Neutrons & X-rays

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

Conclusions & Future Outlook
Neutrons & X-rays
Neutrons & X-rays

Facilities

ISIS & Diamond
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

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$_4$BN$_3$H$_{10}$ desorbs H$_2$ rather than ammonia, has a high storage density, but is not as reversible
- The search goes on…
Superstructures in $\text{Na}_x\text{CoO}_2$

- $\text{CoO}_2$ layer
- Na can occupy $A$ or $C$ position
- Na can occupy $B$ or $C$ position

- Tunable number of $\text{Na}^+$ ions
- $x = 0$ to 1 per $\text{CoO}_2$

Commensurate superstructure

- High flux allows study of tiny crystals (dimensions ~ 0.3mm)
- High resolution enables accurate determination of superlattice
- See surface phases

X-ray diffraction
Commensurate superstructure

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

  $a' = 4a - 3b$

  $b' = a + 3b$

Neutron diffraction
Time-of-flight neutron Laue

- SXD gives 3D diffraction data
- Surveys reciprocal space

12-fold rings ($L=11$)

Crescents ($L=10$)
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

- High resolution allows Bragg peaks from different phases to be resolved
- Single phase at $x = 0.8$
Coexistence of phases $\text{Na}_{0.78}\text{CoO}_2$

- Complicated superstructure!
- Hexagon-of-hexagons
Coexistence of phases $\text{Na}_{0.78}\text{CoO}_2$

- Simple shear deformations give ordered stripe phase
- Coexistence of square and striped phases
Sodium re-ordering transition

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

$T = 150$ K

$T = 350$ K
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

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

Magnetism

Magnetic ordering of Nd

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

2-q magnetic structure
Magnetism

Nd/Pr multilayers

- Resonant x-rays allow the magnetism of the Nd & Pr components to be studied separately
- Neutrons dominated by localised 4f moments
- See 5d polarisation at rare-earth L edges

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

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

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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

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

- Magnetic (charge) peaks filled (open) circles
- $T_N \sim 110$ K
- $T_{CO} \sim 217$ K
- Synchrotron x-ray results different due to surface effects…
Other degrees of freedom

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

- What about orbital ordering?
- $\text{Mn}^{3+}$ is $3d^4$
Other degrees of freedom

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

- Sensitivity of neutron diffraction to orbital ordering is via oxygen displacements
- $\text{Mn}^{3+} (3d^4)$ is Jahn-Teller active
- Jahn-Teller distortion of $\text{MnO}_6$ octahedra small

Other degrees of freedom

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

- Most of the controversy concerns hard x-ray measurements at the Mn K edges
- Transitions to the $4p$ band
- Jahn-Teller distortions dominate, so information similar to neutrons

Charge order

Orbital order
Other degrees of freedom

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

- 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

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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: \( \frac{\Delta E}{E} = \cot \theta d\theta \to 0 \) as \( \theta \to \frac{\pi}{2} \)

• Monochromator & analyzer close to backscattering, e.g. ID16 @ ESRF
Excitations

$\alpha$-SiO$_2$

Energy scan at fixed $Q$
Excitations

$\alpha$-SiO$_2$

Phonon dispersion determined using x-rays agrees with theory
Excitations

\( \alpha\text{-SiO}_2 \)

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

<table>
<thead>
<tr>
<th></th>
<th>Neutrons</th>
<th>Photons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux at sample position</td>
<td>(10^7) cm(^{-2}) s(^{-1})</td>
<td>(10^{10}) mm(^{-2}) s(^{-1})</td>
</tr>
<tr>
<td>Scattering volume</td>
<td>(6 \times 10^4) mm(^3)</td>
<td>(5 \times 10^{-2}) mm(^3)</td>
</tr>
<tr>
<td>Count rate for a typical LA phonon at maximum</td>
<td>215 min(^{-1})</td>
<td>117 min(^{-1})</td>
</tr>
<tr>
<td>time for a scan range of 10 meV transfer</td>
<td>60 min</td>
<td>65 min</td>
</tr>
</tbody>
</table>
Magnetic Excitations

Square Lattice
Parent high-$T_c$ superconductor
La$_2$CuO$_4$

Heisenberg AF on square lattice

\[ \hbar \omega Q = 2S J \sqrt{4 - \cos Q_x \cos Q_y} \]
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)

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

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

Resonant Inelastic X-ray Scattering (RIXS)

- IXS of soft x-rays
- First observation of magnon dispersion using x-rays!
- $\Delta E \sim 140 \text{meV}$
- $\Delta E \sim 30 \text{meV}$ now possible
- Experiment performed on 100nm thin film!

Magnetic Excitations

(\(\text{La, Sr}\))\(_{14}\text{Cu}_{24}\text{O}_{41}\)

- Telephone number compound
- Two-legged ladder of two coupled \(S=\frac{1}{2}\) chains
- Ground state: singlets on rungs
- Excitations: triplons

**Inelastic Neutron Scattering**
Magnetic Excitations

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**Inelastic Neutron Scattering**


Ring exchange!
Magnetic Excitations

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Inelastic Neutron Scattering
Magnetic Excitations

(\text{La, Sr})_{14}\text{Cu}_{24}\text{O}_{41}

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

**Inelastic Neutron Scattering**
Magnetic Excitations

$\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$

- Telephone number compound
- Two-legged ladder of two coupled $S=\frac{1}{2}$ chains
- Ground state: singlets on rungs
- Excitations: triplons

**Inelastic X-ray Scattering**

- 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