Mitglied der Helmholtz-Gemeinschaft

Research at JCNS-2
Lattice dynamics in functional materials

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JCNS-2, PGI-4: Scattering Methods, Prof. Brückel, Forschungszentrum Jülich GmbH, Germany

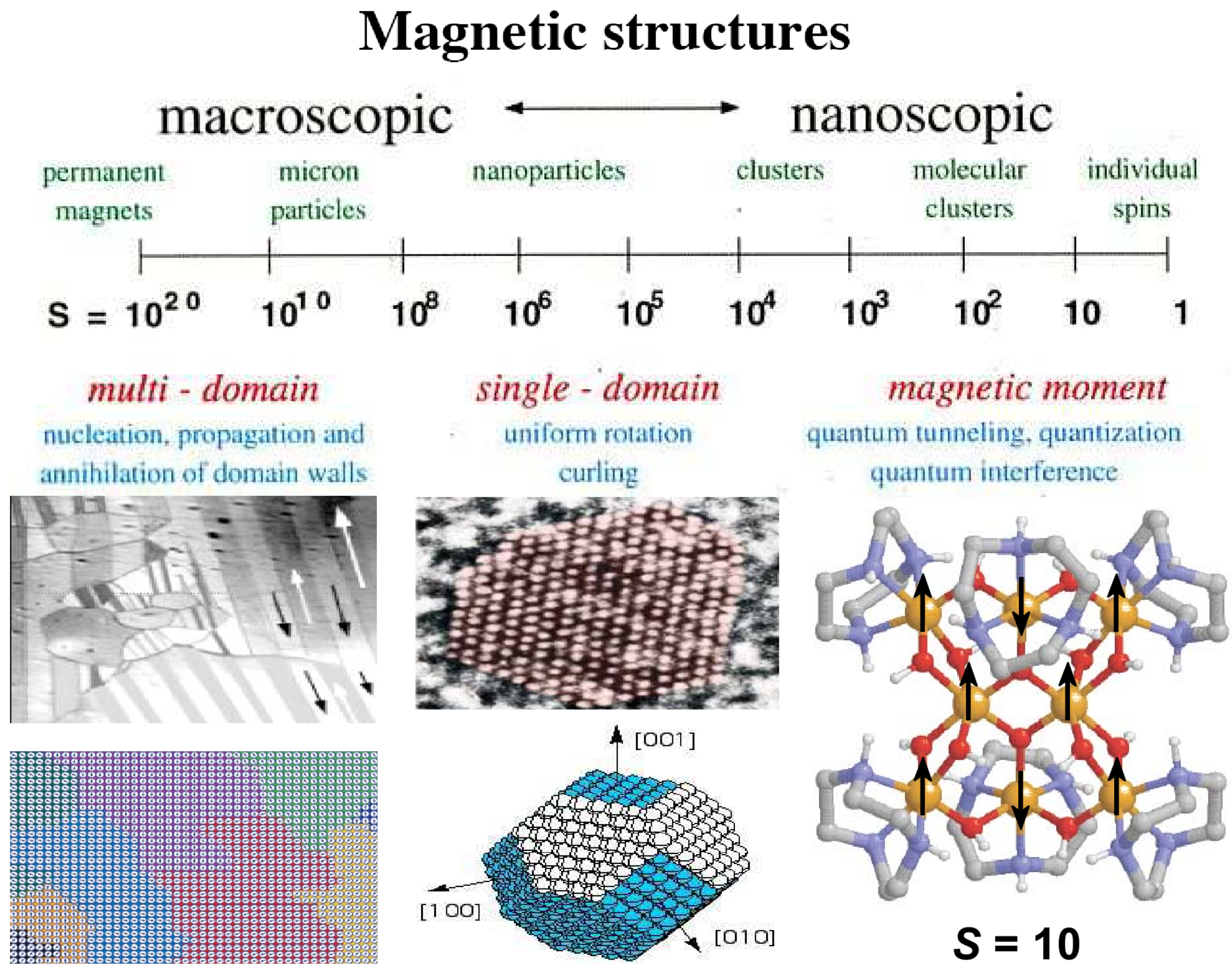
Université de Liège, Faculté des Sciences, Belgium

Tbilisi, August 7th 2012

Outline

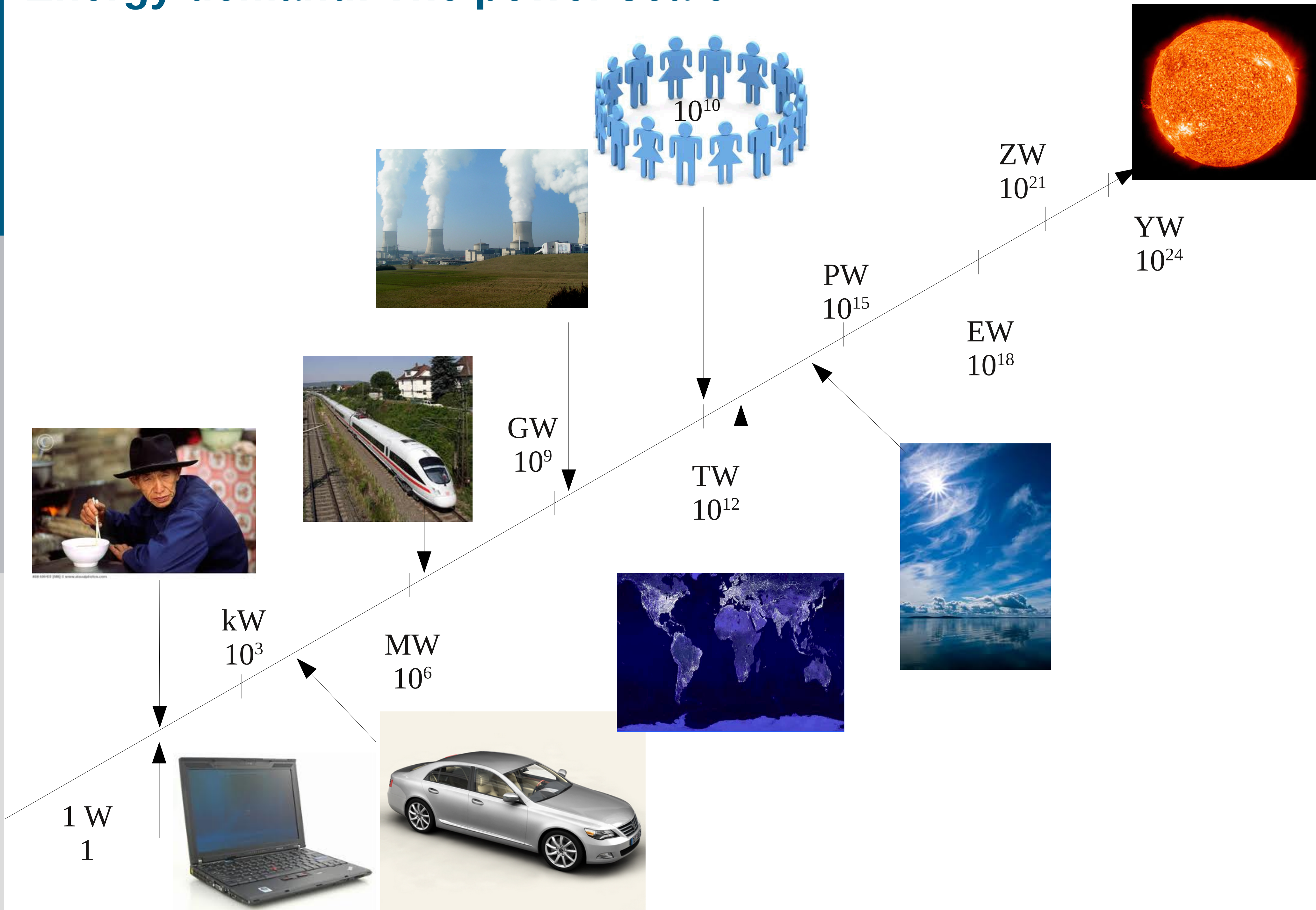
- JCNS-2: scattering methods for information and energy
- '*Lattice dynamics in functional materials*' group
- Thermoelectrics
- Nuclear resonance scattering
- Bulk thermoelectrics
- Nanostructured thermoelectrics

Information demand: the spin scale

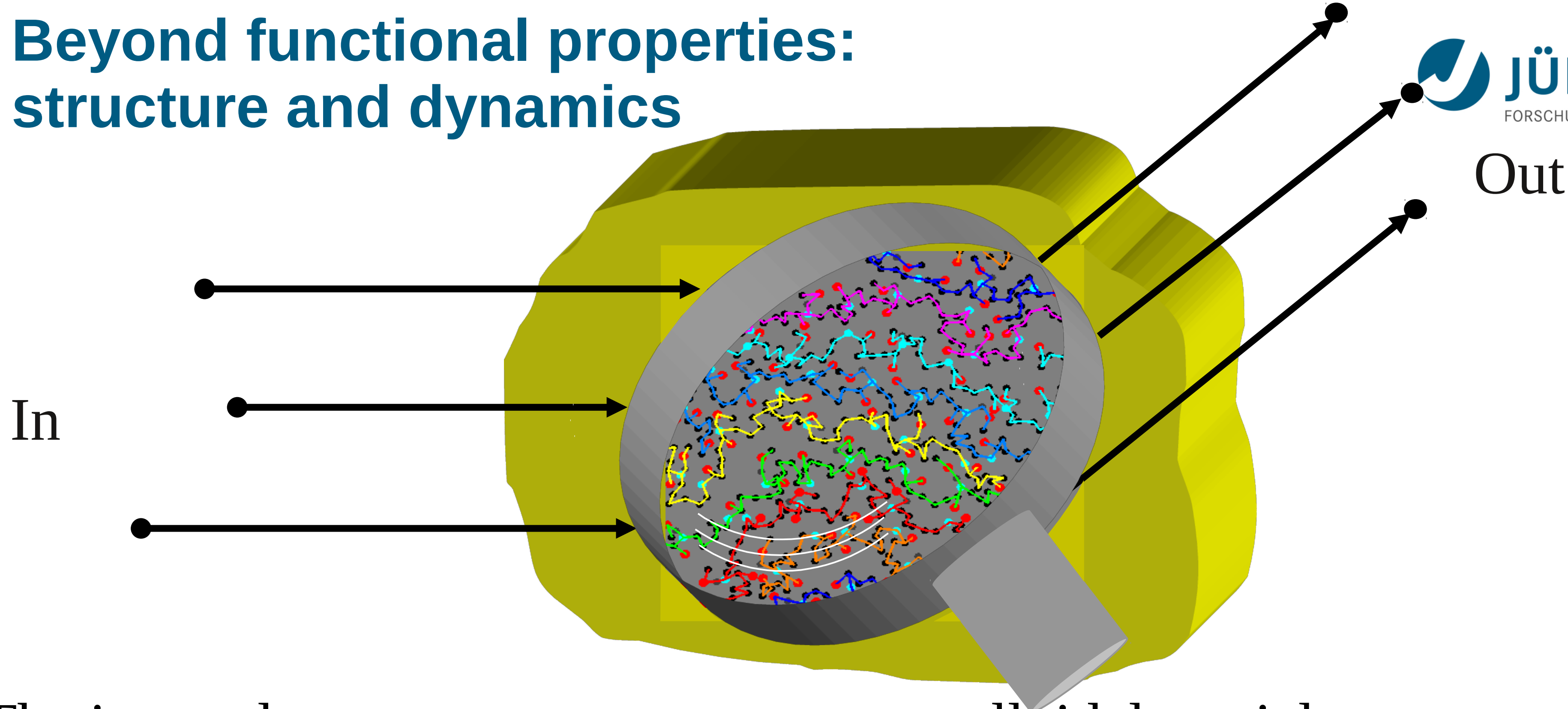


W. Wernsdorfer, *Advances in Chemical Physics*, **118** (2001) 99.

Energy demand: The power scale



Beyond functional properties: structure and dynamics



The internal structure: atoms, colloidal particles ...

& microscopic dynamics: atom movements, ...

Underly functional properties: thermal conductivity, elasticity, viscosity, ...

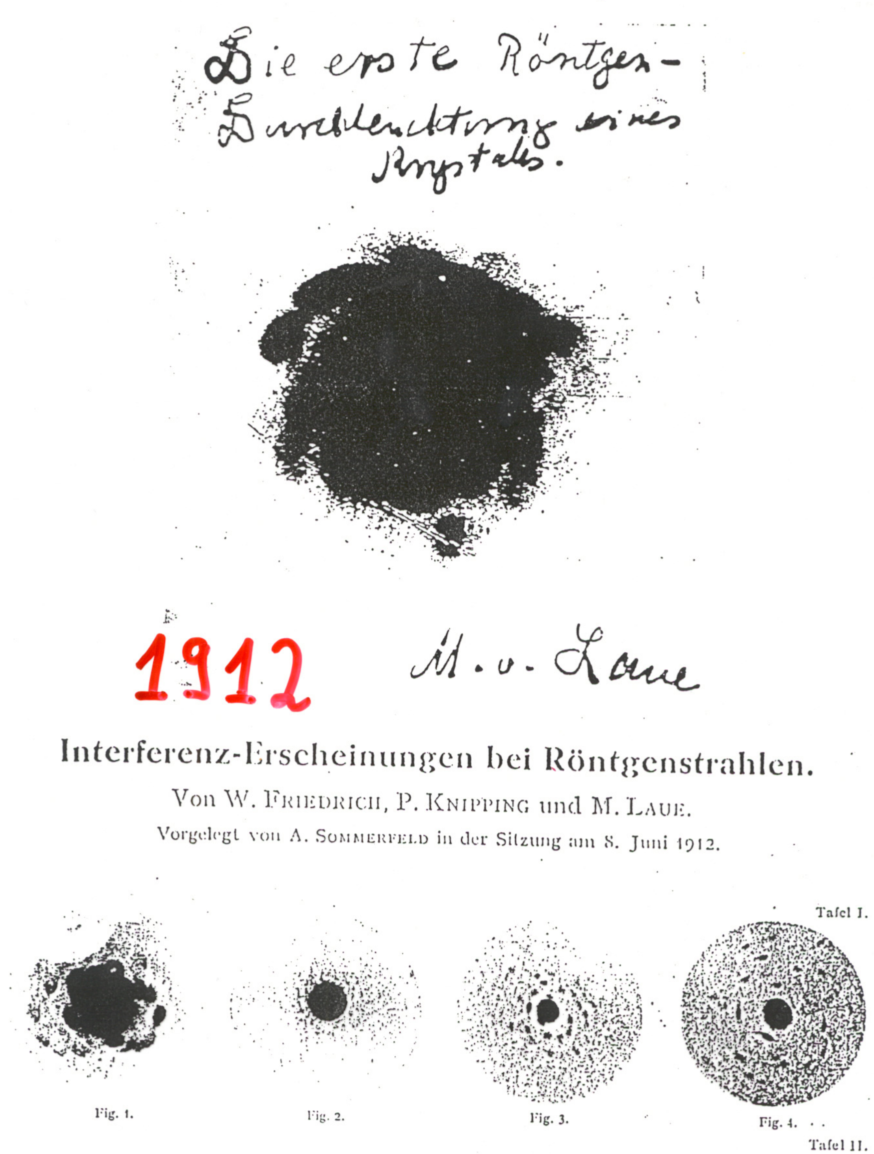
Scattering:

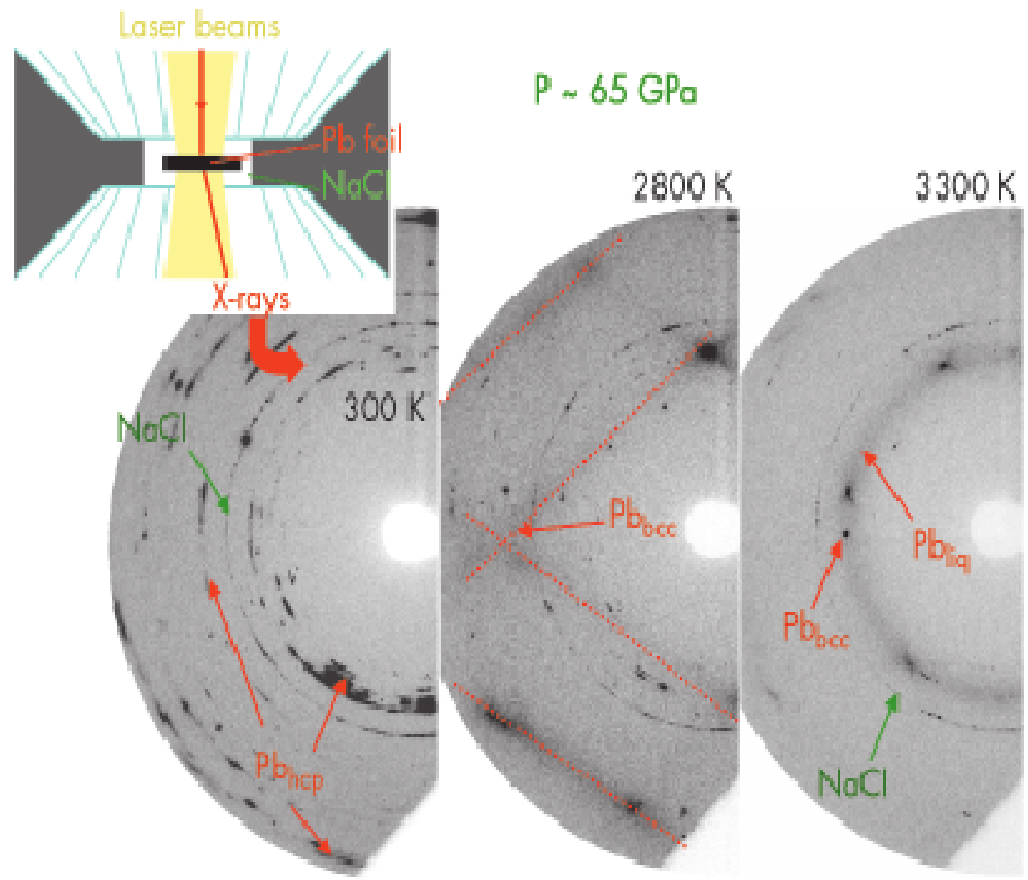
Interaction
sample ↔ radiation

⇒ non-invasive, non destructive probe
for structure & dynamics

A (very) brief history

From groundbreaking to...





A. Dewaele et al., *Phys. Rev. B* **73**, 144106 (2007).

... faster
+ small samples
+ extreme conditions

Breaking New Ground

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JÜLICH
FORSCHUNGSZENTRUM

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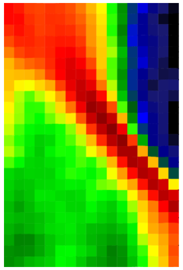
„Lattice dynamics“ group and projects



Thermoelectrics

Bulk materials
Clathrate,
Skutterudites,
Zintl phases

Bi_2Te_3
From bulk to nano,
via films and
nanowires

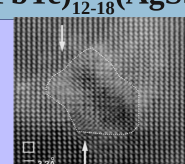
Nanostructured materials

Nanocomposites
Si, MSb_x

SPP 1386
Nanostrukturierte
Thermoelektrika

BMBF
WInG

“NanoKoCh”
LAST $(PbTe)_{12-18}(AgSbTe_2)$



Oxides

Magnetocalorics

Nanoparticles

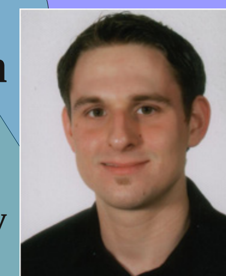
Transition metal oxides

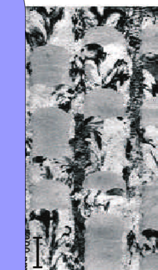
Phase change materials

SFB917 Nanoswitches

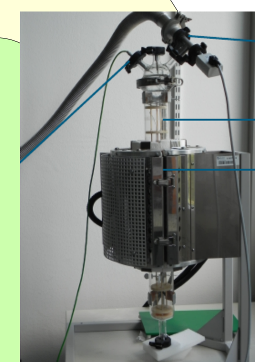
**Thin film
RUS**

Dilatometry





CCMS

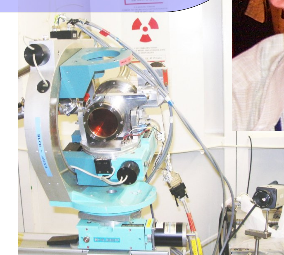


**High-T
RUS**

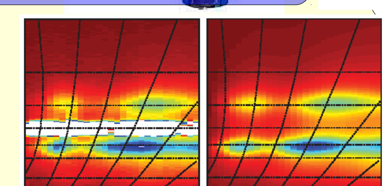
**Mössbauer
spectroscopy**

Superconductors

Neutron
scattering
FRM-II
ILL, SNS



Nuclear scattering
ESRF, APS, Petra III



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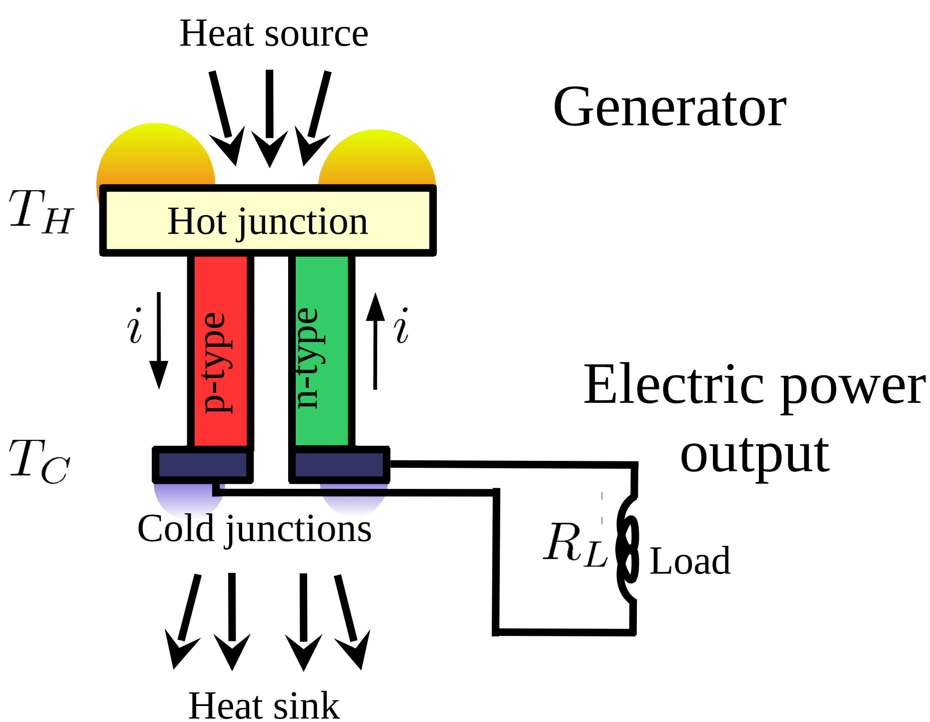
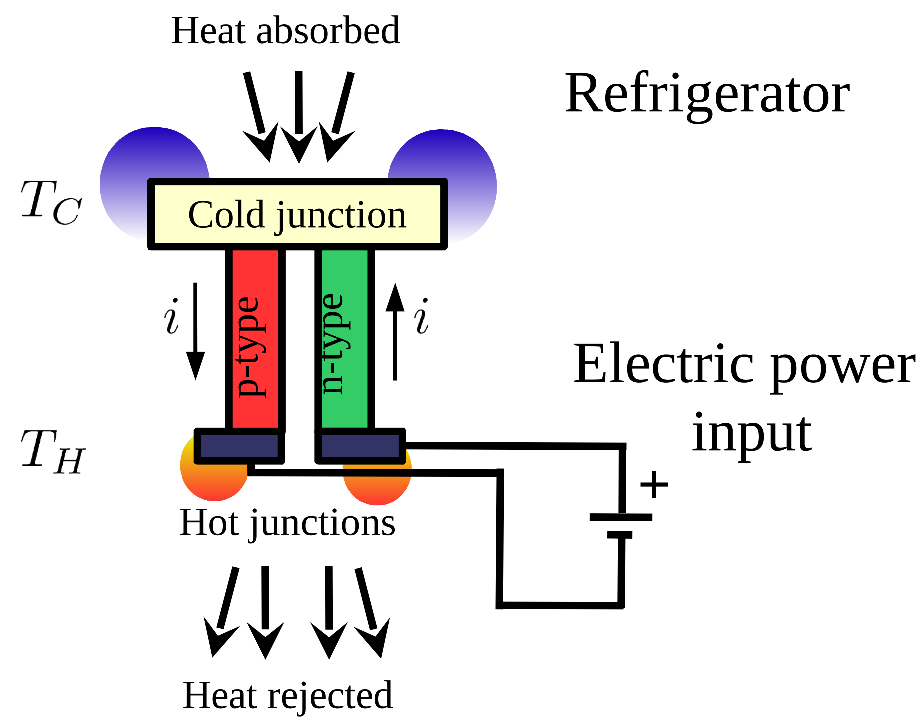
Thermoelectric conversion

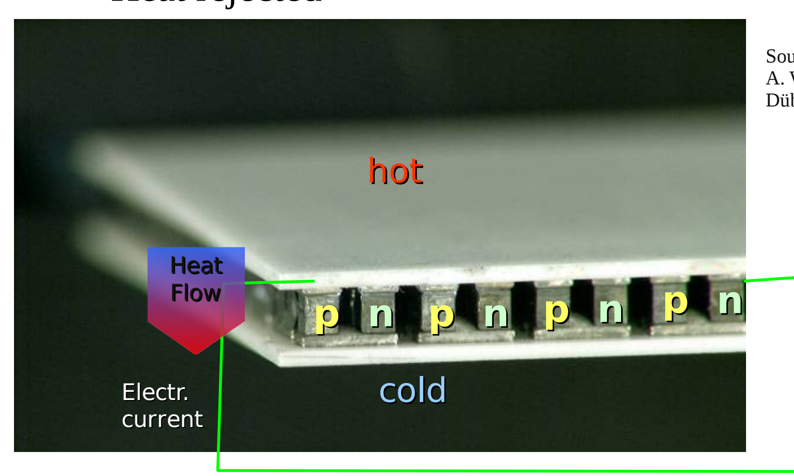
Seebeck effect



Peltier effect



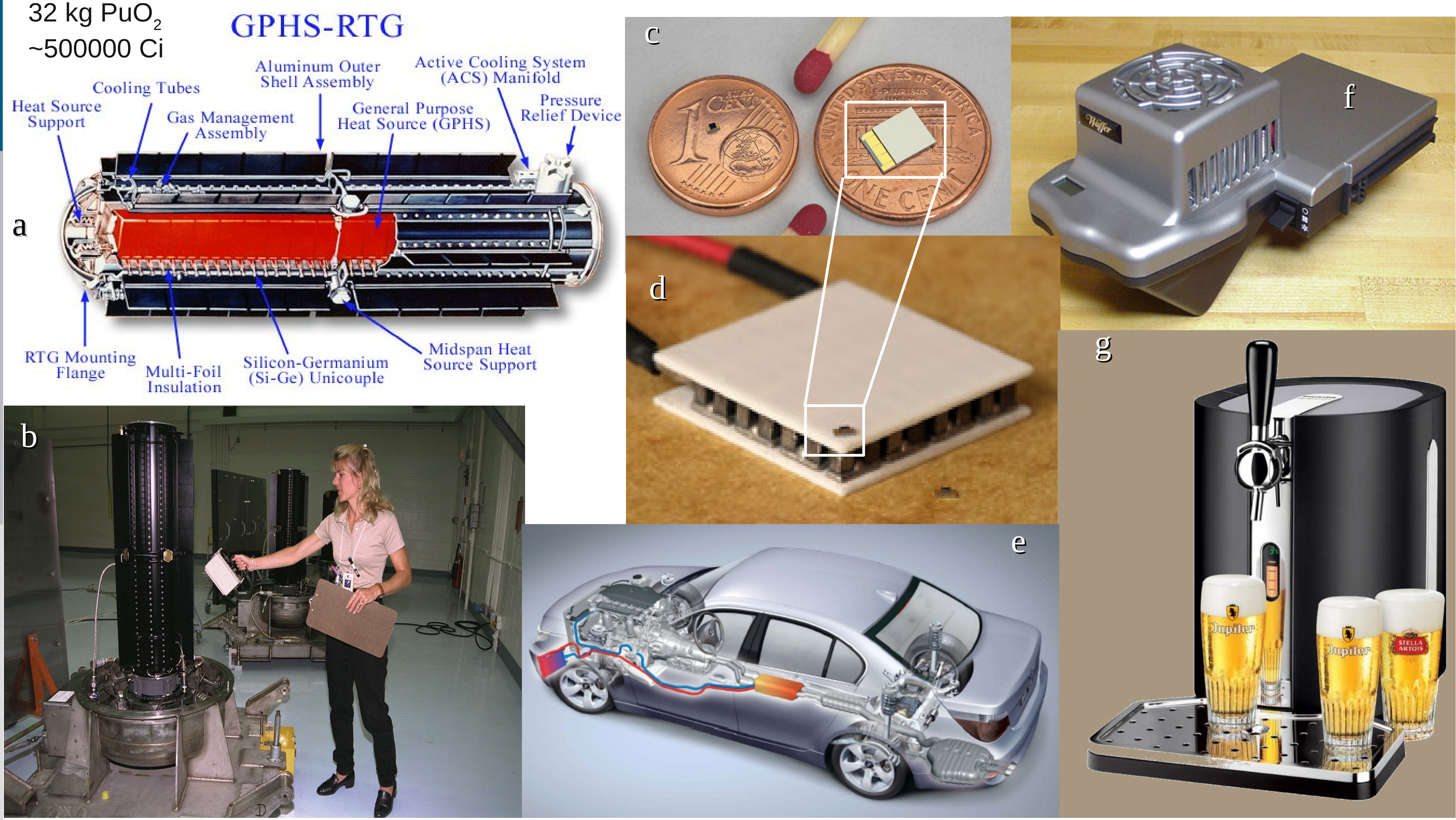
- No moving parts
- Direct conversion: clean and silent
- High power density: small size
- No scale merit, small ΔT



Source:
A. Weidenkaff, EMPA Dübendorf

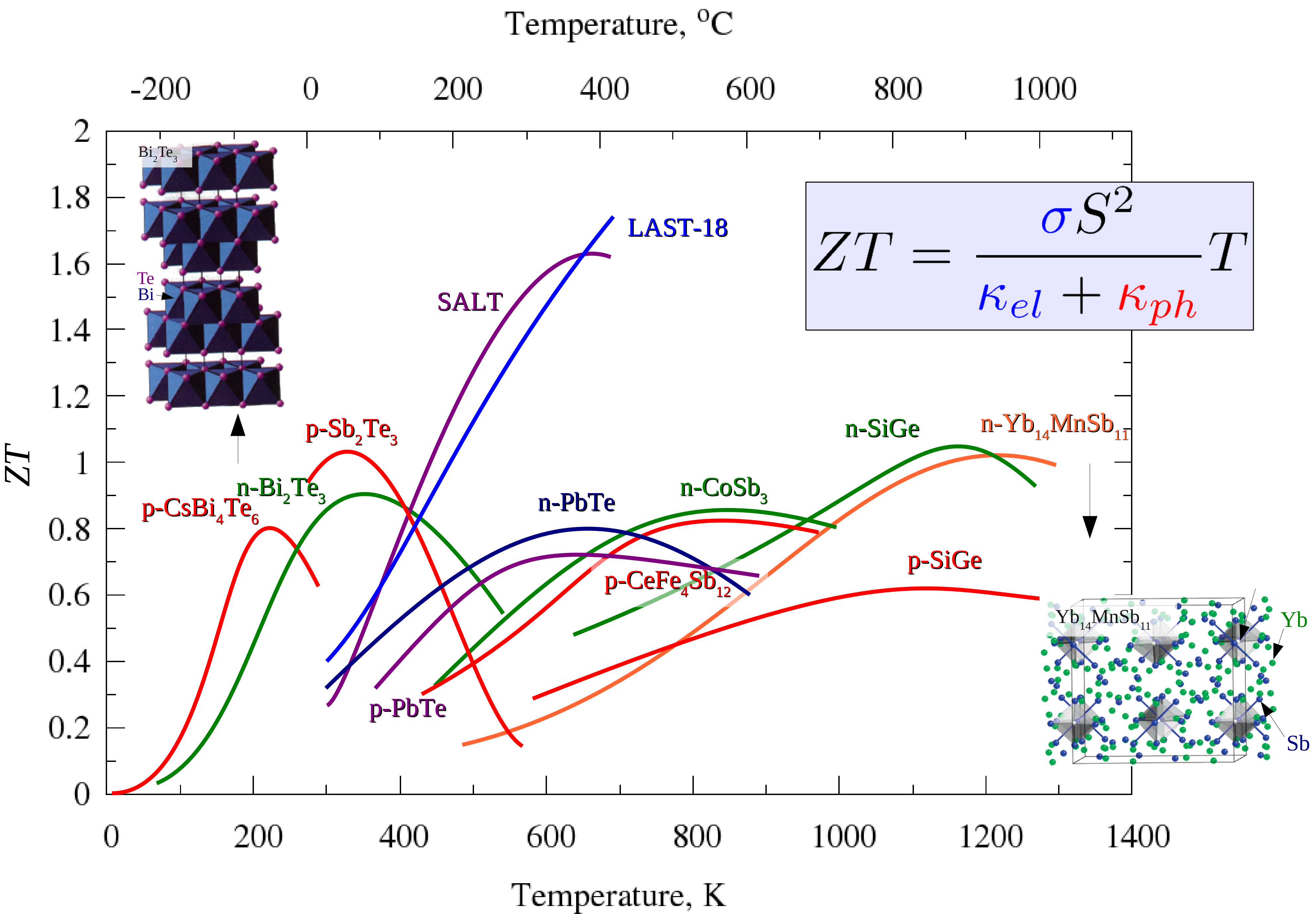
Applications

32 kg PuO_2
~500000 Ci



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

Thermoelectric materials



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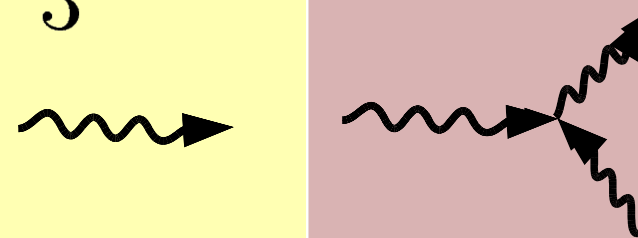
Thermal conductivity

$$\kappa_{ph} = \frac{C_v}{3} < v_s > < l > = \frac{C_v}{3} \langle v_s^2 \rangle \langle \tau \rangle$$



$$\mathbf{J} = -k_B \int_0^\infty g(\omega) \frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \frac{\nu(\omega)^2_{\perp A} \nabla T \tau(\omega)}{V} d\omega$$

R. Hermann et al., Am. J. Phys. **73**, 110 (2005)

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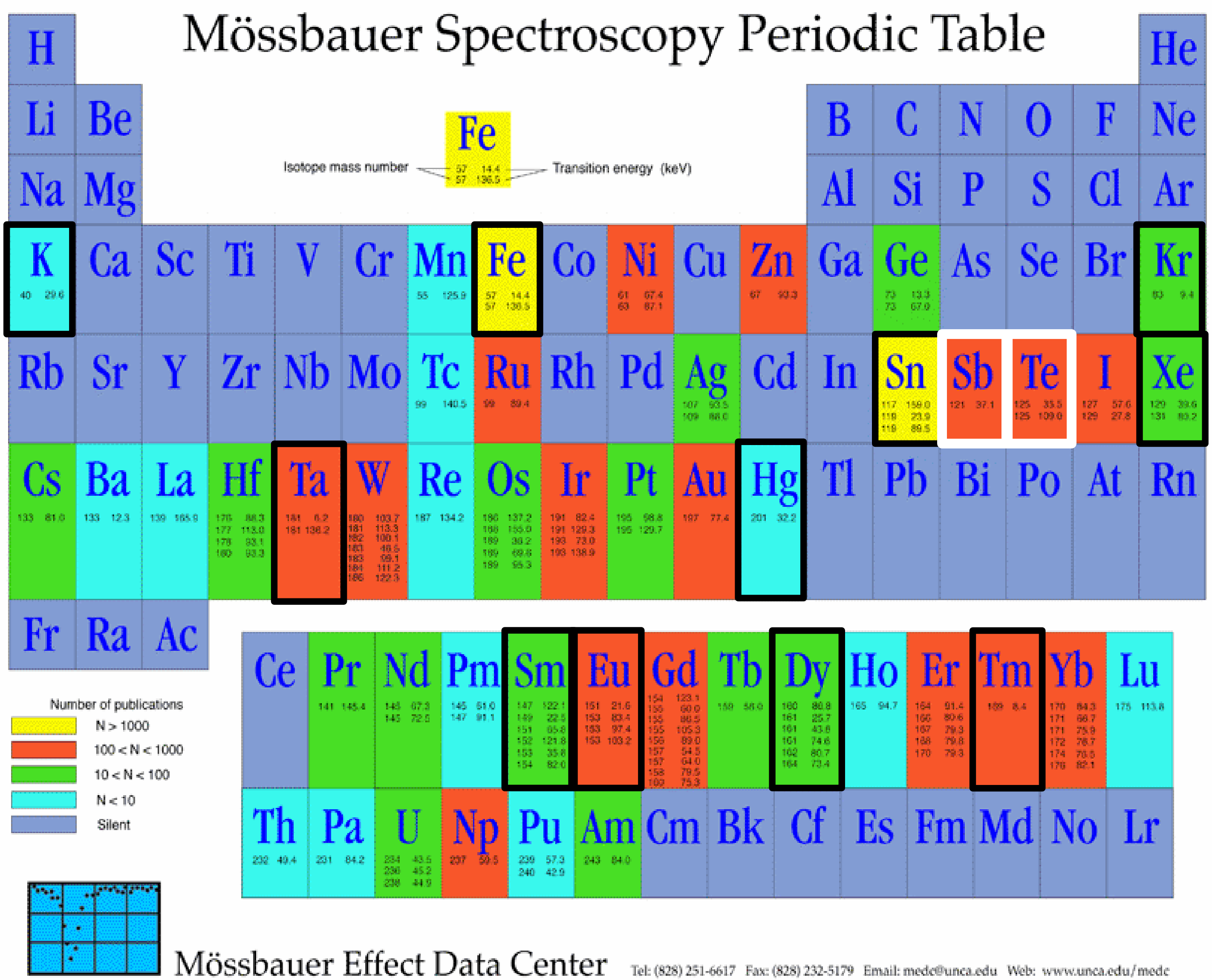
Nuclear resonance scattering & Elements

Mössbauer effect:recoil free emission of γ-rays (1958)

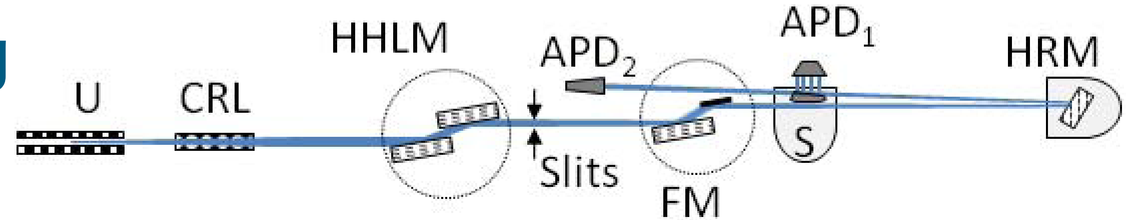
Nuclear **inelastic** scattering: phonon assisted nuclear resonance absorption (1995)

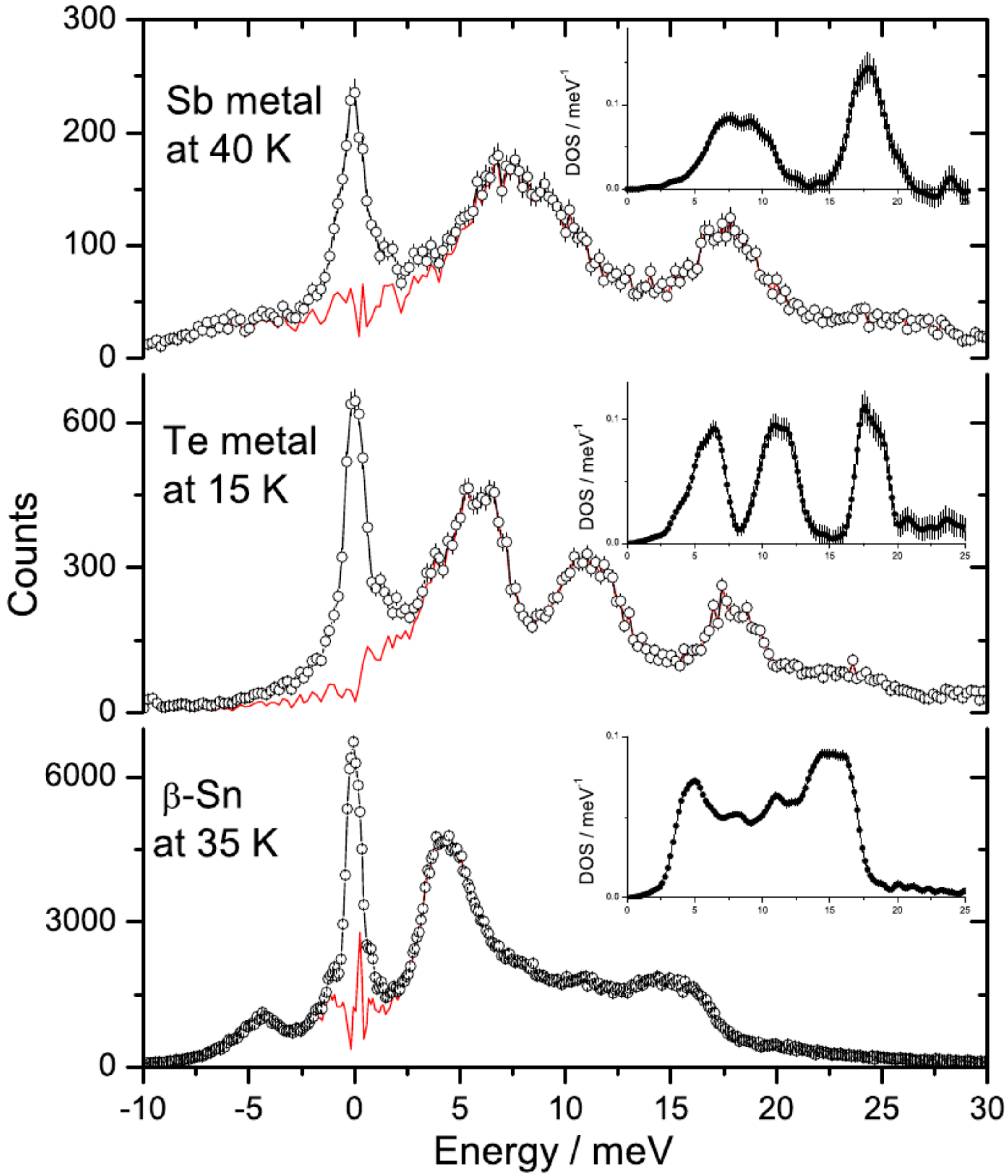


⟺ Successful inelastic measurements

- **Element specific**
- Element blind
- **True DOS**
- No dispersion
- Microfocusing/ small beam
- Small samples
- Isotopic samples

Nuclear inelastic scattering above 20 keV





Sergueev *et al.*, J. Synch. Rad. **18**, 802 (2011).

- Phonon DOS in elemental Sb, Te, or Sn with $\Delta E \sim 1.2$, 1.1, or 1.0 meV
- $E/\Delta E \simeq 3.10^7$, single bounce
- Isotope specific method

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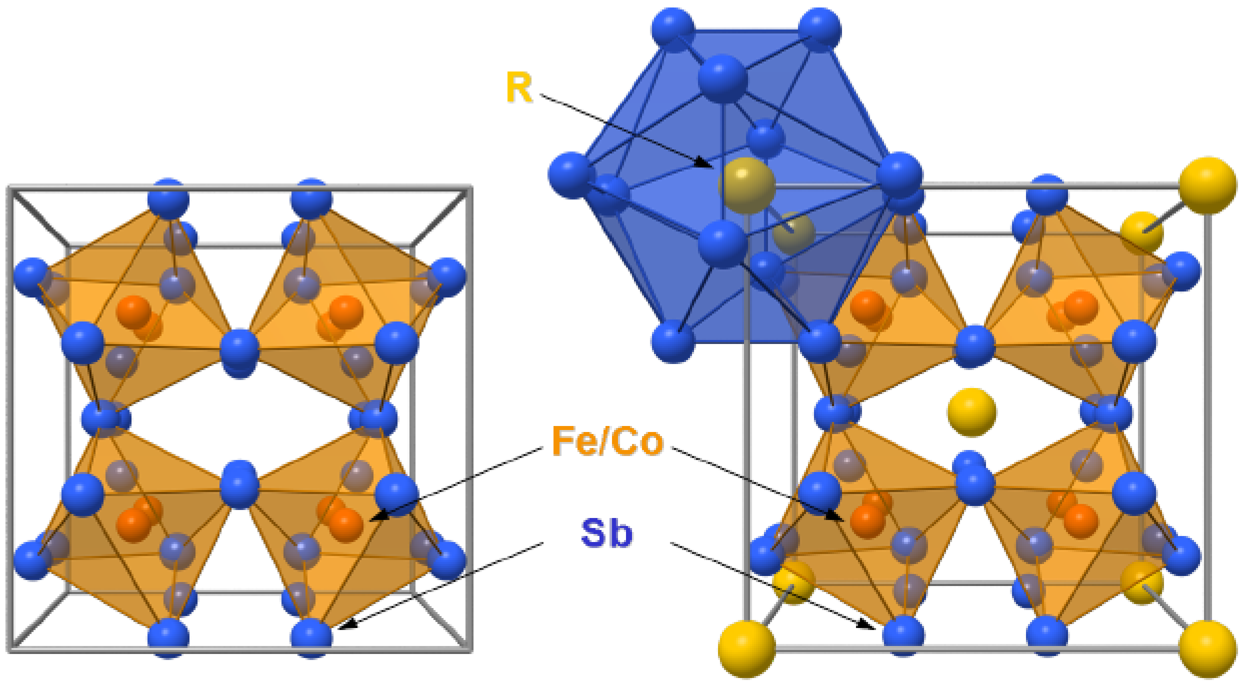
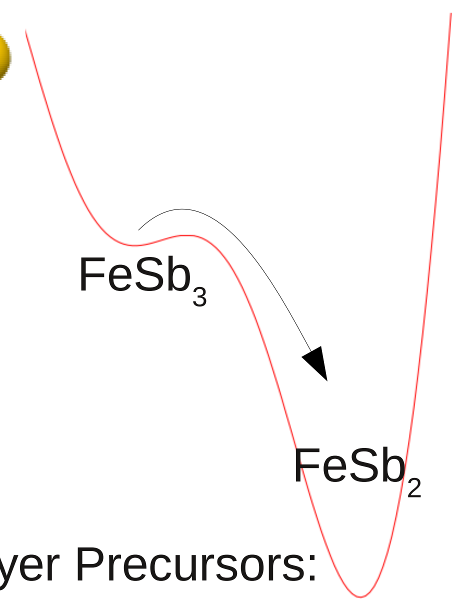
Filled and empty skutterudites



Filling $R_xCo_4Sb_{12}$ requires charge compensation: $\boldsymbol{R}_x(Co,\mathbf{Fe})_4\mathbf{Sb}_{12}$.

Is $CoSb_3$ is a usual reference for filled skutterudite lattice dynamics.

$FeSb_3$ is thermodynamically unstable!

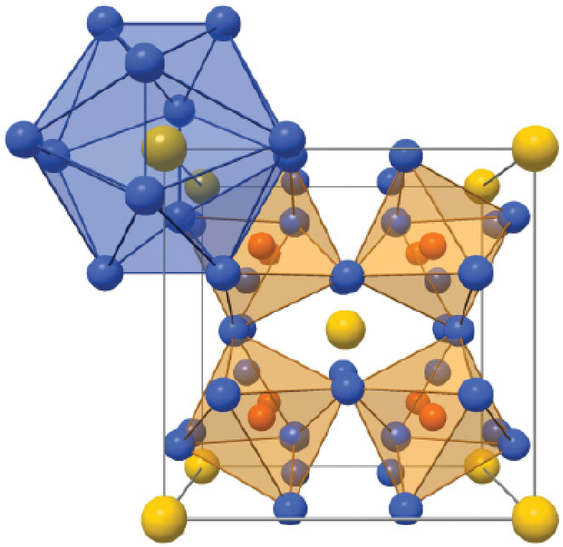


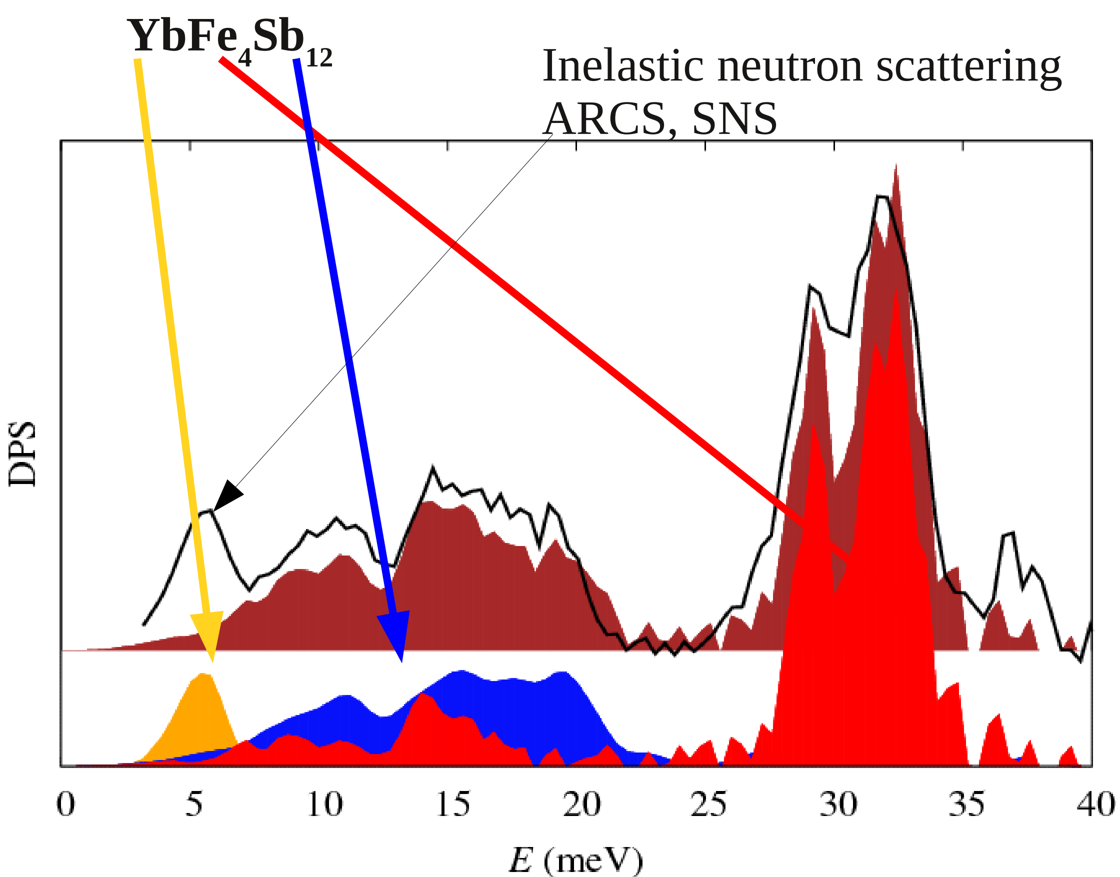
Rational Synthesis of Metastable Skutterudite Compounds Using Multilayer Precursors:

→ „thick“ 1-1.5 µm films of $FeSb_3$

(Hornbostel et al., J. Am. Chem. Soc. 1997, 119, 2665-2668)

Skutterudites – Localized vibrational modes





Moechel A., Sergueev I., Wille H.-C., Voigt J., Prager M., Stone M.B., Sales B.C., Guguchia Z., Shengelaya A., Keppens V., and Hermann R.P.
Lattice dynamics and anomalous softening in the $YbFe_4Sb_{12}$ skutterudite
Phys. Rev B **84**, 184306 (2011). Editor's Selection.

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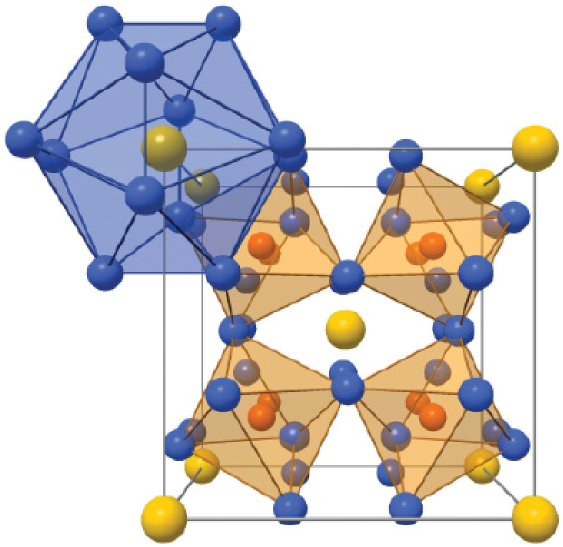

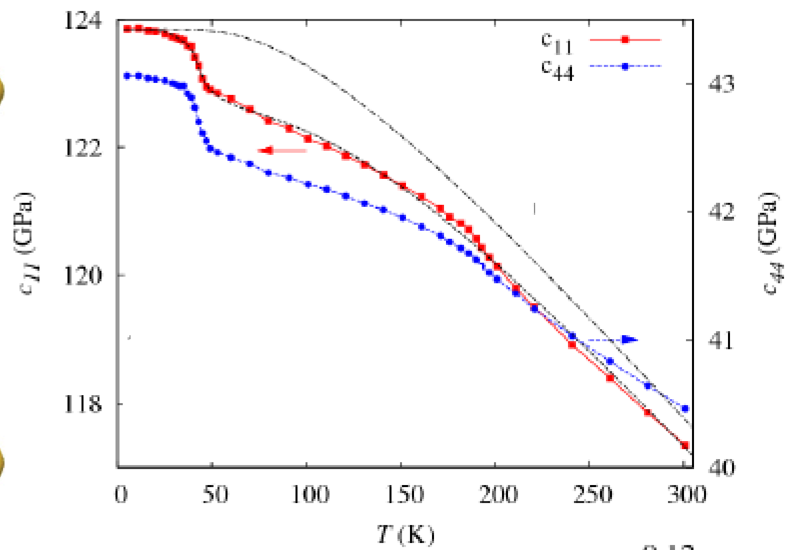

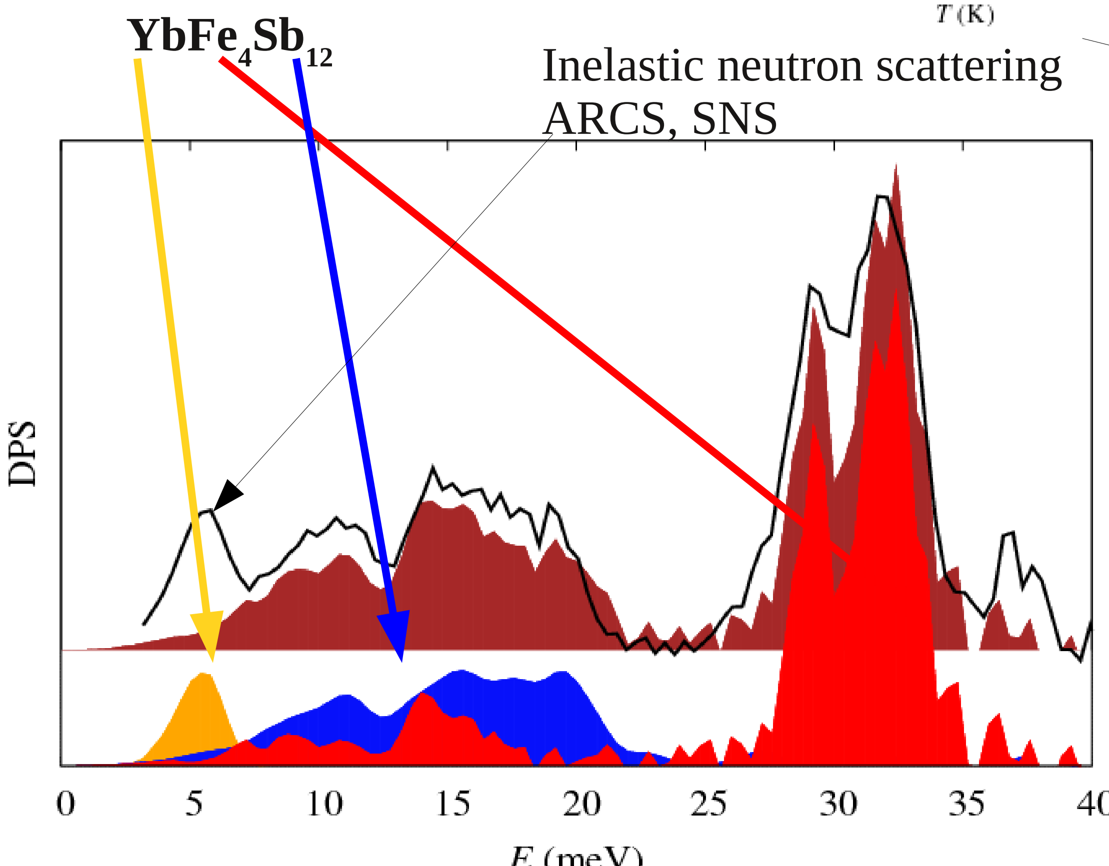

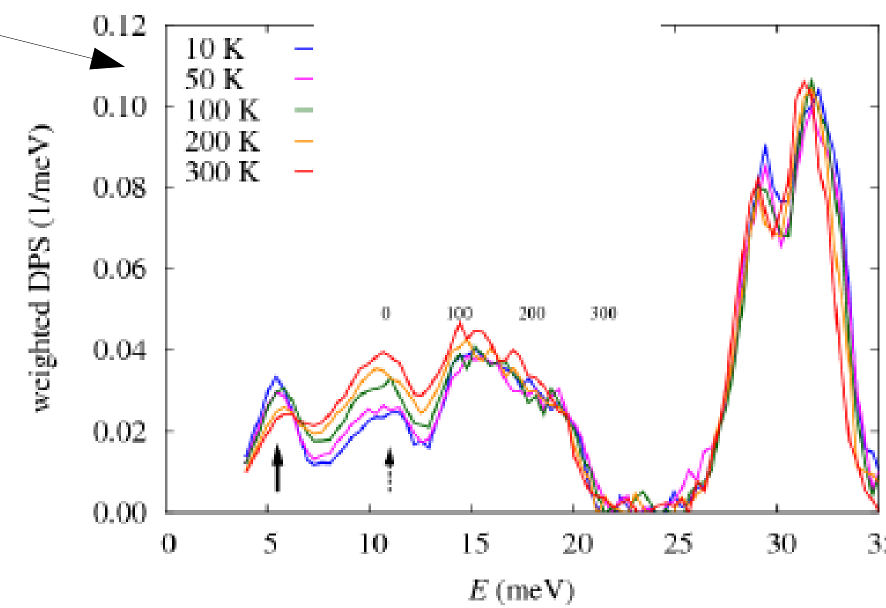

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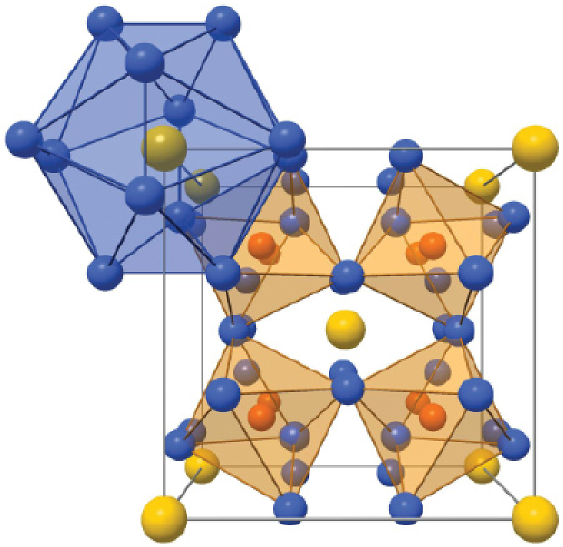

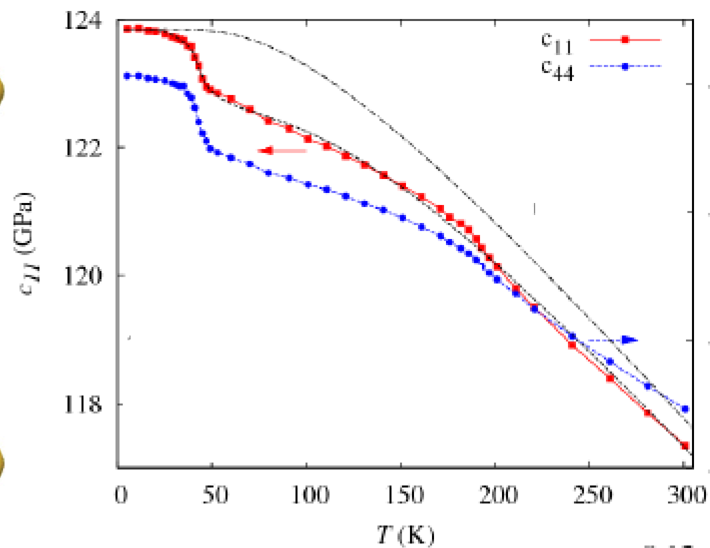

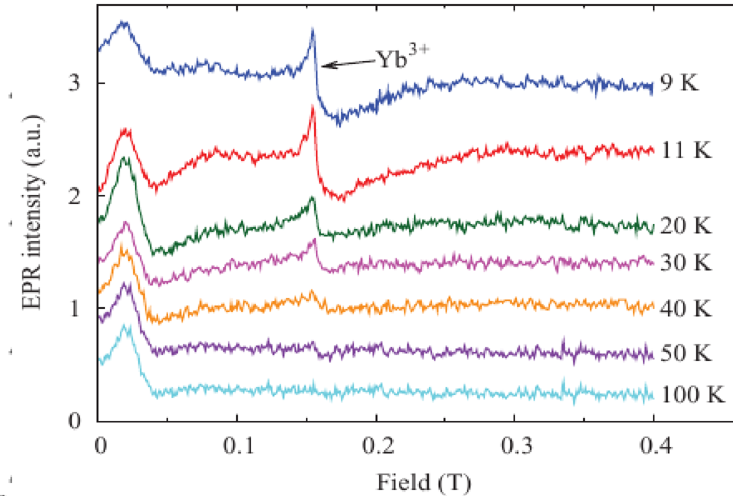

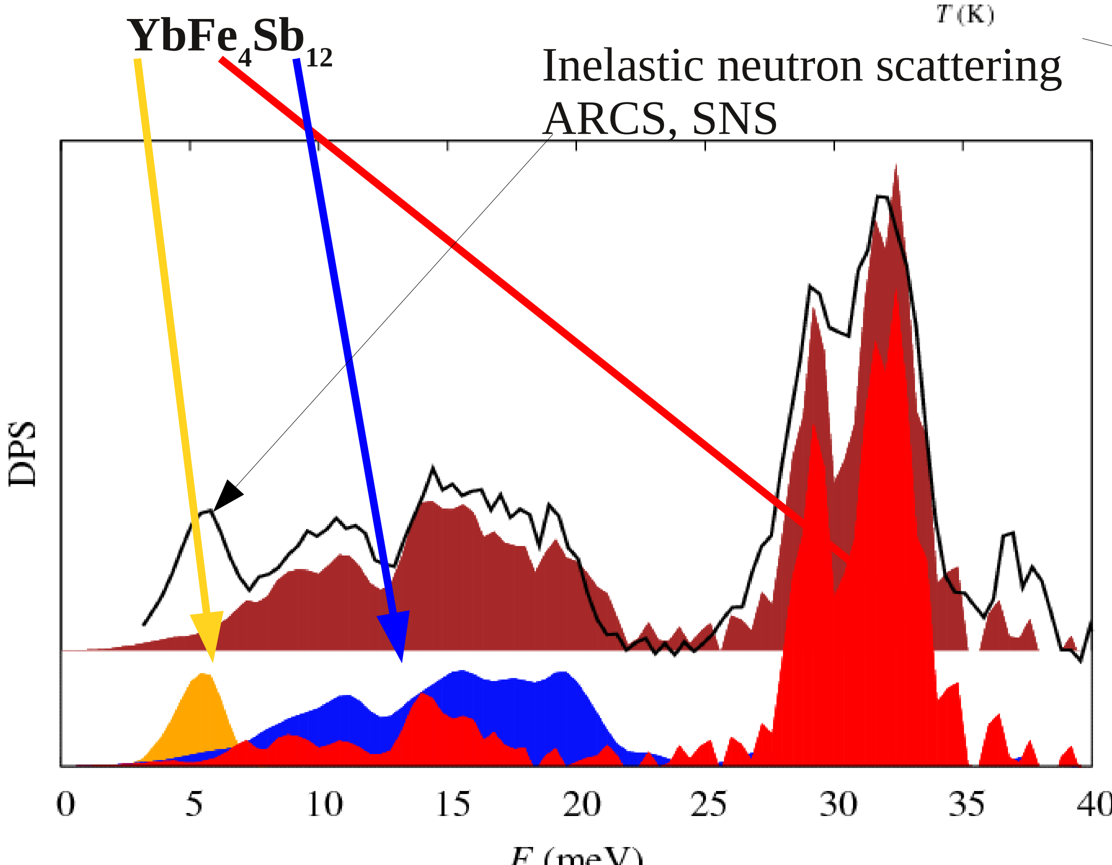

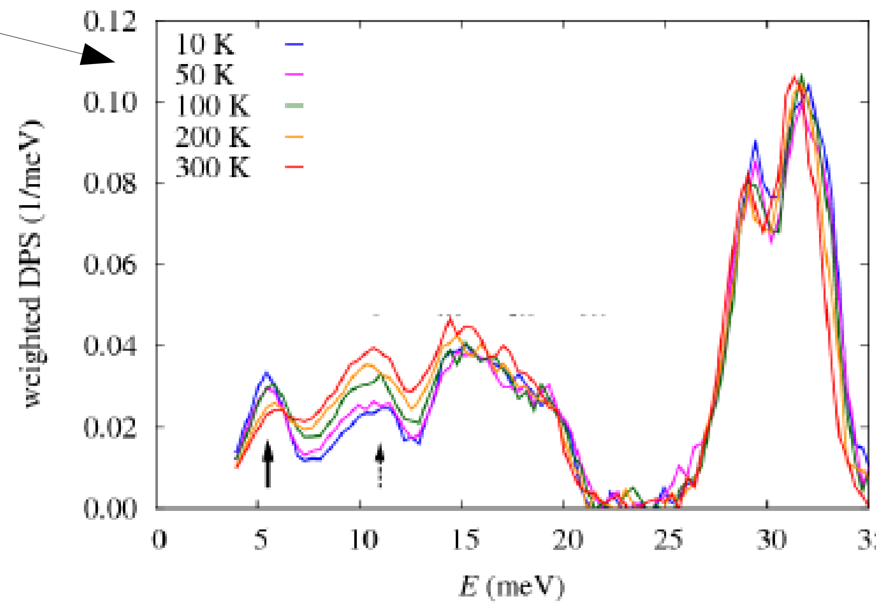

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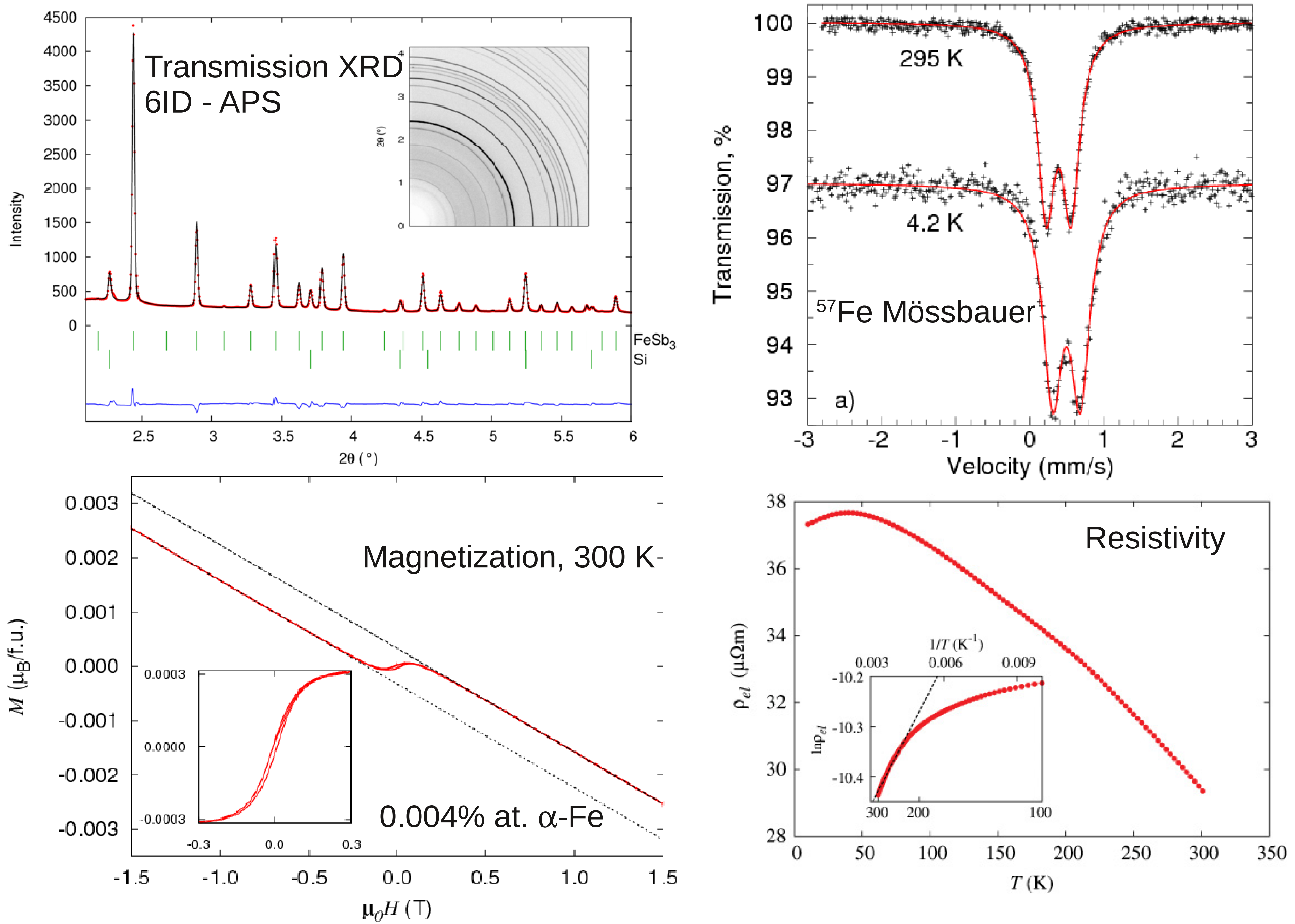
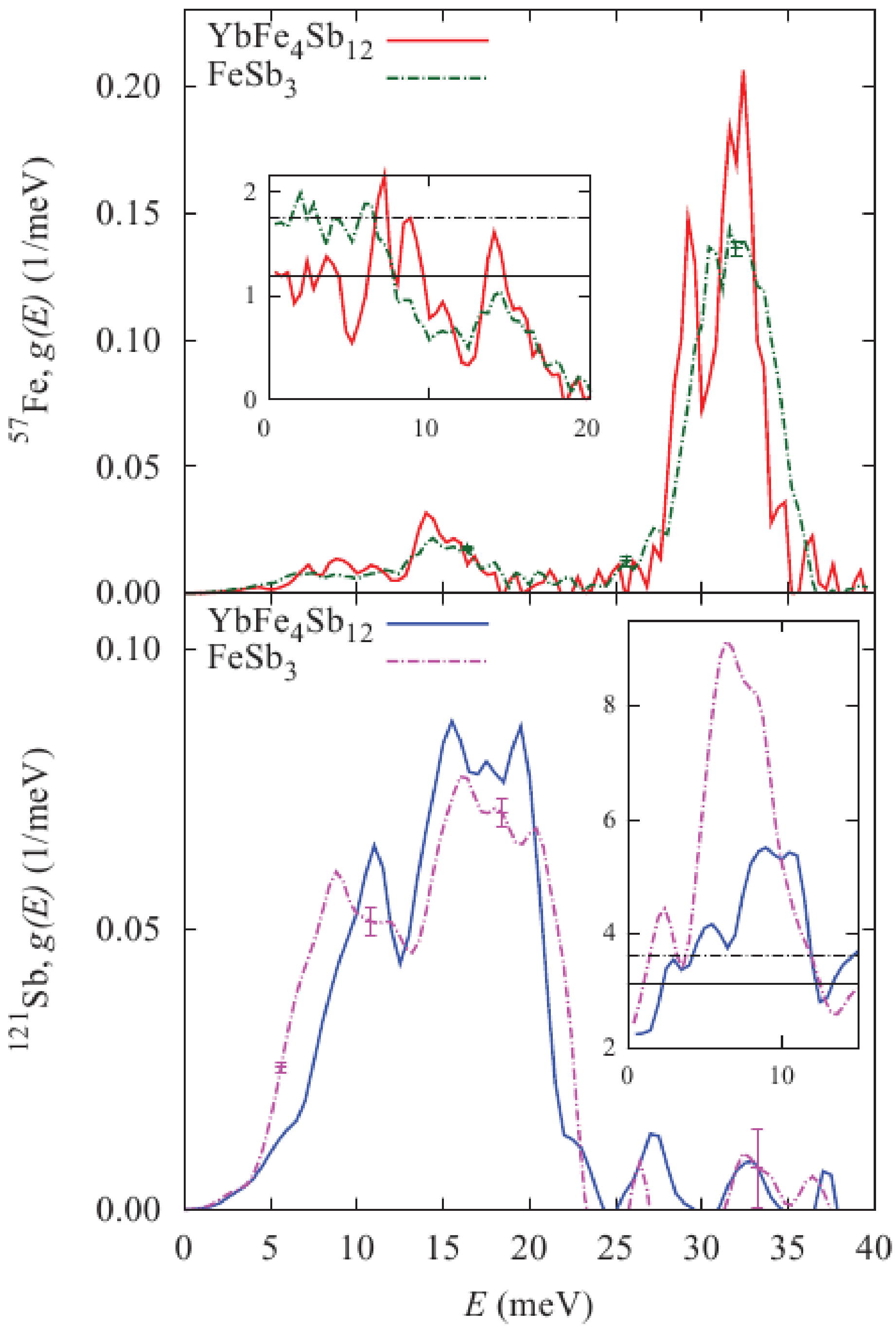
$FeSb_3$: Phase purity and properties ?



Density of phonon states

1.5 µm thick film deposited on kapton foil (David Johnson, U. Oregon).



V_{sound} = 2500 m/s in $YbFe_4Sb_{12}$

V_{sound} = 2390 m/s in $FeSb_3$

V_{sound} = 2920 m/s in $CoSb_3$

F(Sb) = 100 N/m in $FeSb_3$

F(Sb) = 130 N/m in $CoSb_3$

→ $FeSb_3$ and $YbFe_4Sb_{12}$ are significantly softer than $CoSb_3$

→ Beyond filling with Yb, also the soft Fe-Sb framework contributes to the low thermal conductivity

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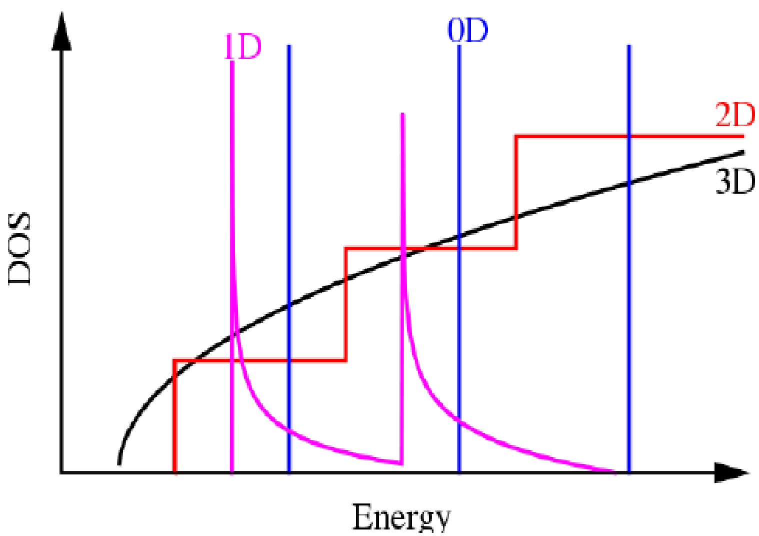
Nanostructured thermoelectrics

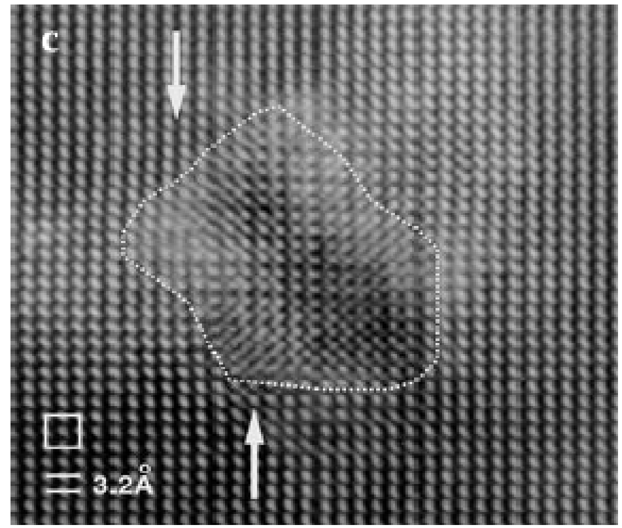
Key idea (Hicks, Dresselhaus,1992):

Electronic band engineering

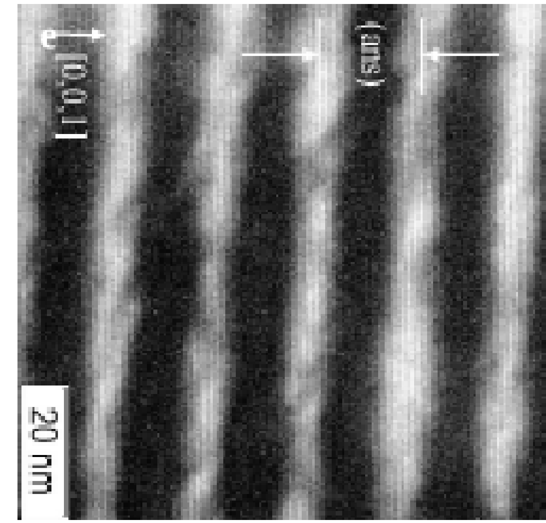
and phonon blocking

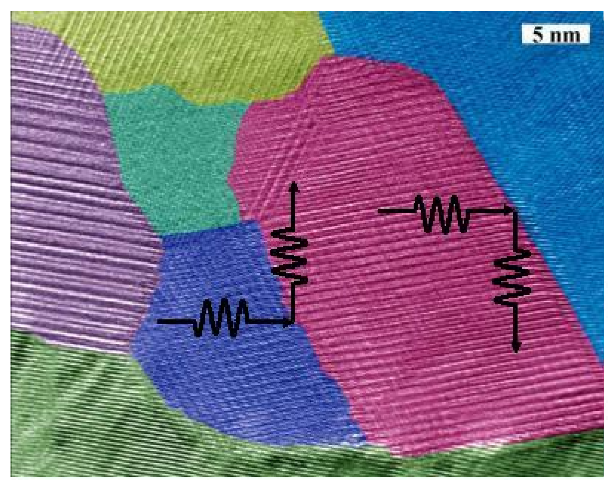


Embedded nanodots
(Kanatzidis group)

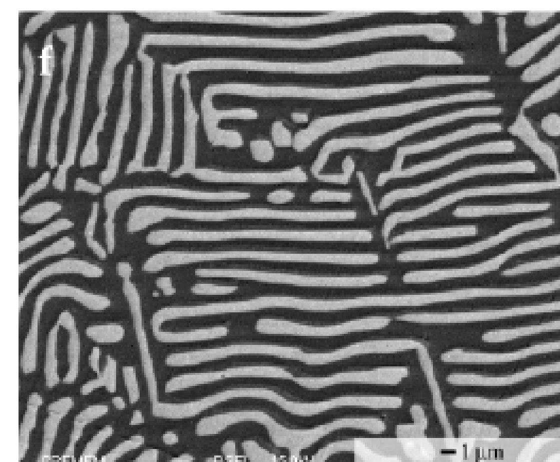


Artificial nanostructures
(N. Peranio, PhD diss., U. Tübingen)





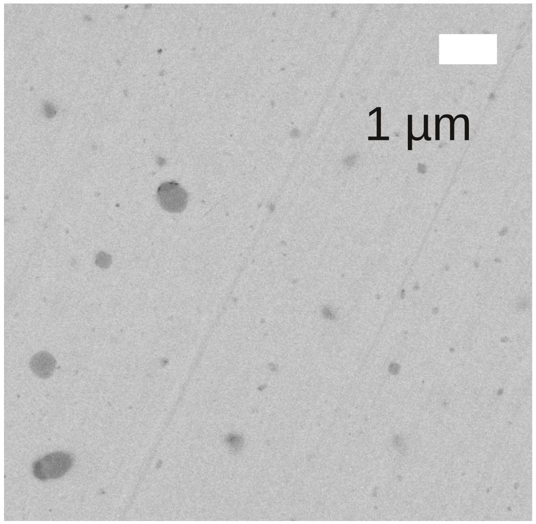
Nanocomposites
(Poudel et al., Science 2008)



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

Jülich Centre for Neutron Science

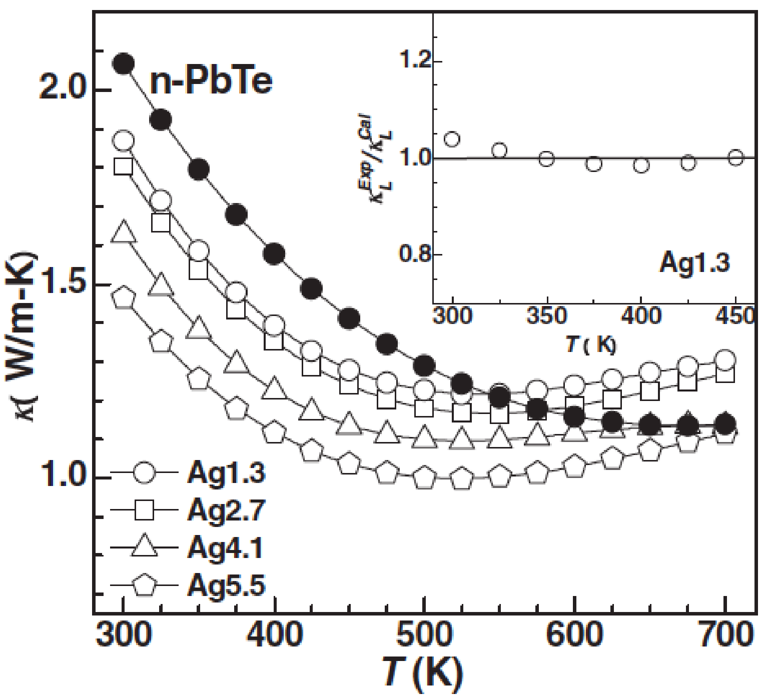
Ag Microinclusions in PbTe



Microstructure (coll. J. Snyder, CalTech)

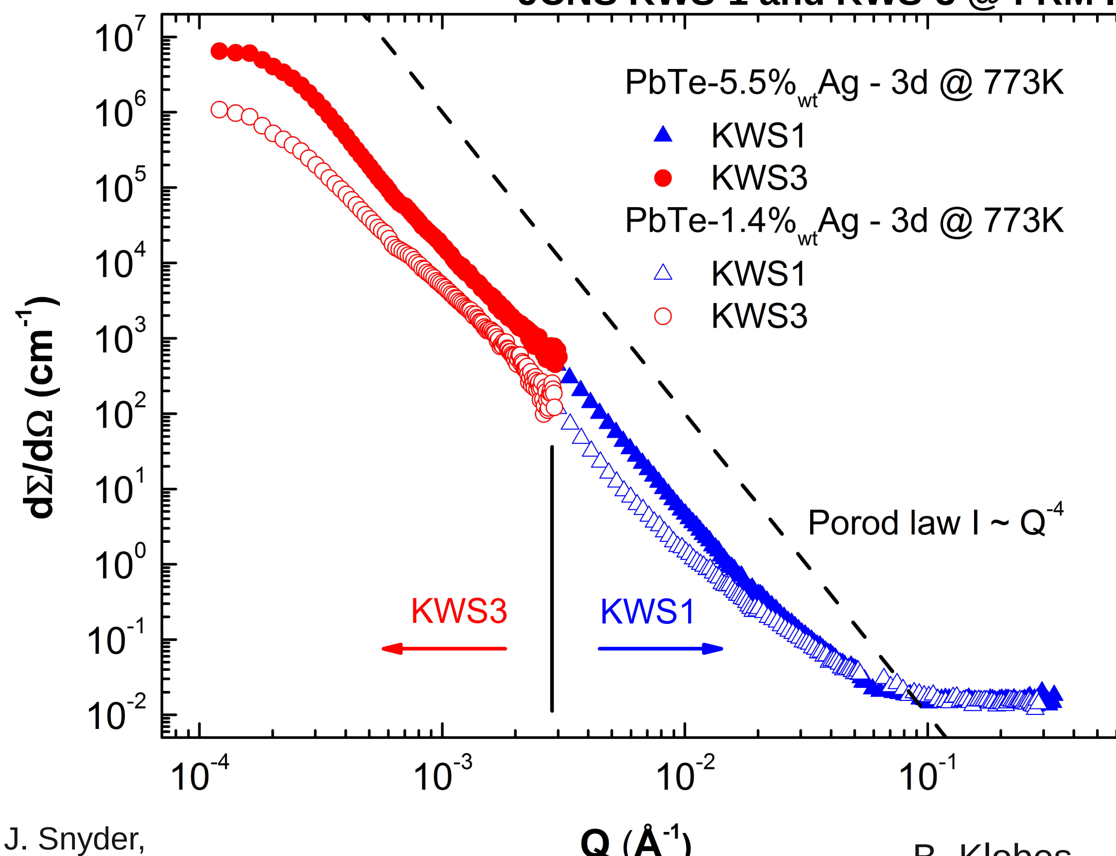
PbTe based alloys

Can the thermal conductivity be correlated with the total internal surface?



Y. Pei, J. Lensch-Falk, E. S. Toberer, D. L. Medlin, and G. J. Snyder, *Adv. Funct. Mater.* **21**, 241 (2011).

JCNS KWS-1 and KWS-3 @ FRM II

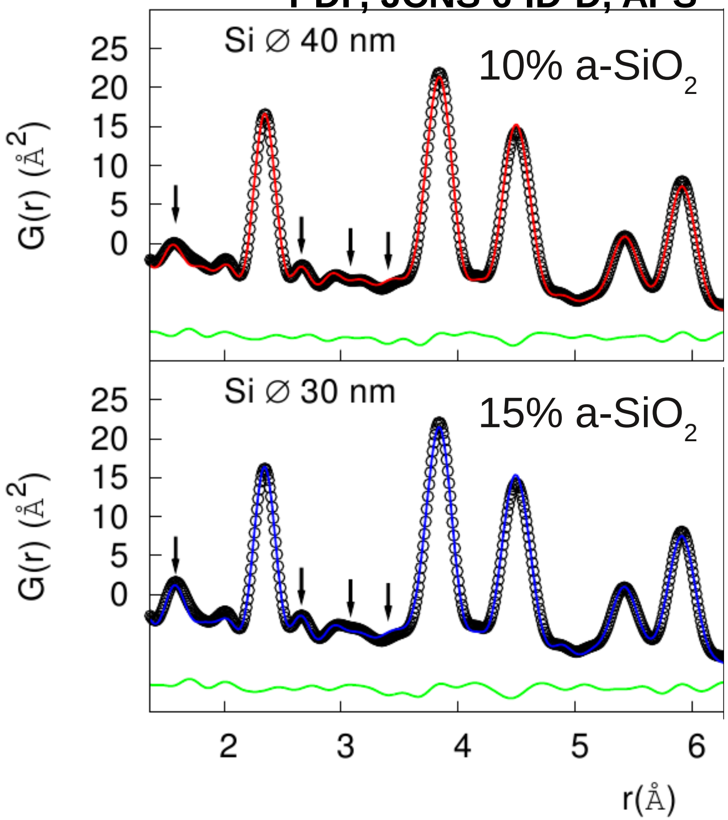


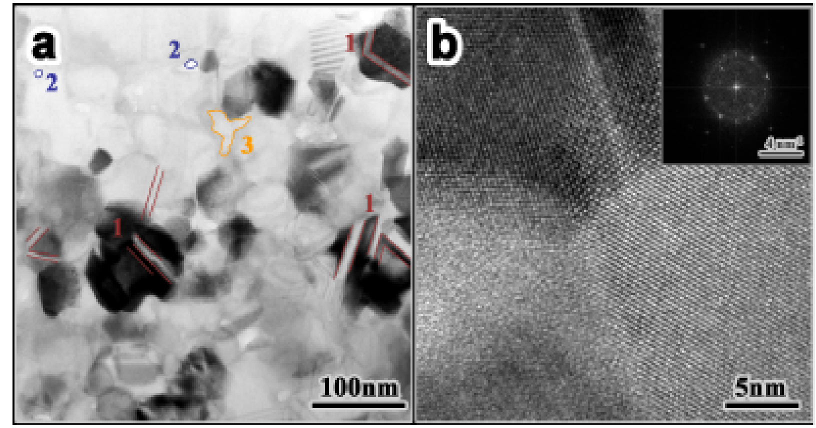
B. Klobes

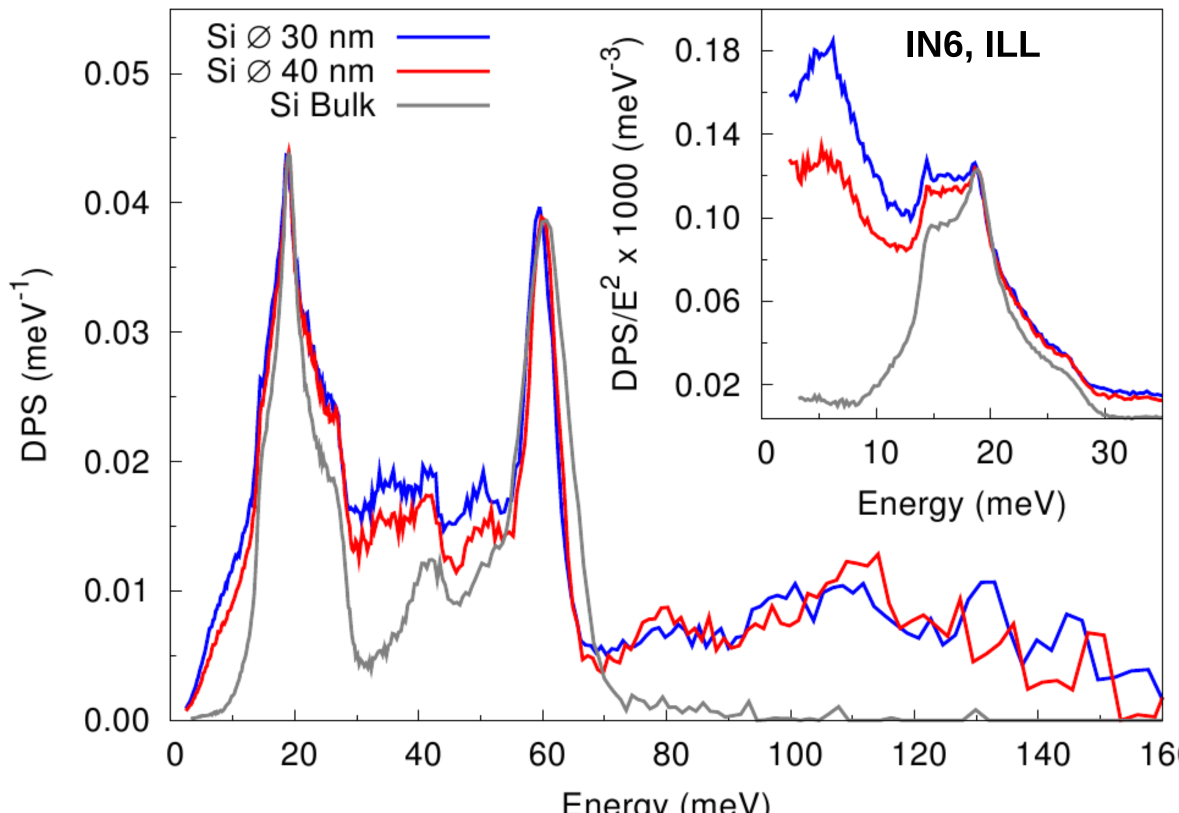
Nanocrystalline silicon

Nanocrystallinity (coll. G Schierning, U Duisburg-Essen)
spark plasma sintered

PDF, JCNS 6-ID-D, APS



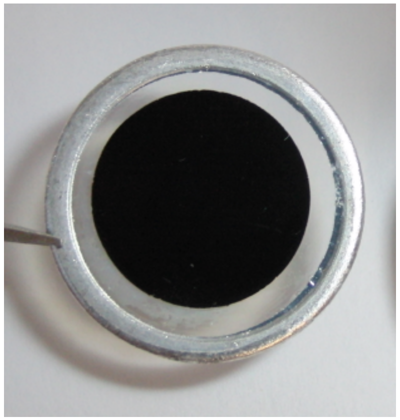




Reaching a quantitative analysis of the amorphous phase content, the impact of the nanostructures on the lattice dynamics

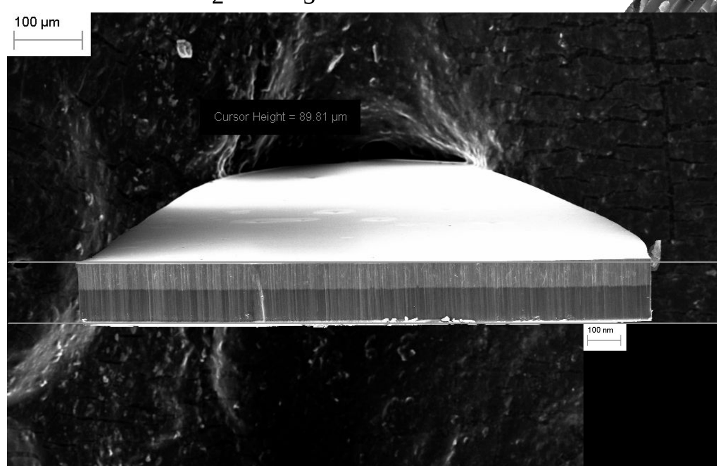
T. Claudio

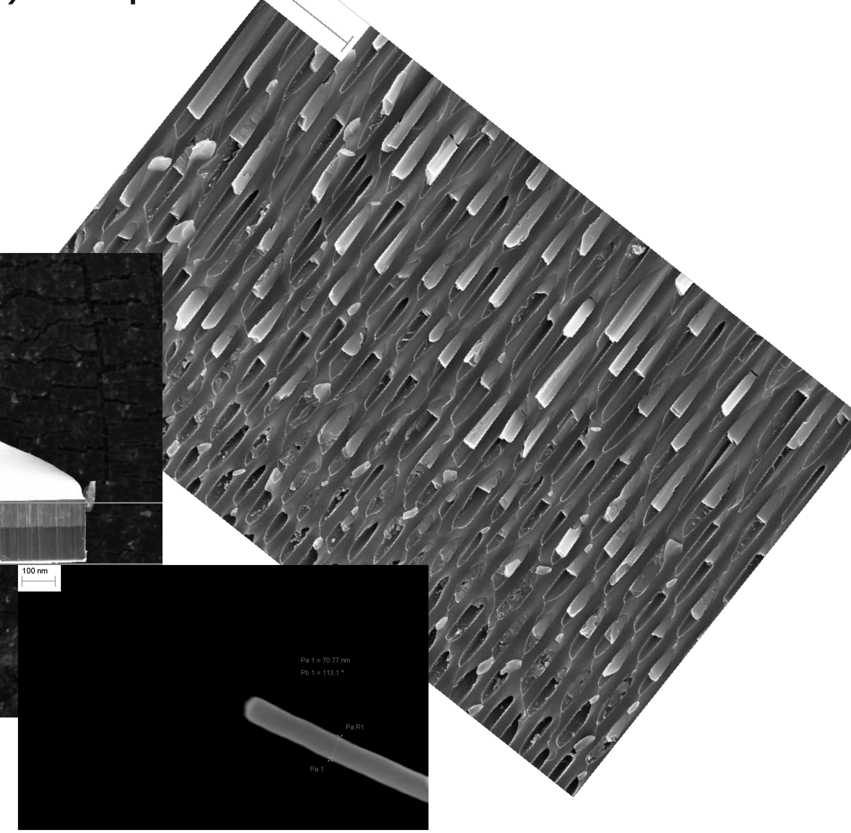
$Bi_2{}^{125}Te_3$ nanowires Ø55 nm



- Novel pulsed electrodeposition process using an anodic Al_2O_3 template (amorphous)
- NW NOT removed from template
- Isotopically enriched (^{125}Te) samples

$Bi_2{}^{125}Te_3$ Nanowires

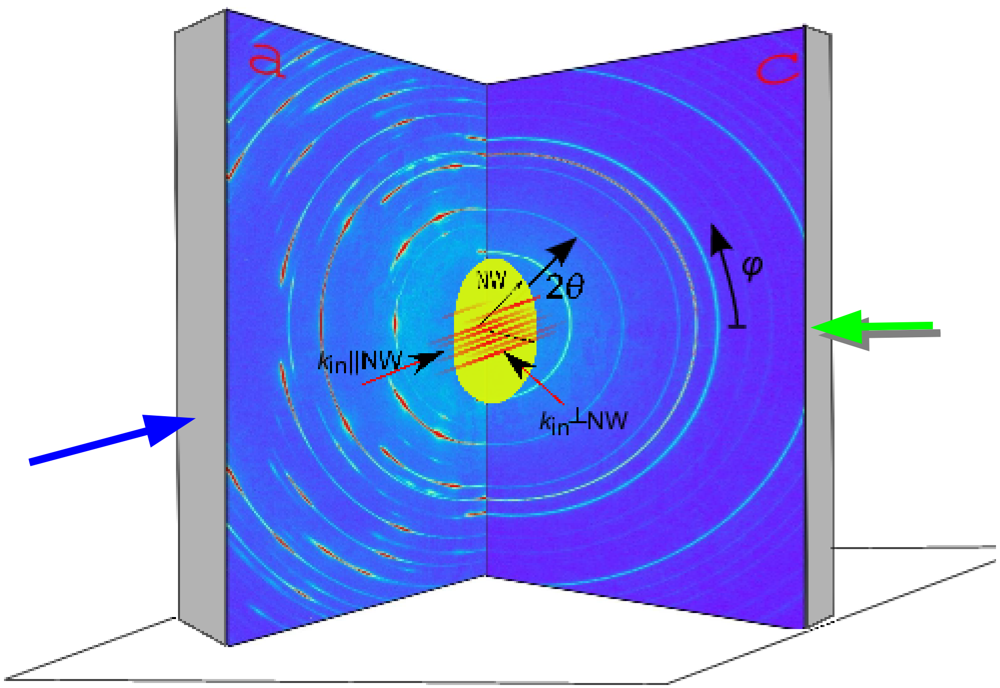


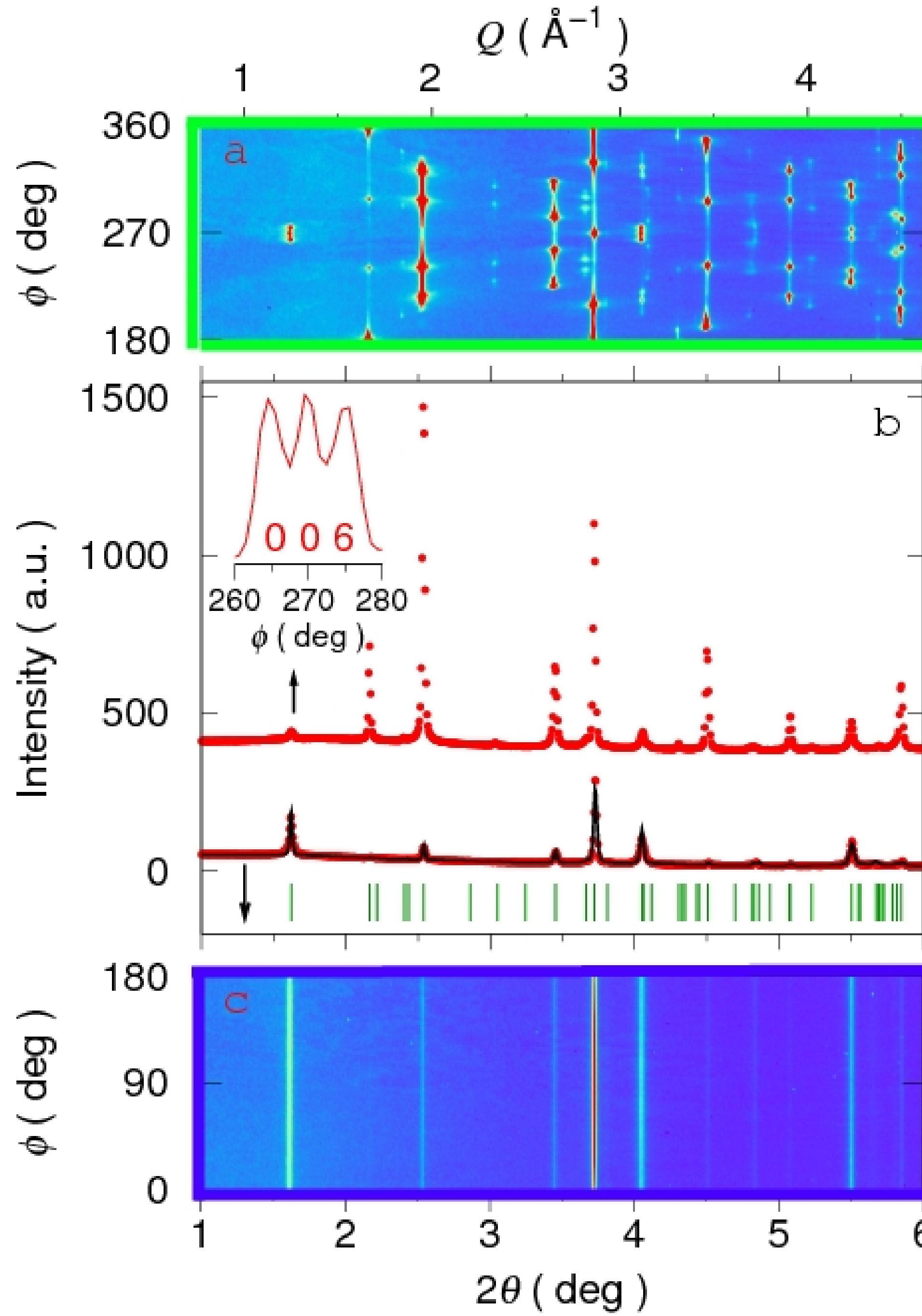


- 16 µm wires, Ø55nm
- 40 µm wires, Ø70nm
- 35 µm wires, Ø250nm

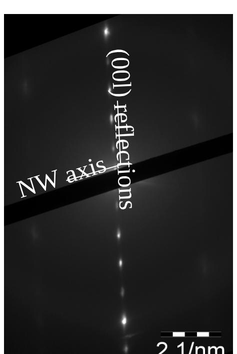
* **W. Töllner, Prof. K. Nielsch, U. Hamburg**

$Bi_2{}^{125}Te_3$ nanowires Ø55 nm



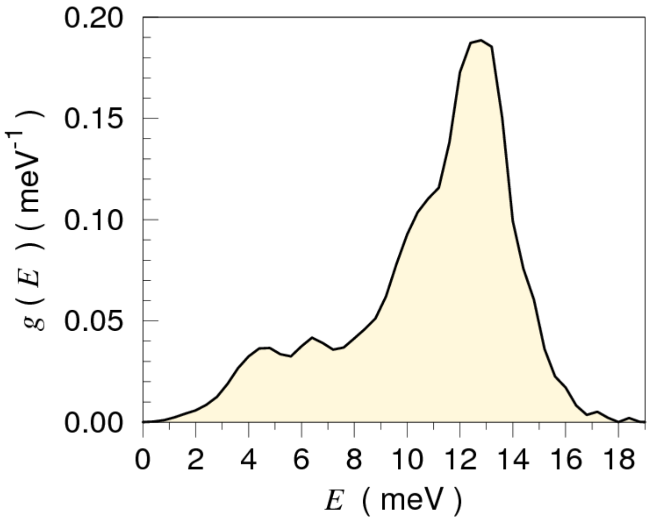


- NW are single crystalline with (0 0 1) twin boundaries
- Larger diameter NW are highly textured
- *c*-axis at 85 deg w/r to NW axis

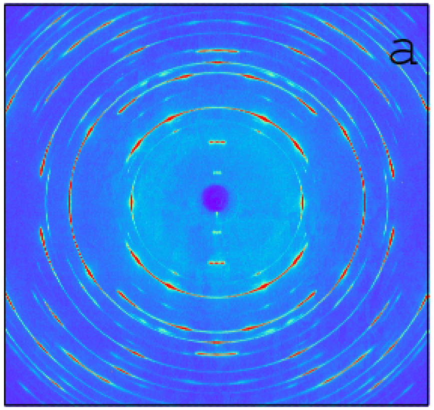


Z. Aabdin, U. Tübingen

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

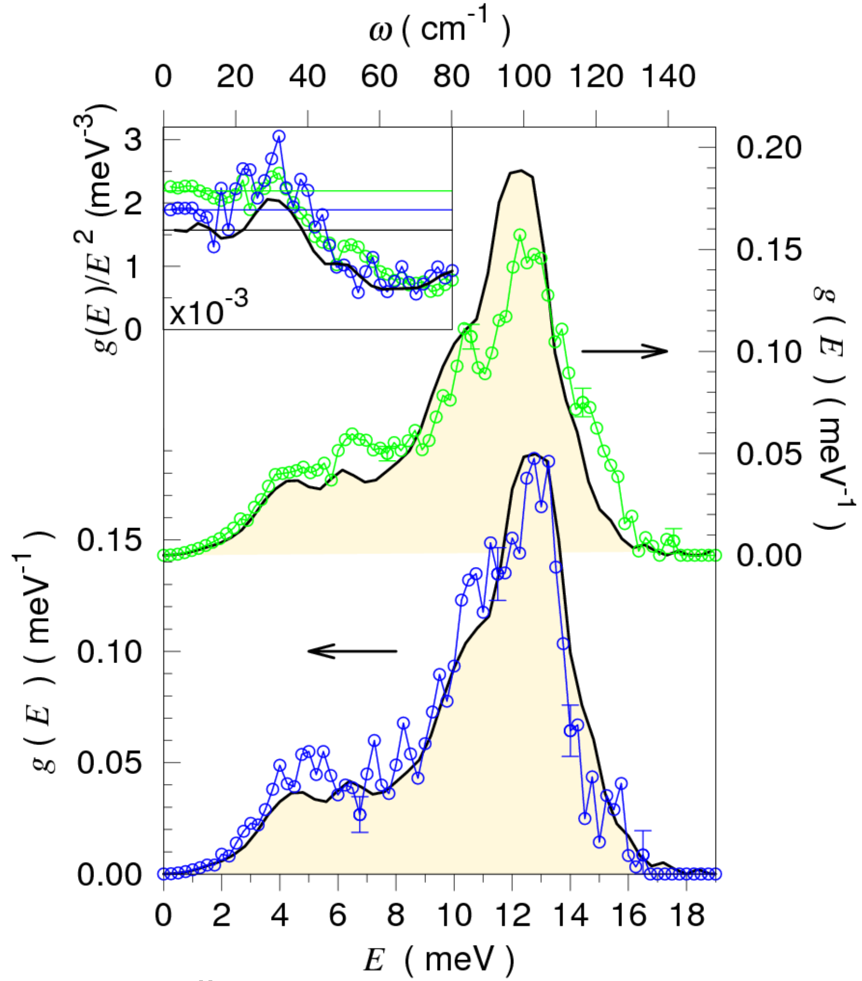


Bulk: v_s = 1750 km/s

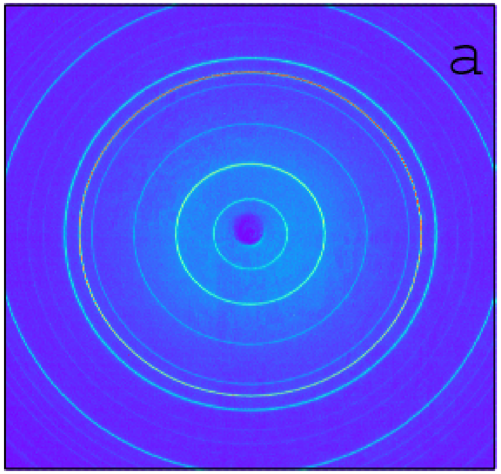


k⊥NW

25% speed of sound reduction

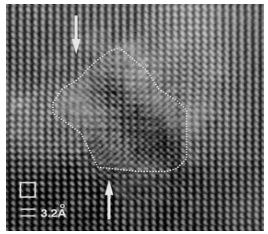


k‖NW



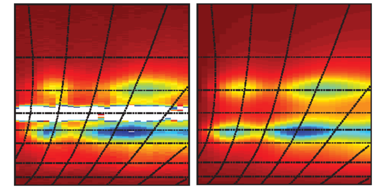
15% speed of sound reduction

Scattering methods



Kanatzidis et al.
JACS 2005

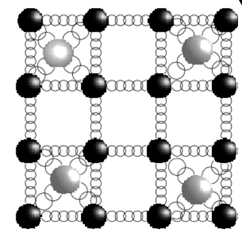
Materials



Jülich Centre for Neutron Science

Understanding

Where are the atoms?
How do they move?

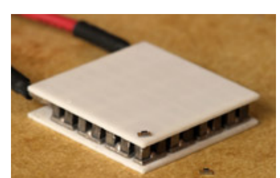


How does structure and dynamics affect the functionality?

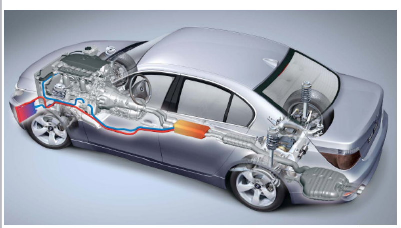
Optimization

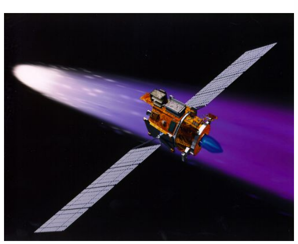
Poudel et al. Science 2008

Devices



Applications





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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

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JÜLICH FORSCHUNGSZENTRUM

Lattice Dynamics in Emerging Functional Materials Group

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