Neutron scattering and numerical simulation: a powerful combination providing unique insights into functional molecules and materials (Chemical Applications)

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Overview

STRUCTURE – *DYNAMICS* - FUNCTION

- Micelles – a new dynamical model
- Endofullerenes – quantum mechanics in a nano lab
- Oxide ion conductors
- Thermoelectric materials

Micelles – a new dynamical model

Sharma, Mitra & Mukho – BARC, Mumbia, India
Bachir Aoun, Eric Pellegrini & Mark Johnson – ILL

Structure & dynamics of micelles

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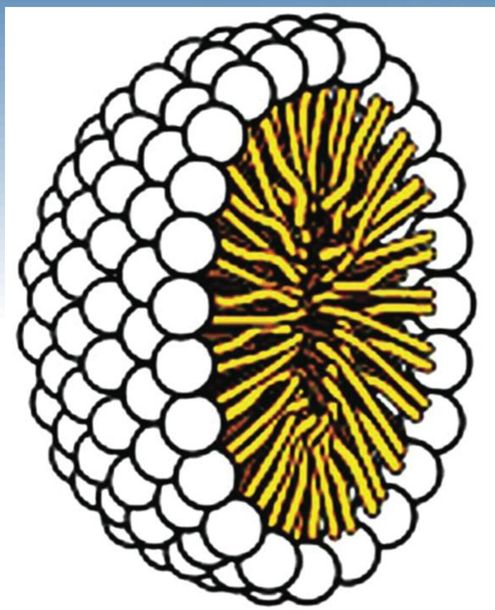
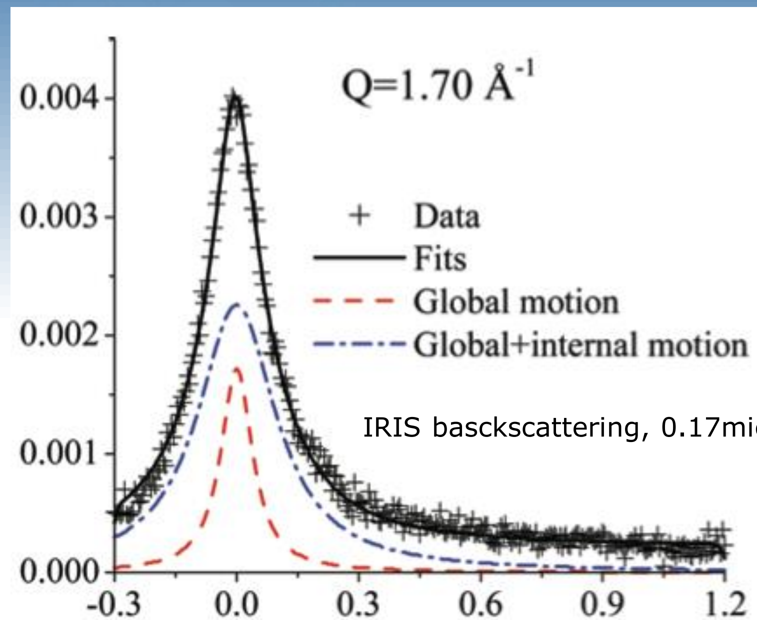
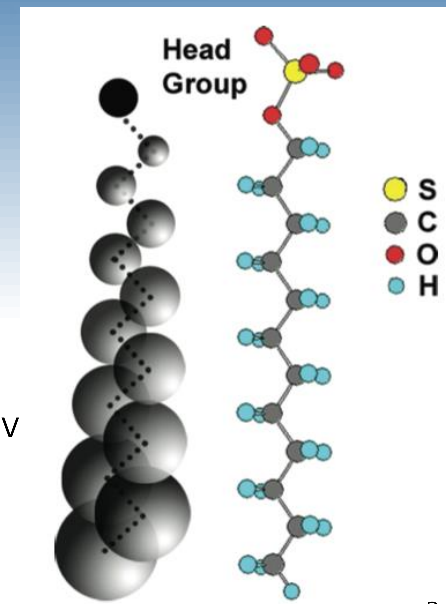




IRIS basckscattering, 0.17micro-eV



$$A(Q) = \frac{1}{12}\sum_{1}^{12}\left[\frac{3 j_1(QR_i)}{QR_i}\right]^2$$

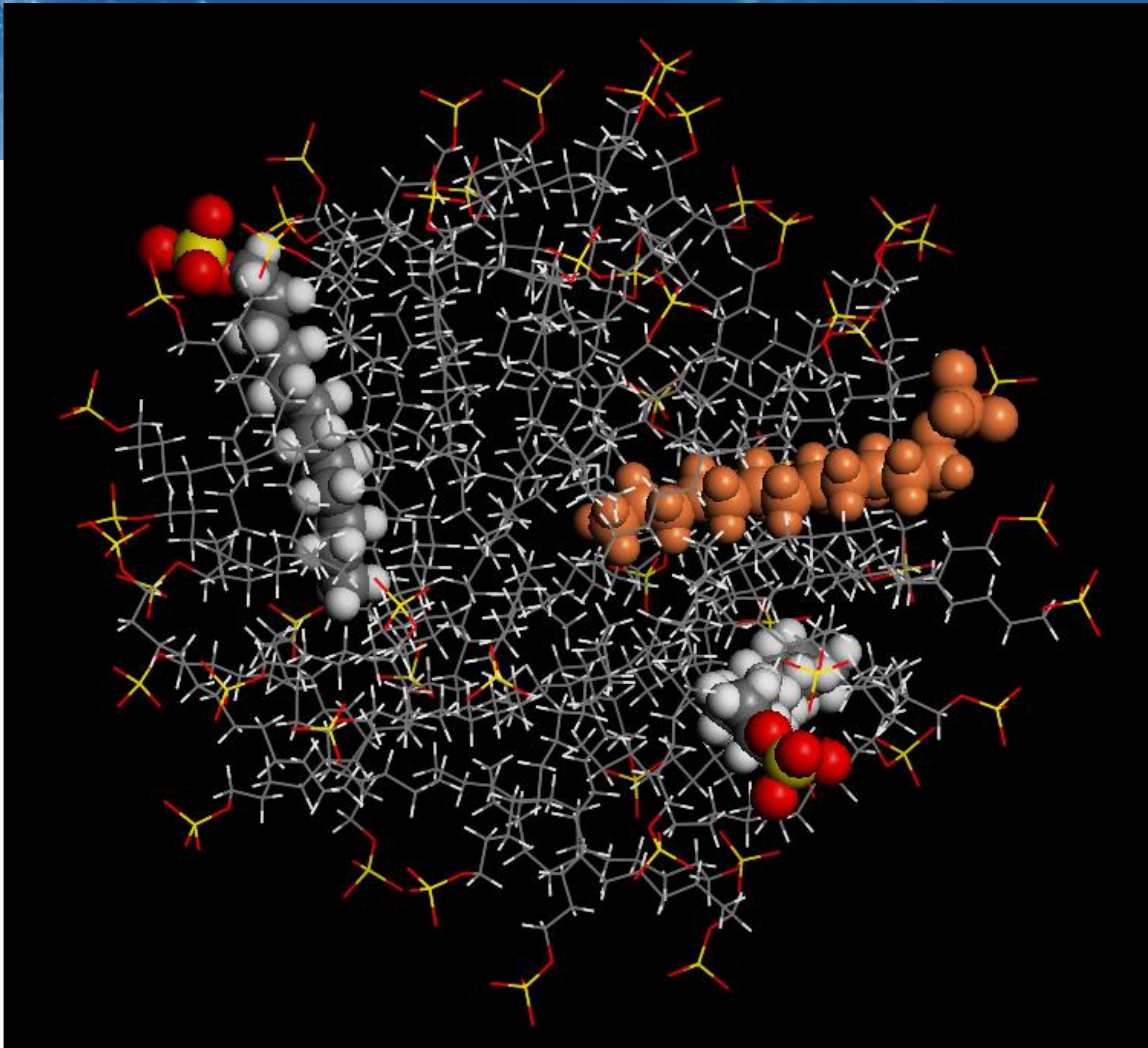
Volino - Dianoux

$$R_i = \frac{i-1}{N-1}\left[R_{\max} - R_{\min}\right] + R_{\min}$$

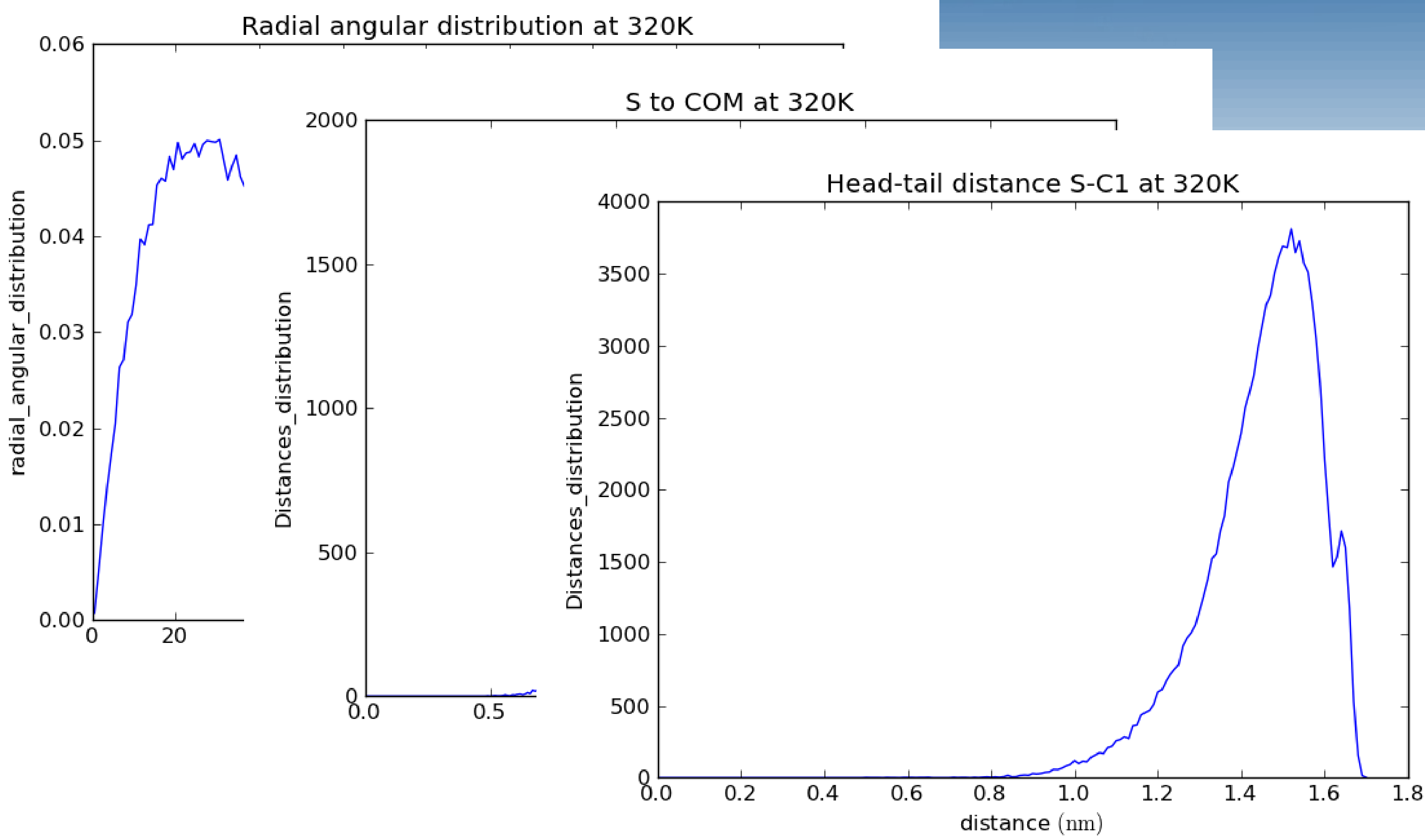
$$S_{micelles}(Q,\omega) = e^{-Q^2\langle u^2\rangle}\left[S_{external}(Q,\omega) \otimes S_{internal}(Q,\omega)\right]$$

$$S_{internal}(Q,\omega) = A(Q)\delta(\omega) + (1 - A(Q))L_{internal}(\Gamma_{internal},\omega)$$

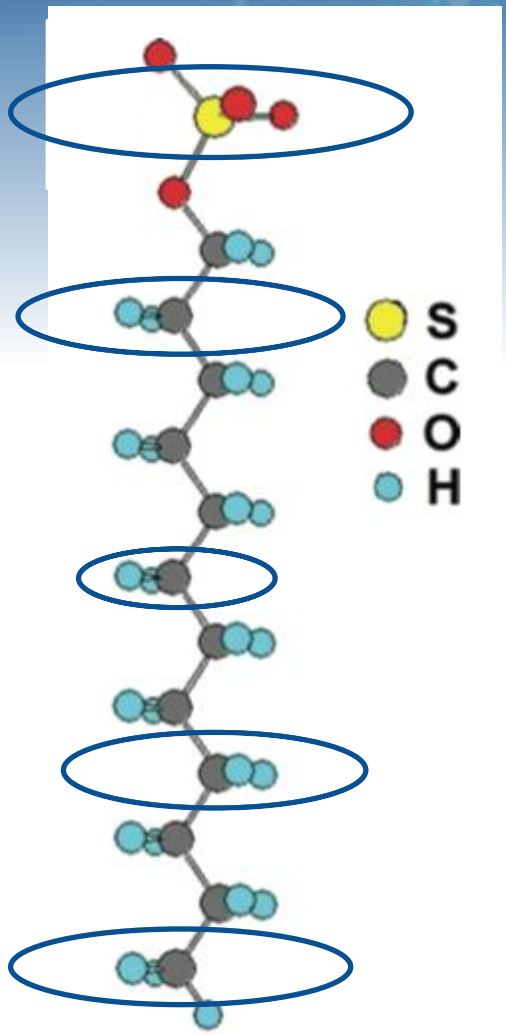
SDS – structural model

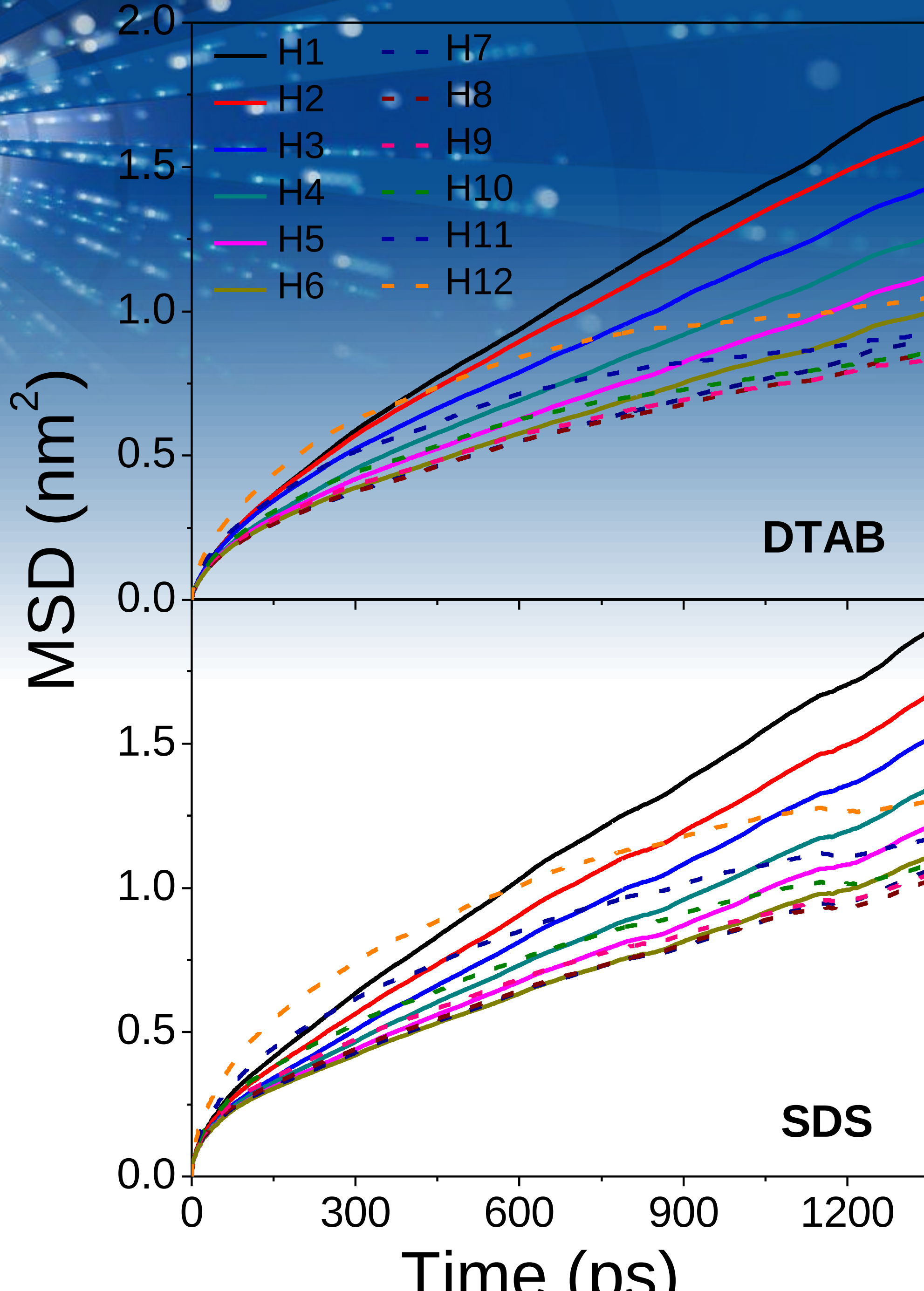


SDS – structural model: 'rough ellipsoid'

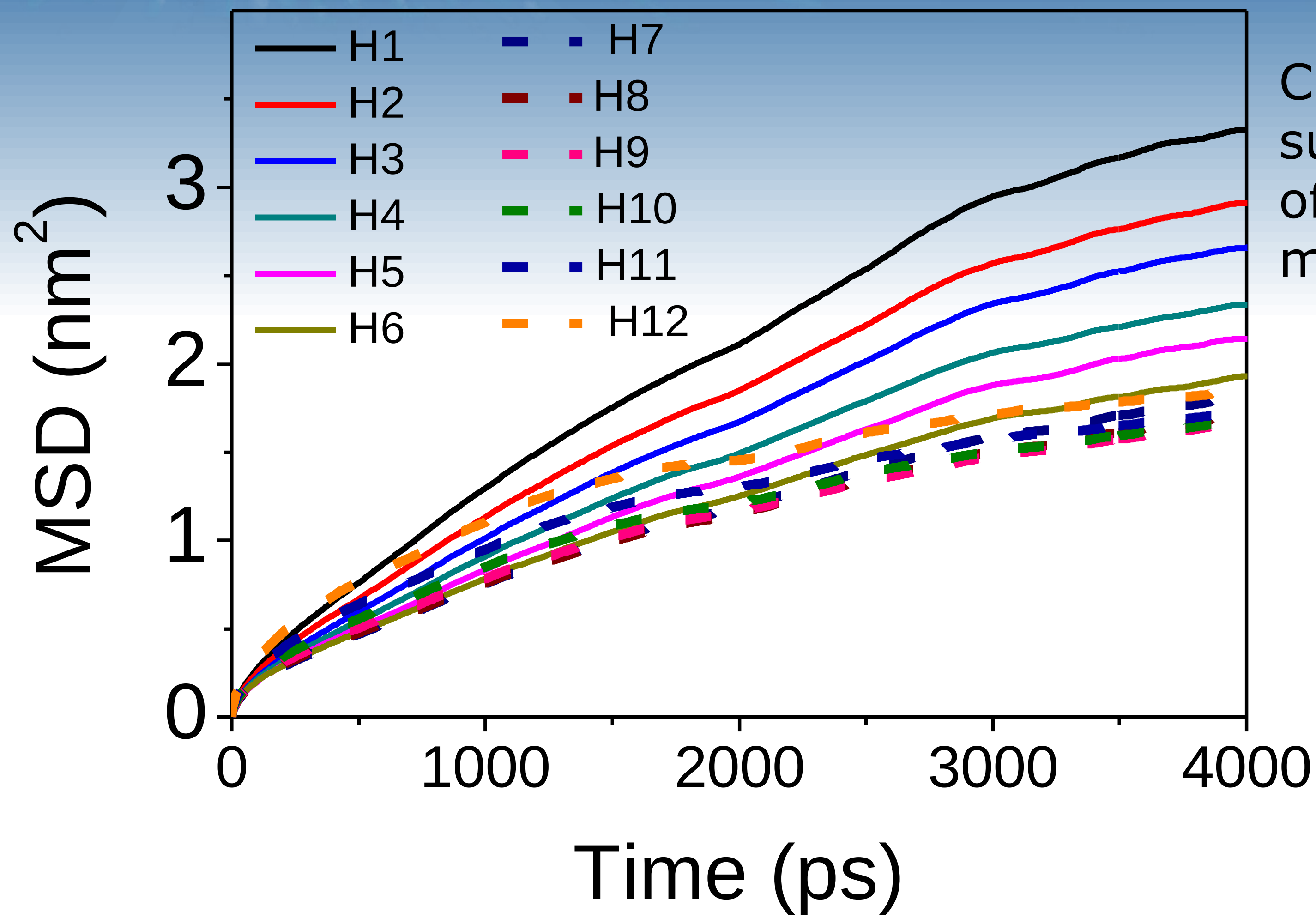


SDS – dynamical model



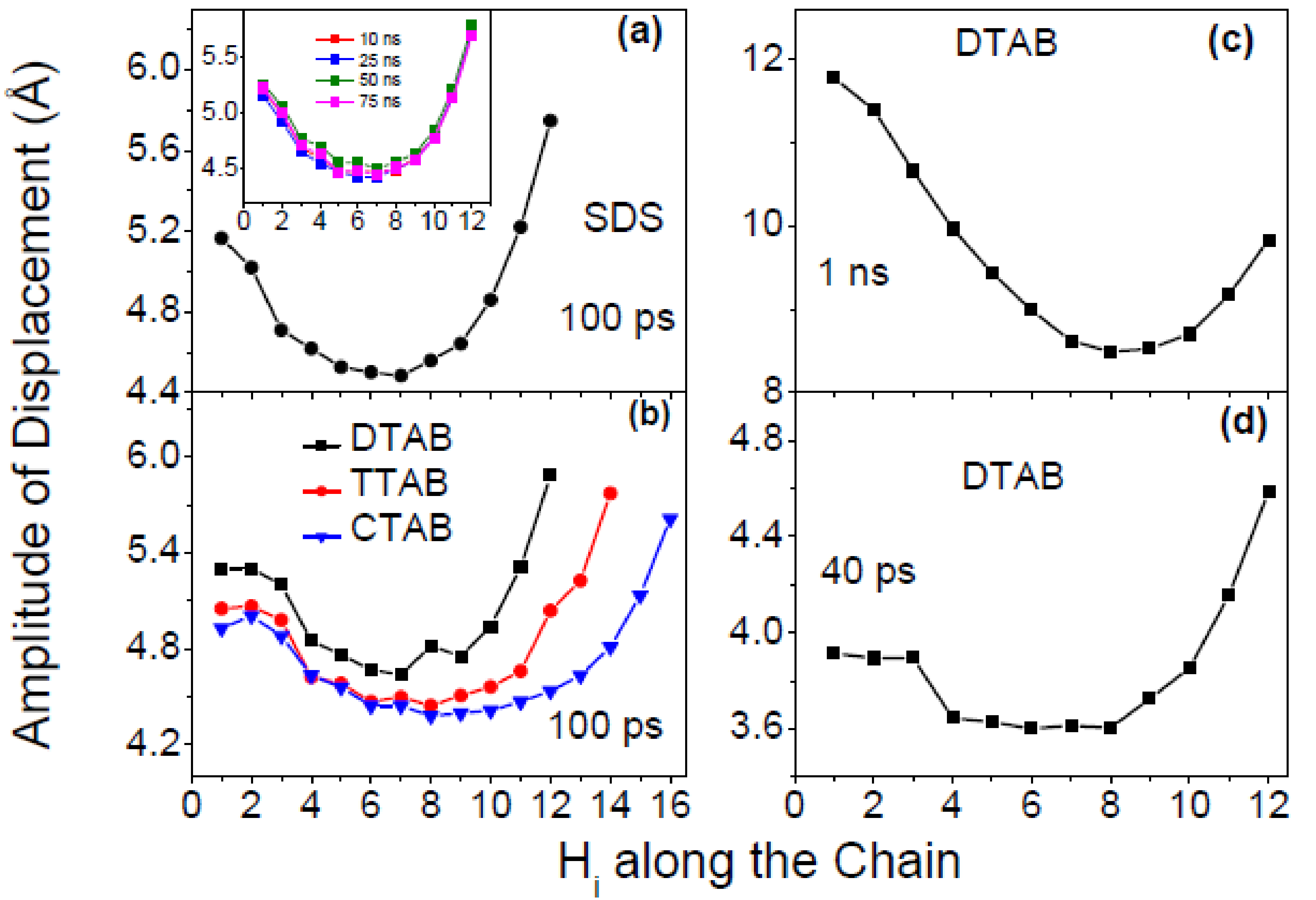


SDS – dynamical model

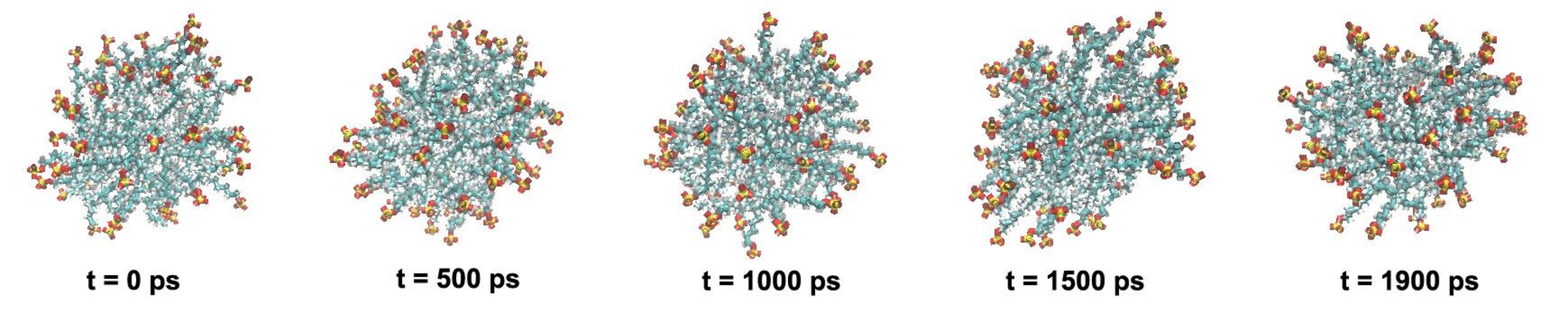


Correct subtraction of global motion

SDS – dynamical model



Micelle – conclusion



- Surface is rough and fluctuating
- Tails can move from surface to centre and back in nanoseconds (analysis of radial distance)
- Head groups are more mobile than tails
- Head group motion is mainly tangential – about 15% of micelle circumference
- Dynamical model can be tested by…

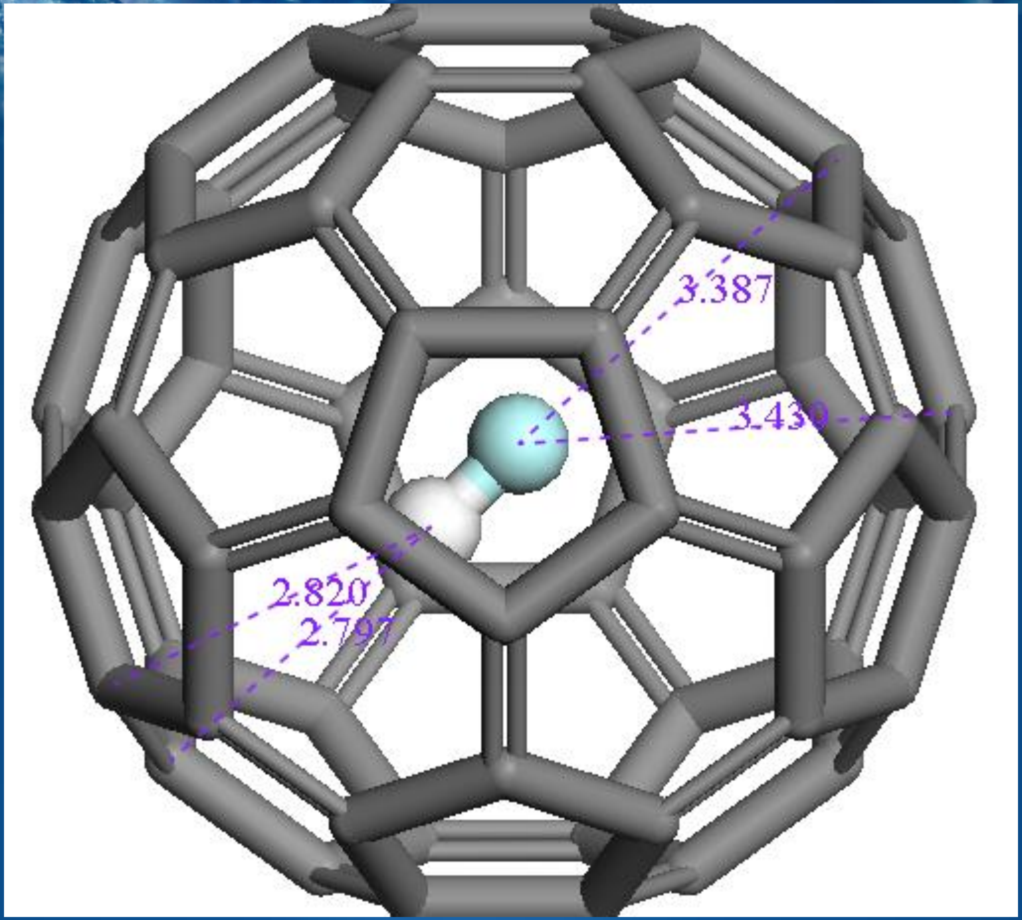
Quantum mechanics in a nano-laboratory

Salvo Mamone & Tony Horsewill – University of Nottingham

Malcolm Levitt & Richard Whitby - University of Southampton

Monica Jimenez, Stef Rols, Jacques Ollivier & Mark Johnson – ILL

Quantum particle in a 'box'



H_2, HD, D_2, HF, H_2O, NH_3, CH_4, etc &
H_2@C70 …

Molecular surgery

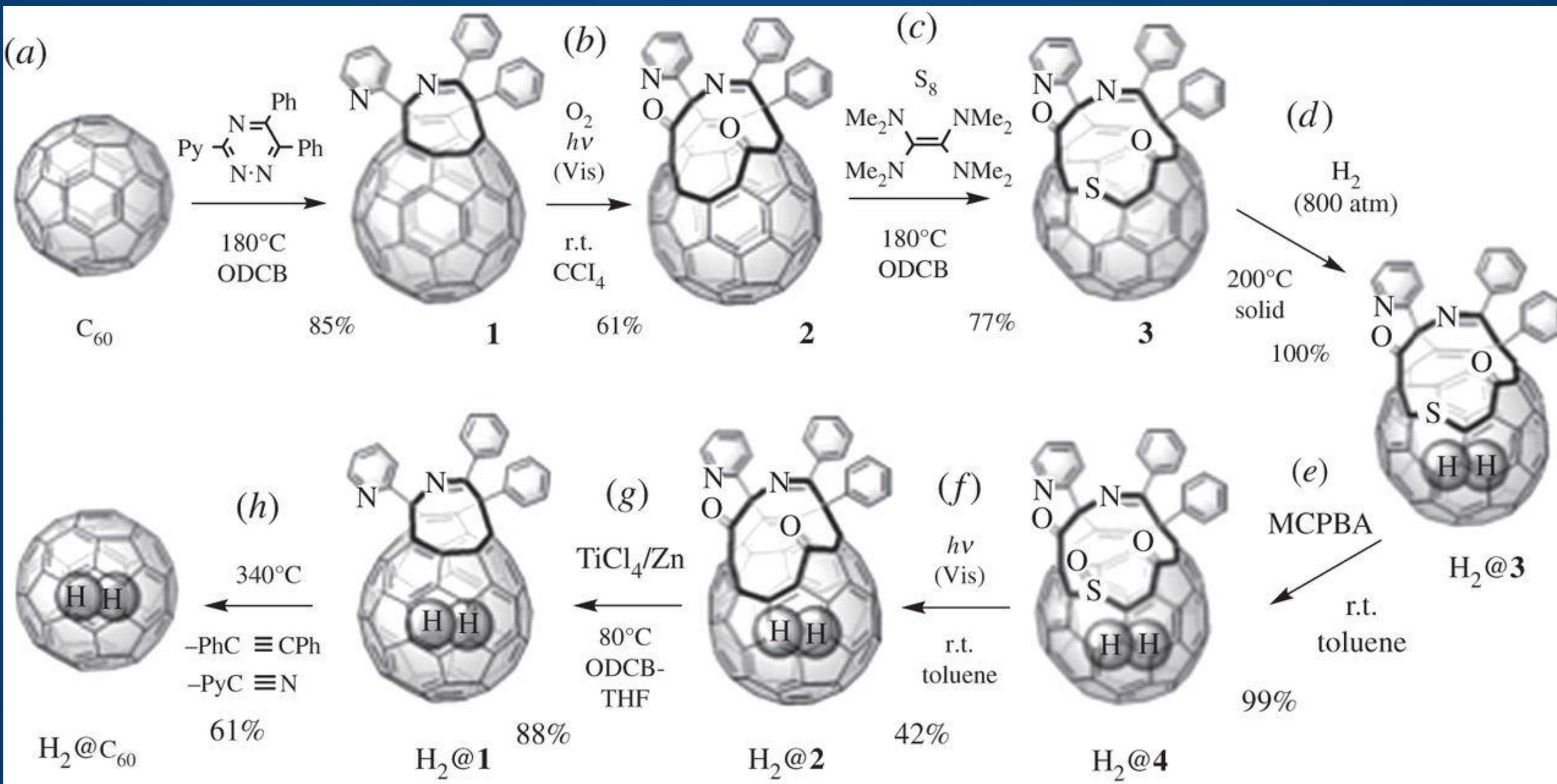
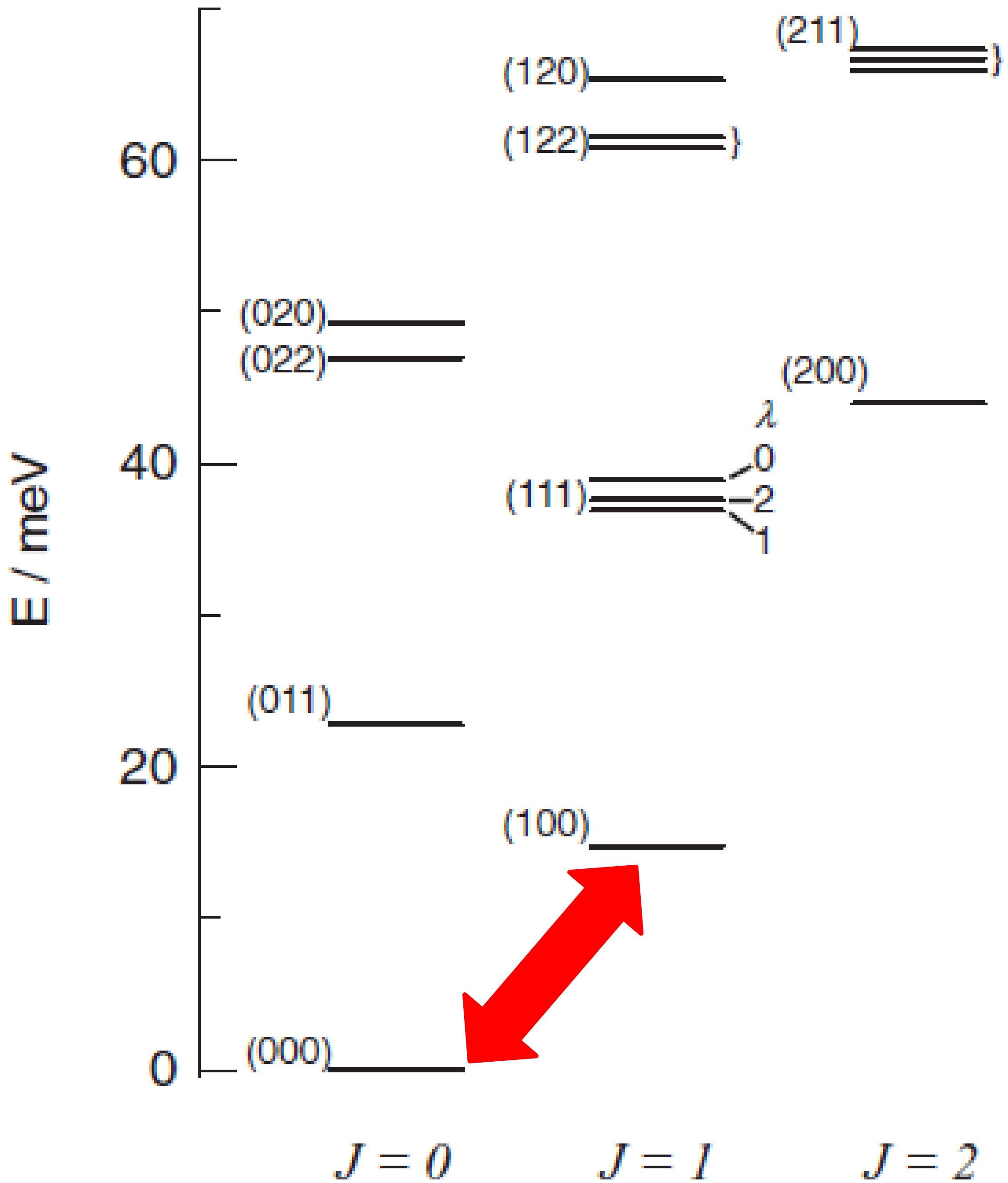
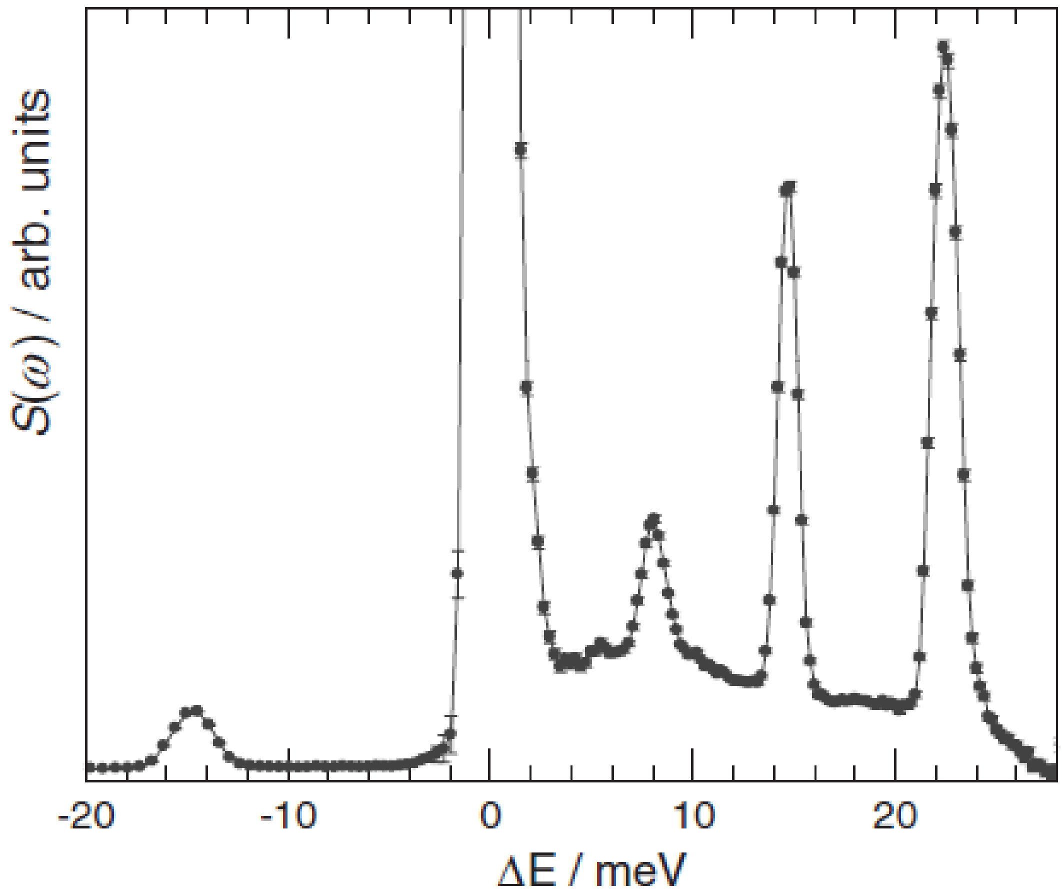


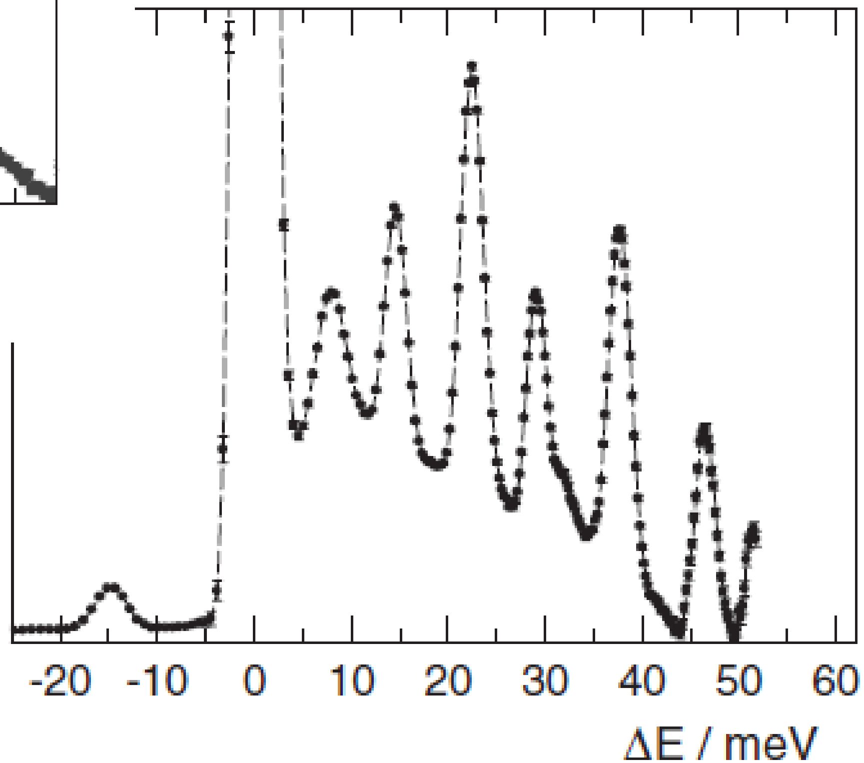
TABLE I.

Initial state (J n l λ)
000 0
100 0
100 0
100 0
100 0
100 0
000 0
100 0
100 0
200 0
200 0
022 2
022 2
020 0
020 0
111 1
100 0

[a]Indicates band cente







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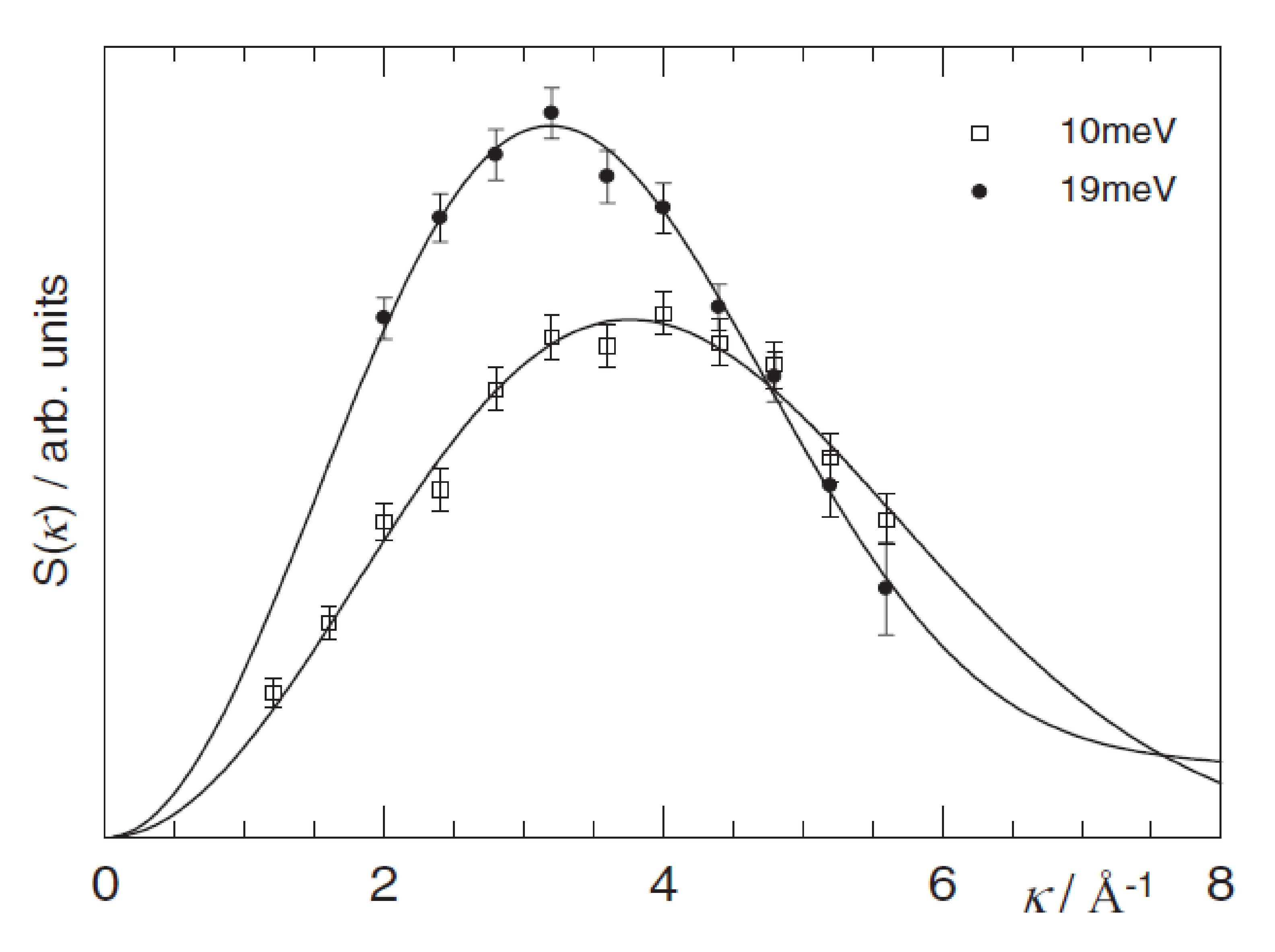
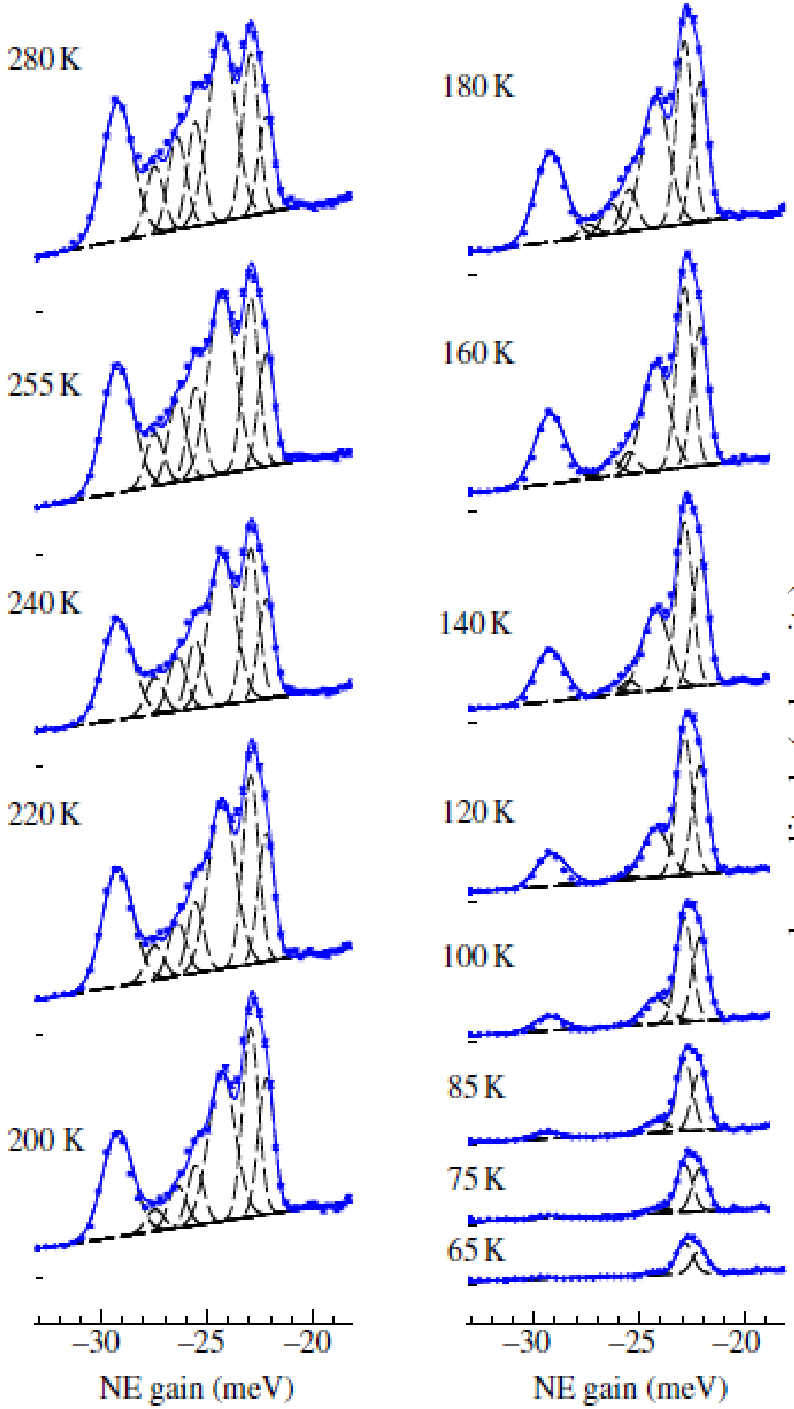
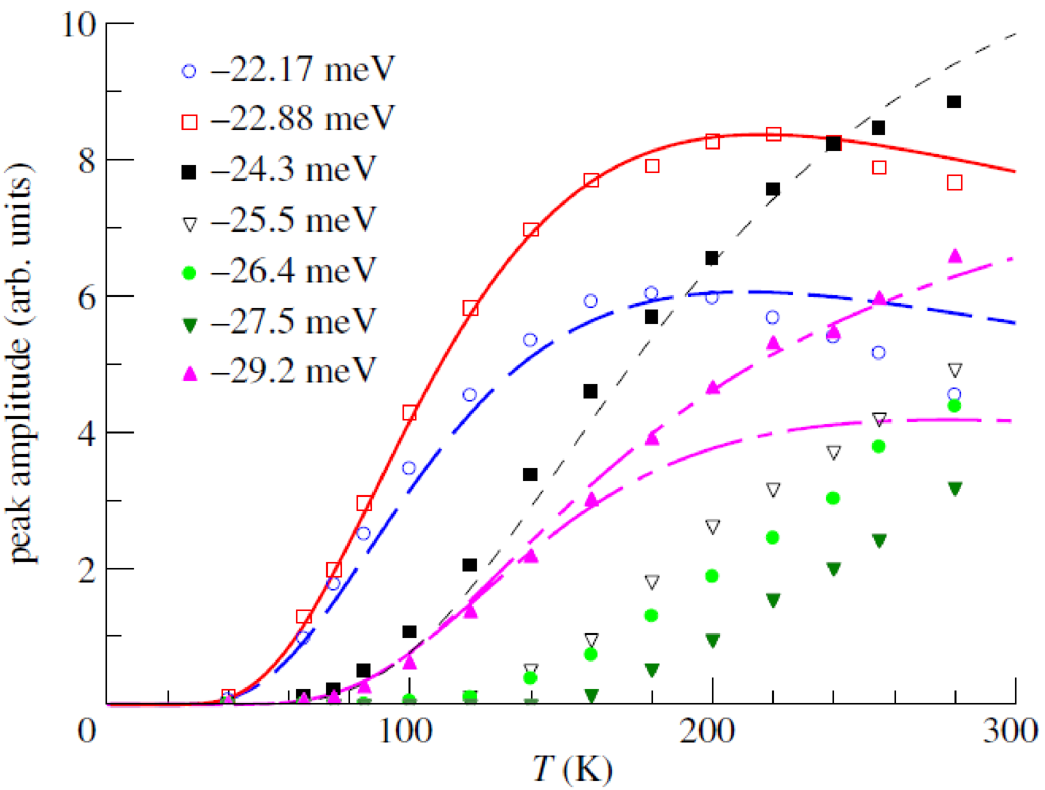
Thermal neutrons

Q – Dependence of transitions

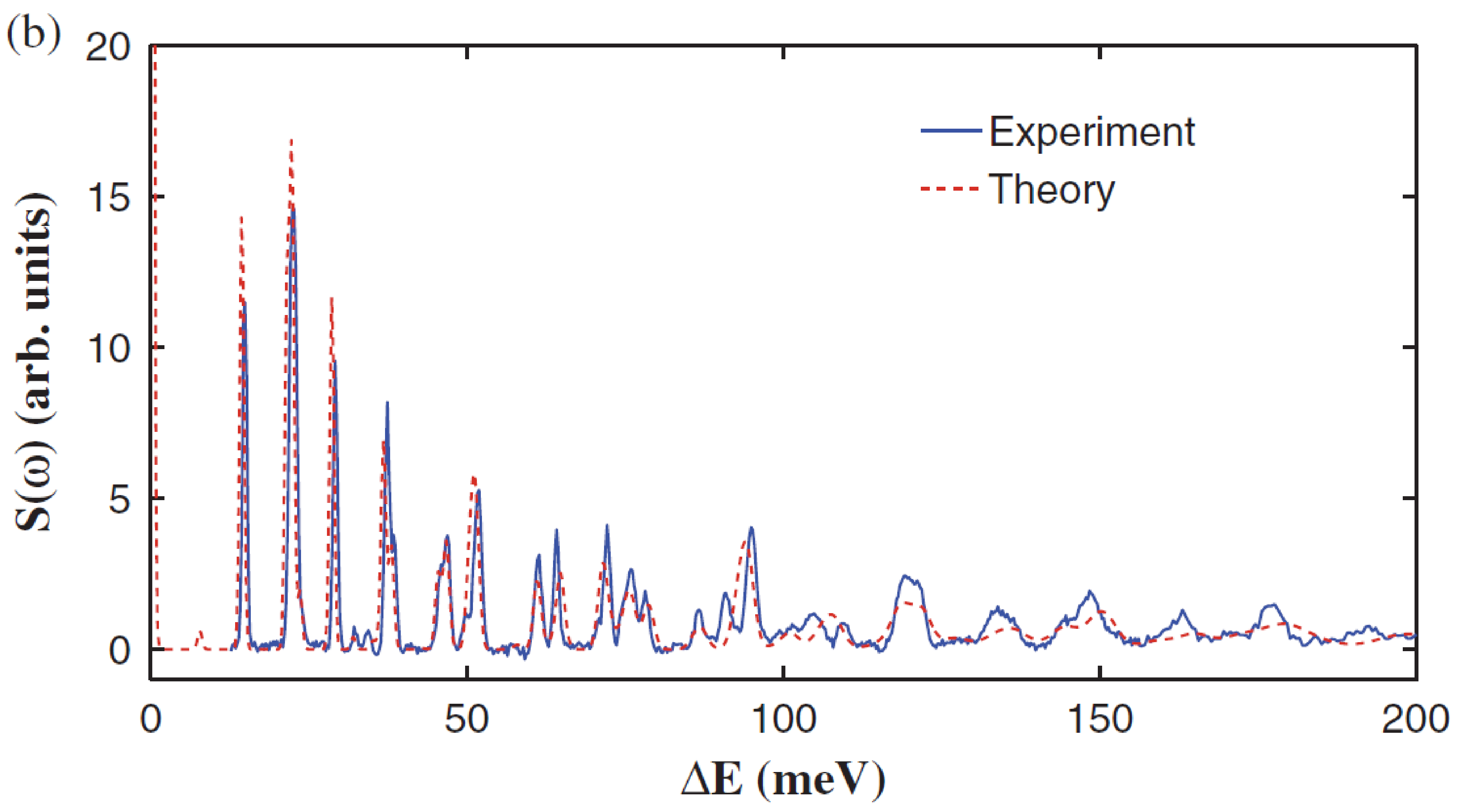


Temperature Dependence of transitions

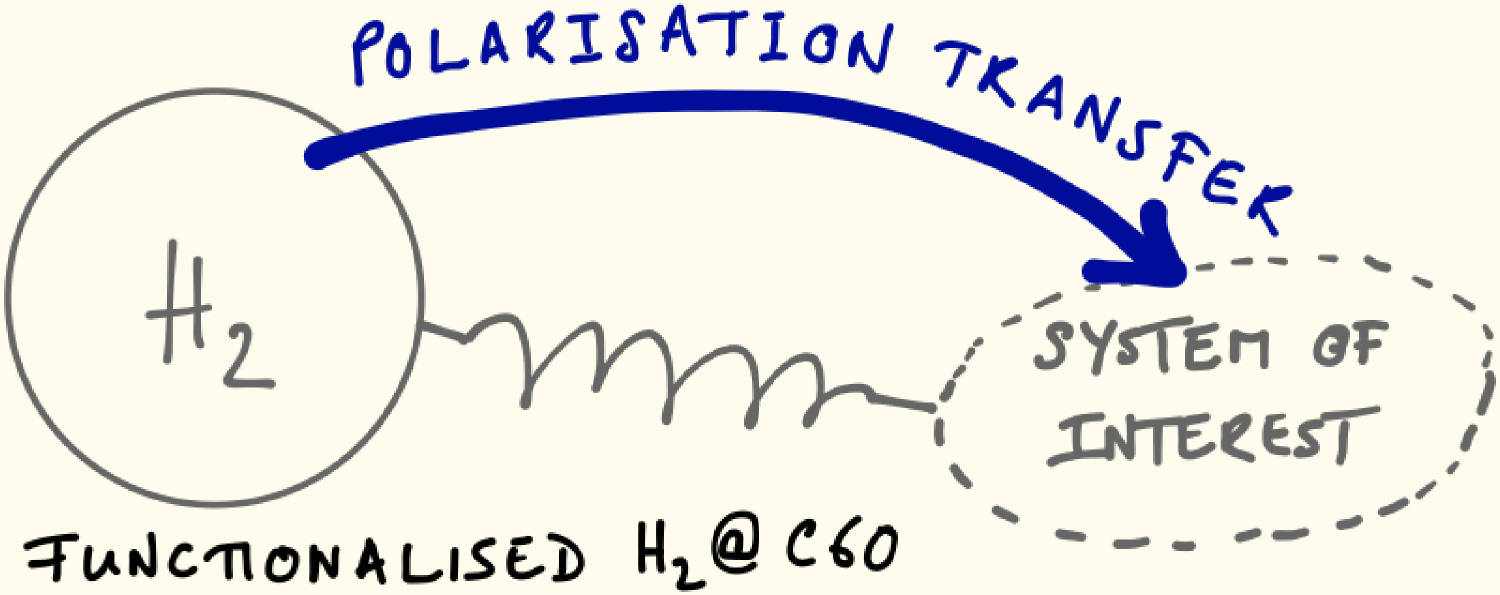




Hot neutrons



Why ?



POLARISATION TRANSFER
H_2
SYSTEM OF INTEREST
FUNCTIONALISED H_2@C60

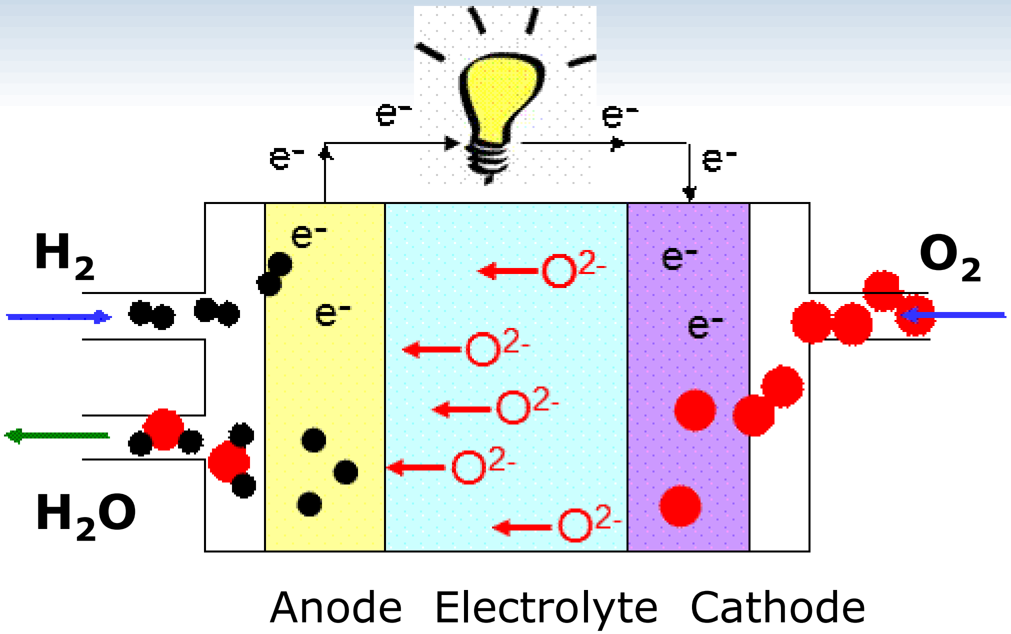
Oxide ion conductors for fuel cell applications

Ivana Evans – University of Durham, UK
Chris Ling – University of Sydney, Australia
Werner Paulus – University of Montpellier, France

Mark Johnson, Stef Rols, Jacques Ollivier, Helmut Schober
Institute Laue Langevin,Grenoble

Fuel cell applications

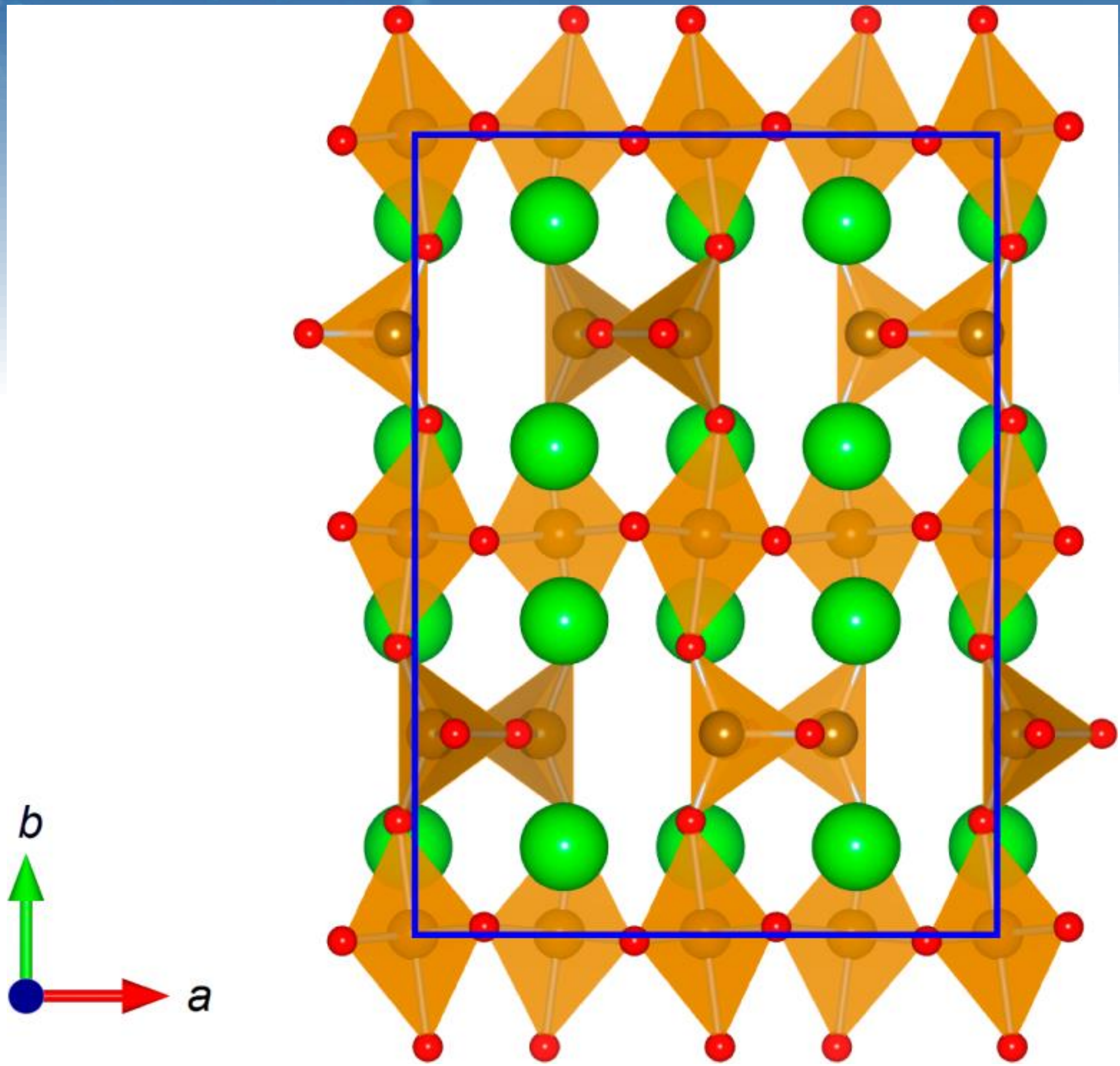
- Clean and efficient energy generation
- Currently used electrolyte: YSZ ($\sigma \sim 10^{-2}$ Scm^{-1} at T > 750°C)
- Current obstacles: device cost and reliability



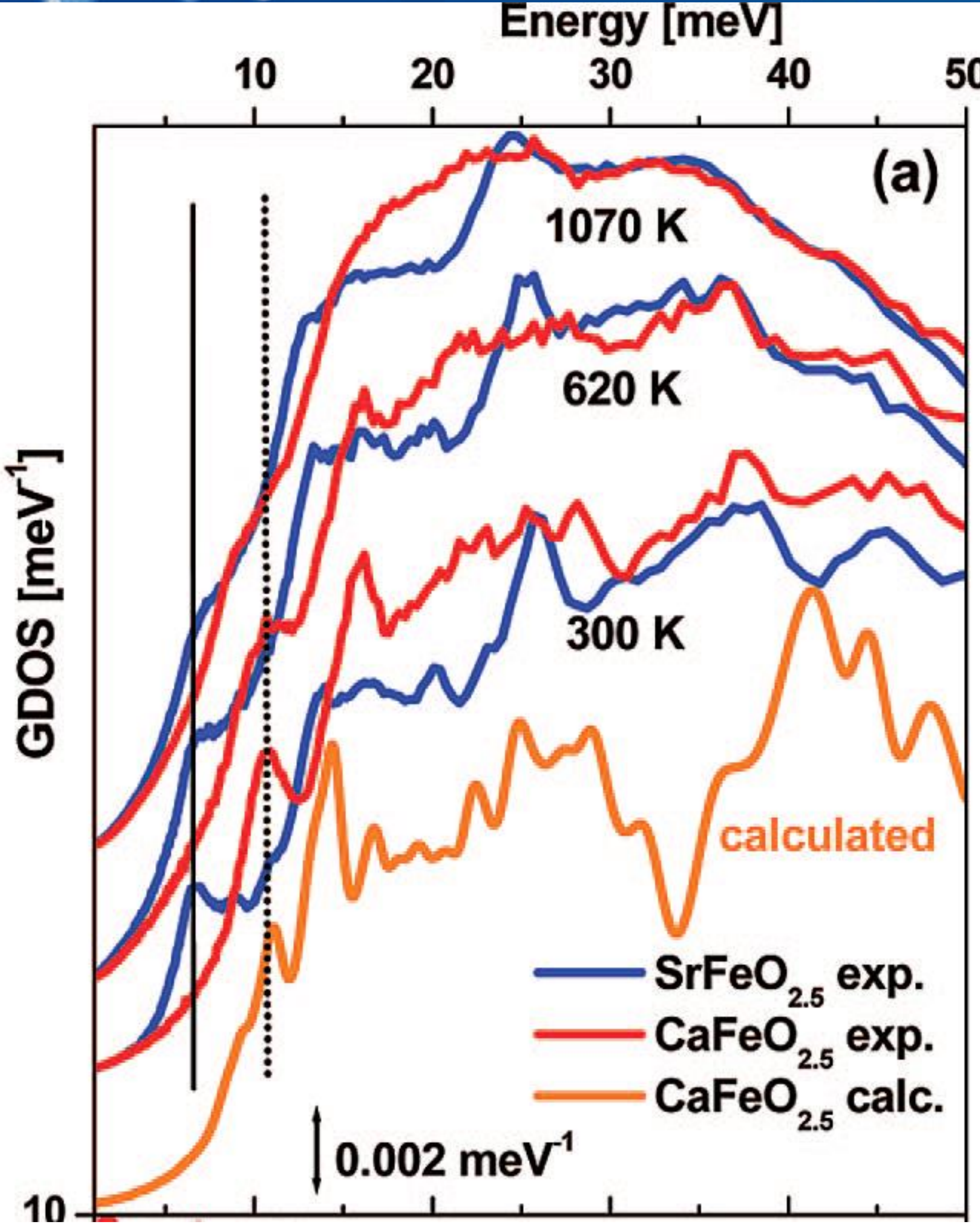
- Aim: lower operating temperature (450-600°C)

Browmillerites – $M_2Fe_2O_5$ (M = Ca, Sr, ...)

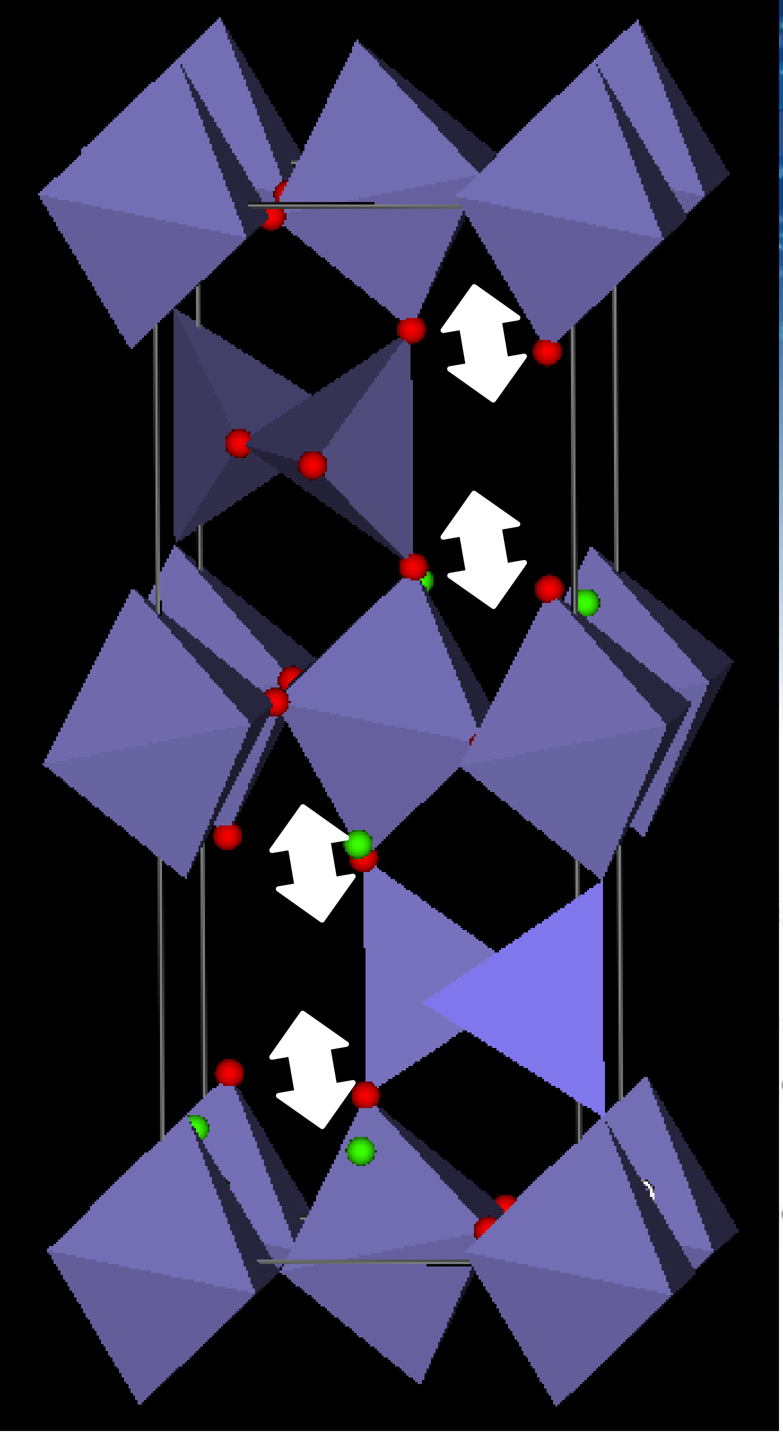
- JACS (2008) v130 p16080

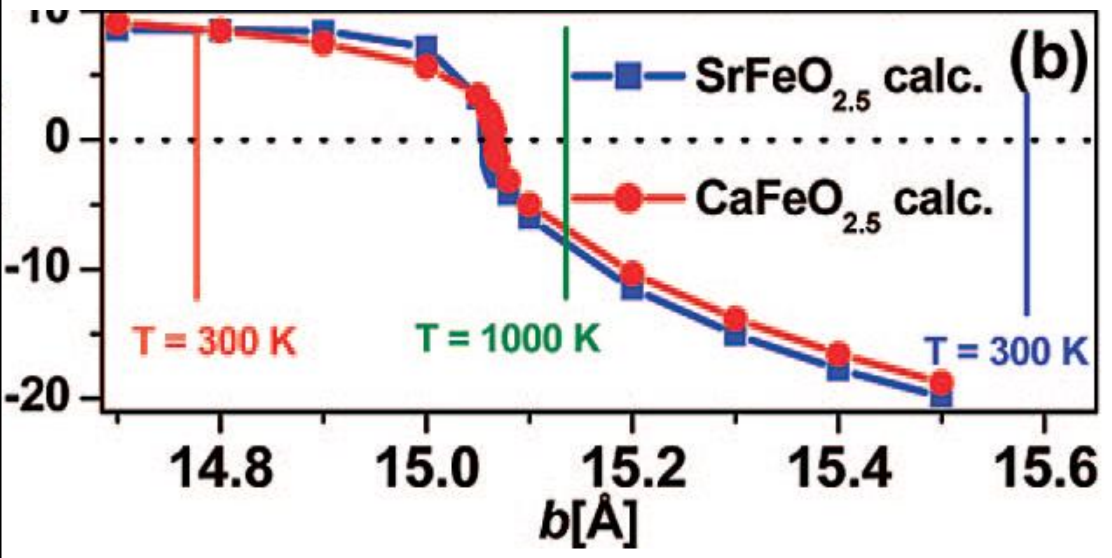


Browmillerites – phonons: INS & DFT



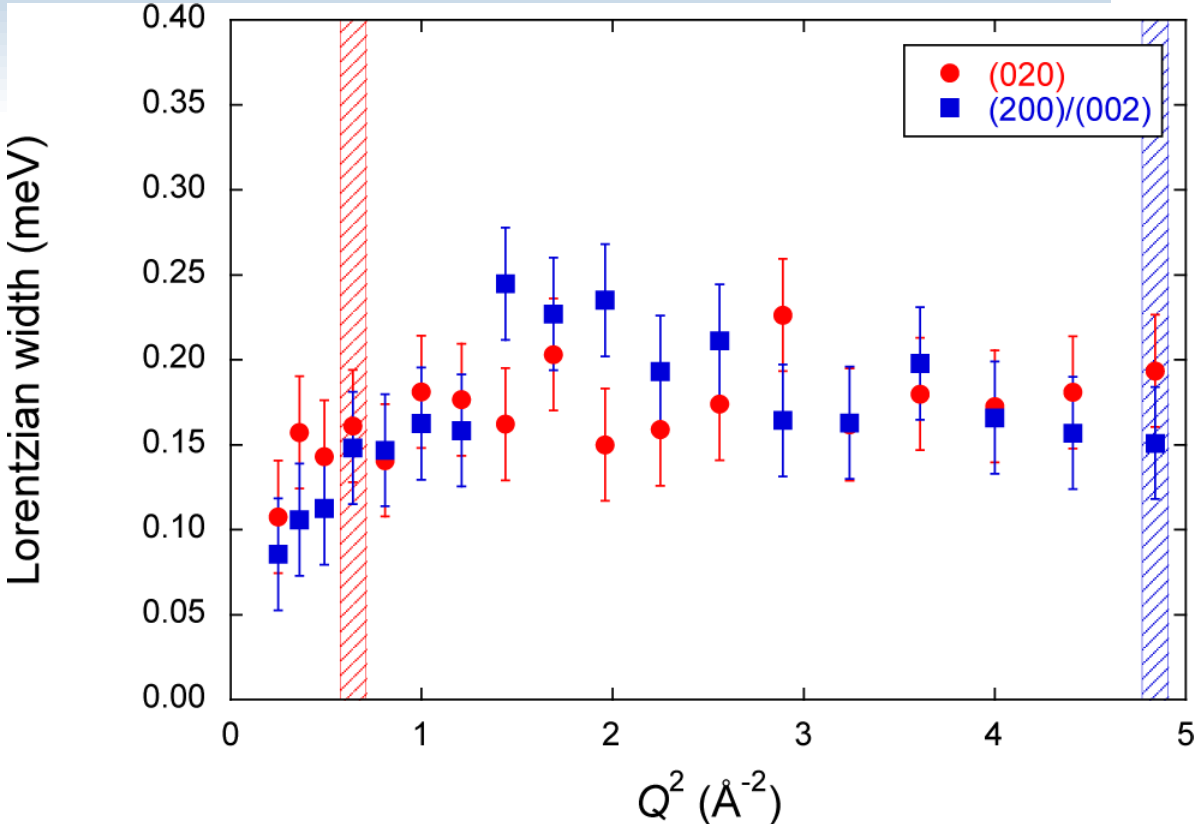
Browmillerites – phonons: INS & DFT

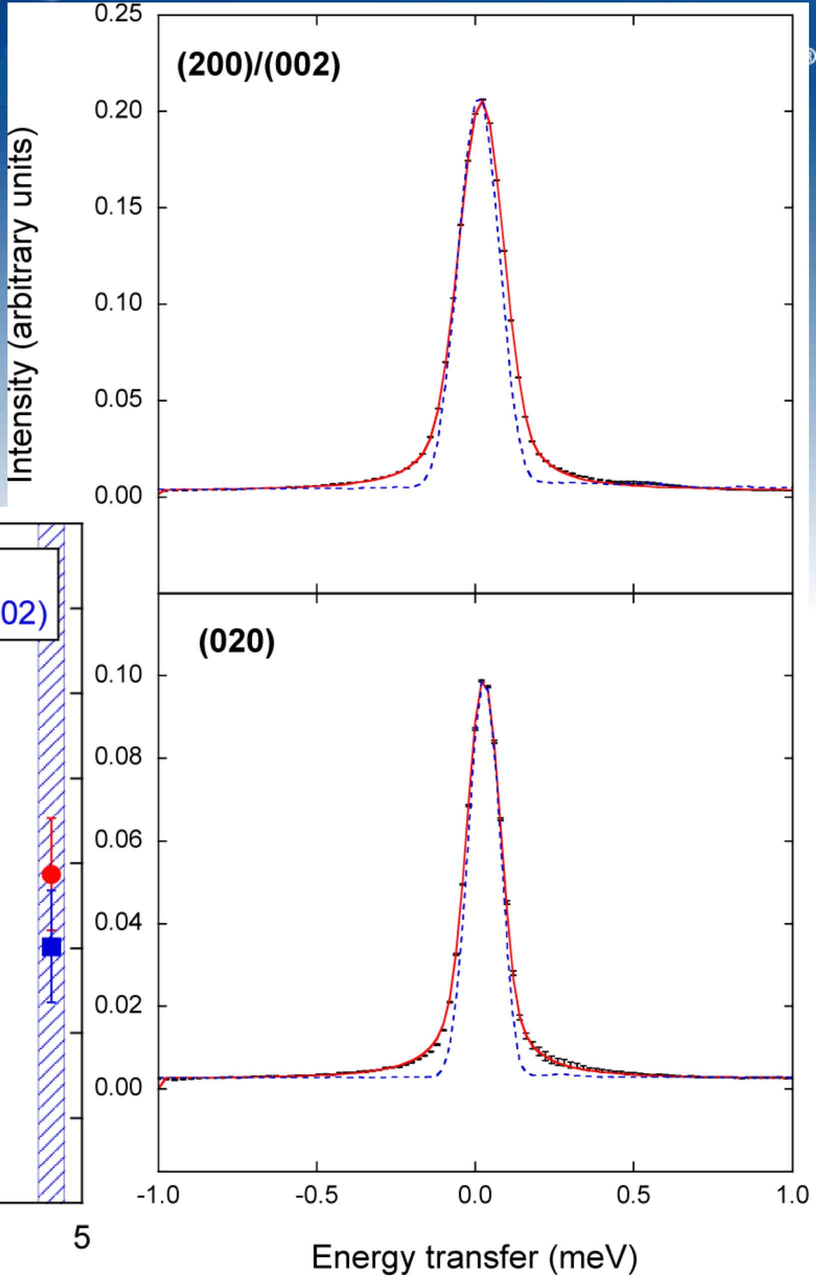




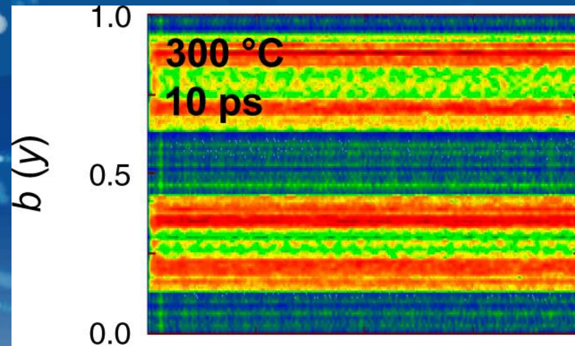
Browmillerites – diffusion: QENS

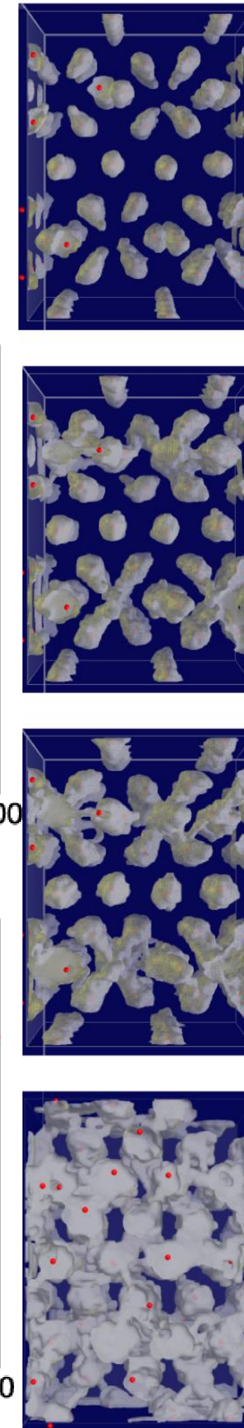
- Chemistry of Materials (2013) v25 p3080

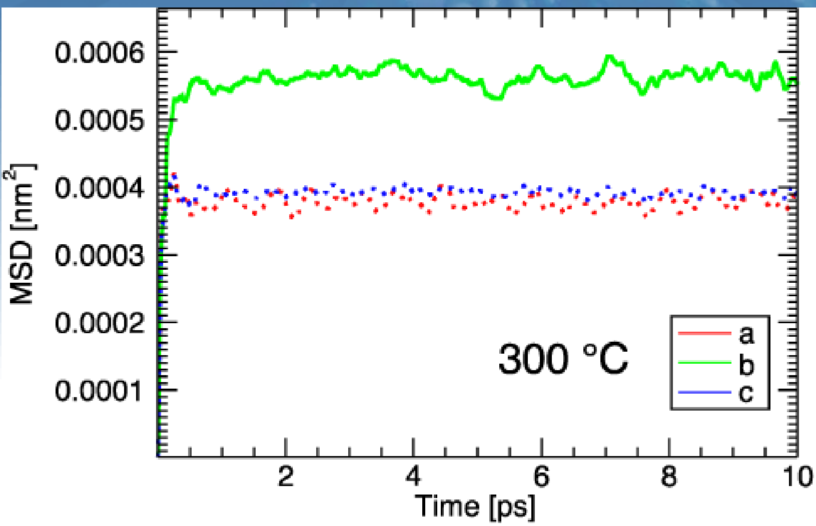


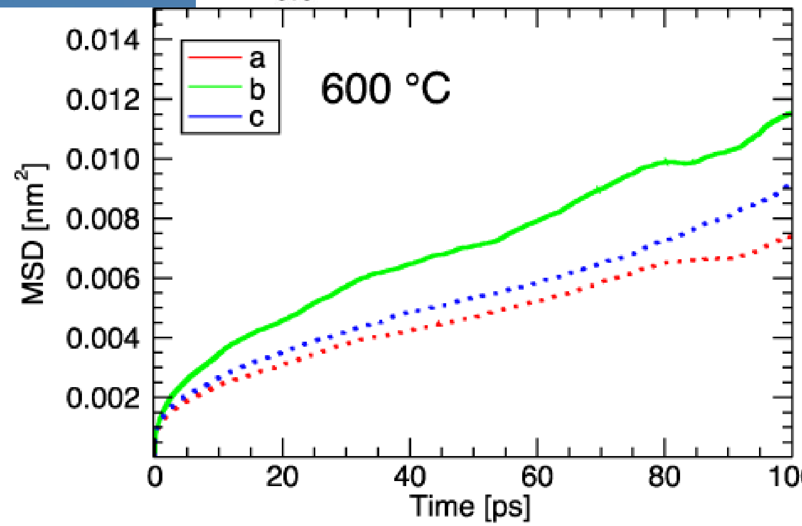


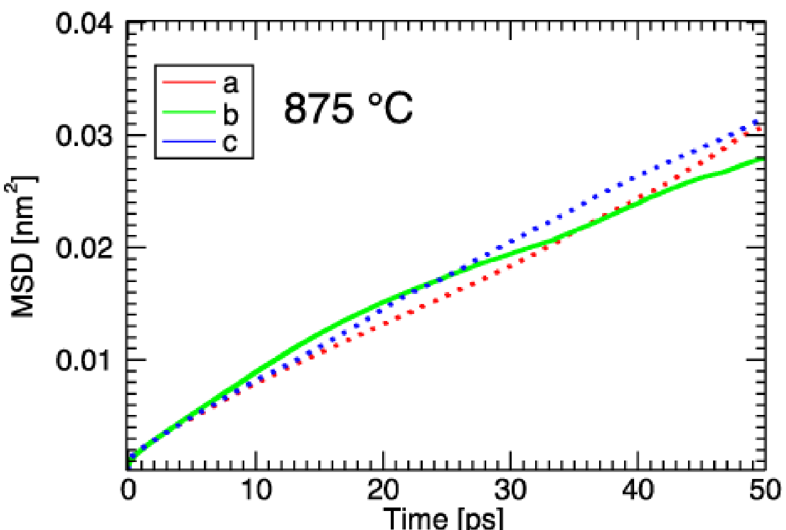
Browmillerites – diffusion: DFT-MD

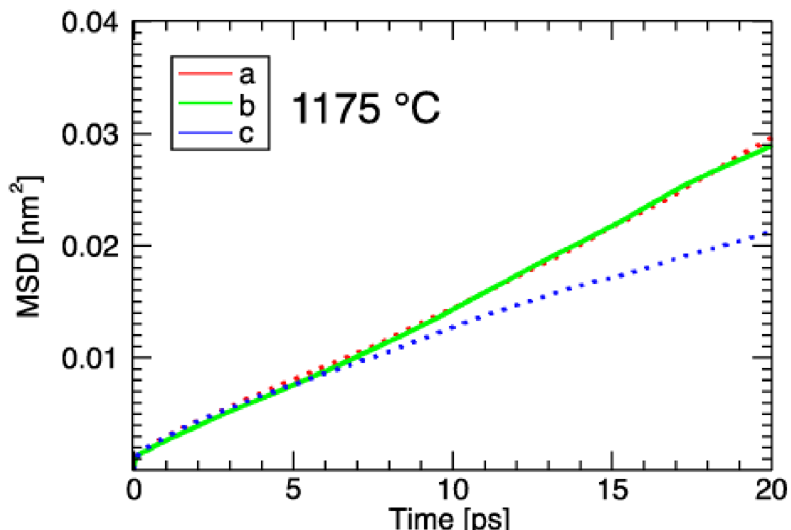












Bismuth-based conductors

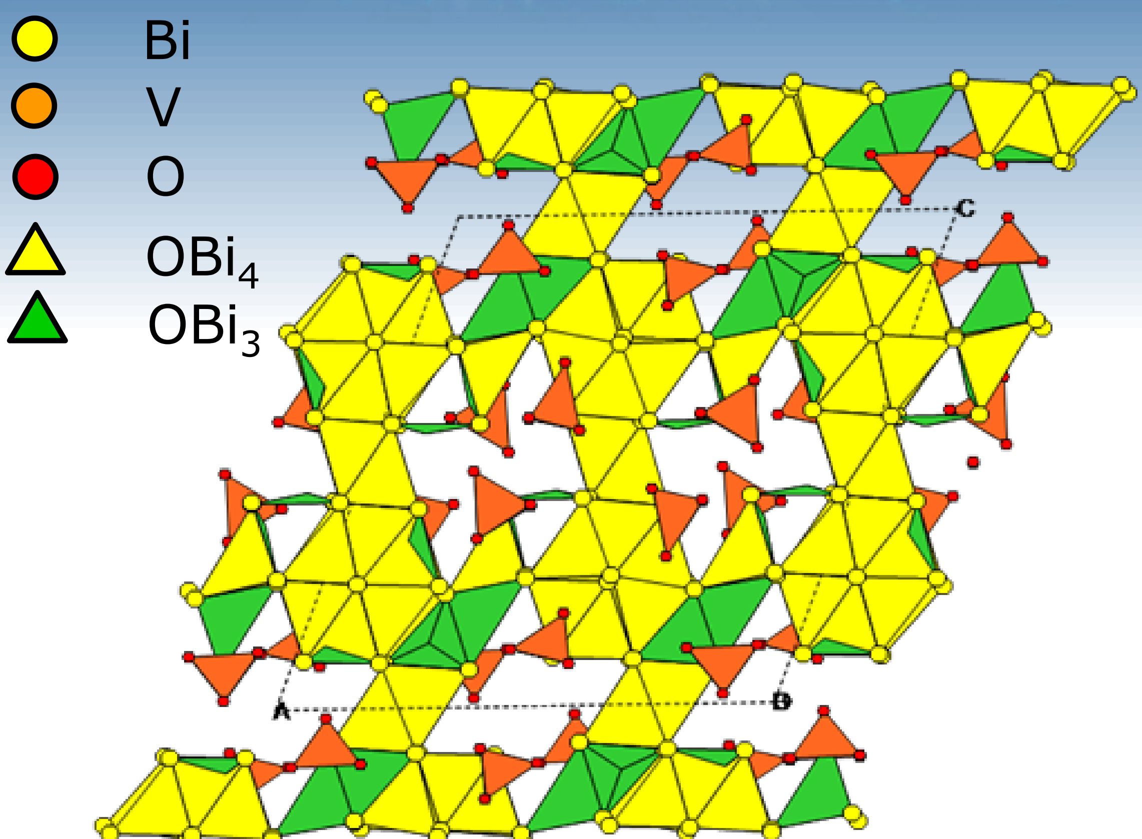
- δ-Bi_2O_3 – best oxide ion conductor: ~1 Scm^{-1}
- 25% O vacancies → vacancy hopping mechanism
- BUT narrow, high temperature stability range

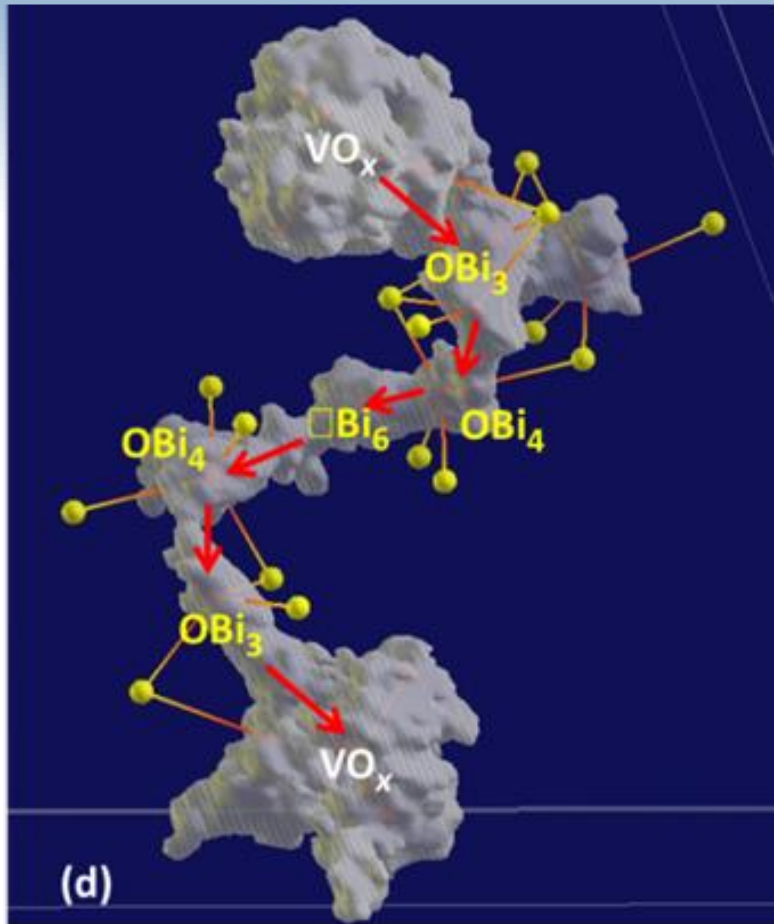
- *Dope with e.g. divalent cation to remove O (Bi^{3+} → Ca^{2+}) → create more vacancies*

- BUT doping with V^{5+} works best: $\sigma \sim 10^{-1}$ Scm^{-1} at T < 500°C
- New conduction mechanism in dual sub-lattice systems: Bi_2O_3 and VO_n
  - Dopant cations have variable coordination; 4,5,6
  - Polyhedral rotation creates dynamic disorder
  - Enhanced vacancy population and conduction in Bi_2O_3 lattice

Vanadate – $Bi_{16}V_2O_{29}$

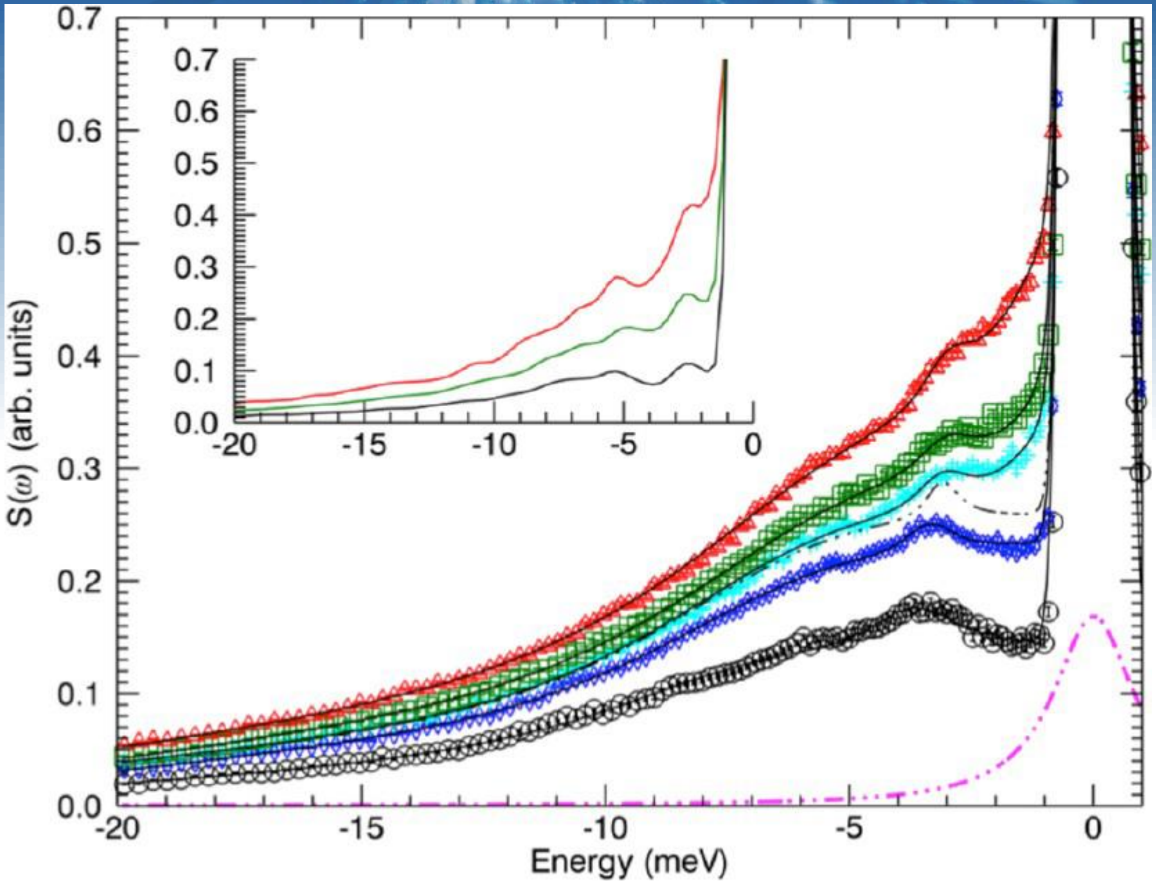
β-form, C2/m

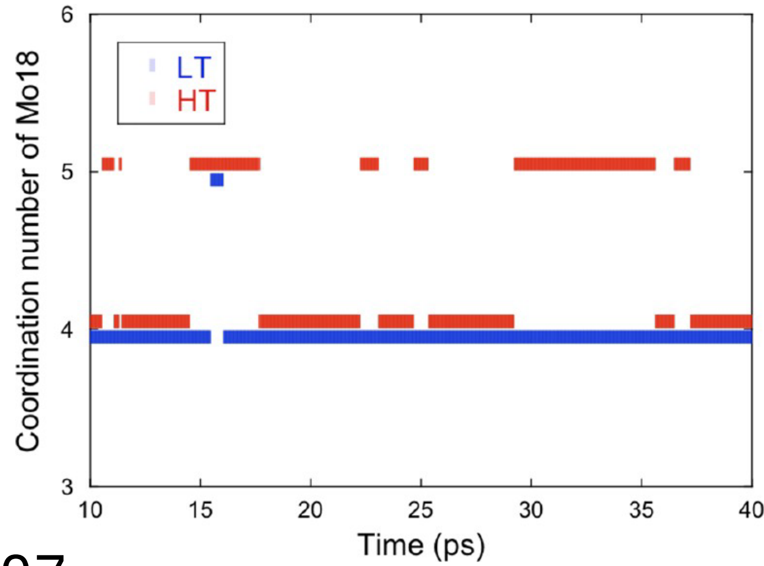




- Angewandte Chimie Int (2012) v51 p690

Molybdate – $Bi_{26}Mo_{10}O_{69}$





- Chemistry of Materials (2012) v24 p4607

Oxide ion conductors – conclusion

- Low frequency vibrations trigger diffusion
- Some structural disorder is essential
  - Variable coordination cations and mixed sub-lattices help
- QENS experiments to go to longer times
  - Measure microscopic diffusion
  - Compare with macroscopic conductivity measurements

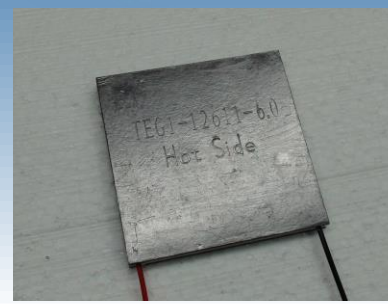
Thermoelectric materials: heat → electricity

Pierre-Francois Lory, Marek Koza, Helmut Schober, *Institute Laue Langevin,Grenoble*

Marc de Boissieu – University of Grenoble, France

Marek Mihalkovic – Bratislava, Slovakia

Thermoelectric materials



http://blog.modernmechanix.com

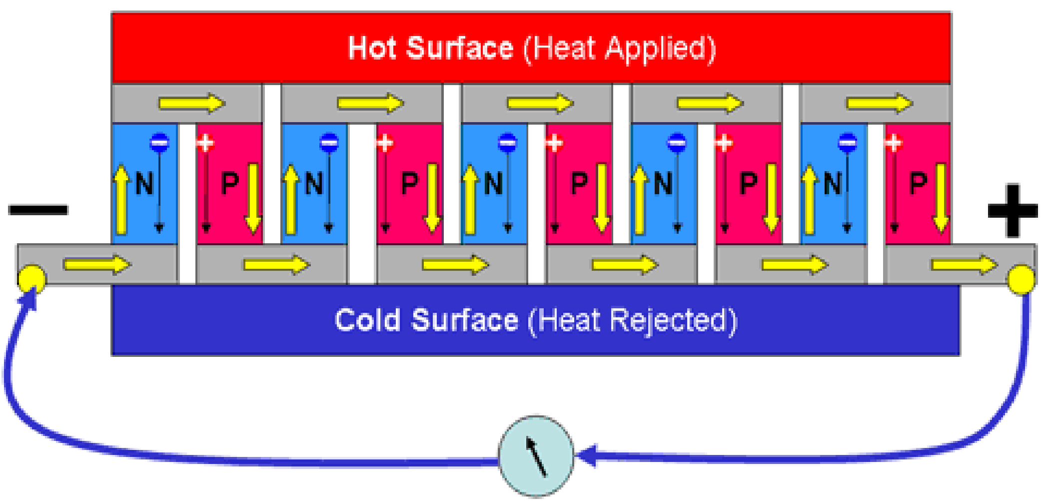
Kerosene Lamp Powers Radio

REMOTE areas of Siberia and China use thermoelectric generators like the one shown here to convert heat from a kerosene lamp into electricity for radios.

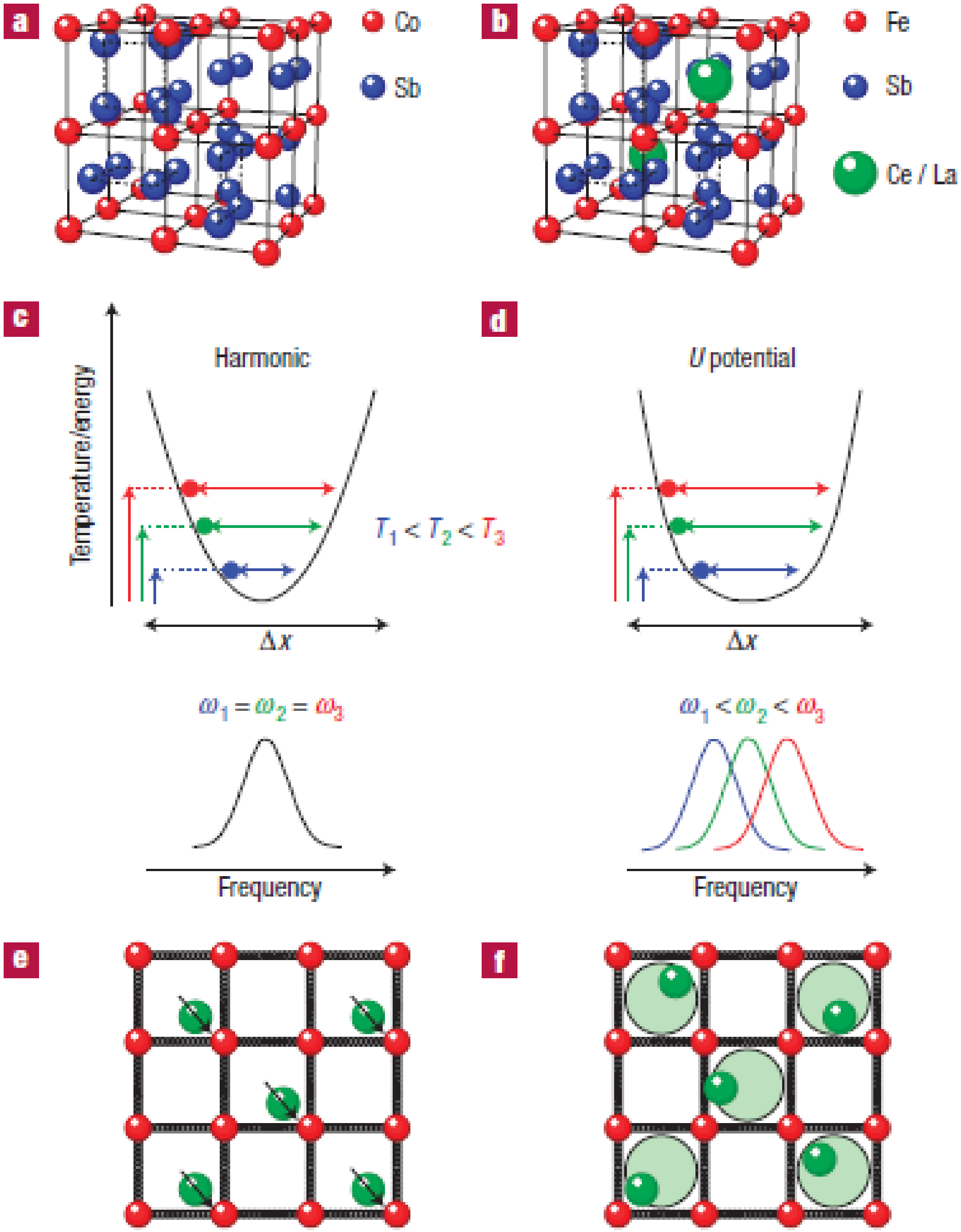
The 20-lb. device is being studied by scientists at the Martin Co., Baltimore, Md., where similar direct conversion principles have been applied to nuclear heat sources. They paid $56 for the Russian-built device.

A series of thermocouples is arranged around the upper portion of the lamp. As each set of elements is heated at one end by the lamp, a small amount of electricity flows through the pair. Metallic fins remove the excess heat.

http://www.mpoweruk.com/thermoelectricity.htm



Thermoelectric Generator (TEG)



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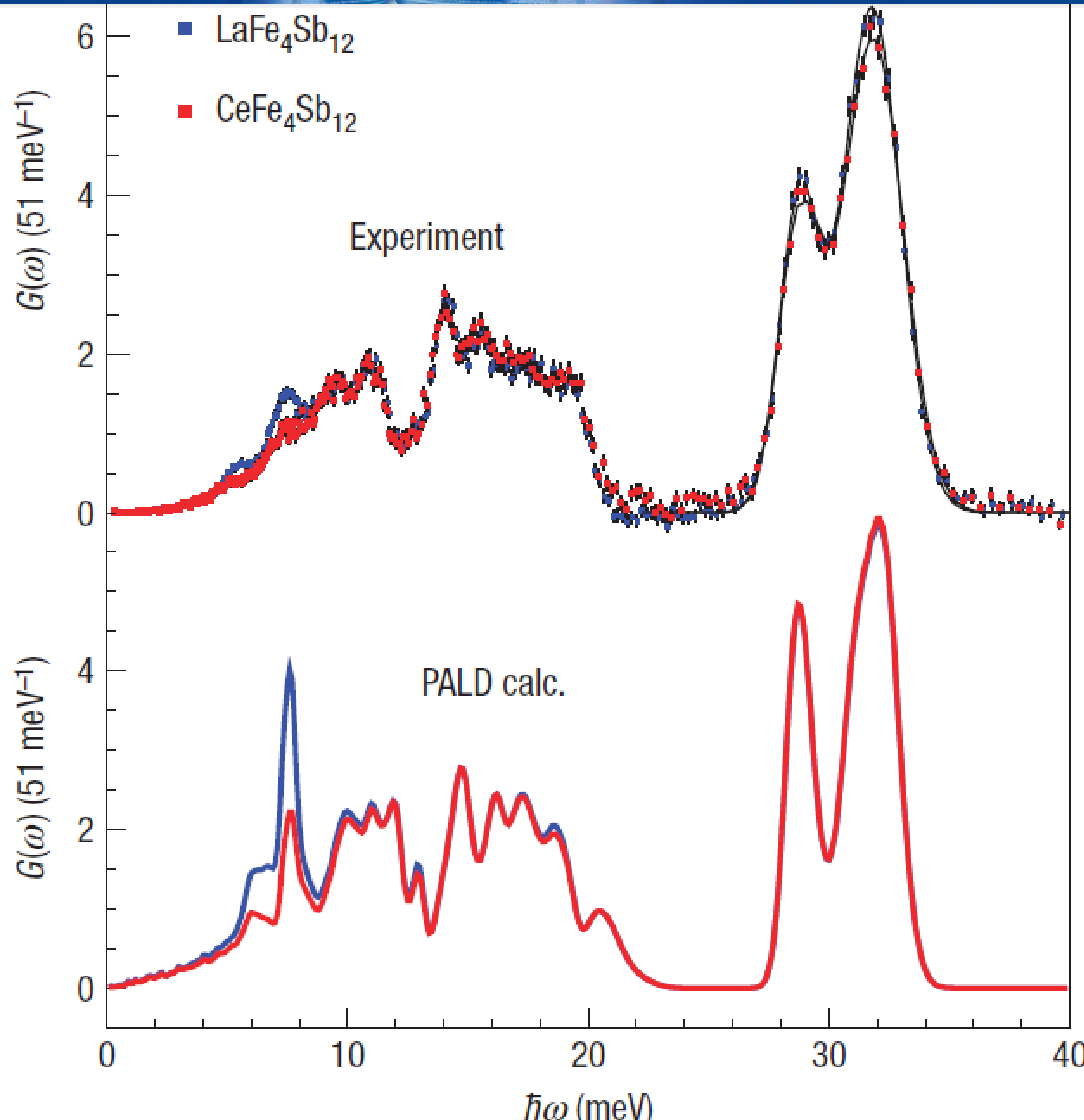
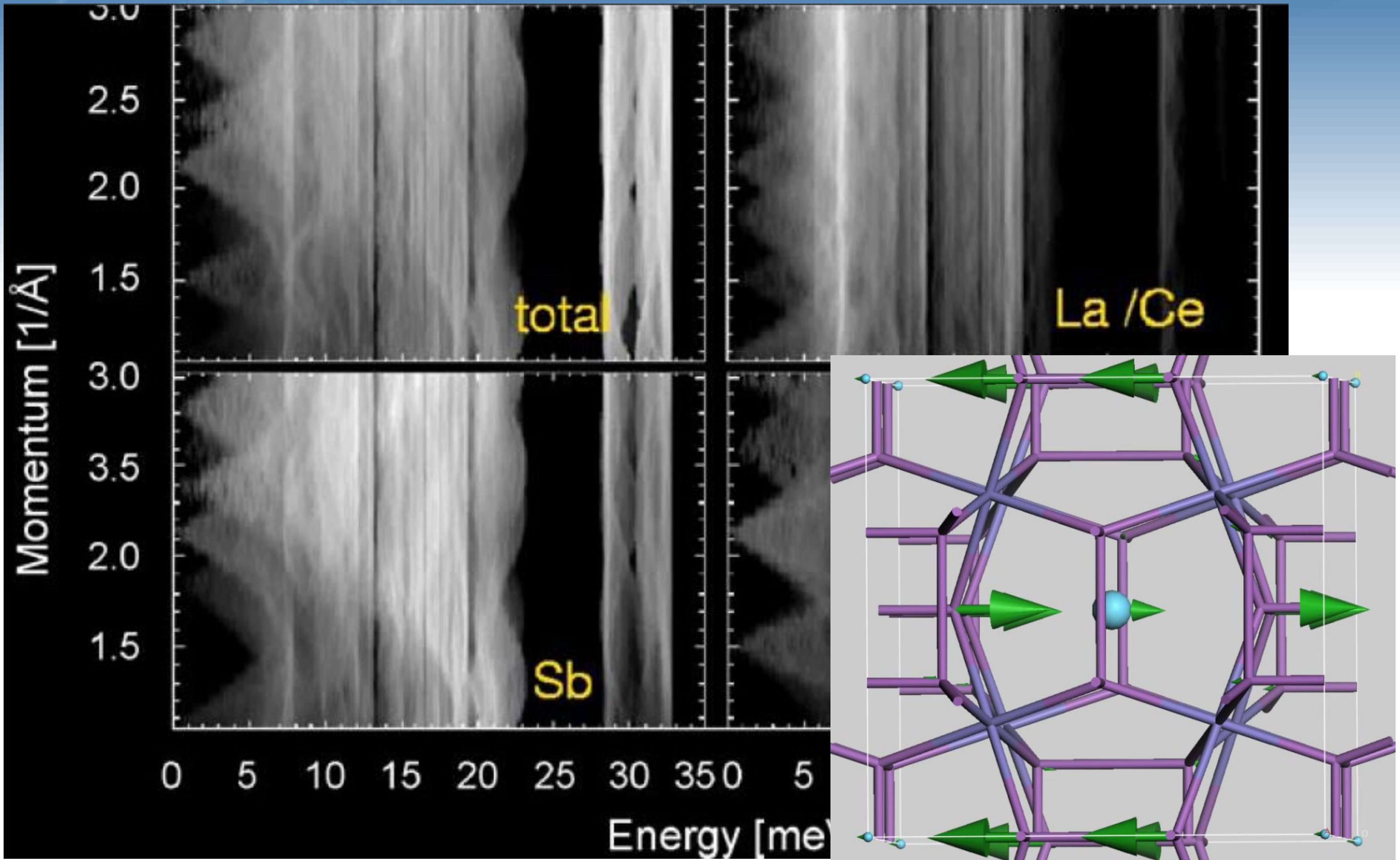
Skutterudites: Cage compounds

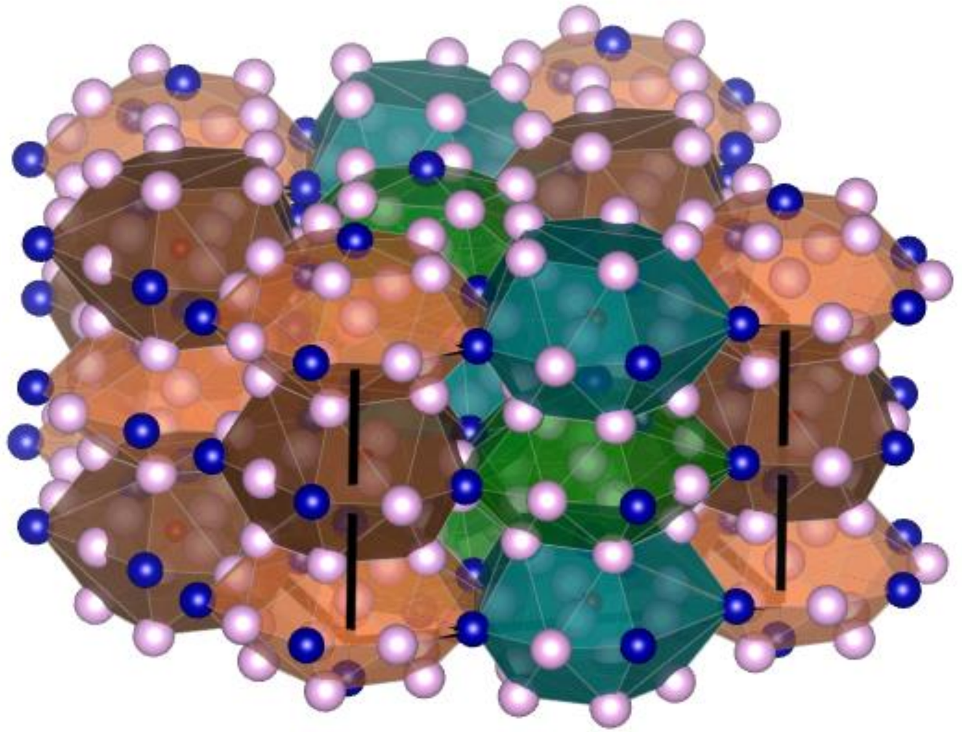
Skutterudites – Vibrational density of states

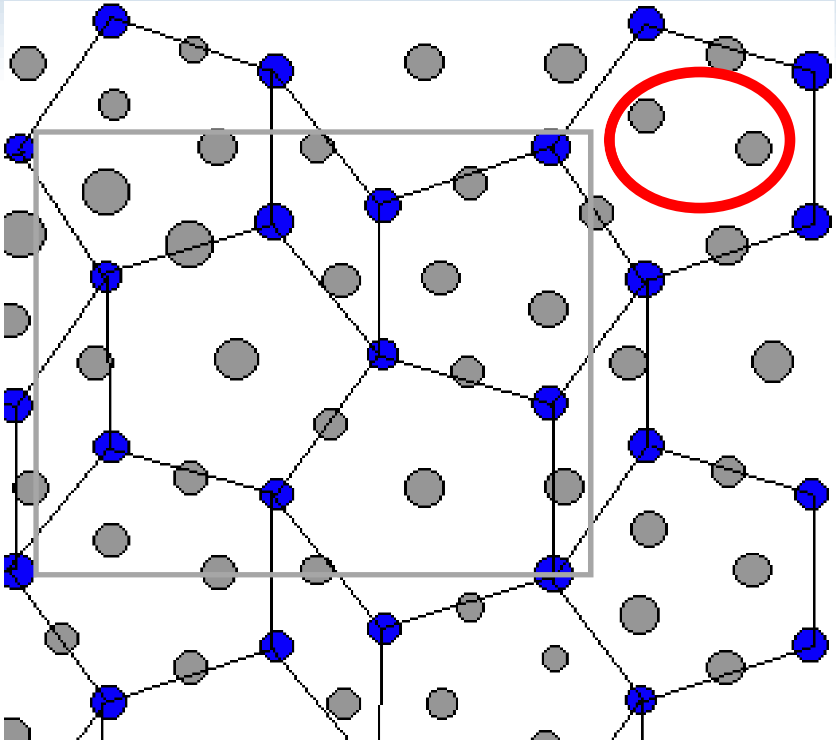


Skutterudites – S(Q,w) from powder-averaged lattice dynamics

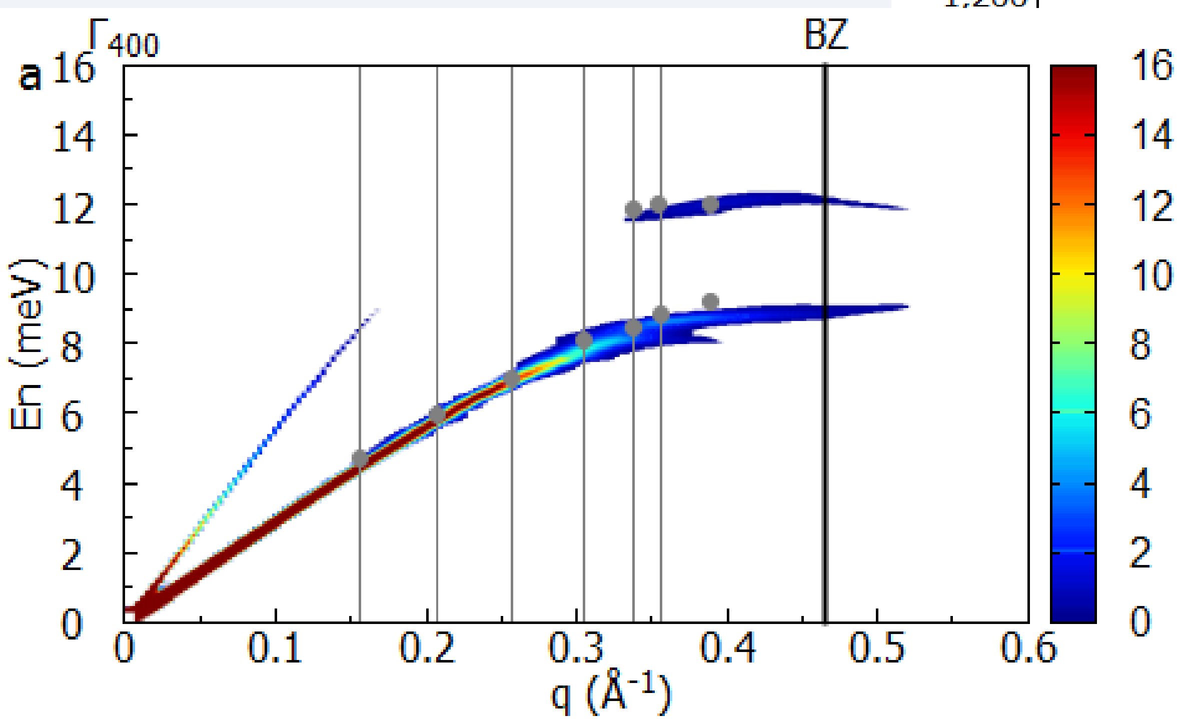


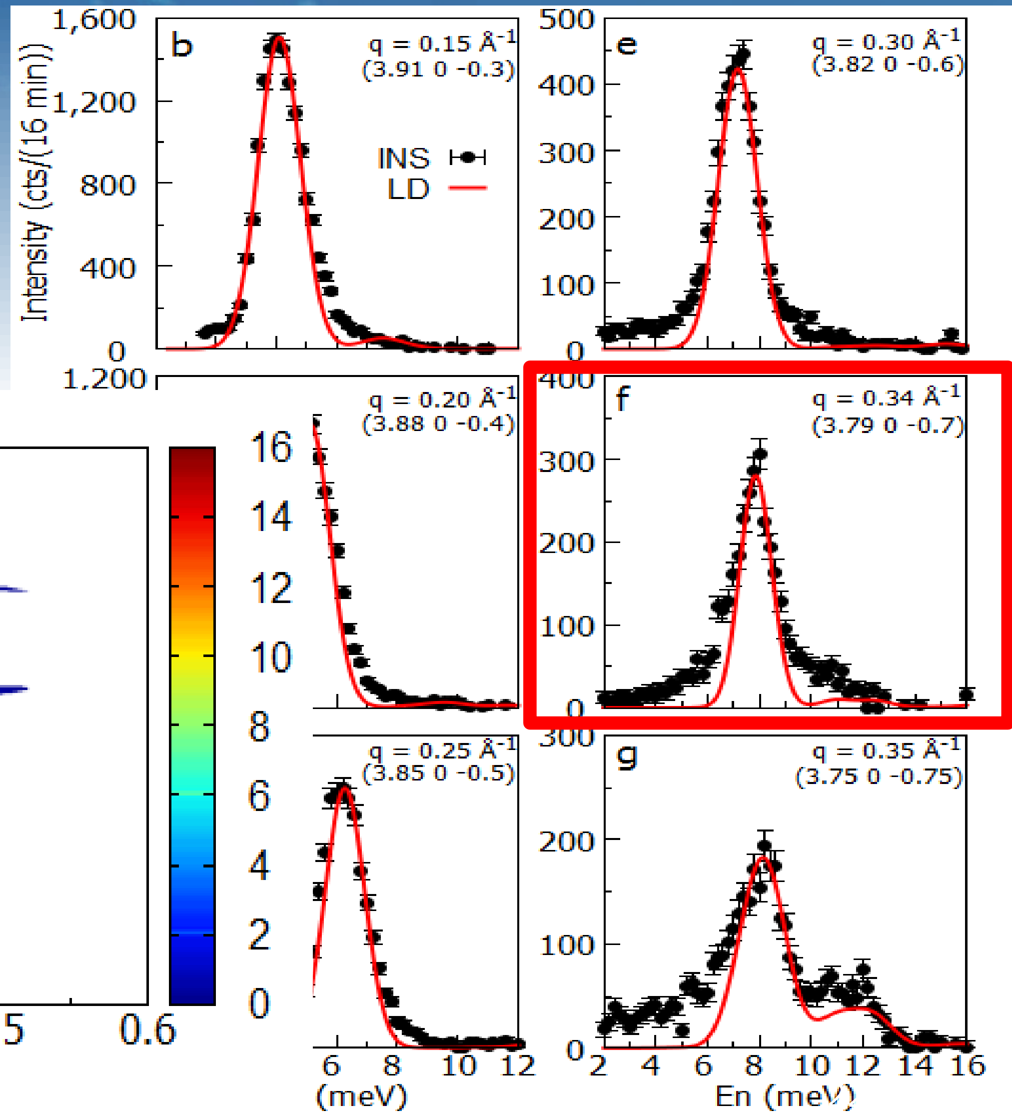
Complex Metallic Alloy – $Al_{13}Co_4$ Quasicrystal approximant



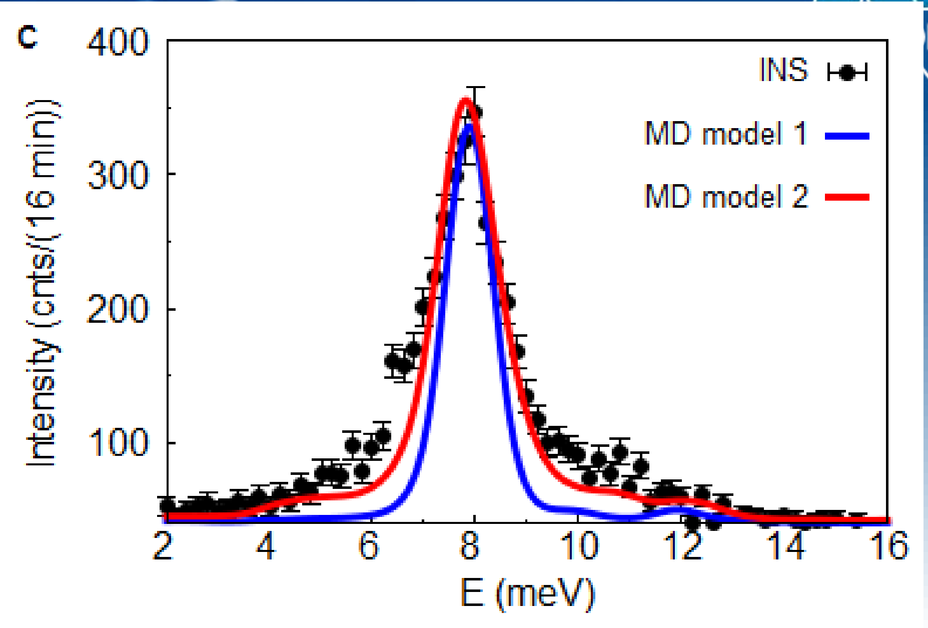


Measuring phonon linewidths - TAS

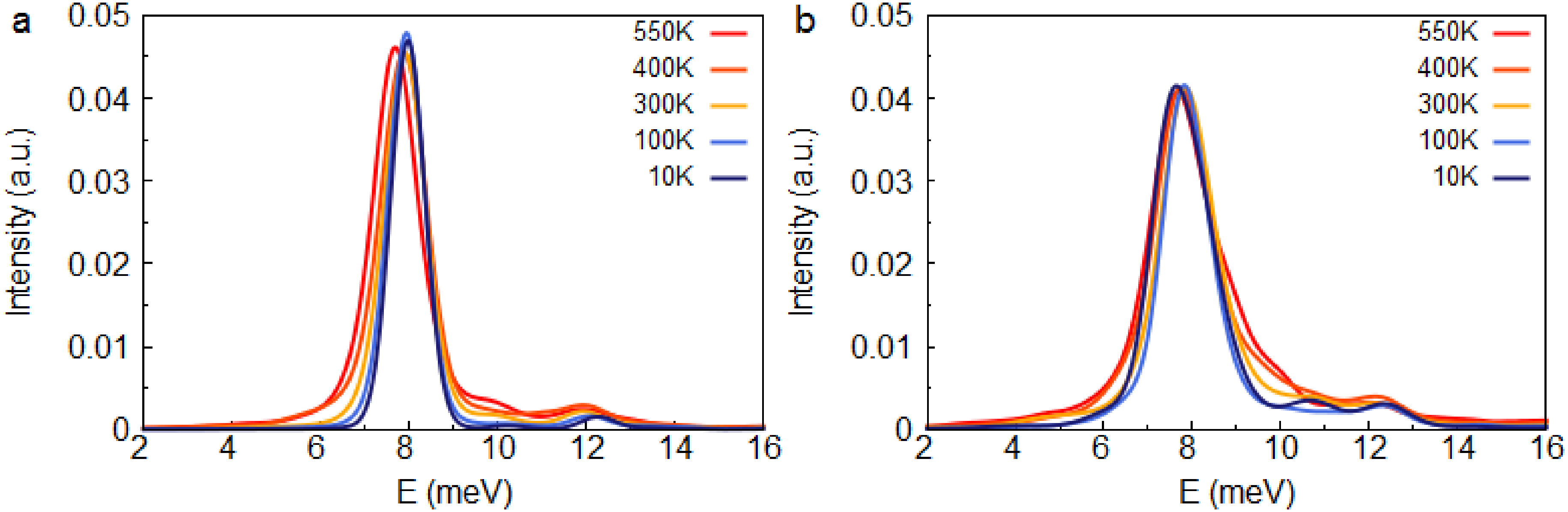




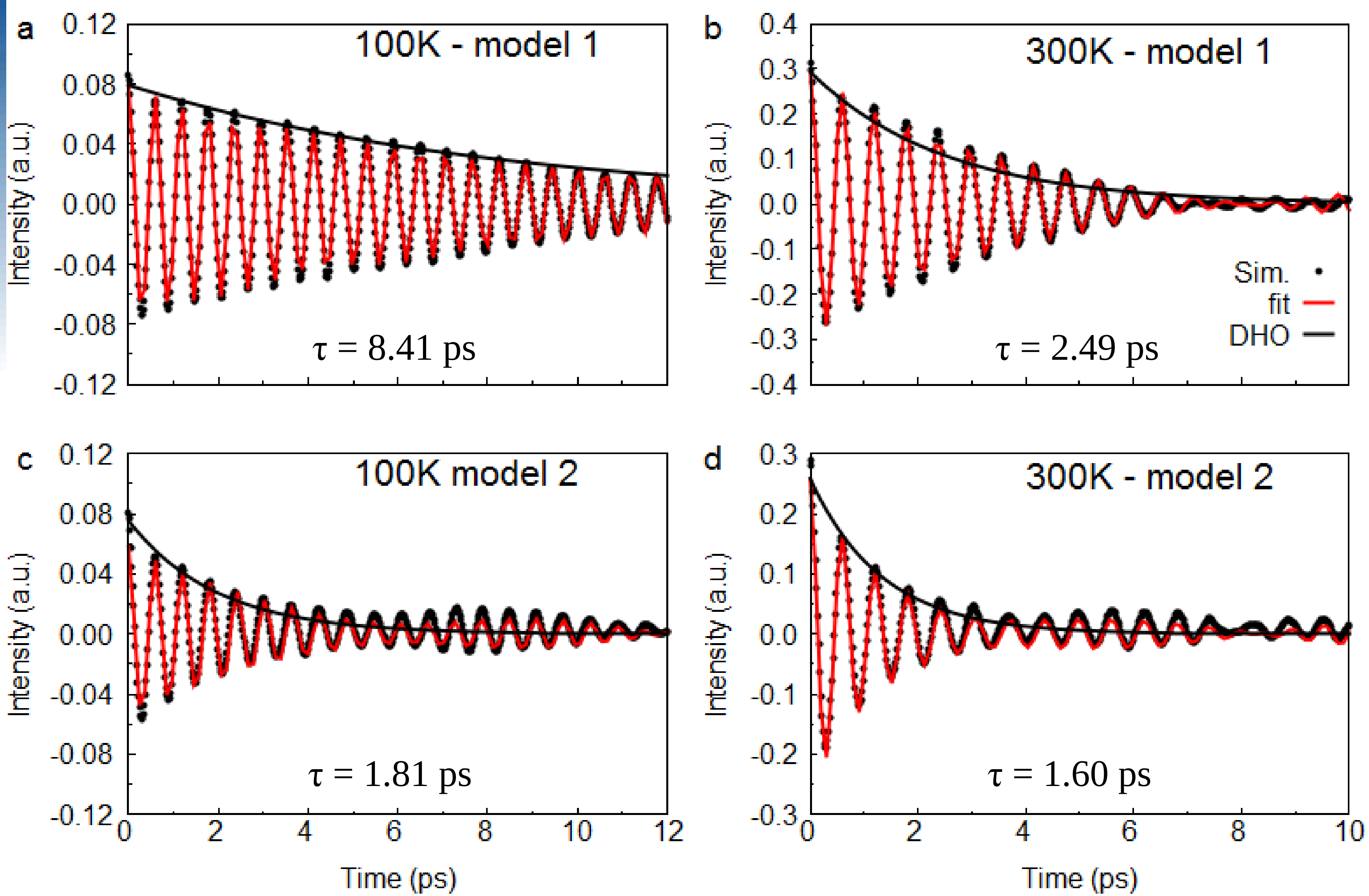
Simulating phonon linewidths - MD



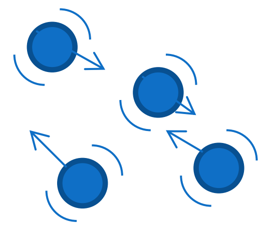
Model 1: ordered | **Model 2: disordered**



In the time domain…



Calculating thermal conductivity



Molecular Dynamics *(LAMMPS)*

Positions, velocities
Energy and forces

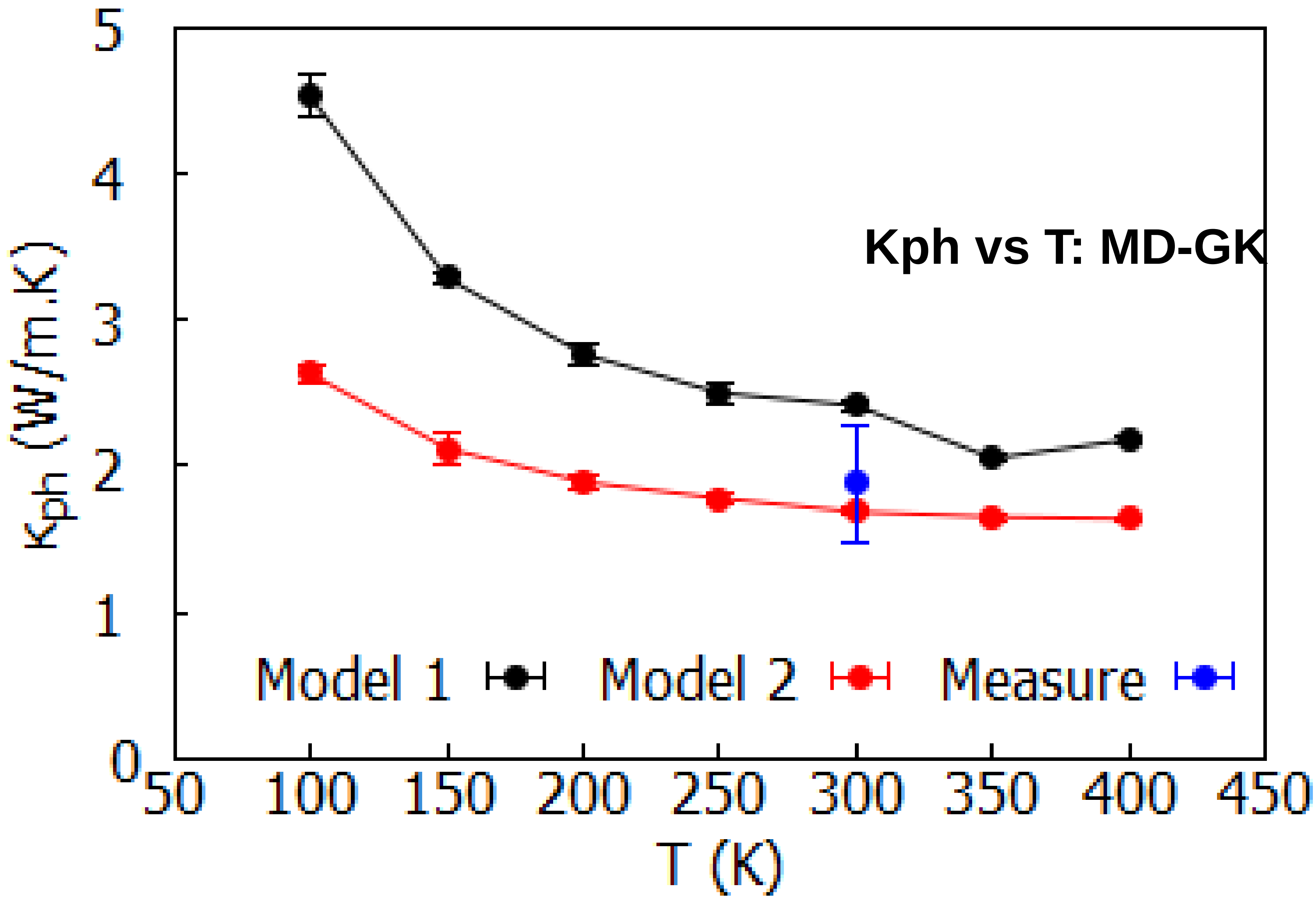
Statistical method

Green-Kubo
Heat Current
$J_i(t)$

$$J_i(t) = \sum_i v_i E_i + \sum_{i \neq j} r_{ij}(F_{ij}.v_j)$$

$$K_{ph}(T) = \frac{V}{3k_B T^2} \int_0^t \sum_{i=x,y,z} \langle J_i(t).J_i(0) \rangle \, dt$$

Thermal conductivity
K_{ph}



Kph vs T: MD-GK
Kph (W/m.K)
5
4
3
2
1
0
50
100
150
200
250
300
350
400
450
T (K)
Model 1
Model 2
Measure

CONCLUSION - THERMOELECTRICS

- Phonon-phonon scattering processes are responsible for reduced phonon lifetimes and low thermal conductivity in Skutterudites.

- Phonon lifetimes in QC approximant are weakly T dependent → defects/disorder is limiting factor


Enjoy exploring potential energy surfaces ☺