Rattling modes in thermoelectric materials

Jon Goff

Outline of talk

Phonon-glass electron-crystal

Highlights - Inelastic X-ray Scattering

- Density Functional Theory

- Thermal conductivity

ROYAL HOLLOWAY UNIVERSITY OF LONDON

Collaborators

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-M. Roger

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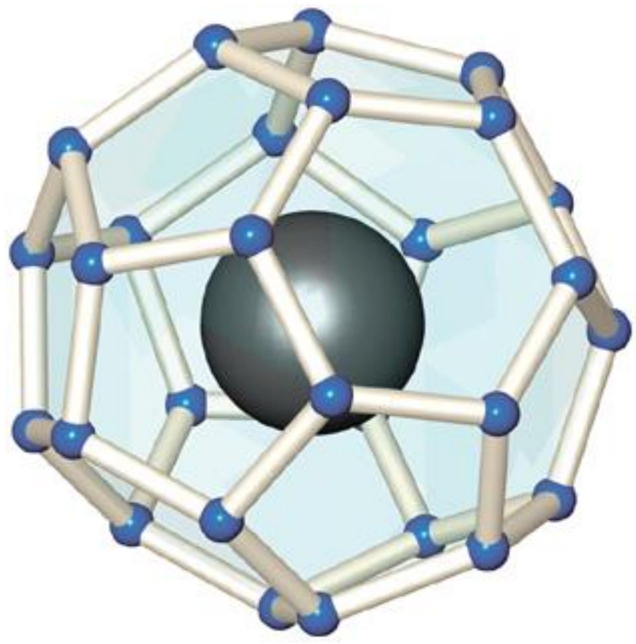
A.T. Boothroyd, L. Gannon

David Voneshen

Phonon-glass electron-crystal

Phonon-glass electron crystal (PGEC)

- Cage forms regular periodic lattice in which electrons or holes move freely
- Loosely bound rattler scatters phonons reducing thermal conductivity to glass-like values
- Skutterudites, clathrates, cobaltates



[Slack, G. A. in *CRC Handbook of Thermoelectrics* (ed. Rowe, D. M.) 407-440 (CRC, Boca Raton, FL USA, 1995).]

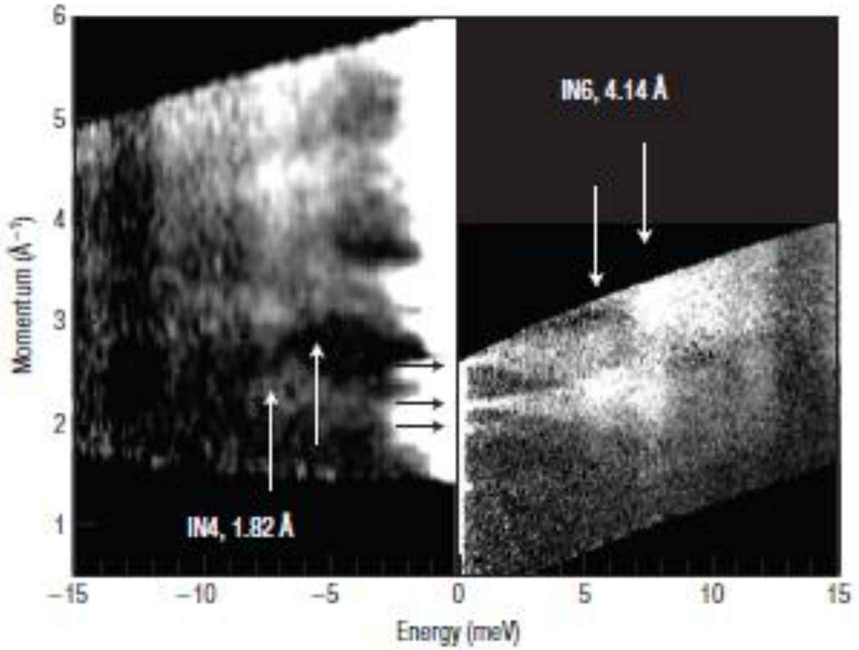
Phonon-glass electron-crystal

$LaFe_4Sb_{12}$ & $CeFe_4Sb_{12}$

- Powder measurements on IN4 & IN6 at the ILL

- See well defined phonons

- Quasi-harmonic coupling between guest & host lattice



[Koza, M. M., *et al*., Breakdown of phonon glass paradigm in La- and Ce-filled Fe_4Sb_{12} skutterudites. *Nature Mater.* **7**, 805-810 (2008).]

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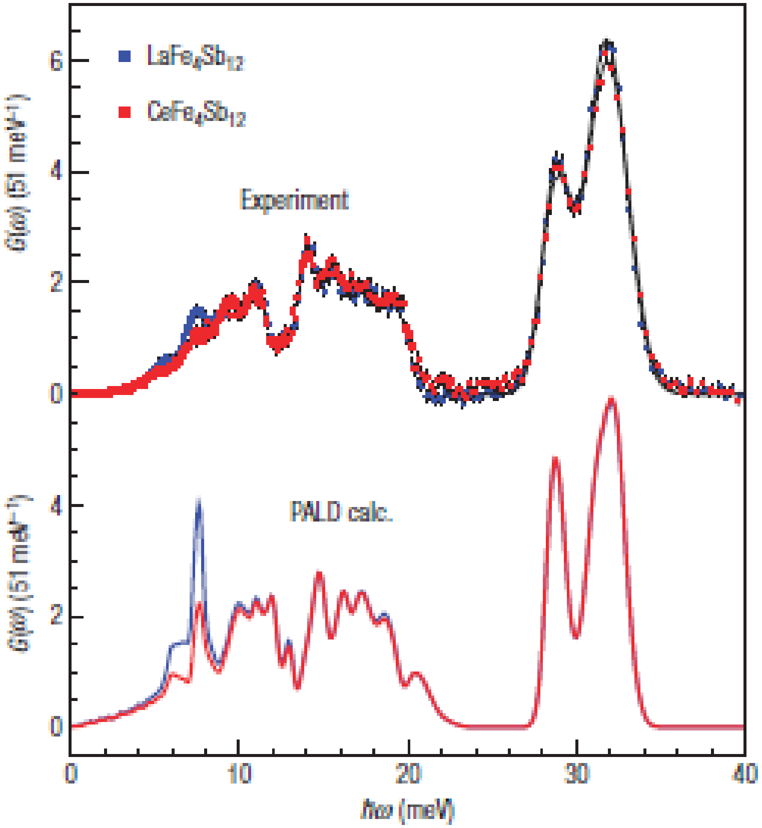

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Avoided crossing in clathrates

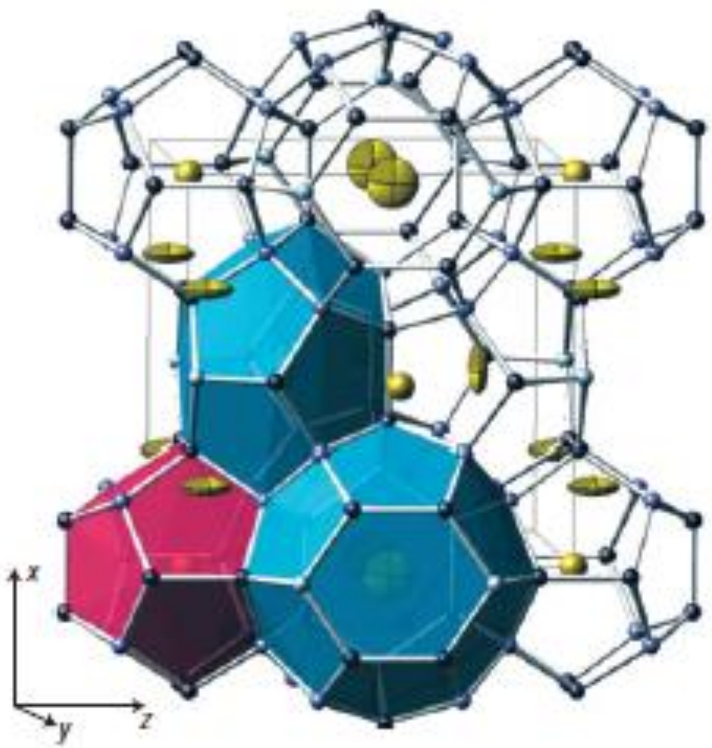
$Ba_8Ga_{16}Ge_{30}$

• Ba guest atoms in cages of Ge & Ga

• Spring model describing interaction between guest atoms and cage walls

• Avoided crossing of acoustic phonon of the cage and flat mode of the guest

• Single-crystal Inelastic Neutron Scattering data from RITA-II at PSI



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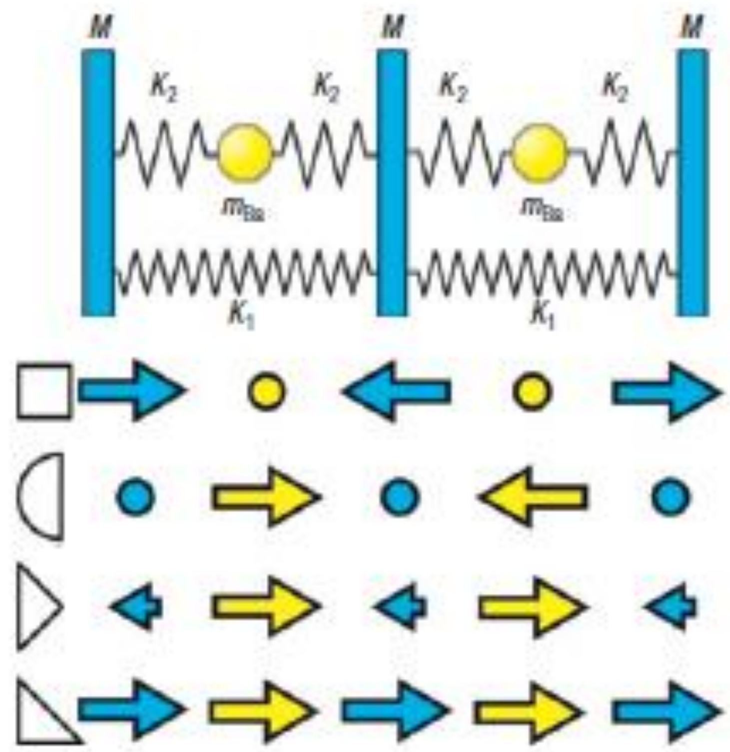

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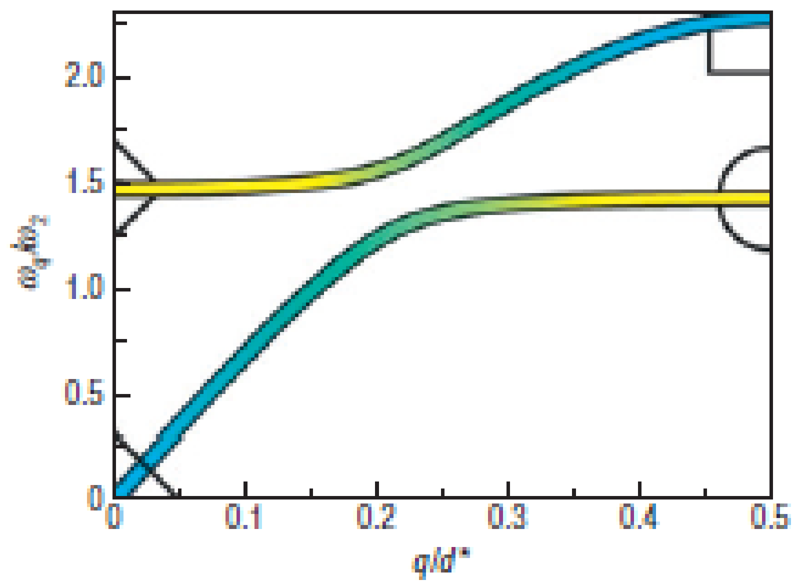

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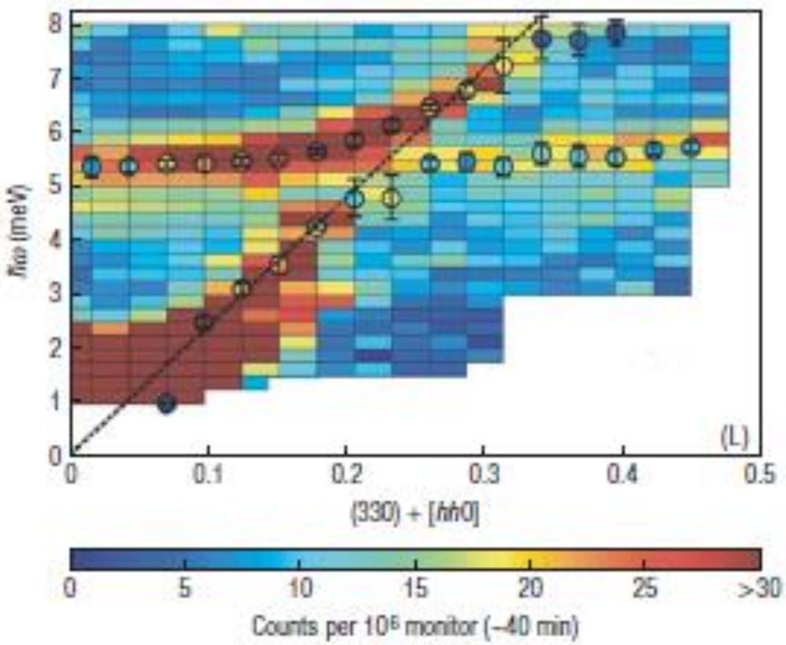

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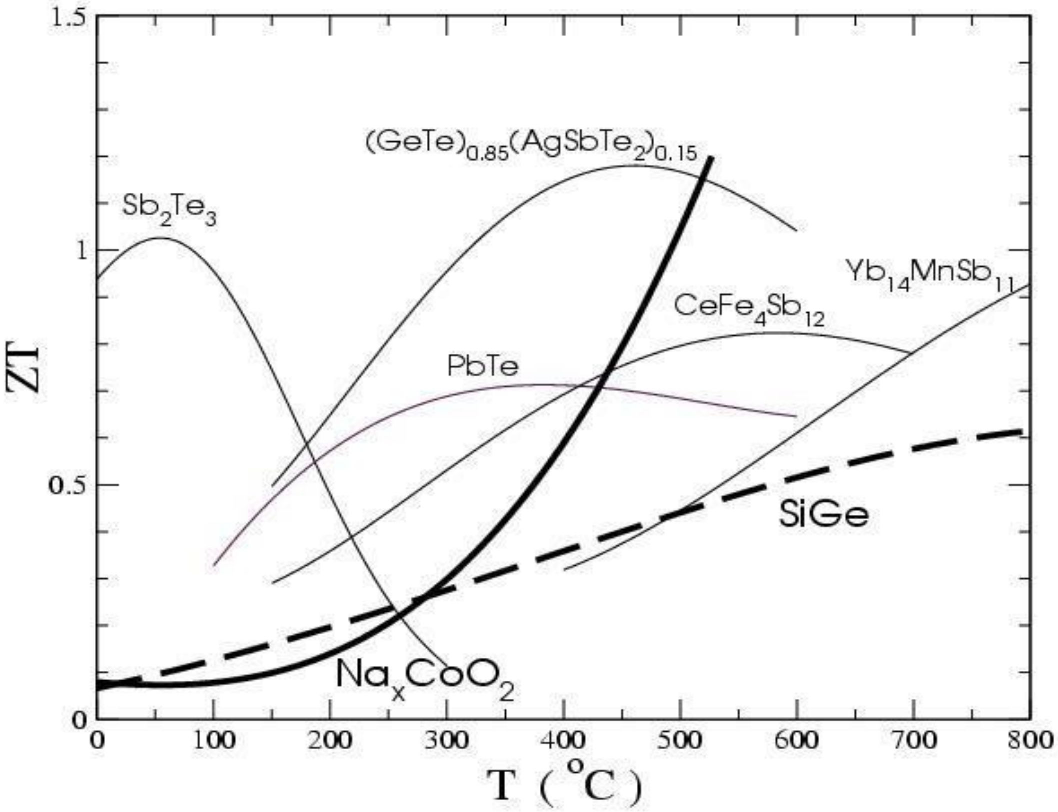
P-type thermoelectric oxides



- Sodium cobaltate better than semiconductors already at high temperatures!

[Terasaki *et al. Phys. Rev. B* **56** R12685 (1997); Wang *et al*. *Nature* **423**, 425 (2003); Lee *et al*. *Nature Mater.* **5**, 537 (2006).]

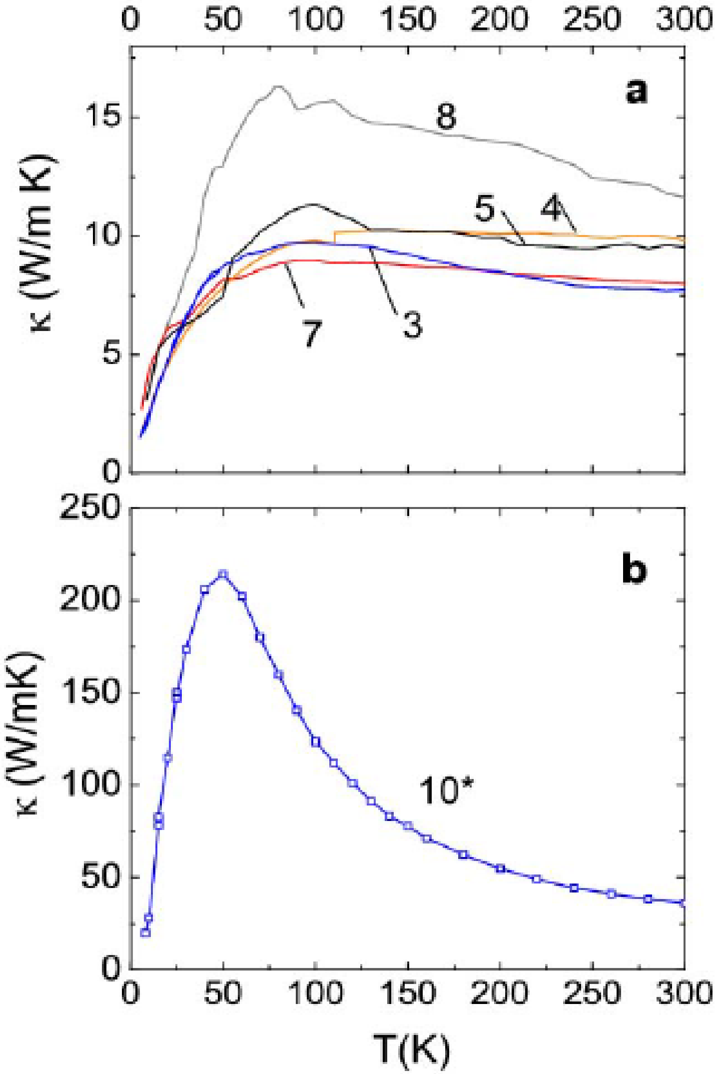
P-type thermoelectric oxides

Thermal conductivity

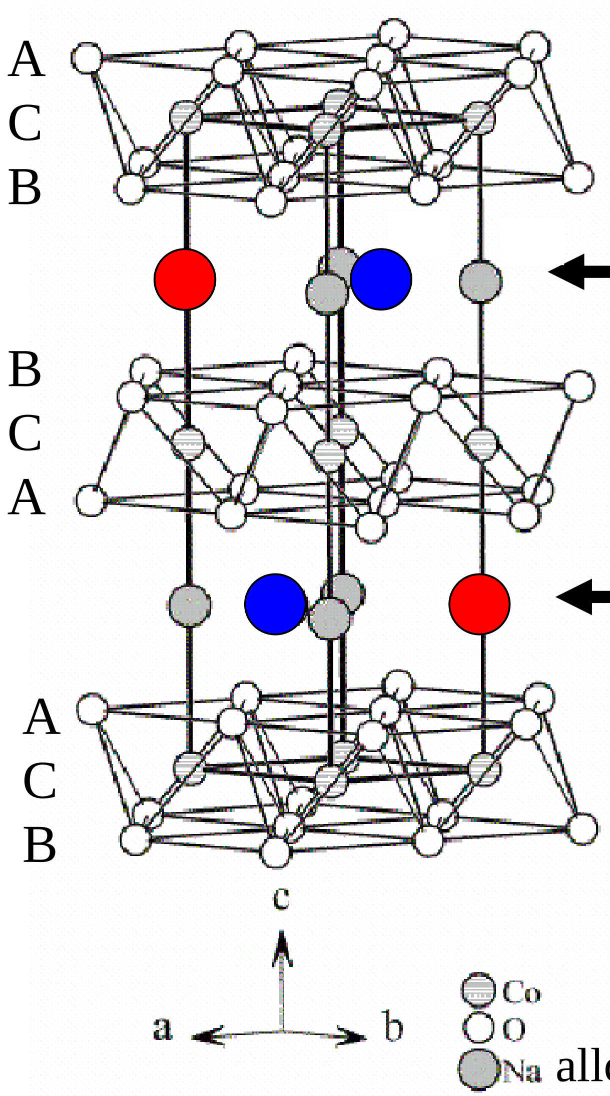
[Supplementary Information Lee *et al*. *Nature Mater.* **5**, 537 (2006)]

- Na_xCoO_2 a few W/mK for high x

- $NaCoO_2$ much higher



Crystallographic structure



CoO_2 layer

Na can occupy A or C position

CoO_2 layer

Na can occupy B or C position

CoO_2 layer

allowed positions

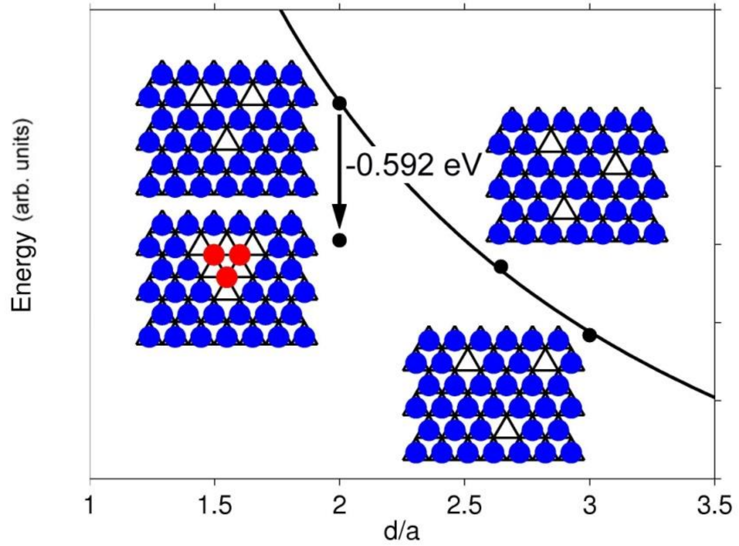
- Tunable number of Na^+ ions
- $x = 0$ to 1 per CoO_2

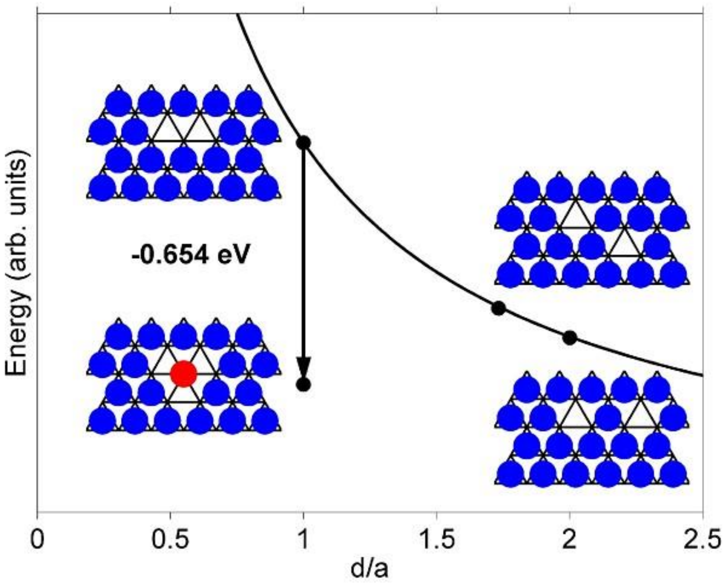
Na1 if C position

Na2 otherwise

Vacancy clustering

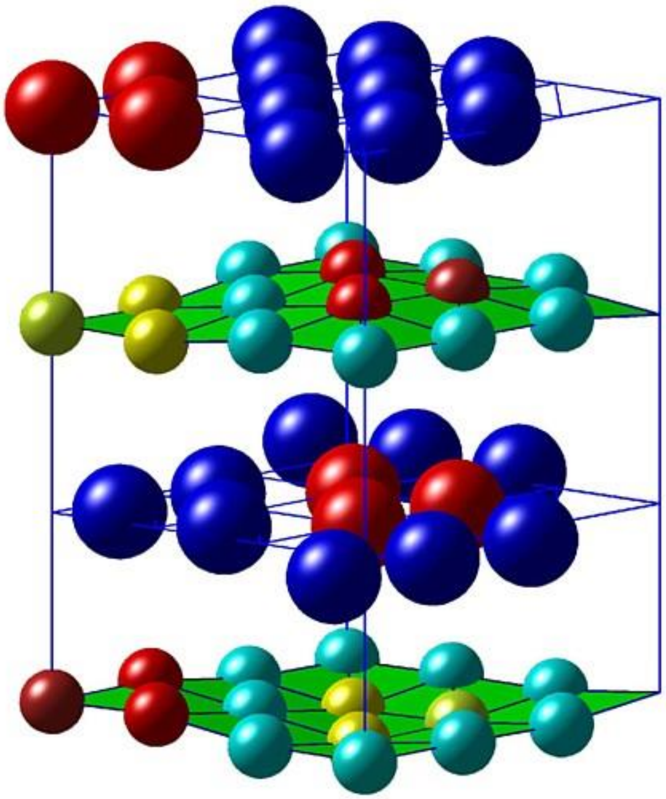
- Vacancies potential varies as 1/*d*
- Promotion of a Na2 to a Na1 site
- Lowers surface energy
- Drives vacancy droplet formation





- Large clusters become unfavourable
- Na1 core cost too high

Neutron diffraction

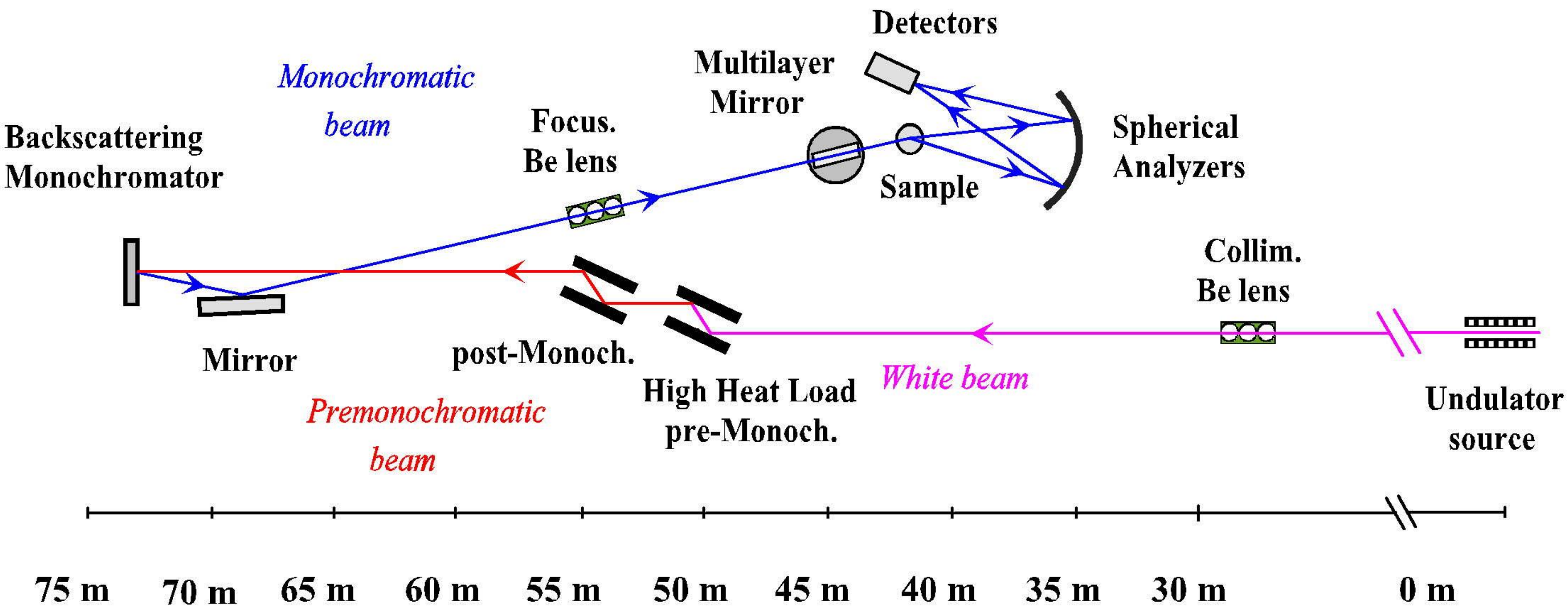


• Are the Na ions inside multi-vacancy clusters rattlers inside cages?

• Are they responsible for low thermal conductivity?

Roger *et al.*, Patterning of sodium ions and the control of electrons in sodium cobaltate. *Nature* **445**, 631 (2007)

Inelastic X-ray Scattering (IXS)



ID28 at the ESRF

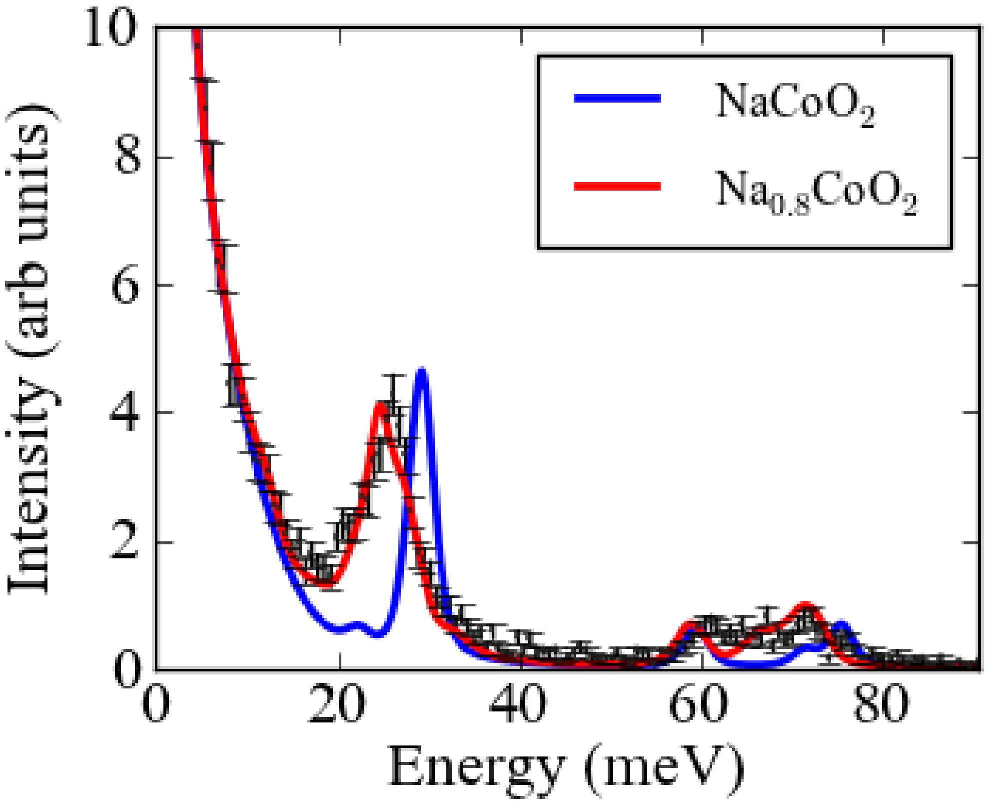
- Study sub-millimetre single crystals throughout Brillouin zone
- Energy resolution ~ 1meV

Inelastic X-ray Scattering (IXS)

ΓM

Q = (1.17,0,0)

Better for $Na_{0.8}CoO_2$



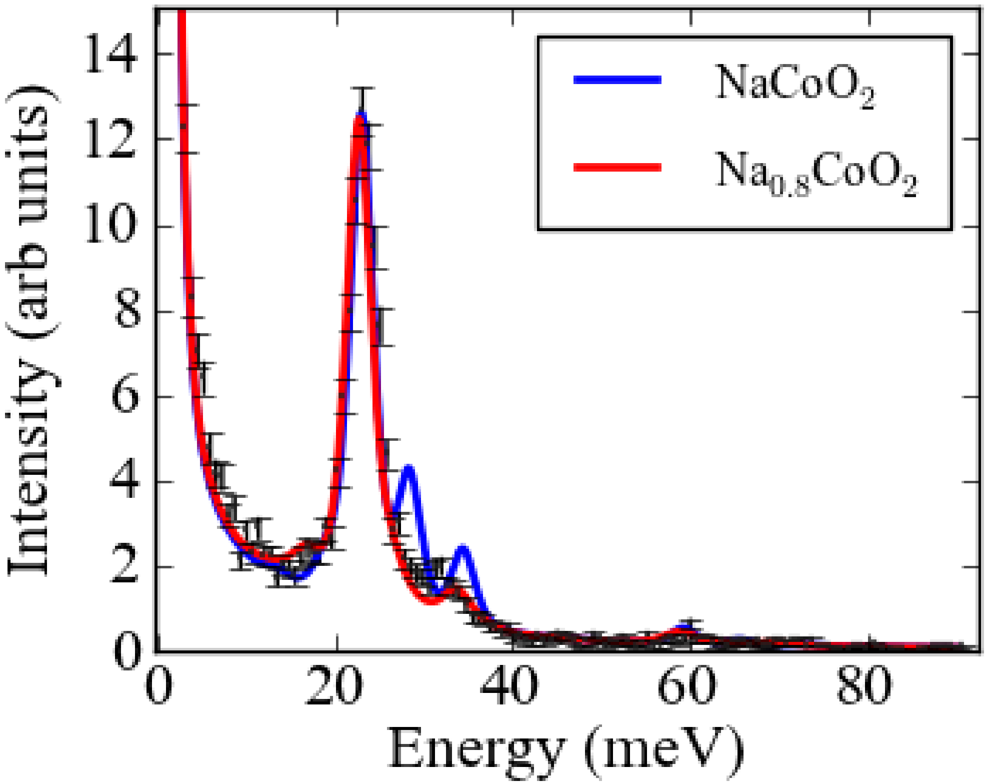
- Typical IXS data in the square phase at *T* ~ 200 K
- Sharp energy line shapes show that it is **not a phonon glass**

Inelastic X-ray Scattering (IXS)

ΓK

Q = (1.1,1.1,1)

Better for $Na_{0.8}CoO_2$



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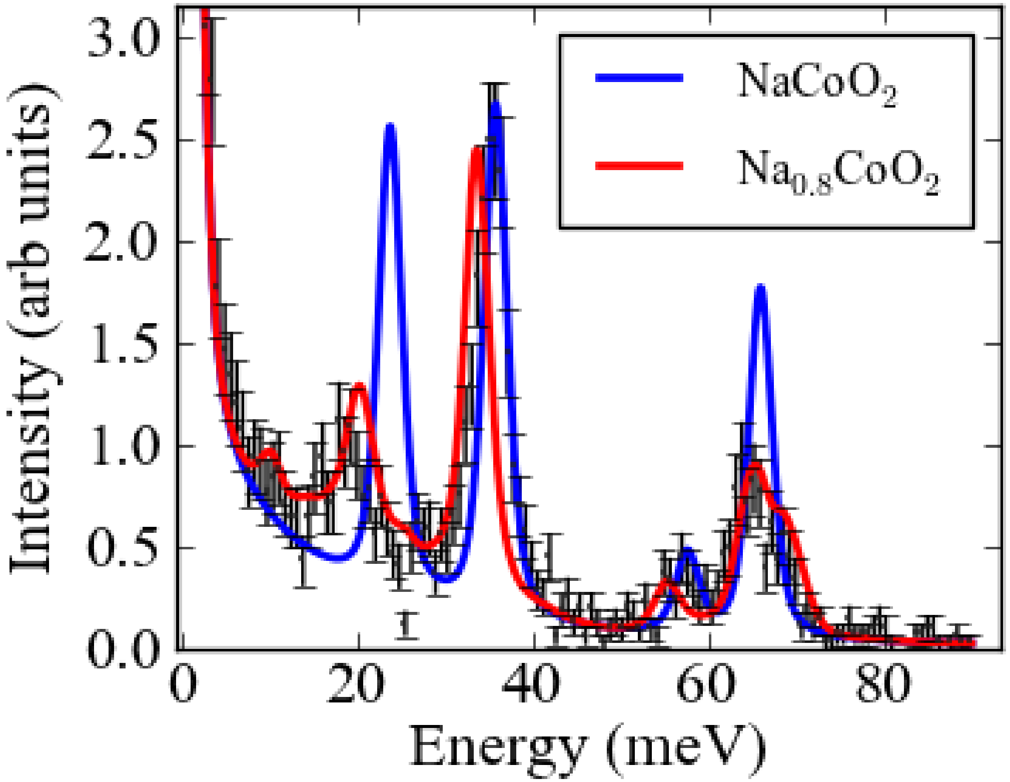
Inelastic X-ray Scattering (IXS)

M

Q = (1.5,1.5,1)

Lose some sharp peaks



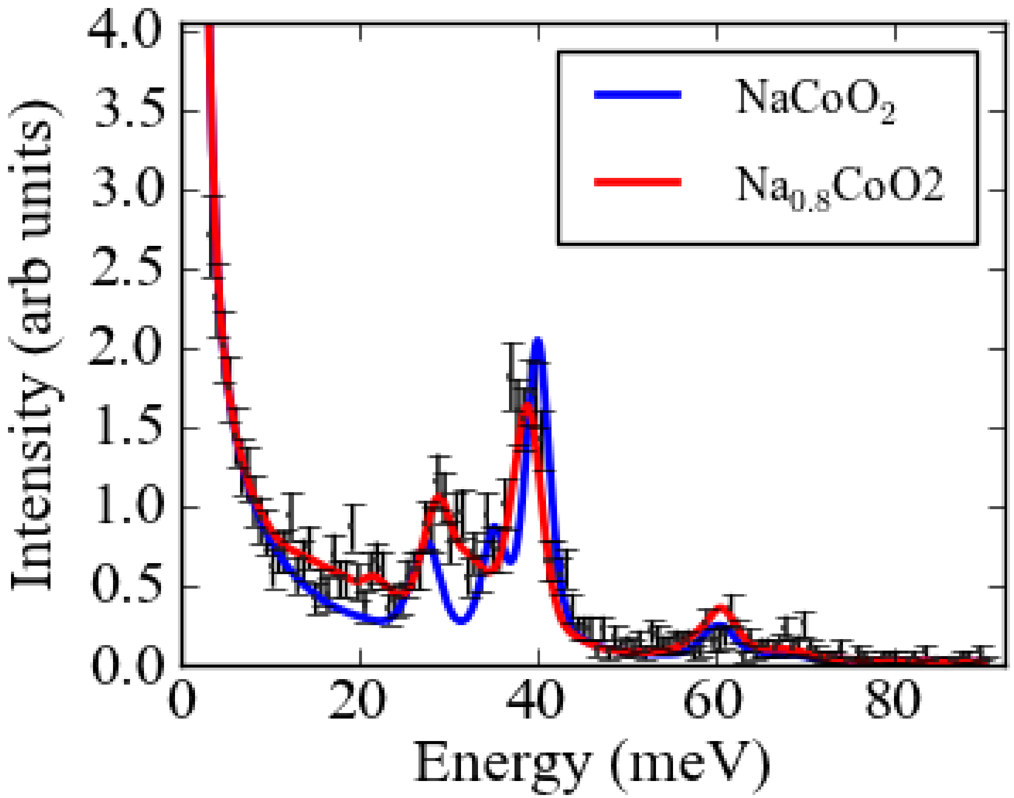
- Typical IXS data in the square phase at $T \sim 200$ K
- Sharp energy line shapes show that it is **not a phonon glass**

Inelastic X-ray Scattering (IXS)

Off axis

Q = (1.175,1.174,1.084)

Data from 9 detectors



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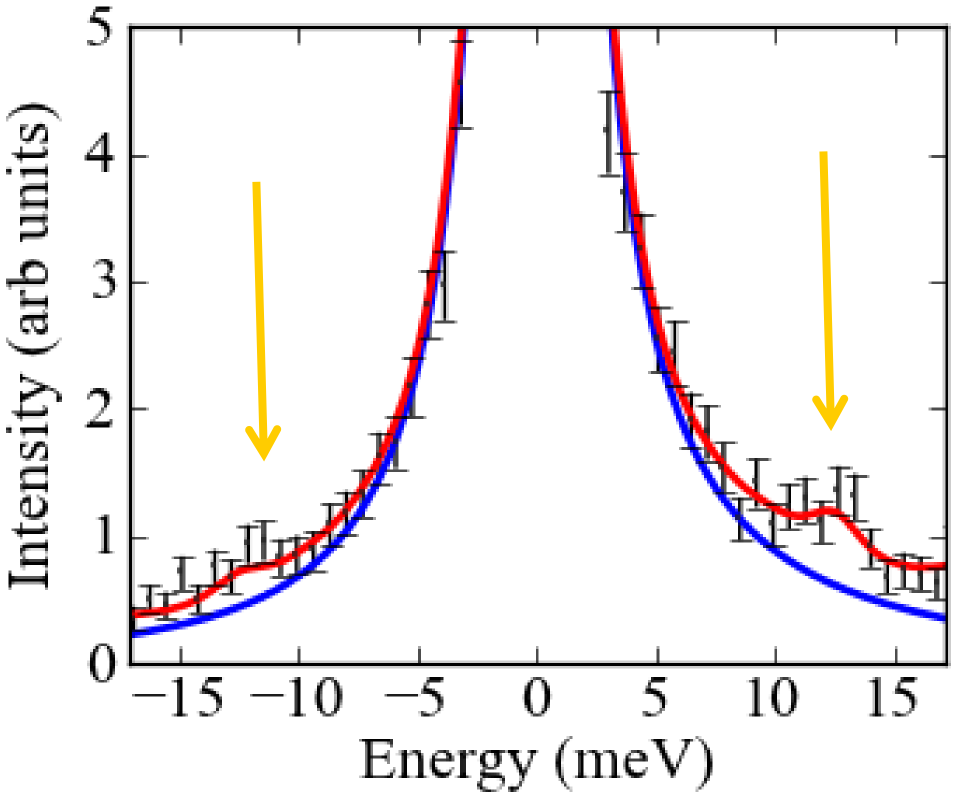
Inelastic X-ray Scattering (IXS)

Low energy transfer

Q = (1.25,1.25,1)

Arrows indicate position of **rattling mode**



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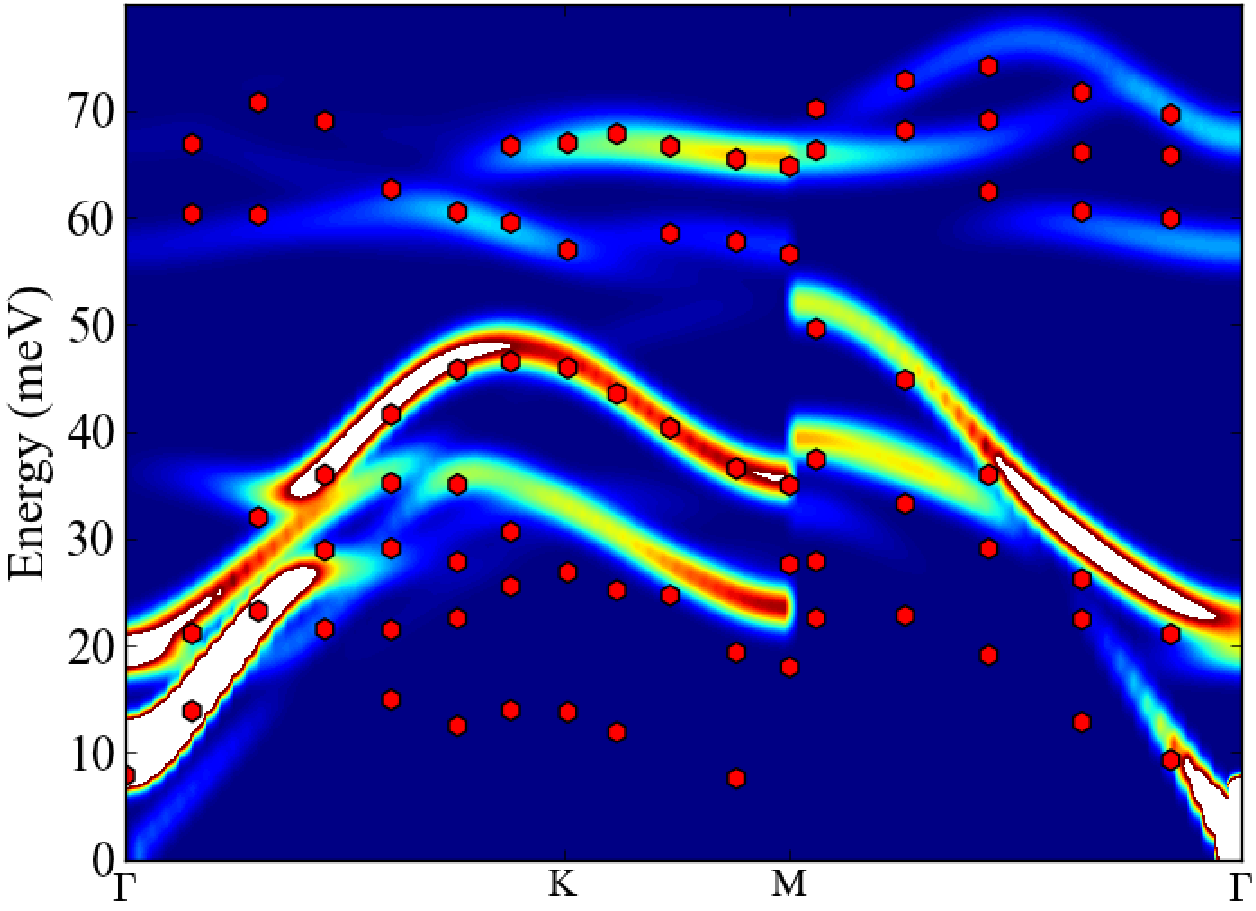
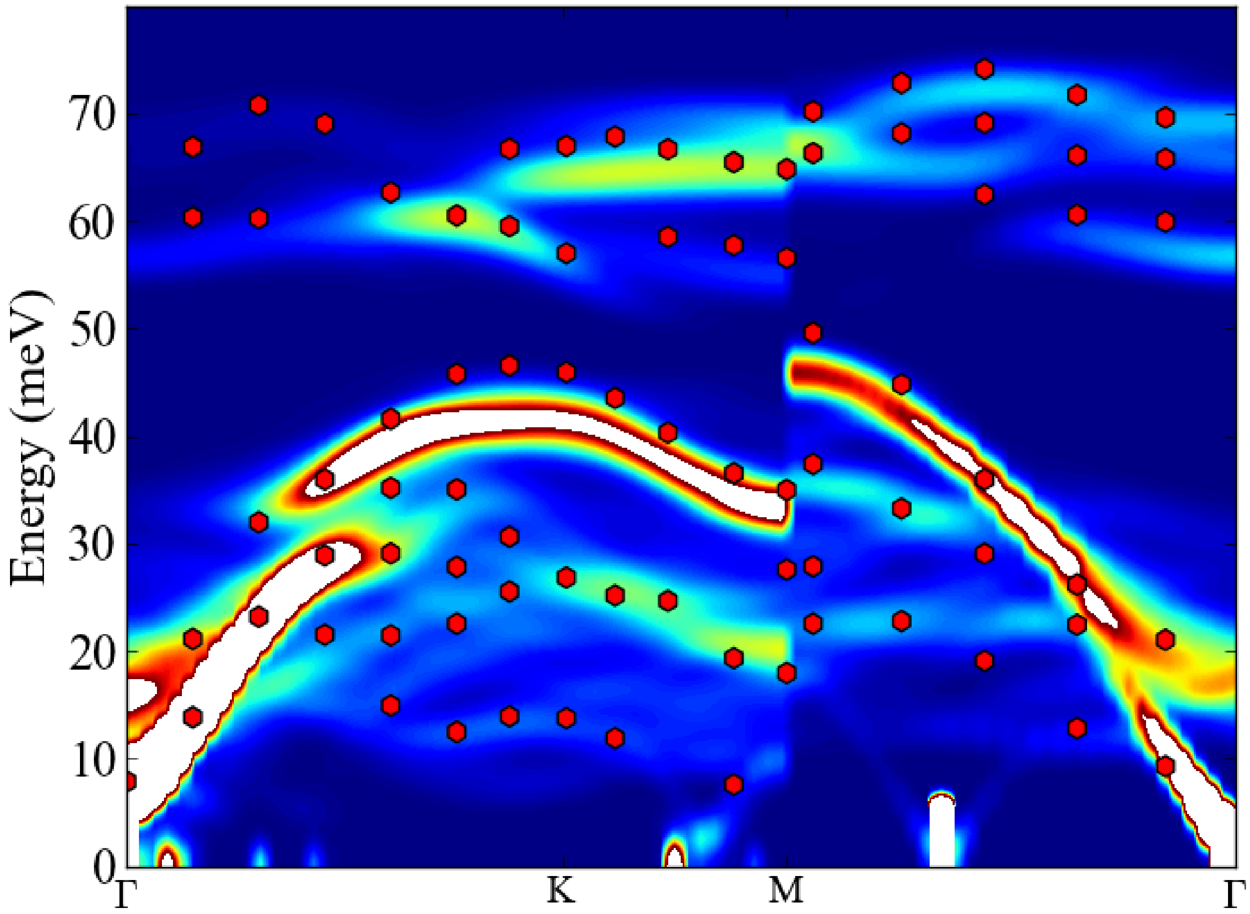


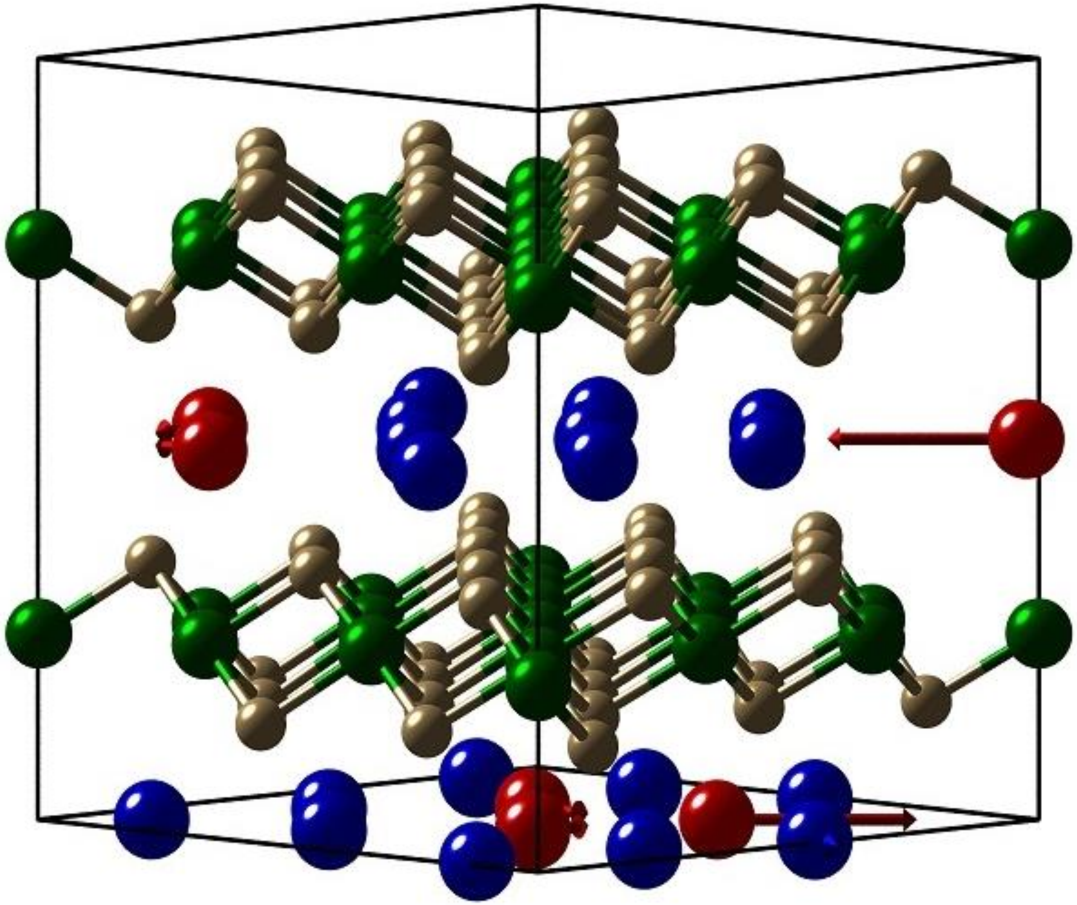
- Phonon dispersion determined by IXS
- CASTEP calculation for **$NaCoO_2$**

Inelastic X-ray Scattering (IXS)



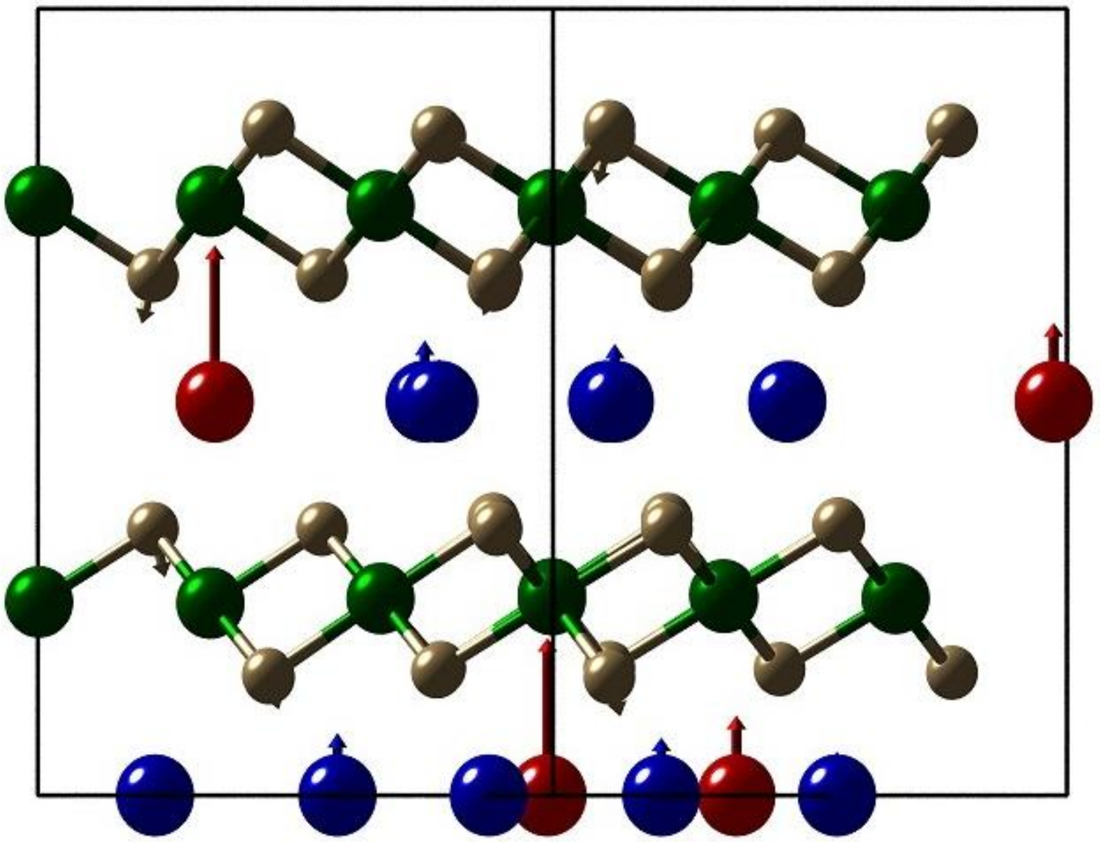
- Phonon dispersion determined by IXS
- CASTEP calculation for $\mathbf{Na_{0.8}CoO}_2$

Phonon modes



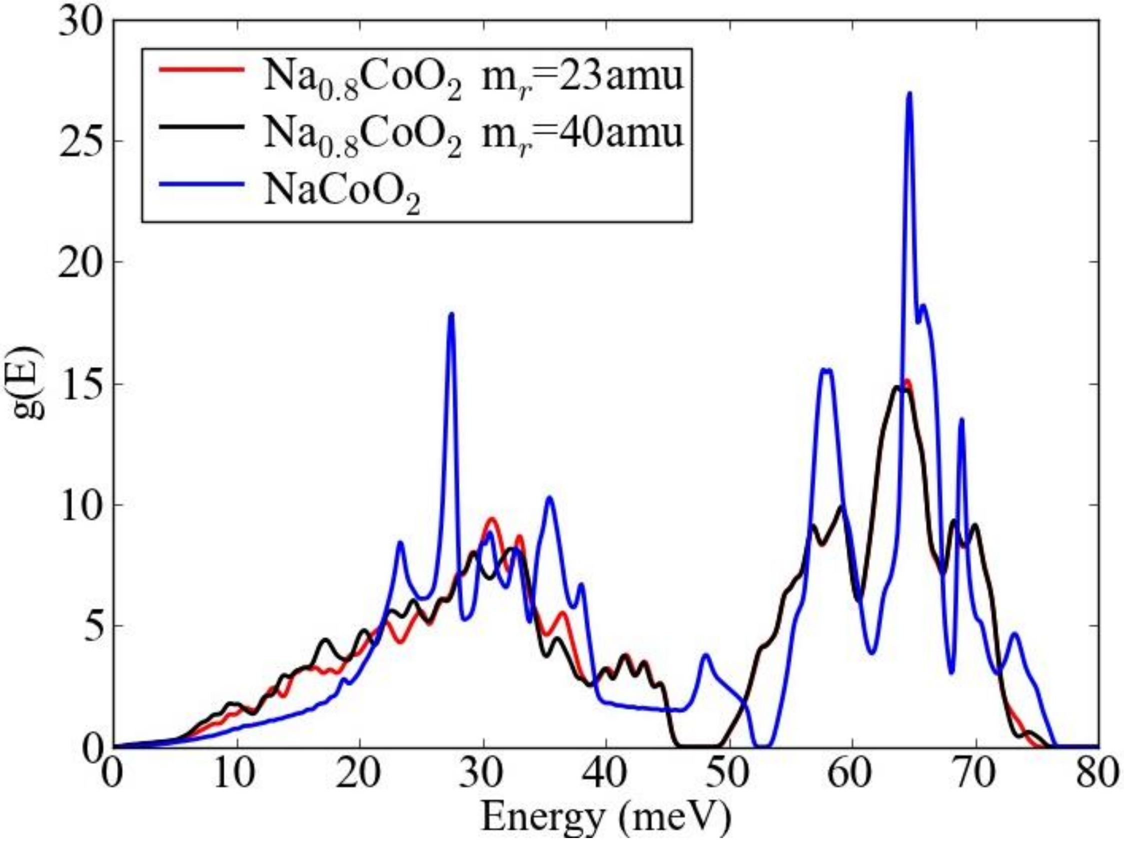
- **Rattling mode** observed using IXS
- Na 2*b* ions have large-amplitude vibrations

Phonon modes



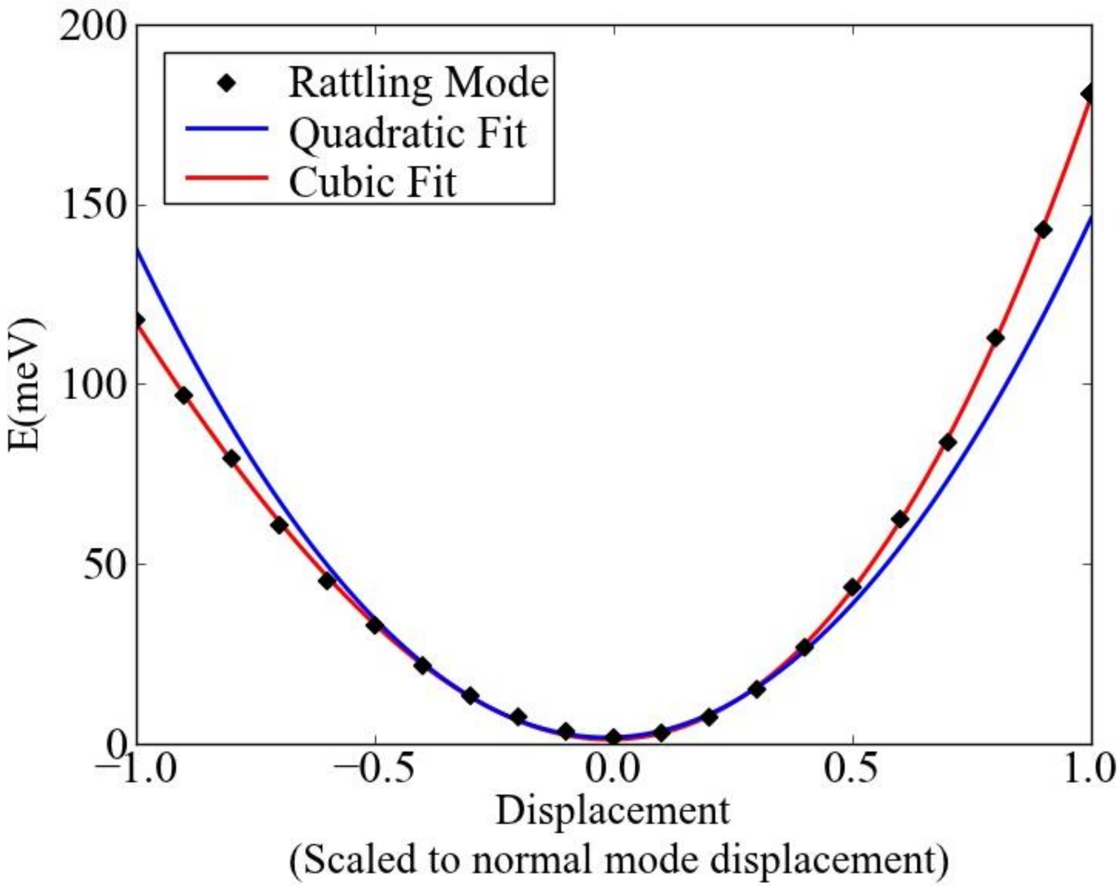
- Effect of rattlers on a typical **optical phonon**
- Na 2*b* ions have large vibrational amplitude

Phonon density of states



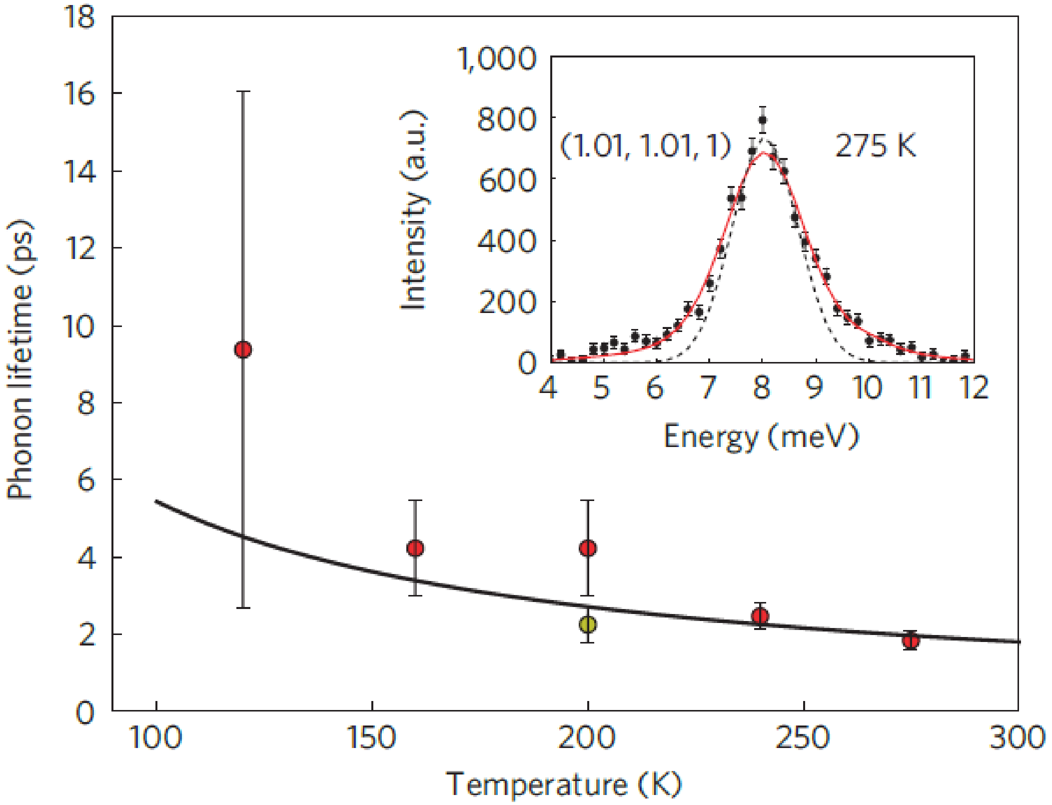
- Rattler only affects modes below E ~ 40 meV
- Transfer from sharp peaks to low energy

Anharmonicity



- **Frozen phonon** calculation for rattling mode
- Asymmetry indicates **anharmonicity**

Phonon lifetimes



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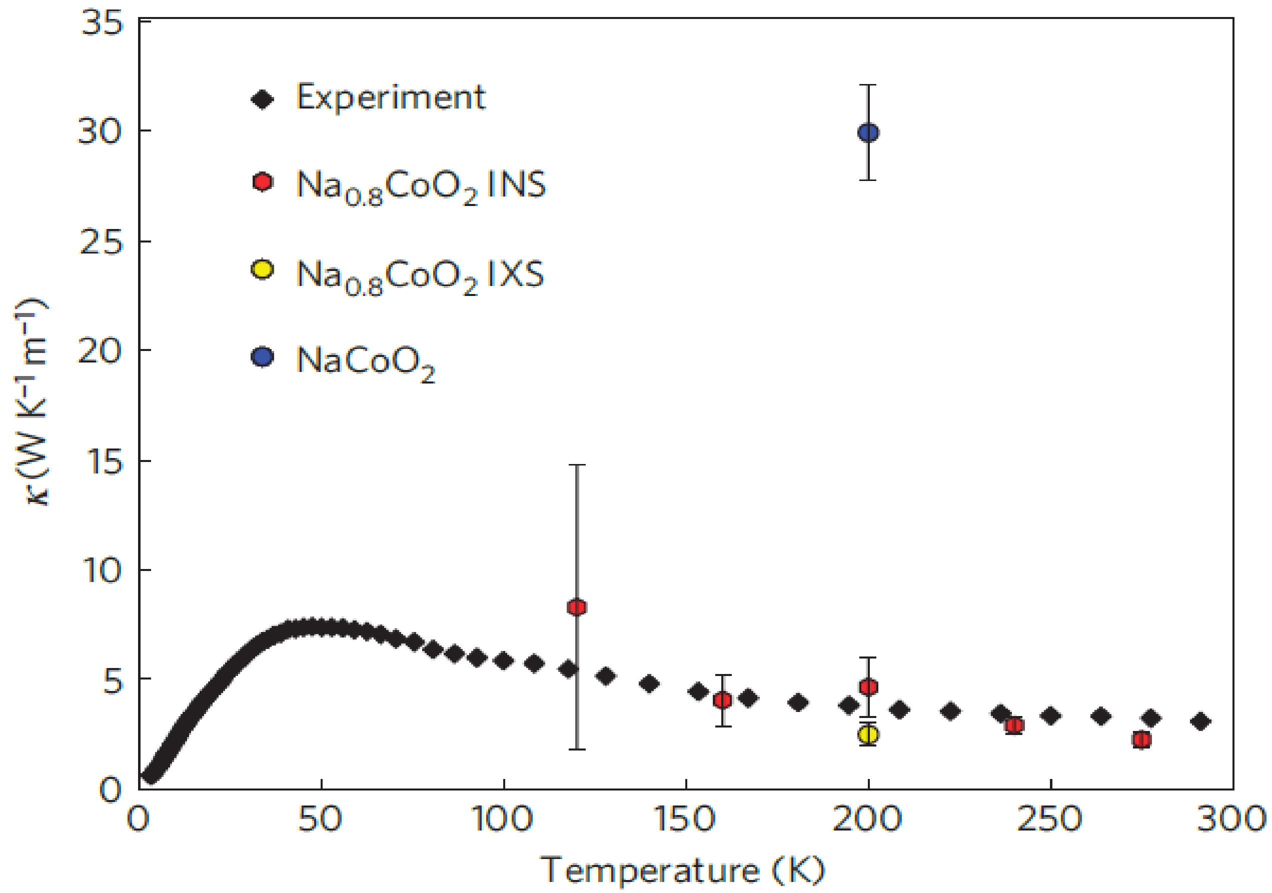
Thermal conductivity



Thermal conductivity given by

$$\kappa^L = \sum_{j,Q} v_{jx}^2(Q)\tau_j(Q,T)c_j(Q,T)$$

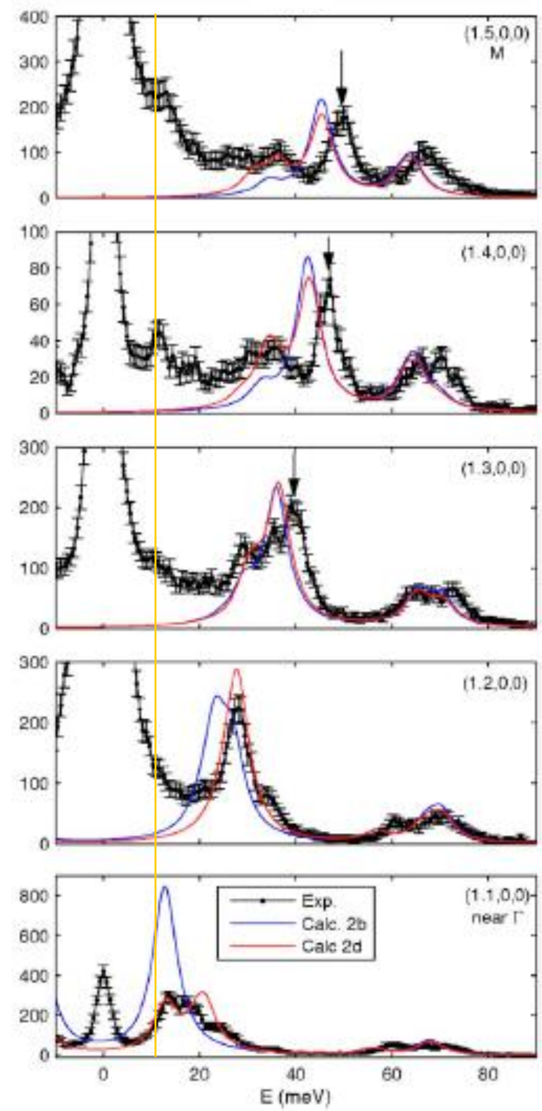
• Quantitative understanding of thermal conductivity

Composition dependence

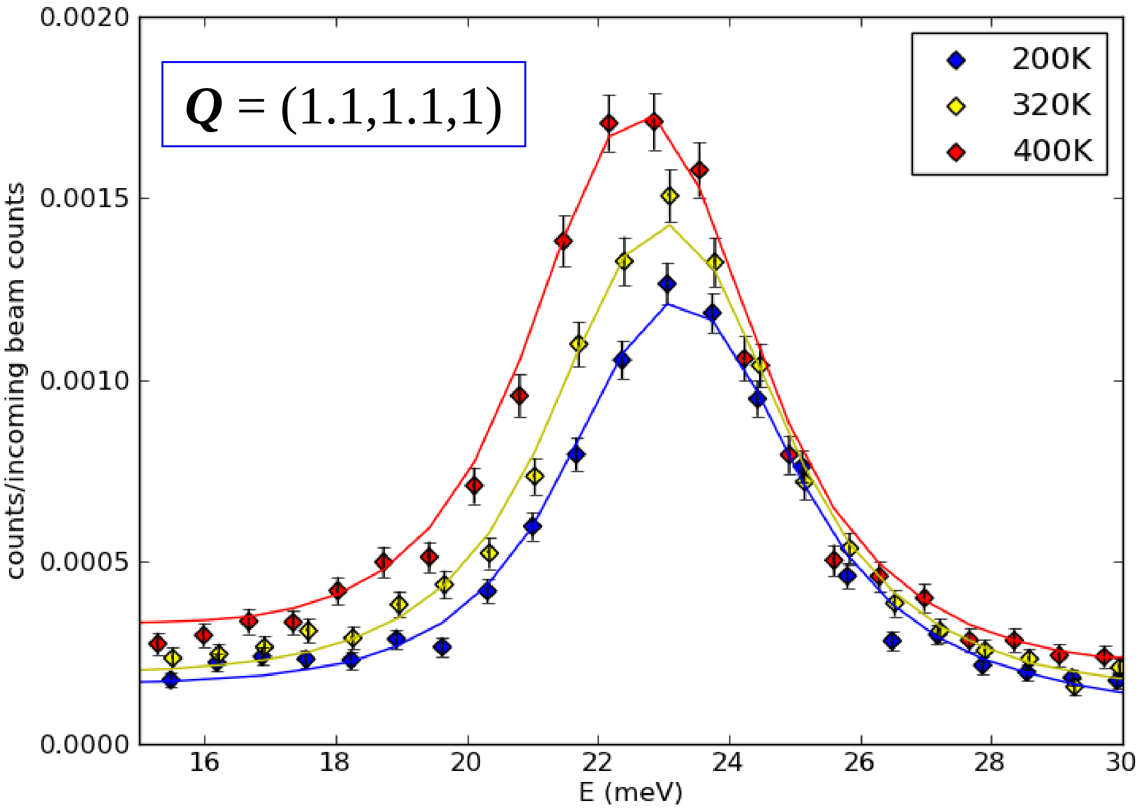
Previous IXS experiment

[Rueff *et al.*, *PRB* **74**, 020504 (2006)]

- $Na_{0.7}CoO_2$ crystal of unknown superstructure
- Rattling mode is golden line
- Rattling modes persist over wide composition range



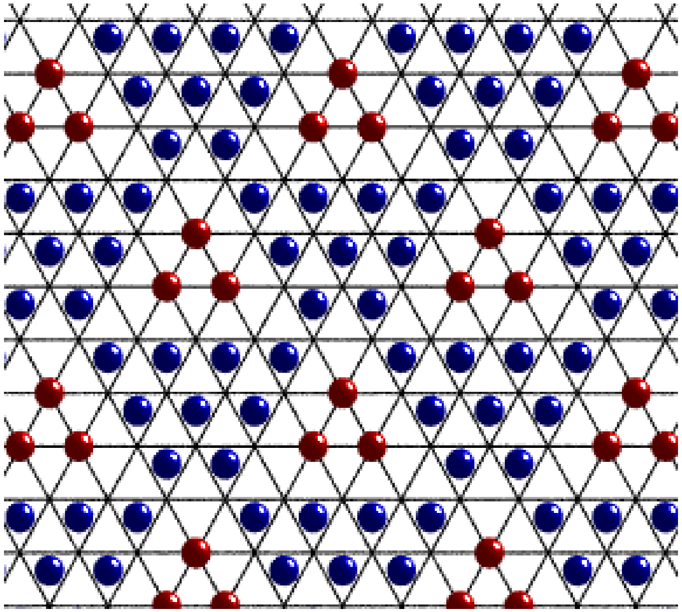
Temperature dependence



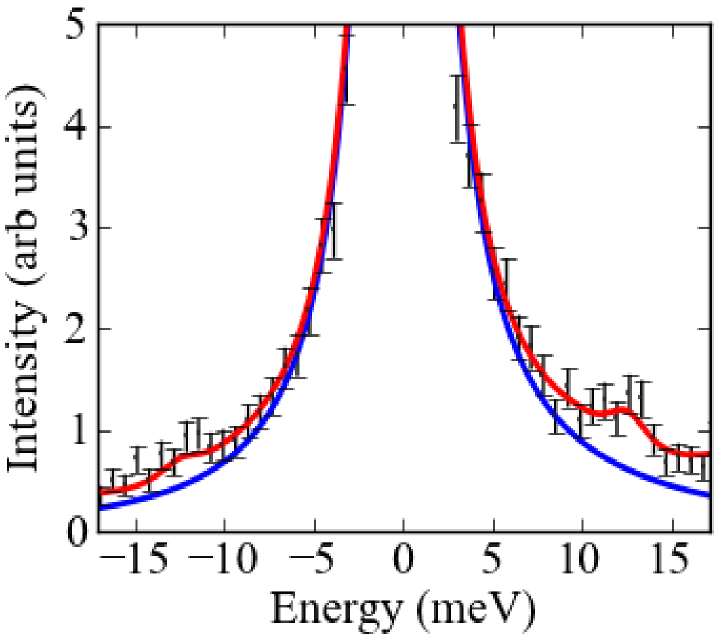
- Renormalisation to lower energy
- Broadening of energy line width

Temperature dependence

Square phase



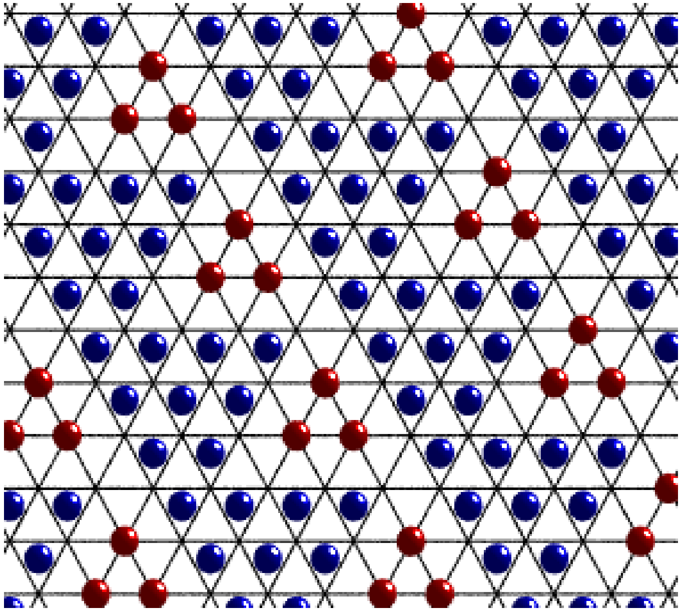
***T* = 200 K**



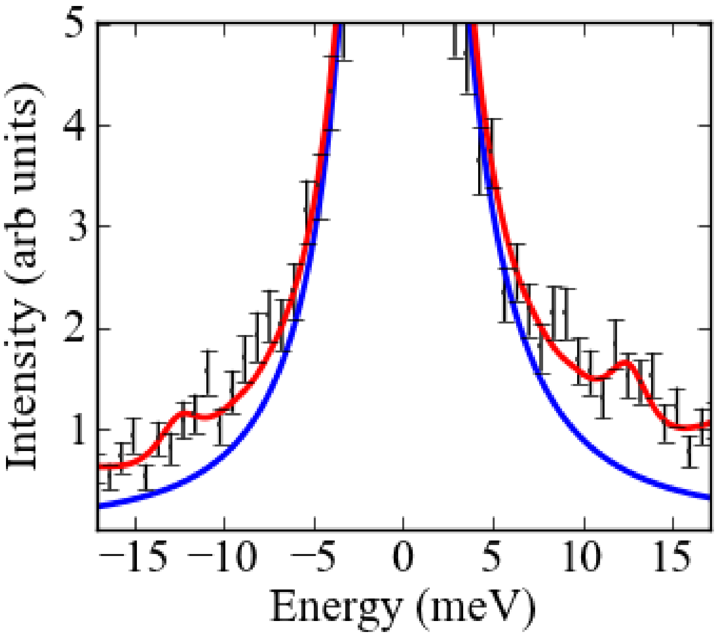
- Rattling mode persists to elevated temperatures
- Important for power recovery applications

Temperature dependence

Striped phase



***T* = 320 K**



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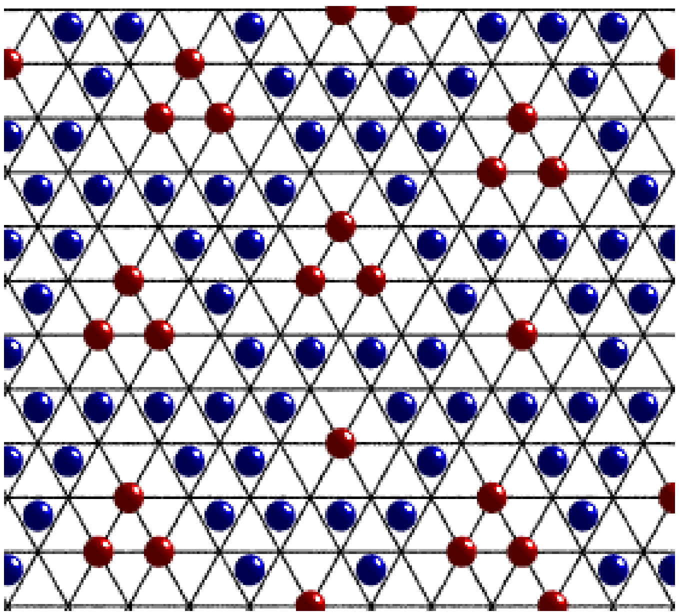
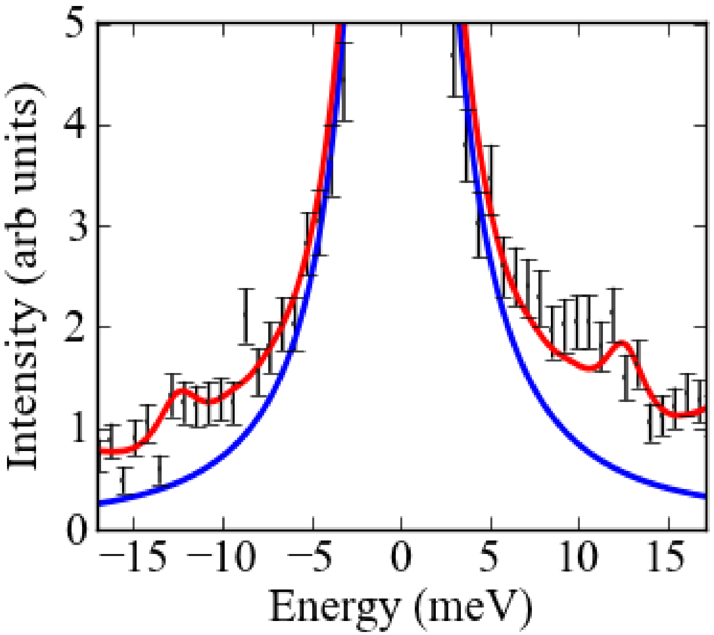
Temperature dependence

Disordered phase



***T* = 400 K**



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Conclusions

[D.J. Voneshen *et al*., Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate. *Nature Mater*. **12**, 1028 (2013)]

- **We have directly observed an Einstein-like rattling mode**

- **Quantitatively account for observation of low thermal conductivity**

- Next stages:

- Apply these techniques to other materials

- Study anharmonicity in this way

→ First principles calculation of thermal conductivity