Materials Crystallography

Structure and Property Relations in Energy Materials

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Acknowledgements

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Thank you for your kind attention!

Facilities:
ESRF
MAX-lab
SPring8

Conclusion

Synchrotron light is a very versatile tools for materials research

Atomic positions and occupancies:
Single crystal and powder diffraction
- including resonant scattering

Vibration characteristics through
Inelastic X-ray scattering

Growth properties of compounds
In situ studies

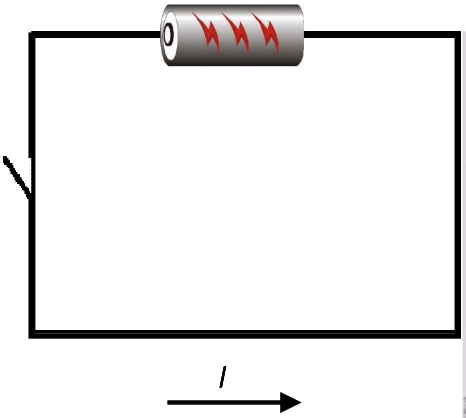
Overview

Thermoelectrics – a short introduction	
Clathrates – the structure	
	Single crystal X-ray and neutron diffraction Resonant diffraction
Zn_4Sb_3	Single crystal diffraction Powder diffraction
Skutterudites	X-ray and Neutron powder diffraction
Photons vs phonons	Inelastic X-ray scattering in $FeSb_2$
In situ X-ray diffraction studies of crystal growth	

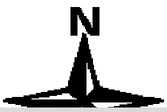
Thermoelectrics - Historical background

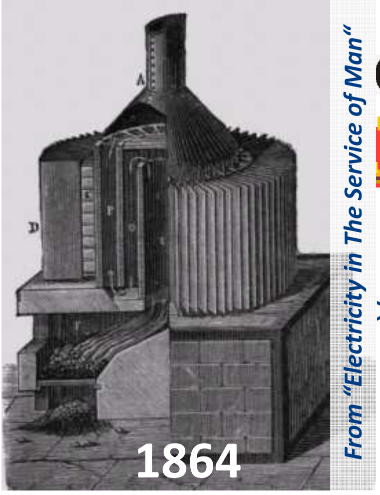
Experiment by H.C. Ørsted:

1820



An electrical current induces a magnetic field.



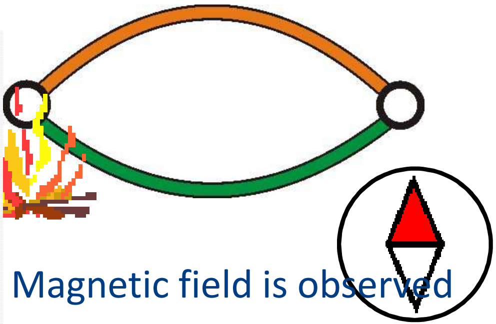


1864

From "Electricity in The Service of Man"

Experiment by T. Seebeck:

1821



Magnetic field is observed > heat causes a current flow.

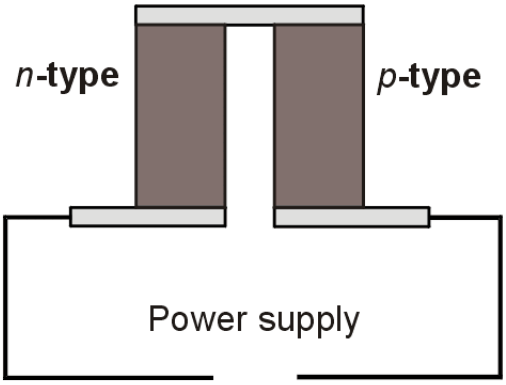
Thermoelectric generator 194 W at 54 V and 3.5 A.

1880 First street light in Broadway, New York

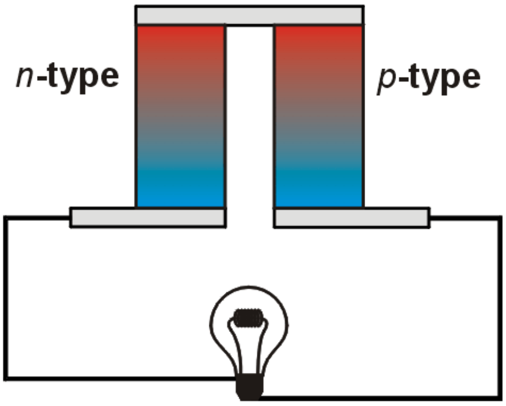
1897 J. J. Thomas discovers the electron

Thermoelectrics

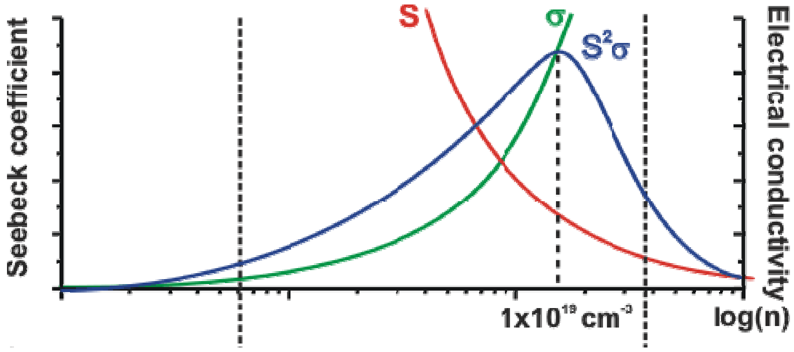
Active Cooling



Power Generation



Thermoelectric figure of merit



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

Power factor $S^2\sigma$
=> Controlled by doping

The Electron Crystal

Electron thermal conductivity κ_e
=> Fixed by Doping.

Lattice thermal conductivity κ_L
⇒ The structure of the material

The Phonon Glass

Application of Thermoelectrics - today

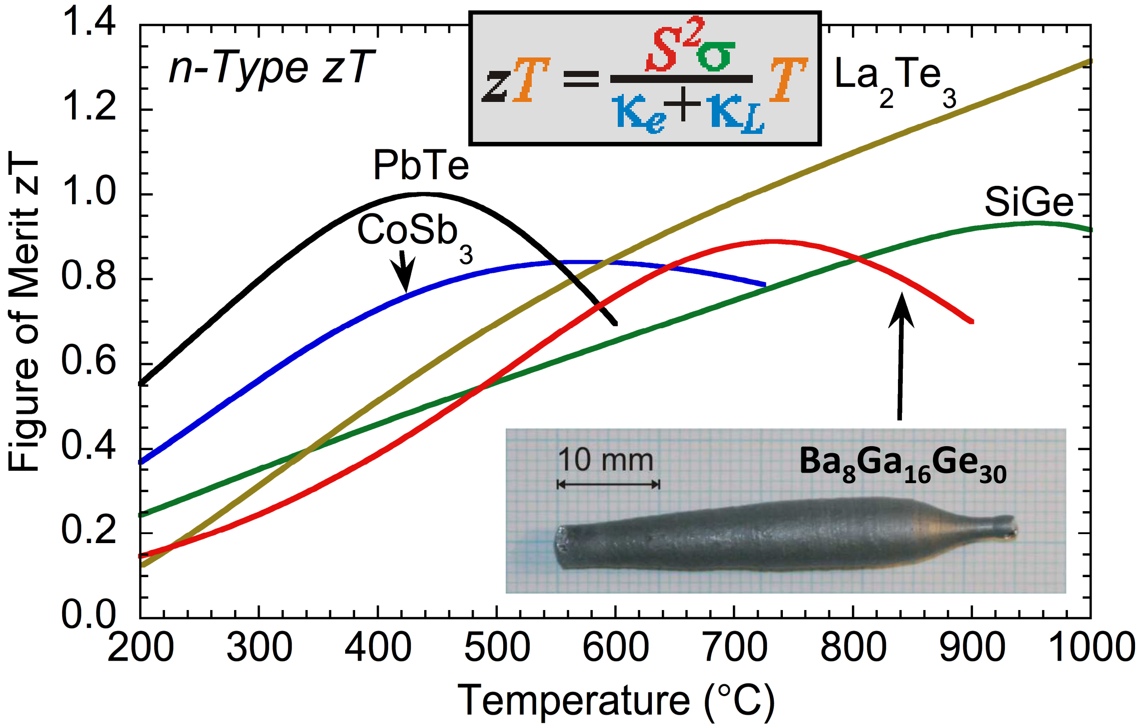
Improved materials could:

revolutionize the cooling industry

and

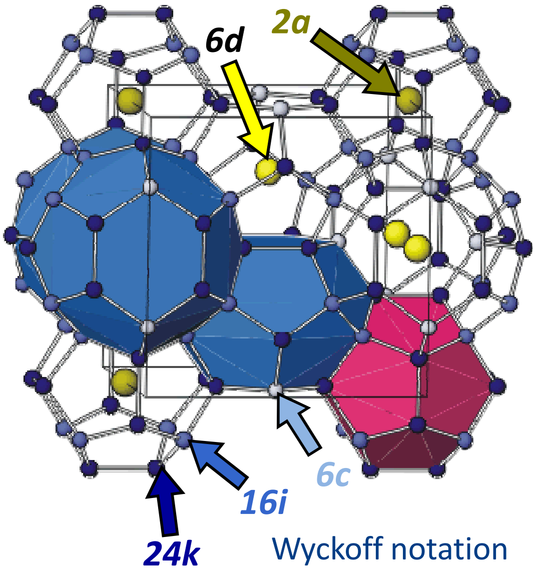
increase fuel efficiency by waste heat recovery.

State-of-the-Art Thermoelectric Materials



zT of 3-4 => paradigm shift in cooling industry.

The clathrate structure



Cages in the unit cell:
- **6 tetrakaidecahedra**
- **2 dodecahedra**

Host	Guest
●	●
Group IV/Group III: (Si, Ge, Sn, Al, Ga, In)	Alkali-(Earth) metals (e.g. Na, Sr, Ba,…,Eu)
Transition metals (e.g. Ni, Pt, Cu, Ag, Au)	Halogens (invers) (Cl, Br, I)
associated with **Electron Crystal**	associated with **Phonon Glasses**
$S^2\sigma$ power factor	κ_L lattice thermal conductivity

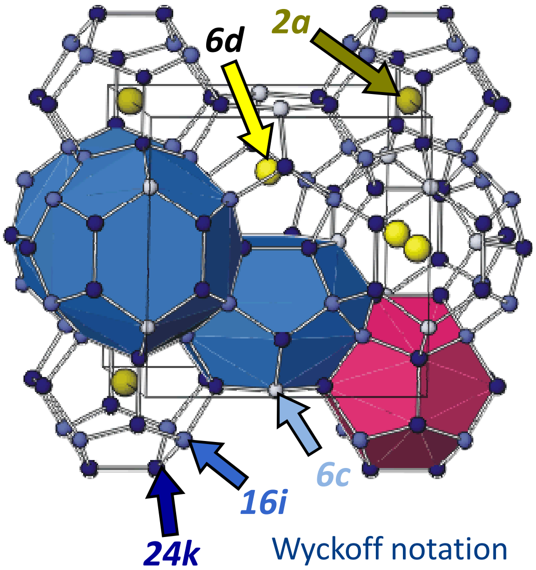
Key Features:

Low thermal conductivity

Tunablility of electrical properties

The clathrate structure

iNANO



Cages in the unit cell:
- **6 tetrakaidecahedra**
- **2 dodecahedra**

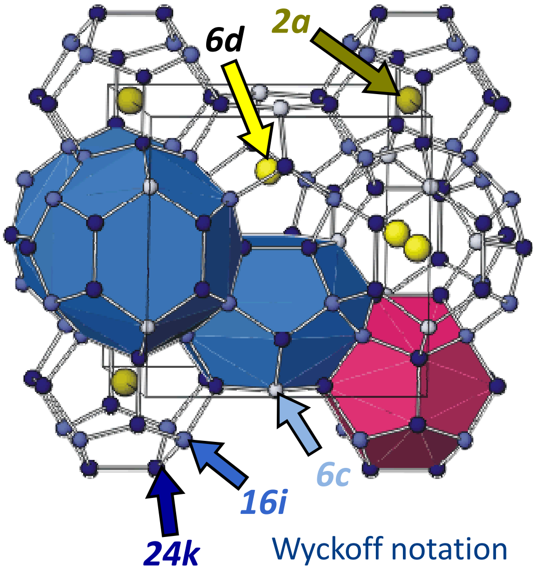
Zintl stoichiometry:
- Host is tetrahedrally bonded: $4e^-$/atom
- Ionic guest donates valence electrons
- Zintl: $4e^-$/atom · 46 host atoms = **$184e^-$**

$Ba_8Ga_{16+x}Ge_{30-x}$

Ba donates $2e^-$	**$= 8 \cdot 2\ e^-$**	**$= 16e^-$**
Ga has 3 valence e^-	**$=16 \cdot 3\ e^-$**	**$= 48e^-$**
Ge has 4 valence e^-	**$=30 \cdot 4\ e^-$**	**$=120e^-$**
Total # e^-		**$=184e^-$**

$x > 0$	**$x < 0$**
Surplus of Ga	**Surplus of Ge**
⇓	⇓
***p-type* carriers**	***n-type* carriers**

The clathrate structure



Cages in the unit cell:
- 6 tetrakaidecahedra
- 2 dodecahedra

$Ba_8Ga_{16+x}Ge_{30-x}$

Ba donates 2*e*$^-$	= 8·2 *e*$^-$	= 16*e*$^-$
Ga has 3 valence *e*$^-$	=16·3 *e*$^-$	= 48*e*$^-$
Ge has 4 valence *e*$^-$	=30·4 *e*$^-$	=120*e*$^-$
Total # *e*$^-$		=184*e*$^-$

Where are the host structure atoms?

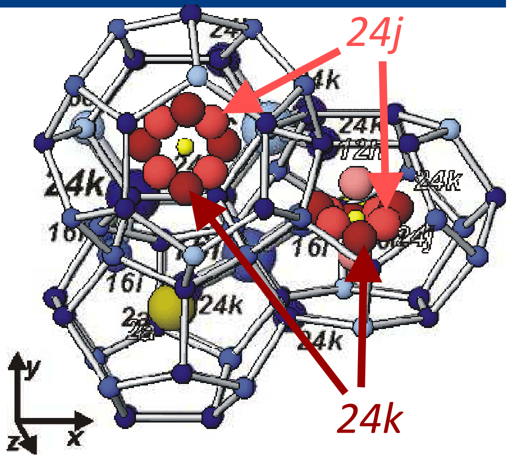
What about the guest atoms?

Look into the literature

Random distribution of Ga/Ge

Guest atom position in the cage has been disputed

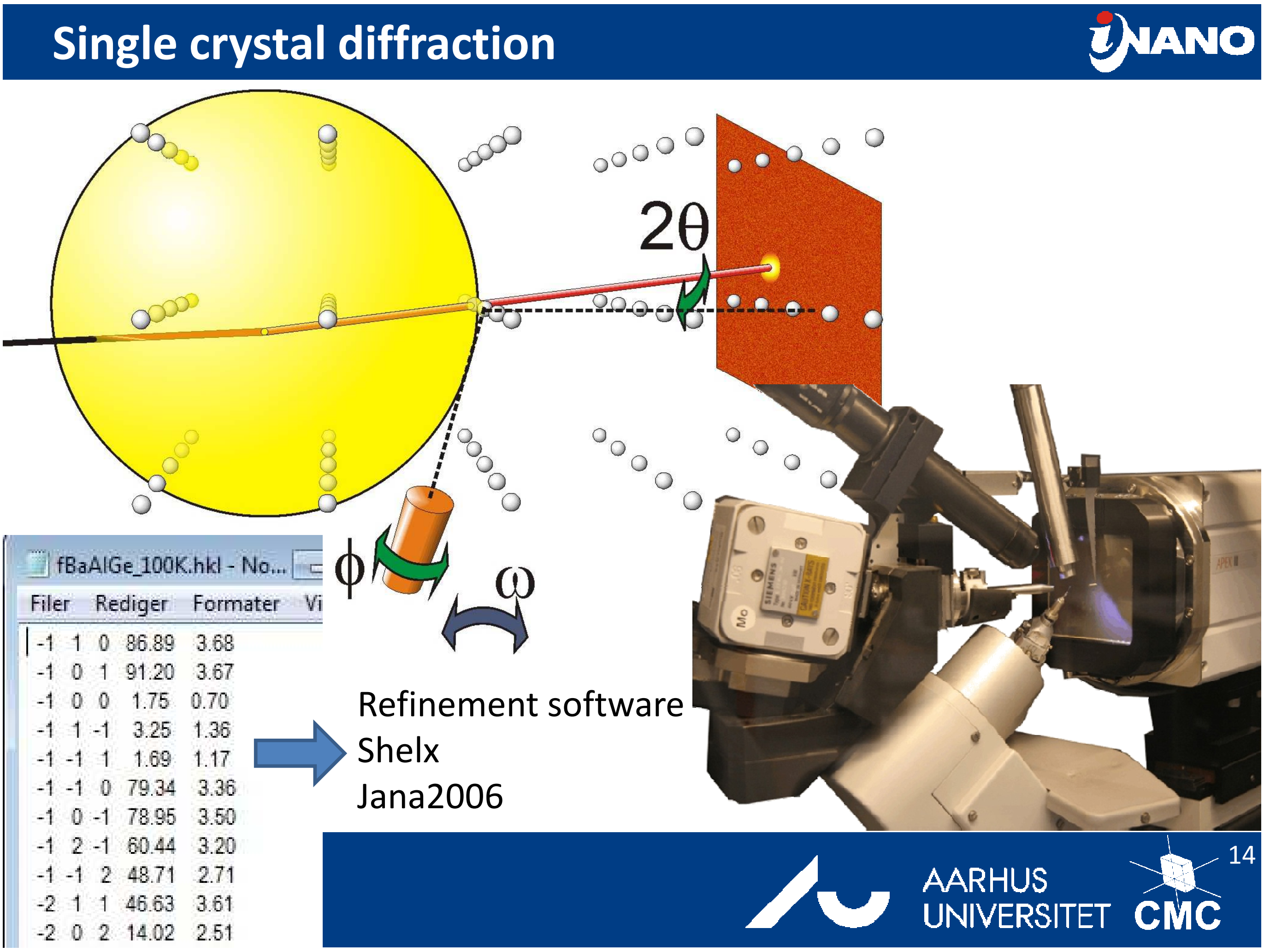
$Ba_8Ga_{16}Ge_{30}$	*6d*
$Sr_8Ga_{16}Ge_{30}$	*24k/24j*
$Eu_8Ga_{16}Ge_{30}$	*24k*



We decided to carry out a single crystal diffraction experiment.

Chakoumakos, et al. *J. Alloys & Comp.* **296** (2000) 80
Chakoumakos, et al. *J. Alloys & Comp.* **322** (2001) 127

Single crystal diffraction



```
-1  1  0  86.89  3.68
-1  0  1  91.20  3.67
-1  0  0   1.75  0.70
-1  1 -1   3.25  1.36
-1 -1  1   1.69  1.17
-1 -1  0  79.34  3.36
-1  0 -1  78.95  3.50
-1  2 -1  60.44  3.20
-1 -1  2  48.71  2.71
-2  1  1  46.63  3.61
-2  0  2  14.02  2.51
```

Refinement software
Shelx
Jana2006

Host structure occupancies

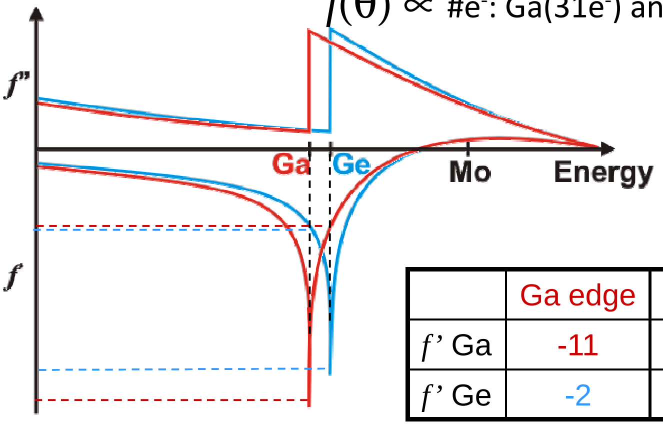
Convention x-ray diffraction: not possible to distinguish Ga/Ge

Problem the scattering power is proportional to the number of electrons

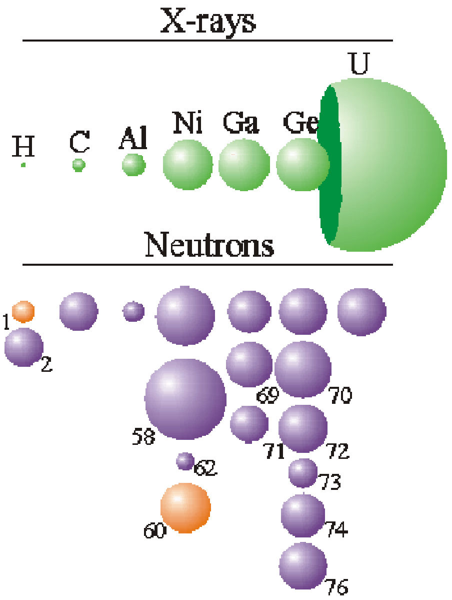
Resonance scattering:

The form factor: $f(\theta,\lambda) = f(\theta) + f'(\lambda) - if''(\lambda)$

$f(\theta) \propto$ #e$^-$: Ga(31e$^-$) and Ge(32e$^-$)



	Ga edge	Ge edge
f' Ga	-11	-2
f' Ge	-2	-10

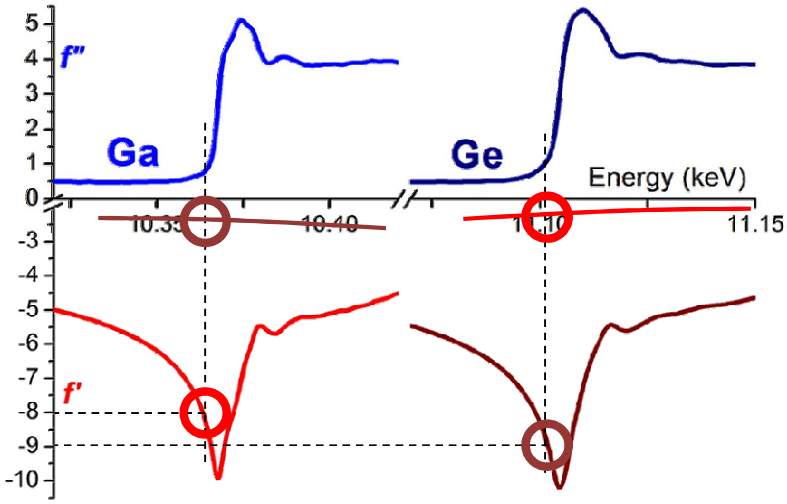


Resonance data was collected at the Swiss-Norwegian Beamlines, ESRF.

M. Christensen et al., Accepted *J. Am. Chem. Soc.*, (2006)

Single crystal diffraction

Flourecence measurement of absorption edge



	Ga edge	Ge edge
f’ Ga	-8.0	-1.8
f” Ga	0.7	4.0
f’ Ge	-2.3	-8.9
f” Ge	0.5	0.7

Contrast:

Ga edge ~ Δf = 7e^-

Ge edge ~ Δf = 6e^-

Host structure occupations

	$Ba_8Ga_{16}Ge_{30}$		$Ba_8Al_{16}Ge_{30}$		
%	*n-type*	*p-type*	*czo*	*norm*	*flux*
6c	76(1)	64(1)	97(1)	66(1)	56(1)
16i	16(1)	17(1)	44(1)	30(1)	24(1)
24k	37(1)	39(1)	5(1)	30(1)	40(1)
6c+24k	113	103	102	96	96
16i+24k	52	56	49	60	64

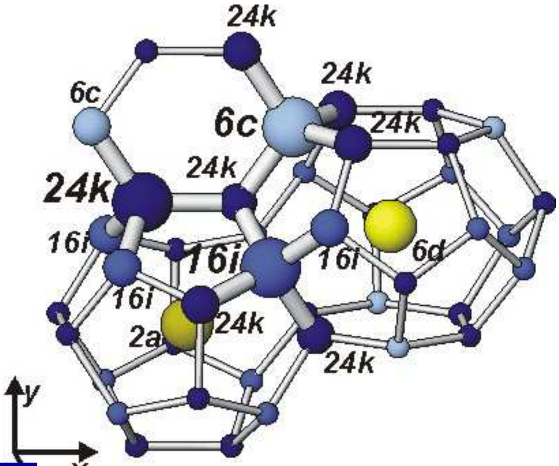
Occupation without causing Ga-Ga bonds.

6c-6c ≤ 100%
16i-16i ≤ 50%
24k-24k ≤ 50%
6c+24k ≤ 100%
16i+24k ≤ 50%

24k(50%)+*6c*(50%)
$Ba_8^{2+}Ga_{15}^{3+}Ge_{31}^{4+}$: $185e^-$

16i(50%)+*6c*(100%)
$Ba_8^{2+}Ga_{14}^{3+}Ge_{31}^{4+}$: $186e^-$

Wyckoff notation:

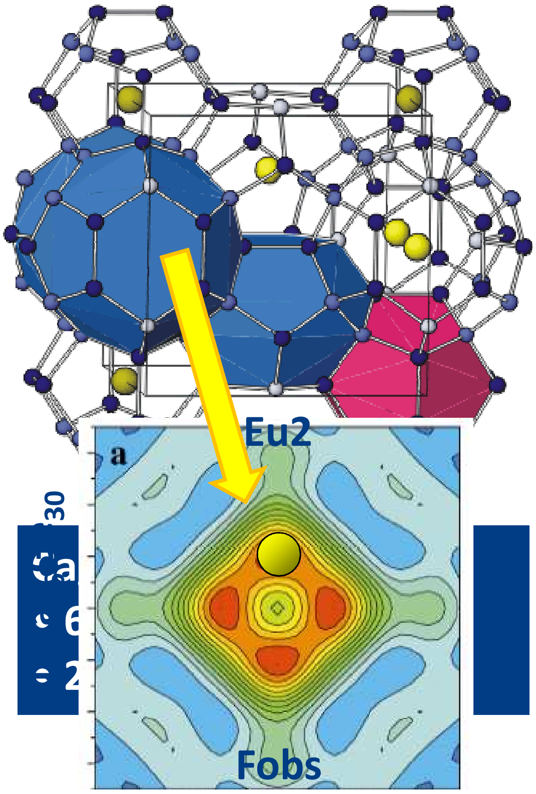


Preferably no bonds
between low valence atoms

☹ Ga-Ga ☹
☺ Ga-Ge ☺
☺ Ge-Ge ☺

M. Christensen *et al.*, *Chem. Mater.* 19 (2007) 4896

Guest atom position



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●	●
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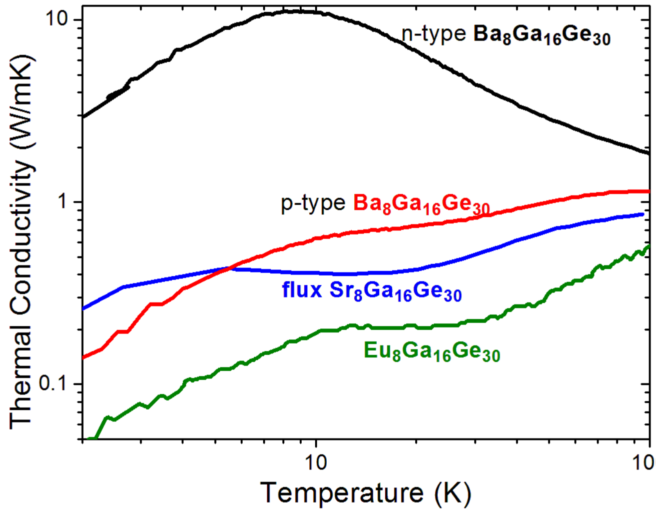
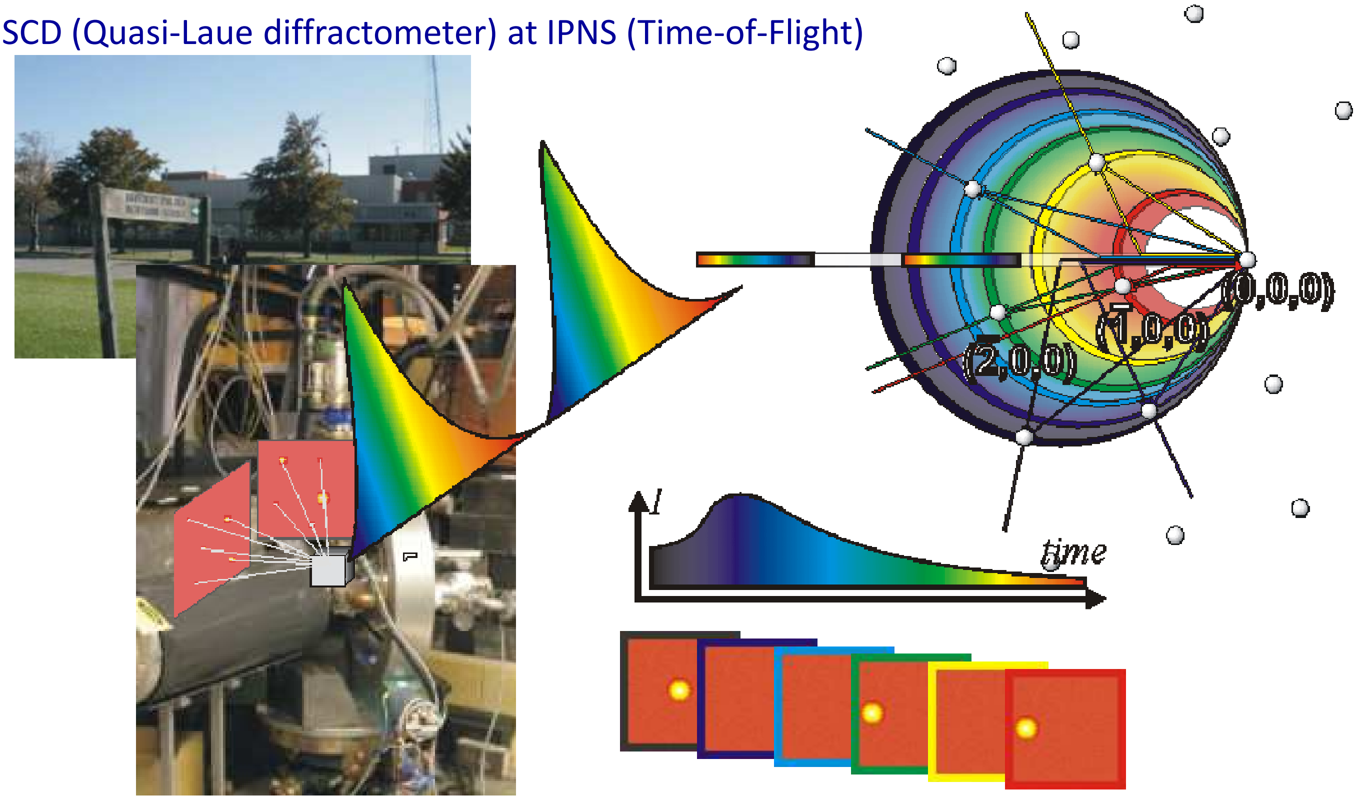


Sales *et al. Phys. Rev. B.* **63** (2001) 245113
Bentien et al. *Phys. Rev. B.* **69** (2004) 045107
Avila *et al. Phys. Rev. B.* **74** (2006) 125109

Time of flight single crystal neutron diffraction

SCD (Quasi-Laue diffractometer) at IPNS (Time-of-Flight)

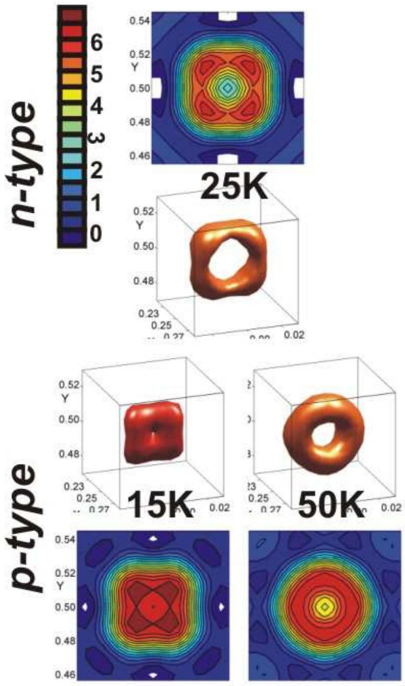


The clathrate structure

Neutron single crystal diffraction

Fourier difference map

F_{obs}-F_{calc}(÷Ba2)

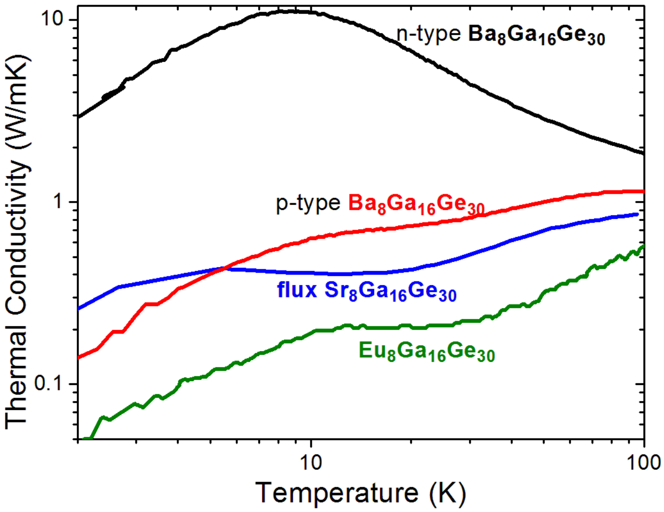


Small difference in Ba position between

n-type $Ba_8Ga_{16}Ge_{30}$ and

p-type $Ba_8Ga_{16}Ge_{30}$

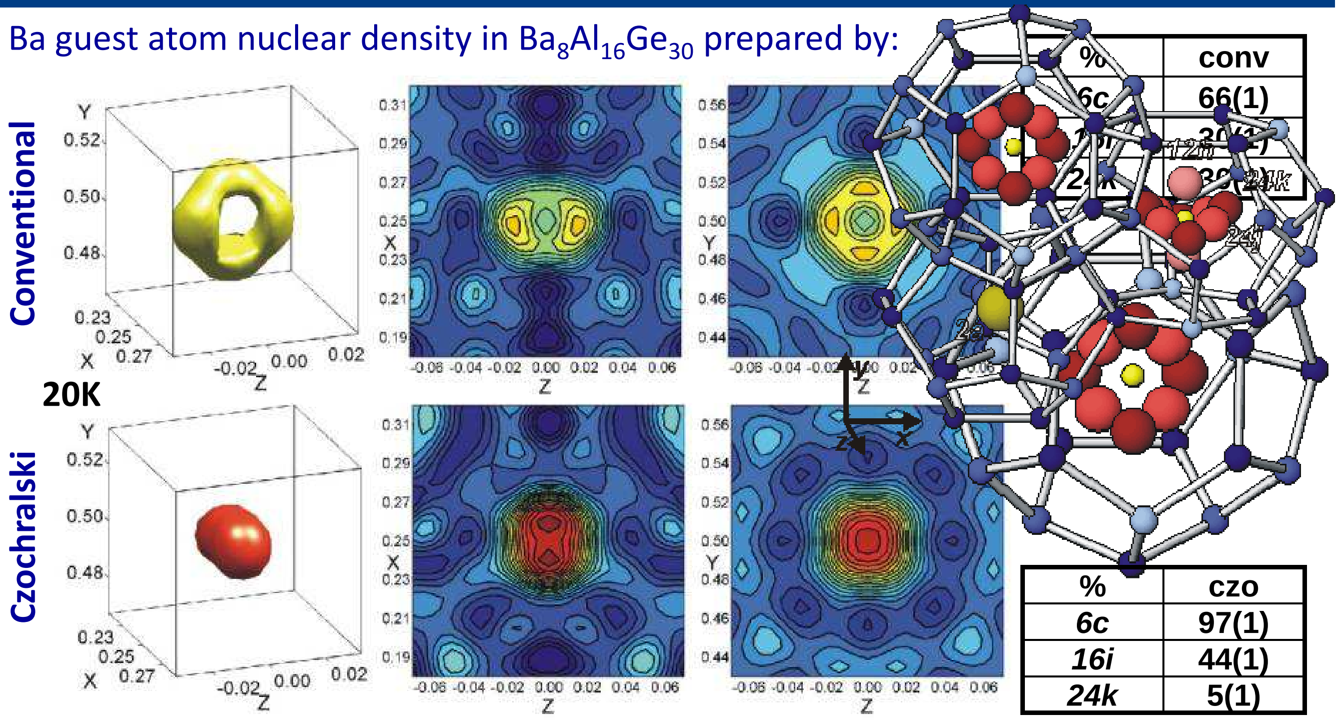
Significant difference in host structure



M. Christensen *et al., J. Am. Chem. Soc.* 128 (2006) 15657

Single crystal neutron diffraction

Ba guest atom nuclear density in $Ba_8Al_{16}Ge_{30}$ prepared by:



%	conv
6c	66(1)
16i	30(1)
24k	30(1)

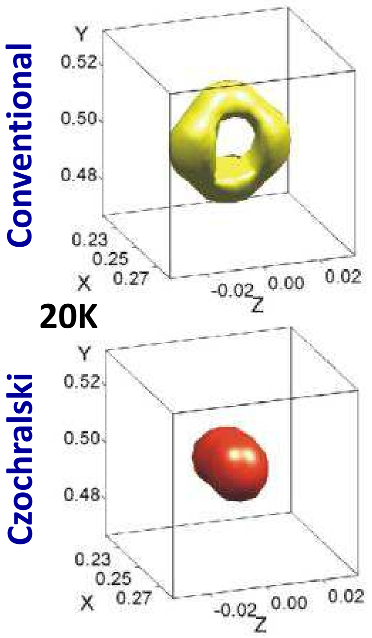
%	czo
6c	97(1)
16i	44(1)
24k	5(1)

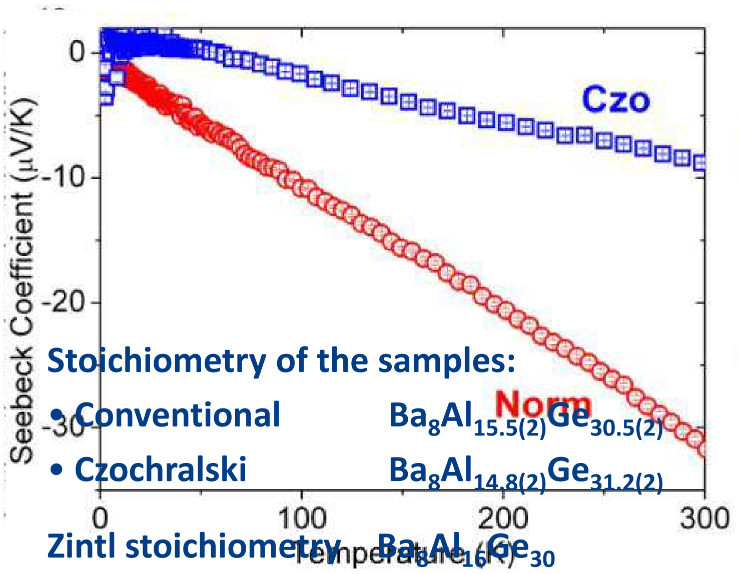
Relation between the host occupancies and guest atom nuclear density!

M. Christensen *et al.*, *Chem. Mater.* 19 (2007) 4896

Thermoelectric properties

Seebeck coefficient
Electrical resistivity
Lattice thermal conductivity





Stoichiometry of the samples:

- **Conventional** $Ba_8Al_{15.5(2)}Ge_{30.5(2)}$
- **Czochralski** $Ba_8Al_{14.8(2)}Ge_{31.2(2)}$

Zintl stoichiometry $Ba_8Al_{16}Ge_{30}$

Normal => Higher resistivity

Larger Seebeck coefficient

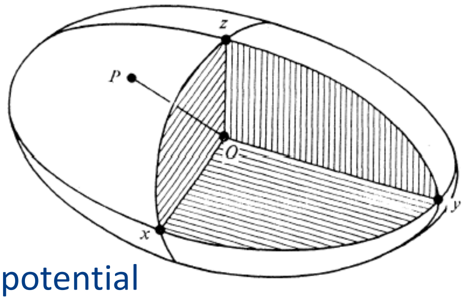
M. Christensen *et al.*, *Chem. Mater.* 19 (2007) 4896

Modelling of thermal vibration

Can we do better than just the Fourier transform?

Harmonic crystal (Anisotropic ellipsoid)

$$T_\kappa(\mathbf{Q}) = \exp(-\tfrac{1}{2}\langle(\mathbf{Q}\cdot\mathbf{u}(\kappa)^2)\rangle), \quad \begin{pmatrix} \langle u_1^2\rangle & \langle u_1u_2\rangle & \langle u_1u_3\rangle \\ \langle u_1u_2\rangle & \langle u_2^2\rangle & \langle u_2u_3\rangle \\ \langle u_1u_3\rangle & \langle u_2u_3\rangle & \langle u_3^2\rangle \end{pmatrix}$$



Anharmonic potentials: Taylor expansion of the crystal potential

$$V = V_0 + V_1 + V_2 + V_3 + V_4 + \dots$$

Isotropic

$$V_1 = \sum_{\alpha\kappa l}\left(\frac{\partial V}{\partial u_\alpha(\kappa l)}\right)_0 u_\alpha(kl),$$

anisotropic

$$V_2 = \frac{1}{2!}\sum_{\alpha\kappa l}\sum_{\alpha'\kappa' l'}\frac{\partial V}{(\partial u_\alpha(\kappa l))_0}\frac{\partial V}{(\partial u_{\alpha'}(\kappa' l'))_0}u_\alpha(\kappa l)u_{\alpha'}(\kappa' l'),$$

Anharmonic

$$V_3 = \frac{1}{3!}\sum_{\alpha\kappa l}\sum_{\alpha'\kappa' l'}\sum_{\alpha''\kappa'' l''}\left(\frac{\partial V}{\partial u_\alpha(\kappa l)}\right)_0\left(\frac{\partial V}{\partial u_{\alpha'}(\kappa' l')}\right)_0\left(\frac{\partial V}{\partial u_{\alpha''}(\kappa'' l'')}\right)_0 \times u_\alpha(\kappa l)u_{\alpha'}(\kappa' l')u_{\alpha''}(\kappa'' l''),$$

$$V_4 = \frac{1}{4!}\dots.$$

Anharmonic modeling

Isolated atom anharmonic potential:

	# Parameters	
Isotropic	**1**	**Scalar**
Anisotropic	**6**	**2nd rank tensor**
Cubic anharmonic	**10**	**3rd rank tensor**
Quadratic anharmonic	**15**	**4th rank tensor**

The number of free parameters

=> high order data is needed for carrying out anharmonic refinements.

The symmetry of a specific atom may reduce the number of free varaiables.

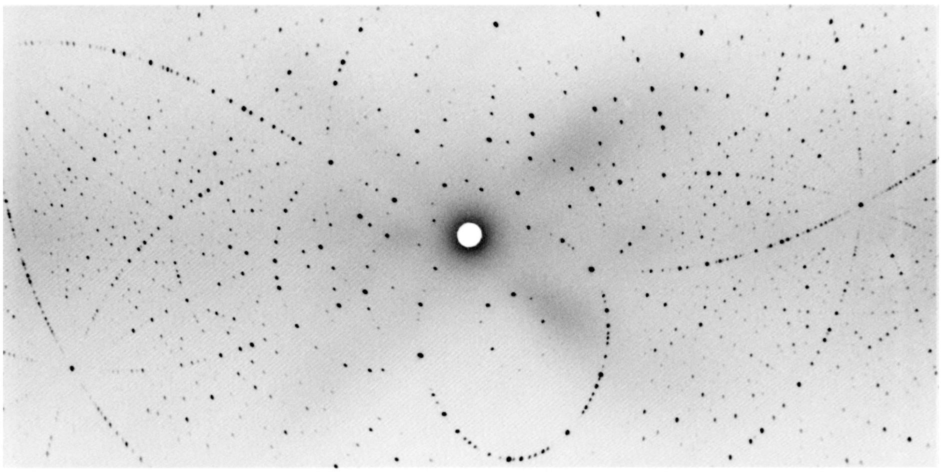
Sr on 6*d* (0.25 0.5 0.0)

Number of free variables:	
Anisotropic:	2
3rd Anharmonic	1
4th Anharmonic	4
Total ADPs	7

High resolution data

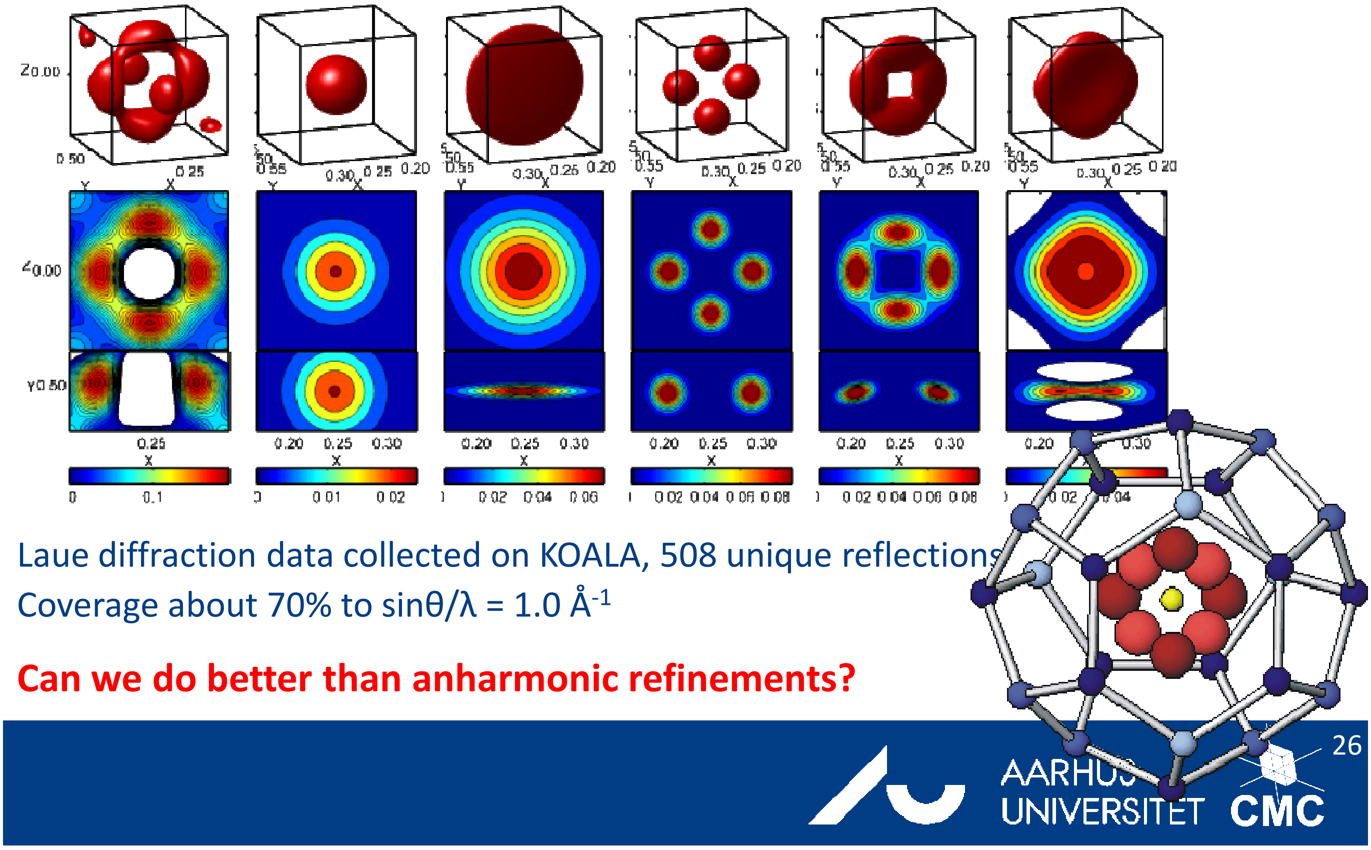
Technique	Advantage	Disadvantage
Monochromatic	High precision	Slow, large crystals
Time-of-flight Laue	Fast, small crystals	Less precise
White beam Laue	Fast, small crystals	Less precise, less coverage

Laue diffraction experiment at KOALA at ANSTO



Single crystal refinements on $Sr_8Ga_{16}Ge_{30}$

15K F_{obs}	6d isotropic	6d anisotropic	24k isotropic	24k anisotropic	6d anharmonic

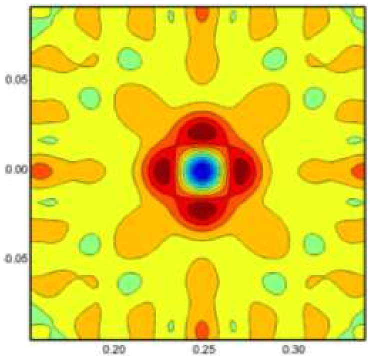


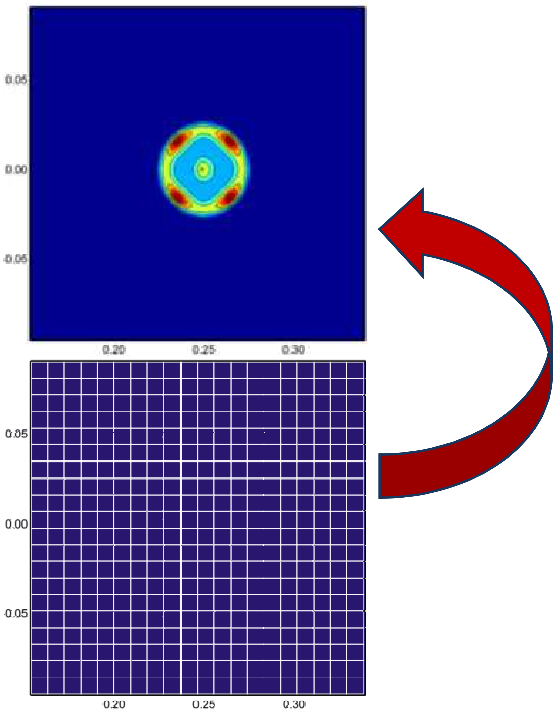
Laue diffraction data collected on KOALA, 508 unique reflections
Coverage about 70% to sinθ/λ = 1.0 $Å^{-1}$

Can we do better than anharmonic refinements?

Maximum entropy method

Nuclear density from Fourier transform of structure factors (F_{hkl})





Maximum entropy method

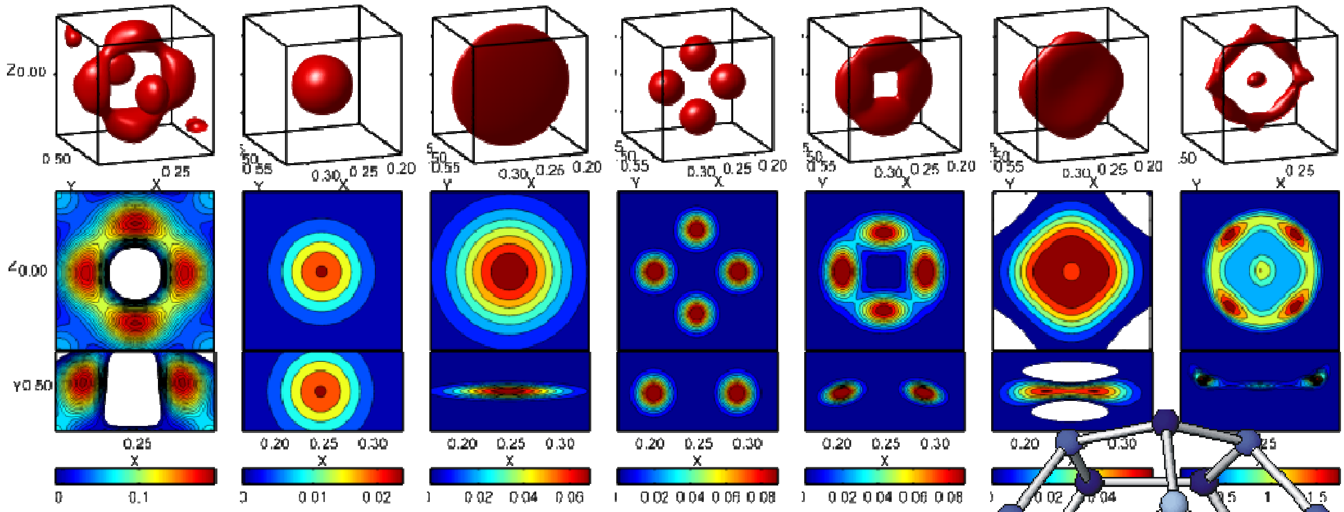
$$S = \sum_N \rho_N \log \frac{\rho_N}{\tau_N}$$

ρ_N is the nuclear density in pixel N,
τ_N is the density of the prior distribution

The density maximization
=> largest entropy
=> flattest and most featureless density, which fits the data.

Single crystal refinements on $Sr_8Ga_{16}Ge_{30}$

F_{obs} | 6d isotropic | 6d anisotropic | 24k isotropic | 24k anisotropic | 6d anharmonic | MEM



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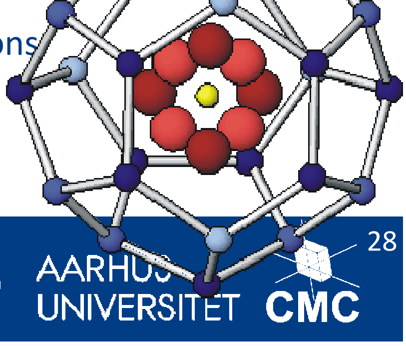

Conclusion – clathrates

$Ba_8Ga_{16}Ge_{30}$ difference in thermal conductivity
=> could not be explained by Ba guest atom position

$Ba_8Al_{16}Ge_{30}$ remarkable difference in host and guest strucutre
=> explain thermoelectric properties

Anharmonic vibration and MEM was used to describe disorder

Acknowledgements:
Dan Bryan (UCSB)
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Jacob Overgaard (Aarhus)
Art Schultz (IPNS)
Mette Schmøkel (Aarhus)
Hans-Peter Weber (SNBL)

Overview

Thermoelectrics – a short introduction

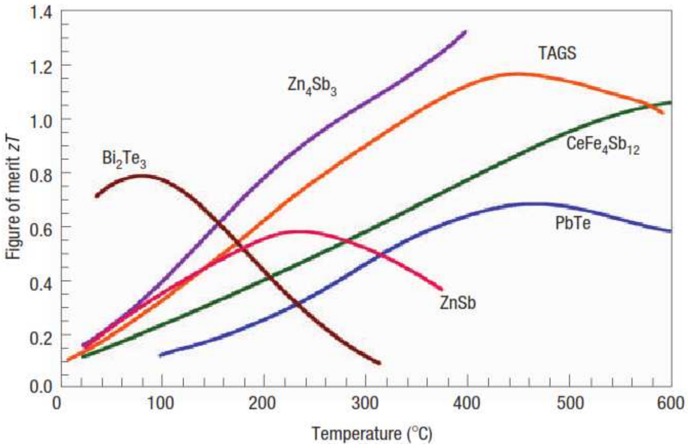
Clathrates – the structure

	Single crystal X-ray and neutron diffraction Resonant diffraction
Zn_4Sb_3	Single crystal diffraction Powder diffraction
Skutterudites	X-ray and Neutron powder diffraction
Photons vs phonons	Inelastic X-ray scattering in $FeSb_2$

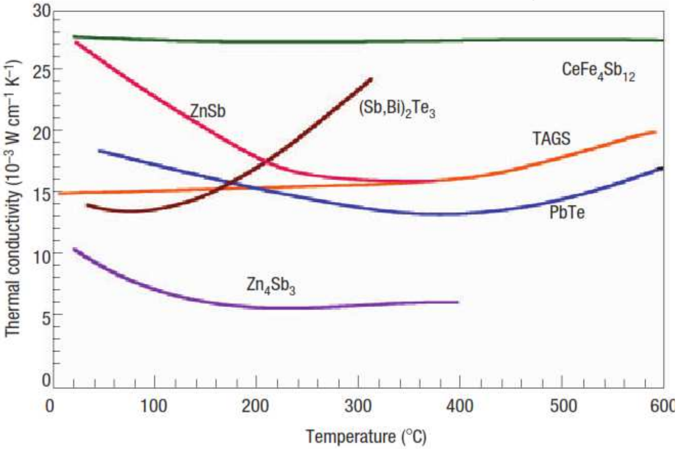
In situ X-ray diffraction studies of crystal growth

Thermoelectric properties of Zn_4Sb_3

Figure of merit zT



Thermal conductivity



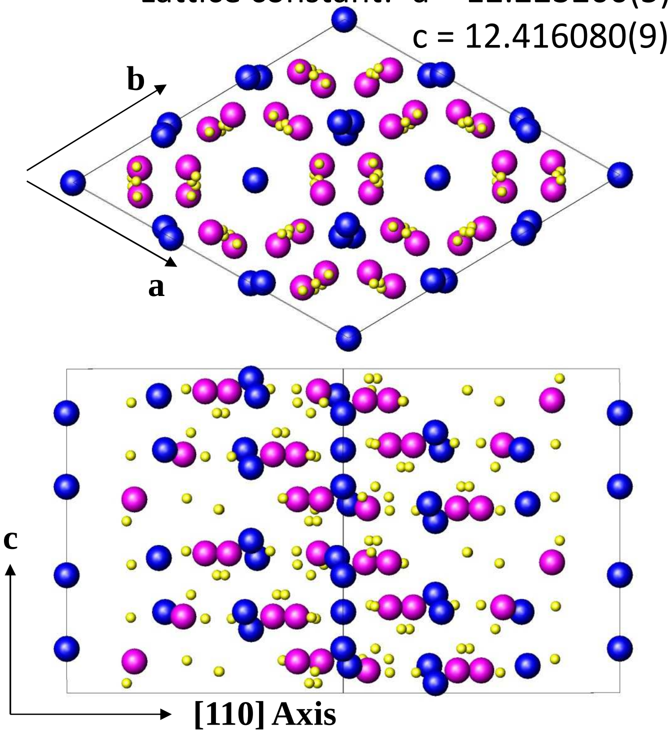
Why is the thermal conductivity of Zn_4Sb_3 so low?

AARHUS UNIVERSITET CMC

The Crystal Structure of Zn_4Sb_3

Space Group : R-3c

Lattice constant: a = 12.223200(5)
c = 12.416080(9)



Original model: Mayer

36*f* Zn 100%
12*c* Sb 100%
18*e* Sb 89%, Zn 11%

Density
6.02 g/cm^3

Empirical Density: 6.36 g/cm^3

New model (single crystal)

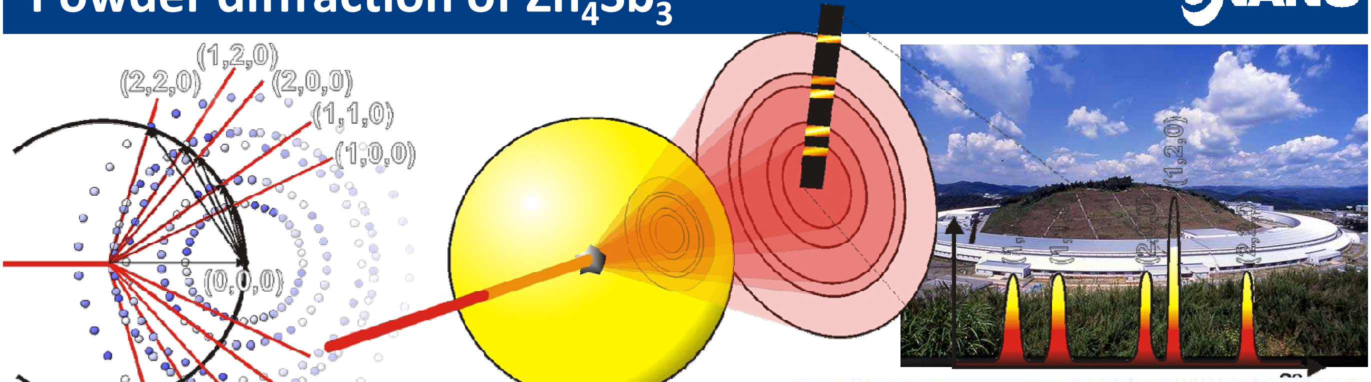
36*f* Zn <100%
12*c* Sb 100%
18*e* Sb 100%

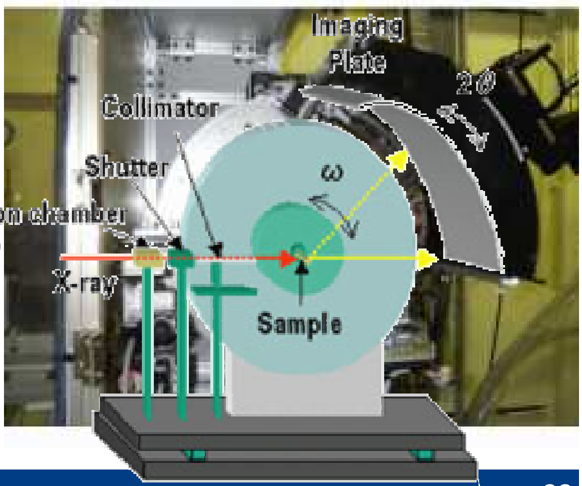
Density
<6.36 g/cm^3

Interstitial Zn site ?

● **Sb**
● **Zn Occupancy 90%**
● **Zn Occupancy 6%**

Powder diffraction of Zn_4Sb_3





Information from powder diffraction data

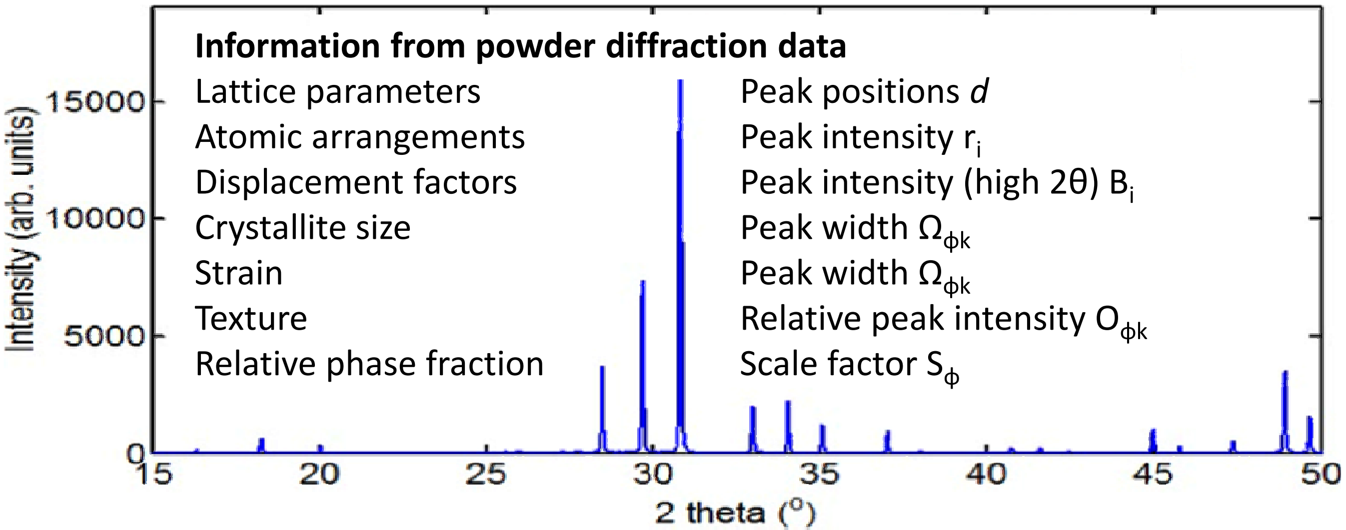
Lattice parameters	Peak positions
Atomic arrangements	Peak intensity
Displacement factors	Peak intensity (high 2θ)
Crystallite size	Peak width
Strain	Peak width
Texture	Relative peak intensity
Relative phase fraction	Scale factor

Powder diffraction of Zn_4Sb_3

Bragg's law: $2d\sin\theta = \lambda$

Structure factor: $F_{hkl} = \sum f_i\, sof_i \exp(-B_i \sin^2\theta_{hkl}/\lambda^2) \exp(2\pi i \mathbf{G}_{hkl}\cdot\mathbf{r}_i)$

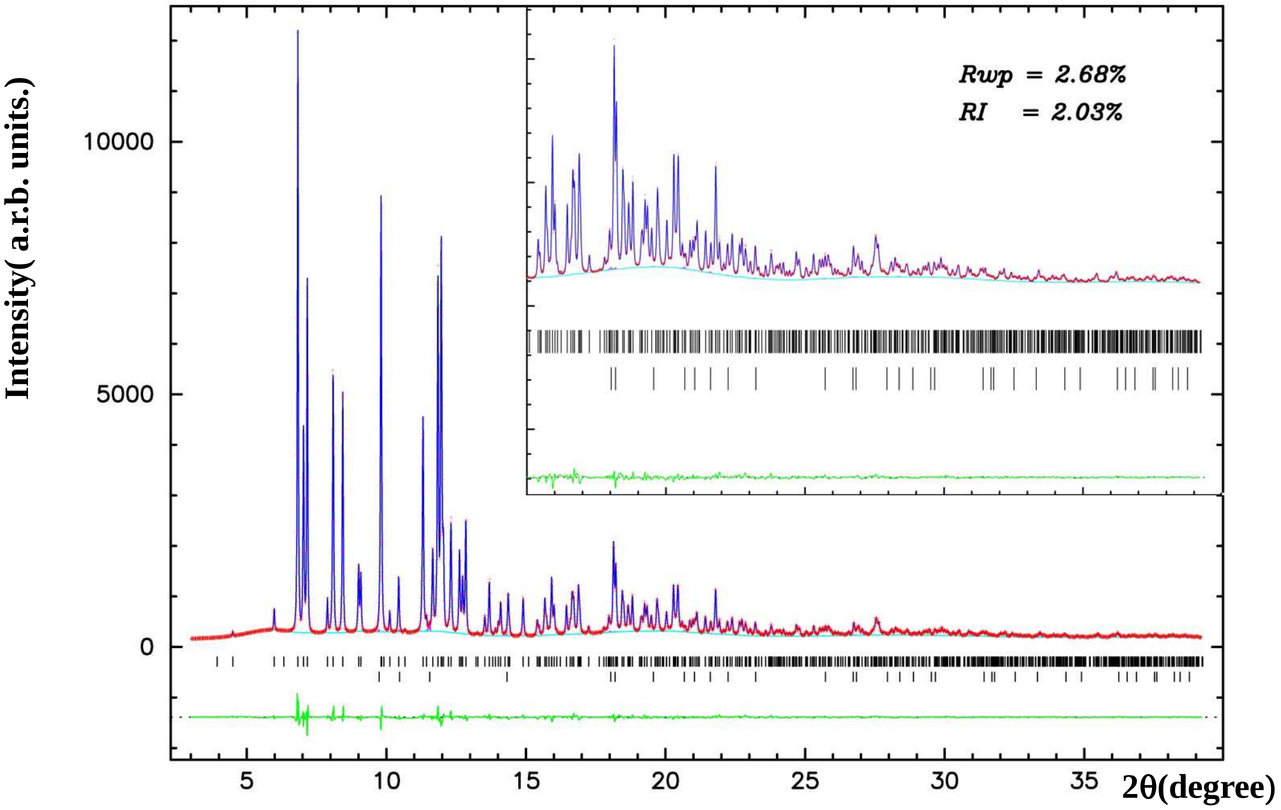
Rietveld function: $y_{ci} = y_{bi} + \sum S_\phi \sum j_{\phi k} LP_{\phi k} O_{\phi k} |F_{\phi k}|^2 \Omega_{\phi k}$



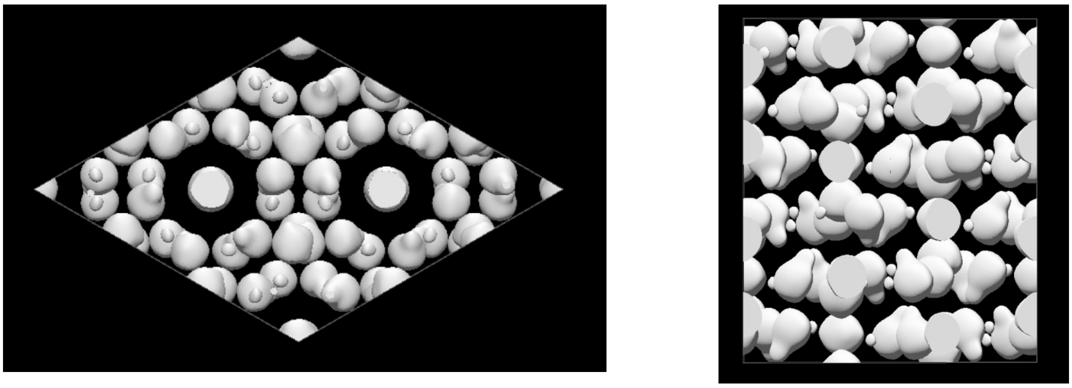
Information from powder diffraction data

Lattice parameters	Peak positions d
Atomic arrangements	Peak intensity r_i
Displacement factors	Peak intensity (high 2θ) B_i
Crystallite size	Peak width $\Omega_{\phi k}$
Strain	Peak width $\Omega_{\phi k}$
Texture	Relative peak intensity $O_{\phi k}$
Relative phase fraction	Scale factor S_ϕ

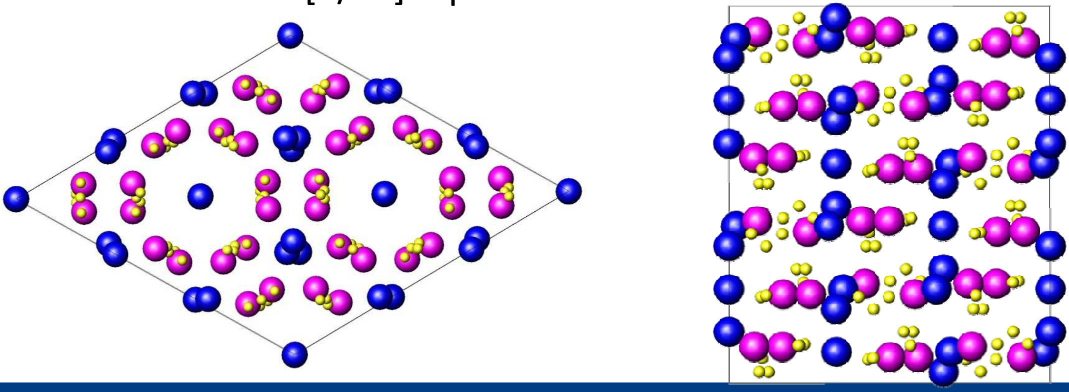
Powder diffraction on Zn_4Sb_3



The MEM Charge Densities of Zn_4Sb_3

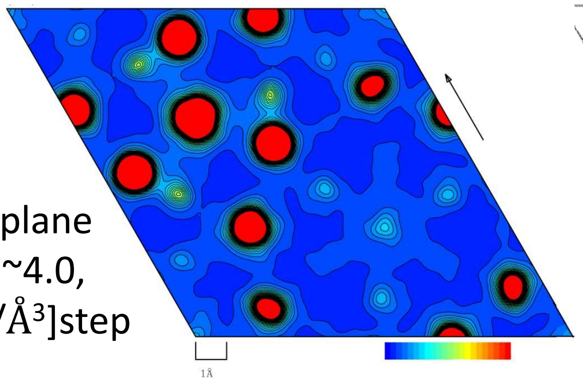


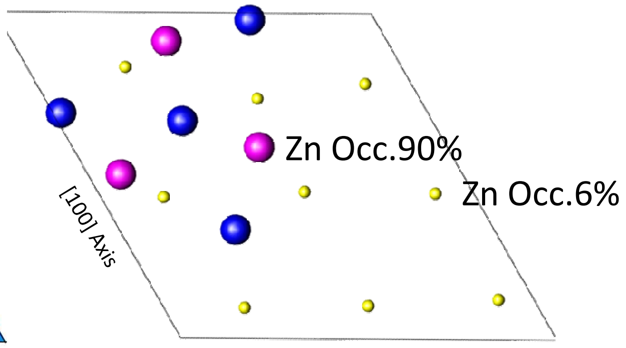
2.0[e/Å^3] equi-contour surface



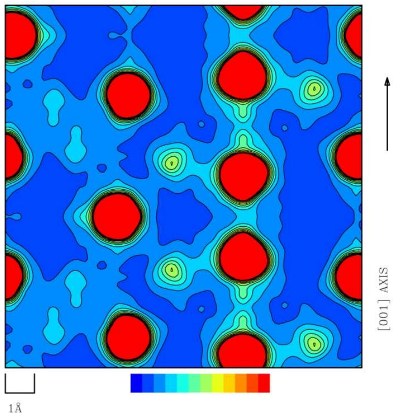
The MEM Charge Densities of Zn_4Sb_3

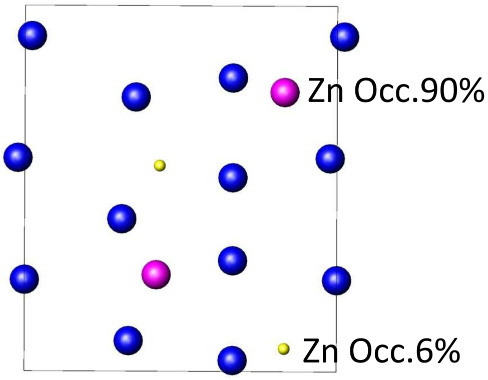
(00l) plane
0.0 ~4.0,
0.2[e/Å^3]step



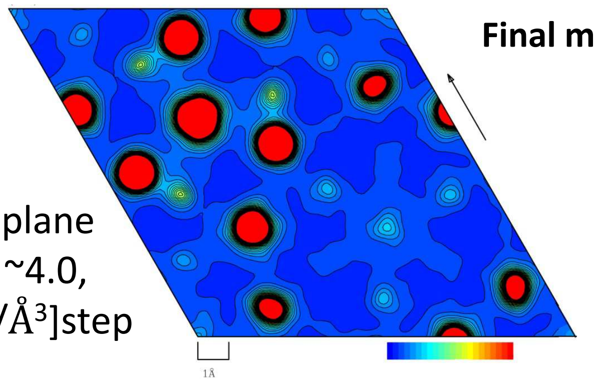


(h00) plane
0.0 ~2.0,
0.2[e/Å^3]step





Conclusion



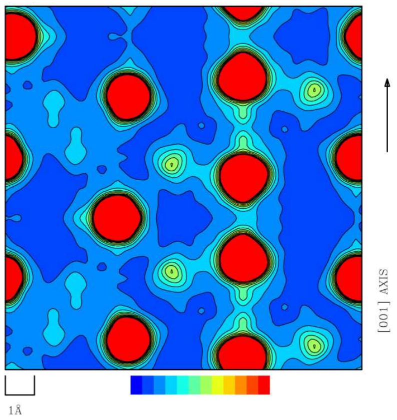
(00l) plane
0.0 ~4.0,
0.2[e/Å^3]step

Final model (single crystal + powder diffraction)

36*f* Zn 90%
12*c* Sb 100%
18*e* Sb 100%
3x Zn interstitial sites ~6%
Chemical formula $Zn_{39}Sb_{30}$

Density
6.37 g/cm^3

Empirical Density: 6.36 g/cm^3



(h00) plane
0.0 ~2.0,
0.2[e/Å^3]step

Electron counting:

18*e*: 18 x Sb^{3-} = 54 e^-
12*c*: 12 x Sb^{2-} = 24 e^-
Total e^- = 78 e^-

$\Rightarrow$ 39 Zn^{2+} 32 from 36*f*
7 from interstitial Zn

Conclusion

The low thermal conductivity could be explained by
Interstial atoms in the structure
MEM help confirming the atomic positions

The new structure agrees with
Electron counting
Density in correspondance with measurements

Acknowledgements: Bo B. Iversen (Aarhus)
Eiji Nishibori (SPring8)
Jeff Snyder (JPL)

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Skutterudites

Skutterudites have promising thermoelectric properties:

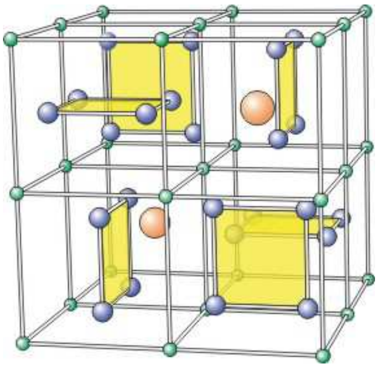
Brutto formula: GCo_4Sb_{12}

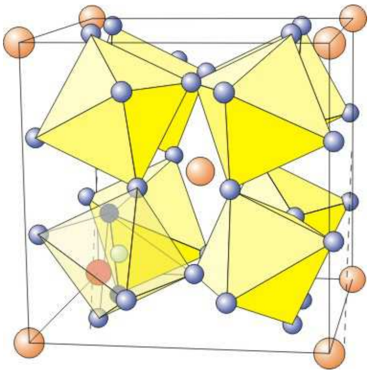
Possible ways of optimization:

- Filling – Guest atoms in the voids.
- Nano structuring.
- Substitution of **Co** by **Fe** or **Ni**.

X-Rays source problems:

- Weak contrast between **Fe**, **Ni**, and **Co**.
- Problem with conventional **Cu** Kα sources:
  - High Fluorescence due to **Co** and **Fe**.

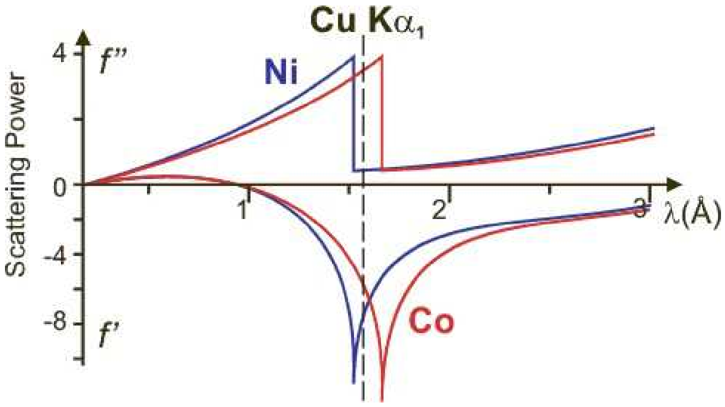


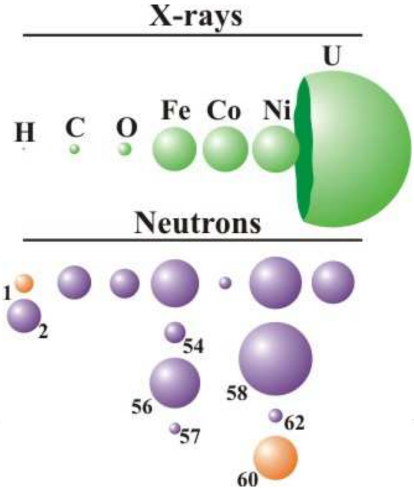


X-rays vs. Neutrons

X-Rays; high background,
comparable scattering length

Neutrons; isotope specific
scattering length





General problems:

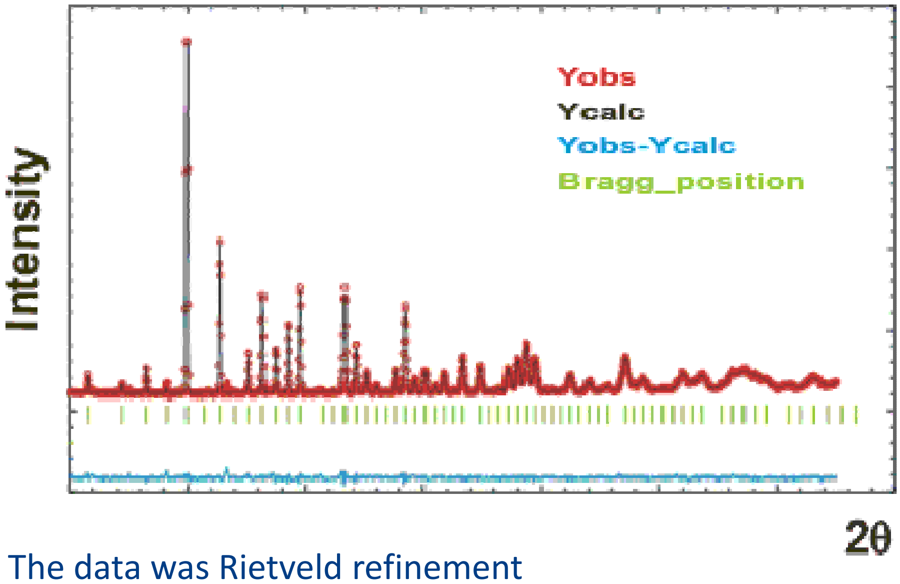
High background => hides small impurities.

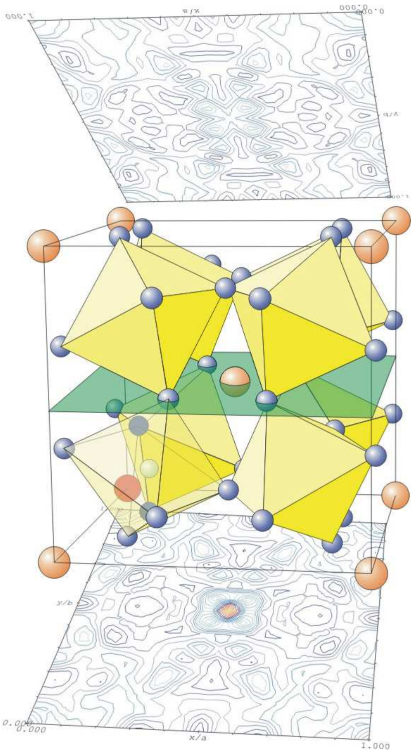
Broad peaks => difficult to resolve closely spaced peaks.

Comparable scattering power => hard to distinguish atoms.

Skutterudite $Ni_{1.2}Co_{2.8}Sb_{12}$

Neutron data measured at Studvik, Sweden





The data was Rietveld refinement

A difference Fourier map reveal an interstitial atom.

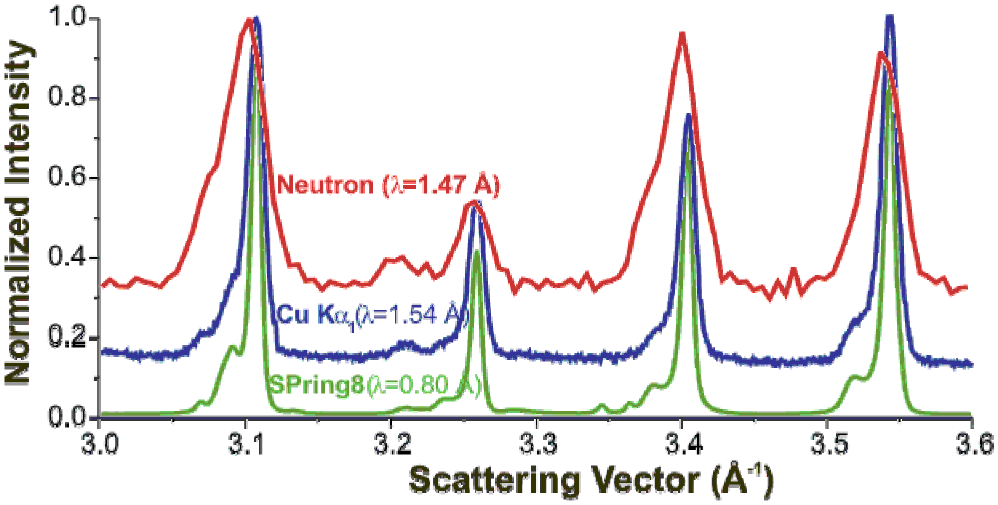
Skutterudite $Ni_{4x}Co_{4(1-x)}Sb_{12}$

Sample with x = 0.3 investigates by

Conventional Cu Kα radiation (λ = 1.54Å)

Neutron scattering (λ = 1.47Å)

Synchrotron radiation (λ = 0.80Å)



A combined refinement was carried out

Case I; $Ni_{4x}Co_{4(1-x)}Sb_{12}$

Phase analysis of combined refinement

$Co_{3.76}Ni_{0.24}Sb_{12}$	72.7%
$Co_{0.92}Ni_{3.08}Sb_{12}$	16.4%
$NiSb_2$	5.8%
Sb	4.84%
CoSb	0.29%

Total amount of Co and Ni relative to Sb of 12

	Powder phase analysis	**Atomic absorption**
Ni	1.2(1)	**1.2**
Co	2.9(1)	**3.0**
Sb	12.0(1)	**12.0**

Theoretical calculation of phase stability supports the interpretation of the data.

Conclusion

Take care when analyzing powder diffraction data
Data does not always reveal what they are

Very good correspondence between atomic absorption and careful phase identification.

Acknowledgement:
Luca Bertini (ISTM)
Carlo Gatti (ISTM)
Bo B. Iversen (Aarhus)
Mamoun Muhammed (KTH)
Eiji Nishibori (SPring8)
Häkon Rundlöf (Studsvik)
Mamoun Toprak (KTH)

Overview

Thermoelectrics – a short introduction

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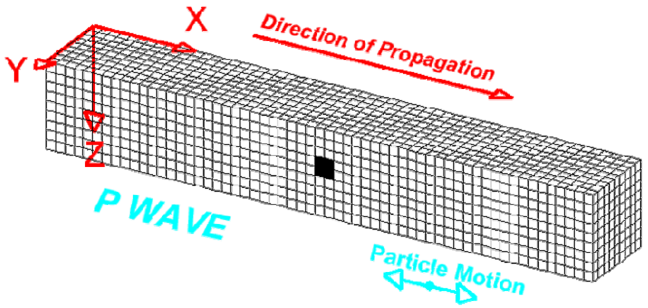
Photons vs Phonons

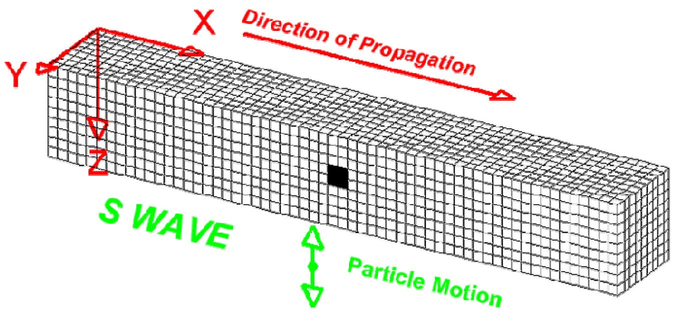
Photon	**Phonon**
”Massless” energy	Mass displacement
Energy package in air/vacuum	Energy package in solids
Photons have direction	Phonons have direction **k**
Photons have energy	Phonons have energy E
Photons have polarization	Phonons have polarization **e**

Phonon propagation

Longitudinal phonon



Transvers phonon



http://web.ua.es/en/urs/disclosure/seismic-wave-propagation.html

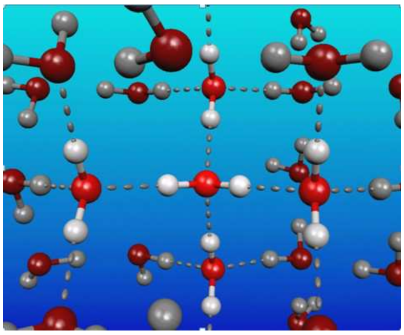
Scattering - a reminder

Elastic scattering

$E_{in} = E_{out}$

$\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{G}$ **G** integer Miller indices

Tells us where atoms are



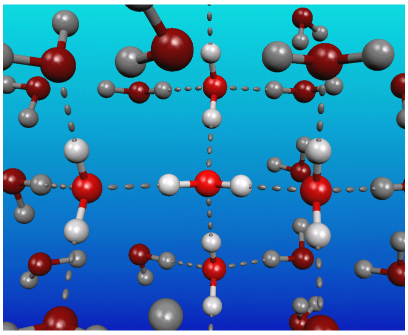
Inelastic scattering

$E_{in} = E_{out}\, E \pm \hbar\omega$

$\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{G}$ **G** fractional Miller indices

Tells us additionally what atoms do

- Phonons/atomic vibrations
- Molecular dynamics
- Diffusion processes



Unfortunately the inelastic signal is very weak

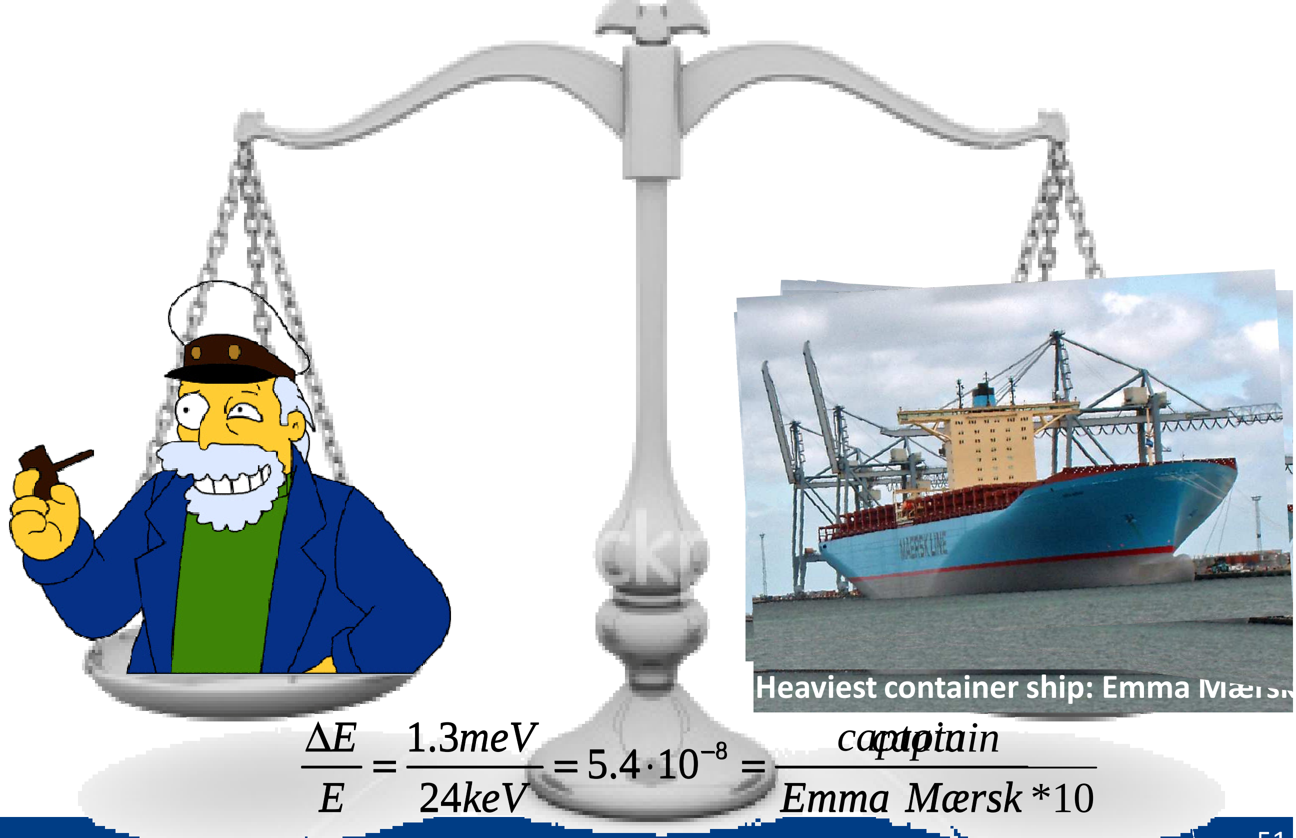
Approximately 10^6 times weaker than the elastic signal

Comparison: X-rays, Raman and neutrons

Phonons have typical energies of: E = 0-100 meV
Phonon wave vectors **G** > 0.5 Å^{-1}

X-ray:	**Raman (light):**	**Neutron:**
$\lambda \sim 1.3$ Å	$\lambda \sim 500$ nm	$\lambda \sim 2.8$ Å
$Q_{max} \sim 10$ Å^{-1}	$Q_{max} \sim 3 \cdot 10^{-3}$ Å^{-1}	$Q_{max} = 4.4$ Å^{-1}
$E_{in} \sim 10$ keV	$E_{in} \sim 2.5$ eV	$E_{in} \sim 10$ meV
$\Delta E/E_{in} \sim 10^{-7}$	$\Delta E/E_{in} \sim 4 \cdot 10^{-4}$	$\Delta E/E_{in} \sim 10^{-1}$
Sample size:		
$<1mm^3$	$<<1mm^2$	$>>1cm^3$

If this were a show on Discovery channel



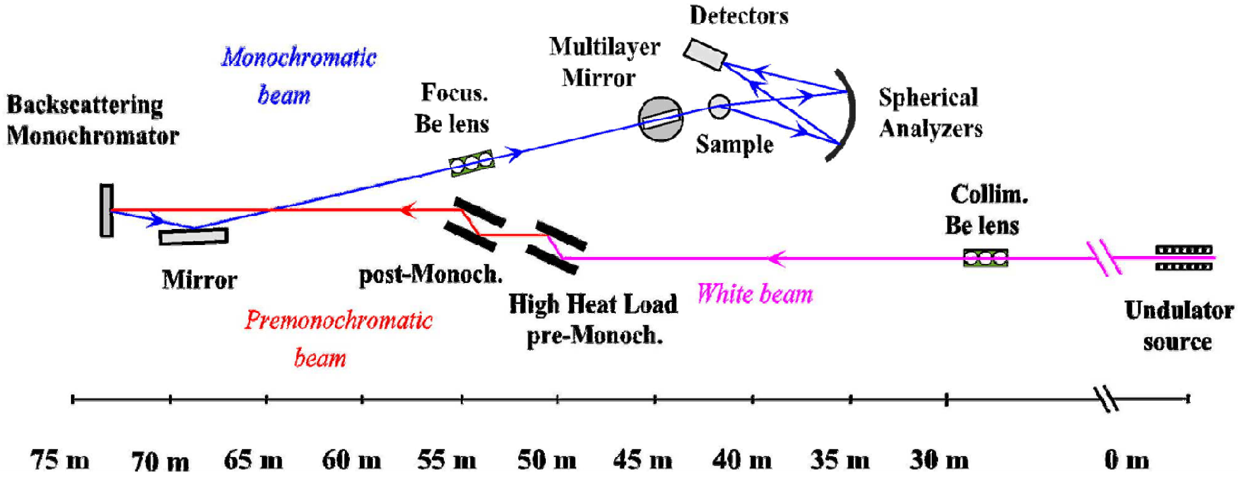
Heaviest container ship: Emma Mærsk

$$\frac{\Delta E}{E} = \frac{1.3meV}{24keV} = 5.4\cdot 10^{-8} = \frac{captain}{Emma\ Mærsk * 10}$$

Courtesy Sebastian Christensen

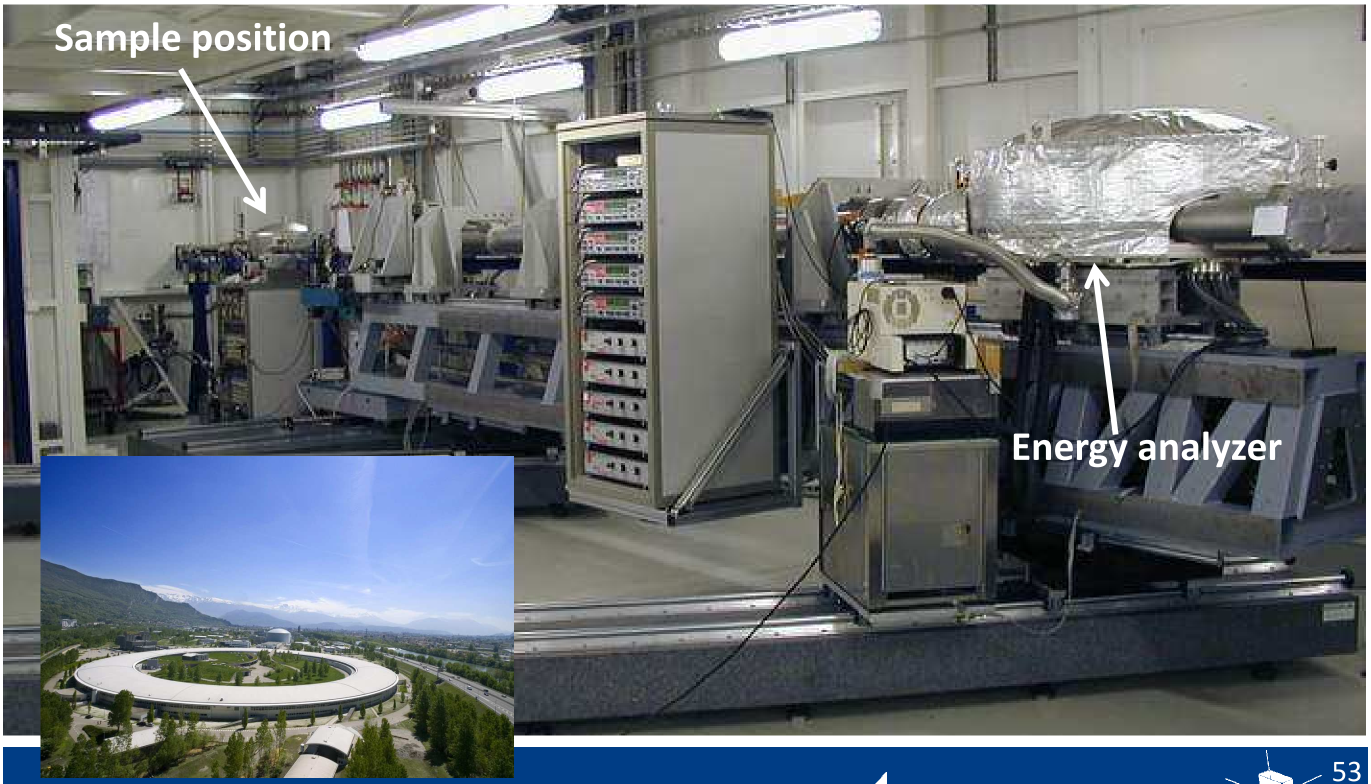
Schematic instrument setup

- Extremely well monochromatized incoming beam
- Very good angular resolution for energy detection

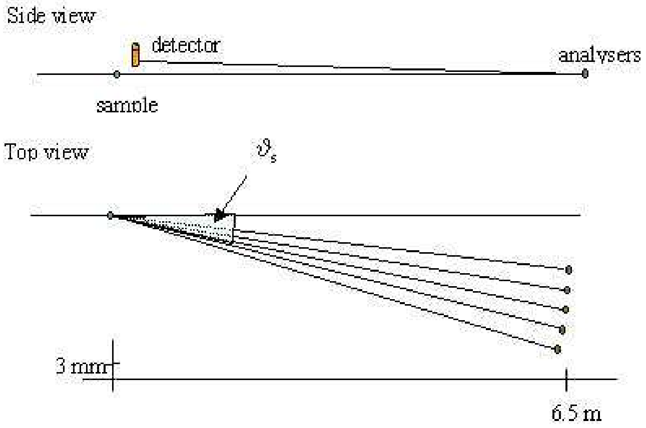


Pictures from the experimental hutch:

The ID28 beamline @ ESRF



Detection and energy scans



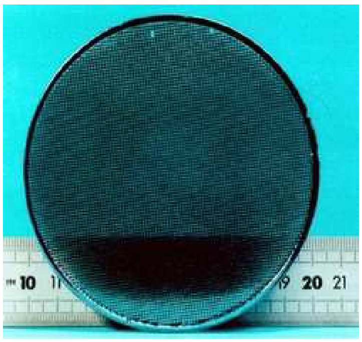
The incoming energy is kept fixed and change in outgoing energy is changed

The detected energy is changed by

How to change energy?

precision.

9 different Q-values are measured simultaneous.

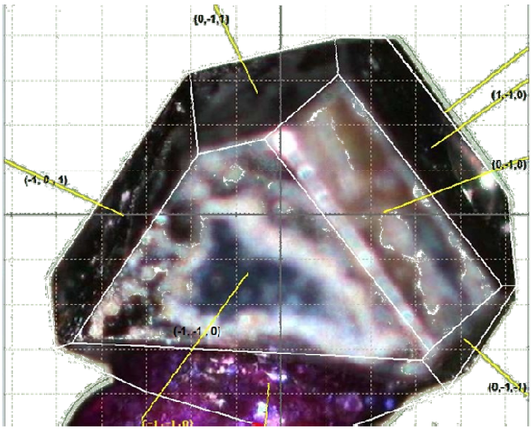


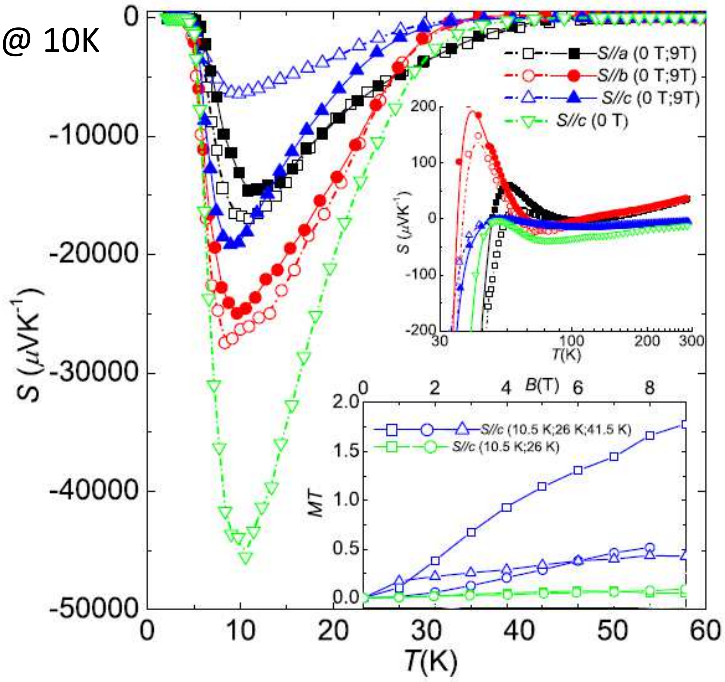
Analyzer crystal
Si(13,13,13)
12000 individual crystals glued onto a spherical Si substrate

Study of $FeSb_2$

Colossal Seebeck reported: -45000µV/K @ 10K

Calculations have so far not been able to reproduce the peak Seebeck value



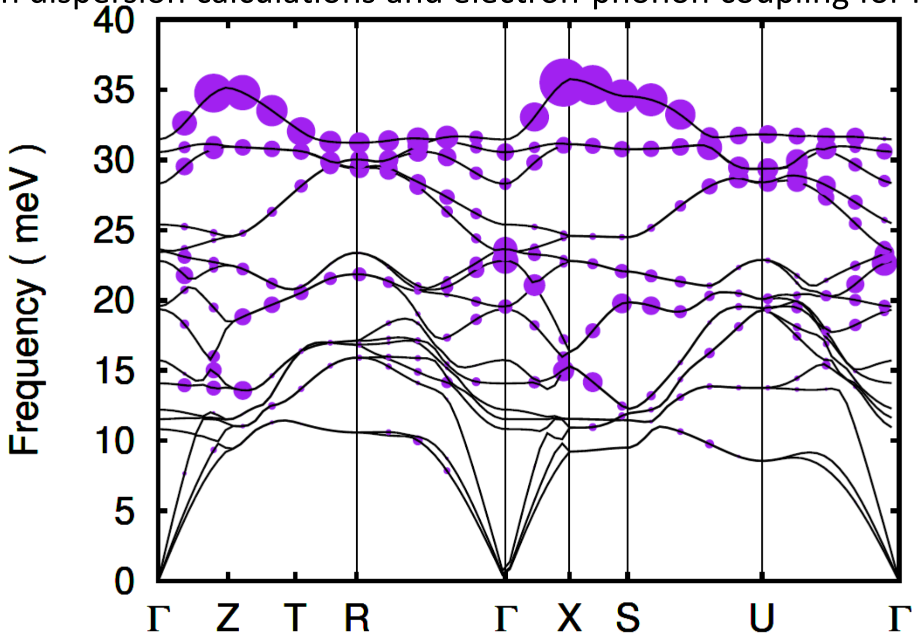


Experiments done in reflection mode
Crystal was cut to prepare a (100) surface next to (110)

A. Bentien et al. EPL, 80 (2007) 17008

DFT calculations of phonon dispersion

Phonon dispersion calculations and electron-phonon coupling for $FeSb_2$



Size of ● indicates the strength of e-p-coupling at that point.
First we focused on the X point

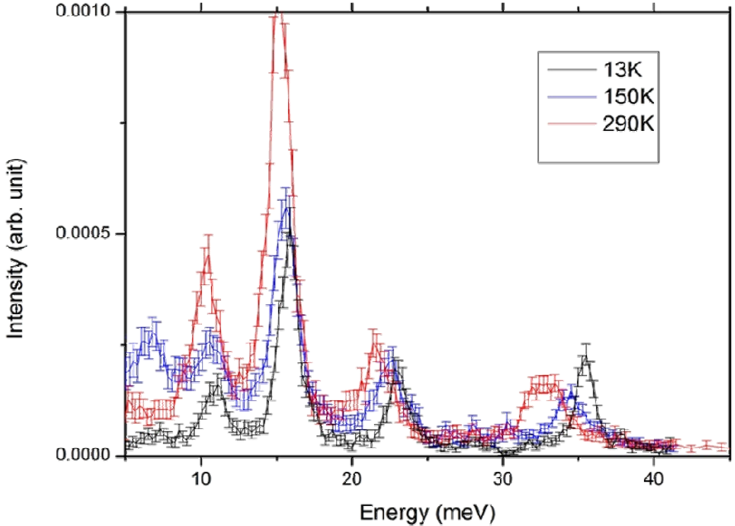
M.S. Diakhate et al. Phys. Rev. B **84,** 125210, (2011)

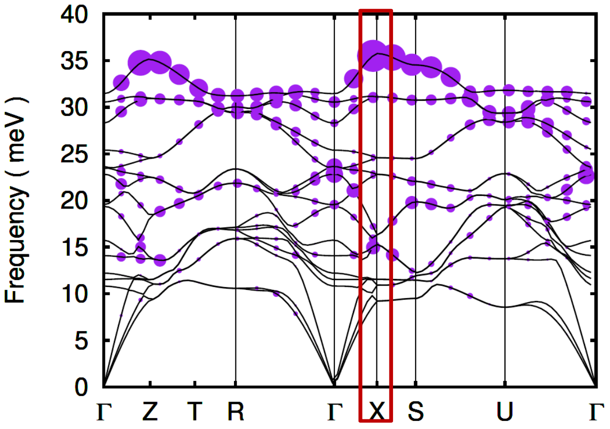
How the data looks

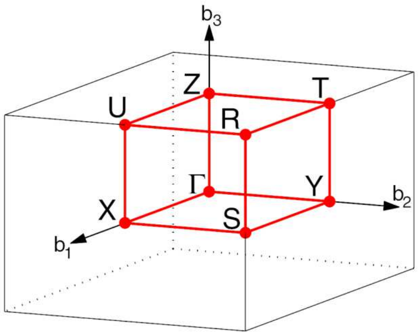
X=(4.5,0,0)

Not all phonon branches are detected in a given experimental setup due to symmetry

Data fitted with Lorentzians convoluted with experimental resolution function.



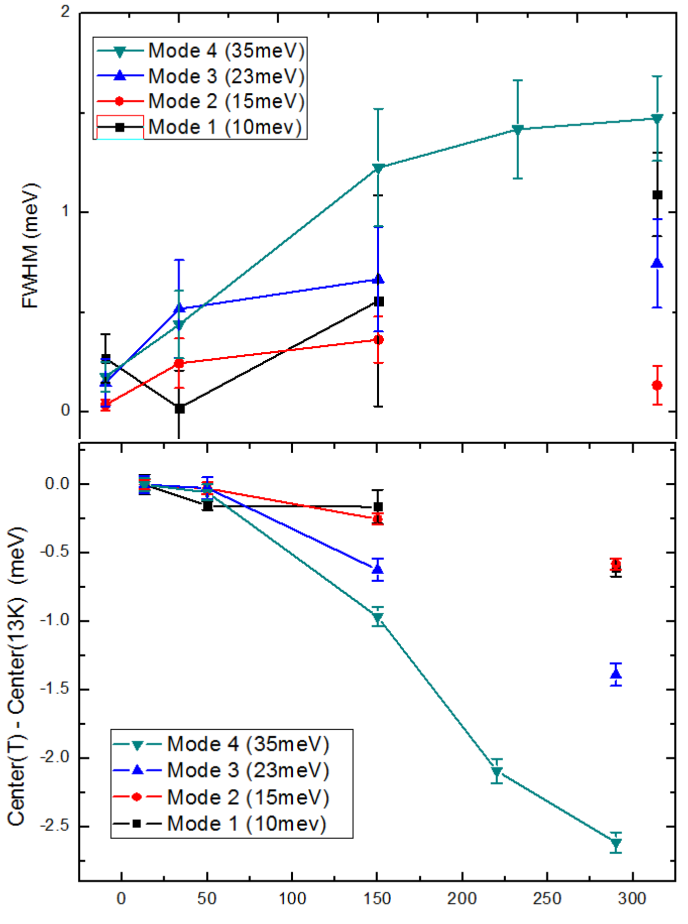




Results

Signs of E-P-coupling when temperature is increased

- Broadening of phonon mode
- Decrease of phonon energy



Mode 4 shows significantly stronger e-p-coupling than modes 2+3

Apparent broadening of mode 1 is most likely an artifact of scattering from ice

Conclusions on $FeSb_2$ study

Theoretical calculations are confirmed at high symmetry position.

Off-high symmetry positions - some discrepancies that need to be explained.

Still no apparent explanation for the colossal low temperature Seebeck.

Acknowledgement:
Sebastian Christensen (Aarhus)
Raphael Hermann (Jülich)
Michael Krisch (ESRF)
Anna Möchel (Juüich)
Ilya Sergueev (ESRF)
Martin Søndergaard

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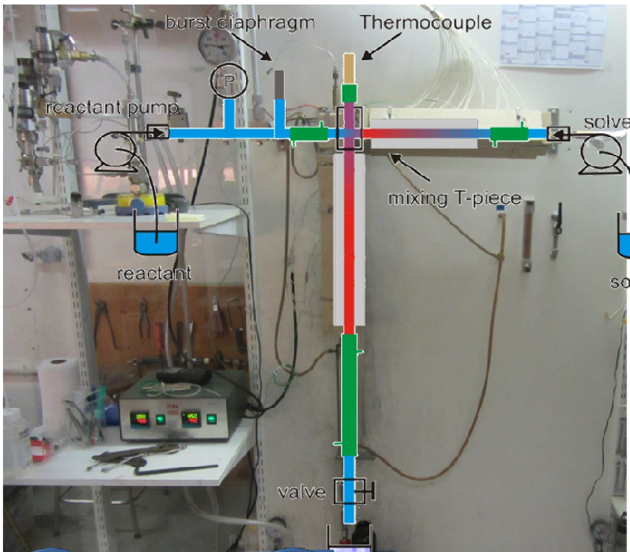
Pressure cooking

Because you want your ~~husband~~ colleagues to say you're the smartest, best ~~cook~~ chemist ever, even though you spend less time in the ~~kitchen!~~ laboratory

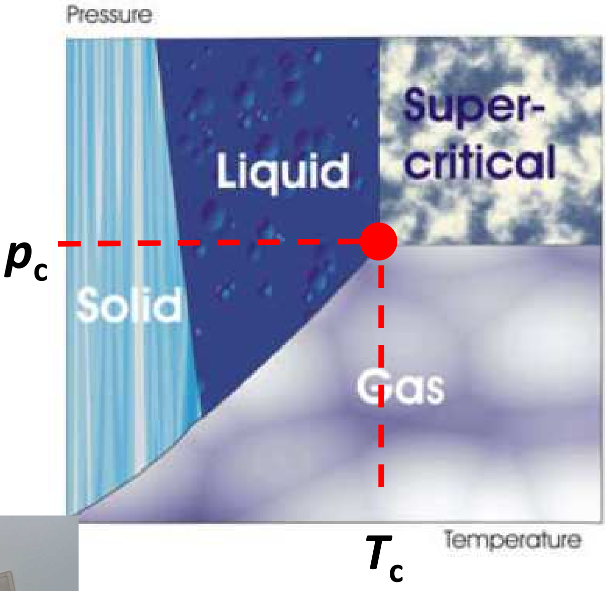
Advertisement for WEAR-EVER from 1967

Pressure cooker anno 2010



Wash
Centrifuge
Dry

Synthesis in supercritical water

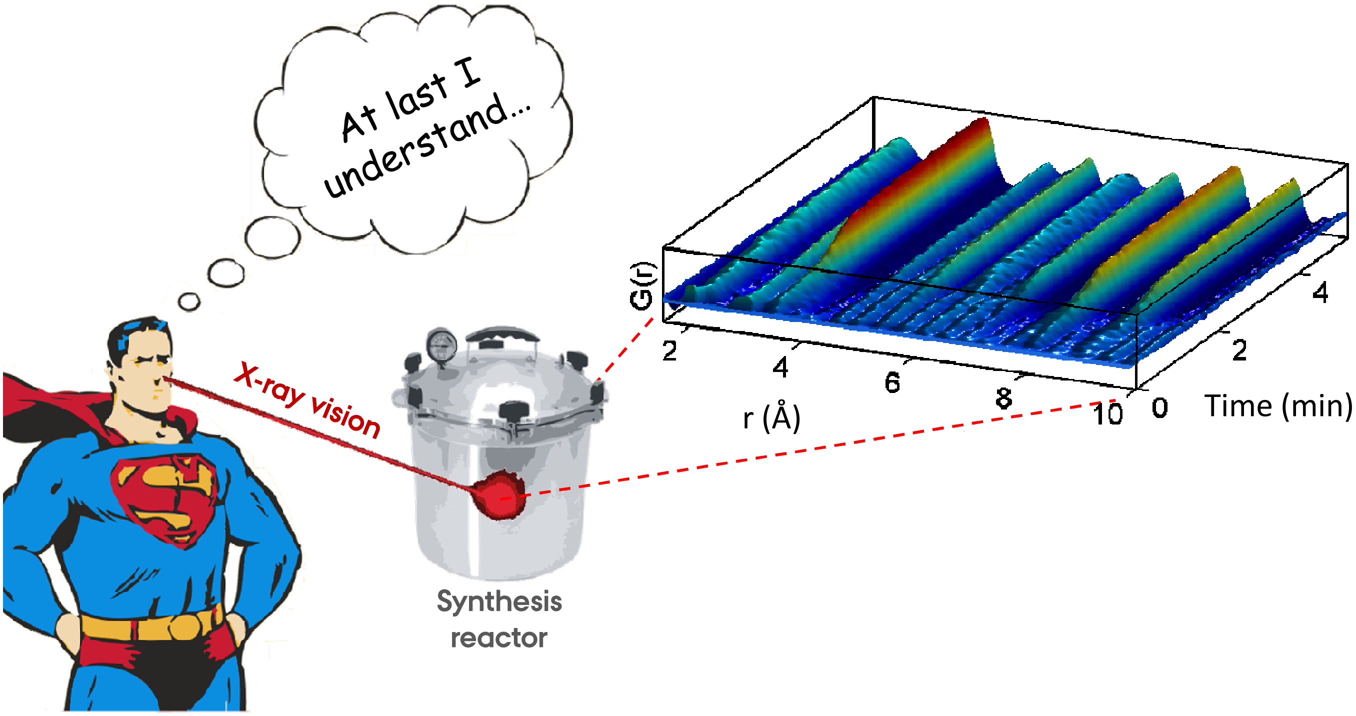


Fast heating rates

=> instant nucleation

=> minimal particle growth

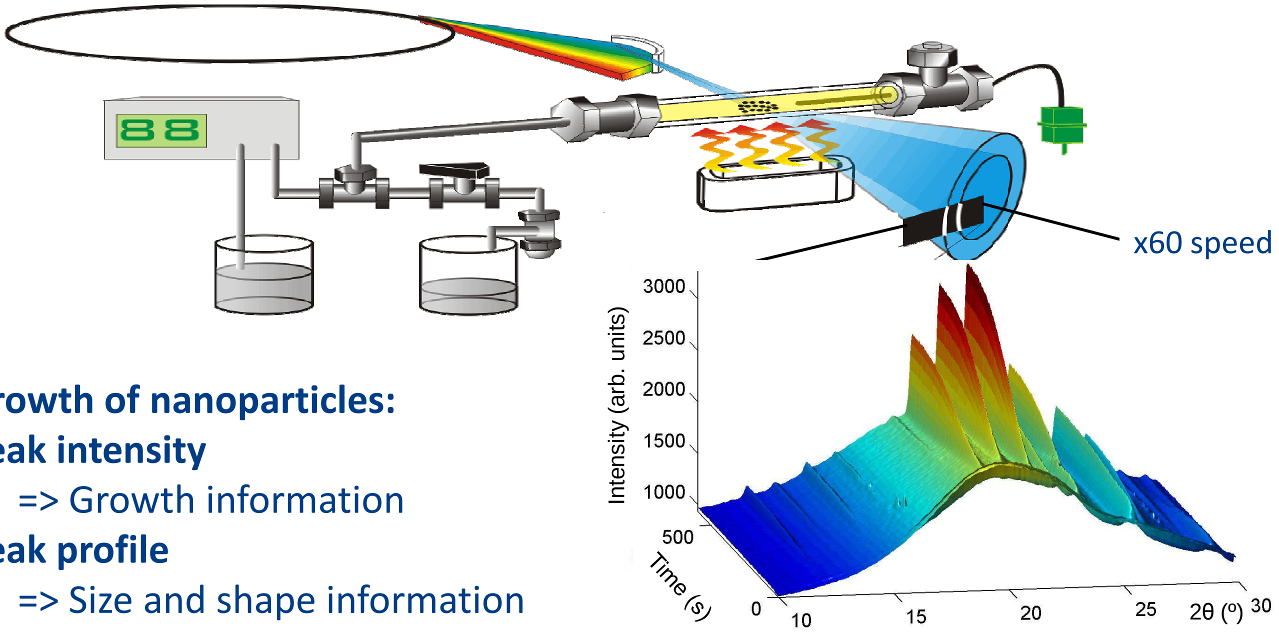
What happens in the synthesis?



In situ X-ray diffraction

***In situ* X-ray characterization** of synthesis products allow observation of

=> **Crystal growth**



x60 speed

Growth of nanoparticles:

Peak intensity

=> Growth information

Peak profile

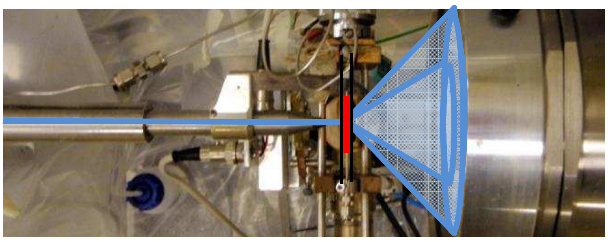
=> Size and shape information

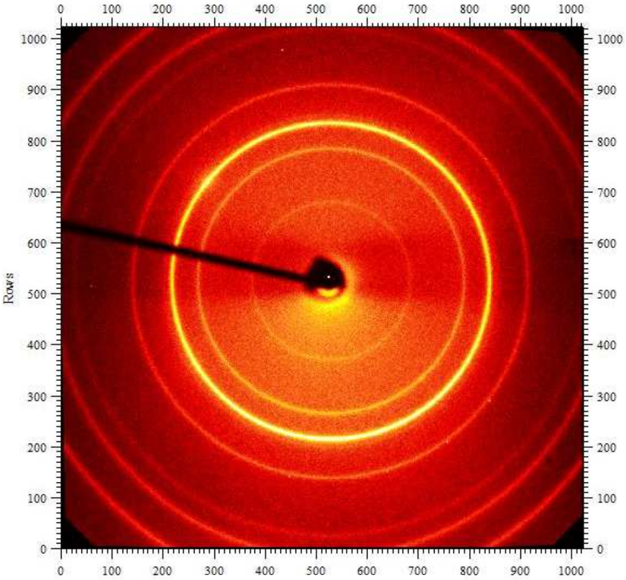
Growth of nanoparticles

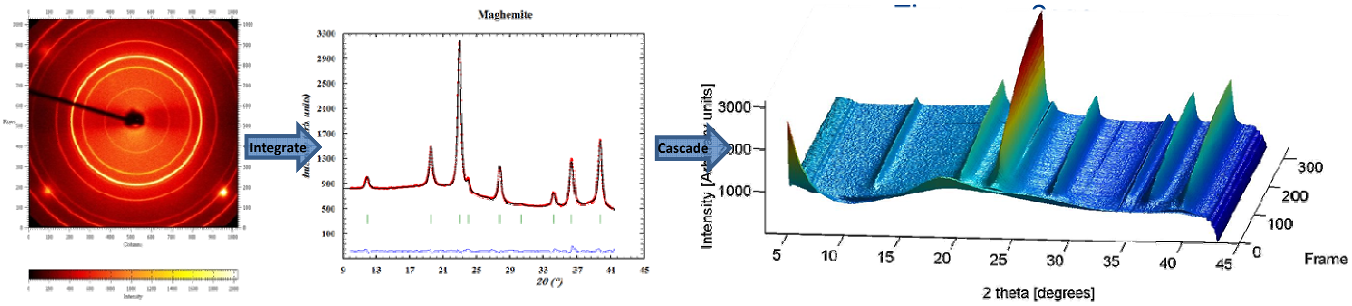
In situ growth of Fe_2O_3 nanoparticles

Pressure: 250 bar

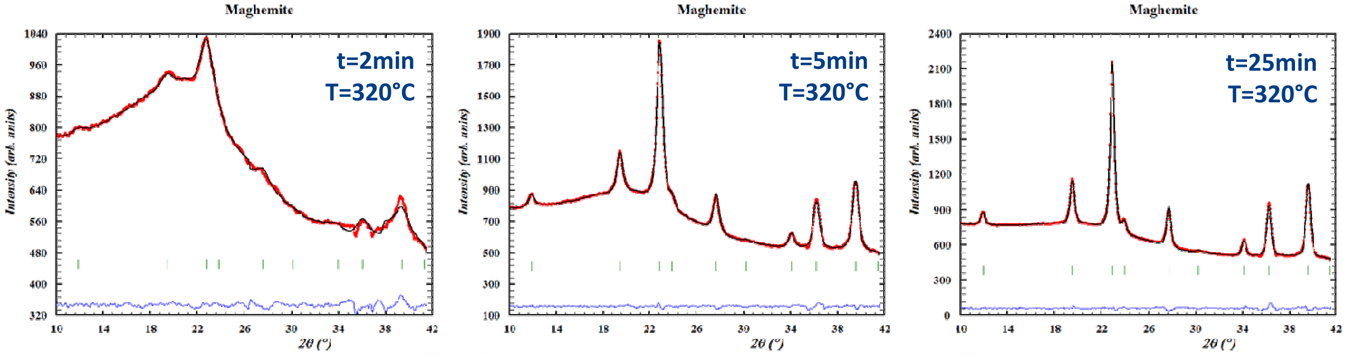
Variable temperature



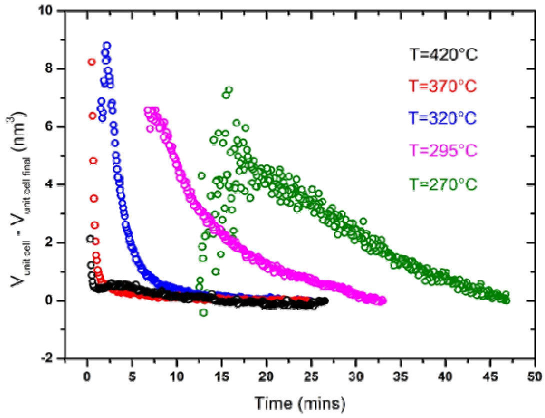




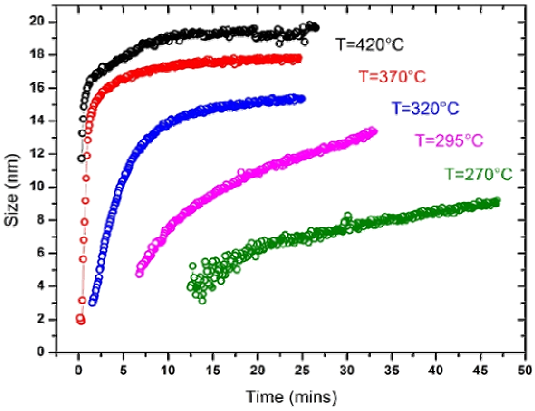
Rietveld results



Unit Cell Volume



Crystallite Size



Avrami kinetics - Fits

Plot:

Reation rate as a function of time.

Reaction rate defined as

$V(t) / V_{inf}$,

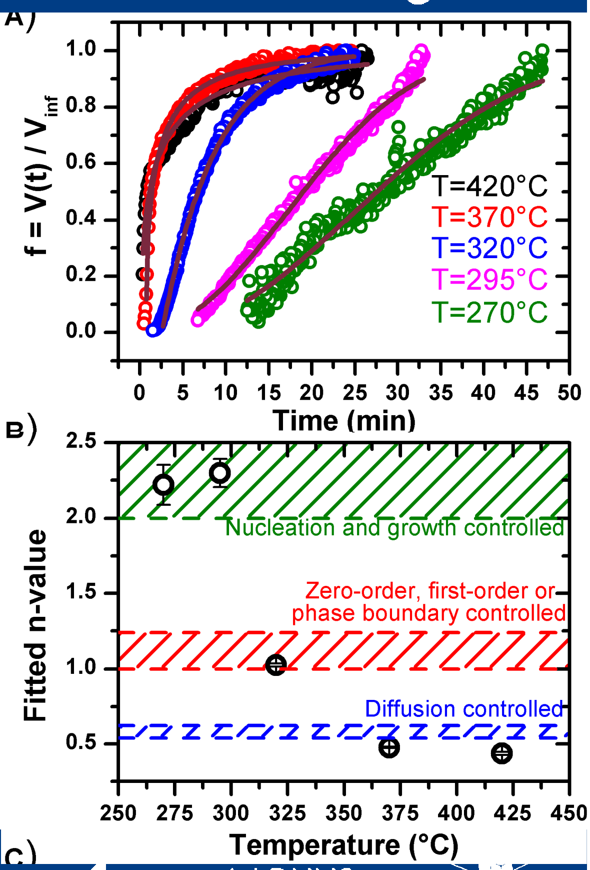
with V_{inf} being the final crystallite volume.

Fit:

Johnson-Mehl-Avrami equation:

$$f = V(t) / V_{inf} = 1-\exp[-(k(t-t_0))^n]$$

n Identifies the limiting mechanism for growth and estimate the activation energy from k.



Activation energy

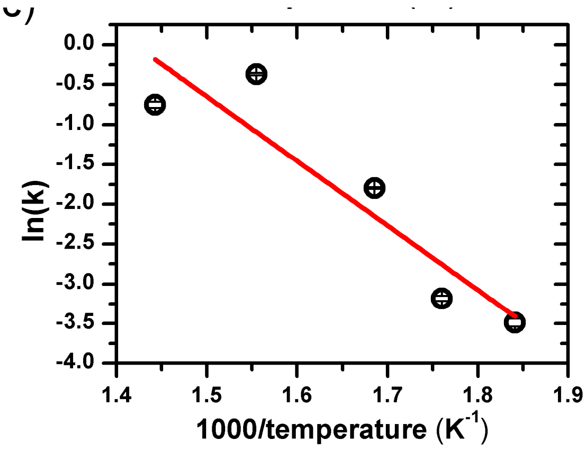
Activation energy:
Calculated from the Arrhenius equation:

$\mathbf{k = k_0 exp(-E_a/(RT))}$

$\ln(k) = -(E_a/RT)+\ln(k_0)$

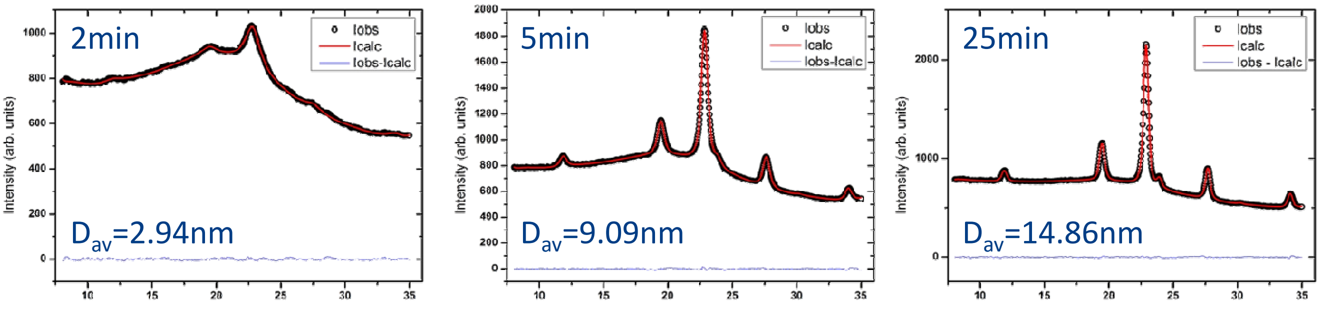
$E_a = - R*\Delta y/\Delta x =$ **67.4 kJ/mol**

Previously reported:
0.71 eV = 68.5 kJ/mol



Whole Powder Pattern Modeling (WPPM)

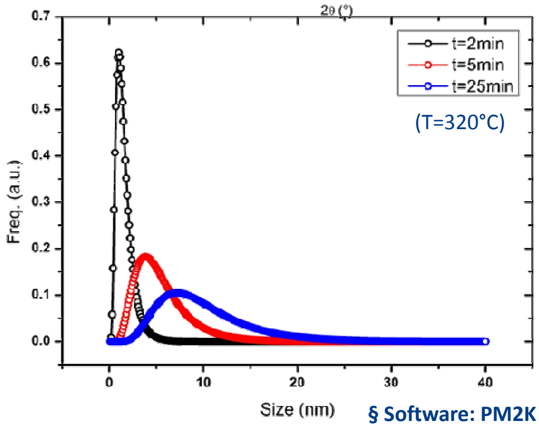
2M NH_4-Fe(III)-Citrate, T=320°C



LogNormal distribution:

$$g(D) = \frac{1}{D\sigma\sqrt{2\pi}} exp\left[-\frac{1}{2}\left(\frac{lnD-\mu}{\sigma}\right)^2\right]$$

$$D_{Volume\ avg.} = \frac{3}{4} exp\left[\mu + \frac{7}{2}\sigma^2\right]$$



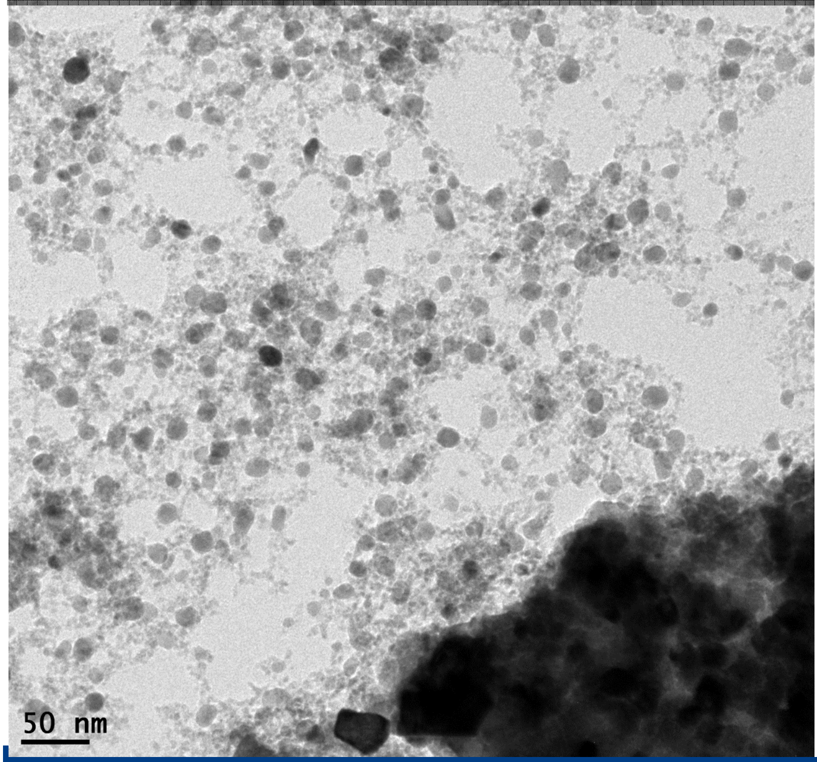
§ Software: PM2K

* P. Scardi and M. Leoni, “Whole Powder Pattern Modelling,” *Acta Crystallogr. A*, 58, 190–200 (2002).

** Matteo Leoni, Rosa Di Maggio, Stefano Polizzi and Paolo Scardi, *J. Am. Ceram. Soc.*, **87** [6] 1133–1140 (2004)

Transmission Electron Microscopy (TEM)

Sample: *2M NH4-Fe(III)-Citrate -> 25 min at 390°C*

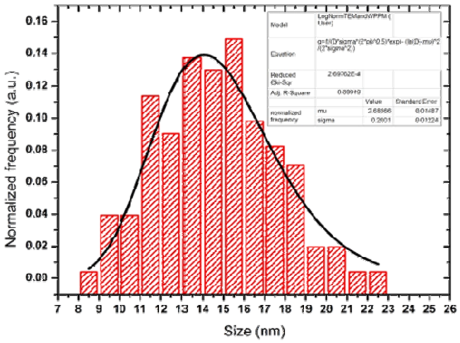


Fit with LogNormal distributon:

$$g(D) = \frac{1}{D\sigma\sqrt{2\pi}} exp\left[-\frac{1}{2}\left(\frac{lnD-\mu}{\sigma}\right)^2\right]$$

$$D_{Number\ avg.} = \exp\left(\mu + \frac{1}{2}\sigma^2\right)$$

Mean size = **14.93nm**



Size comparison

PXRD(Rietveld):

$$D_{av} = \frac{0.94\lambda}{FWHM\cos(\theta)}$$

(Scherrer – volume weighted)

PXRD(WPPM):

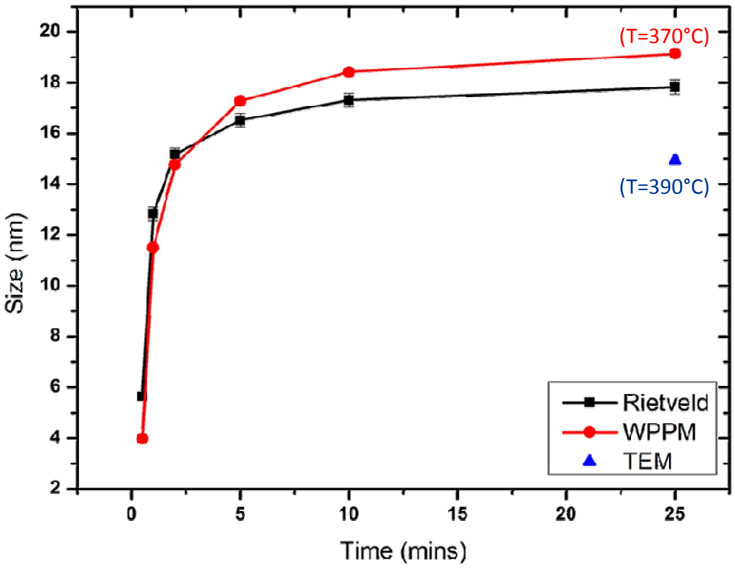
$$D_{av} = \frac{3}{4} exp\left[\mu + \frac{7}{2}\sigma^2\right]$$

(LogNormal – volume weighted)

TEM:

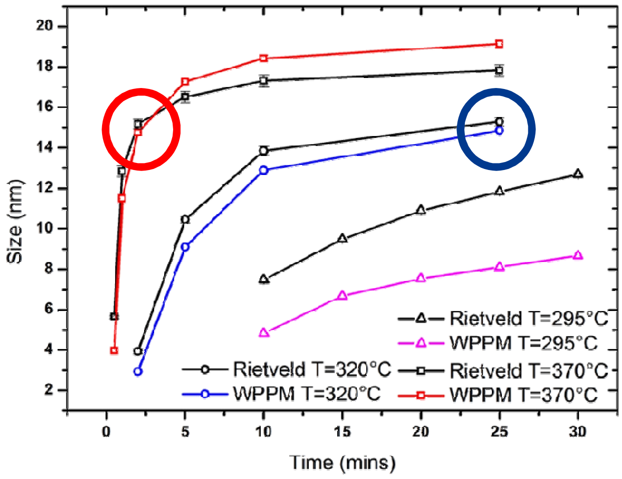
$$D_{av} = exp\left(\mu + \frac{1}{2}\sigma^2\right)$$

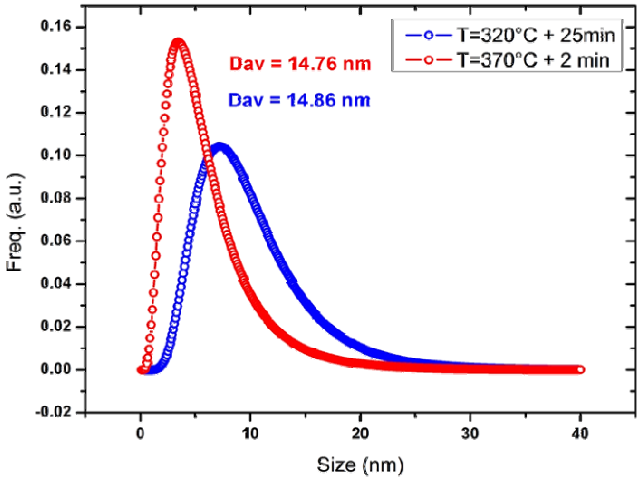
(LogNormal – number weighted)



Size comparison

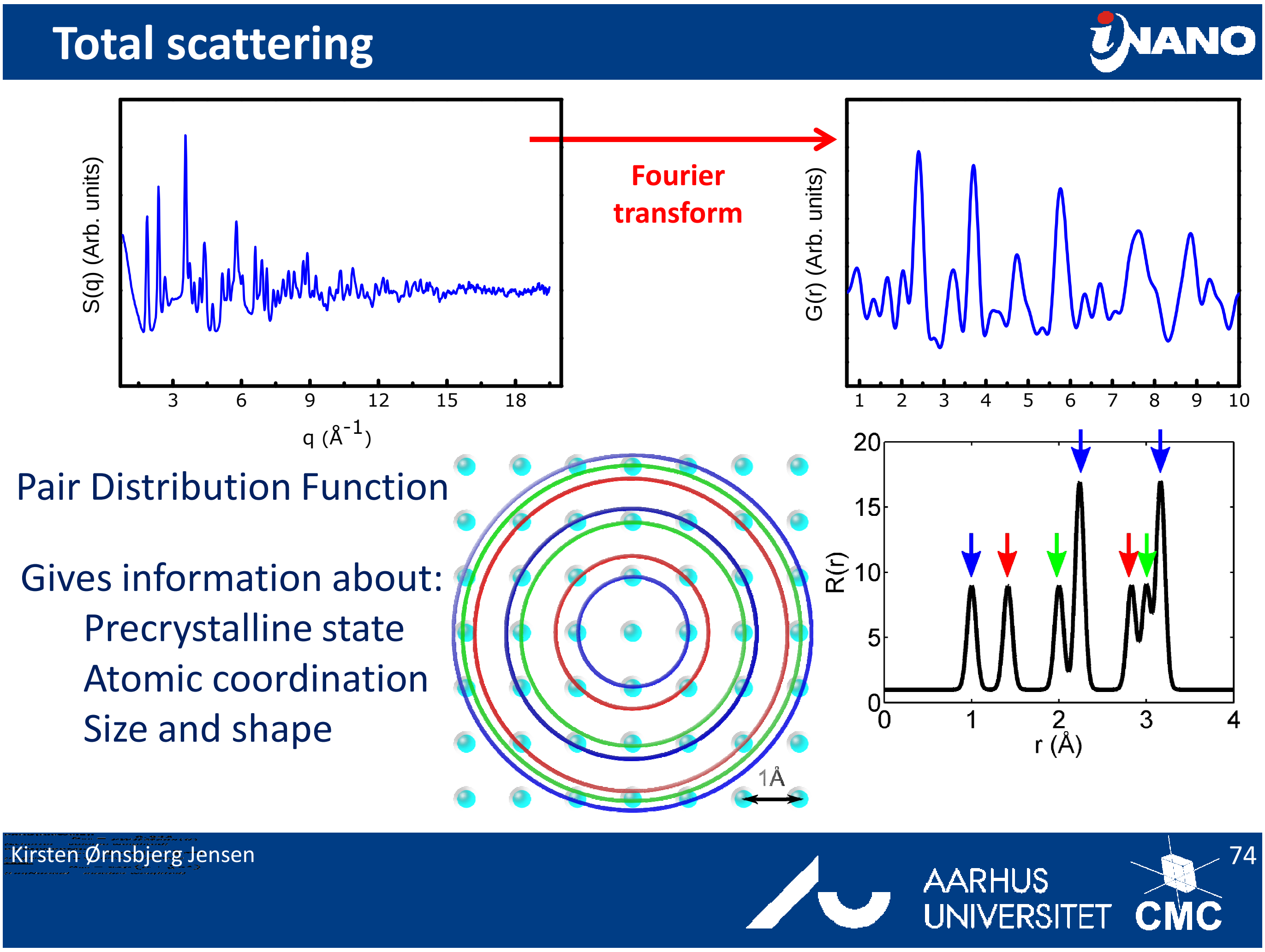
Rietveld vs. WPPM sizes:





* Same average size but different distributions!

-> High temperature + short reaction time gives narrower size distribution!

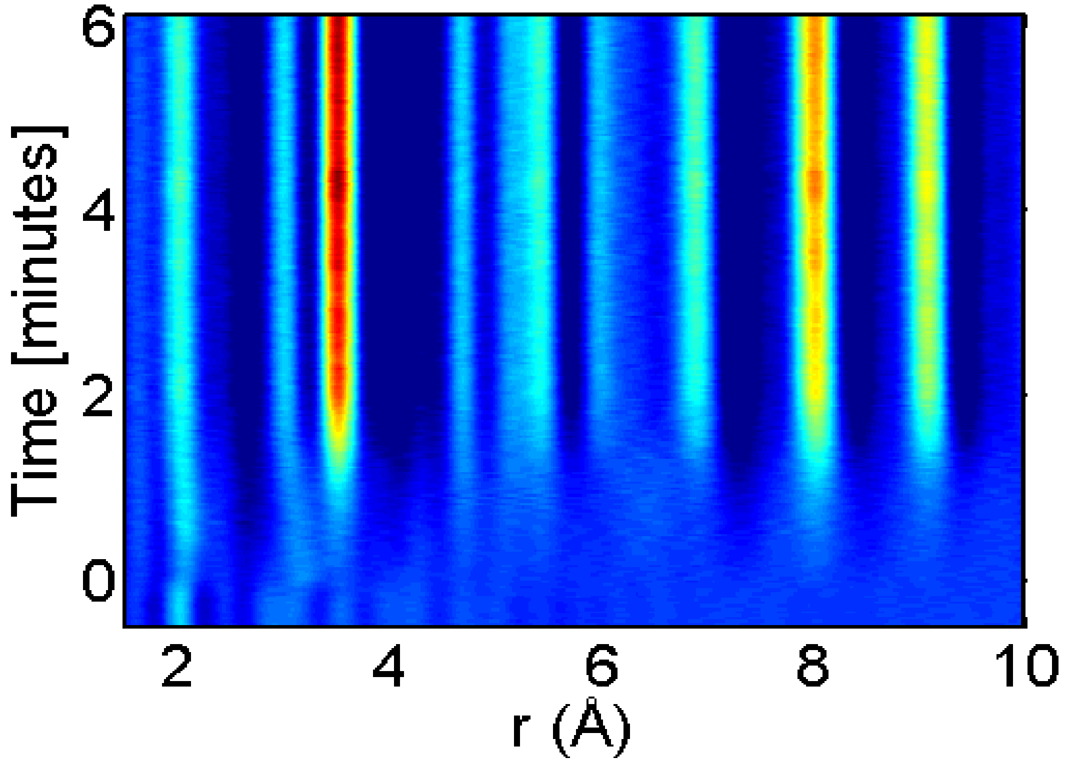


Total scattering

Pair Distribution Function

Gives information about:
- Precrystalline state
- Atomic coordination
- Size and shape

Pair distribution function analysis



Conclusion

- Particles size can be controlled by reaction temperature or by substituting a surfactant free iron(III) source.
- Different mechanisms limit the growth depending on the reaction temperature.
- The size distributions broaden as reaction temperature or reaction time is increased.

Acknowledgements:	Henrik Andersen (Aarhus) Espen Bøjesen (Aarhus) Bo B. Iversen (Aarhus) Kirsten Jensen (Aarhus) Nina Lock (Aarhus) Christoffer Tyrsted (Aarhus)

Conclusion

Synchrotron light is a very versatile tools for materials research

Atomic positions and occupancies:
Single crystal and powder diffraction
- including resonant scattering

Vibration characteristics through
Inelastic X-ray scattering

Growth properties of compounds
In situ studies