


*Réunion GDR Thermoélectricité
Phonons et thermoélectricité.*

M. de Boissieu

SIMaP

Sciences, Engineering, Material and Process

CNRS, Grenoble-INP, Université Joseph Fourier

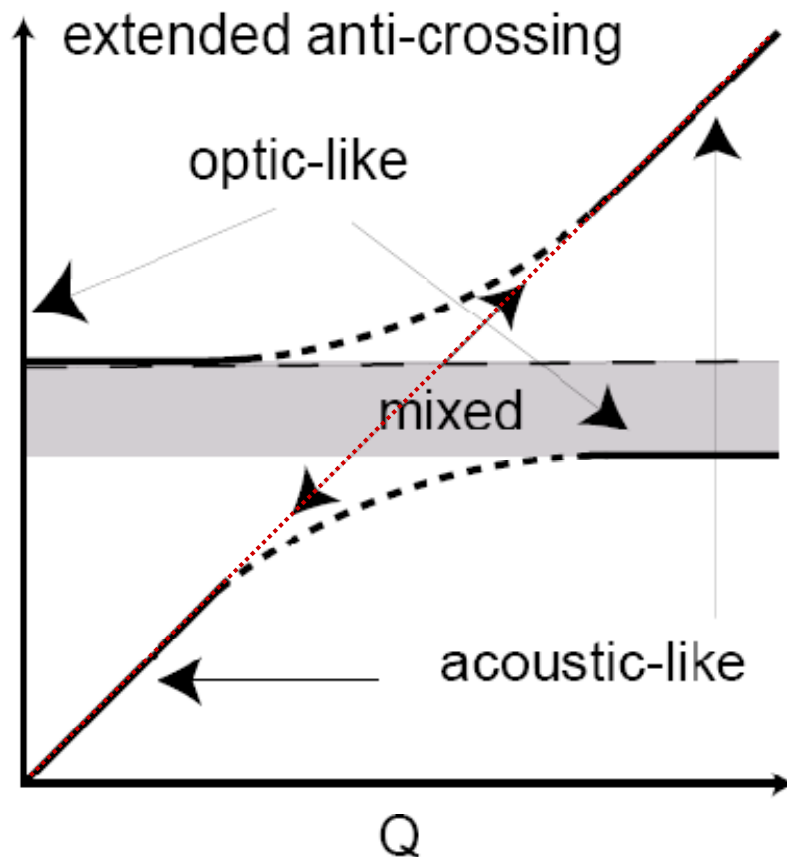
- 
- Phonons dans les matériaux thermoélectriques.
 - Faible conductivité thermique, ‘phonon glass electron crystal’; Clathrates ‘Rattling modes’.
 - Chaleur spécifique.

 - Relation entre conductivité thermique et phonons dans les thermoélectriques et cage compounds??
 - Nature de l’interaction phonon-phonon responsable de la durée de vie faible des phonons acoustiques.



Phonon and the phonon glass electron crystal scenario

- What is the mechanism of reduced phonon lifetime?
- Hypothesis: interaction of the rattler low energy mode with the acoustic phonons (those carrying heat)
- ‘Anticrossing’ of phonon branch and finite lifetime of phonon
- Inelastic X-ray or neutron scattering allows in principle to measure both.
- **Best if on single crystals.**



- Anti-crossing
- Ouverture d'un gap
- 'Mode de résonance': l'onde acoustique est 'réfléchi' par le Xe (défaut, analogie avec un bord de zone).
- Le caractère 'acoustique' se transmet à la branche 'optique'
- Interaction entre les modes, durée de vie finie. Calcul perturbatif permet de calculer le temps de vie

Clathrates Hydrates: ‘rattling’

- Insertion à l’intérieur des cages. Effet de la taille de l’atome à l’intérieur de la cage. Couplage entre le mode localisé et les modes de la structure hôte.

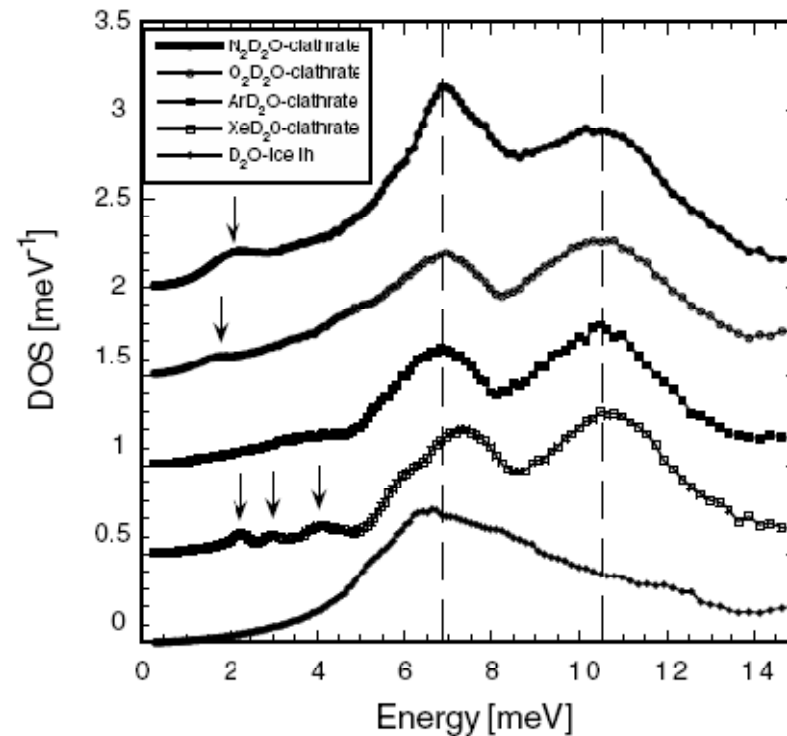
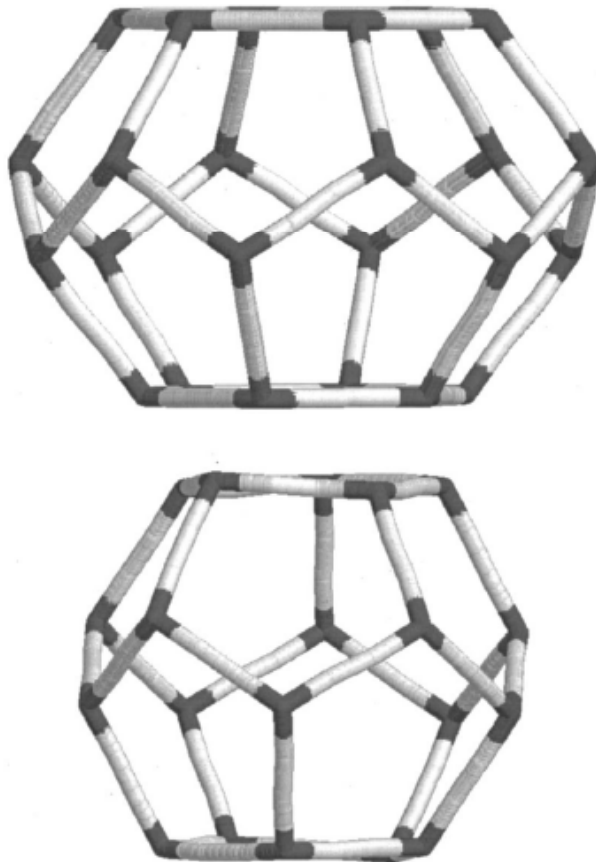
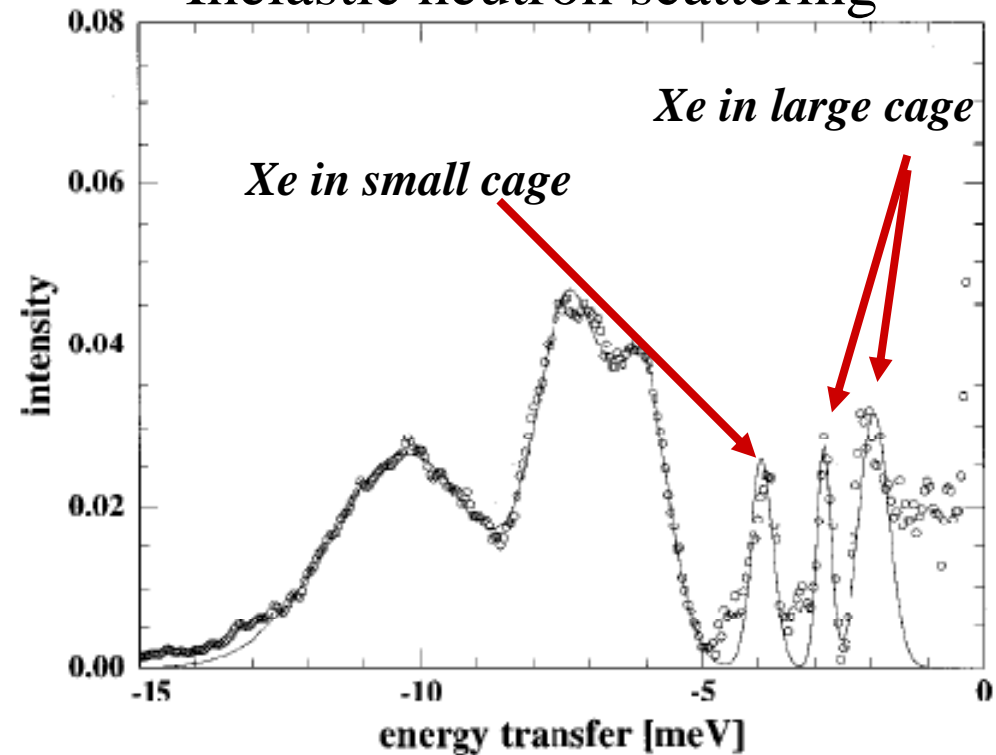
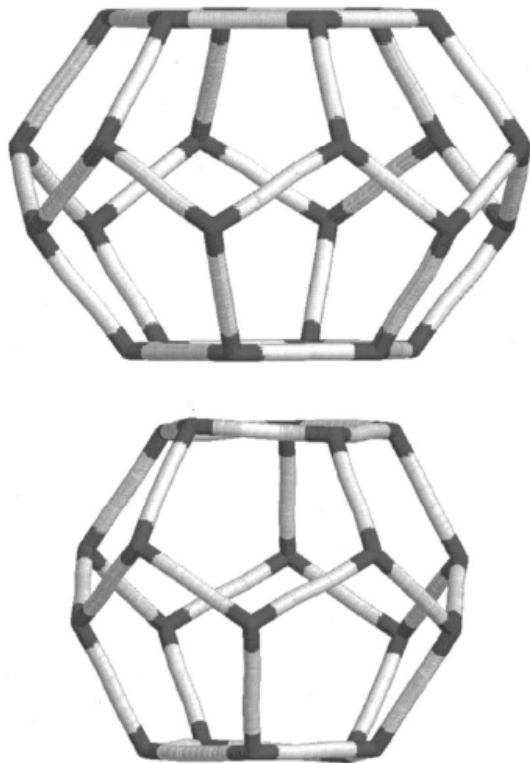


Fig. 2. Generalized density of states $G(\omega)$ for a selection of clathrate hydrates and comparison with hexagonal ice. Arrows indicate well-identified peaks originating from guest vibrations.

Xe Clathrate hydrate (Tse et al)

Mesure de la GVDOS
Inelastic neutron scattering



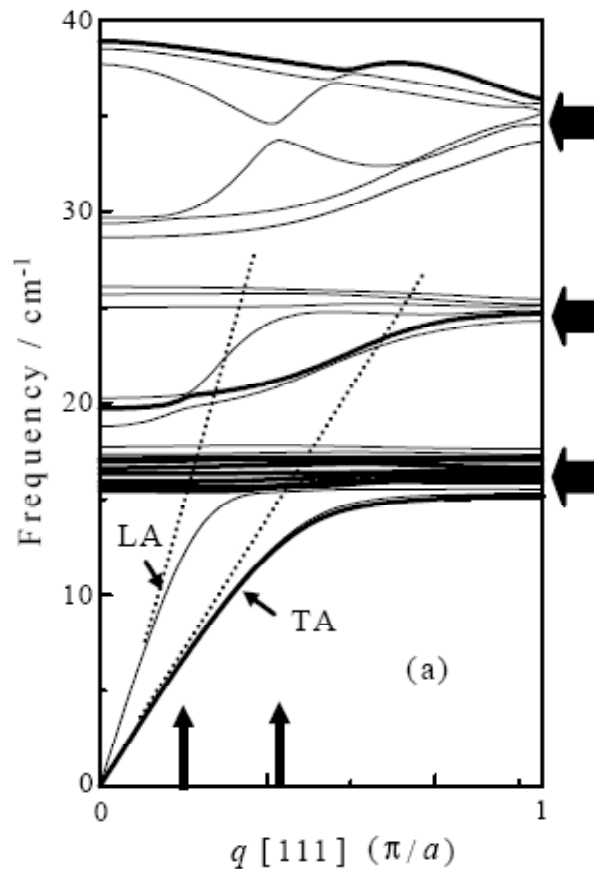
Mise en évidence de modes localisés, Xe dans les cages.

Energie vibration, plus faible dans les grandes cages. Anisotropie:

2 modes. Xe est un gros atome. J. Chem. Phys., Vol. 116, No. 9, 1 March 2002

Xe Clathrate hydrate (Tse et al)

- Calcul des courbes de dispersion: modes localisés
- Calcul du temps de vie des phonons acoustiques: modèle perturbatif. Xe comme un défaut et mode de résonance.

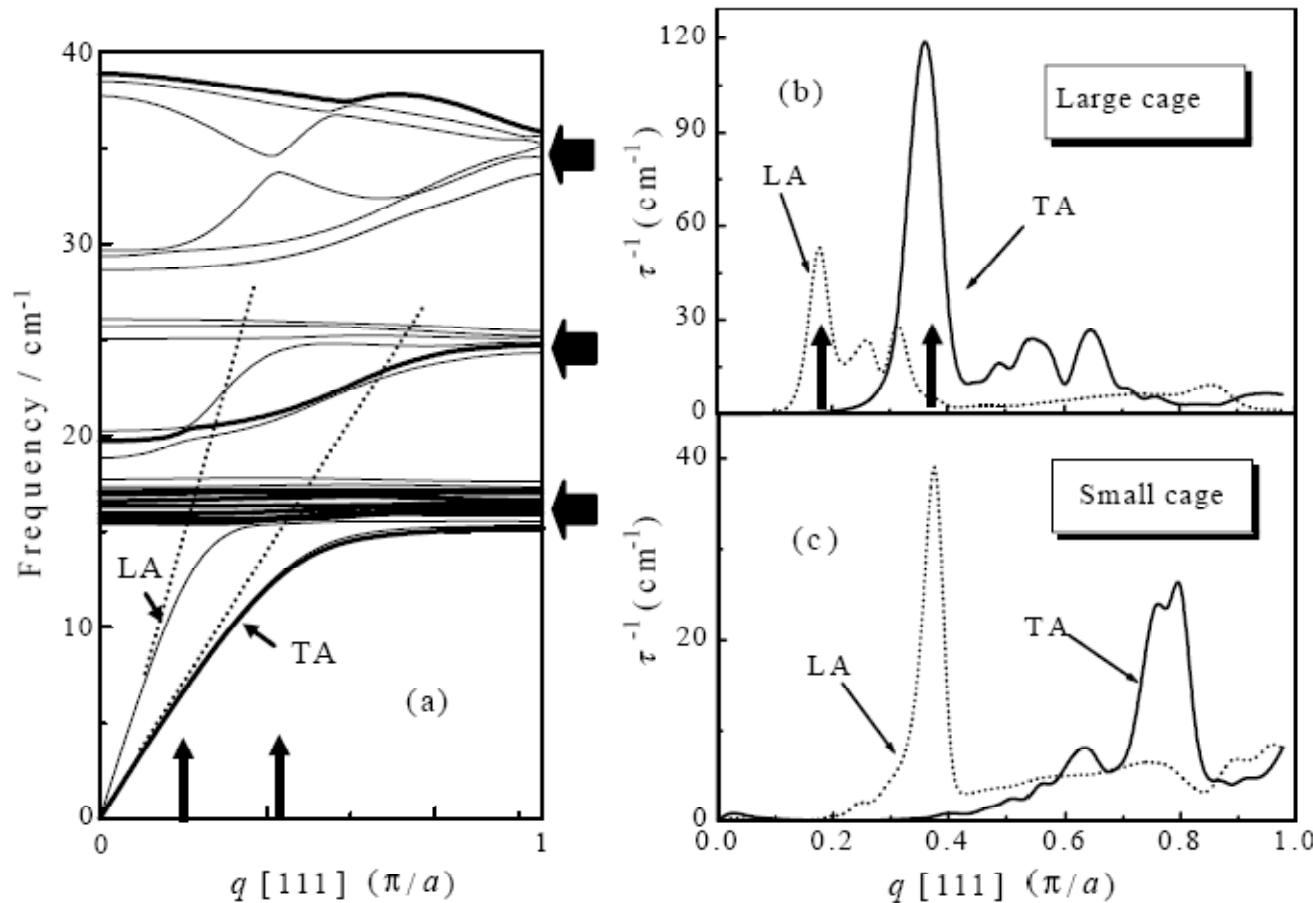


Importance de l'interaction entre le mode acoustique et les modes localisés (ou modes optiques).

Les phonons acoustiques transportent l'énergie thermique

Croisement de deux branches: propriétés de symétrie imposent un 'anti-crossing'

- Anticrossing et durée de vie
- Modèle qualitatif. Permet d'expliquer la conductivité.
- Nécessite d'autres mesures pour confirmer ce modèle



Inverse du temps de vie:
 Largeur du mode en fréquence.

Clathrates Hydrates: anharmonicit ?

- Si l'atome ins r  est plus petit (ex N2), le potentiel devrait  tre fortement anharmonique: vall e tr s large et ensuite potentiel raide sur les bords de la cage.
- Variation  nergie du mode avec T: signature d'anharmonicit . E diminue quand T diminue ('exploration' du fond du potentiel)

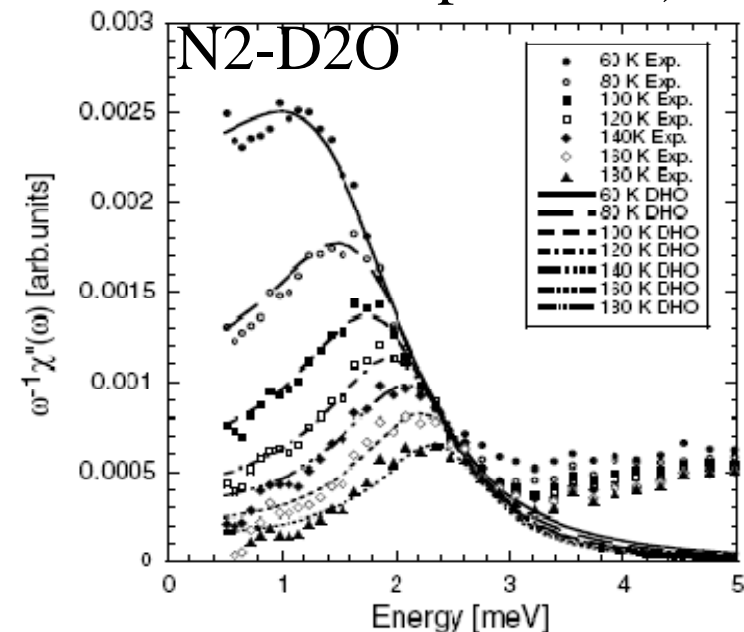
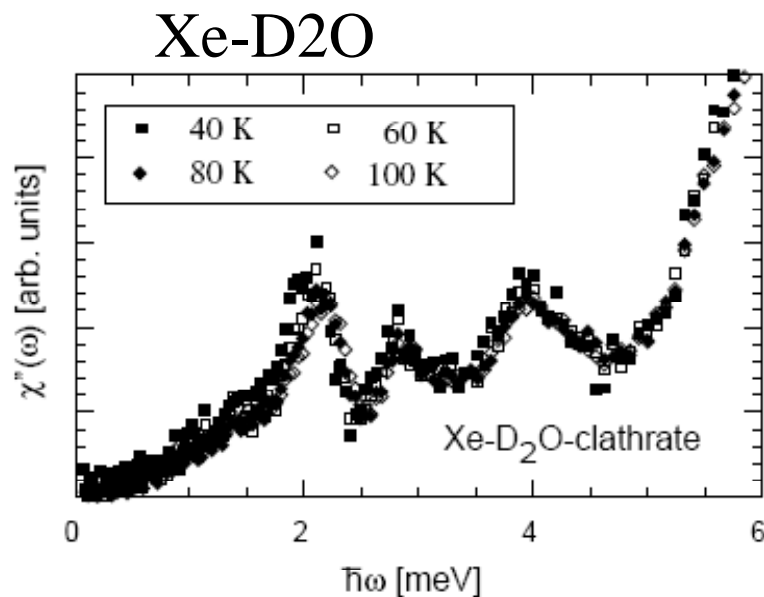



Fig. 6. Dynamic susceptibility multiplied by the inverse frequency for N₂-D₂O clathrate as a function of temperature. As in Figure 5 the data have been summed over the scattering angle to obtain better statistics. The shift with temperature is not influenced by this, i.e. it is found Q-independent.



Thermoelectrics: cage compounds

- Phonon glass/electron crystal
- Phonon ‘tayloring’: rattling mode, size effect
- However the microscopical mechanism responsible for the low thermal conductivity are not well understood.

Skutterudite: rattling?

Phonons in thermoelectrics – no evidence for the 'phonon glass' scenario in La/CeFe₄Sb₁₂ skutterudites.

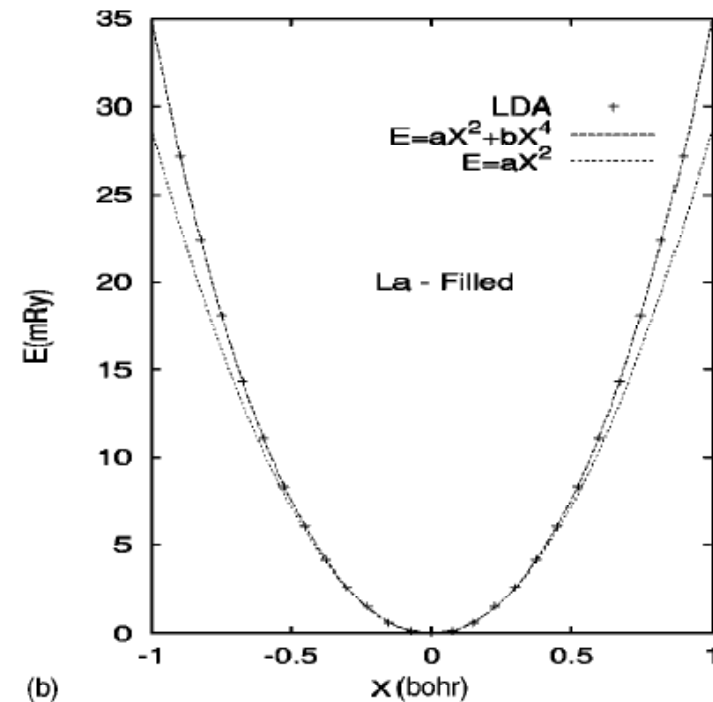
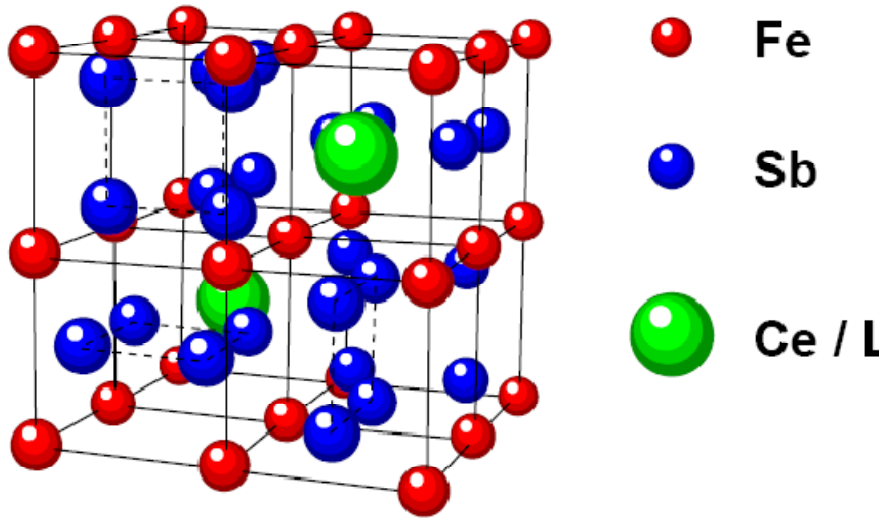
Michael Marek Koza¹, Mark Robert Johnson¹, Romain Viennois², Hannu Mutka¹, Luc Girard³, Didier Ravot³

¹Institut Laue Langevin, 6 Rue Jules Horowitz, B.P. 156, 38042 Grenoble, Cedex 9, France.

²DPMC, Universite de Geneve, 24 quai Ernest Ansermet, CH-1211 Geneva, Switzerland.

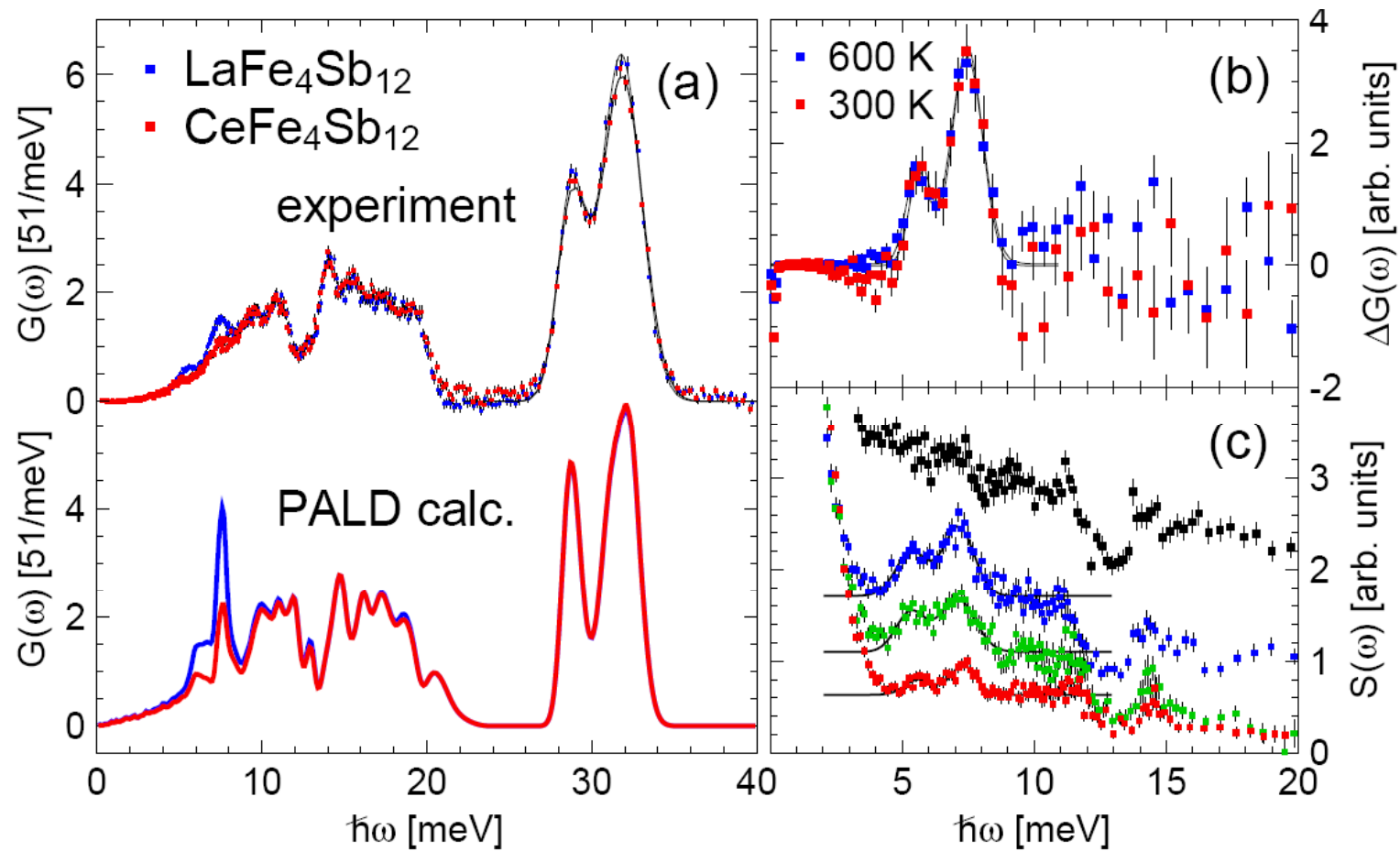
³LPMC, Universite de Montpellier II, pl. Eugene Bataillon, 34095 Montpellier, France.

Nature Materials 7, (2008), p. 805.

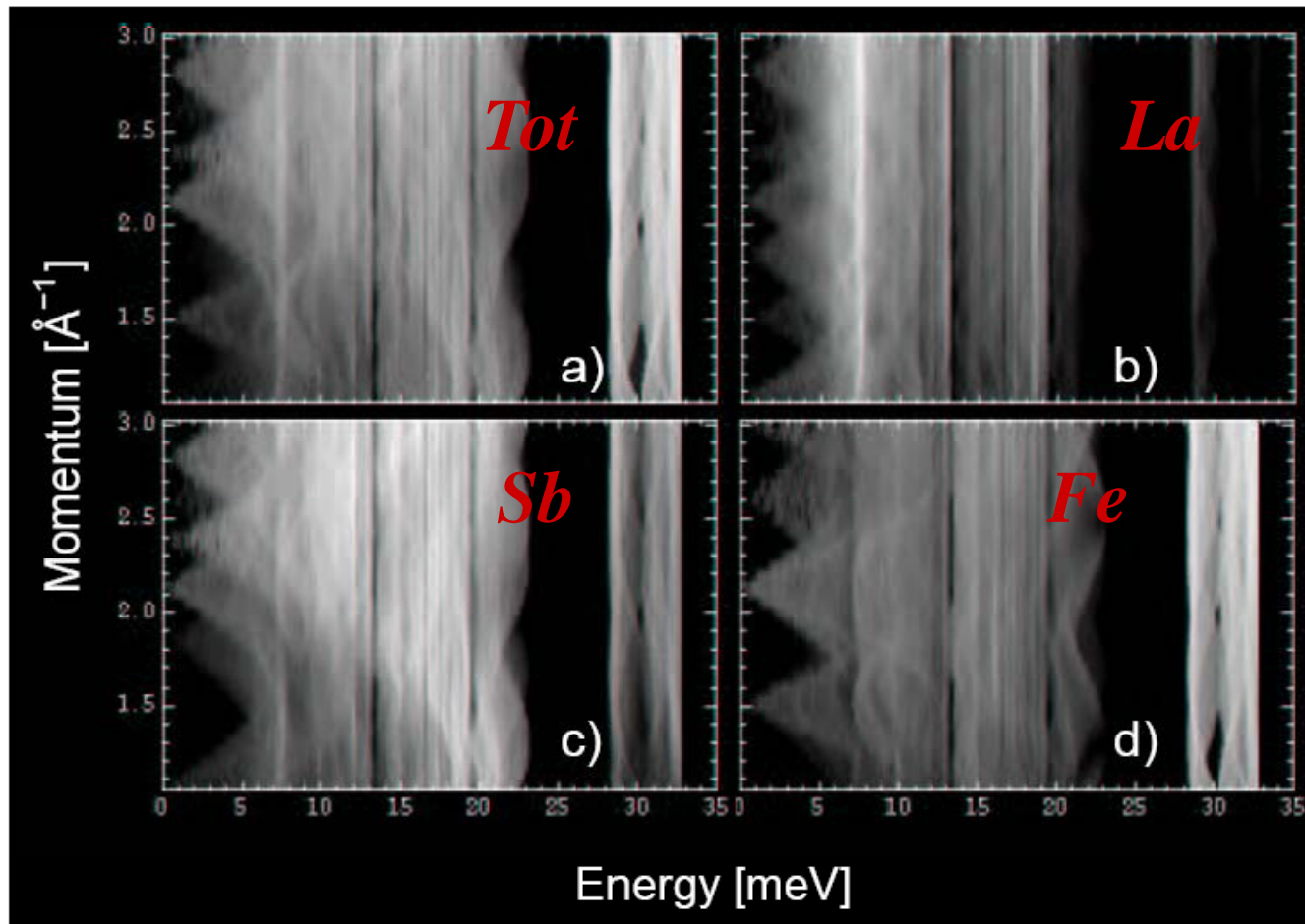


(b) *Feldman et al, PRB, 61,2000 R2209*

Skutterudite: rattling?



Skutterudite: rattling?



Simulation

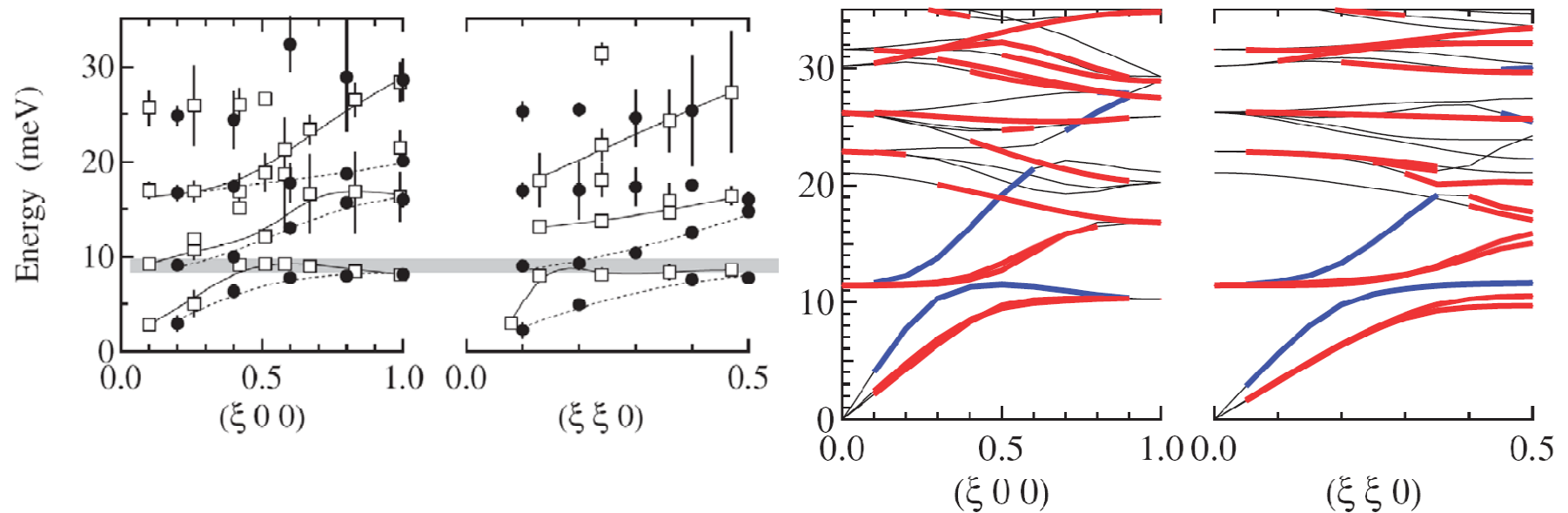
Simulation
montre qu'il
y a un
couplage
entre le mode
localisé et le
réseau

Harmonic
Crystals

Mais: Nature
du mode de
basse
énergie?

Inelastic X-ray scattering in single crystal of the $\text{SmRu}_4\text{P}_{12}$

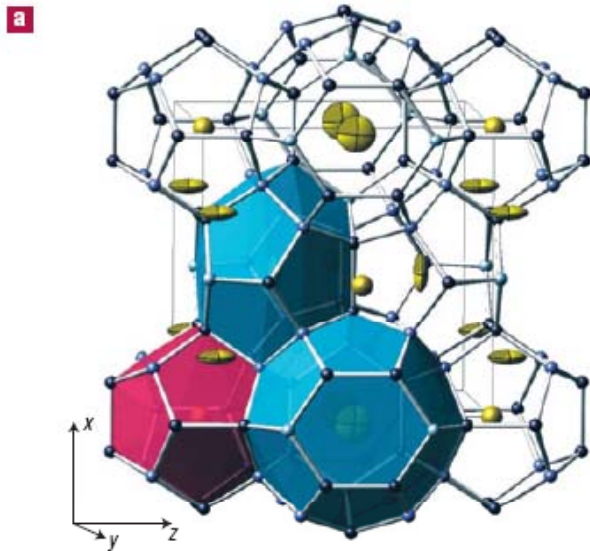
- Tsutsui S., Kobayashi H., Ishikawa D., *et al.*, *J. Phys. Soc. Jpn.*, Vol. 77, (2008), p. 033601.



Anticrossing is clearly visible, as expected in the phonon glass scenario..
Somehow contradicts the arguments of Koza et al.

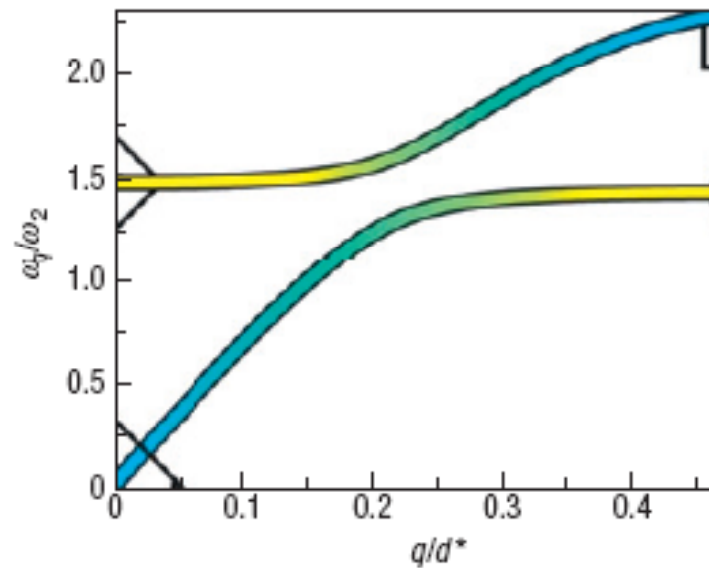
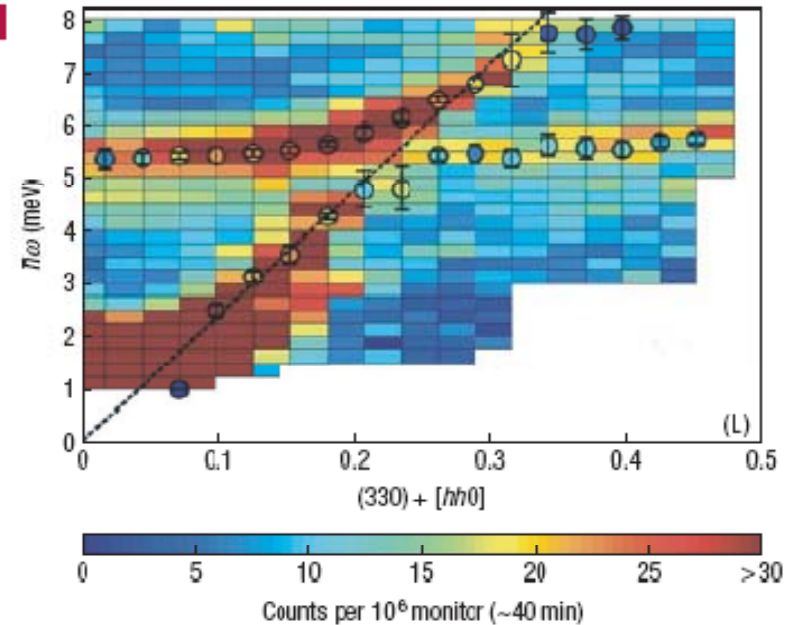
Avoided crossing of rattler modes in thermoelectric materials

MOGENS CHRISTENSEN^{1*}, ASGER B. ABRAHAMSEN², NIELS B. CHRISTENSEN^{2,3,4}, FANNI JURANYI³, NIELS H. ANDERSEN², KIM LEFMANN^{2*}, JAKOB ANDREASSON⁵, CHRISTIAN R. H. BAHL^{2*} AND BO B. IVERSEN^{1†}



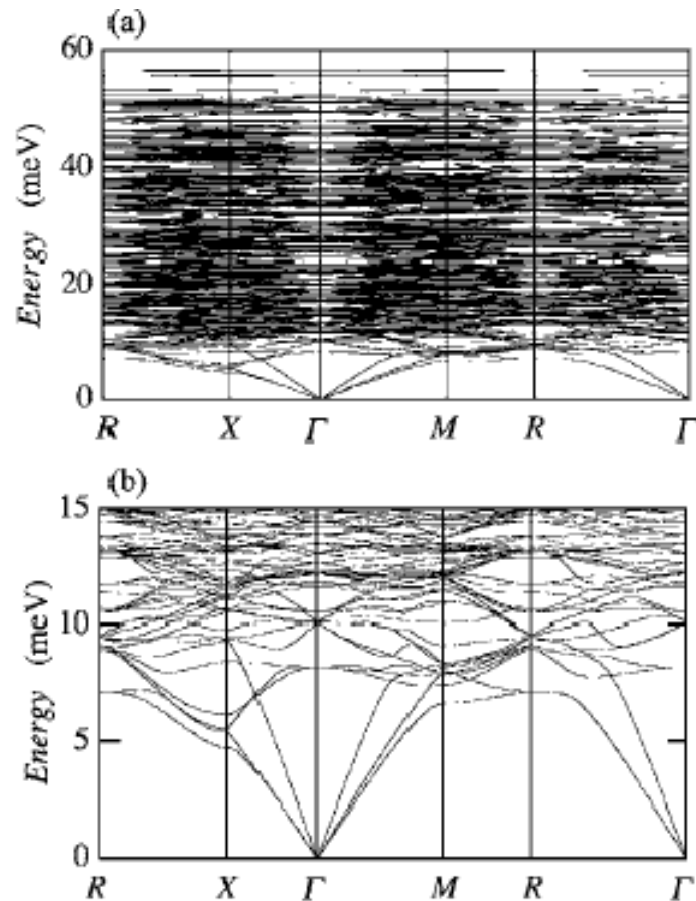
- BaGaGe Clathrates
- Large single grains: inelastic neutron scattering
- Data in qualitative agreement with the rattling scenario

Christensen M., Abrahamsen A. B., Christensen N. B., *et al.*,
Nature Mater, Vol. 7, (2008), p. 811

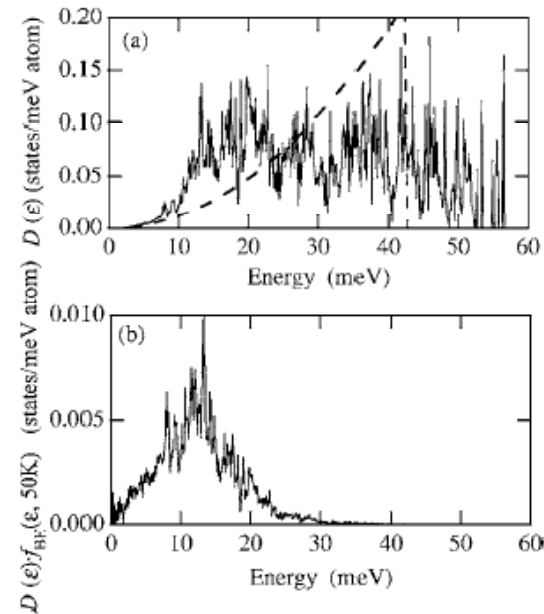
d**c**

Data in agreement with a simple scenario
 However, not enough to explain the low thermal conductivity:
low lying optical modes due to the complex structure are
 important: Umklapp process.

Complexité structurale



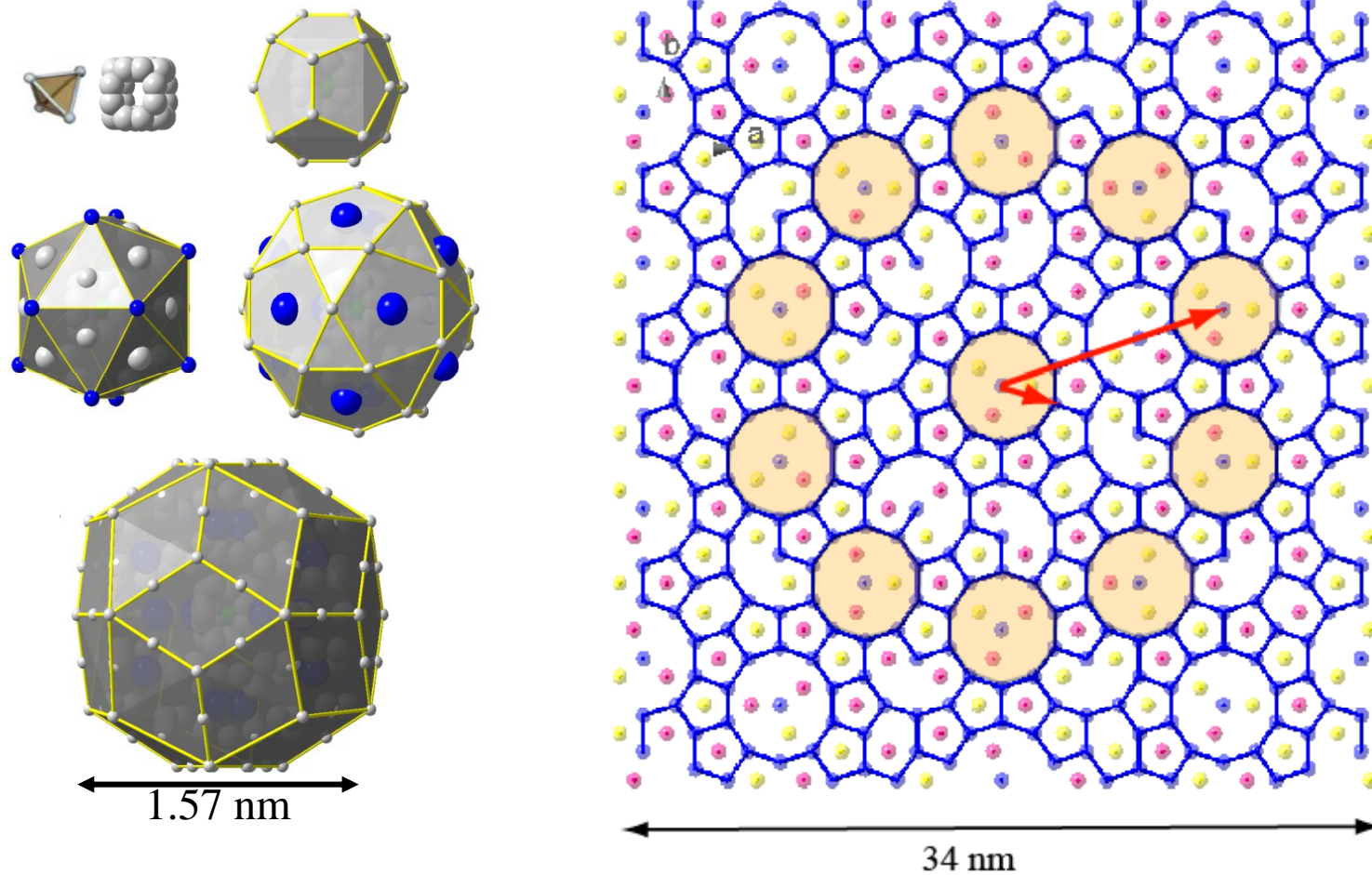
*Takeuchi et al, Phys Rev B, 74
(2006) 54206*



Complexité: Grand nombre de modes optiques à basse énergie

Conductivité réduite, par umklapp. Par rapport à un système simple, beaucoup plus de possibilités

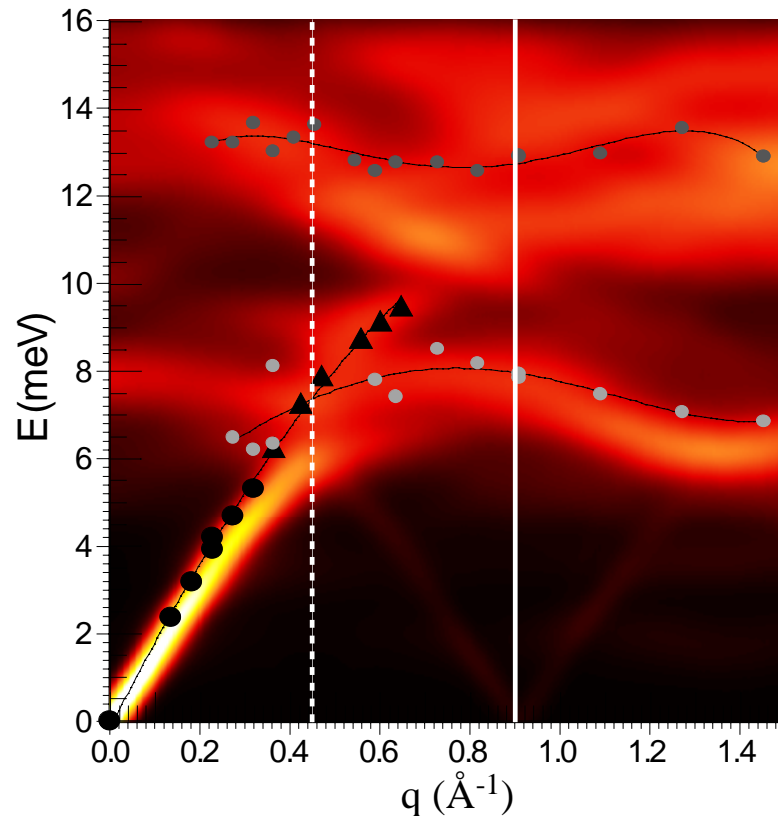
Mesure et simulation de la dynamique de phase ZnMgSc quasicristalline et approximante



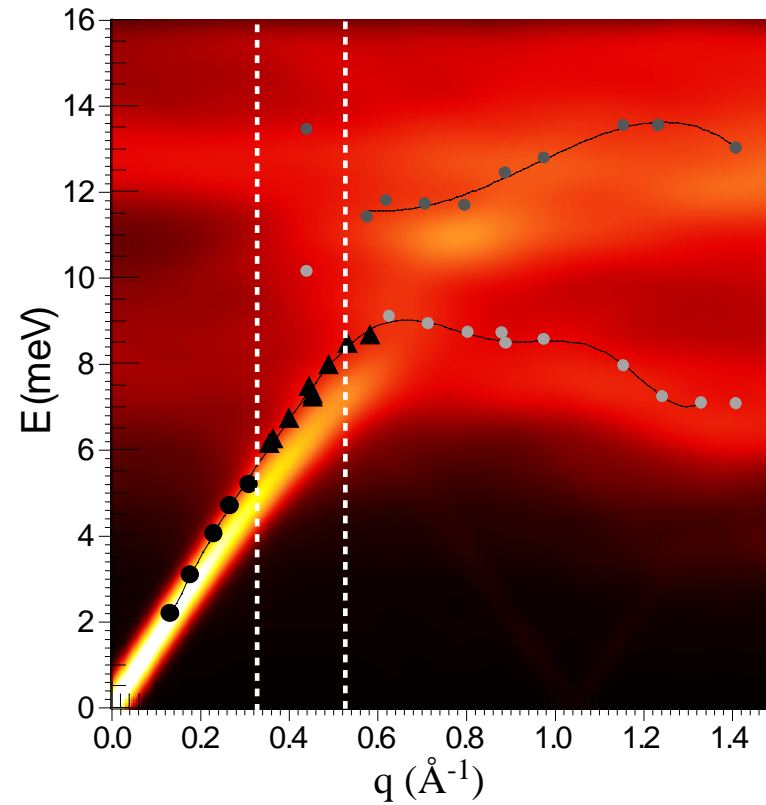
Takakura H., Gomez C. P., Yamamoto A., de Boissieu M. and Tsai A. P.: *Nature Mat.* 6 (2007) 58-63.

Comparison simulation-measurement Transverse modes

Cristal Zn-Sc



QC Zn-Sc



Good agreement. Differences QC and 1/1 are well reproduced.

de Boissieu M., Francoual S., Mihalkovic M., Shibata et al.: Nature Mat. 6 (2007) 977-984

Simulation and interpretation of thermal lattice conductivity

VOLUME 86, NUMBER 11

PHYSICAL REVIEW LETTERS

12 MARCH 2001

Theoretical Study of the Lattice Thermal Conductivity in Ge Framework Semiconductors

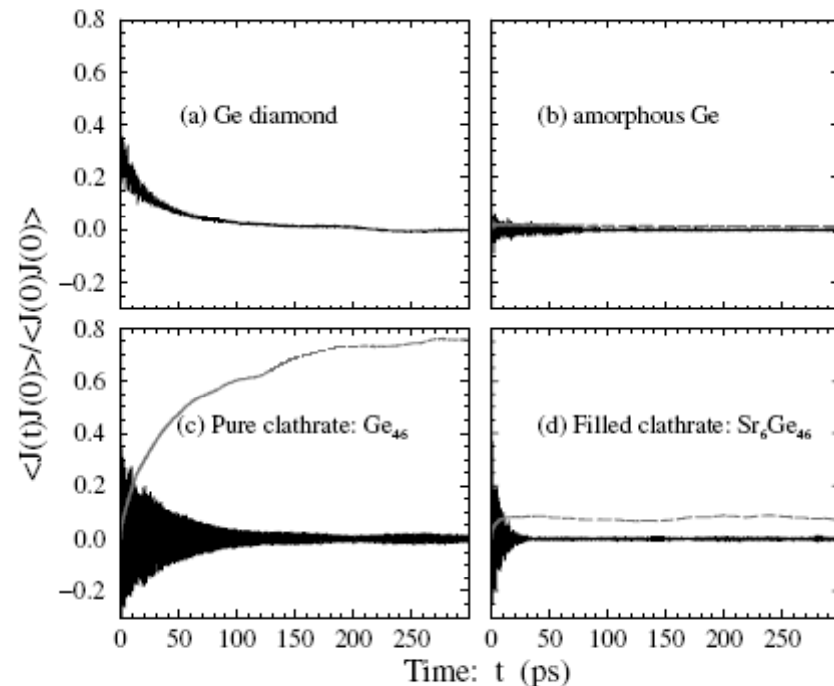


FIG. 2. The normalized time-dependent correlation function $g(t)$ at room temperature for (a) d -Ge, (b) a -Ge, (c) the guest-free clathrate framework Ge_{46} , and (d) the guest-containing clathrate $\text{Sr}_6\text{Ge}_{46}$. The time integration of $g(t)$ is also shown as a dashed curve in (b)–(d).

- MD and Green-Kubo calculation of equilibrium fluctuations.
- Ge filled/unfilled
- Effect of both complexity and filling.

Simulation and interpretation of thermal lattice conductivity

PRL 103, 015901 (2009)

PHYSICAL REVIEW LETTERS

week ending
3 JULY 2009

Mechanisms for Thermal Conduction in Methane Hydrate

Niall J. English*

*The SEC Strategic Research Cluster and the Centre for Synthesis and Chemical Biology,
School of Chemical and Bioprocess Engineering, Conway Institute of Biomolecular and Biomedical Research,
University College Dublin, Belfield, Dublin 4, Ireland*

John S. Tse†

Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2, Canada

TABLE I. Acoustic relaxation times and contributions to the overall thermal conductivity based on fitting procedure, in $\text{Wm}^{-1} \text{K}^{-1}$, for SI MH, EH, and ice *Ih* at two selected temperatures.

Type	T (K)	$\tau_{\text{sh,ac}}$ (ps)	Short-range acoustic	$\tau_{\text{int,ac}}$ (ps)	Medium-range acoustic	$\tau_{\text{lg,ac}}$ (ps)	Long-range acoustic	Optic	Total
SI	30	0.38 ± 0.062	0.21			4.4 ± 0.39	0.69	0.15	1.05 ± 0.06
	265	0.046 ± 0.005	0.06	0.33 ± 0.16	0.05	2.1 ± 0.27	0.40	0.13	0.64 ± 0.05
Empty SI	30	0.44 ± 0.056	0.20			6.1 ± 0.49	0.99	0.22	1.41 ± 0.06
	265	0.057 ± 0.0047	0.08			2.2 ± 0.23	0.43	0.16	0.67 ± 0.05
Ice	30	0.47 ± 0.068	0.24			8.2 ± 0.58	1.31	0.24	1.79 ± 0.08
	220	0.23 ± 0.034	0.11			2.4 ± 0.23	0.72	0.20	1.03 ± 0.07

Conclusion

- La question des mécanismes réduisant la conductivité thermique reste encore ouverte
- Nécessité de données expérimentales, notamment de diffusion inélastique des neutrons sur mono-cristaux: seul moyen d'avoir une information sur la nature des modes et leur durée de vie.
- Couplage des mesures avec des simulations
- Simulations de la conductivité thermique
- Nécessité d'une approche théorique pour interpréter les résultats des simulations et des expériences.

