Neutrons & X-rays

Jon Goff

Royal Holloway, University of London

Outline of talk

Examples
- Structures (crystallography, superstructures)
- Magnetism (bulk samples, multilayers)
- Other degrees of freedom (charge, orbital)
- Excitations (phonons, magnons)

Conclusions & Future Outlook

Royal Holloway University of London

Neutrons & X-rays

Facilities

ILL & ESRF

Neutrons & X-rays

Facilities

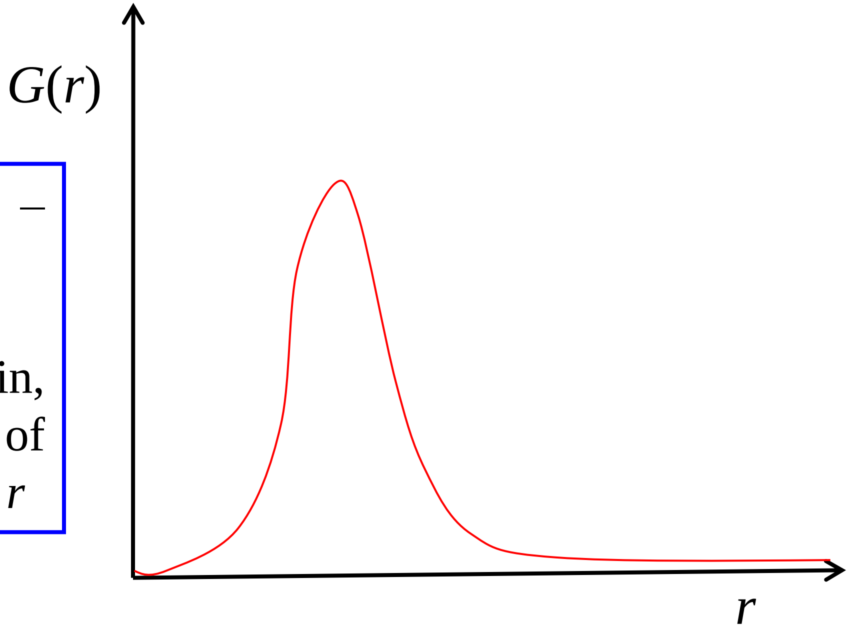
ISIS & Diamond

Neutrons & X-rays

Facilities

G(*r*) is the neutron source – synchrotron correlation function

Given a neutron source at the origin, what is the probability, *G*(*r*), of finding a synchrotron at a distance *r*

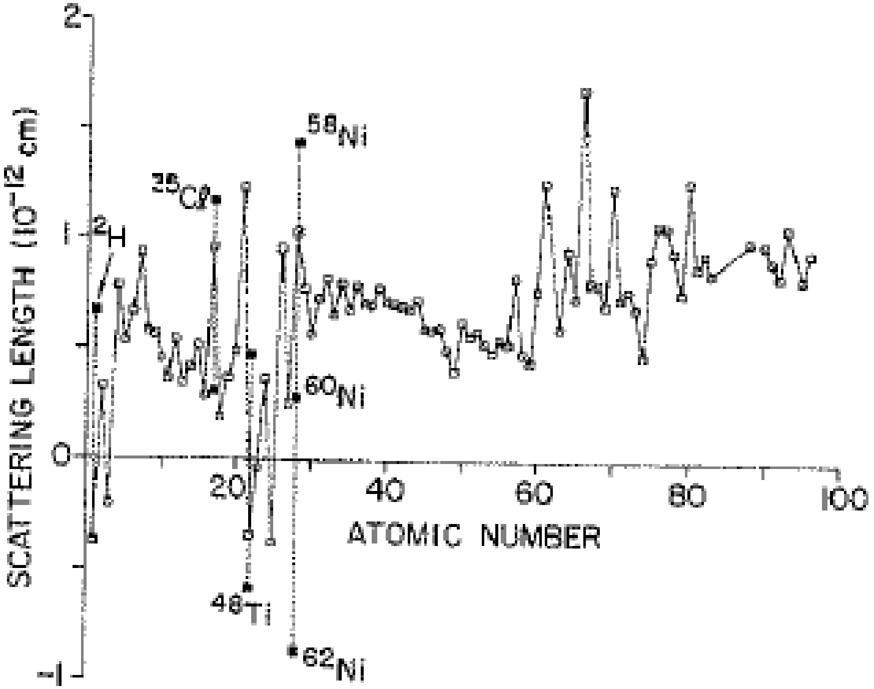


Why is there usually a synchrotron next to a neutron source?

Crystallographic structure

Structural cross sections

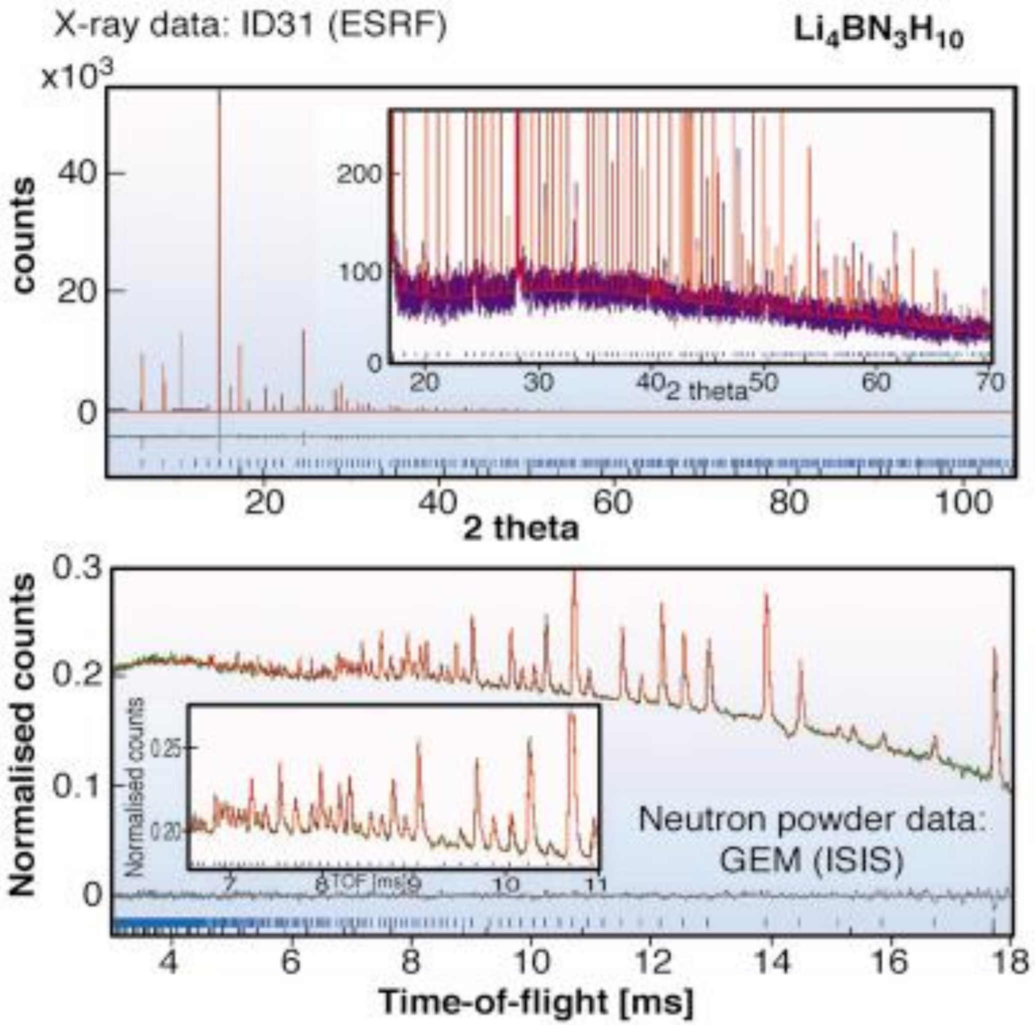
• Neutrons interact with nuclei and scattering length varies irregularly with Z
• X-rays interact with electrons and form factor varies as Z^2
• Neutrons good for light elements (H, Li, O, Na, etc.)
• Neutrons discriminate between nearby elements in periodic table (but anomalous x-ray diffraction useful too!)



Crystallographic structure

Hydrogen storage

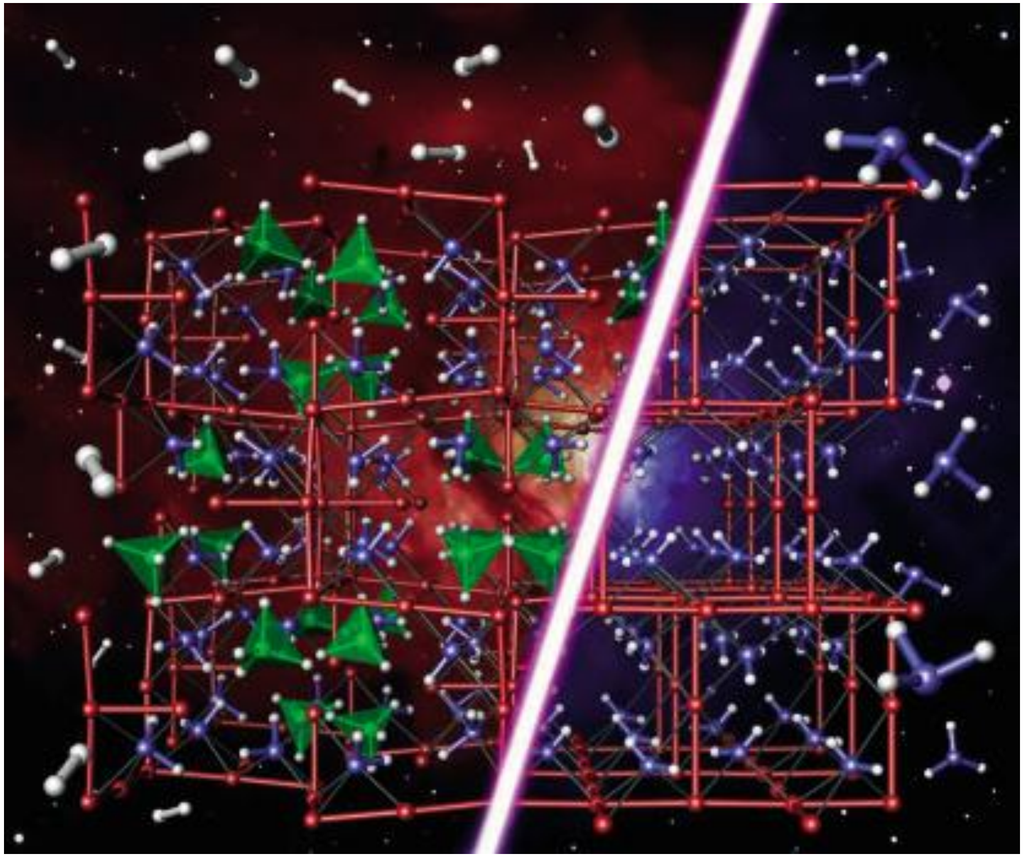
- High storage densities
- Rapid charge and discharge at acceptable temperatures
- Synchrotron x-rays to search compositions
- Neutron diffraction determines location of hydrogen
- In-situ studies



Crystallographic structure

$Li_4BN_3H_{10}$ $LiNH_2$

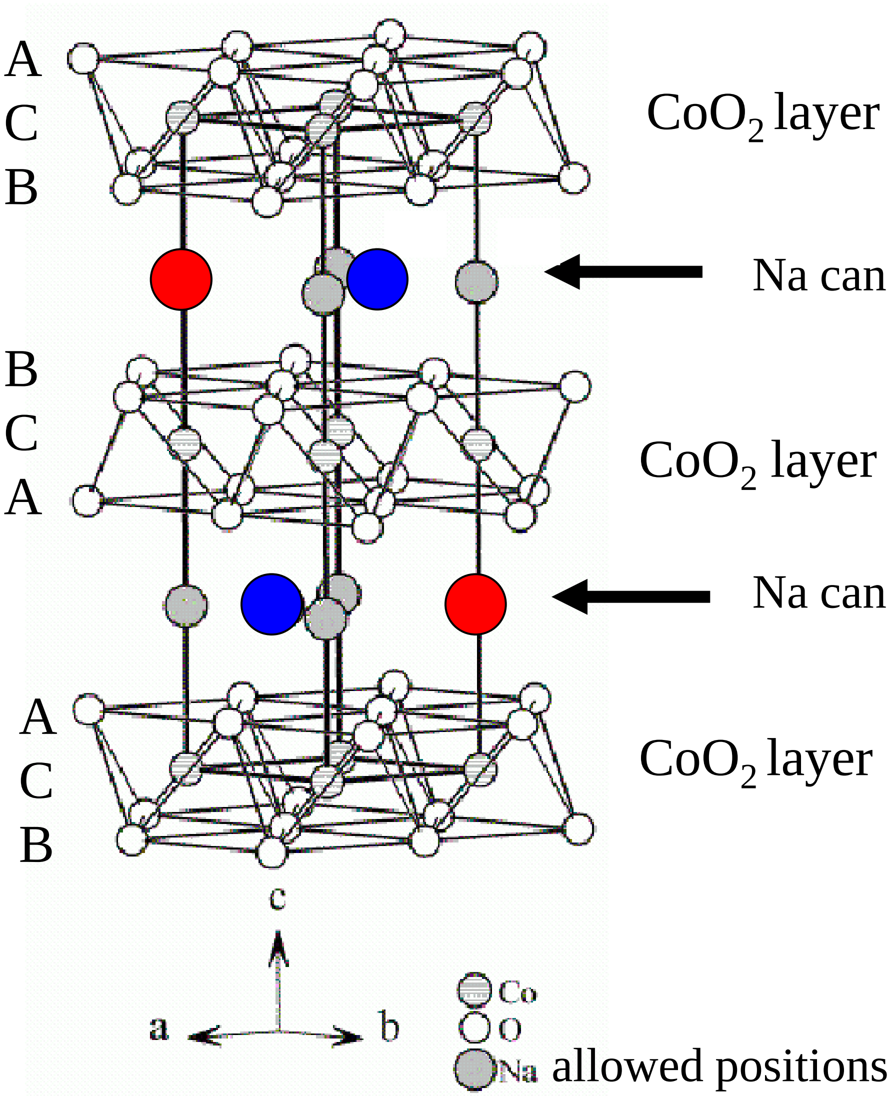
Hydrogen storage



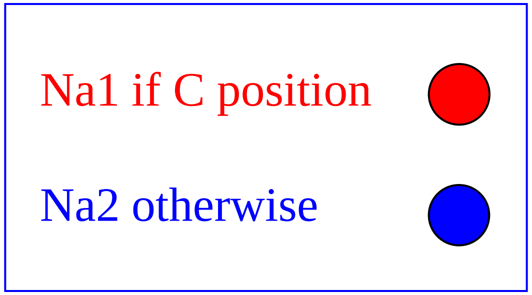
- NH_2 & BH_4 groups isoelectronic
- Neutrons can distinguish between them
- $LiNH_2$ high storage density & reversible, but gives off harmful ammonia
- Structurally similar $Li_4BN_3H_{10}$ desorbs H_2 rather than ammonia, has a high storage density, but is not as reversible
- The search goes on…

Superstructures in Na_xCoO_2

Roger *et al.*, *Nature* **445**, 631 (2007)



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



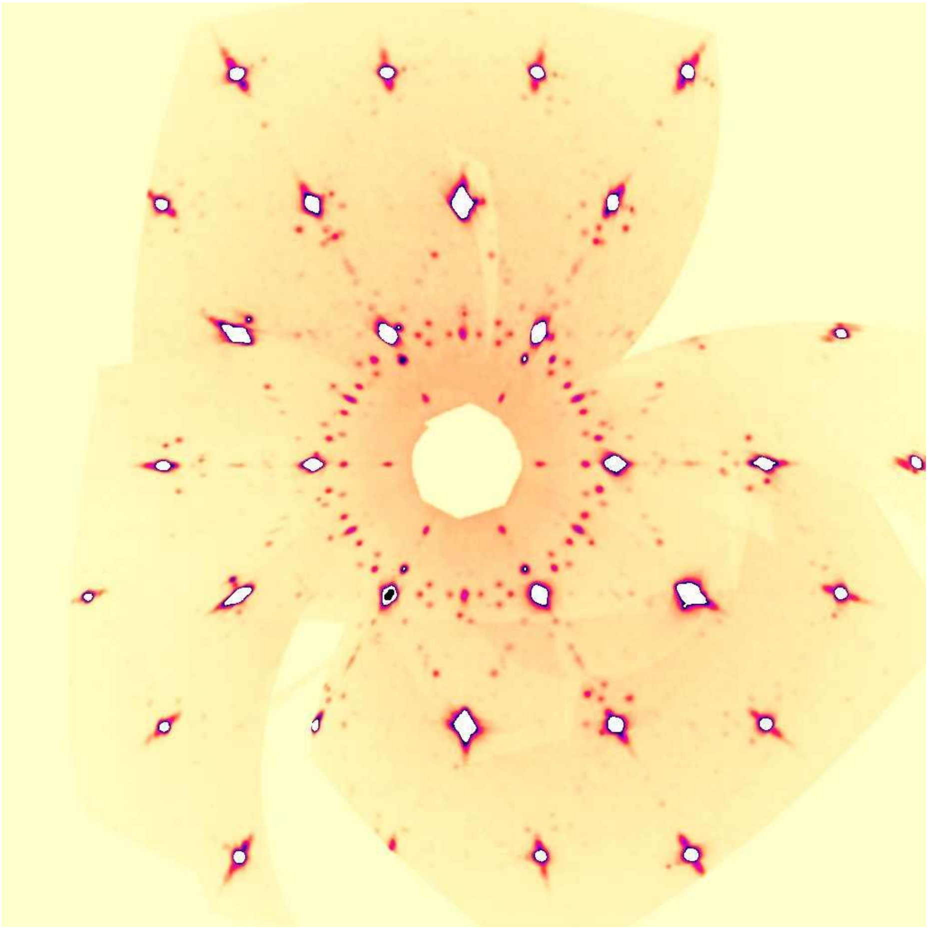
Commensurate superstructure

X-ray diffraction

• High flux allows study of tiny crystals (dimensions ~ 0.3mm)

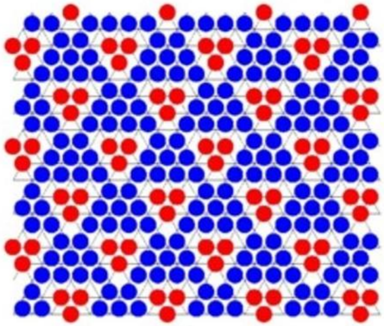
• High resolution enables accurate determination of superlattice

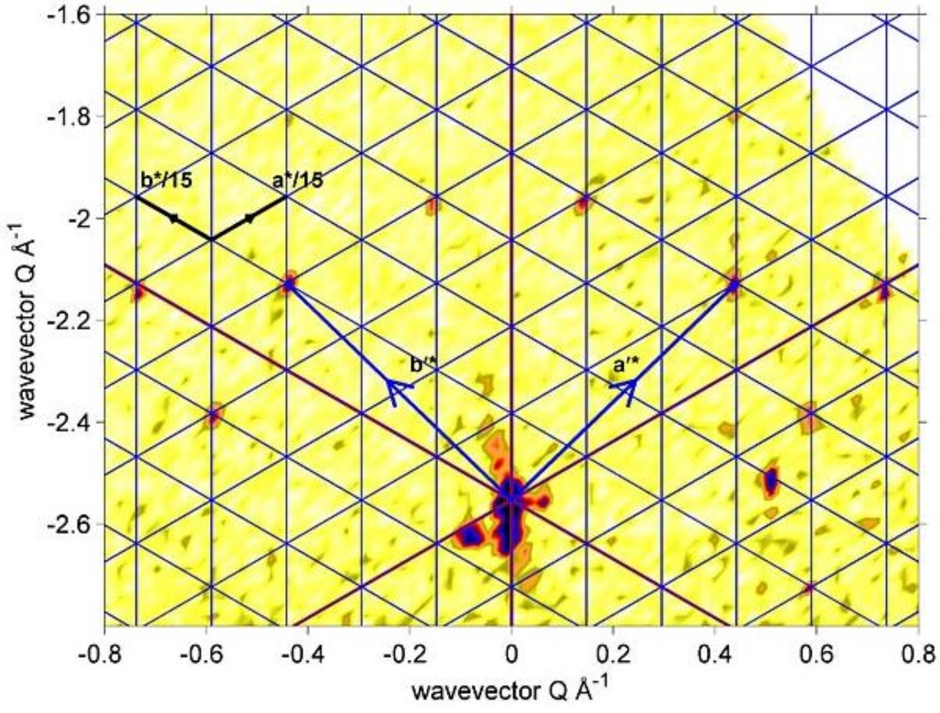
• See surface phases



Commensurate superstructure

Neutron diffraction

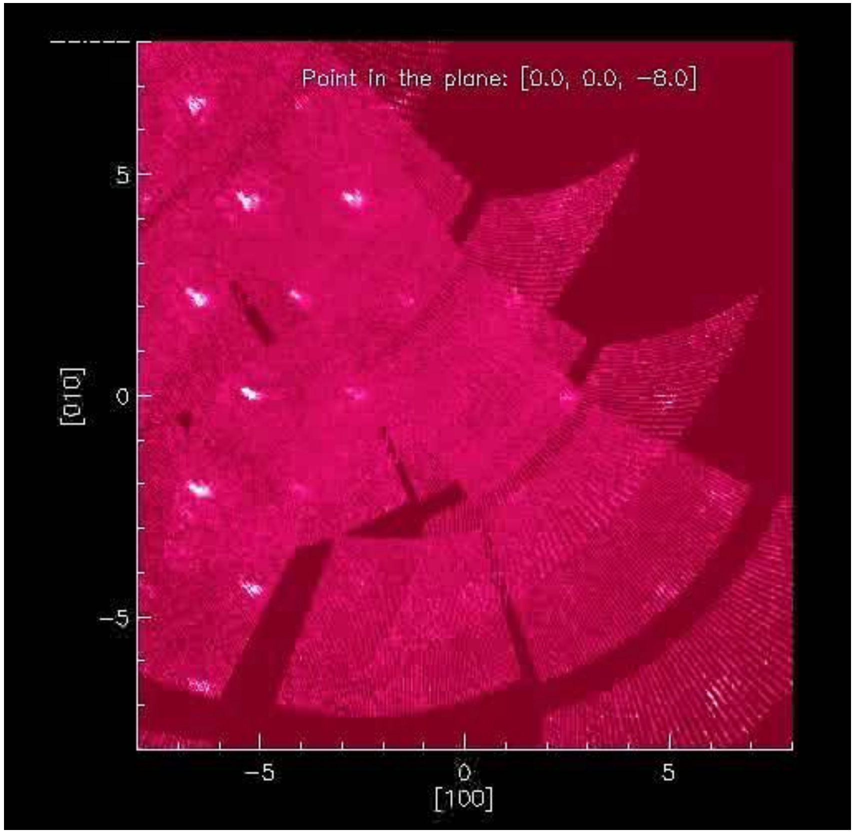




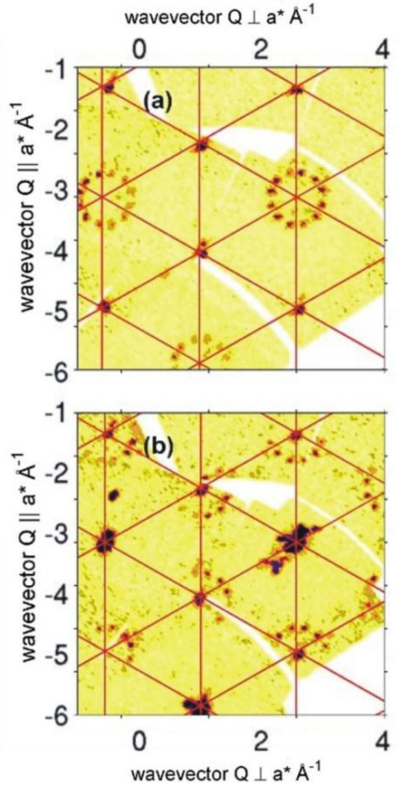
- Measure bulk properties
- Commensurate supercell
- Agrees with x = 4/5 trivacancy cluster model
- Supercell:

$$\boldsymbol{a}' = 4\boldsymbol{a} - 3\boldsymbol{b}$$
$$\boldsymbol{b}' = \boldsymbol{a} + 3\boldsymbol{b}$$

Time-of-flight neutron Laue



12-fold rings (L=11)



Crescents (L=10)

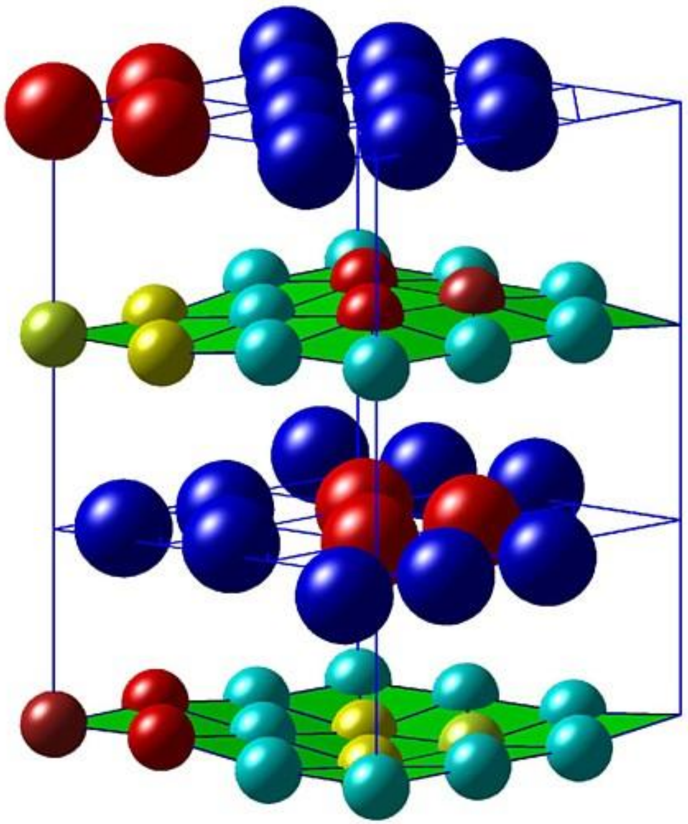
- SXD gives 3D diffraction data
- Surveys reciprocal space

One-parameter model

- Trivacancy clusters in successive layers as far apart as possible

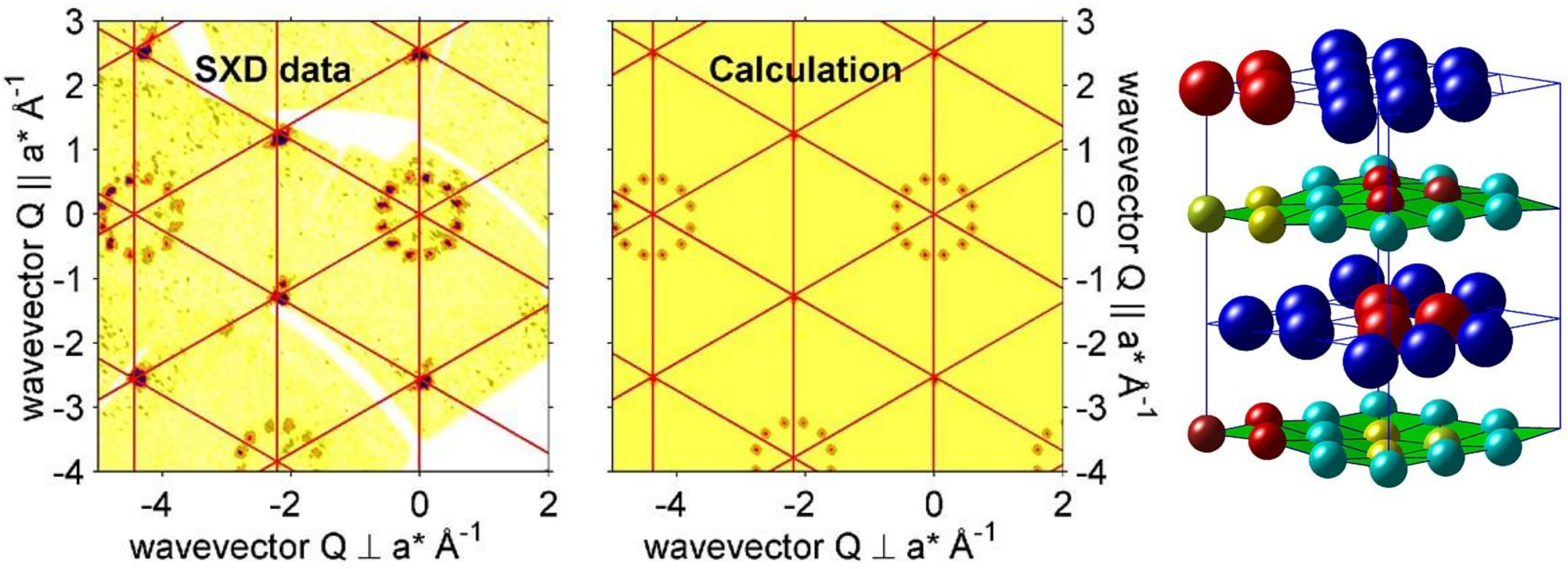
- Calculate potential gradient at Co ions – gives distortion

- Move O to keep Co-O bond length constant



Neutron diffraction

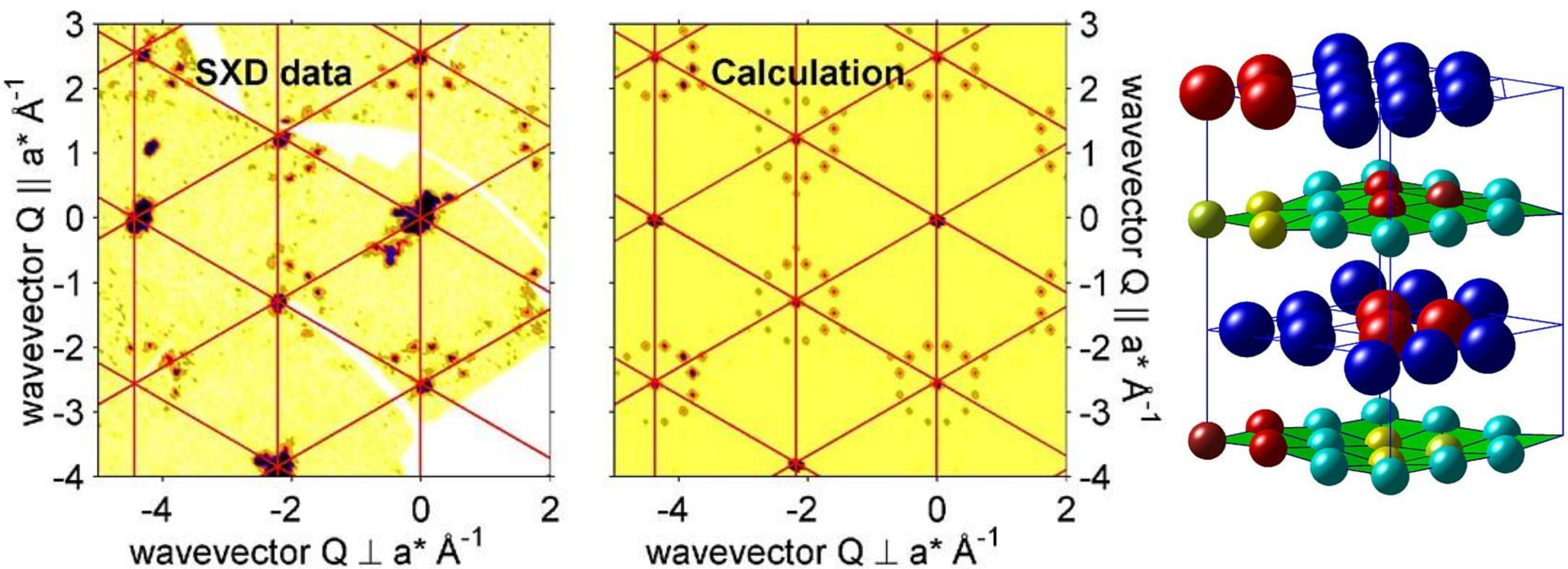
12-fold rings, L = 11, T = 150 K



Very good agreement with our one-parameter model

Neutron diffraction

Crescent shaped, L = 10, T = 150 K



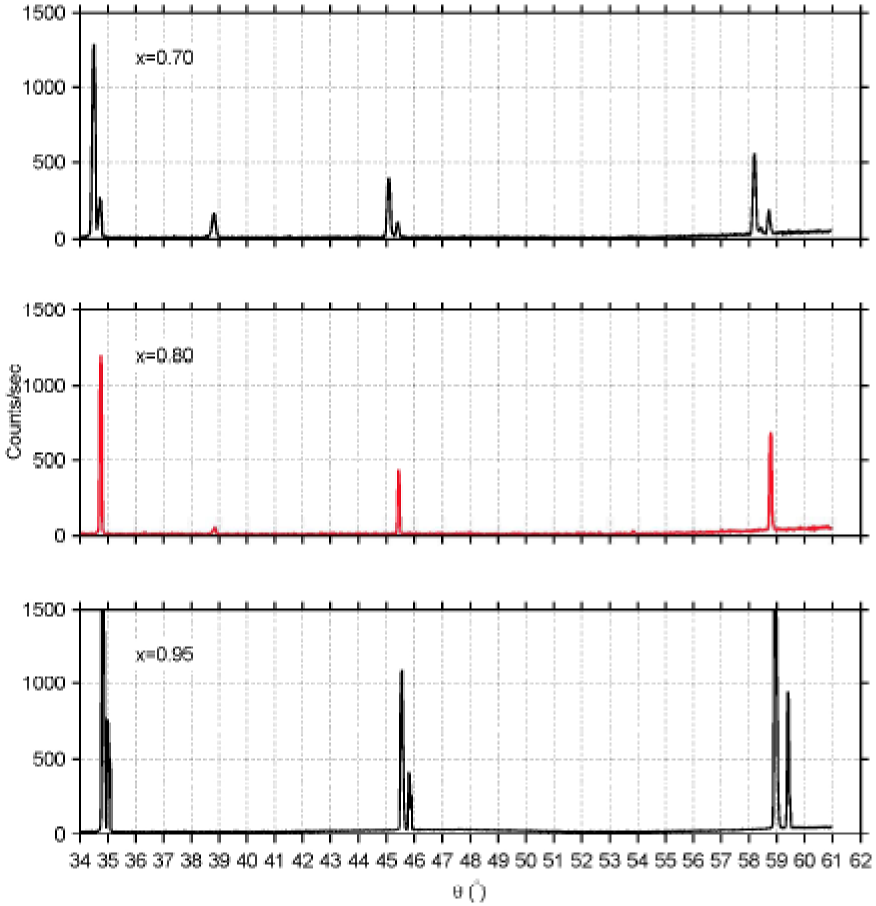
Very good agreement with our one-parameter model

Coexistence of phases

X-ray diffraction data

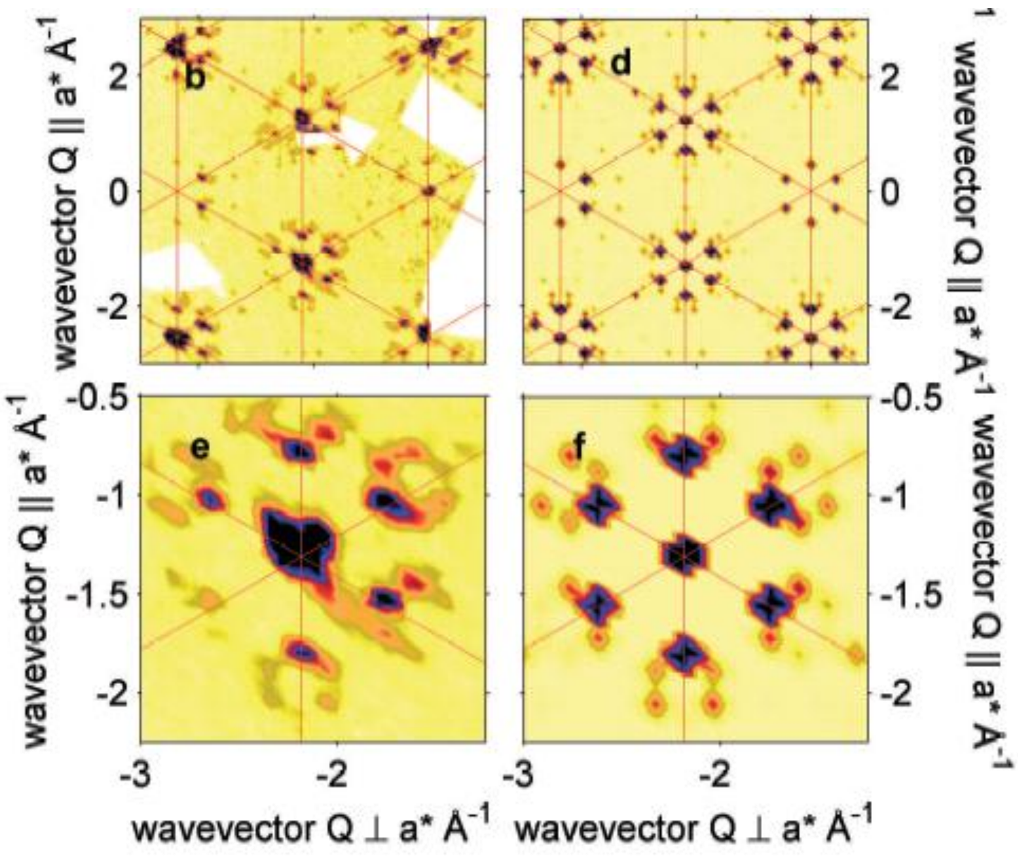
- High resolution allows Bragg peaks from different phases to be resolved

- Single phase at $x = 0.8$



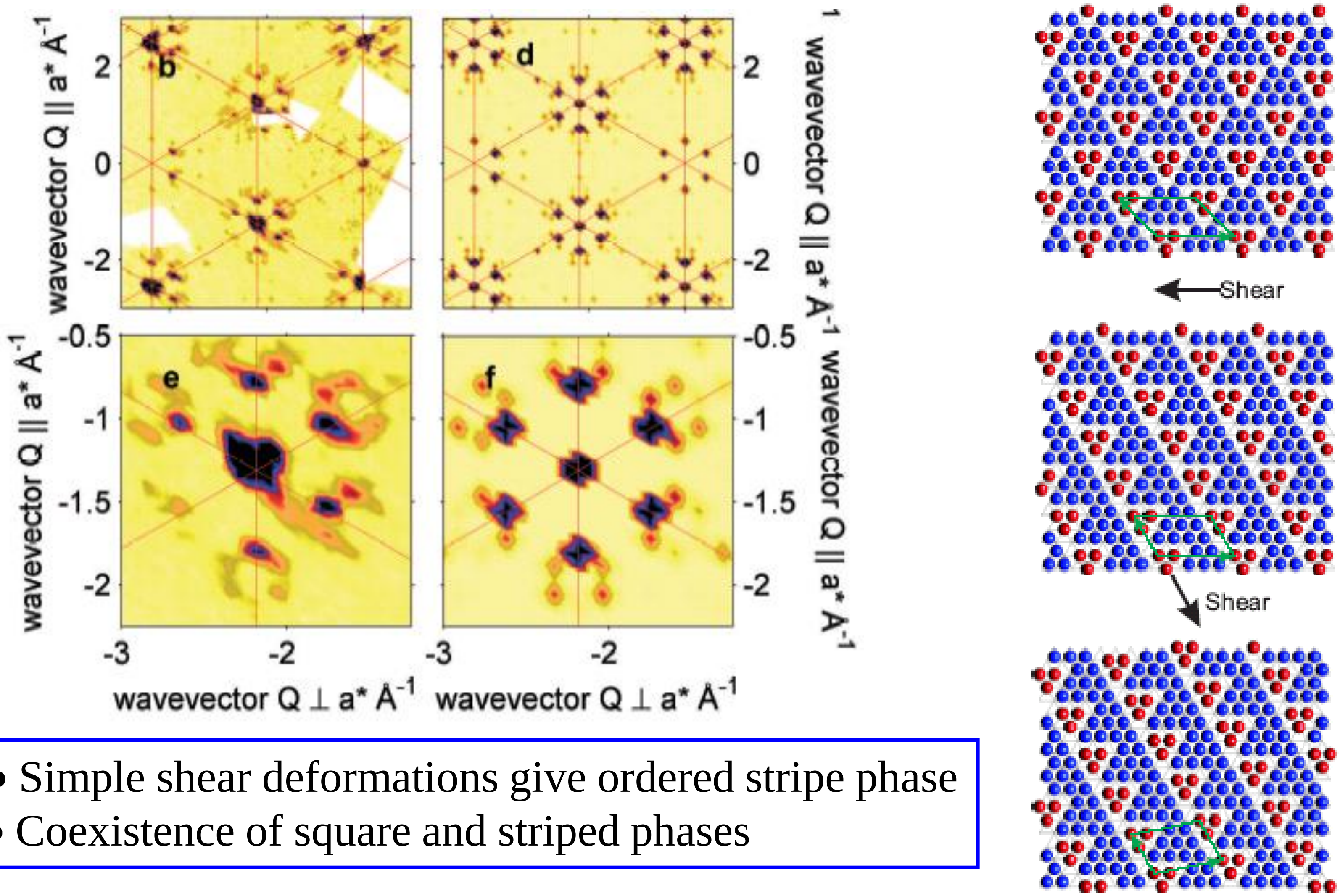
Coexistence of phases $Na_{0.78}CoO_2$

SXD data **Calculation**



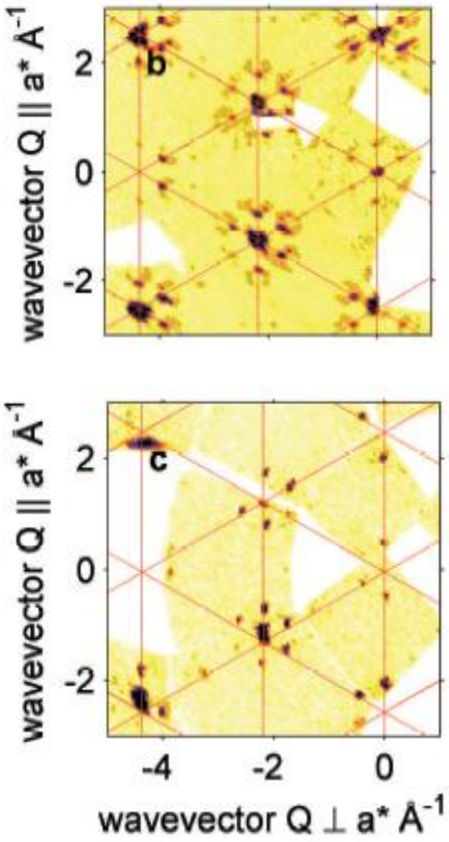
- Complicated superstructure!
- Hexagon-of-hexagons

Coexistence of phases $Na_{0.78}CoO_2$



- Simple shear deformations give ordered stripe phase
- Coexistence of square and striped phases

Sodium re-ordering transition



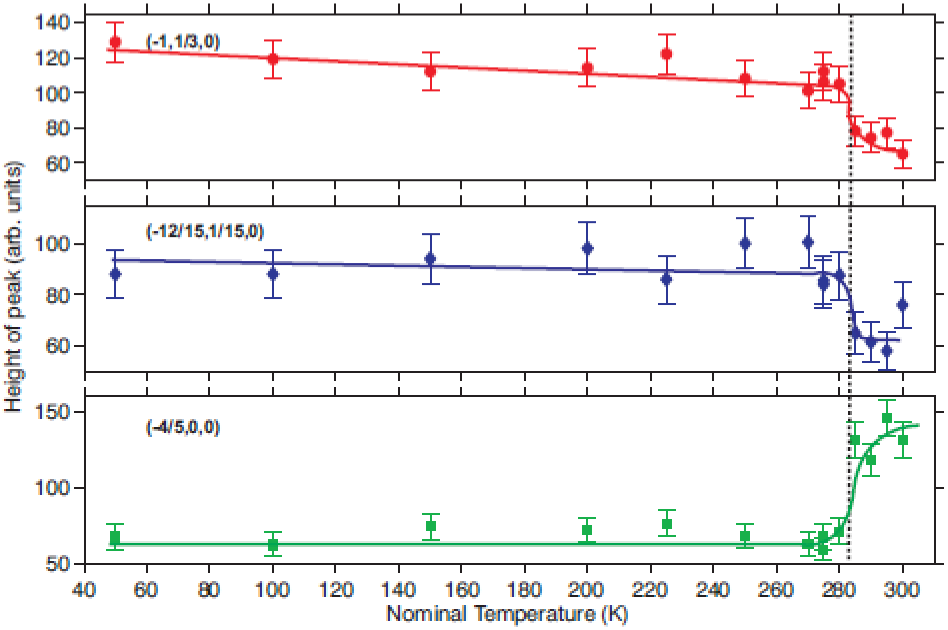
T = 150 K

T = 350 K

Samples of composition *x* = 0.75, 0.78 & 0.92 transform to the same superstructure in the vicinity of room temperature

Sodium re-ordering transition

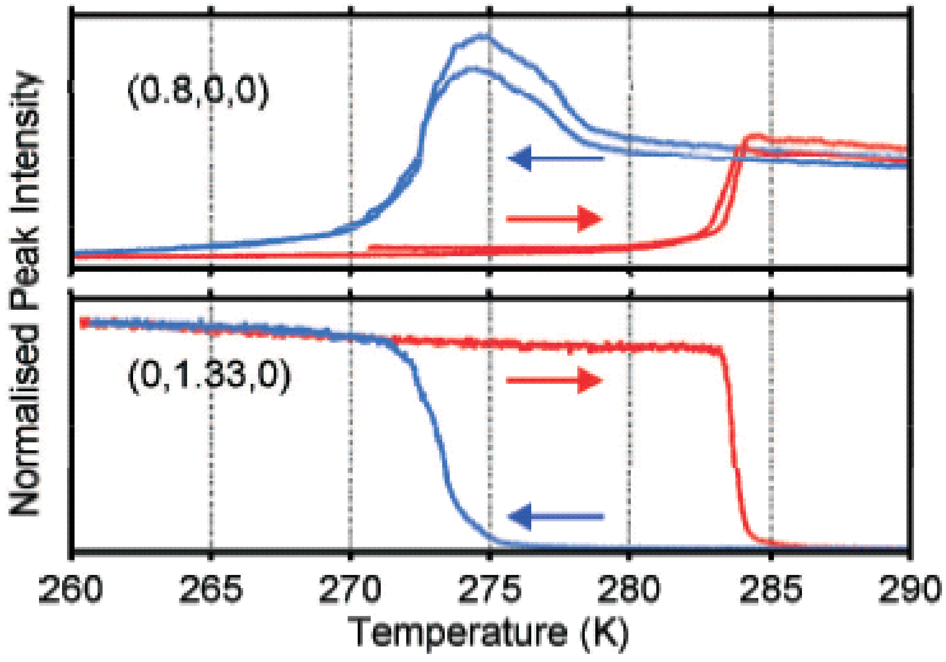
Neutron diffraction



- SXD several hours per exposure, so not ideal for phase transitions
- Reactor source better, but not ideal in this case

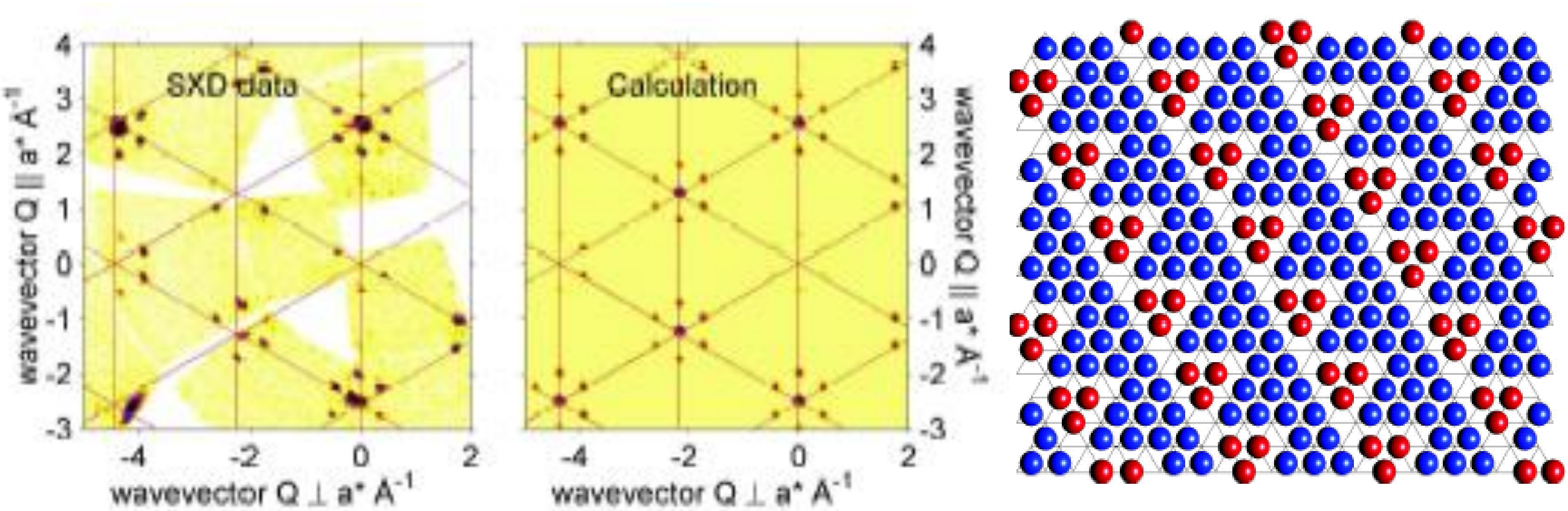
Sodium re-ordering transition

Synchrotron x-rays



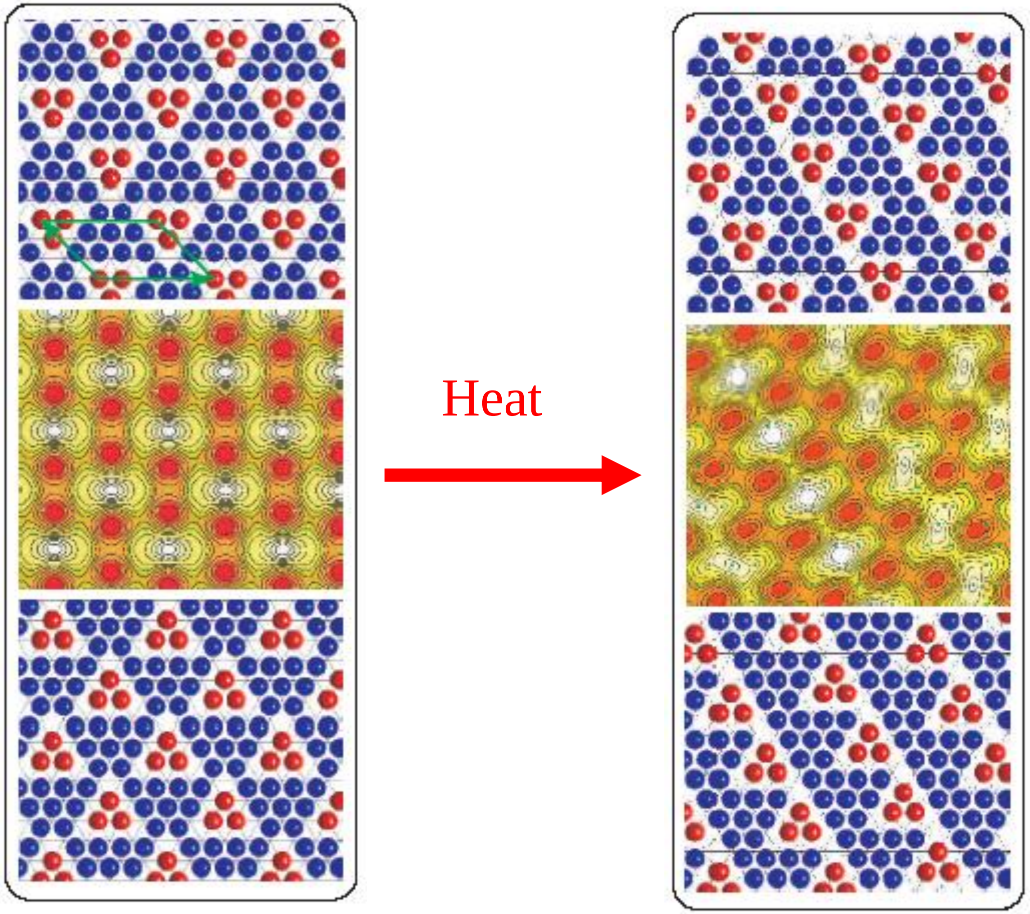
- The hysteresis in the re-ordering transition using synchrotron x-rays
- Ideal for studies of phase transitions – extra features observed

Sodium re-ordering transition



- The high-temperature disordered stripe phase
- The stripes are ordered, but the locations of the clusters within stripes varies randomly from stripe to stripe

Sodium re-ordering transition



- Crystal – stripe transition
- Change in dimensionality

Magnetism

Magnetic order

Neutrons

- Cross section simple and comparable to nuclear cross section
- By far the dominant technique for solving magnetic structures
- Complicated structures require polarised neutrons

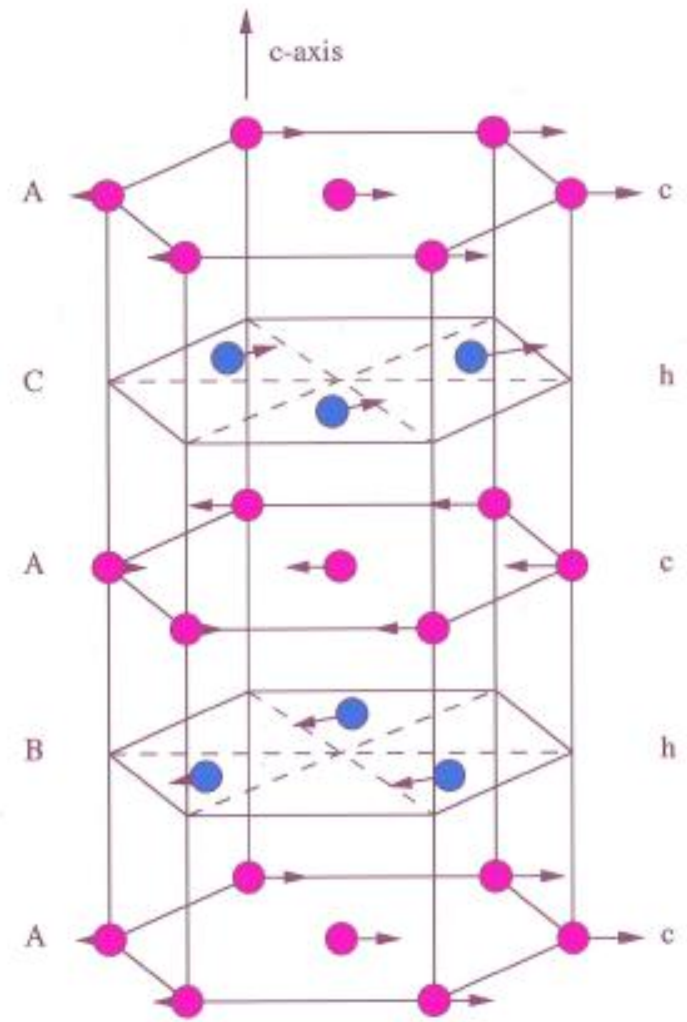
Synchrotron x-rays

- Generally complicated weak cross section and, if detectable at all, potentially additional information on magnetic structures
- Non-resonant x-rays separate *S* and *L*
- Resonant x-rays give species-specific information
- More accurate determination of propagation vectors than neutrons
- Information on electronic state

Magnetism

Magnetic ordering of Nd

Neutron diffraction
• Incommensurate structure
Moon *et al.*, *J. Appl. Phys.* **35,** 1041 (1964)

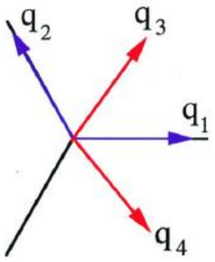


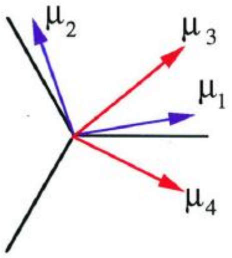
Magnetism

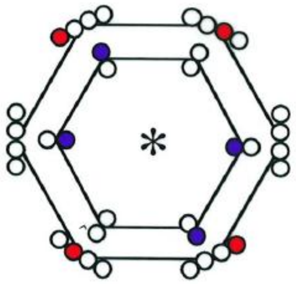
Magnetic ordering of Nd

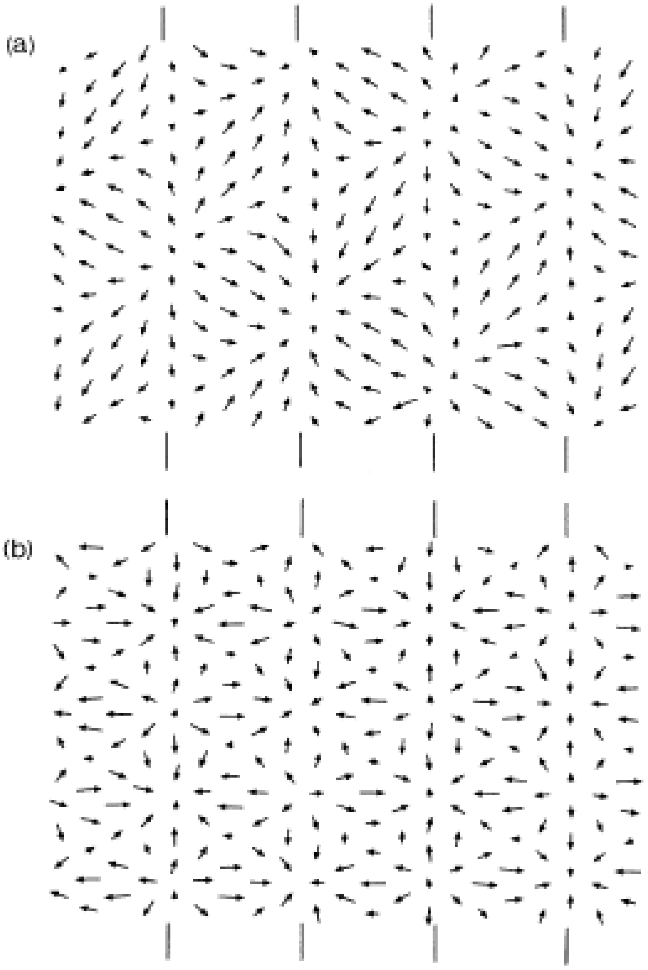
Neutron diffraction
- Solve multi-q structures using diffraction harmonics
- Quadruple-q at low temperature

Forgan *et al.*, *Phys. Rev. Lett.* **62**, 470 (1989)









Magnetism

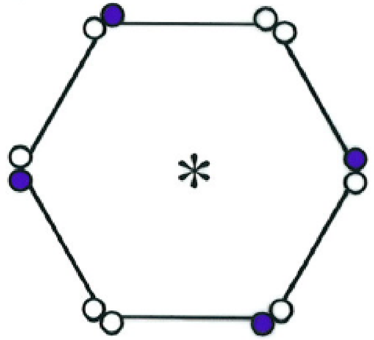
Magnetic ordering of Nd

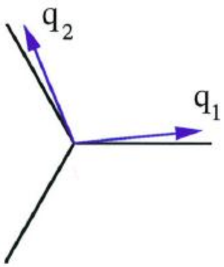
2-*q* magnetic structure

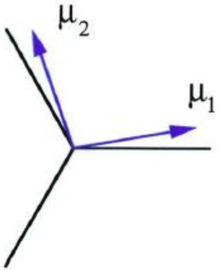
Resonant x-ray scattering

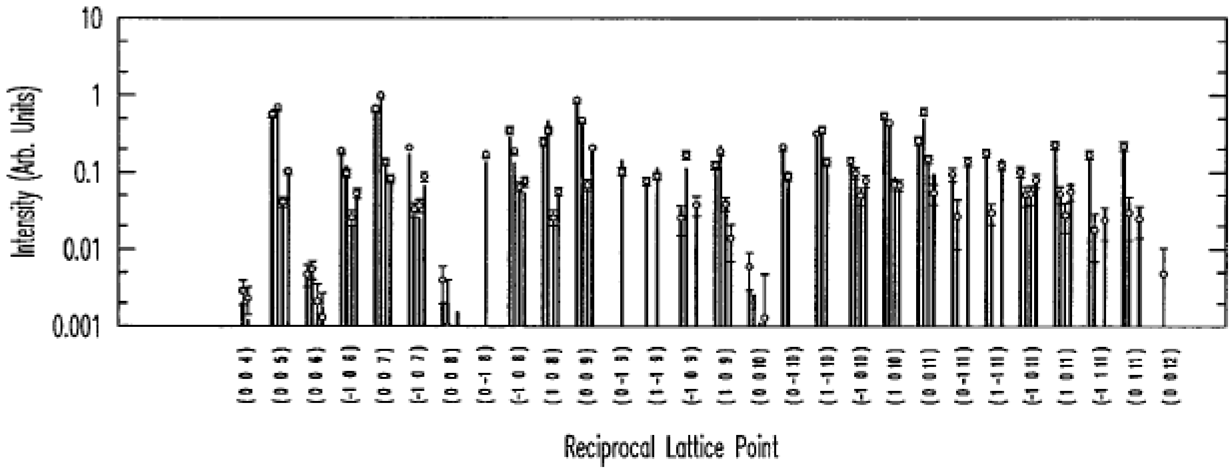
- Focus on single domain
- Solve 2-q structure using x-rays

Watson *et al.*, *Phys. Rev. B.* **57**, R8095 (1998)





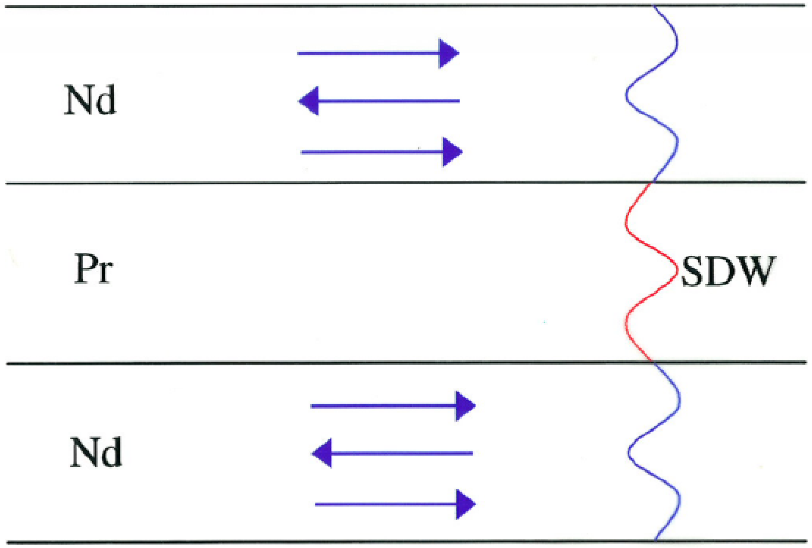




Magnetism

Nd/Pr multilayers

• Resonant x-rays allow the magnetism of the Nd & Pr components to be studied *separately*
• Neutrons dominated by localised 4*f* moments
• See 5*d* polarisation at rare-earth L edges
Goff *et al., J. Phys.: Condens. Matter* **11,** L139 (1999).

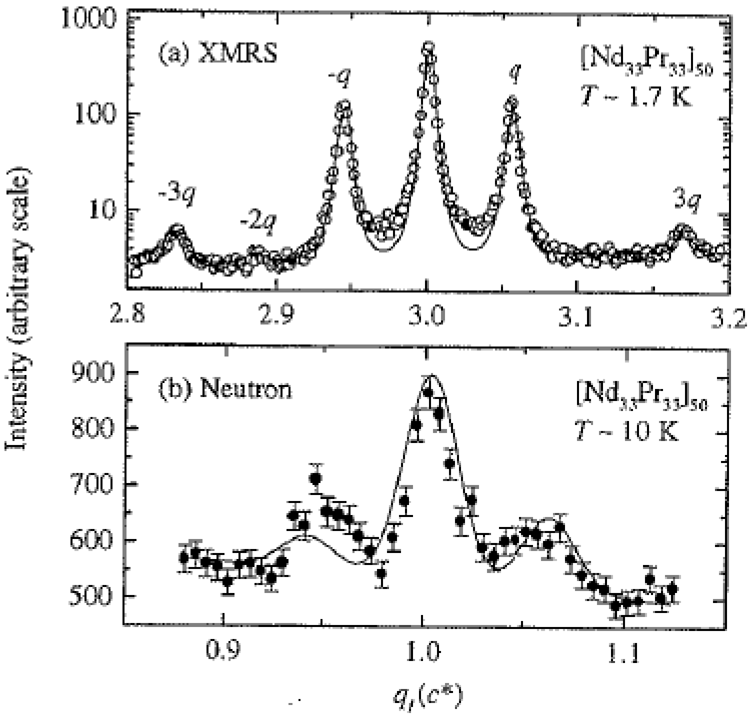


Magnetism

Nd/Pr multilayers

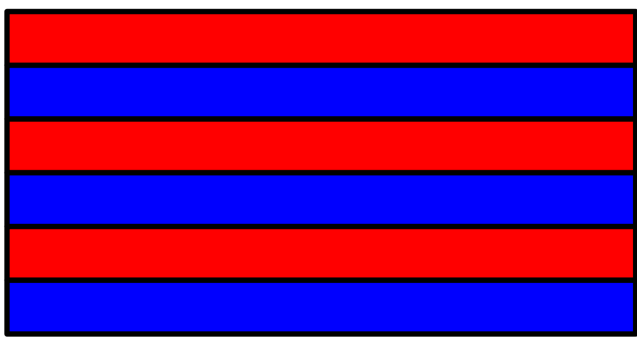
- Resonant x-rays give much better signal-to-background from tiny magnetic volumes
- Obtain better magnetization profile through multilayer stack
- More accurate incommensurate wave vectors
- More information on magnetic correlation lengths

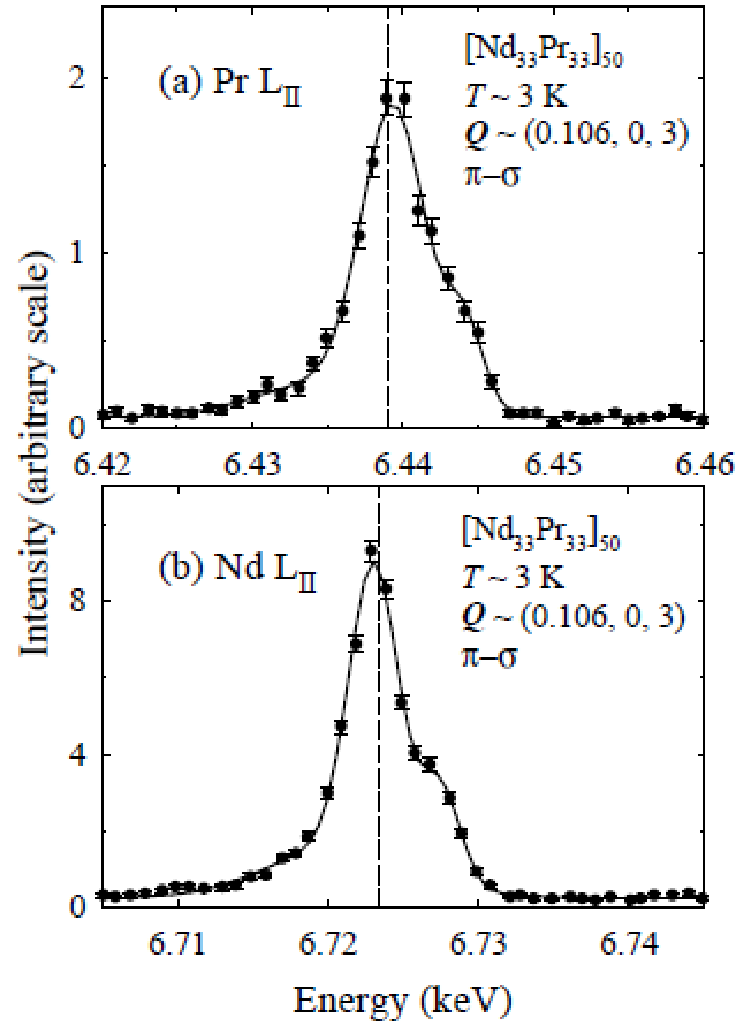
Goff *et al., J. Phys.: Condens. Matter* **11,** L139 (1999).



Magnetism

Nd/Pr multilayers

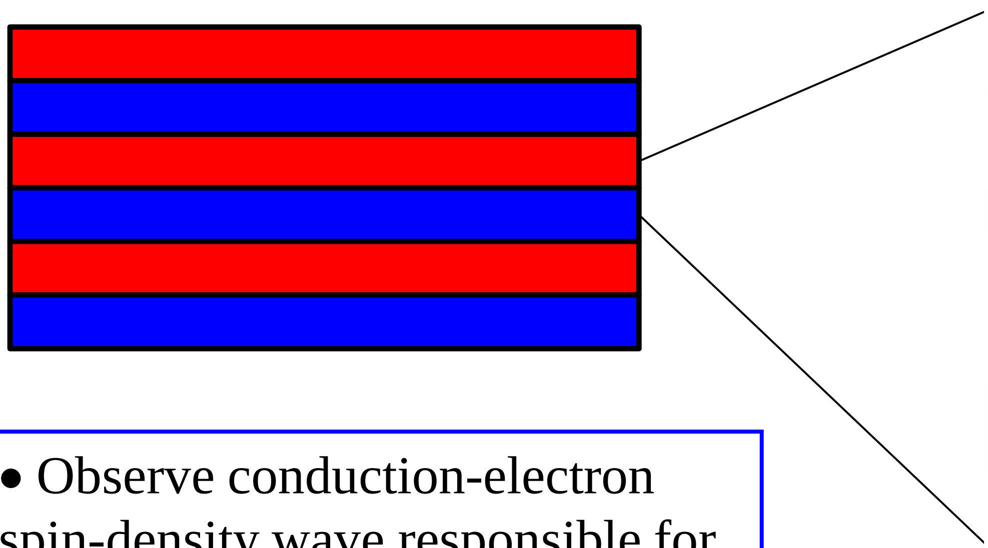


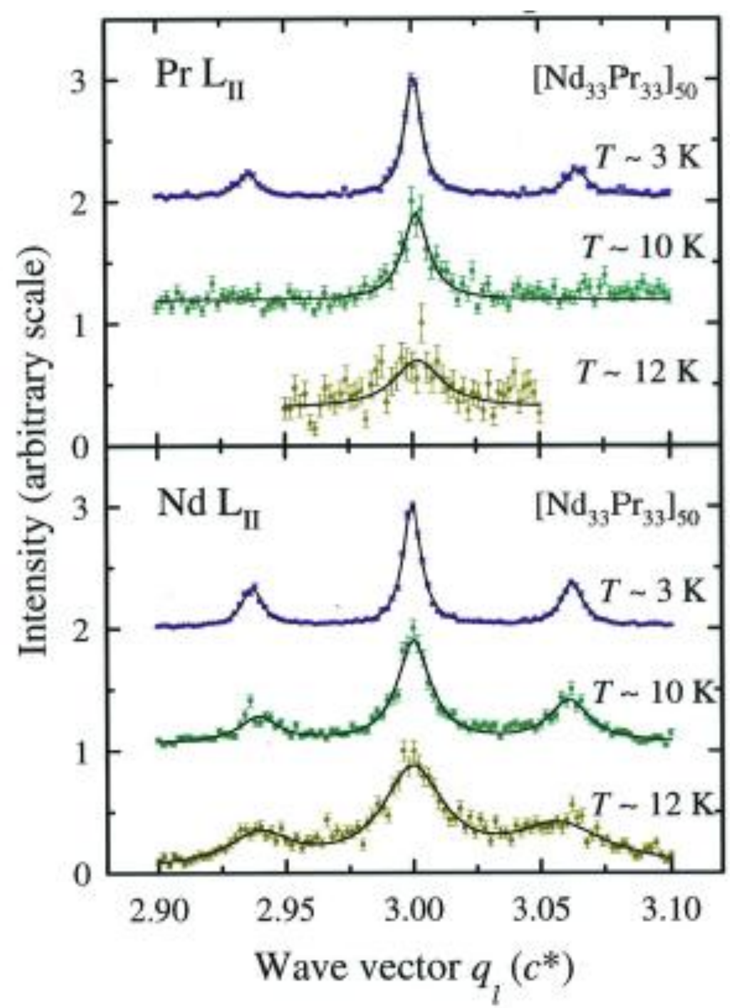


- Observe conduction-electron spin-density wave responsible for the propagation of magnetic order in magnetic multilayers

Magnetism

Nd/Pr multilayers





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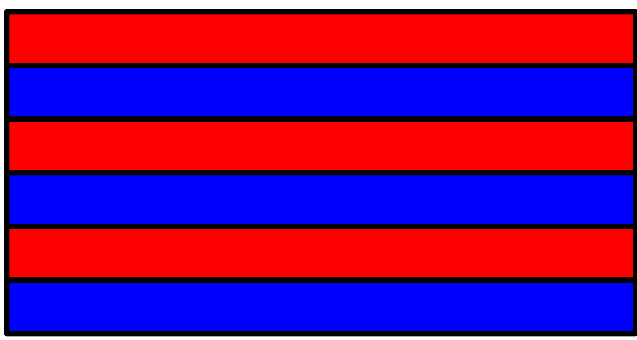
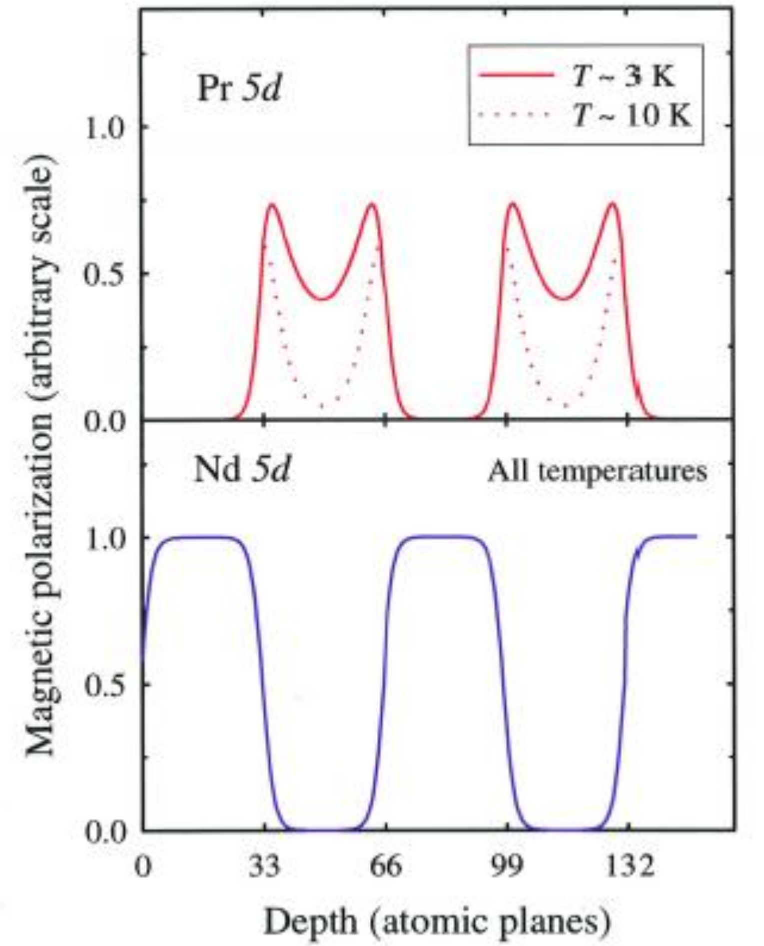
Magnetism

Nd/Pr multilayers



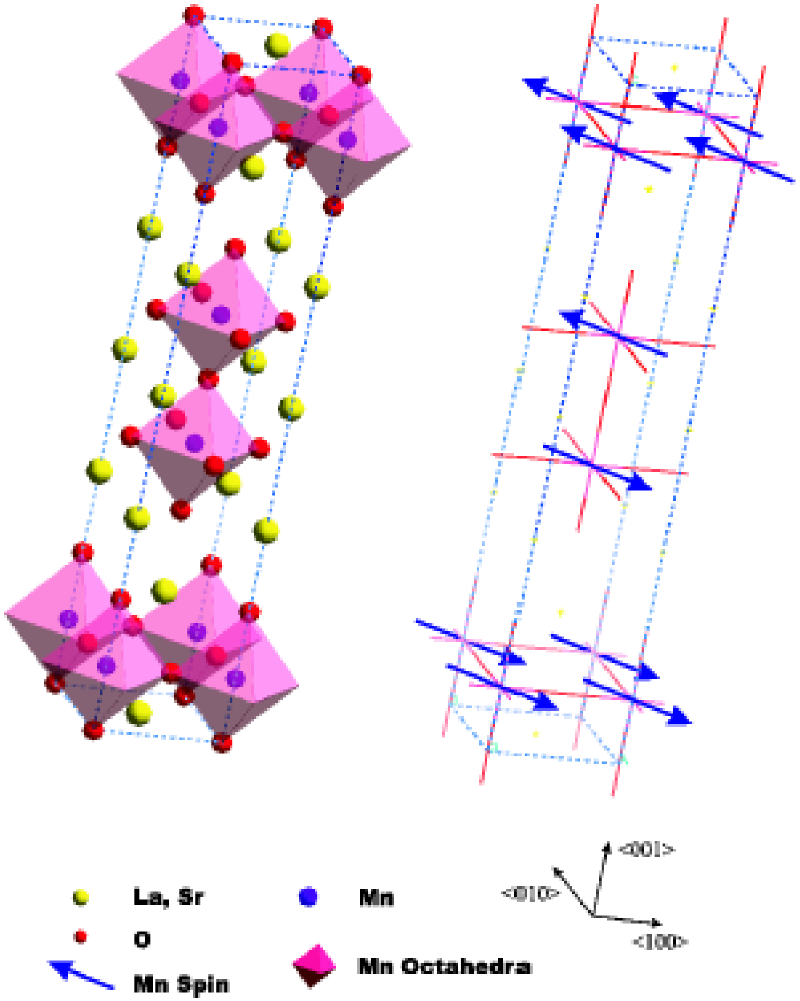


- Observe conduction-electron spin-density wave responsible for the propagation of magnetic order in magnetic multilayers

Other degrees of freedom

$La_{0.5}Sr_{1.5}MnO_4$

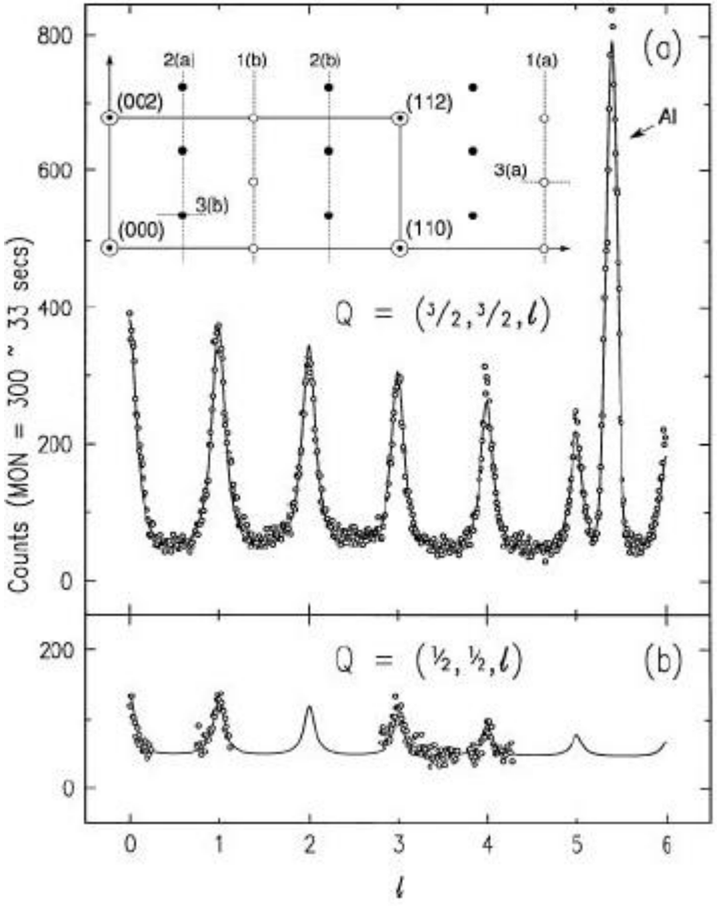
- Prototypical strongly correlated electron system with spin, charge, orbital and lattice degrees of freedom
- Spin structure originally proposed by Goodenough *Phys. Rev.* **100**, 564 (1955)
- Much controversy in recent years…



Other degrees of freedom

$La_{0.5}Sr_{1.5}MnO_4$

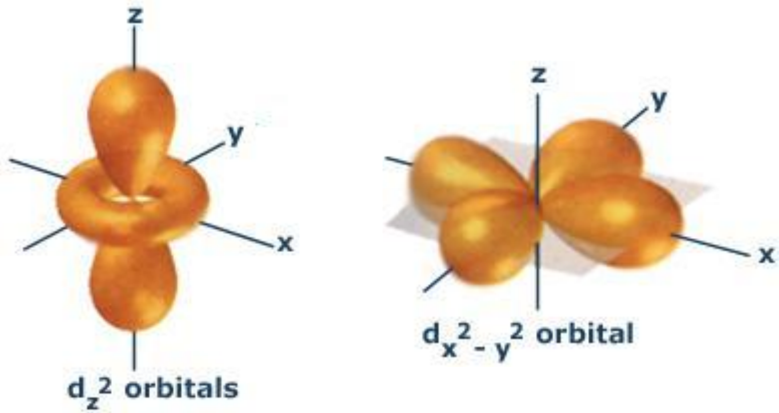
• Spin and charge ordering determined by Sternlieb *et al.*, *Phys. Rev. Lett.* **76**, 2169 (1996)
• Magnetic (charge) peaks filled (open) circles
• T_N ~ 110 K
• T_{CO} ~ 217 K
• Synchrotron x-ray results different due to surface effects…



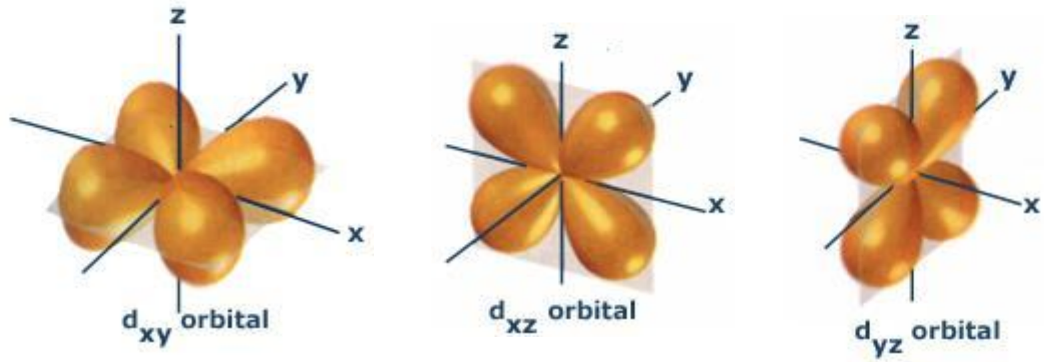
Other degrees of freedom

$La_{0.5}Sr_{1.5}MnO_4$

e_g



t_{2g}



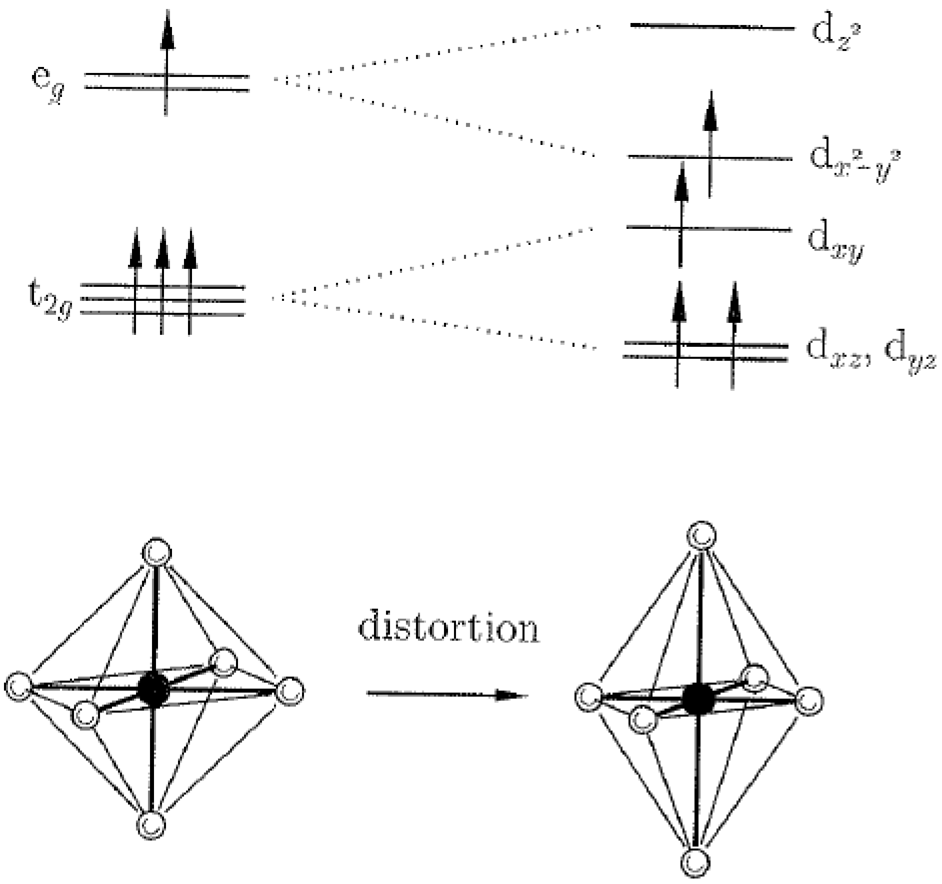
- What about orbital ordering?
- Mn^{3+} is $3d^4$

Other degrees of freedom

$La_{0.5}Sr_{1.5}MnO_4$

- Sensitivity of neutron diffraction to orbital ordering is via oxygen displacements
- Mn^{3+} ($3d^4$) is Jahn-Teller active
- Jahn-Teller distortion of MnO_6 octahedra small

Sternlieb *et al.*, *Phys. Rev. Lett.* **76**, 2169 (1996)

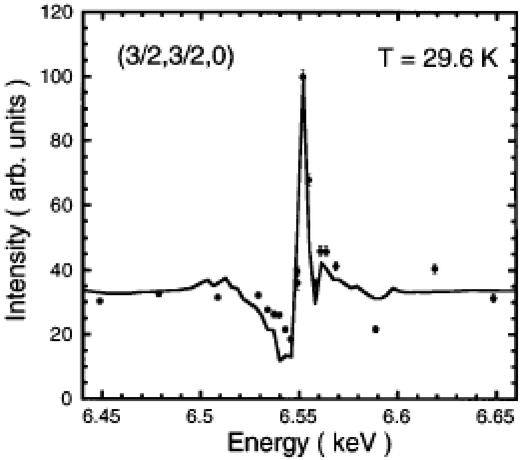


Other degrees of freedom

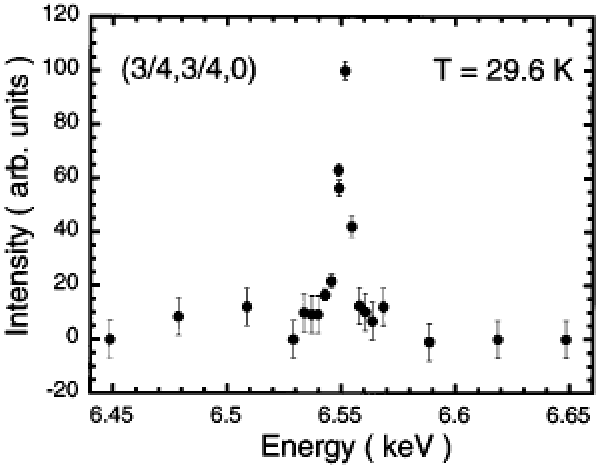
$La_{0.5}Sr_{1.5}MnO_4$

- Most of the controversy concerns hard x-ray measurements at the Mn K edges
Murakami *et al.*, *Phys. Rev. Lett.* **80**, 1932 (1998)
- Transitions to the 4*p* band
- Jahn-Teller distortions dominate, so information similar to neutrons
Benfatto *et al.*, *Phys. Rev. Lett.* **83**, 636 (1999)

Charge order



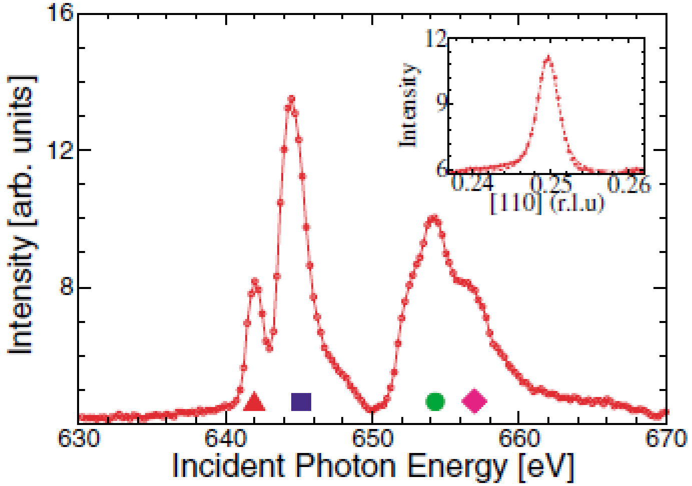
Orbital order

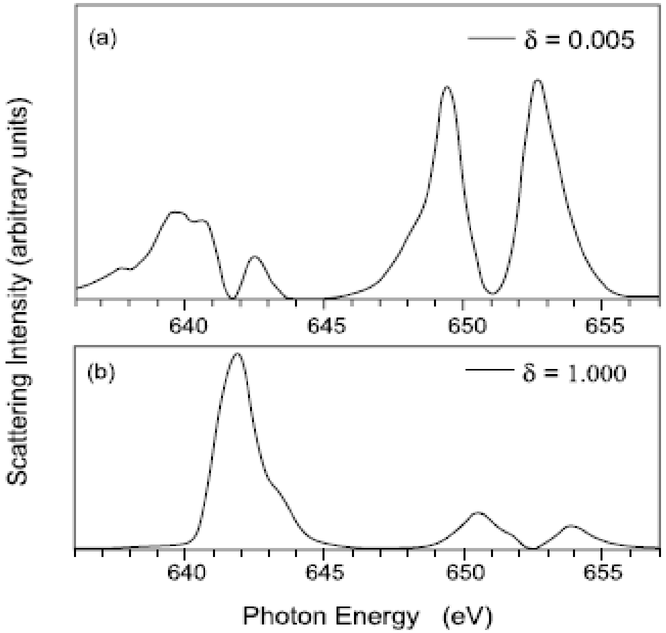


Other degrees of freedom

$La_{0.5}Sr_{1.5}MnO_4$

• Mn L-edge resonances in the soft x-ray range directly probe *d*-electrons
• Resonant lineshape due to direct orbital ordering and Jahn-Teller distortions
Wilkins *et al.*, *Phys. Rev. Lett.* **91,** 167205 (2003)





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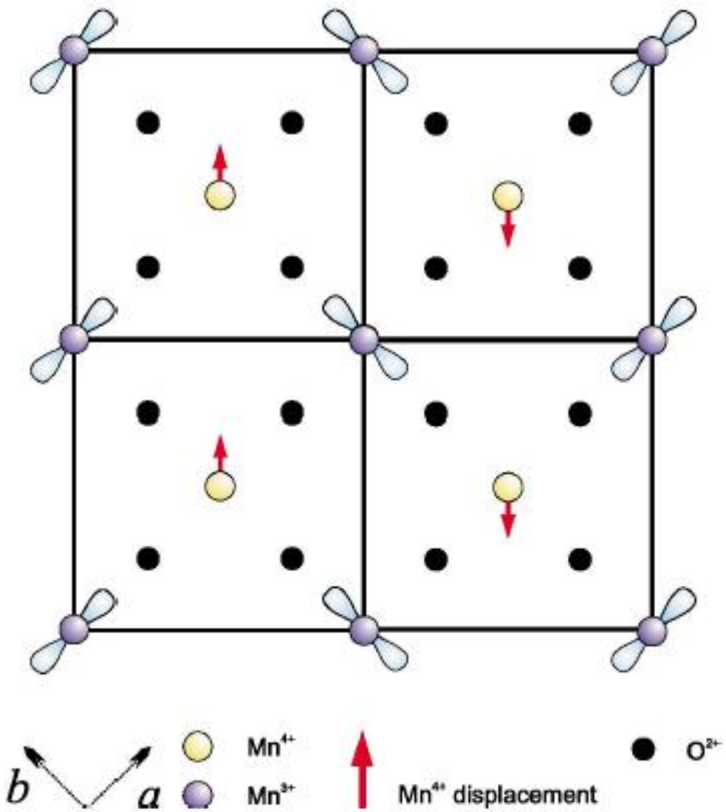


Excitations

Neutrons

• Thermal neutron wavelengths ~1Å and energies ~100meV are well matched to interatomic distances and excitation energies in condensed matter

• Measure the energy spectrum over entire Brillouin zone!

X-rays

• Photons with wavelength of ~1Å have an energy of ~12keV, so need an energy resolution of 1 part in 10^7 – backscattering

• Small samples

• High pressure

• Charge and orbital excitations

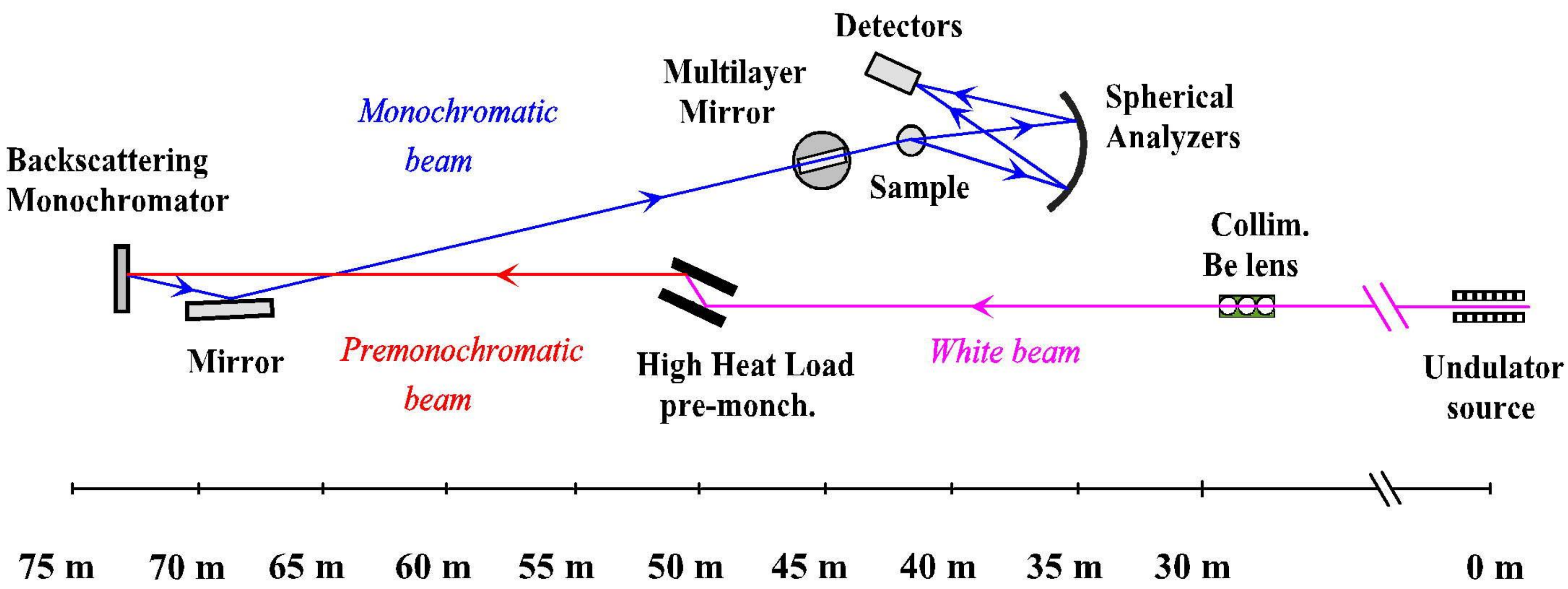
• Dispersions at low Q

• High frequency excitations

Excitations

Inelastic X-ray Scattering

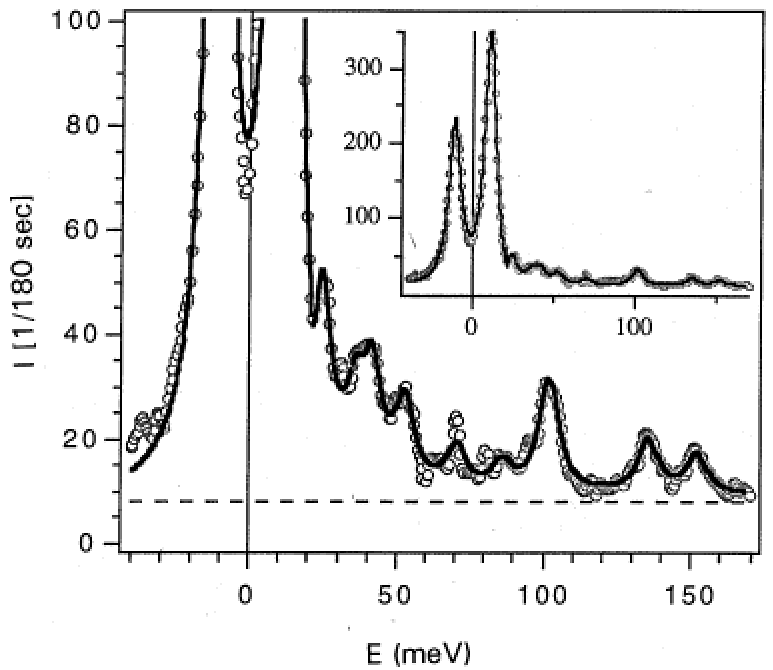
- Differentiate Bragg's law: $\frac{\Delta E}{E} = \cot\theta \, d\theta \rightarrow 0$ as $\theta \rightarrow \frac{\pi}{2}$
- Monochromator & analyzer close to backscattering, e.g. ID16 @ ESRF



Excitations

α-SiO_2

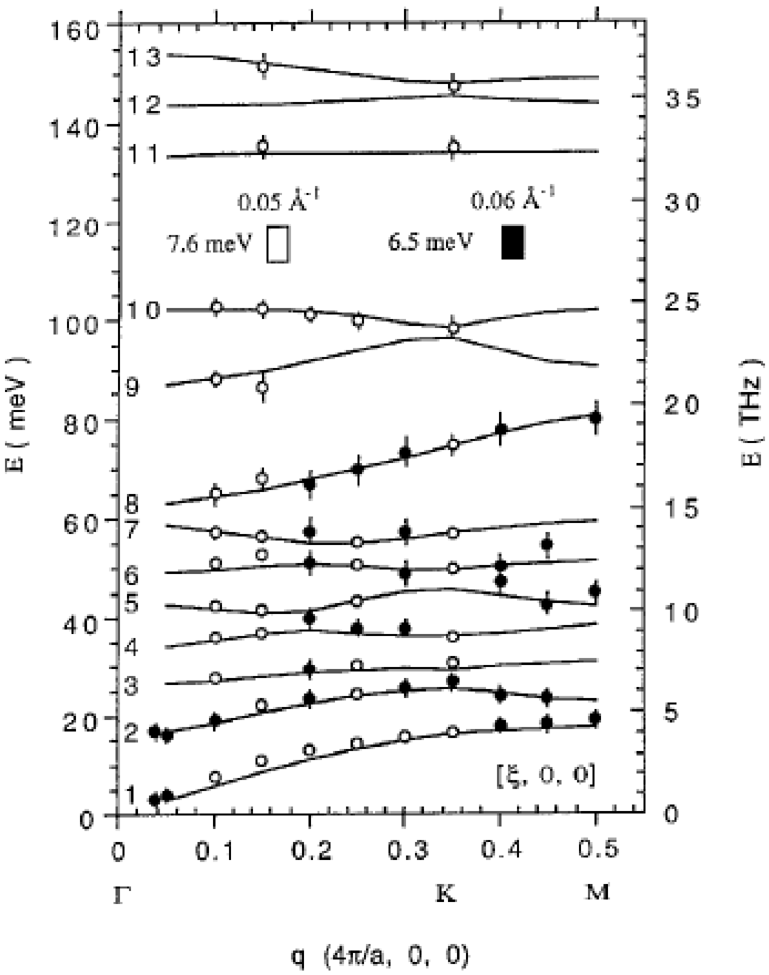
Energy scan at fixed *Q*
Halcoussis *PhD Thesis* (1997)



Excitations

α-SiO_2

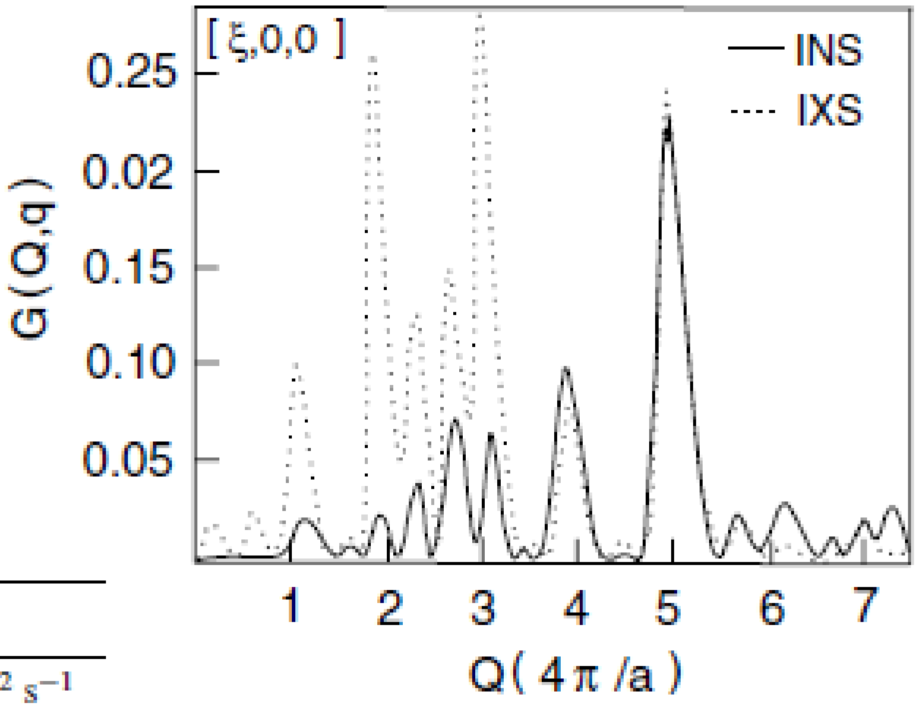
Phonon dispersion determined using x-rays agrees with theory



Excitations

α-SiO_2

For x-rays the counting statistics is similar for a crystal 1 million times smaller!

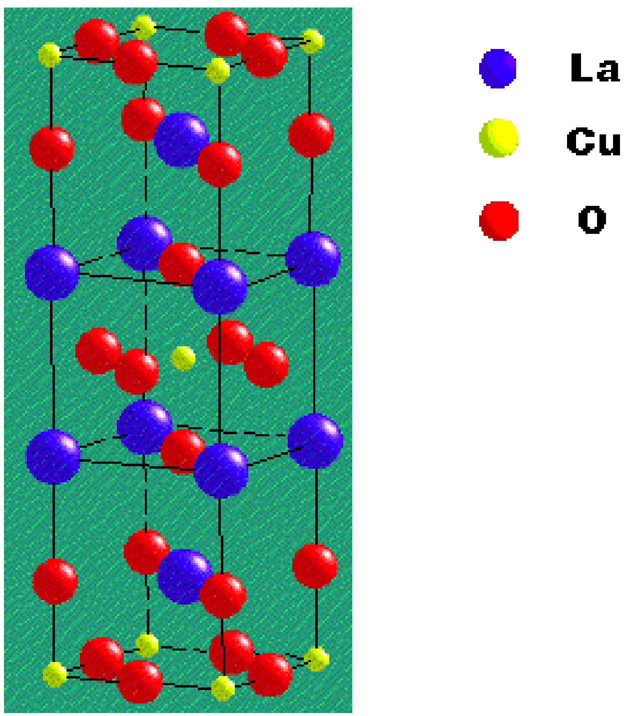


	Neutrons	Photons
Flux at sample position	10^7 cm^{-2} s^{-1}	10^{10} mm^{-2} s^{-1}
Scattering volume	6×10^4 mm^3	5×10^{-2} mm^3
Count rate for a typical LA phonon at maximum	215 min^{-1}	117 min^{-1}
time for a scan range of 10 meV transfer	60 min	65 min

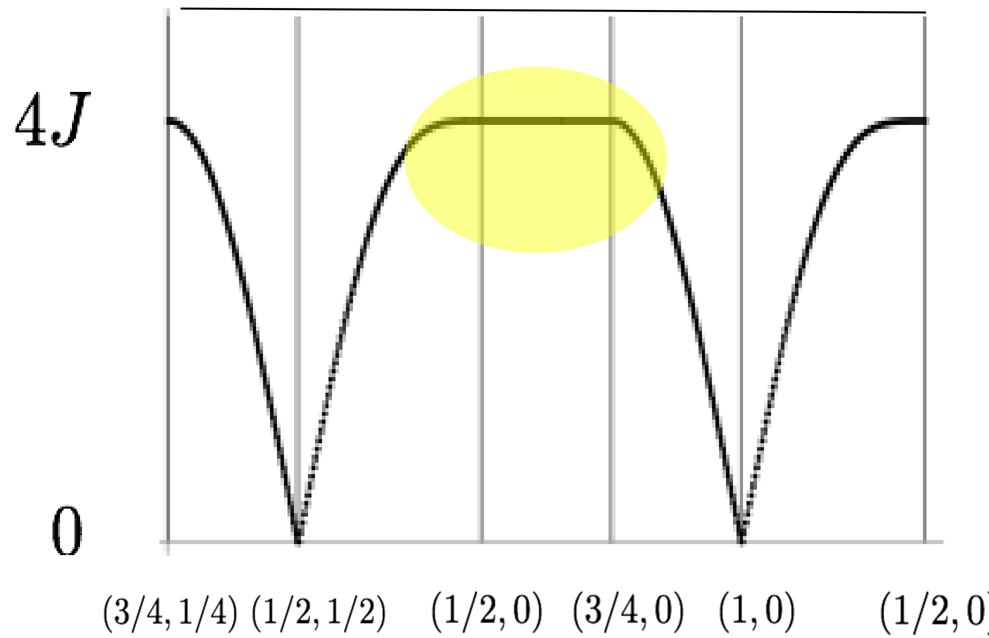
Magnetic Excitations

Square Lattice

Parent high-*Tc* superconductor La_2CuO_4



Heisenberg AF on square lattice

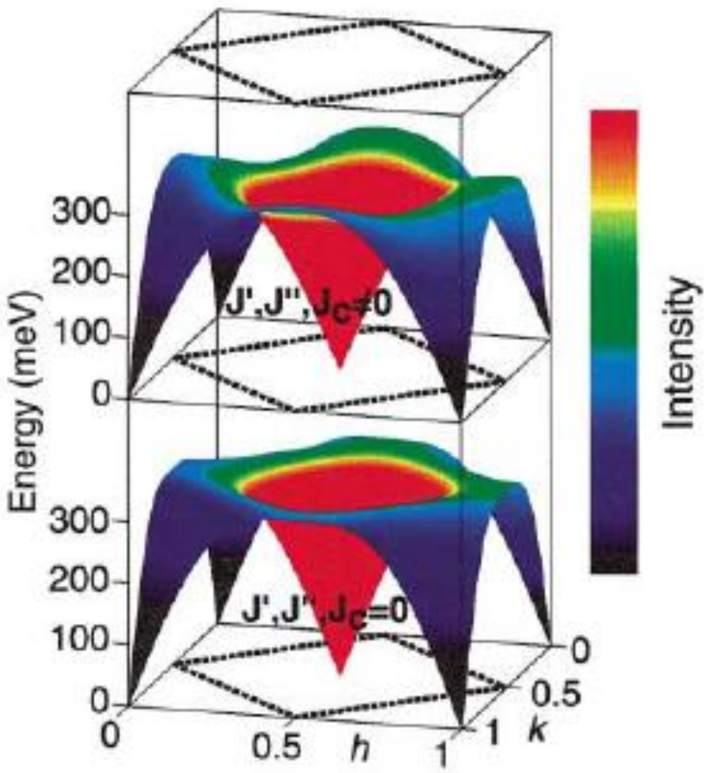


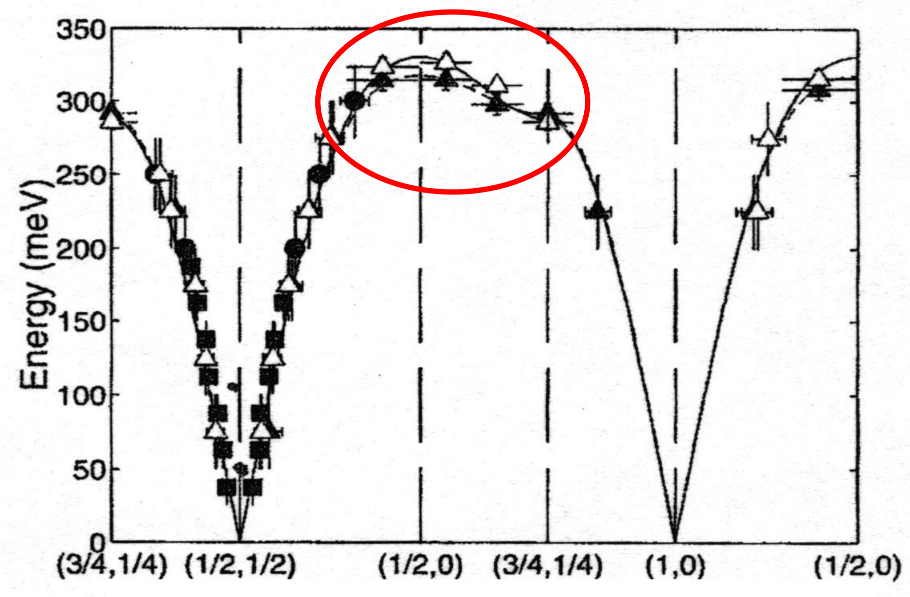
$$\hbar\omega(\underline{Q}) = 2SJ\sqrt{4 - (\cos Q_x + \cos Q_y)^2}$$

Magnetic Excitations

Inelastic Neutron Scattering (INS)

Coldea *et al.*, *PRL* **86,** 5377 (2001)





Tour de force of INS

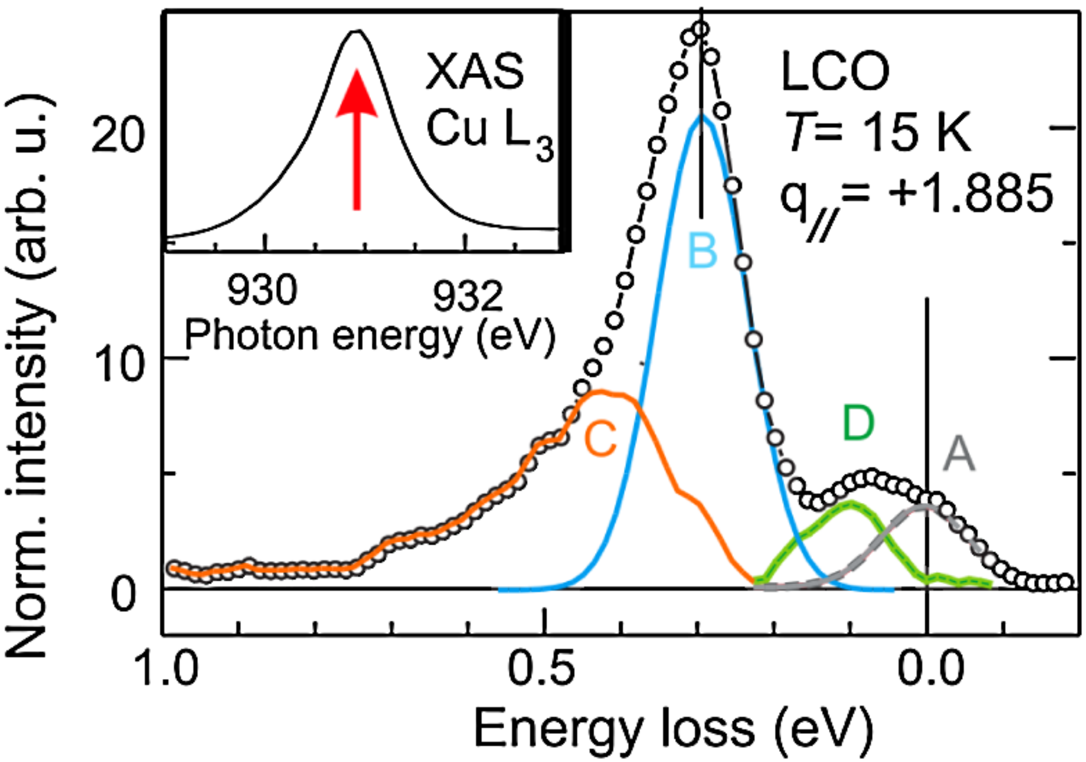
Determine spin Hamiltonian

Magnetic Excitations

Resonant Inelastic X-ray Scattering (RIXS)

Braicovich *et al.*, *PRL* **104,** 077002 (2010)

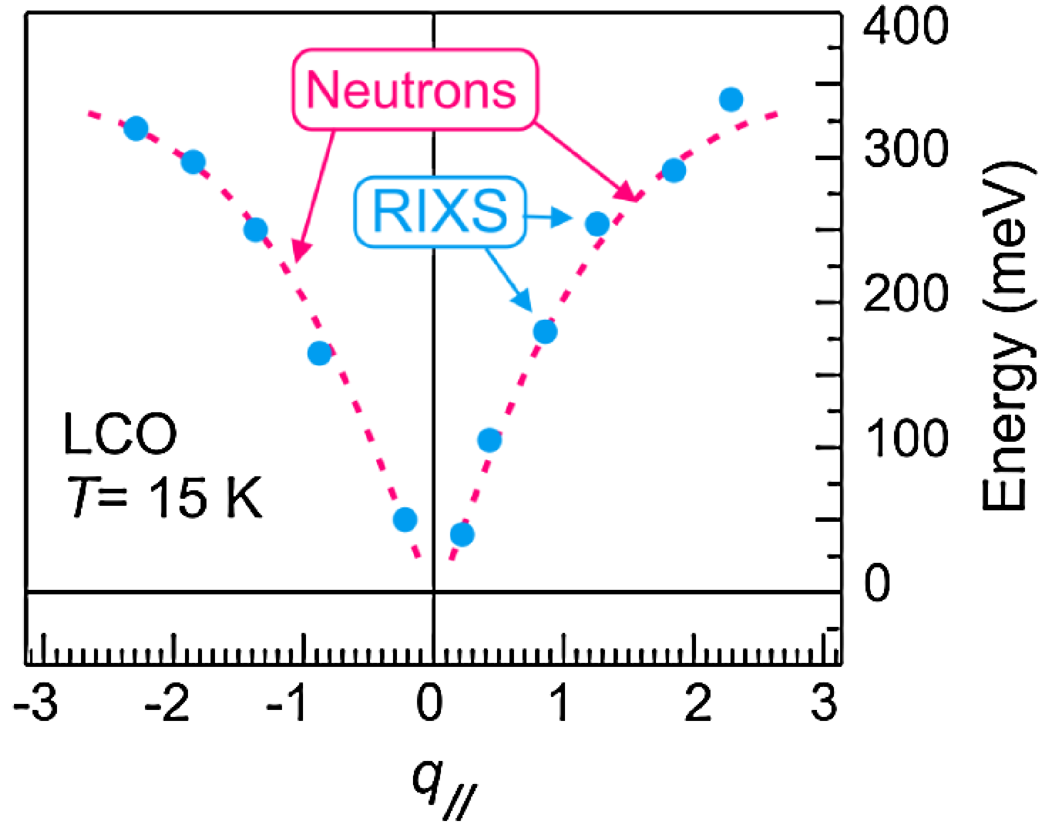
- IXS of soft x-rays
- A elastic scattering
- B single magnon
- C multiple magnon
- D optical phonons



Magnetic Excitations

Resonant Inelastic X-ray Scattering (RIXS)

Braicovich *et al.*, *PRL* **104,** 077002 (2010)



- IXS of soft x-rays
- First observation of magnon dispersion using x-rays!
- ΔE ~ 140meV
- ΔE ~ 30meV now possible
- Experiment performed on 100nm thin film!

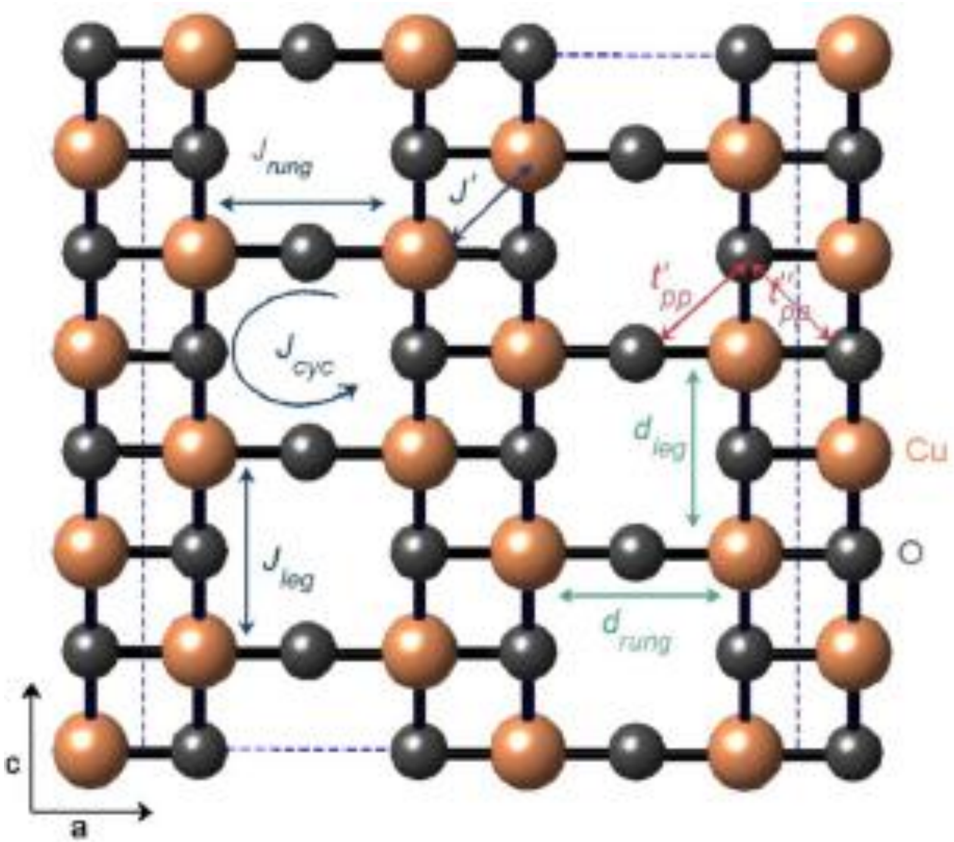
Magnetic Excitations

$(La,Sr)_{14}Cu_{24}O_{41}$

- Telephone number compound
- Two-legged ladder of two coupled S=½ chains
- Ground state: singlets on rungs
- Excitations: triplons

Inelastic Neutron Scattering

Notbohm *et al.*, *Phys. Rev. Lett.* **98**, 027403 (2007)



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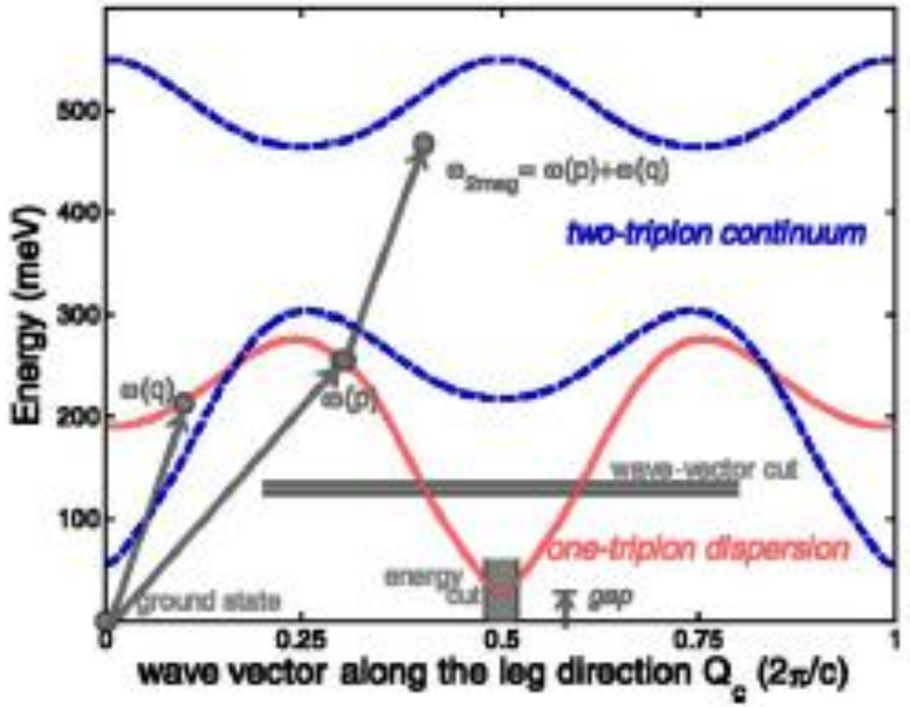

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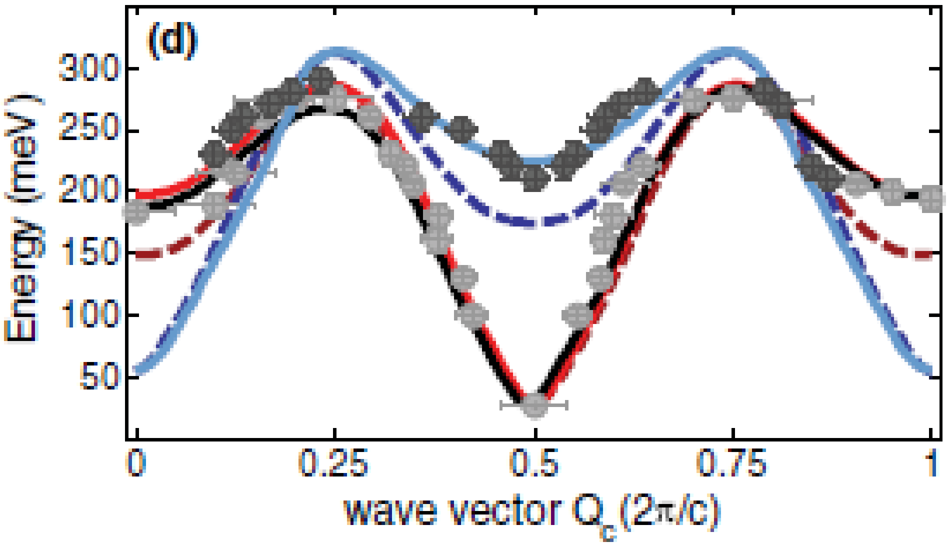

Ring exchange!

Magnetic Excitations

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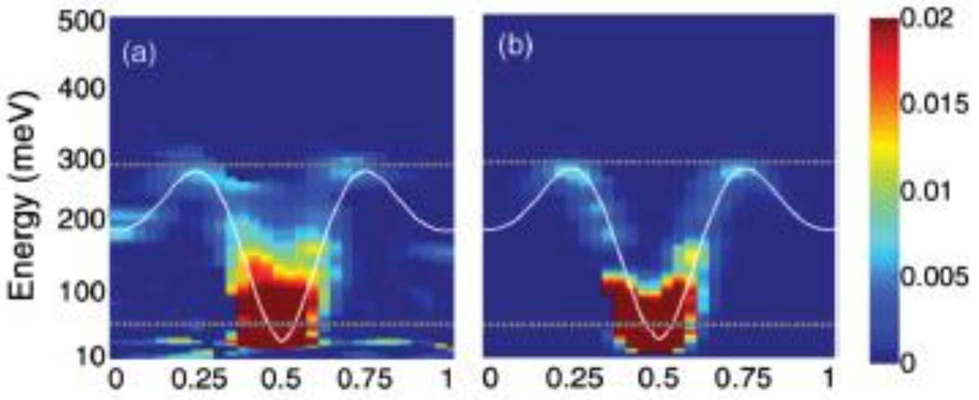
Inelastic Neutron Scattering

Notbohm *et al.*, *Phys. Rev. Lett.* **98**, 027403 (2007)

One-triplon excitations



Magnetic Excitations

$(La,Sr)_{14}Cu_{24}O_{41}$

Two-triplon excitations

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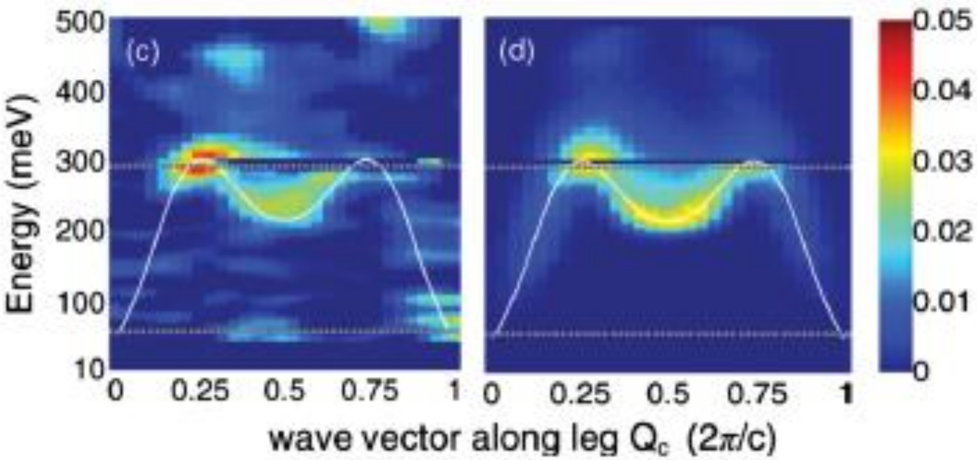
Inelastic Neutron Scattering
Notbohm *et al.*, *Phys. Rev. Lett.* **98**, 027403 (2007)



Magnetic Excitations

$Sr_{14}Cu_{24}O_{41}$

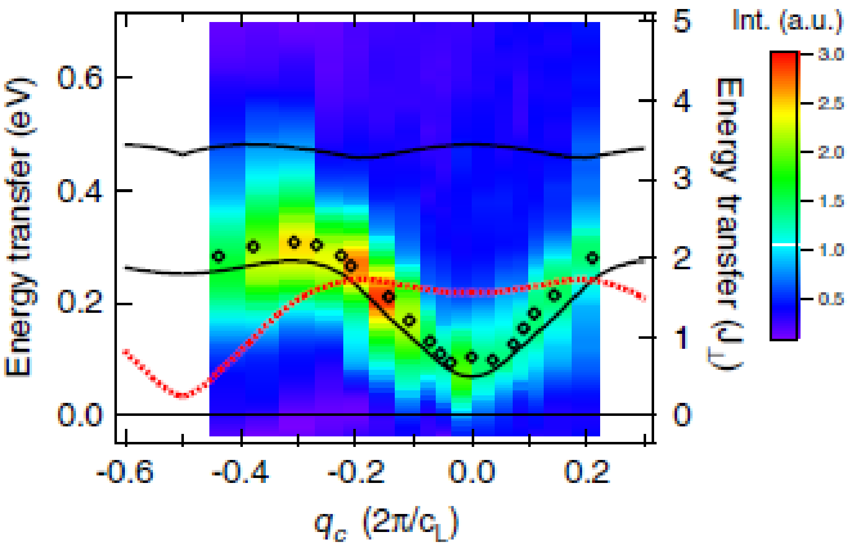
Two-triplon excitations

- Telephone number compound
- Two-legged ladder of two coupled S=½ chains
- Ground state: singlets on rungs
- Excitations: triplons

Inelastic X-ray Scattering

Schlappa *et al.*, *Phys. Rev. Lett.* **103**, 047401 (2009)

- Electric dipole: $\Delta L=\pm 1$, $\Delta S=0$
- Measure across whole BZ



Conclusions & Future Outlook

Structures
- X-rays primary technique for structures
- Neutrons locate light elements

Magnetism
- Neutrons primary technique due to simple, large cross section
- X-rays can provide additional information, e.g. element specific

Charge & orbital degrees of freedom
- Neutrons indirect probe, since detect accompanying oxygen distortions
- Resonant x-rays potentially couple to charge & orbital ordering directly

Excitations
- Neutrons primary technique for excitations
- X-rays enable the study of tiny samples