Microscopic Dynamics of Thermoelectric Materials

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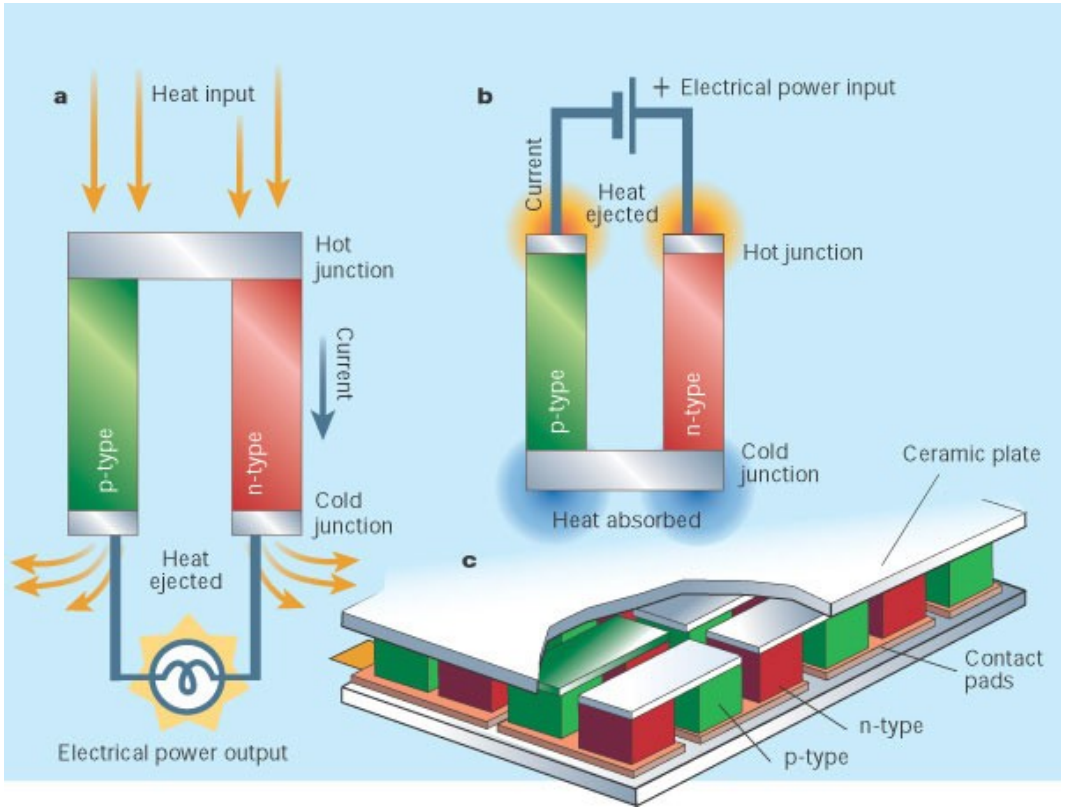
Overview

- Introduction into the Phonon Glass Electron Crystal concept and rattling modes idea
- The merit of inelastic and elastic neutron scattering and the approach to the study of polycrystalline matter
- Results for filled skutterudite compounds
- Comparison with other open-framework compounds
- Summary and Outlook

Thermoelectric Effect

Cronin B. Vining, *Nature* 413, 577, (2001)



a) Conversion of thermal to electrical energy (Seebeck effect)

b) Cooling (pumping heat) by application of electrical power (Peltier effect)

c) Thermoelectric module

Thermoelectric materials are efficient converters of thermal to electrical energy !

Figure of merit :

$$Z = S^2a/k \qquad \text{with} \qquad k = k_{electr.} + k_{lattice}$$

S = Seebeck coefficient (dV/dT), a = electrical conductivity, k = thermal conductivity

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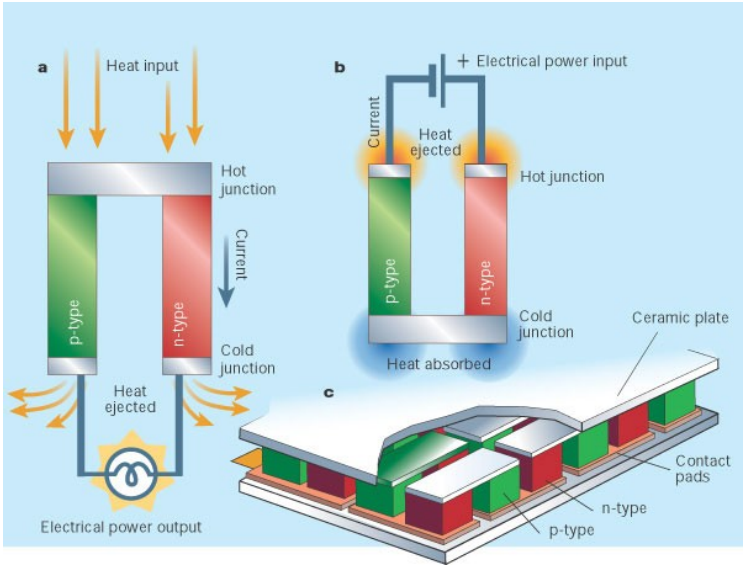


Figure of merit : $Z = S^2a/k$

Thermal conductivity :

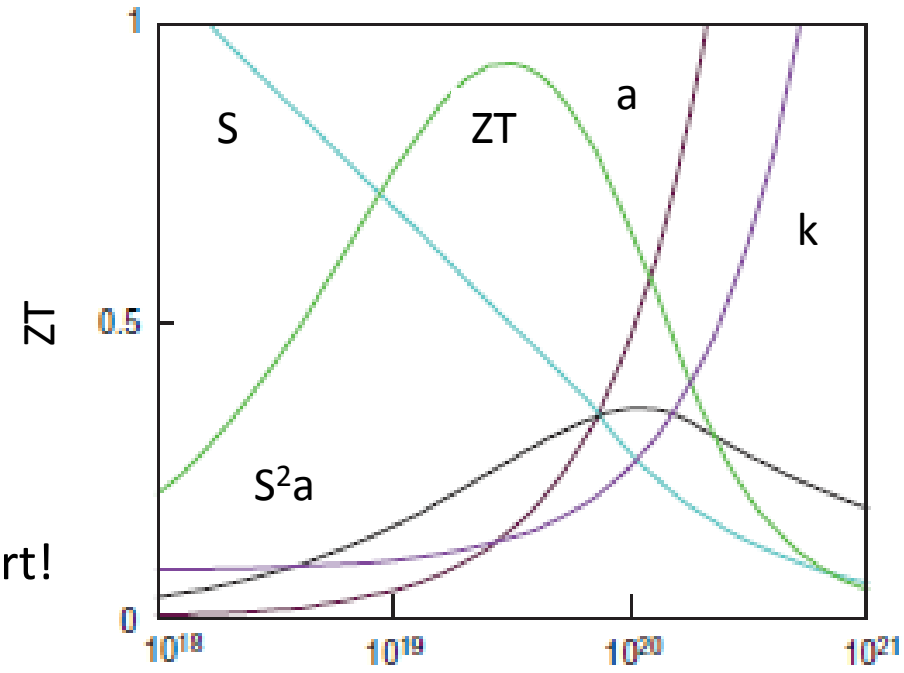
$k = k_{electr.} + k_{lattice}$

Dimensionless FoM : ZT

S^2a and $k_{electr.}$ limited by n ~ $10^{19\text{-}20}$

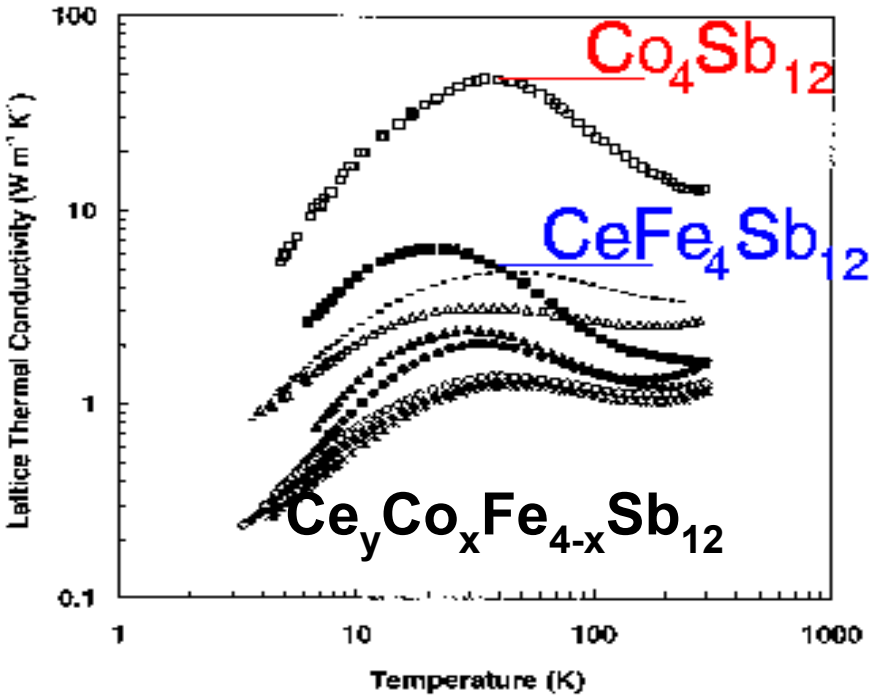
Working Hypothesis :

Manipulate $k_{lattice}$ without perturbing Bloch symmetry for electronic transport!



G.J. Snyder & E.S. Toberer,
Nature Materials 7, 105, (2008)

Lattice Thermal Conductivity



Lattice thermal conductivity of skutterudite compounds :

Ternary compound exhibits a lattice thermal conductivity suppressed by at least one order of magnitude. Effect must be mediated by the vibrational properties (phonons ?) of the crystals.

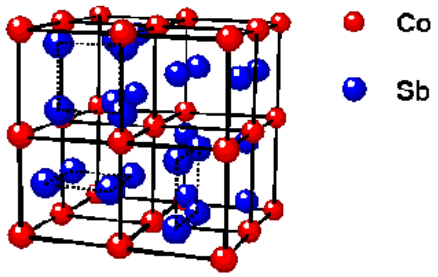
G.P. Meisner et al., *PRL* 80, 3551 (1998)

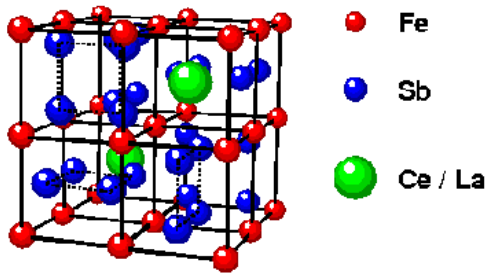
MT_4X_{12}- Skutterudite

Space group: Im-3

Cubic structure with M on bcc-sites

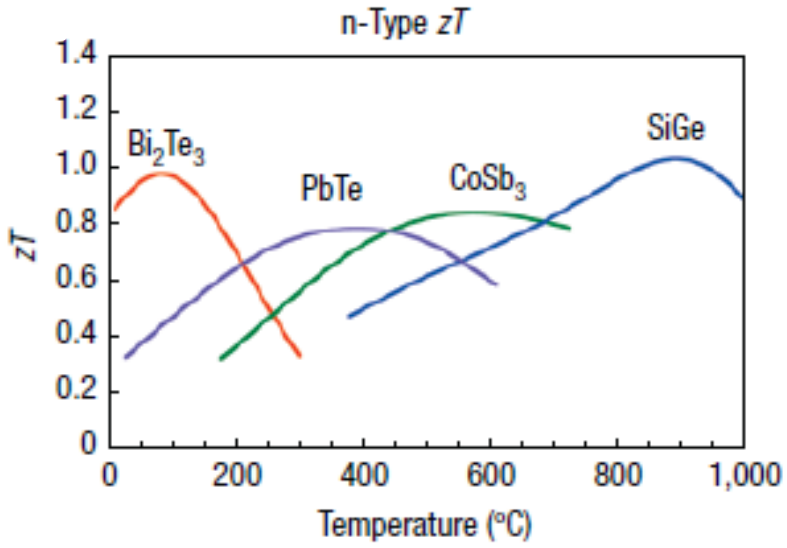
d = 9.2 Å for $LaFe_4Sb_{12}$

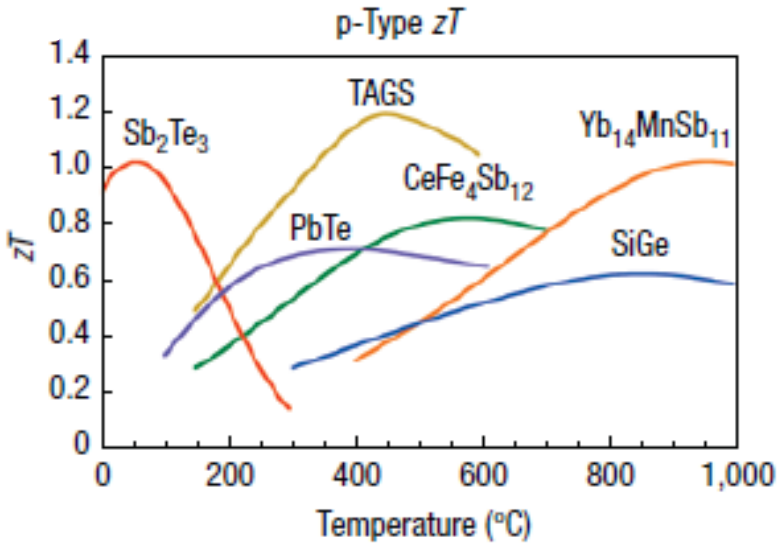




Thermoelectric Performance of Skutterudites

G.J. Snyder & E.S. Toberer, Nature Materials 7, 105 - 114 (2008)





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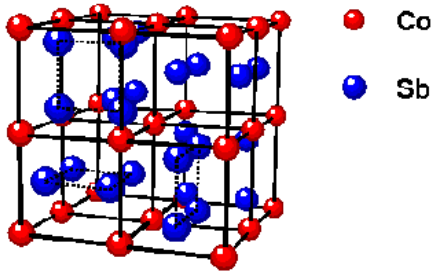
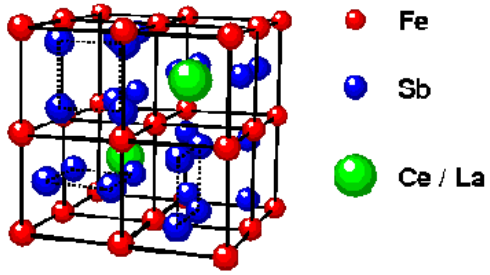


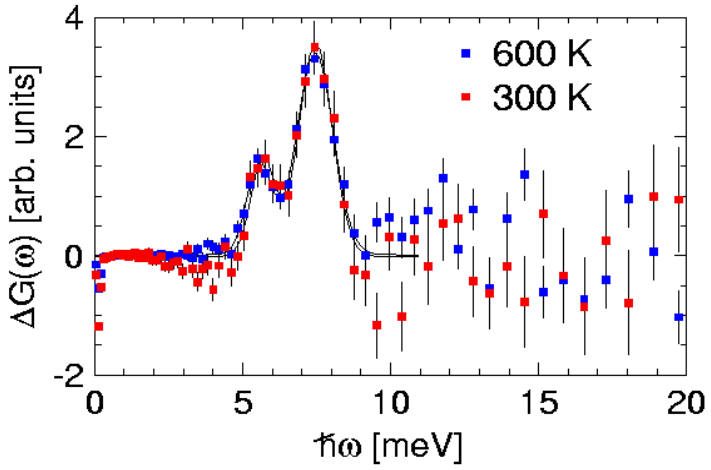


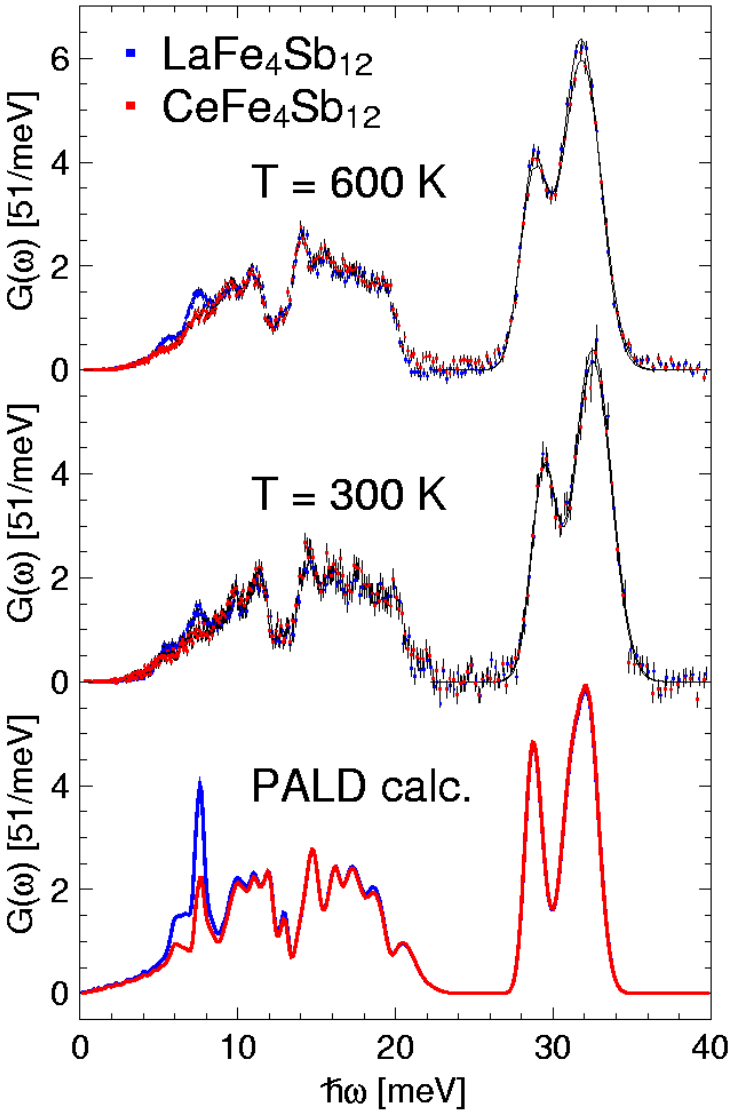
Phonon Density of States of Skutterudites

INS contrast experiment at IN6@ILL

	S.C.S.	A.M.U.	S.P.
La	9.7	138.9	7.0
Ce	2.9	140.1	2.1
Fe	11.6	55.9	20.8
Sb	3.9	121.8	3.2

S.C.S. = scattering cross section in barns
A.M.U. = atomic mass unit
Scattering Power S.P. = C.S./A.M.U.*100





M.M. Koza et al., *Nature Materials* 2008
V. Keppens et al., Nature 1998, R.P. Hermann et al., *PRL* 2003, G.J. Long et al., *PRB* 2005

Apparent Perception upon the Lattice Dynamics

From Literature :

Einstein mode

Rattling mode

Isolated oscillator

Off-center motion

Local vibrational mode

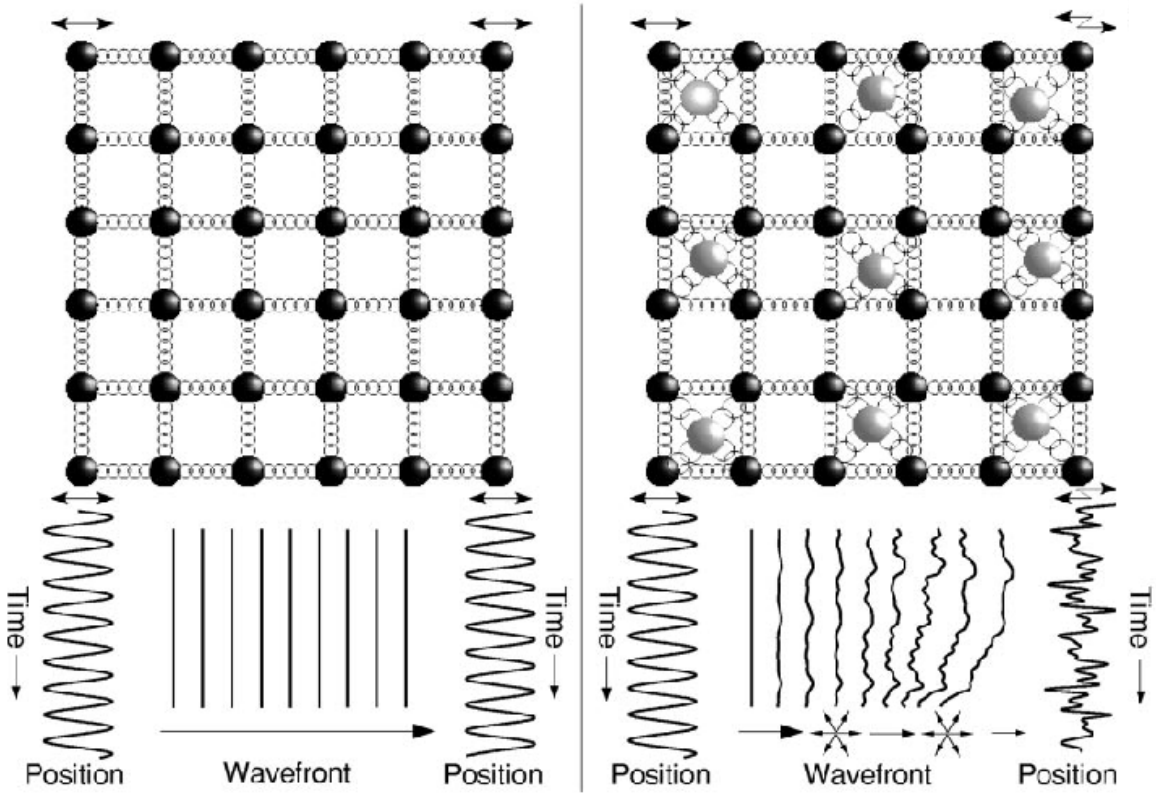
Incoherent phonons

Independent vibrations

Decoupled dynamics

...

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

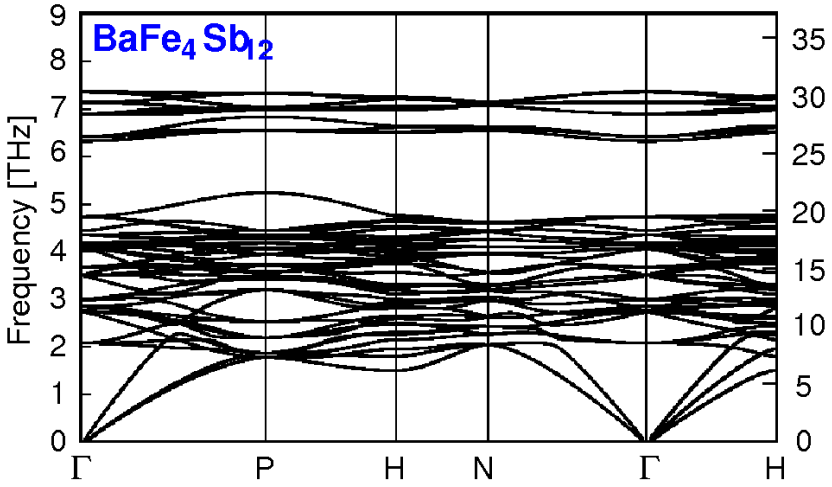


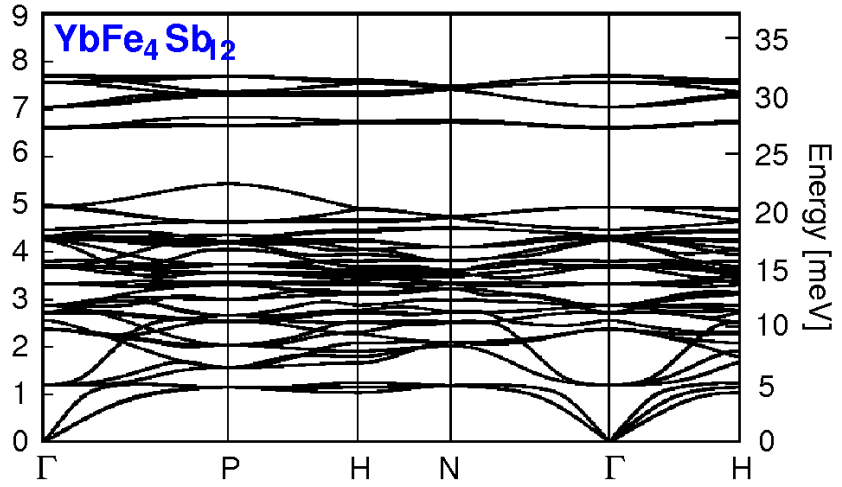
B.C. Sales et al., *PRB 56*, 15081, (1997)

Phonon Glass and Electron Crystal - PGEC !

Results from Computer Modelling

Ab initio modelling of skutterudite compounds : Phonon dispersion from lattice dynamics calculations





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MFe_4Sb_{12}, M = **La**, **Ce**, ^Eu, Nd, Yb, *Tl

Experimental work :

"M. Rotter et al. *PRB* 77, 144301 (2009)

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LD calculation work :

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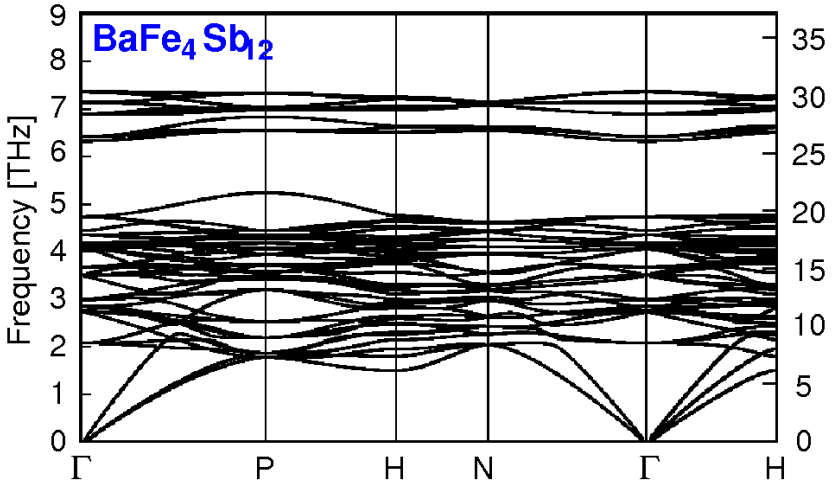

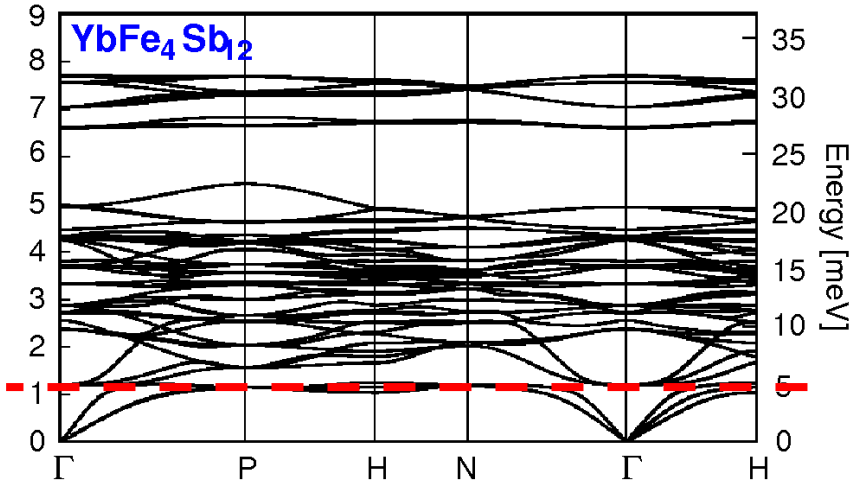

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Rattling mode, Einstein mode, isolated oscillator, local vibrational mode, incoherent phonons, independent vibrations, decoupled dynamics, ...

Results from Computer Modelling

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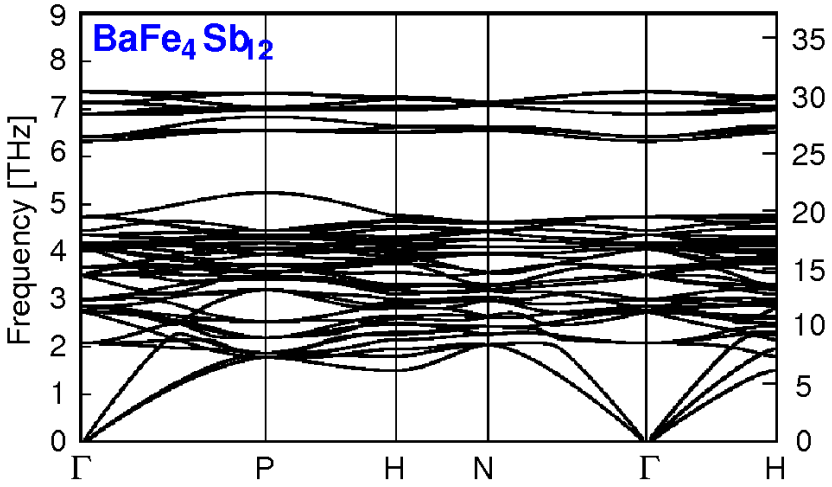

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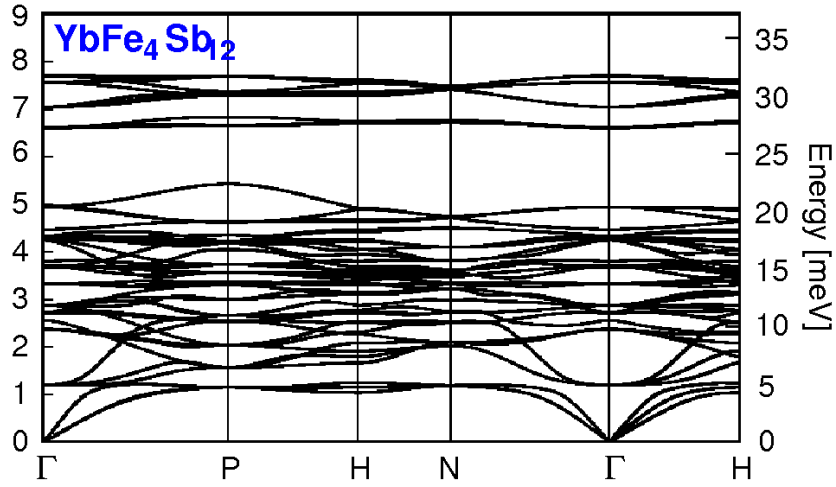

MFe_4Sb_{12}, M = **La**, **Ce**, ^Eu, Nd, Yb, *Tl

The Callaway Model : $\kappa_{\mathrm{lattice}} = 1/3 \cdot C \cdot v \cdot l$

specific heat C - via density of states from dispersion relations

velocity of sound v - from dispersion relations

mean free path l, phonon life time $\tau = l/v$ - **infinite !!!**

Results from Computer Modelling

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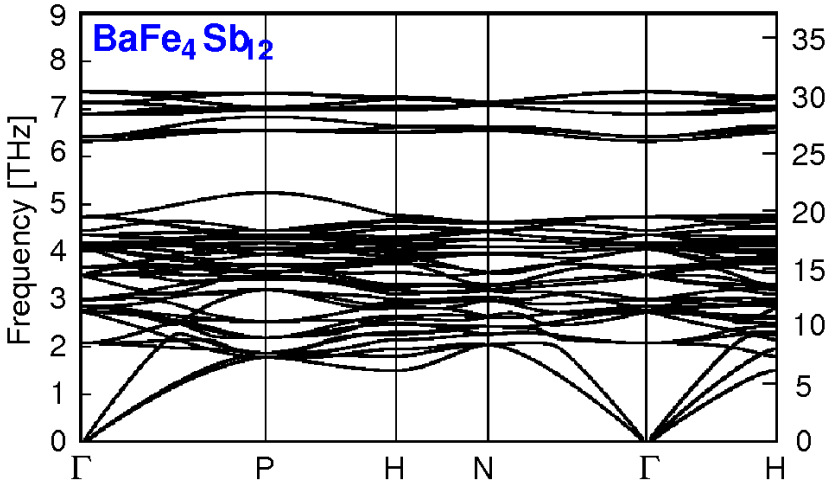

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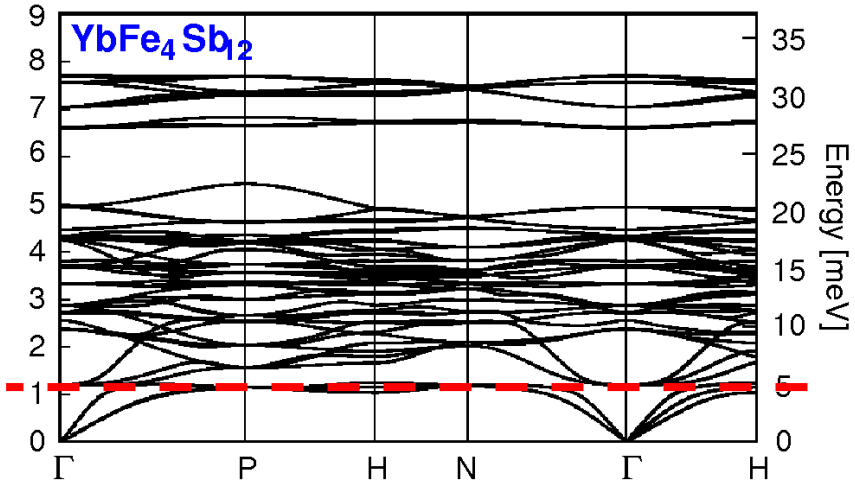


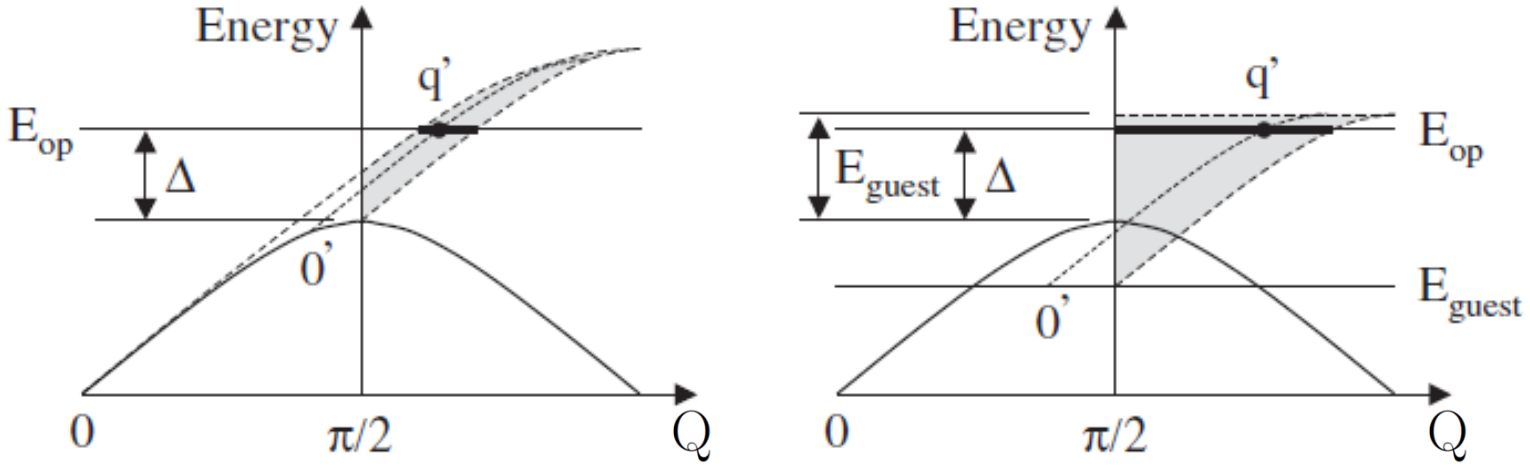
MFe_4Sb_{12}, M = **La**, **Ce**, ^Eu, Nd, Yb, *Tl

A set of normal modes is sufficient to characterize the vibrational response, the associated thermodynamic and material properties.

Applies as well to the rattling mode, Einstein mode, isolated oscillator, local vibrational mode, incoherent phonons, independent vibrations, decoupled dynamics, ...

A Gedankenexperiment

‘Conceptual diagram of phonon dispersion relations. …’

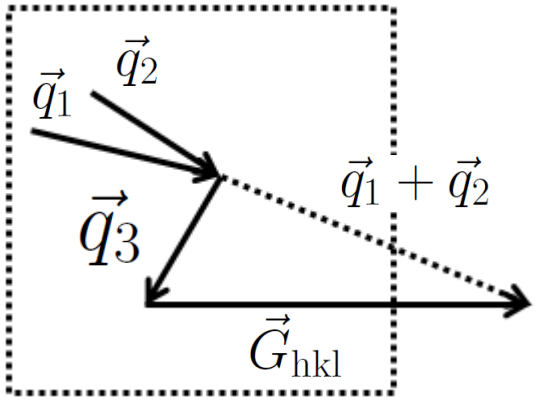


C.H. Lee et al., *J. Phys. Soc. Jpn.* 75, 123602, (2006)

Umklapp scattering :

$$\hbar\omega_1 + \hbar\omega_2 = \mathrm{E_{op}}$$

$$\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{G}_{\mathrm{hkl}}$$



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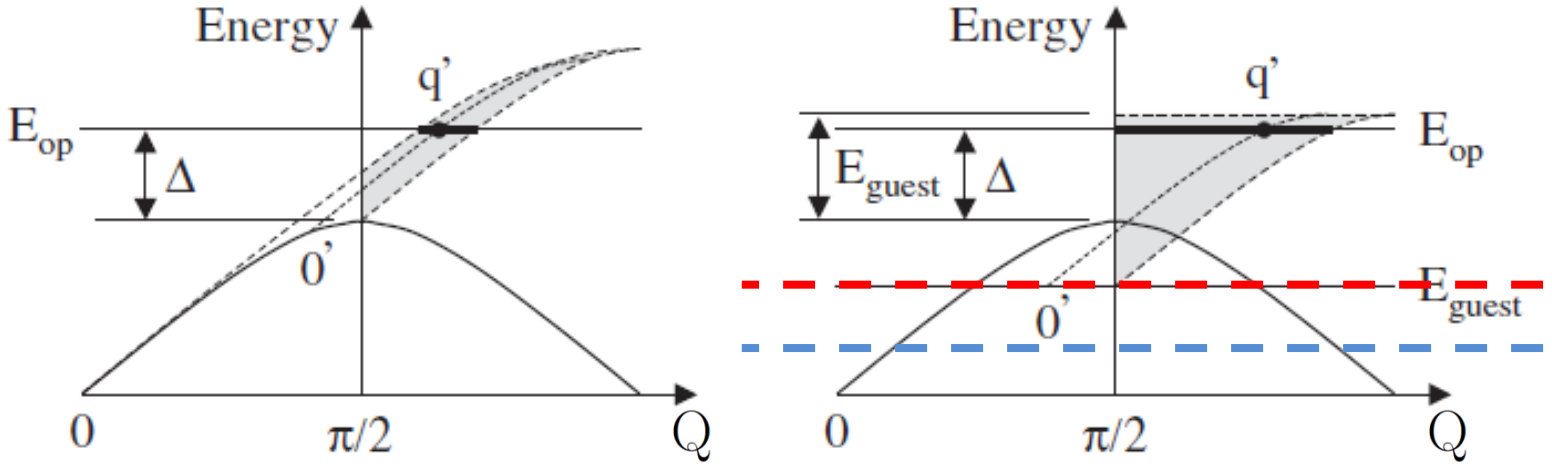


C.H. Lee et al., *J. Phys. Soc. Jpn.* 75, 123602, (2006)

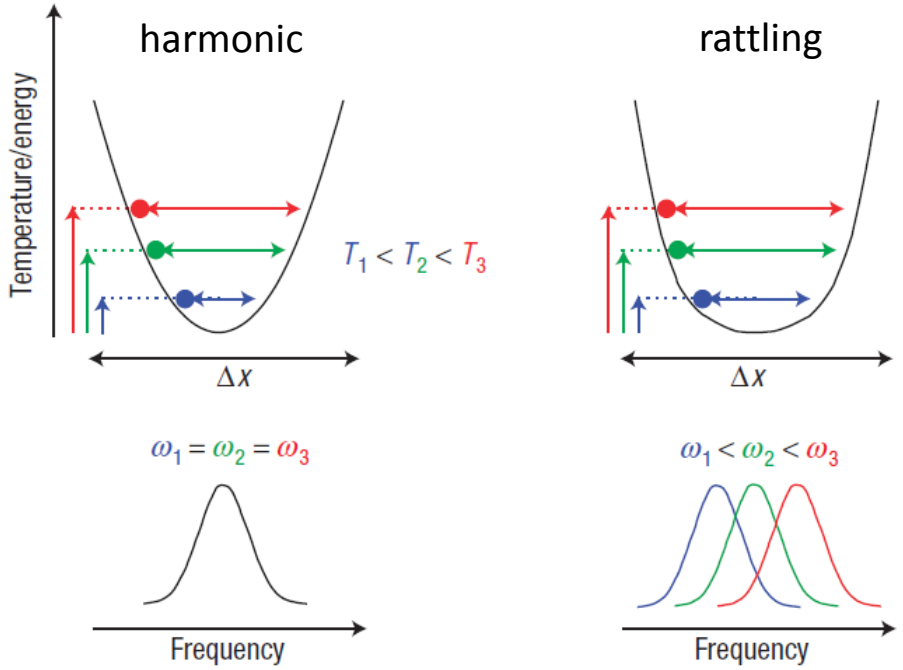
Umklapp scattering : $\hbar\omega_1 + E_{guest} = E_{op}$

Condition to meet : $E_{guest} \geq \Delta$

Puzzle to solve : $E_{guest} < \Delta$

Another Gedankenexperiment

Particle in a box : isolated oscillator concept



normal modes

$$\frac{\partial^2 U(x)}{\partial x^2} = \text{const.}$$

thermal expansion

~~$$\frac{\partial^3 U(x)}{\partial x^3} < 0$$~~

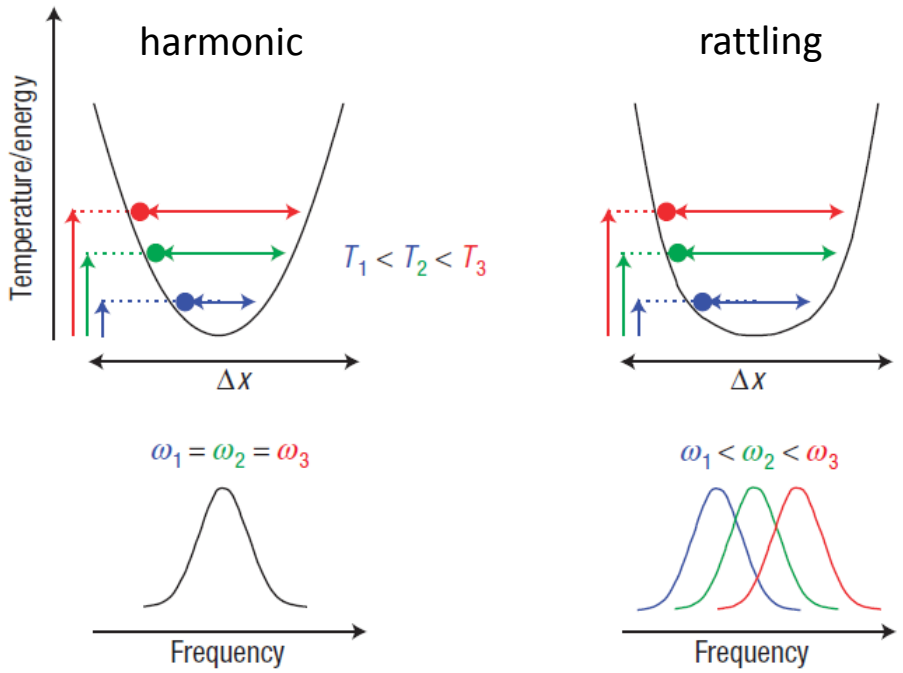
rattling term

$$\frac{\partial^4 U(x)}{\partial x^4} > 0$$

$$U(x) = U_\circ + \frac{1}{2}\frac{\partial^2 U(x)}{\partial x^2}x^2 + \cancel{\frac{1}{6}\frac{\partial^3 U(x)}{\partial x^3}x^3} + \frac{1}{24}\frac{\partial^4 U(x)}{\partial x^4}x^4 + \ldots$$

Another Gedankenexperiment

Particle in a box : isolated oscillator concept



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$$\frac{\Delta\omega}{\Delta T} = 0 \qquad \frac{\Delta\omega}{\Delta T} < 0 \qquad \frac{\Delta\omega}{\Delta T} > 0$$

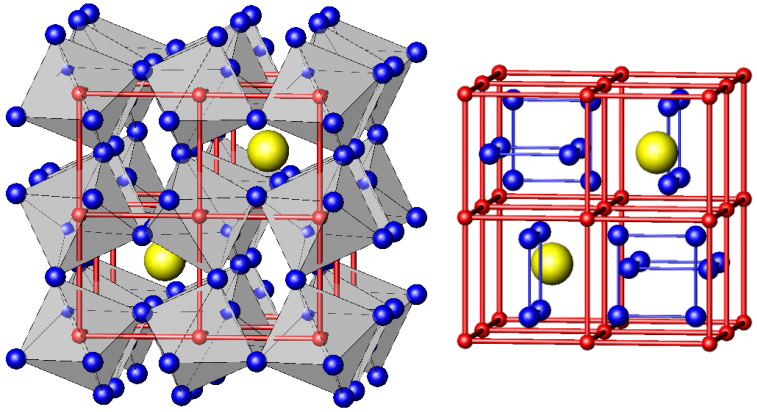
Rattling Modes and PGEC

- Do rattling modes (RMs) exist ? What are RMs ?

  - weakly-bonded, isolated, individual oscillators, ...

- Are RMs responsible for PGEC ?
- Are RMs the adequate means to break thermal transport ?
- How weak must a coupling be to generate a RM ?
- How strong must a coupling be to perturb thermal transport ?
- What are the conditions to turn a classical RM into a quantum mechanical oscillator ?
- ...

Open-Framework Compounds



MFe_4Sb_{12} - Skutterudite

M = **Ca^{2+}**, **Sr^{2+}**, **Ba^{2+}**, **La^{3+}**, Ce, Eu, Nd, **Yb^{2+}**, Tl, ...

Space group: Im-3

Cubic structure with M on bcc-sites

d = 9.2 Å

LaT_4X_{12} - Skutterudite

T = Fe, Ru, Os

X = As, Sb

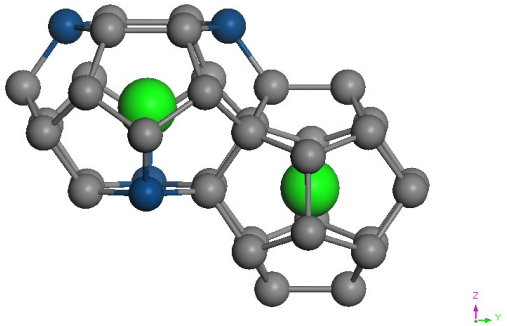
Clathrates, Clathrate-hydrates

Ba_8Ge_{43}, $Ba_8M_xGe_{46-x}$ M = Zn, Pd, ...

Ba_8Si_{46}, $Ba_{24}Si_{100}$

M_8Sn_{44} M = K, Rb, Cs

d = 11 – 22 Å

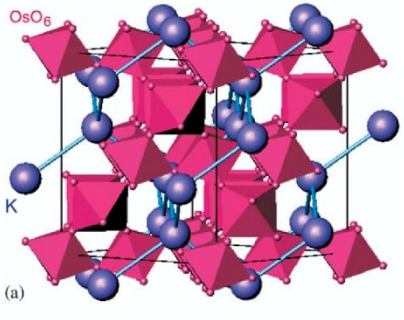


MV_2Al_{20}

M = Sc, Y, Al, Ga, La, Ce

Space group: Fd-3m

d = 14.5 Å



Beta - Pyrochlores

MOs_2O_6, M = K, Rb, Cs

Space group: Fd-3m

d = 10.1 Å

Why Inelastic Neutron Scattering ?

INS contrast experiment at IN6@ILL

	S.C.S.	A.M.U.	S.P.
La	9.7	138.9	7.0
Ce	2.9	140.1	2.1
Fe	11.6	55.9	20.8
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S.C.S. = scattering cross section in barns
A.M.U. = atomic mass unit
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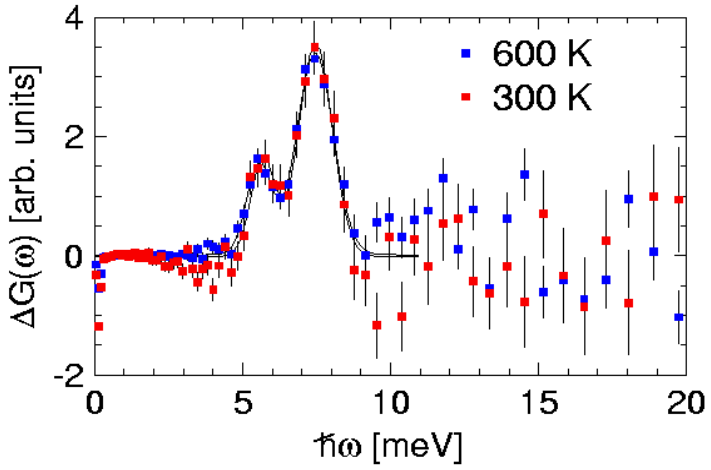
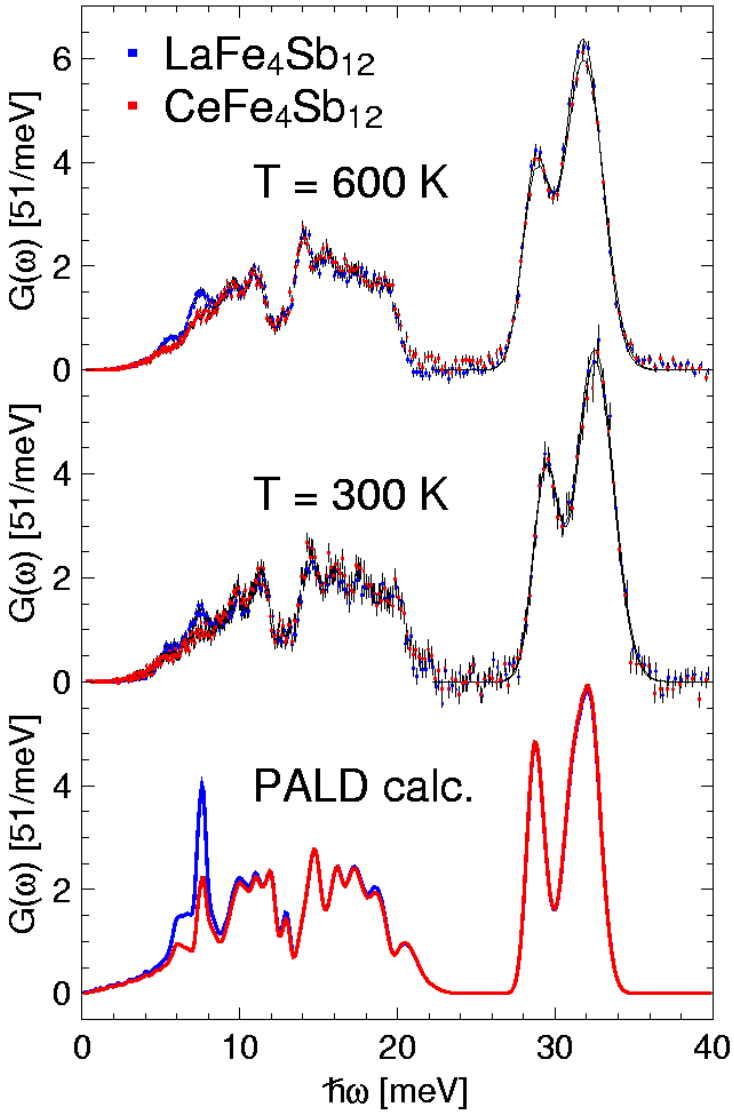




M.M. Koza et al., *Nature Materials* 2008
V. Keppens et al., Nature 1998, R.P. Hermann et al., *PRL* 2003, G.J. Long et al., *PRB* 2005

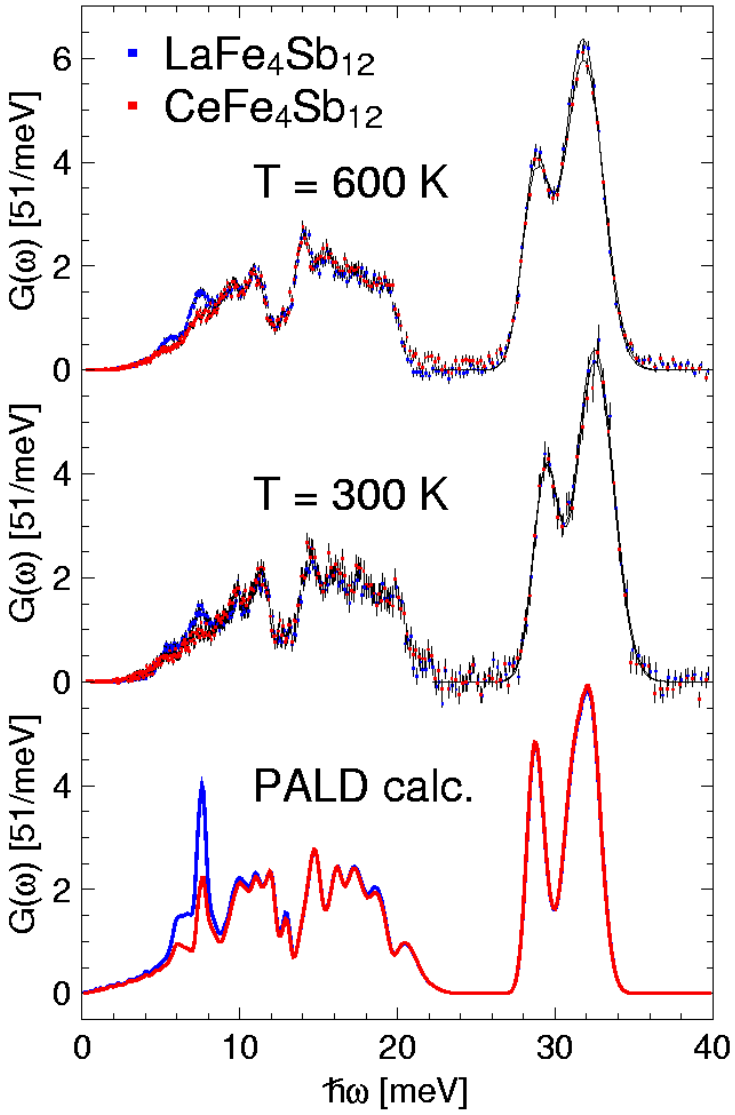
Why Inelastic Neutron Scattering ?

Mode energies in meV

INS	Raman*	LD calc.
5.5	-	-
7.5	-	7.2
9.5	-	-
11.5	11.5	11.4/11.5
13.0	12.5	12.5/12.6
14.5	15.1	15.0/15.4
16.0	16.2	15.9
17.5	18.1	17.3/17.9/18.2
19.0	19.1	18.4/18.6/18.9
20.0	20.0	
21.5	21.3	21.1

*J.L. Feldman et al., *PRB* 68, 94301 (2003)

Black - Raman active
Blue - IR active
Red - neither ... nor



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11.5	11.5	11.4/11.5
13.0	12.5	12.5/12.6
14.5	15.1	15.0/15.4
16.0	16.2	15.9
17.5	18.1	17.3/17.9/18.2
19.0	19.1	18.4/18.6/18.9
20.0	20.0	
21.5	21.3	21.1

*J.L. Feldman et al., *PRB* 68, 94301 (2003)

30 mm

© Sandro Maggia, http://minernet.it/

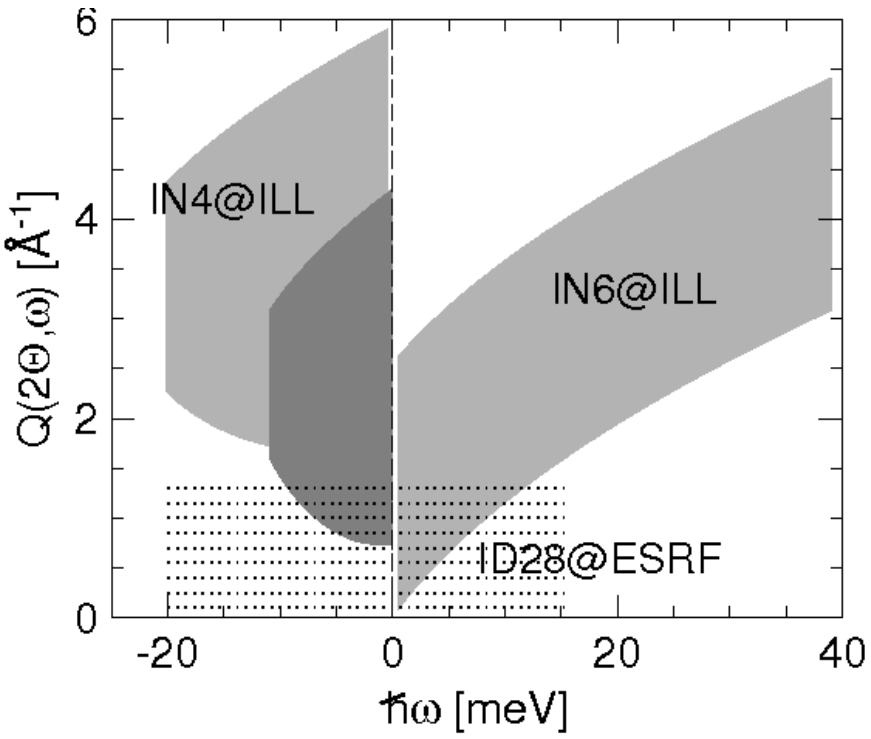
Compounds form readily as polycrystals and powders.

Their high reflectivity makes optic experiments very difficult.

The Merit of Inelastic Neutron Scattering

- High energy resolution of 1-500 microeV.
- Relaxed selection rules governing scattering process and thus capability of monitoring all vibrational eigenstates.
- Moderate and weak absorption effects.
- Capability of sampling large areas of the energy-momentum phase space simultaneously.
- Sensitivity to bulk properties, requiring however samples of sufficient volume ~1 cm^3.
- ...

Phase Space Coverage by INS and IXS Spectrometers



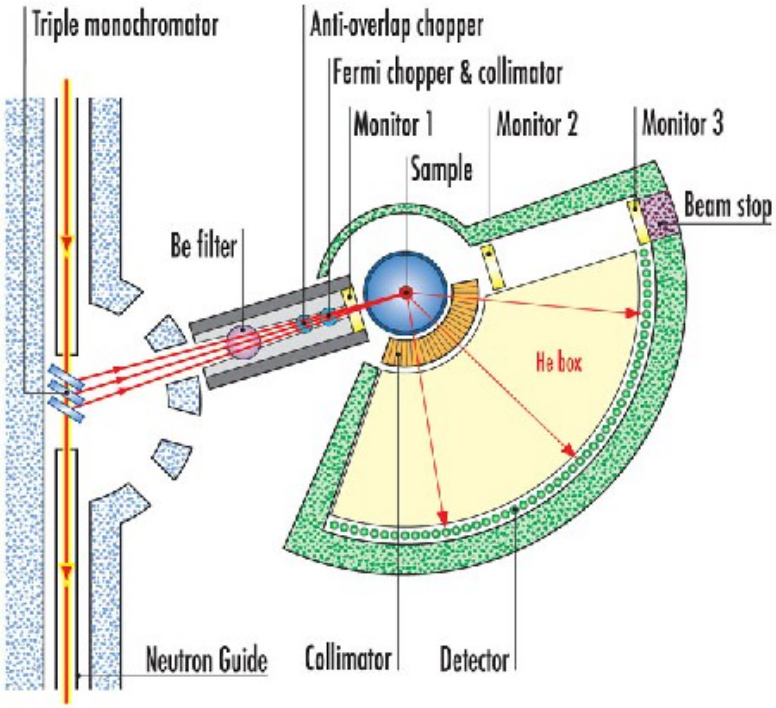
Time of flight spectroscopy

IN6@ILL 'cold' spectrometer :

dE = 0.1 - 0.2 meV

IN4ILL 'thermal' spectrometer :

dE = 0.5 – 1.0 meV



X-ray spectroscopy

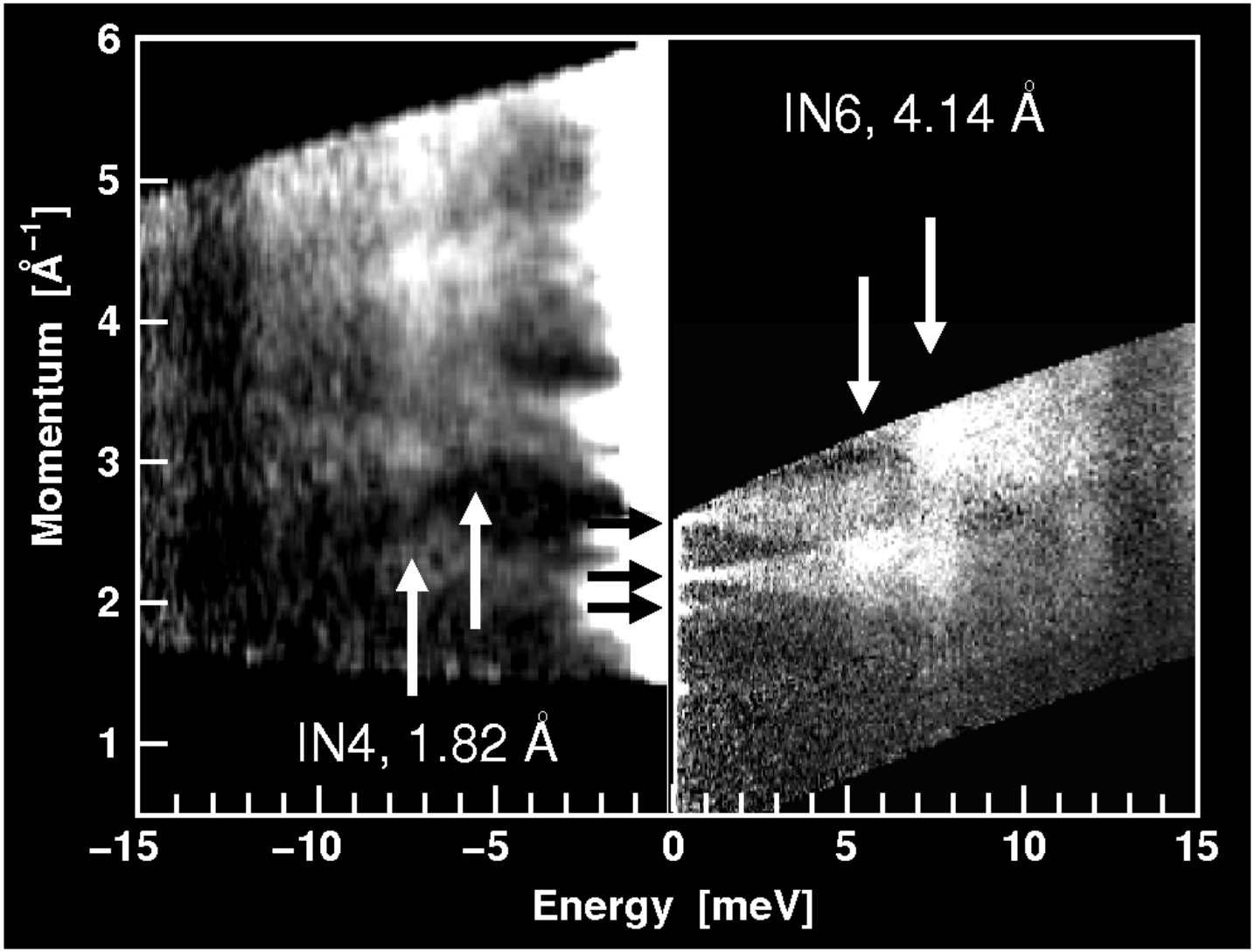
ID28@ESRF

dE = 1.5 meV

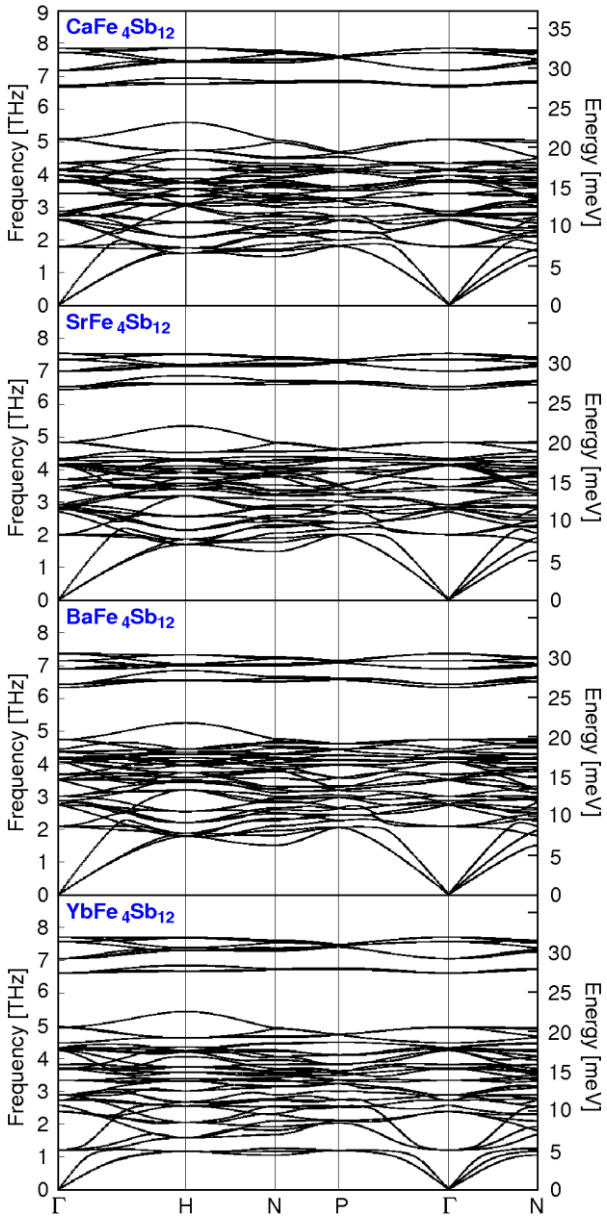
Plus any other experimental technique that helps to verify/improve calculations !

Phase Space Coverage by INS and IXS Spectrometers

S(Q,w) of $LaFe_4Sb_{12}$



Ab Initio Powder Averaged Lattice Dynamics



All energy and force calculations performed with Vienna Ab-initio Simulation Package (VASP DFT) with PAW-GGA (LDA) potentials.

All lattice dynamics phonon calculations performed with the 'direct method' implemented in the package PHONON.

Powder Average Lattice Dynamics (PALD) :

Random generation of Q – points in the spherical coordinate space $(r,2\theta,\varphi)$ matching the natural sampling of the phase space by the time of flight neutron scattering technique.

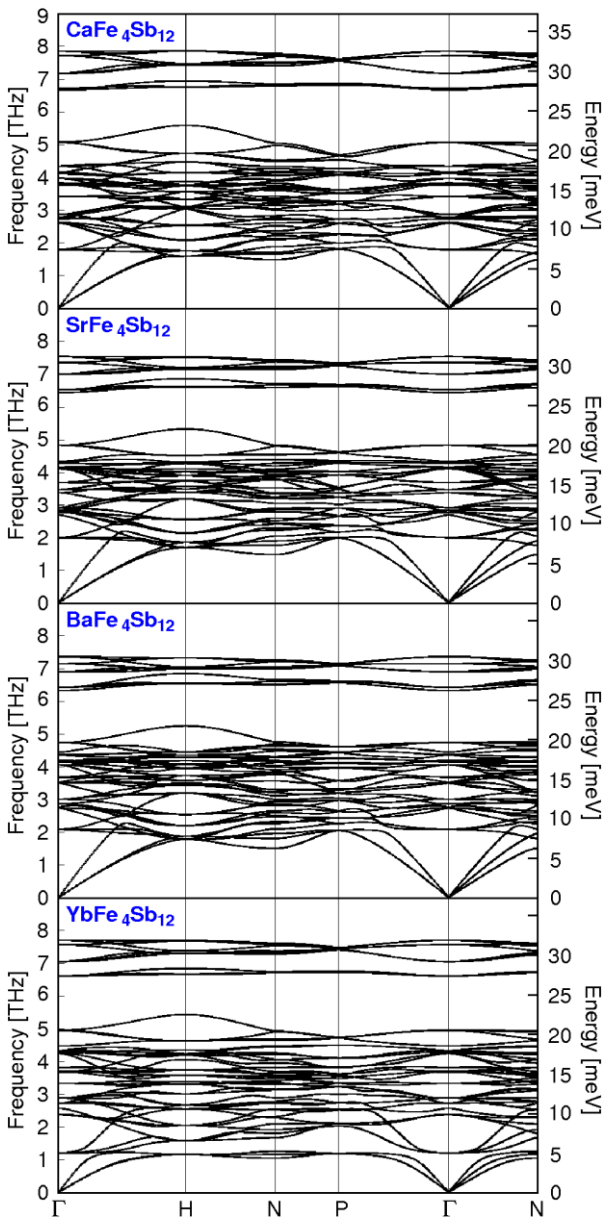
Calculation effort depends on the Q resolution required.

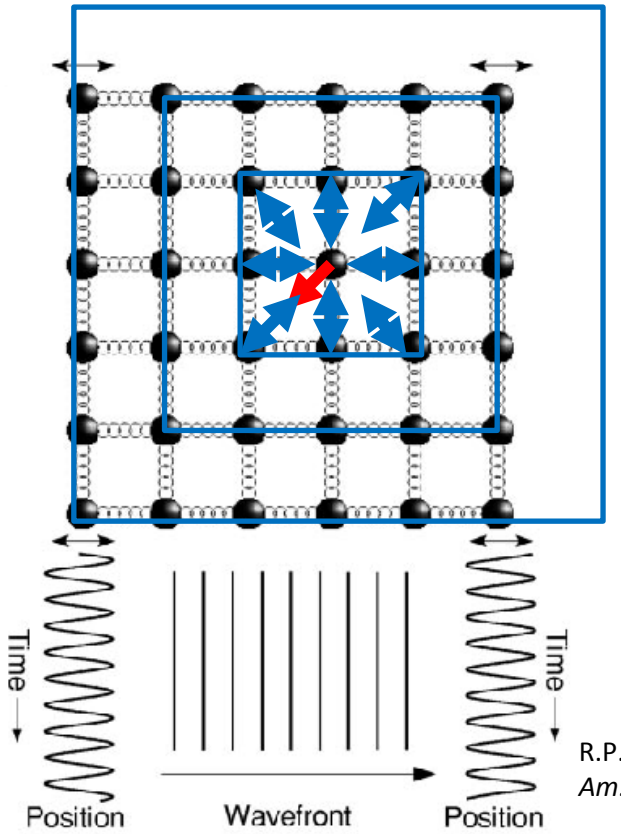
Neutron and x ray specific signals and partial (self- and cross-correlations) contributions can be calculated.

Labor intensive work.

M.M. Koza et al., *Phys. Rev. B 84, 014306 (2011)*

Ab Initio Powder Averaged Lattice Dynamics





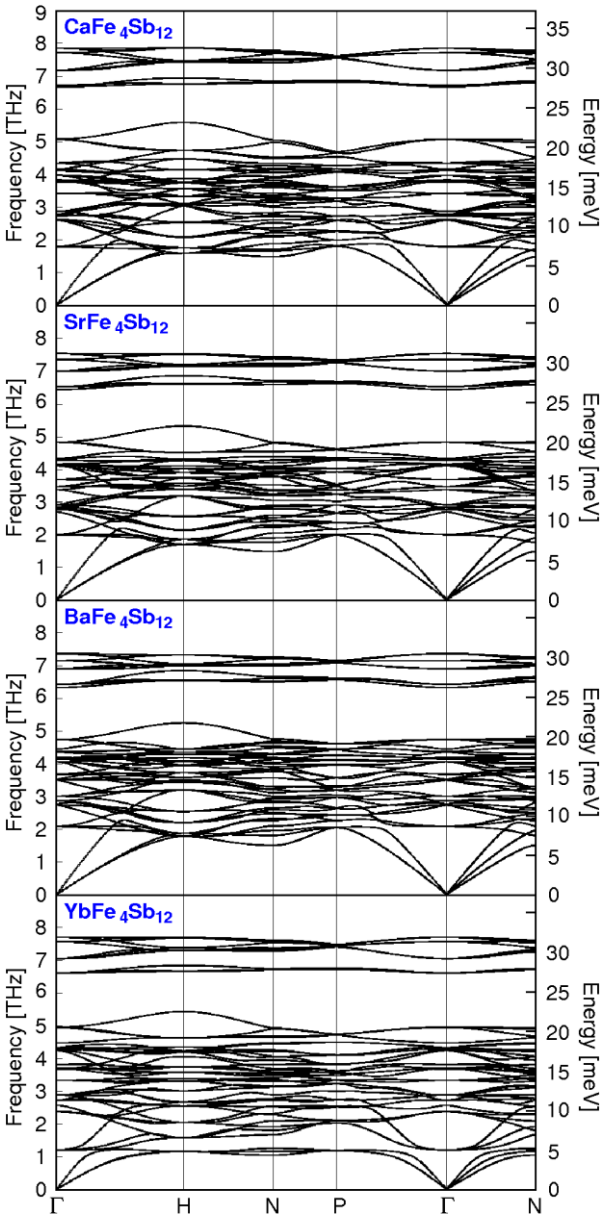
R.P. Hermann et al., *Am. J Phys.* **73**, 110, (2005)

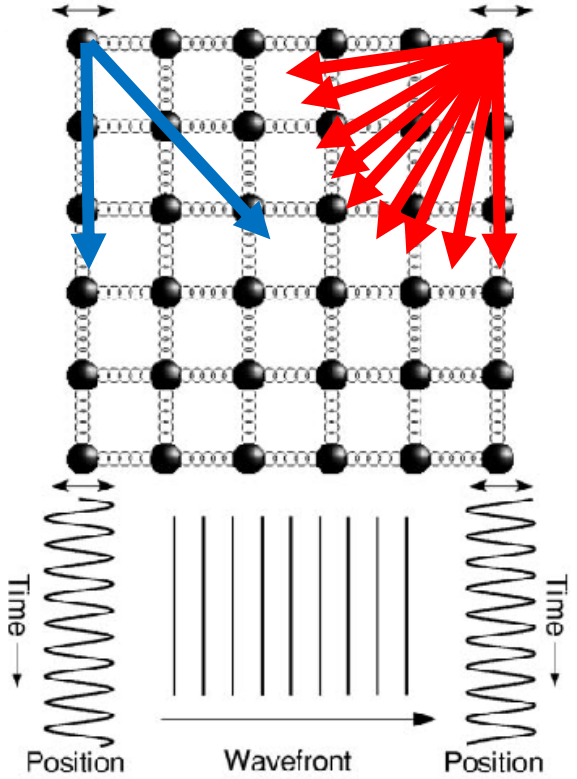
Displacement of symmetry non-equivalent atoms.

Calculation of forces - Hellmann-Feynman theorem.

Precision is dependent on the size of the simulation box size !

Ab Initio Powder Averaged Lattice Dynamics



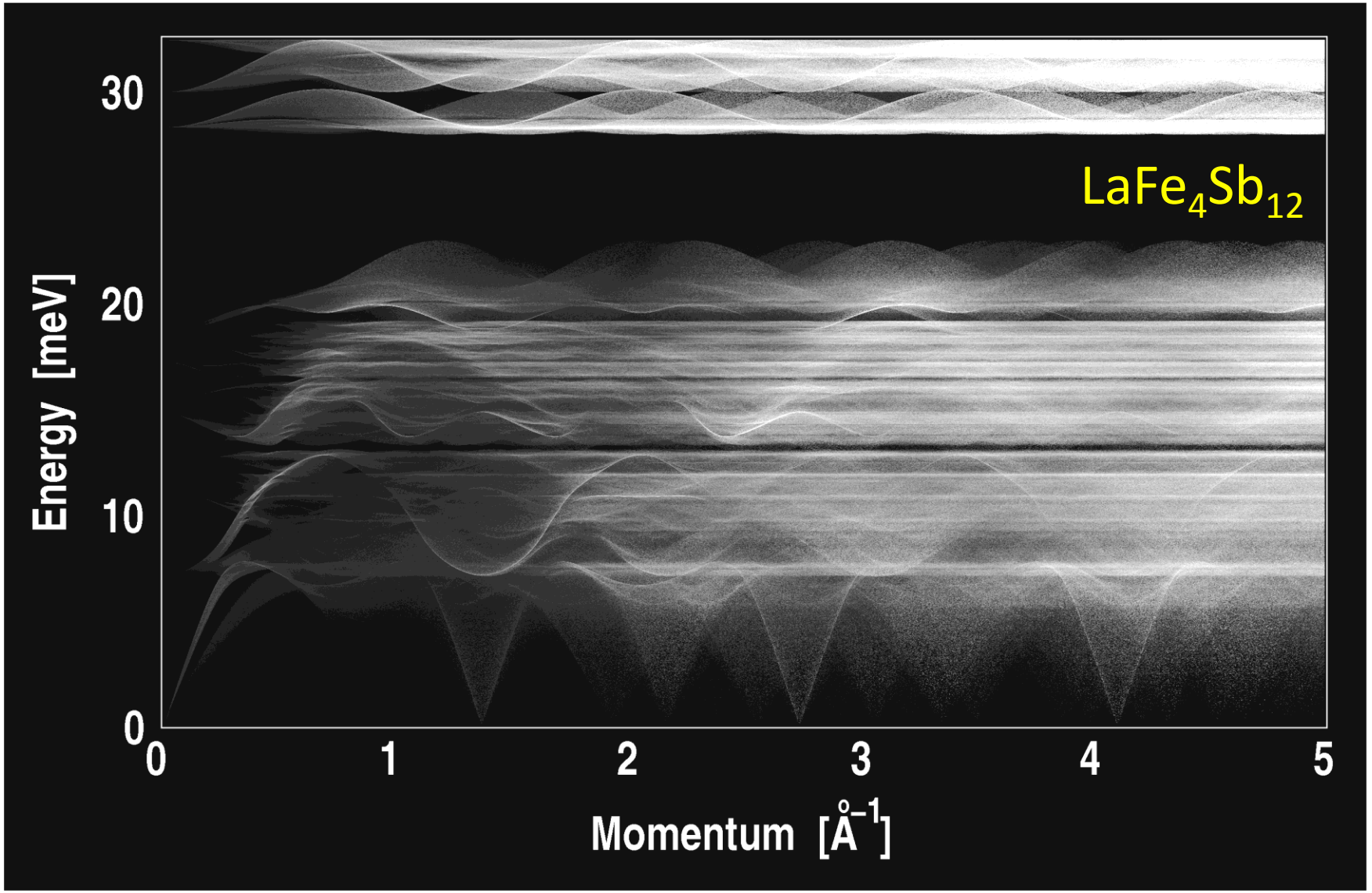


R.P. Hermann et al., *Am. J Phys.* **73**, 110, (2005)

Standard lattice dynamics calculation is performed along high symmetry directions in reciprocal space.

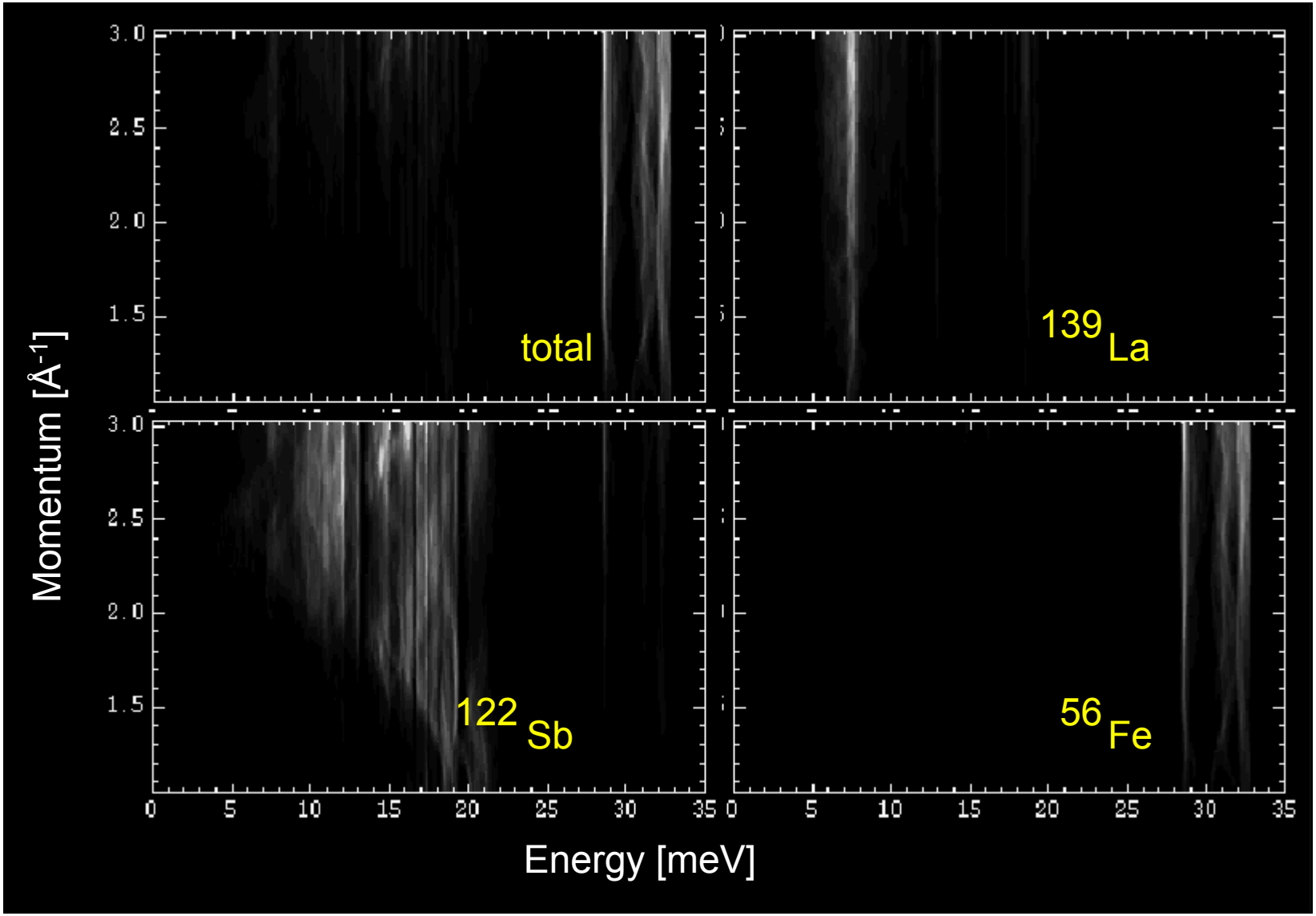
Powder Averaged Lattice Dynamics calculates the dispersion in any possible direction at random.

Ab Initio Powder Averaged Lattice Dynamics



Total S(Q,w) of $LaFe_4Sb_{12}$, 350 - 400 Gbyte of data plus 50 Gbyte for each partial signal

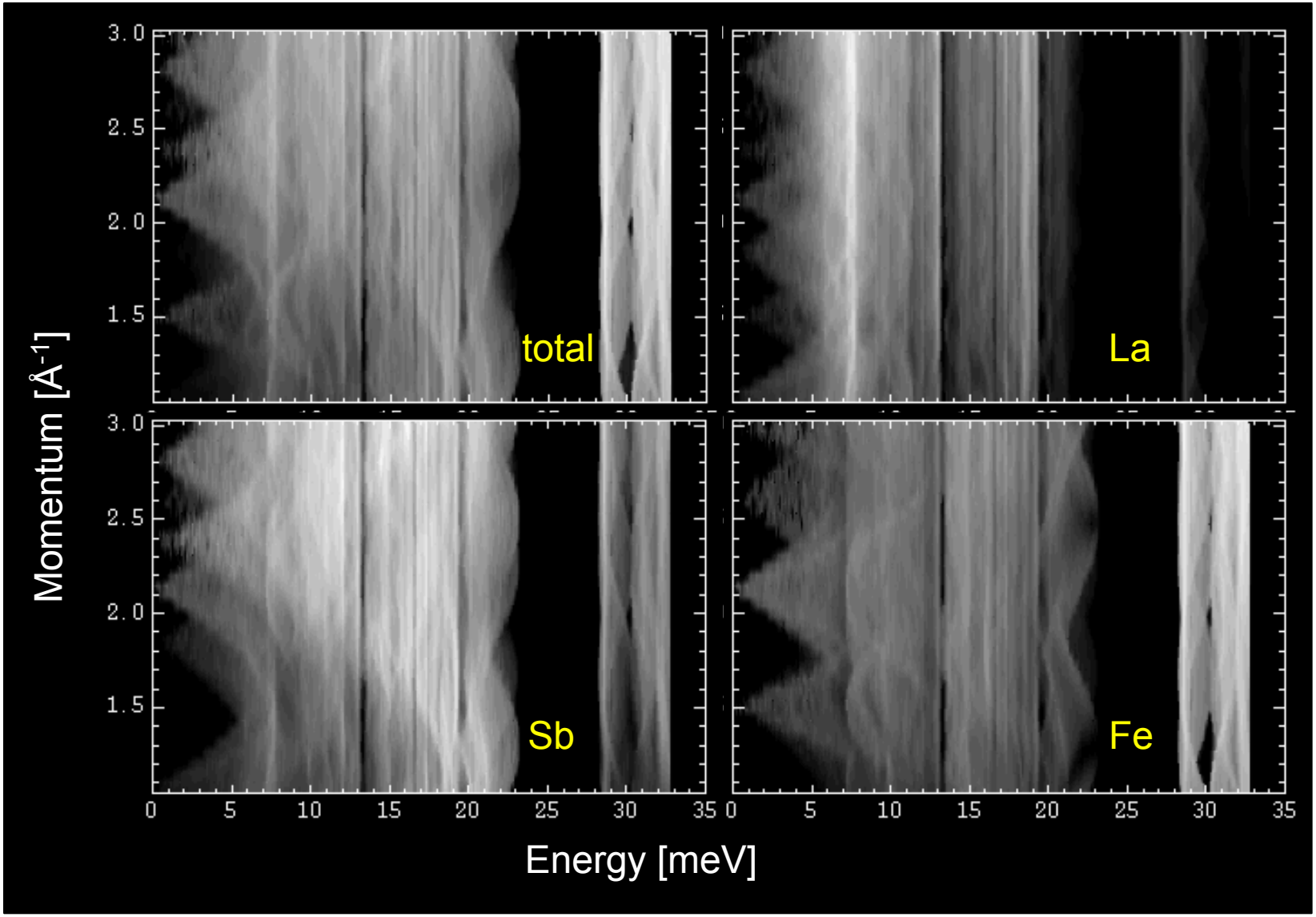
First Principle Powder Averaged Lattice Dynamics



Linear intensity scale !

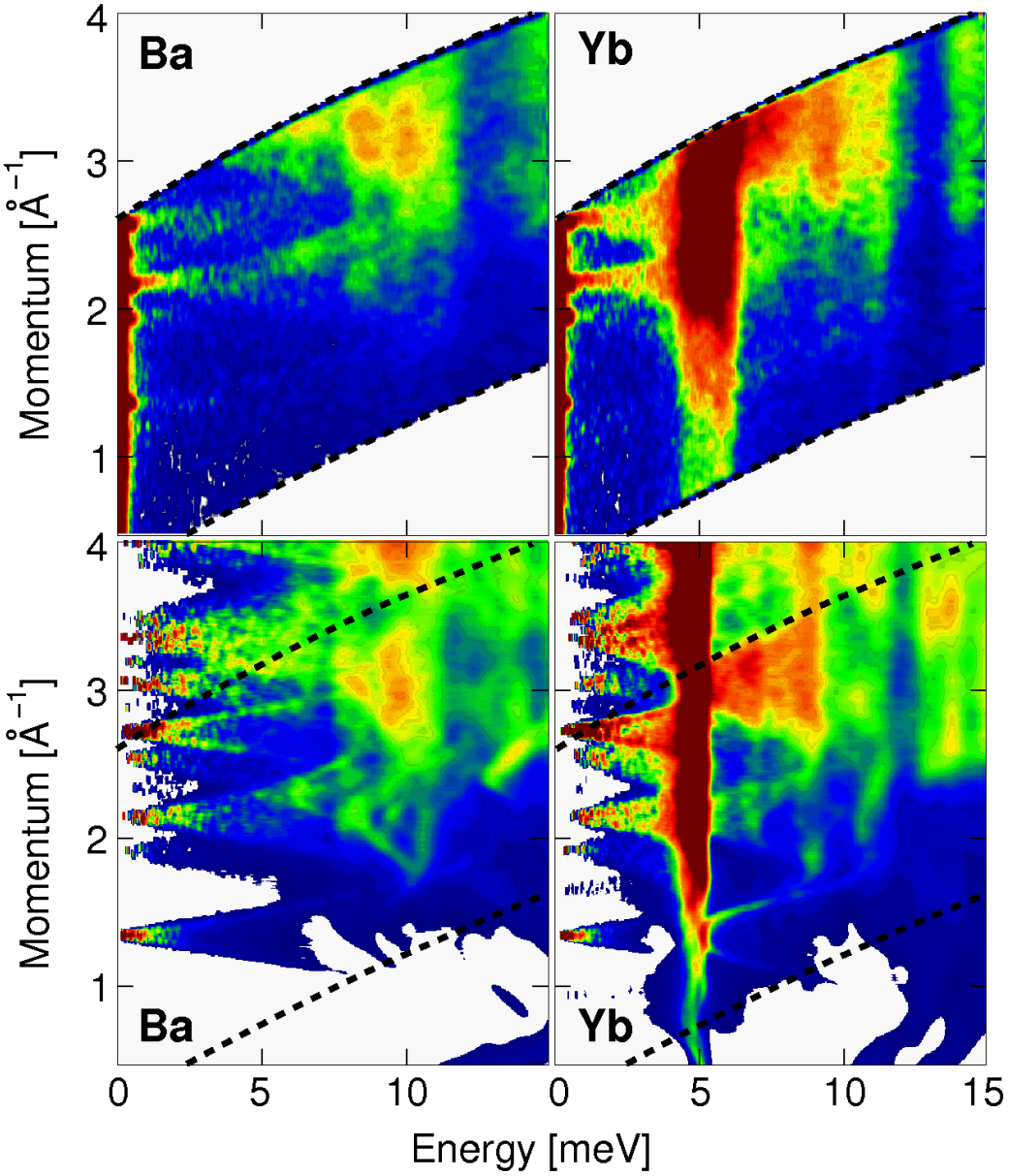
$$\omega \propto \sqrt{(K/M)} \qquad S(Q,\omega) \propto \sigma/M$$

First Principle Powder Averaged Lattice Dynamics



Logarithmic intensity scale !

Powder INS from IN6@ILL and PALD

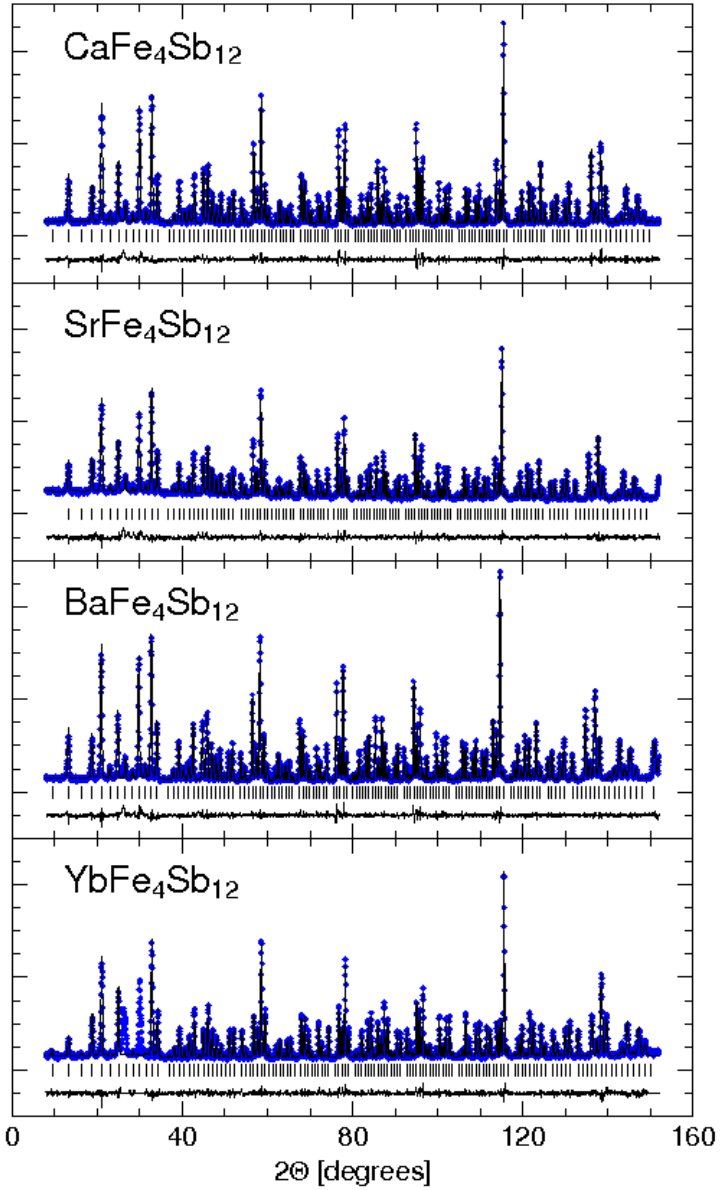


S(Q,w) of MFe_4Sb_{12}

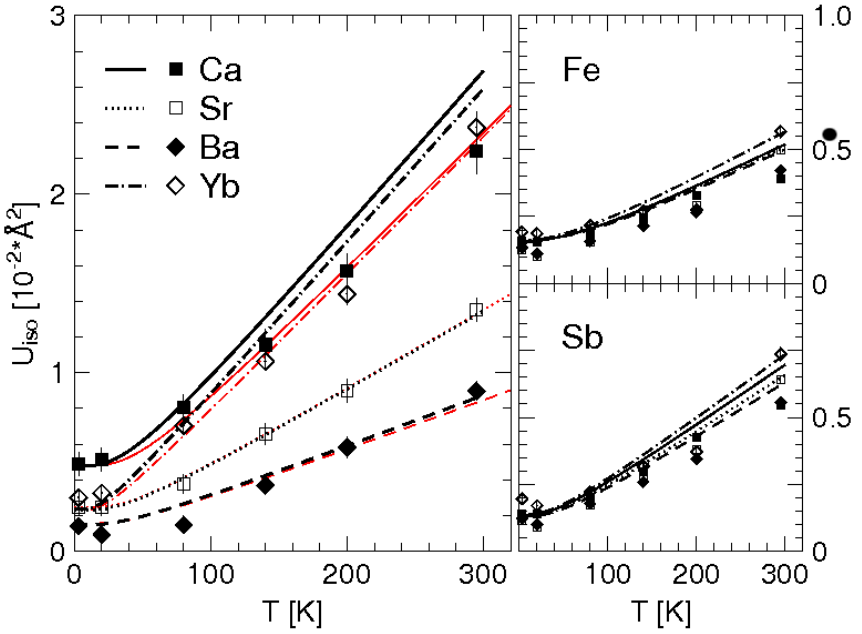
	σ_{tot}	A.M.U.	S.P.
Ca	2.8	40.1	7.0
Sr	6.3	87.6	7.2
Ba	3.4	137.3	2.5
La	9.7	138.9	7.0
Ce	2.9	140.1	2.1
Yb	23.4	174.0	13.5
Fe	11.6	55.9	20.8
Sb	3.9	121.8	3.2

S.P. = σ_{tot} /A.M.U. * 100

Diffraction Results and Temperature Effects



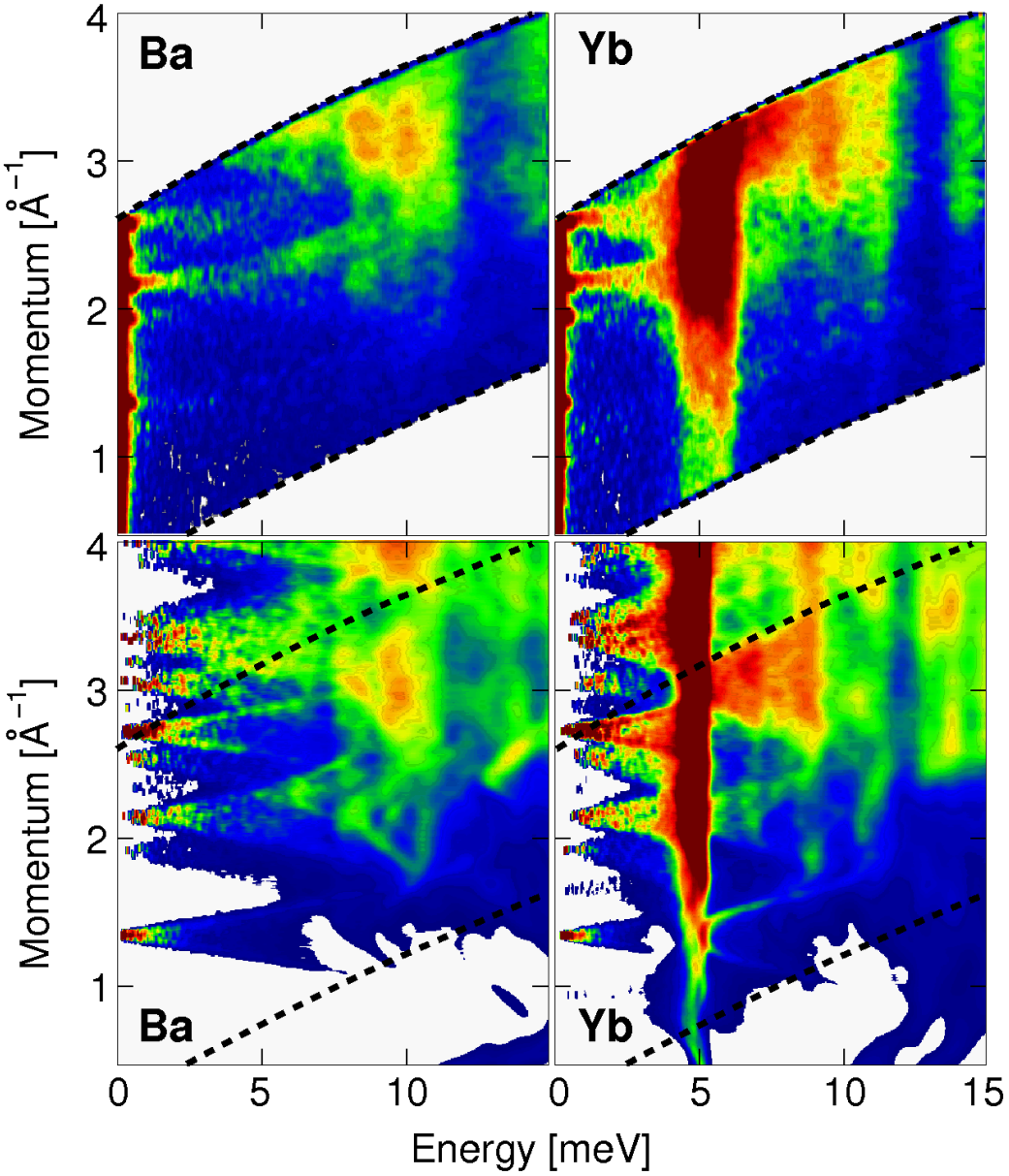
Mean Square Displacement :



Lattice Parameters and Ionic Radii in Angstrom :

	Ca	Sr	Ba	Yb
A.I. calc.	9.19	9.21	9.24	9.18
T = 3 K	9.14	9.16	9.18	9.13
Radius	1.26	1.40	1.56	1.28

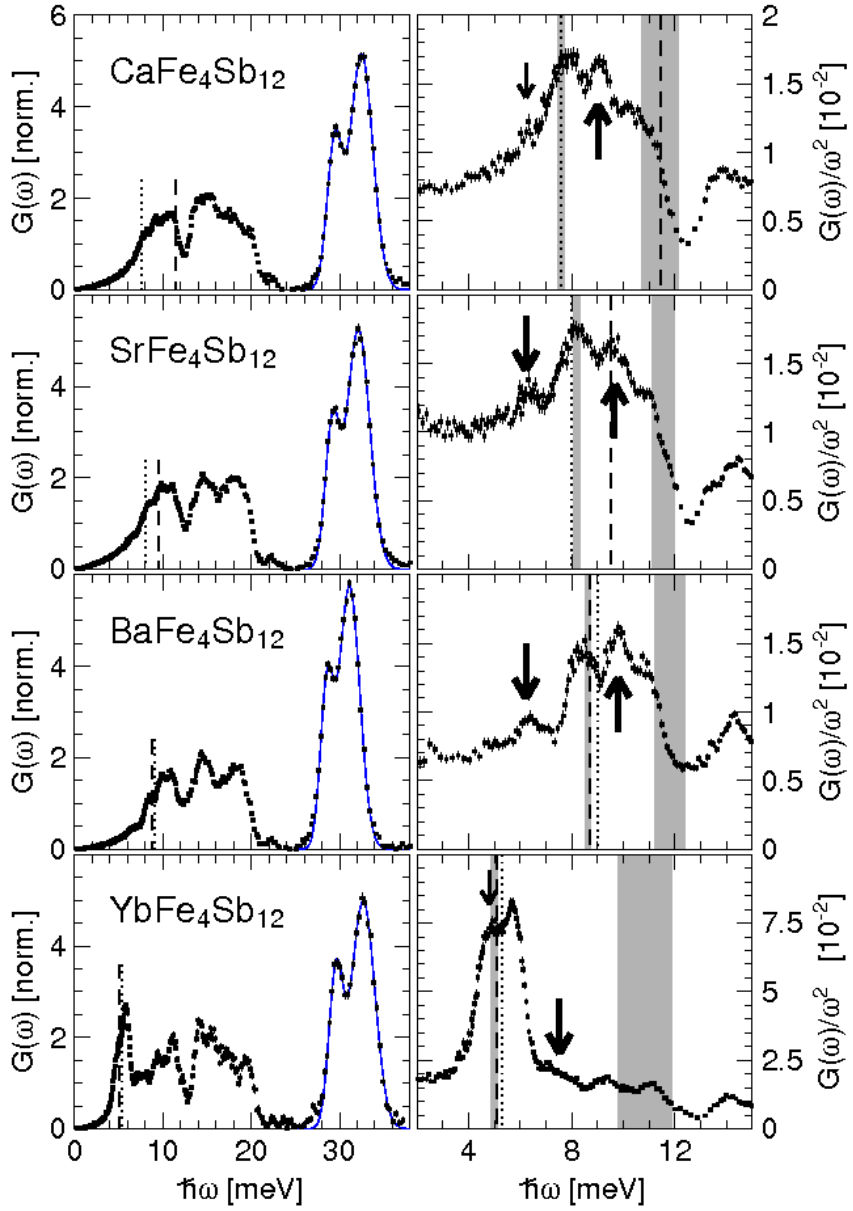
Powder INS from IN6@ILL and PALD



Generalized Density of States from momentum integrated signal :

incoherent approximation

Generalized Density of States from IN6@ILL

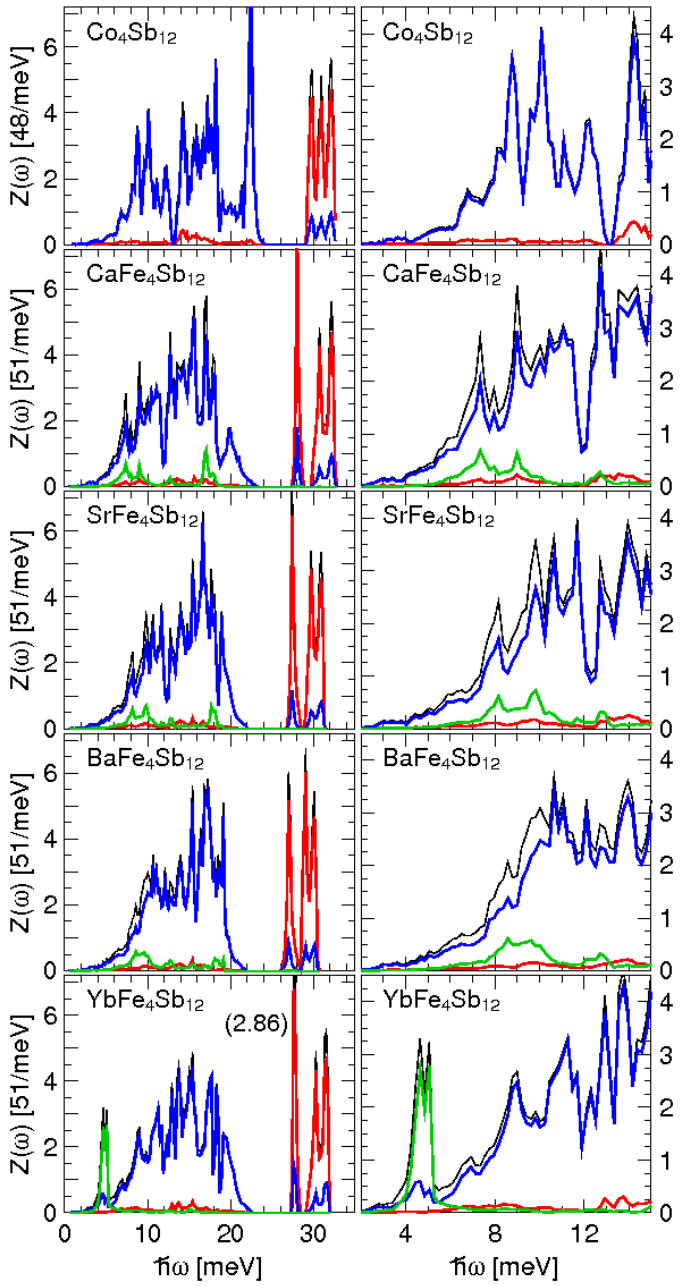


Characteristic Energies in meV :

	Ca	Sr	Ba	Yb
G(ω)	-	6.5	6.5	4.9
	-	-	-	5.7
	8.0	8.2	8.4	7.5
	9.2	9.9	9.9	9.4
	11.5	11.1	10.9	11.1
U(r)	9.6	8.8	8.8	4.6
MSD	10.8	9.6	9.7	5.2
c(T)*	7.6	8.0	9.0	5.3

*W. Schnelle et al., *PRB* 77, 094421 (2008)

Phonon Density of States from Lattice Dynamics



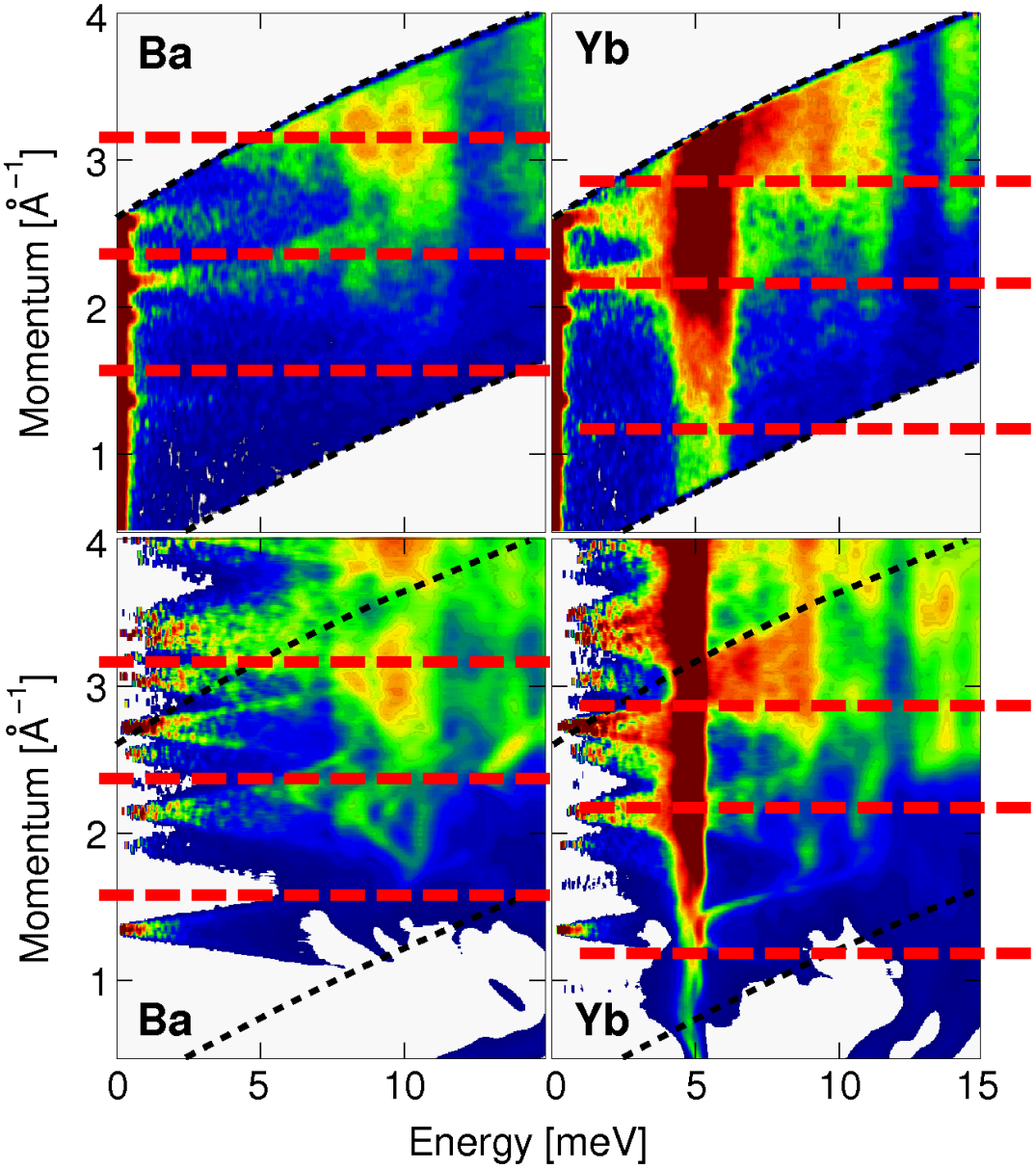
Characteristic Energies in meV :

	Ca	Sr	Ba	Yb
G(ω)	-	6.5	6.5	4.9
	-	-	-	5.7
	8.0	8.2	8.4	7.5
	9.2	9.9	9.9	9.4
	11.5	11.1	10.9	11.1
U(r)	9.6	8.8	8.8	4.6
MSD	10.8	9.6	9.7	5.2
c(T)*	7.6	8.0	9.0	5.3

*W. Schnelle et al., *PRB* 77, 094421 (2008)

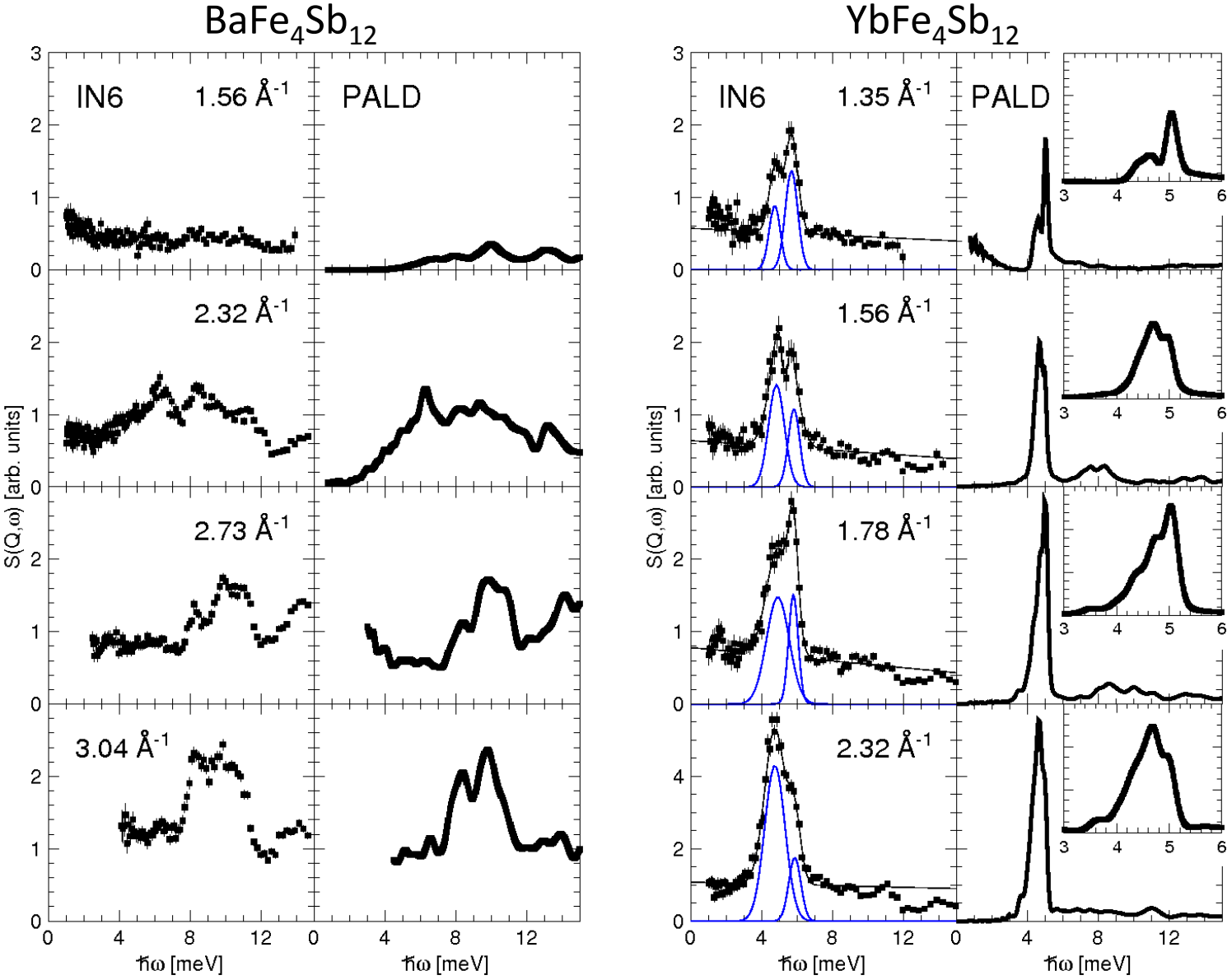
Strong localization present in MFe_4Sb_{12} with M = La, Eu, Nd, Yb, Tl .

Powder INS from IN6@ILL and PALD

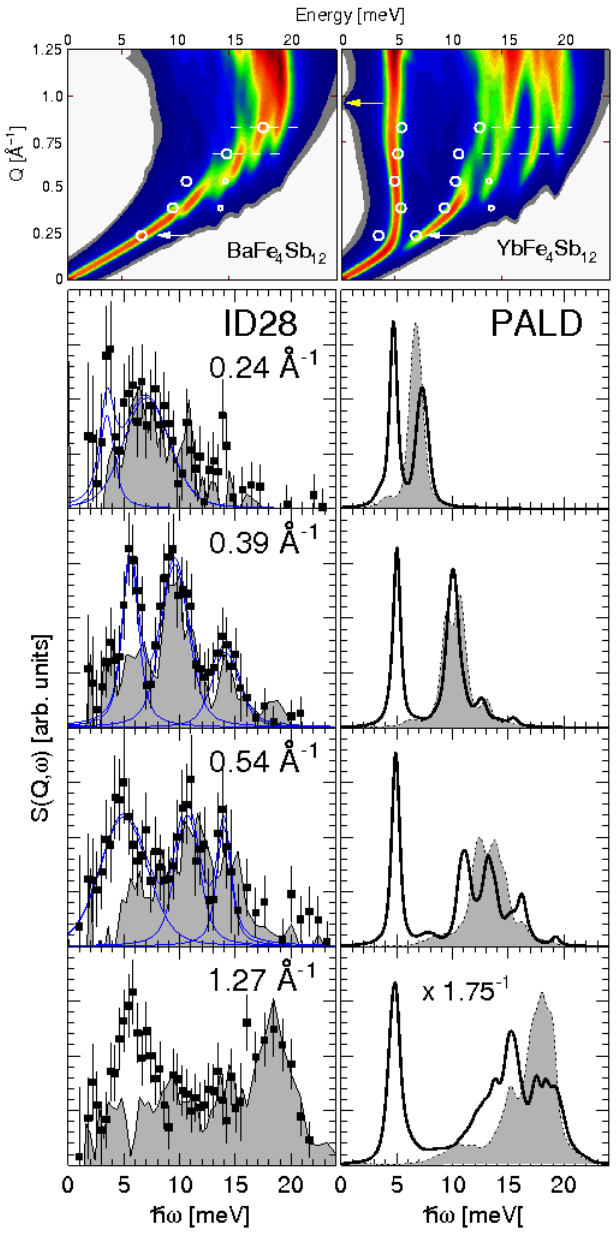


Spectra at constant momentum Q.

Dynamic Structure Factor from IN6@ILL and PALD



Dynamic Structure Factor from ID28@ESRF and PALD



Mode energies in meV :

	$YbFe_4Sb_{12}$		$BaFe_4Sb_{12}$
Q	E1	E2	E1
2.42	3.5(1)	7.0(4)	6.8(2)
3.92	5.6(1)	9.6(1)	9.8(1)
5.36	5.0(1)	10.7(1)	11.1(3)
6.85	5.3(2)	11.0(5)	14.9(4)
8.27	5.8(4)	13(2)	18.3(2)

Longitudinal velocity of sound :

$YbFe_4Sb_{12}$: 4400(250) m/sec

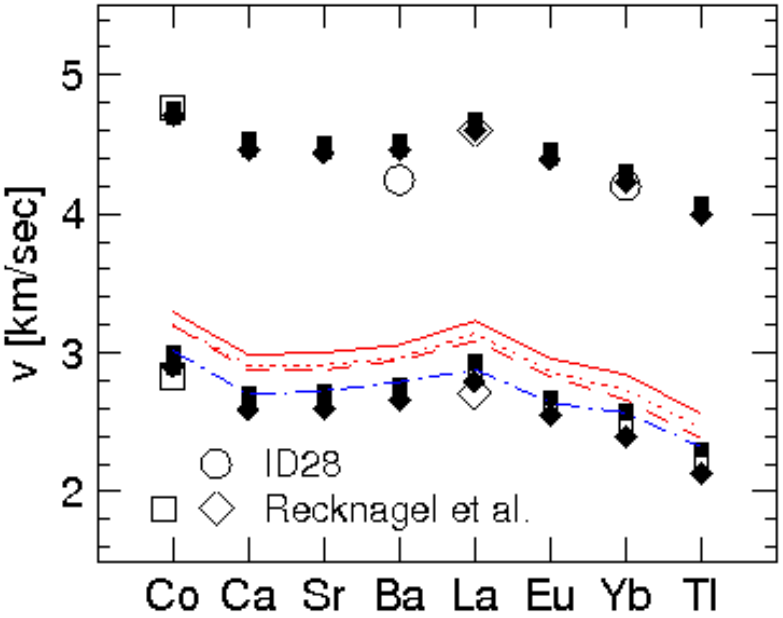
$BaFe_4Sb_{12}$: 4270(130) m/sec

Scattering power : Z^2

Absorption : Z^4

PALD and Material Properties

Velocity of sound of Co_4Sb_{12} and MFe_4Sb_{12}



	C_{11}/GPa	C_{44}/GPa	T_{debye}/K
$^{+}Co_4Sb_{12}$	164	59	319
$^{*}Co_4Sb_{12}$		61	327
$^{*}CaFe_4Sb_{12}$	132	49	300
$^{*}LaFe_4Sb_{12}$		57	315
$^{+}LaFe_4Sb_{12}$	162	58	310

$^{+}$V.Keppens et al., Nature, 1998

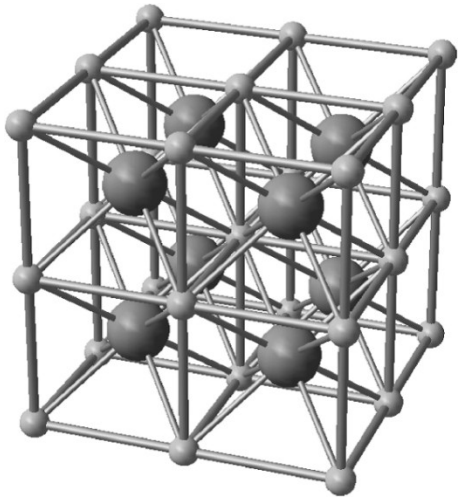
*L.Zhang et al., Mat.Sci.&Eng. B, 2010

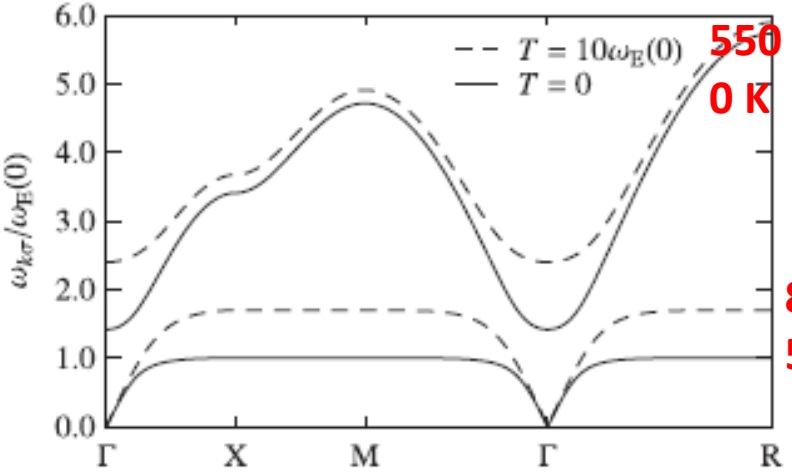
Material properties : elastic constants, bulk and Young's moduli and Poisson ratio :

	d [Å]	$\bar{v}_{DL}$ [m/sec.]	T_{DL} [K]	v_t [m/sec]	v_l [m/sec]	T_{Debye} [K]	c_{11} [GPa]	G [GPa]	E [GPa]	ν	B [GPa]
Co	9.096	3094	322	2929(45)	4719(20)	336(4)	167(1)	64(2)	152(3)	0.19(1)	81(1)
Ca	9.180	2679	278	2637(44)	4487(31)	307(4)	149(2)	51(2)	127(3)	0.24(1)	80(1)
Sr	9.210	2707	281	2646(50)	4462(30)	307(4)	150(2)	53(2)	130(4)	0.23(1)	80(1)
Ba	9.240	2769	288	2703(47)	4479(28)	312(4)	154(2)	56(2)	136(4)	0.21(1)	80(1)
La	9.169	2857	297	2856(58)	4632(33)	331(5)	169(2)	64(3)	153(5)	0.19(1)	83(1)
Eu	9.172	2659	276	2603(53)	4418(28)	303(4)	154(2)	54(2)	132(4)	0.23(1)	83(1)
Yb	9.176	2541	264	2475(72)	4263(30)	289(6)	145(2)	49(3)	122(5)	0.25(2)	80(2)
Tl	9.211	2300	239	2216(70)	4034(29)	259(6)	131(2)	39(2)	101(5)	0.28(2)	78(2)

Beyond the Harmonic Approximation

A. Yamakage et al., *J. Phys. Soc. Japan* 78, 064602 (2009)





550 K

0 K

8 meV @ 550 K

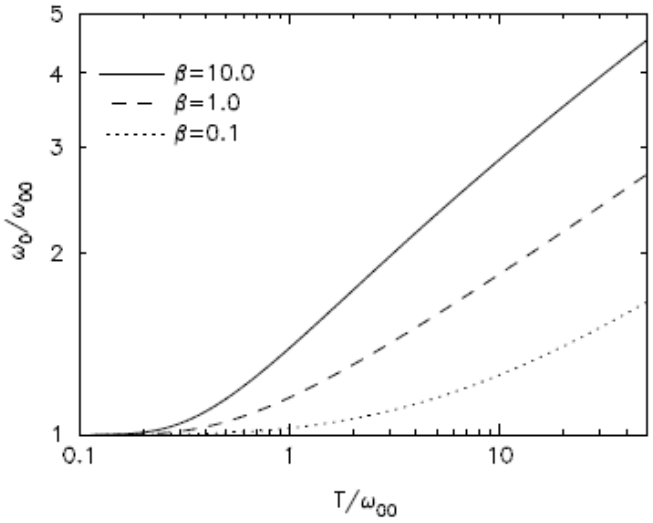
5 meV @ 0 K

T. Dahm and K. Ueda, *PRL* 99, 187003 (2007)

Temperature dependence of guest-dominated modes

$$U(x) \approx A \cdot x^2 + B \cdot x^4$$

$$\beta \propto B/M^2/\omega_{oo}{}^3$$

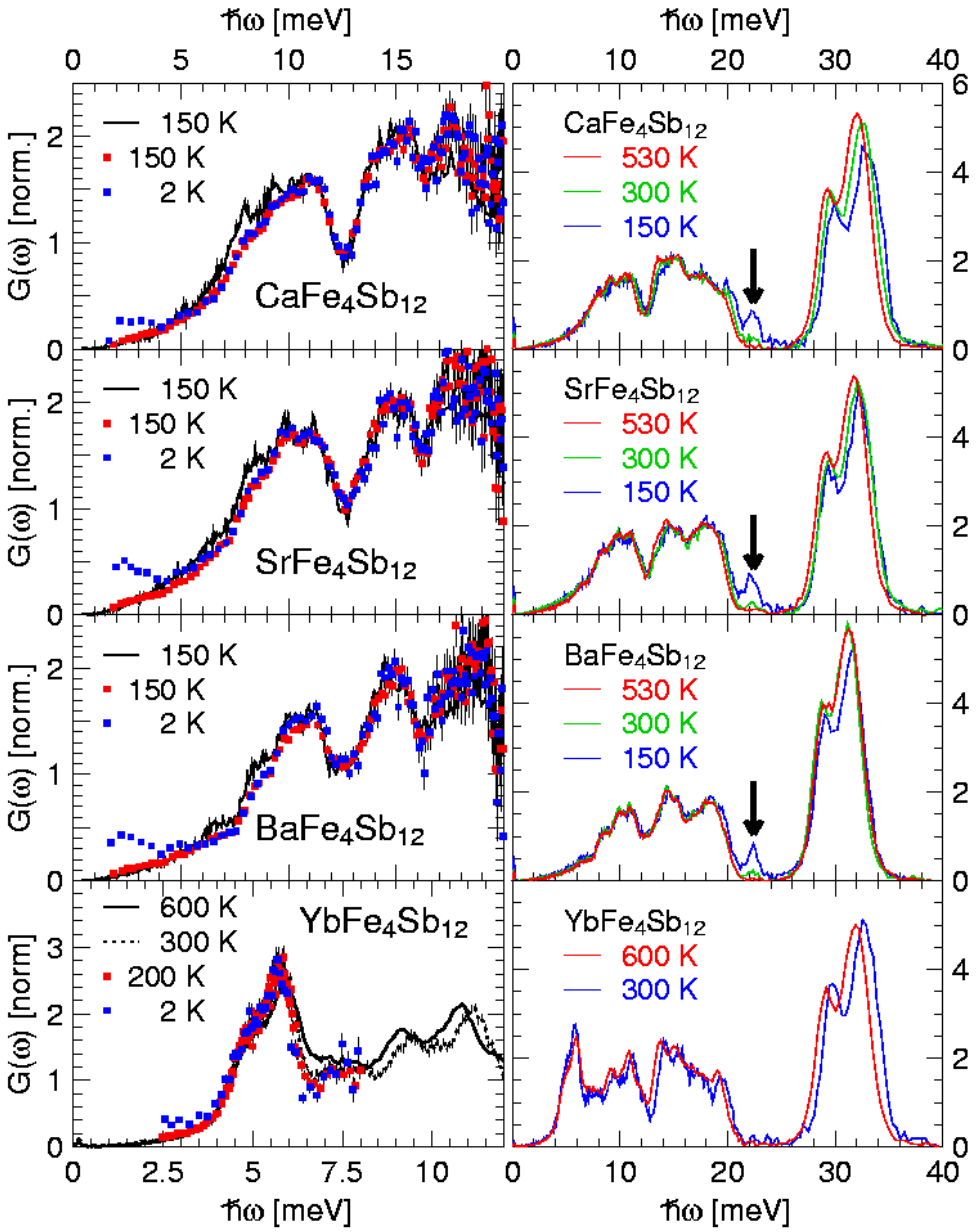


10

1.0

0.1

Beyond the Harmonic Approximation



normal modes

$$\frac{\partial^2 U(x)}{\partial x^2} = \text{const.} \qquad \frac{\Delta\omega}{\Delta T} = 0$$

thermal expansion

$$\frac{\partial^3 U(x)}{\partial x^3} < 0 \qquad \frac{\Delta\omega}{\Delta T} < 0$$

rattling term

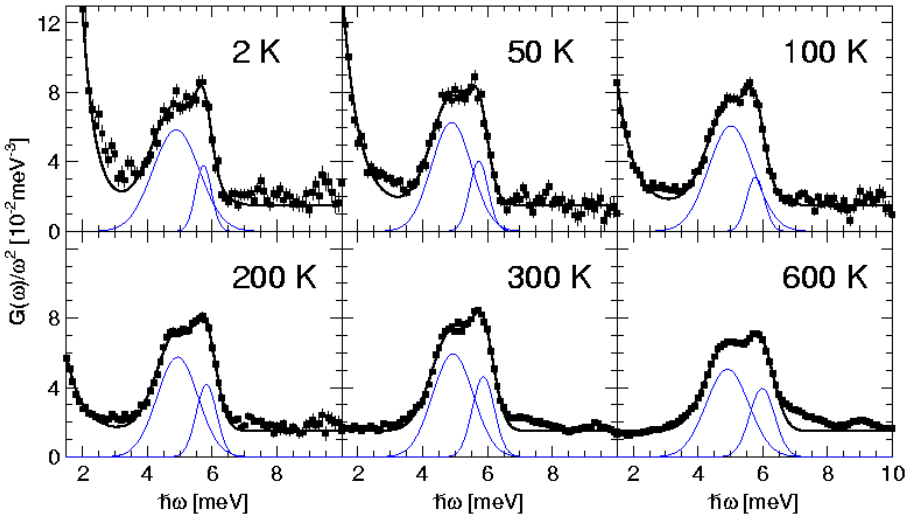
$$\frac{\partial^4 U(x)}{\partial x^4} > 0 \qquad \frac{\Delta\omega}{\Delta T} > 0$$

Energy shift between 300 and 550/600 K, ionic radii of cations and lattice parameters at 2 K

	Ca	Sr	Ba	Yb
Δω/meV	0.6	0.2	0.1	0.8
R/Å	1.26	1.40	1.56	1.28
d/Å	9.14	9.16	9.18	9.13

Beyond the Harmonic Approximation

Temperature dependence of Yb - dominated modes in $YbFe_4Sb_{12}$:

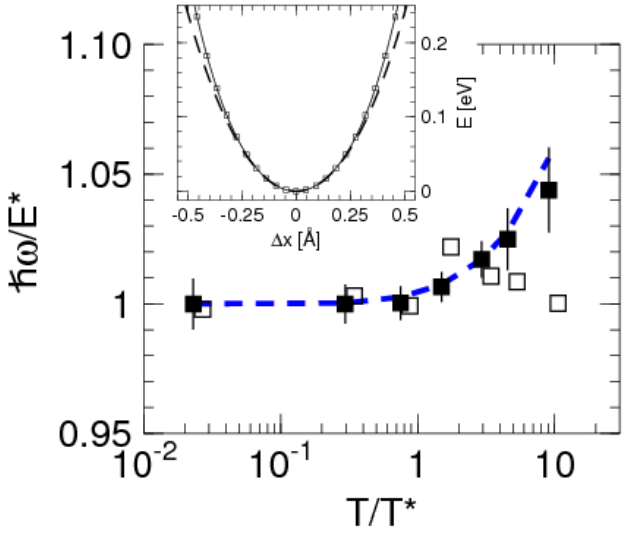


Relative changes of characteristic energies :

$A = 0.88$ eV/A^2

$B = 1.16$ eV/A^4

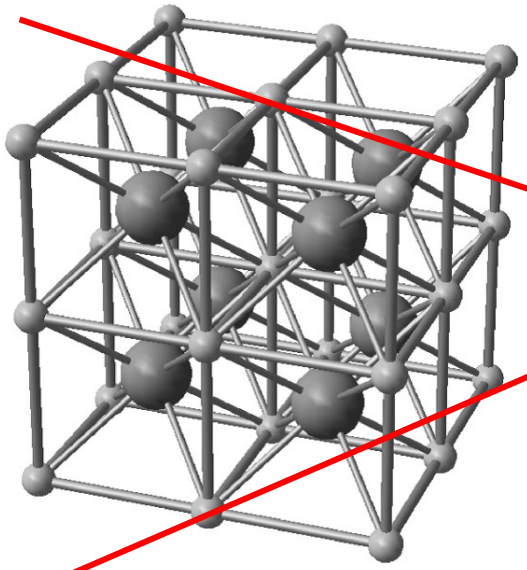
$\beta = 0.013(3)$



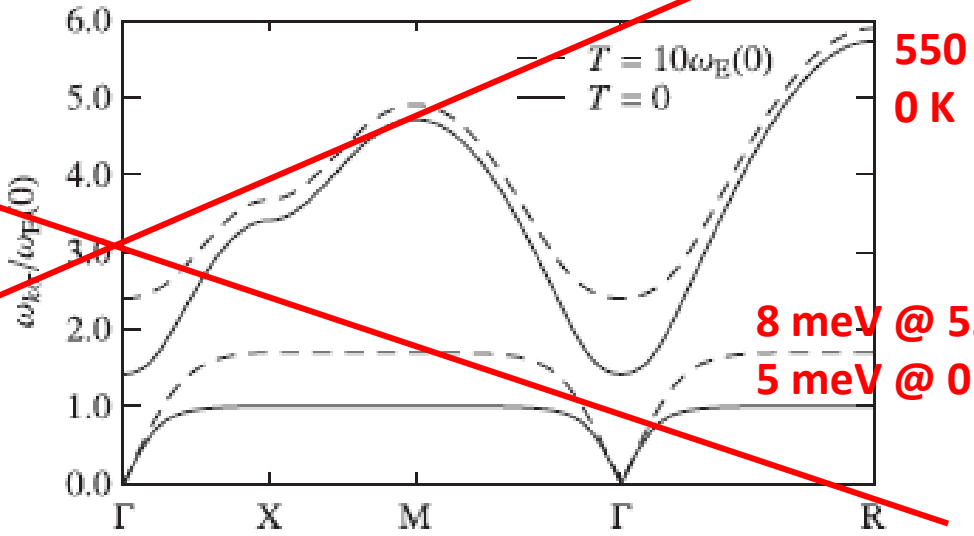
$$\frac{\Delta\omega}{\Delta T} > 0$$

Beyond the Harmonic Approximation

Modelling anharmonicity in filled skutterudites :



A. Yamakage et al., *J. Phys. Soc. Japan* 78, 064602 (2009).



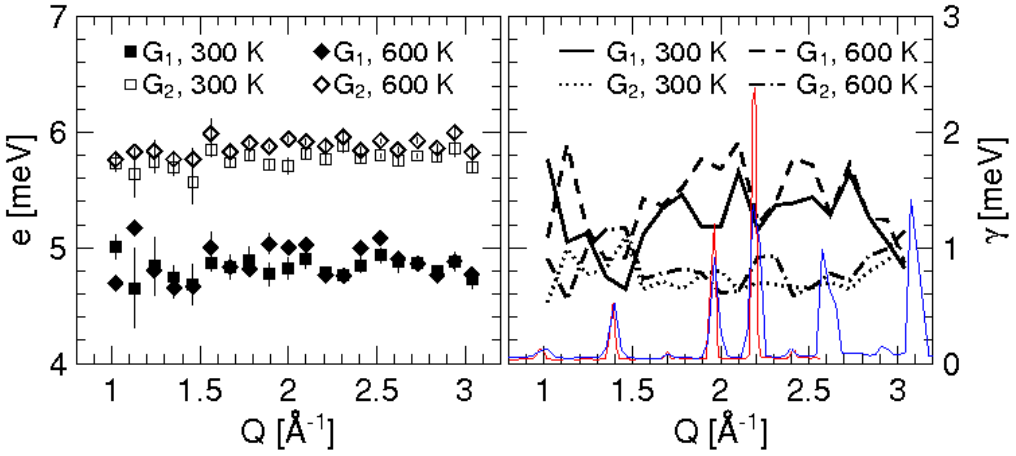
550 K

0 K

8 meV @ 550 K

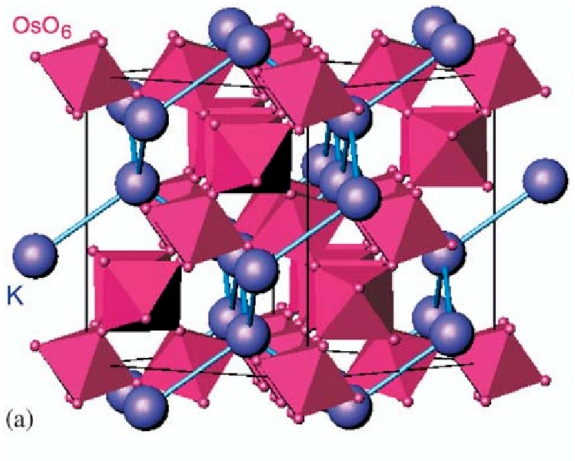
5 meV @ 0 K

Q-resolved temperature dependence of low-energy modes derived from IN6@ILL data :

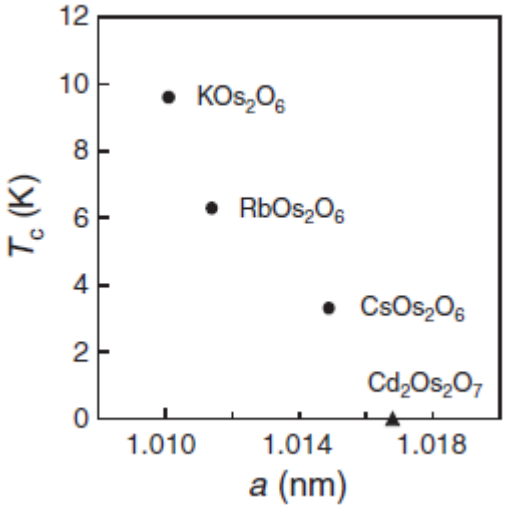


Low-Energy Modes and Superconductivity

Beta – Pyrochlores : MOs_2O_6 , M = K, Rb, Cs, space group: Fd-3m



Shigeki YONEZAWA*, Yuji MURAOKA and Zenji HIROI
Journal of the Physical Society of Japan
Vol. 73, No. 7, July, 2004, pp. 1655–1656



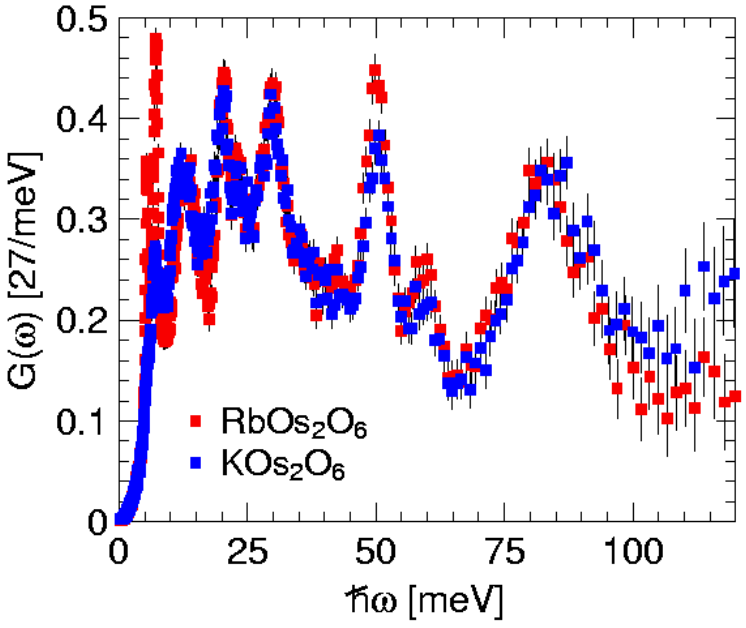
PHYSICAL REVIEW B 78, 104307 (2008)

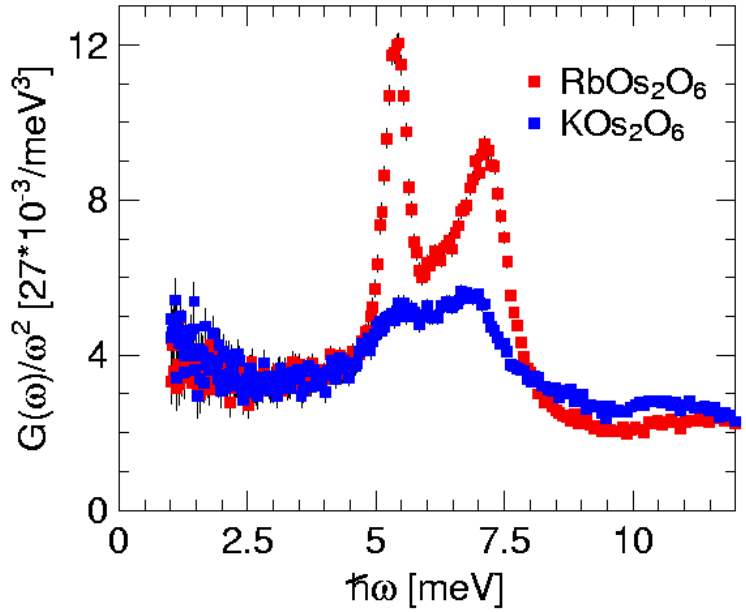
Generalized density-of-states and anharmonicity of the low-energy phonon bands from coherent inelastic neutron scattering response in the pyrochlore osmates AOs_2O_6 (A=K, Rb, Cs)

Hannu Mutka,* Michael Marek Koza, and Mark Robert Johnson
Institut Laue Langevin, 6 Rue Jules Horowitz, B.P. 156, 38042 Grenoble Cedex 9, France

Zenji Hiroi, Jun-Ichi Yamaura, and Yohei Nagao
Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
(Received 22 July 2008; published 30 September 2008)

Low-Energy Modes and Superconductivity



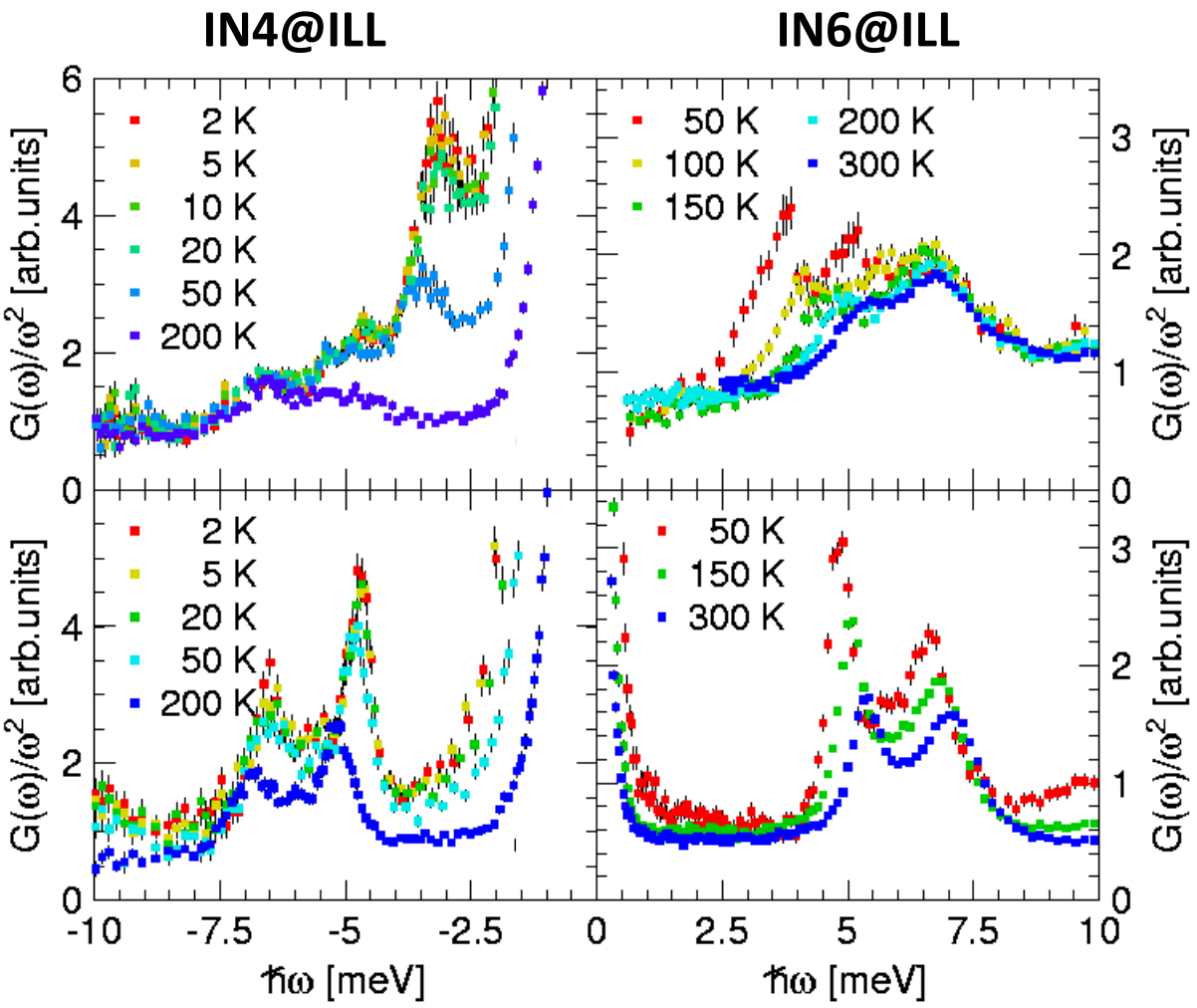


INS contrast experiment at IN6@ILL

	σ_{tot} [barns]	A.M.U.	S.P
Os	14.7	190.2	7.7
O	4.23	16.0	26.4
K	1.96	39.1	5.0
Rb	6.8	85.5	8.0

H. Mutka et al., *Phys. Rev.* B 78, 104307 (2008)

Low-Energy Modes and Superconductivity

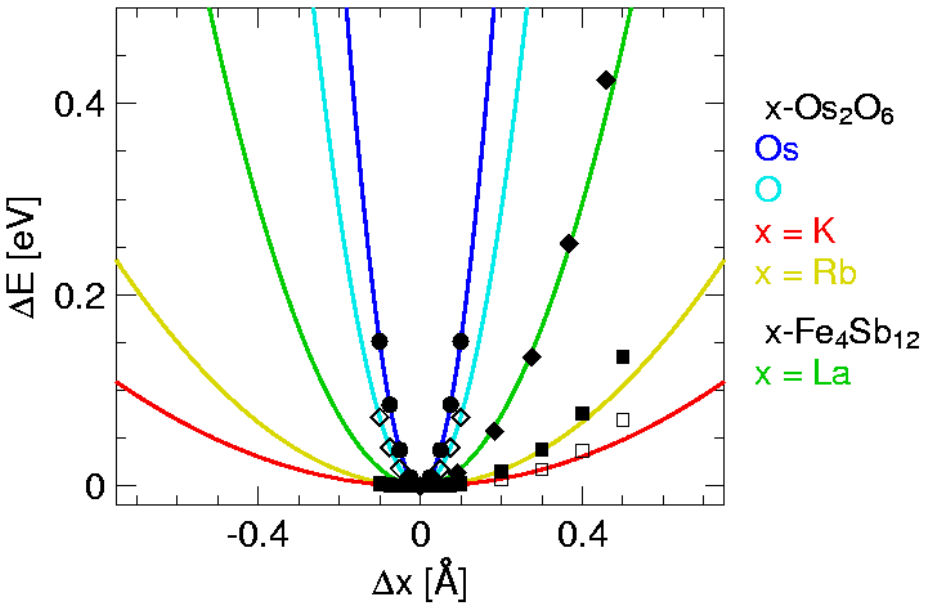


T. Dahm and K. Ueda, *PRL* 99, 187003 (2007)
matching resistivity data :

β = 6.3

Restoring Forces from Ab Initio Calculations

Potentials calculated *ab initio*

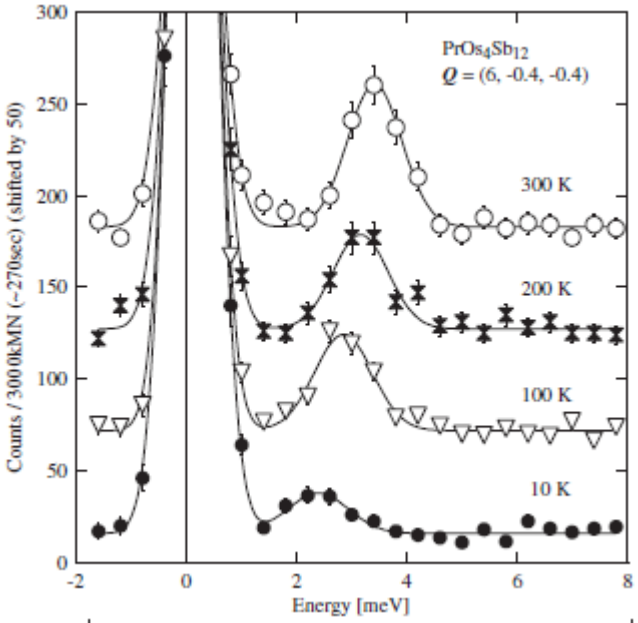


Restoring forces are non-isotropic in particular for Sb in MFe_4Sb_{12}.

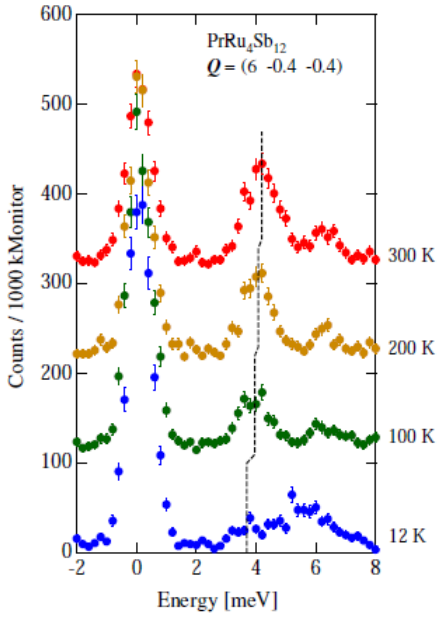
Restoring Forces

	K [eV/Å^2]
Os	15.1
O	7.2
K	0.2
Rb	0.4
Ca	0.9
Sr	1.6
Ba	2.5
La	2.0
Yb	0.9
Fe	5.1-5.4
Sb	2.4-5.0

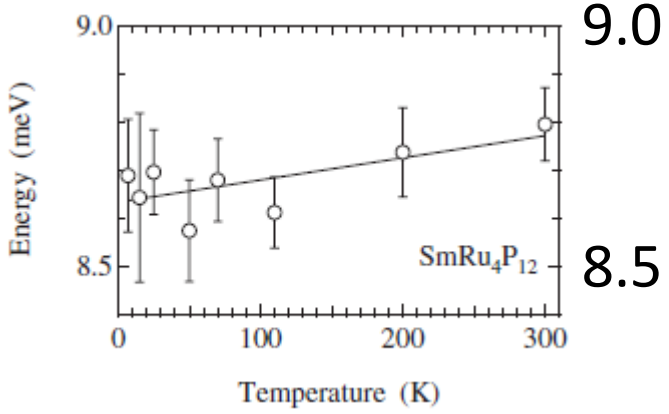
Anharmonicity in Other Skutterudite Compounds ?



$PrOs_4Sb_{12}$ by K.Iwasa et al.
Physica B 378-380, 194, (2006)

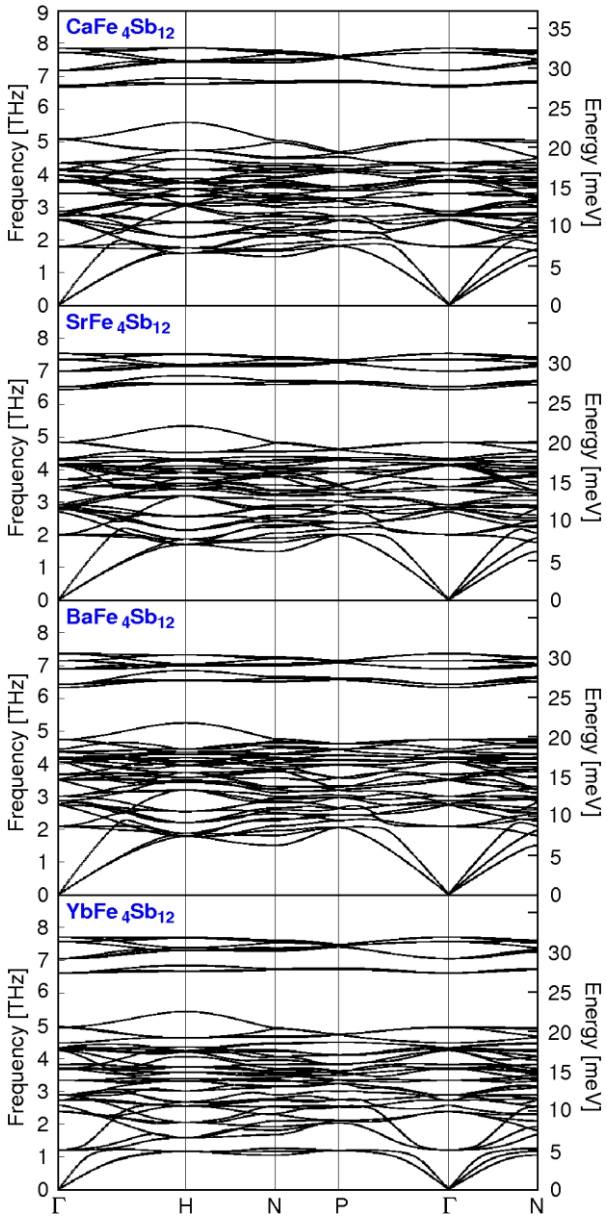


$PrRu_4Sb_{12}$
K.Iwasa et al.,
Journal of Physics: Conference Series 92, 012122, (2007)



$SmRu_4P_{12}$ by S.Tsutsui et al., J. Phys. Soc. Jpn. 77, 33601, (2008)

Ab Initio Powder Averaged Lattice Dynamics



The dynamics of different MFe_4Sb_{12} compounds (M = Ca, Sr, Ba, La, Eu, Nd, Yb, Tl) can be well reproduced by a set of normal modes.

Low energy modes of M = Ca, Sr, Ba, La, Nd, Yb containing compounds do not show appreciable anharmonic behaviour.

For $YbFe_4Sb_{12}$ low-energy modes indicate the significance of a quartic anharmonic term.

Modelling $k_{lattice}$ of $CoSb_3$ and $LaFe_4Sb_{12}$

N. Bernstein et al., *Phys. Rev.* B 81, 134301, (2010)

Model	*A*-Fe	*A*-Sb	*A*-La	*B*-La	α	α^*	γ^*	v_s^*
Unfilled-FSM-cf	1.63	2.14			6.71	7.76	1.48	2836
Filled-FSM-cf	1.80	2.06	5.03 ± 0.09	4.1 ± 1.6	9.31(7.95,7.41)	10.9(9.73)	2.00 (1.78)	2813
Unfilled-FS-cf	1.54	2.00			5.26	6.29	1.33	2932
Filled-FS-cf	1.67	1.92	5.10 ± 0.03	–7.3 ± 0.4	7.53	8.80	1.84	2908
Unfilled-LK	2.10	2.28			1.74	3.46	0.68	2462
Filled-LK	2.32	2.13	5.14 ± 0.02	–6.4 ± 0.4	4.28	6.49	1.24	2383
Filled-LDA	1.55*	1.94*	5.12*					2912
Unfilled Exp.[a]						6.36	0.95,1.5	3082
Filled Exp.[b]	1.14	1.79	4.69			9	1.5	2946

Feldman et al. *PRB* 2000

Feldman et al. *PRB* 1996

Feldman et al. *PRB* …

Chakoumakos et al. *AC* 55, 341 (1995)

Thermodynamic expansivity α, Gruneisen parameter γ and velocity of sound υ at T = 300 K from MD and LD calculations.

Result:

- Simulated $LaFe_4Sb_{12}$ exhibits a thermnal conductivity reduced by a factor of 2 in comparison to Co_4Sb_{12}.
- A reduction by 5 is correct.
- However, anharmonicity - cubic as well as quartic -is requires to approximate the perturbation of lattice thermal conductivity.

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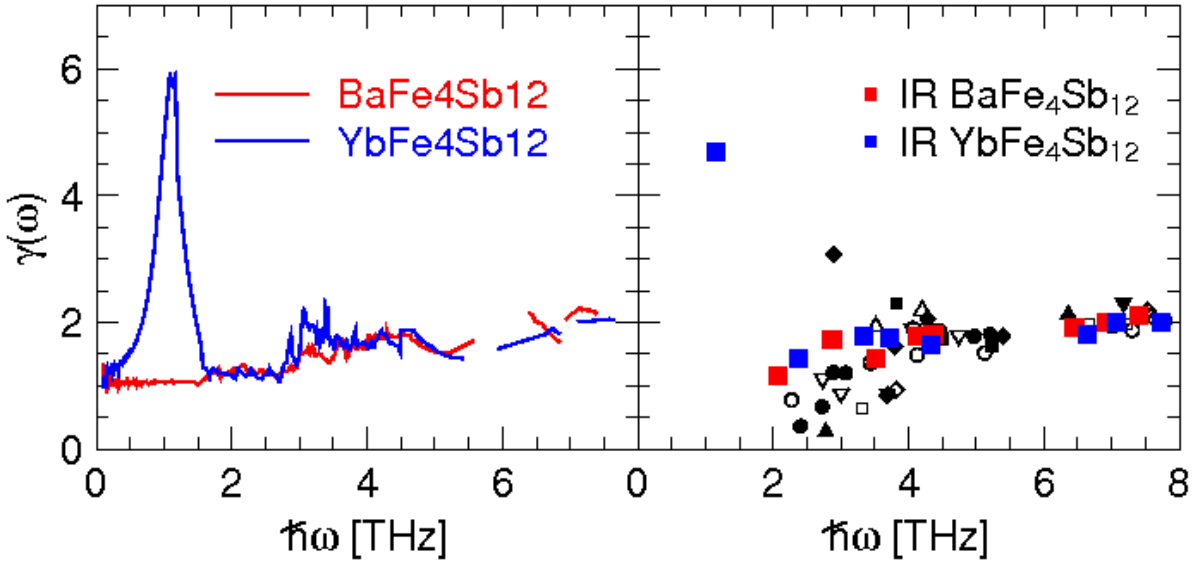
LD calculated mode Gruneisen parameter [dln(w)/dln(V)] :



Optimized harmonic dynamics

Optimization of the anharmonic content

Summary

• Our approach to the problem of powdered materials : different scattering techniques, *ab initio* + PALD calculations, complementary experimental tools.

• Experimental results on filled skutterudites can be reproduced by *ab initio* lattice dynamics calculations.

• Response to T and p of low-energy modes indicates the relevance of a quartic (rattling) term in bonding potential. However, effect is not strongly pronounced and not globally present!

• Cubic and quartic anharmonic terms can be tuned appreciably in MOs_2O_6 and MV_2Al_{20} by cation M variation.

• Computation work requires super-cells of 200-500 atoms to match the inelastic response from experiments limiting other .

• We are more or less prepared to approach the thermal conductivity modelling .

Thank You for Your Attention !