattering

Schweika *et al.* PRL **99** 125501 (2007)



Zn_4Sb_3 - Inelastic neutron scattering

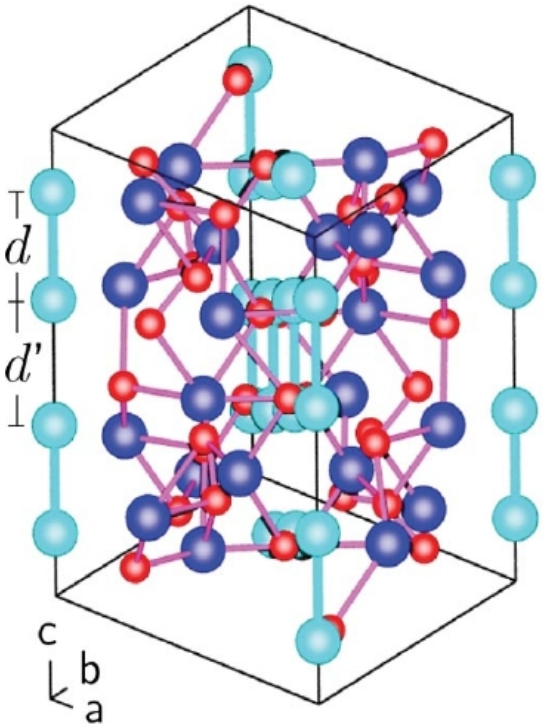
Schweika *et al.* PRL **99** 125501 (2007)

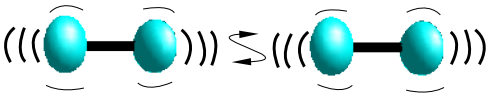
E = 5.23(2) meV

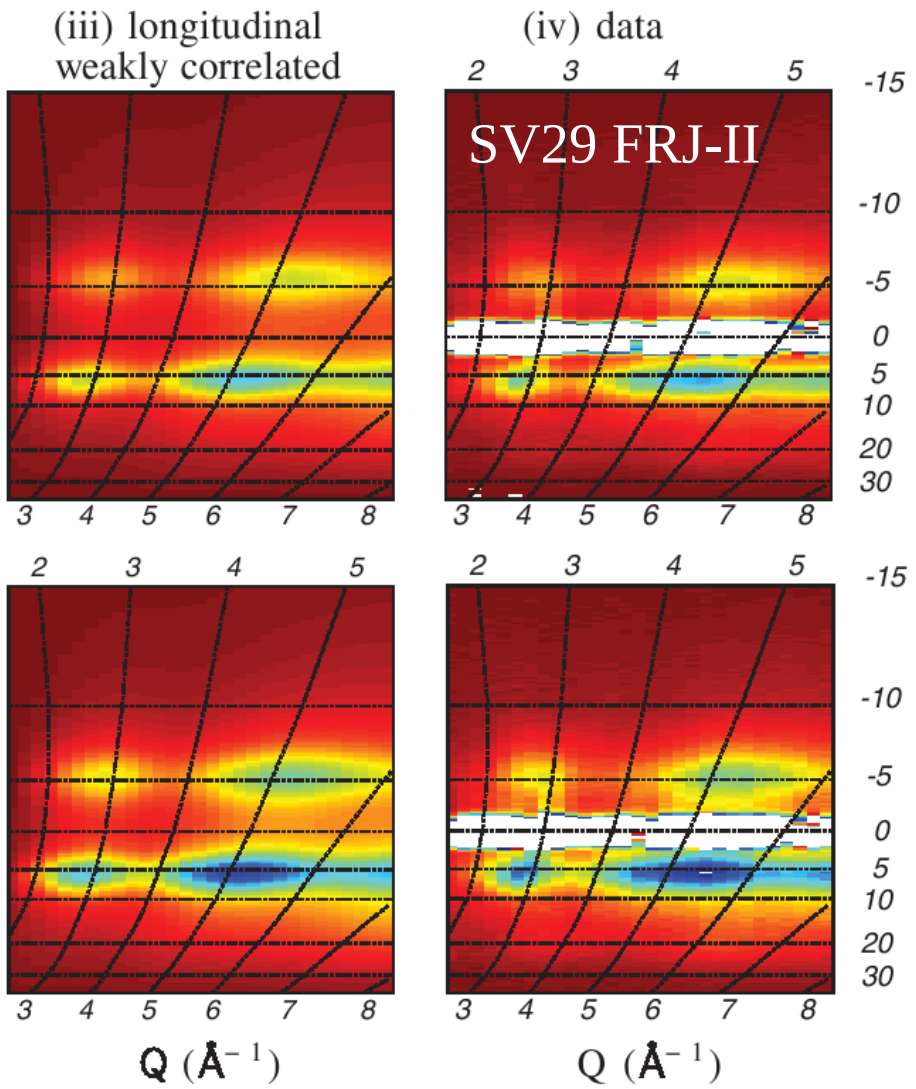
Γ = 1.69(5) meV

$d_{Sb\text{-}Sb}$ 2.754(15) Å

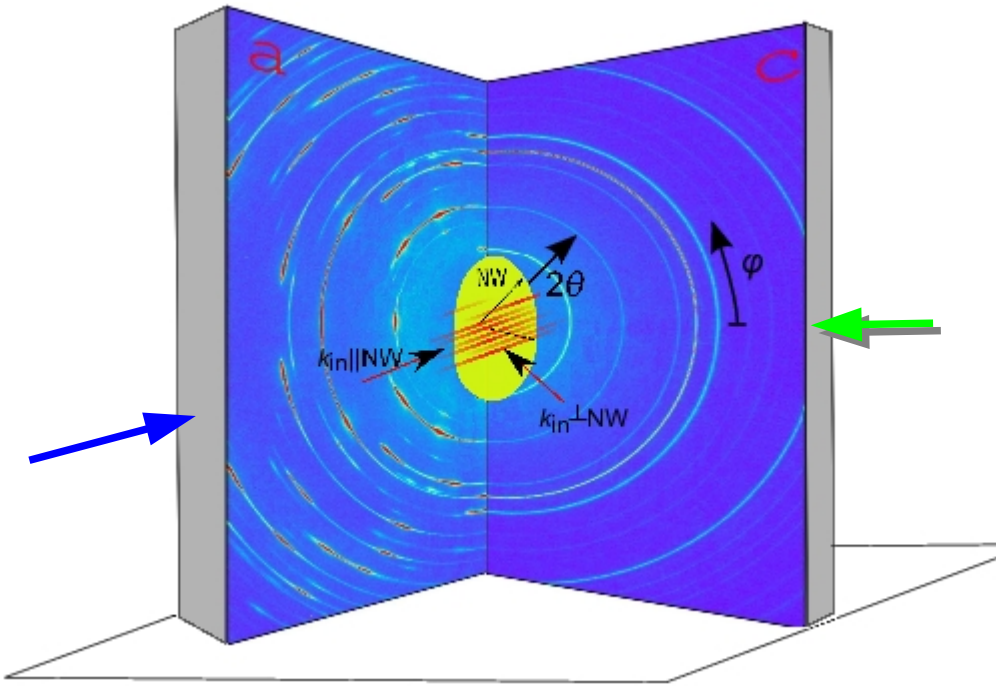
u^2_{33} = 0.04 Å



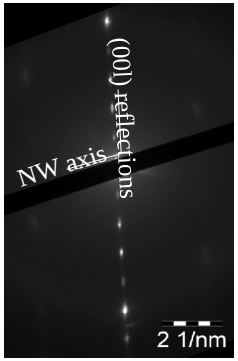


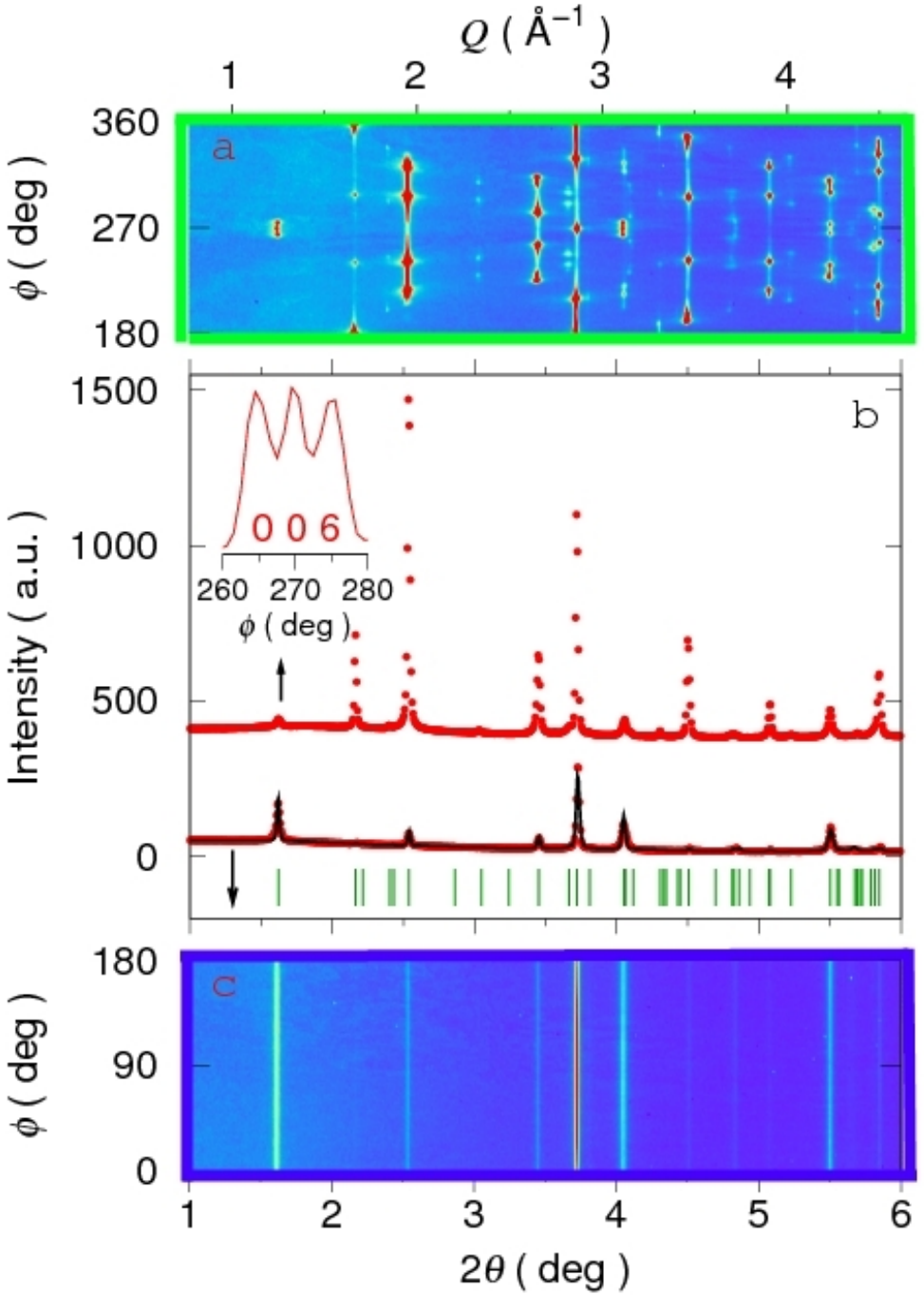


$Bi_2{}^{125}Te_3$ nanowires Ø55 nm



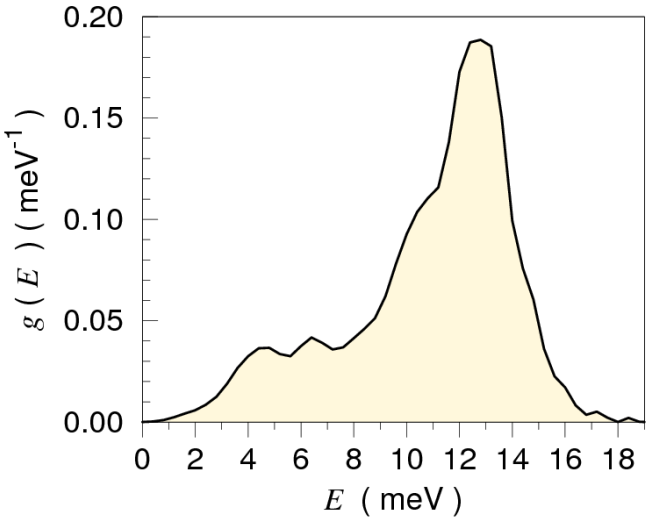
- NW are single crystalline with (0 0 1) twin boundaries
- Larger diameter NW are highly textured
- *c*-axis at 85 deg w/r to NW axis



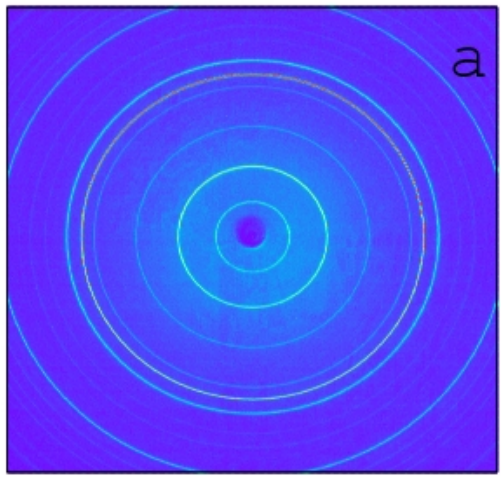


Z. Aabdin, U. Tübingen

$Bi_2{}^{125}Te_3$ nanowires Ø55 nm: ^{125}Te phonons

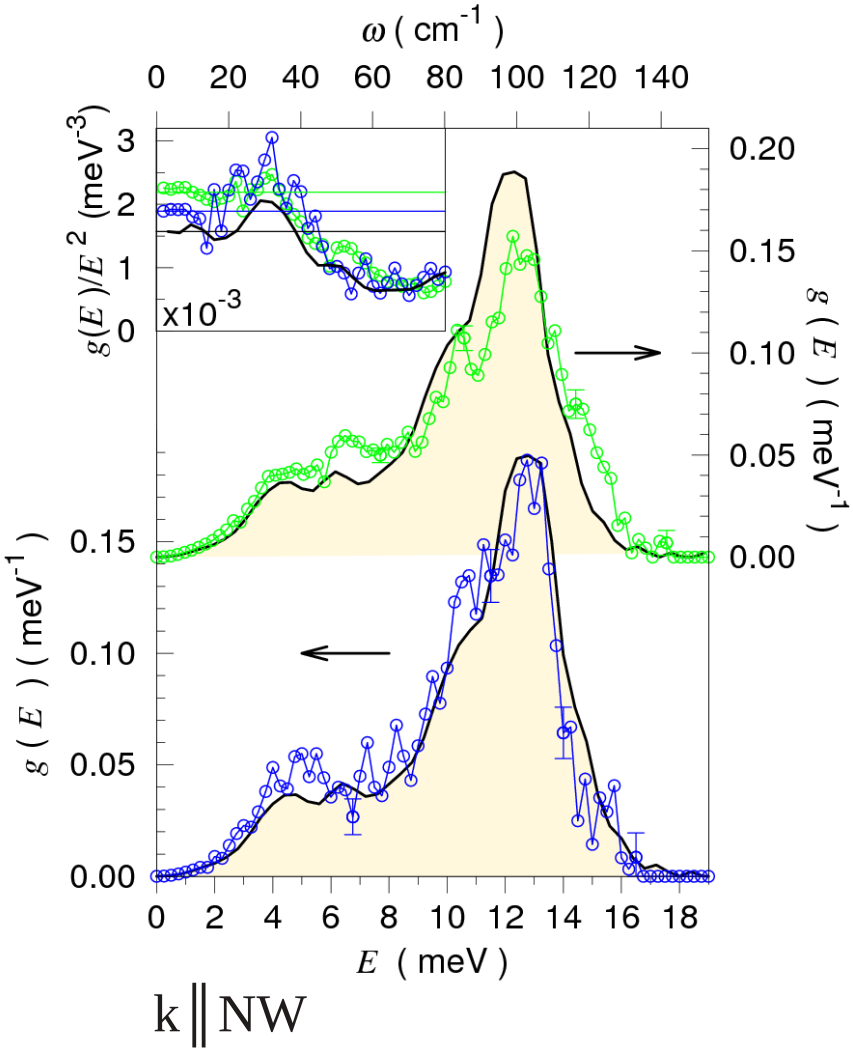


Bulk: v_s = 1750 km/s



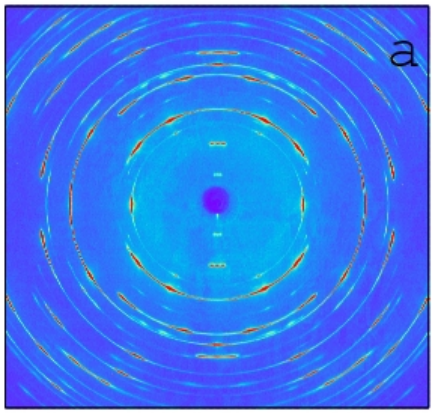
k⊥NW

25% speed of sound reduction

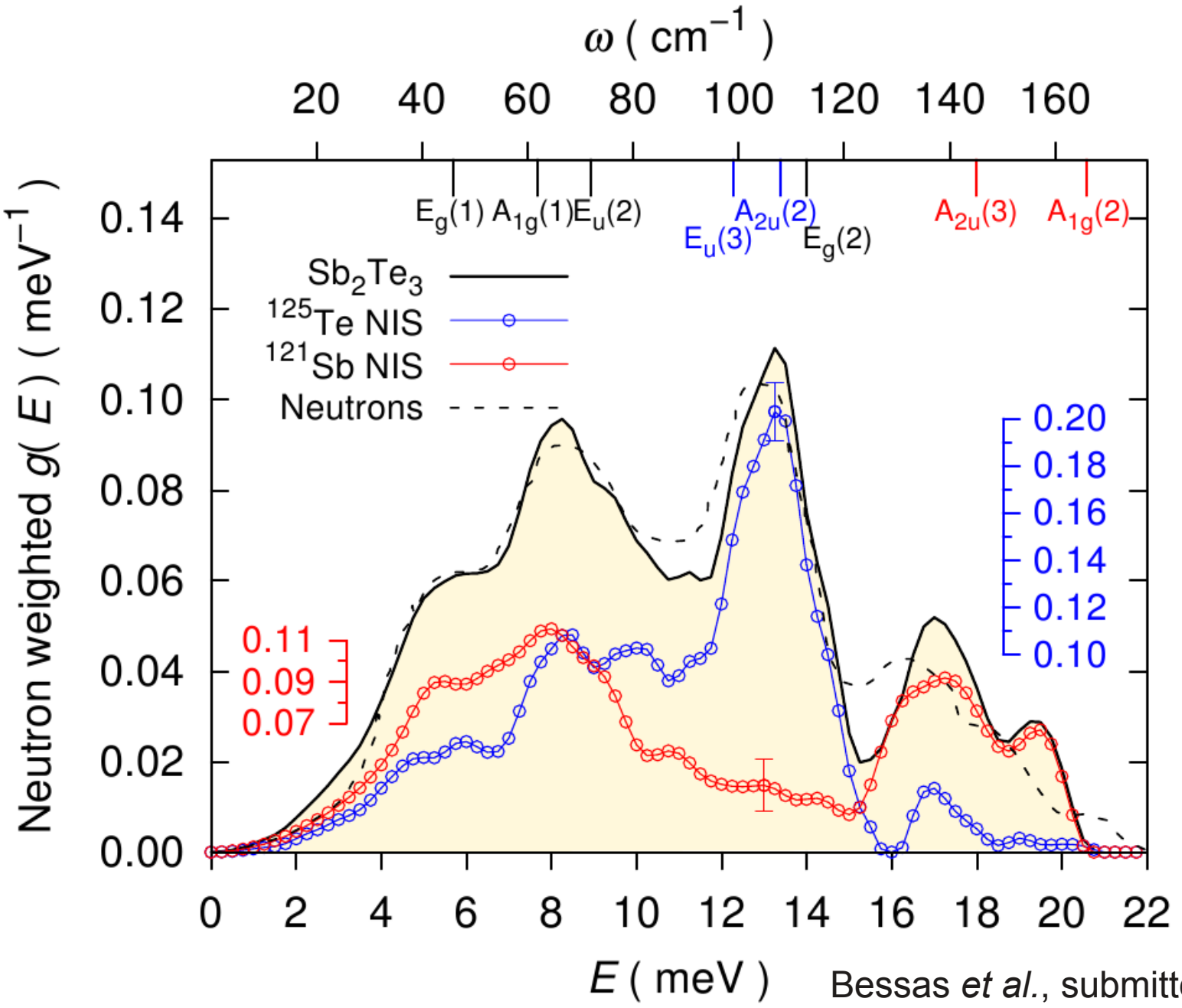


k∥NW

15% speed of sound reduction

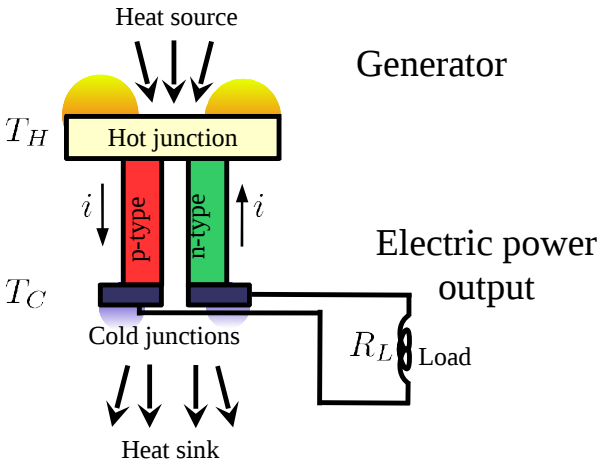


Density of phonon states – Bulk Sb_2Te_3



Bessas *et al.*, submitted, June 2012.

Generator efficiency



$$\eta = |\frac{P}{\dot{Q}}| = |\frac{R_L I^2}{\dot{Q}}|$$

Peltier heat loss ($\pi I<0$) Joule heat gain Thermal conductivity loss

$$\dot{Q} = -\pi_{ab} I - \frac{I^2}{2}[\rho_a + \frac{\rho_b}{B}]L + (\kappa_a + B\kappa_b)\Delta T/L$$

Optimization for maximal efficiency yields

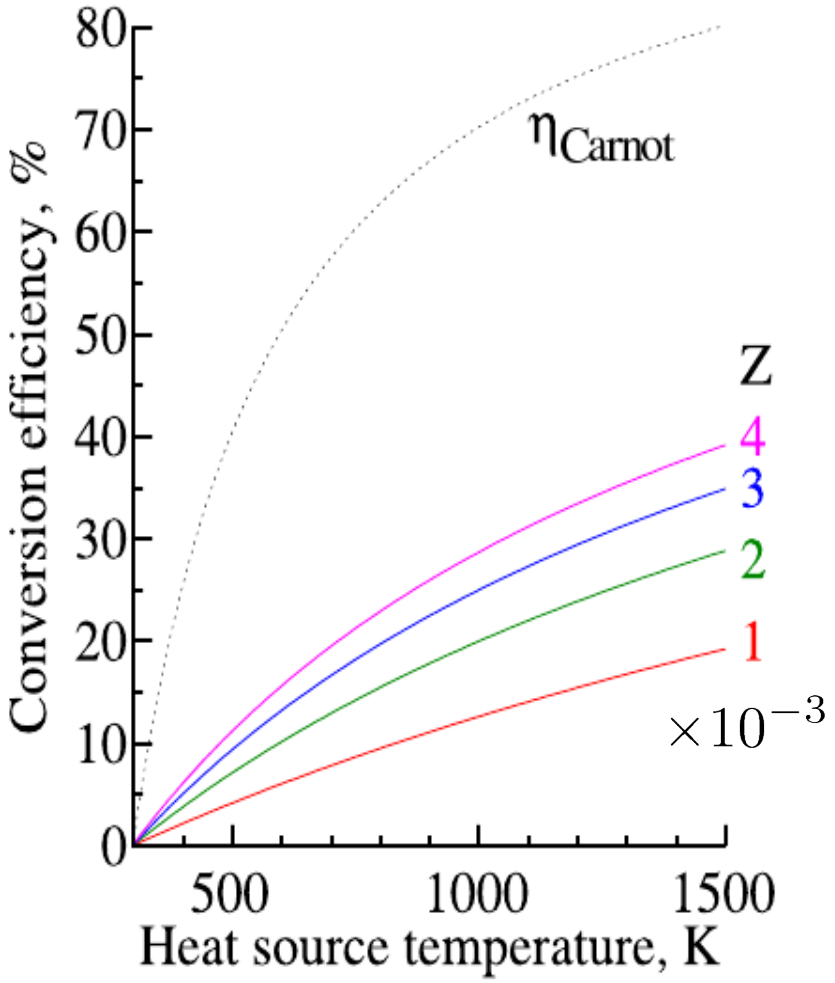
$$\eta = \eta_C \frac{\sqrt{1 + Z_{ab}T_{av}} - 1}{\sqrt{1 + Z_{ab}T_{av}} + T_C/T_H}$$

with

$$Z_{ab} = \alpha_{ab}^2 / [(\rho_a \kappa_a)^{1/2} + (\rho_b \kappa_b)^{1/2}]^2$$

Considering a single material $\boxed{Z = \frac{\alpha^2}{\rho\kappa} = \frac{\alpha^2 \sigma}{\kappa}}$

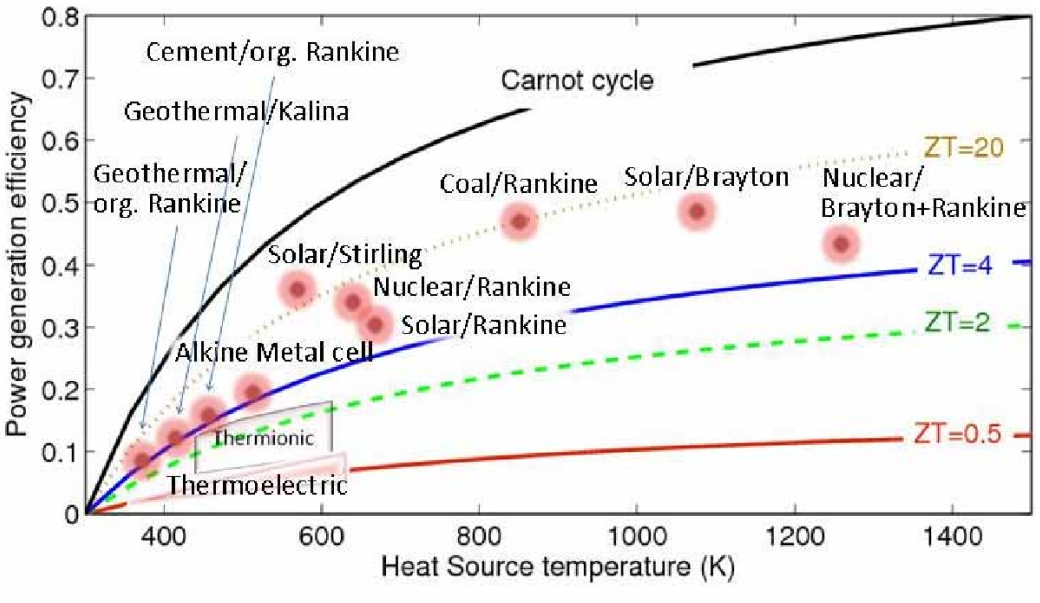
Generator conversion efficiency



Cold point: 300 K

$$Z = \frac{\alpha^2 \sigma}{\kappa}$$ → Power factor

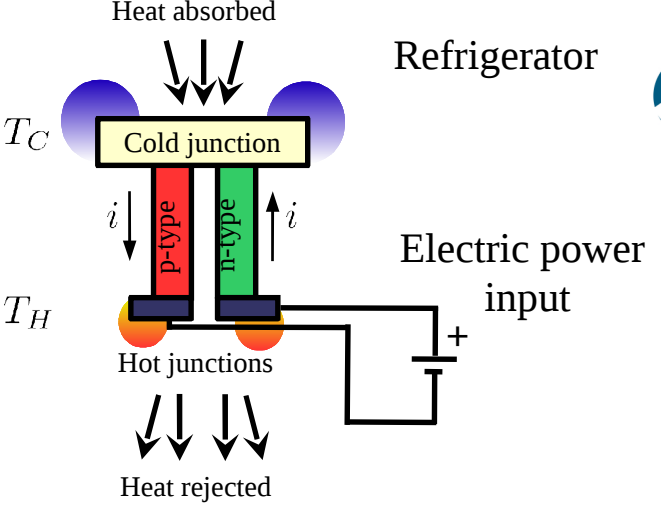
Source: A. Shakouri, U Santa Cruz



Adapted from Cronin Vining, Nature Materials 2009

NB: *Z* is the figure of merit [1/K], *ZT* is the dimensionless figure of merit.

Refrigerator efficiency



$$COP = |\frac{\dot{Q}}{P}| = |\frac{\dot{Q}}{VI}|$$

$$P = RI^2 + \alpha_{ab}\Delta T I$$

Peltier cooling Joule heating Thermal conductivity

$$\dot{Q} = \alpha_{ab} T_C I - \frac{I^2}{2} R - (\kappa_a + B\kappa_b)\Delta T / L)$$

$$R = [\rho_a + \frac{\rho_b}{B}]L$$

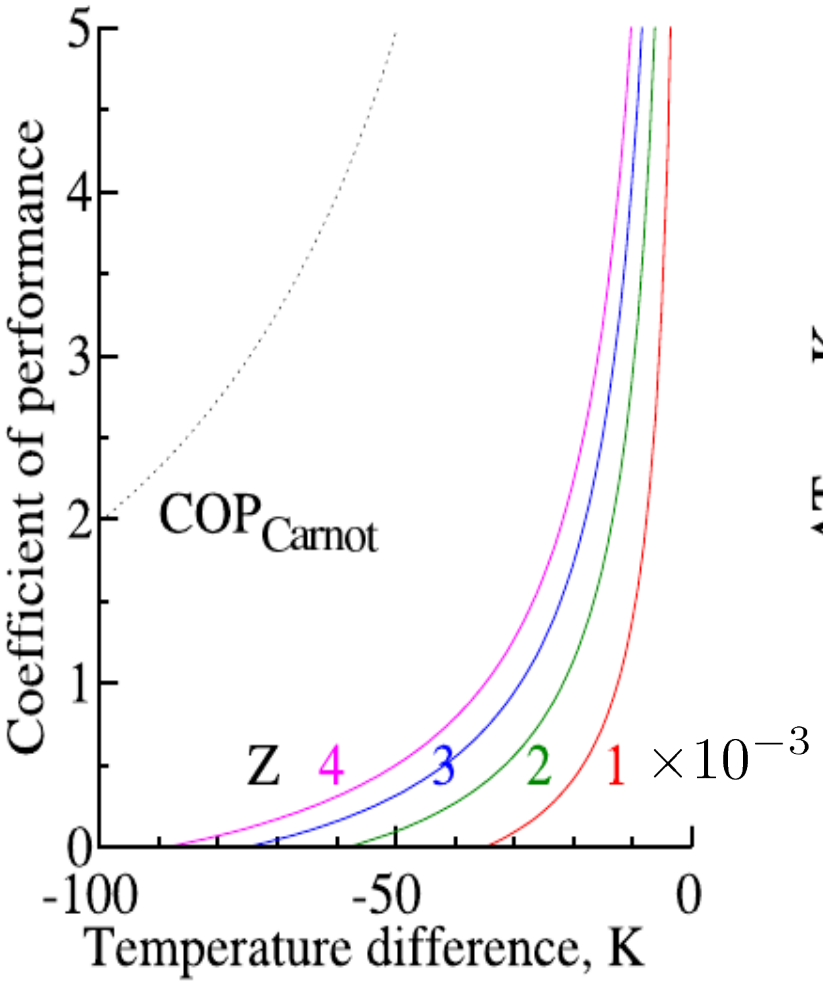
Optimization for maximal cooling power yields

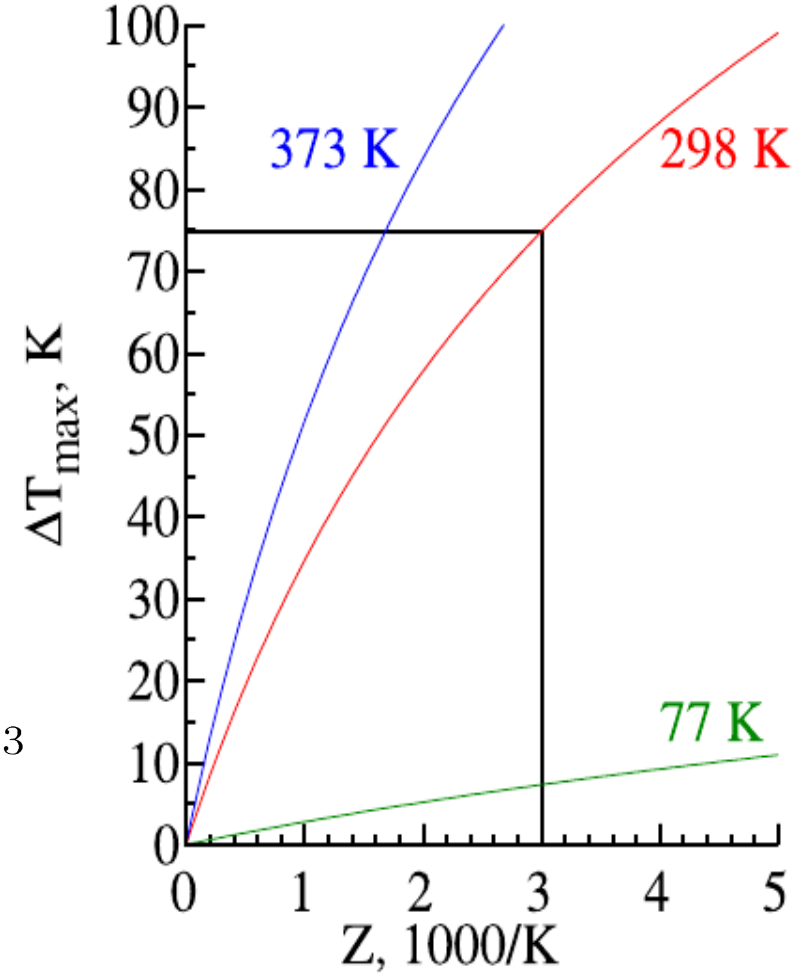
$$\Delta T = Z T_C^2 / 2 \qquad I_o = \alpha_{ab} T_C / R$$

Optimization for maximal efficiency yields

$$COP = \frac{T_C}{T_H - T_C} \frac{\sqrt{1 + Z_{ab} T_{av}} - T_H / T_C}{\sqrt{1 + Z_{ab} T_{av}} + 1}$$

Refrigerator conversion efficiency





Hot point: 300 K

Material efficiency

$$Z = \frac{\alpha^2 \sigma}{\kappa} \longrightarrow \text{Power factor}$$

$$\alpha^2 = (\alpha_b - \alpha_a)^2$$

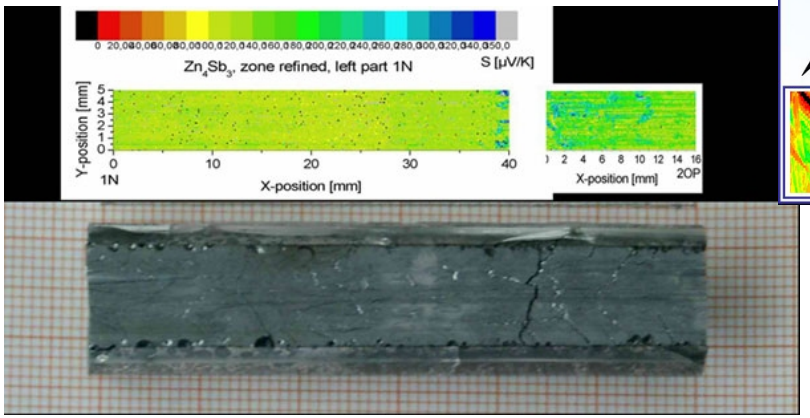
Opposite sign of the thermopower in both legs.

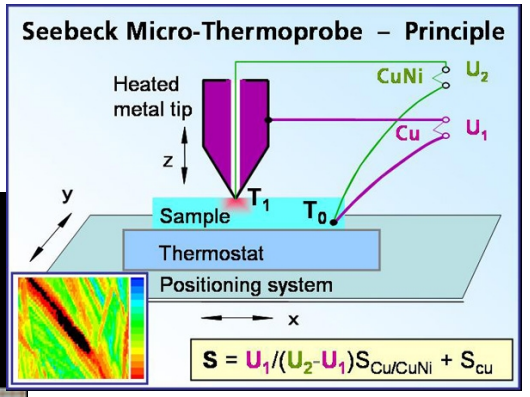
$$\alpha_{n+p} = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p}$$

Avoid bipolar conductivity

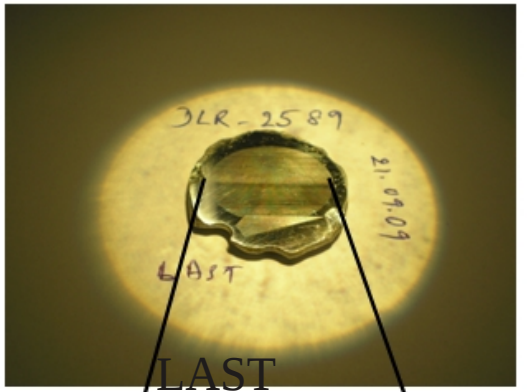
In as cast materials, inhomogeneities are observed.

Zn_4Sb_3



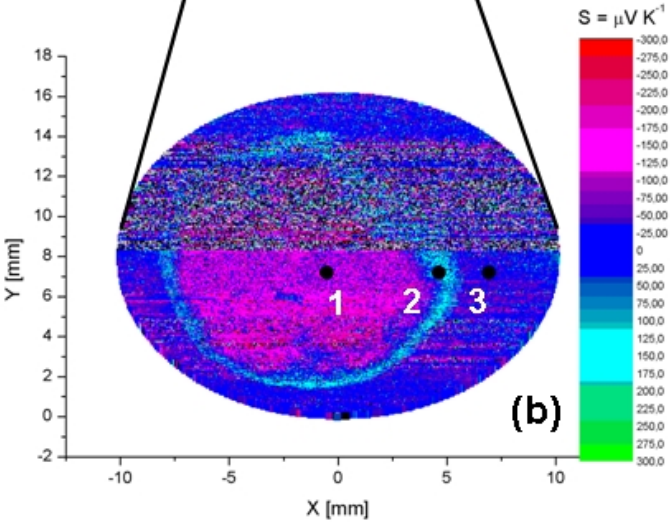


Source: DLR



(a)

LAST



Typical values and requirements

Goal: $ZT = \frac{\alpha^2 \sigma}{\kappa} T = 1$

Suppose: $\kappa_l = 0$

$$\kappa_e/\sigma \approx L \cdot T \quad \Rightarrow \quad ZT = \frac{\alpha^2 \sigma}{\kappa_e} T = \alpha^2/L = 1$$

$$\alpha = \sqrt{L} = 157 \mu \mathrm{V/K}$$

Compare with Sommerfeld model for the free electron gas

$\alpha \sim -c_v/3ne$ $\qquad$ $\alpha = -142(k_B T/E_F)\mu V/K$

$c_v = \pi^2/3k_B^2 T g(E_F)$ $\qquad$ $E_F \sim 10000\ K$

Slack „limit“ for the minimal thermal conductivity in bulk crystalline materials

$\kappa_{min} \simeq 0.25 - 0.5\ \mathrm{Wm^{-1}K^{-1}}$

$\kappa_{air} \simeq 0.024\ \mathrm{Wm^{-1}K^{-1}}$

Characterization

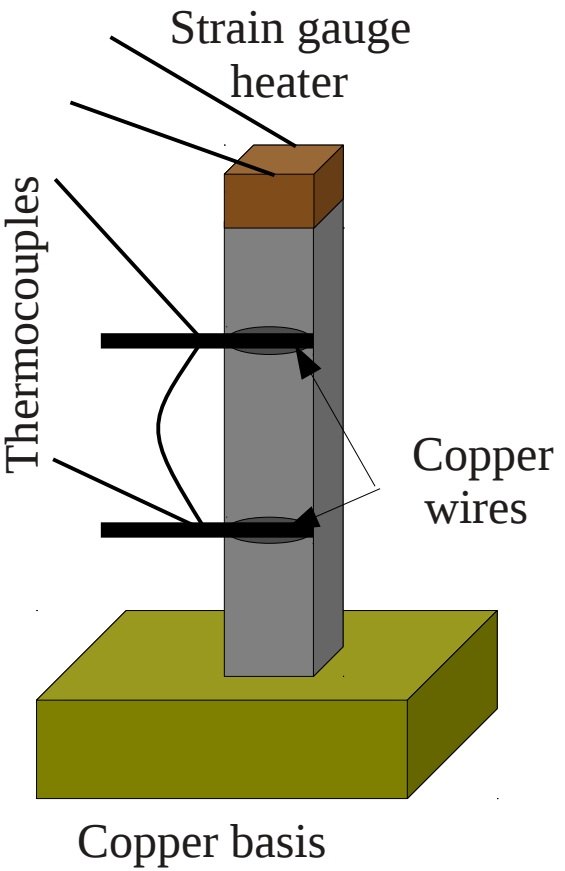
$$Z = \frac{\alpha^2 \sigma}{\kappa}$$

Complex problem:

- 3 quantities must be measured
- Error bars are often large on *ZT*
- High temperature measurements are challenging

(radiative losses, corrosion, ...)

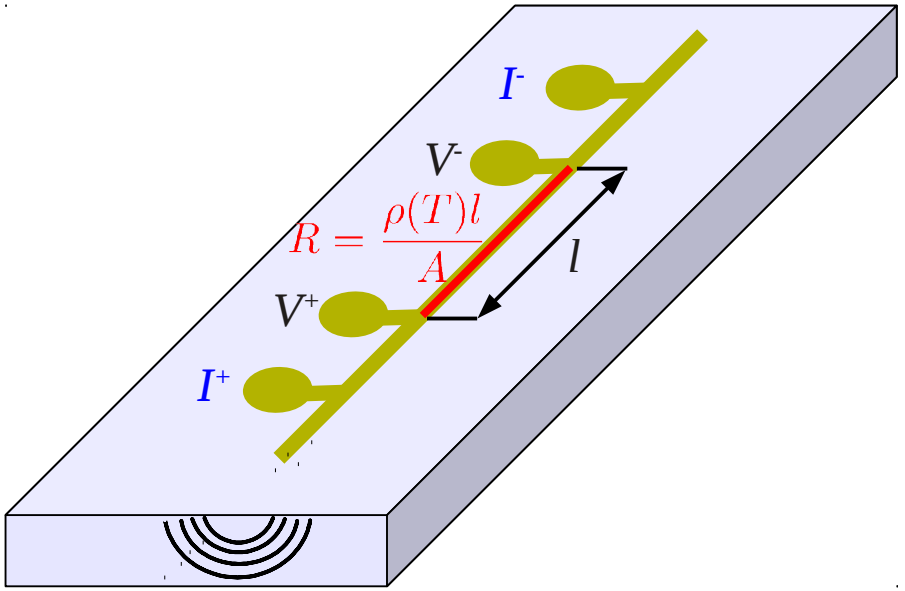
Four point thermal conductivity and Seebeck measurements

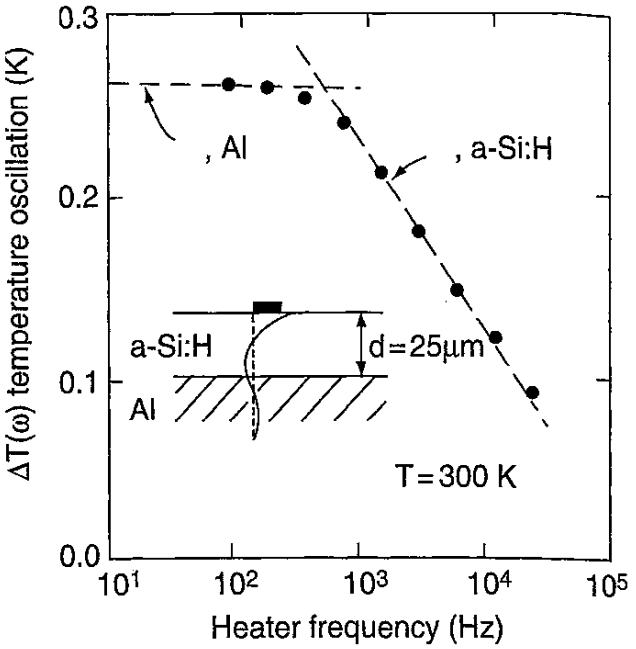


Characterization

AC thermal transport: „3ω“ method

$$V = IR = I_0 e^{i\omega t}\left(R_0 + \frac{dR}{dT}\Delta T\right) = V_1 e^{i\omega t} + V_3 e^{i3\omega t}$$





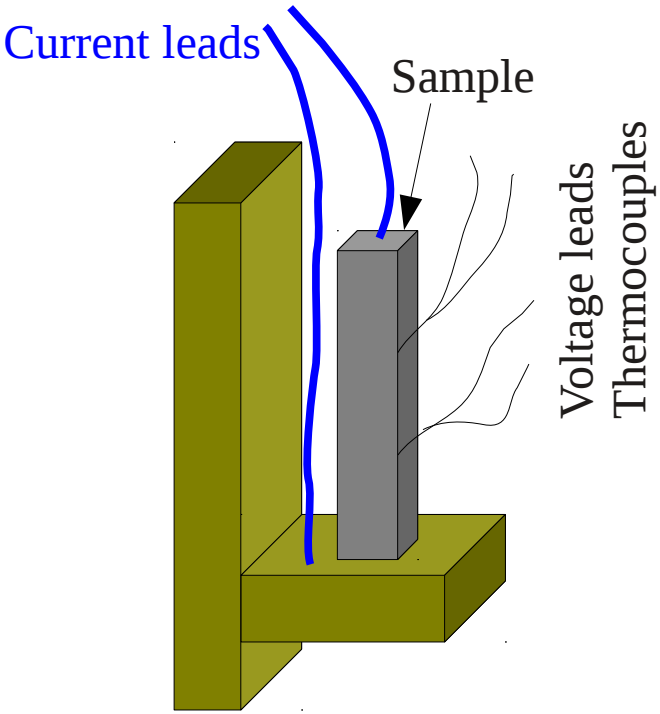
$$\kappa = \frac{V_1^3(\omega)\ln(\omega_1/\omega_2))}{4\pi l R^2[V_3(\omega_2) - V_3(\omega_1)]}\frac{dR}{dT}$$

Applicable for films

Characterization

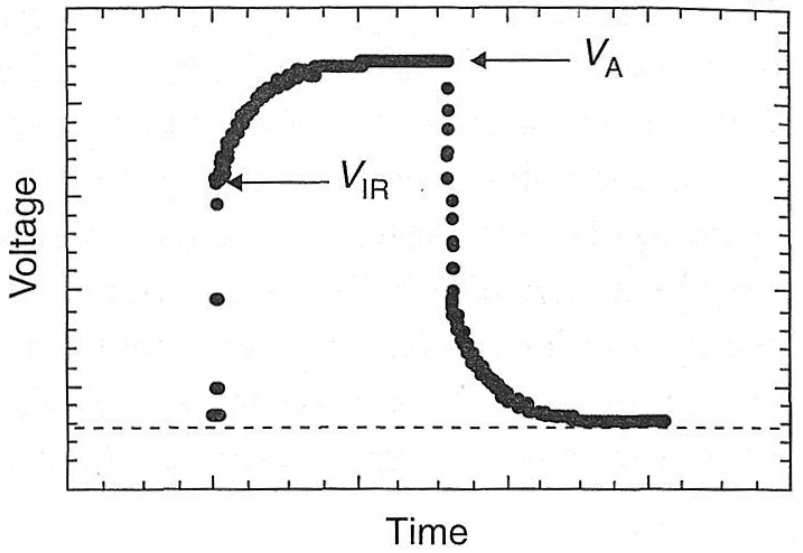
Z-Meter - Harman method

Measures the „device Z“, but requires high-Z materials



Fast Slow

$$V_A = V_R + V_{TE}$$



$$ZT = (\frac{V_A}{V_{IR}} - 1)$$