Inelastic Neutron Scattering (INS)

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Seminar Overview

· Introduction to INS
  - Principles and Instrumentation
  - Advantages and Disadvantages Over Other Techniques
  - Selection Rules for Magnetic INS

· Applications
  - Ground State Zero-Field-Splitting of non-Kramers Ions
  - Exchange Coupling in Molecular Clusters
The Technique Provides a Measure of Energy and Momentum Transfer Between the Neutron and Sample

\[ \text{Incoming Neutrons} \quad \vec{k} \quad \text{Sample} \quad \vec{Q} \quad \text{Scattered Neutrons} \quad \vec{k}' \]

Energy Transfer: \[ \hbar \omega = \frac{\hbar^2}{2m} (k^2 - k'^2) \]

Momentum Transfer: \[ \hbar \vec{Q} = \hbar (\vec{k} - \vec{k}') \]
Schematic of a Time-of-Flight (TOF) INS Spectrometer

One measures the time it takes for neutrons to travel from the sample to a position on the detector bank.
Incoming “white” neutron beam
- Incident energy selection
- Scattering by the sample
- Final energy selection

Allows the measurement of inelastic excitations at a given point in reciprocal space.
## Principal Facilities for INS in Europe

<table>
<thead>
<tr>
<th>Facility</th>
<th>Organisation</th>
<th>Location</th>
<th>TYPE</th>
<th>Description of Instruments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILL</td>
<td>Institut Laue-Langevin</td>
<td>Grenoble, France</td>
<td>High-flux reactor</td>
<td><a href="http://www.ill.fr/index_sc.html">http://www.ill.fr/index_sc.html</a></td>
</tr>
<tr>
<td>ISIS</td>
<td>Rutherford Appleton Laboratory</td>
<td>Oxford, UK</td>
<td>Pulsed neutron facility</td>
<td><a href="http://www.isis.rl.ac.uk/instruments/index.htm">http://www.isis.rl.ac.uk/instruments/index.htm</a></td>
</tr>
<tr>
<td>BENSIC</td>
<td>Berlin Neutron Scattering Centre</td>
<td>Hahn-Meitner-Institut, Berlin, Germany</td>
<td>Cold neutron guides</td>
<td><a href="http://www.hmi.de/bensc/instrumentation/instrumentation_en.html">http://www.hmi.de/bensc/instrumentation/instrumentation_en.html</a></td>
</tr>
</tbody>
</table>

The list is by no means complete. See also: http://www.neutron-eu.net/en/index.php
Variation of INS Intensity with Q, differs for Magnetic and Phonon Transitions
In general:

- Ability to detect low energy excitations limited by the width of the elastic line
- Momentum transfer increases with increasing energy transfer: favours detection of phonon rather than magnetic transitions
- Resolution becomes poorer with increasing energy transfer
- Practical range of magnetic INS: ~0.5 to ~500 cm$^{-1}$, depending on sample, and instrument configuration.
Advantages of INS Over Other Techniques

- Direct Determination of Energy Levels in Zero Magnetic Field
- Change in Intensity and Energy as a Function of Q Carries Useful Information Concerning the Wavefunctions

Disadvantages of INS Over Other Techniques

- Several Grams of Sample Must be Used
- Often Necessary to Use Fully Deuteriated Samples
Background due to incoherent scattering from protons often precludes the observation of magnetic transitions.
Magnetic Scattering Selection Rules
Powdered Sample, Unpolarised Neutron Beam

Basis $|S, M_S\rangle$

$I_{\text{INS}}(Q = 0) \propto \exp\left(-\frac{E_i}{kT}\right)\left(2|\langle \Psi_f | \hat{S}_z | \Psi_i \rangle |^2 + |\langle \Psi_f | \hat{S}_+ | \Psi_i \rangle |^2 + |\langle \Psi_f | \hat{S}_- | \Psi_i \rangle |^2 \right)$

$\Delta M_S = \pm 1,0 \quad \Delta S = \pm 1,0$

Basis $|L, S, M_L, M_S\rangle$

$I_{\text{INS}}(Q = 0) \propto \exp\left(-\frac{E_i}{kT}\right)\left(\langle \psi_i | k\hat{L}_z + g_e \hat{S}_z | \psi_f \rangle \langle \psi_f | k\hat{L}_z + g_e \hat{S}_z | \psi_i \rangle + \langle \psi_i | k\hat{L}_x + g_e \hat{S}_x | \psi_f \rangle \langle \psi_f | k\hat{L}_x + g_e \hat{S}_x | \psi_i \rangle + \langle \psi_i | k\hat{L}_y + g_e \hat{S}_y | \psi_f \rangle \langle \psi_f | k\hat{L}_y + g_e \hat{S}_y | \psi_i \rangle \right)$

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  - Exchange Coupling Parameters in Molecular Clusters
Ground State Zero-Field-Splittings of non-Kramers Ions

Case Studies

1. \([\text{Mn}(\text{OD}_2)_6]^{3+}\)
2. \([\text{V}(\text{OD}_2)_6]^{3+}\)
3. \([\text{Fe}(\text{OD}_2)_6]^{2+}\)
4. \([\text{Fe}(\text{imidazole})_6]^{2+}\)
5. \([\text{Cr}(\text{OD}_2)_6]^{2+}\)

INS is complementary to other spectroscopic techniques, for the characterisation of transition metal complexes. The main advantage of INS is that it affords the direct determination of the low-lying electronic structure in zero magnetic field.
Why is the Characterisation of Integer-Spin Transition Metal Complexes Difficult?

Kramers Ions are Amenable to Study by Electron Paramagnetic Resonance:
In Non-Kramers Transition Metal Ions, the Zero-field Splitting is generally large compared to $\hbar \nu$:

Values of $|D|$ in $S = 2$ systems are in the range 2 to 6 cm$^{-1}$
1. Determination of Ground State Zero-Field-Splittings of non-Kramers Ions using INS

TOF Inelastic Neutron Scattering Spectra of Cs[Mn\textsuperscript{III}(OD\textsubscript{2})\textsubscript{6}](SO\textsubscript{4})\textsubscript{2}⋅6D\textsubscript{2}O


\[ D = -4.524(1) \text{ cm}^{-1} \]
\[ E = 0.276(1) \text{ cm}^{-1} \]

1 meV ~ 8.06554 cm\textsuperscript{-1}
States of the $d^2$ electronic configuration in octahedral and trigonal fields

Energies of states of the $^3T_{1g}$ term as a function of a positive trigonal field. $\lambda$ is set to 100 cm$^{-1}$.
2. High-Field EPR and Inelastic Neutron Scattering Studies of the \([V(OH_2)_6]^{3+}\) cation

High-Field EPR Spectrum of \([V(OH_2)_6]^{3+}\) Doped Caesium Aluminium Sulphate

Data modelled with an \(S=1\) Spin Hamiltonian

Inelastic Neutron Scattering Spectrum of \([V(OH_2)_6]^{3+}\) in Guanidinium Vanadium Sulphate

\[\begin{align*}
D / \text{cm}^{-1} &= 4.8713(1) \\
g_{||} &= 1.95188(3) \\
g_{\perp} &= 1.8662(4) \\
A_{||} / \text{cm}^{-1} &= 0.00988(4) \\
A_{\perp} / \text{cm}^{-1} &= 0.0080(6)
\end{align*}\]

Experimental and Theoretical Electronic Raman Profiles of \( \text{C(NH}_2)_3[\text{V}^{\text{III}}(\text{OH}_2)_6](\text{SO}_4)_2 \)

Mössbauer Study of Cs[Fe^{II}(OH_2)_6](PO_4)

Shows phase transition beautifully, but does not readily yield low temperature electronic structure

Data Collected and Analysed by Eckhard Bill
3. **Inelastic neutron data of CsFe(D$_2$O)$_6$PO$_4$**

10 K INS Spectrum of a powdered sample of CsFe(D$_2$O)$_6$PO$_4$

Simulated spectrum consists of a sum of two spectra, each calculated using an $S=2$ Spin Hamiltonian with the following parameters:

Species 1:
- $D=11.999$ cm$^{-1}$
- $E=2.1117$ cm$^{-1}$

Species 2:
- $D=12.121$ cm$^{-1}$
- $E=1.346$ cm$^{-1}$

Direct determination of energies of low-lying states by INS
HFMF-EPR data of CsFe(D₂O)₆PO₄

HF-EPR spectrum (5K, 284.9973 GHz) of a powdered sample of CsFe(D₂O)₆PO₄ fitted using two $S=2$ Spin Hamiltonians:

Species 1:
- $D=11.999$ cm⁻¹
- $E=2.1117$ cm⁻¹
- $g_x=2.22$, $g_y=2.22$, $g_z=2.32$

Species 2:
- $D=12.121$ cm⁻¹
- $E=1.346$ cm⁻¹
- $g_x=2.32$, $g_y=2.22$, $g_z=2.32$

EPR data simulated with zero-field-splitting parameters from INS. The EPR experiments then yield the $g$ values.
$^5T_{2g}$ ($O_h$) term as a function of the trigonal field, with $\lambda$ set to 100 cm$^{-1}$.

$J=1$ ground state perturbed by trigonal field:
Model Data with $S=1$ spin-Hamiltonian

$^5A_{1g}$ ($D_{3d}$) ground term perturbed by trigonal field:
Model Data with $S=2$ spin-Hamiltonian
Inelastic neutron data for Fe(II)(Imidazole)$_6$(NO$_3$)$_2$

INS spectra (incident wavelength 2.2 Ångstrom) of a powdered sample of deuterated Fe(Im)$_6$(NO$_3$)$_2$ at various temperatures.

Ground state energies ($^5$A) fitted using the ligand field Hamiltonian:

$$\hat{H} = Dq \frac{-28\sqrt{\pi}}{3} (Y^0_4 + \sqrt{10/7}(Y^2_4 - Y^{-3}_4))$$

$$+ \Delta \frac{-14\sqrt{\pi}}{3\sqrt{5}} Y^0_2 + \lambda \hat{L} \cdot \hat{S}$$

operating in the $^5D$ manifold.
Magnetisation data reproduced using the ligand field Hamiltonian:

\[
\hat{H} = D q \frac{-28\sqrt{\pi}}{3} \left( Y_4^0 + \sqrt{\frac{10}{7}} (Y_4^3 - Y_4^{-3}) \right) \\
+ \Delta \frac{-14\sqrt{\pi}}{3\sqrt{5}} Y_2^0 + \lambda \hat{L} \cdot \hat{S} \\
k(\hat{L} + 2\hat{S}) \beta B
\]

operating in the 5D manifold using the parameters obtained from INS. Orbital reduction factor, \( k = 0.95 \).
Calculated energies of the lower three energy levels as a function of field directed parallel and normal to the three-fold axis.

Experimental and calculated resonant field positions for HFMF-EPR.

Inelastic Neutron Scattering Spectra of (ND₄)₂[Crᴵᴵ(OD₂)₆](SO₄)₂

High-Field EPR Spectra and Simulations of (ND₄)₂[Cr^{II}(OD₂)₆](SO₄)₂

Five Parameters Required to Model the EPR Data with an S=2 Spin-Hamiltonian. With INS, the Zero-Field Transitions are Obtained Directly.
Variation of the zero-field-splitting parameters $D$ and $E$ with temperature, obtained by least-squares refinement of the eigenvalues of:

$$\hat{H} = D \left[ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right] + E \left[ \hat{S}_x^2 - \hat{S}_y^2 \right]$$

to the energies of the INS transitions.
Variable Temperature X-band EPR Spectra and Simulations of $(\text{ND}_4)_2[\text{Cr}^{\text{II}}(\text{OD}_2)_6](\text{SO}_4)_2$
5. **Variation of Cr-O bond distances with temperature**

Unable to account for the data using static model
Calculated Potential Energy Surface of \([\text{Cr(OD}_2\text{)}_6]^{2+}\) in \((\text{ND}_4)_2[\text{Cr}^{\text{II}}(\text{OD}_2\text{)}_6](\text{SO}_4)_2\) at 10 K

Degeneracy of Distorted Configurations Lifted by Anisotropic Strain
Hamiltonian for the System

\[ H = H_0 + H_{ph} + H_{JT} + H_{st} \]

\[ H_{ph} = \left[ 0.5 \hbar \omega (P^2_{\theta} + P^2_{\varepsilon} + Q^2_{\theta} + Q^2_{\varepsilon}) + A_3 (3Q_{\theta} Q^2_{\varepsilon} - Q^3_{\varepsilon}) \right] U_{\tau} \]

\[ H_{JT} = A_1 (Q_{\theta} U_{\theta} + Q_{\varepsilon} U_{\varepsilon}) + A_2 \left( (Q^2_{\varepsilon} - Q^2_{\theta}) U_{\theta} + 2Q_{\theta} Q_{\varepsilon} U_{\varepsilon} \right) \]

\[ H_{st} = e_{\theta} U_{\theta} + e_{\varepsilon} U_{\varepsilon} \]

\[ Q_{\theta} \sim 2\Delta z^2 - \Delta x^2 - \Delta y^2 \] and \[ Q_{\varepsilon} \sim \Delta x^2 - \Delta y^2. \]

\[ U_{\tau} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_{\theta} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_{\varepsilon} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]

5.

Eigenvalues and Eigenvectors

\[ \langle \psi | Q_\theta | \psi \rangle \]
\[ \langle \psi | Q_\varepsilon | \psi \rangle \]

Cr-O Bond Lengths

Timescale \( \sim 10^{-14} - 10^{-13} \)

\[ I_{INS} \propto \exp \left( \frac{-E_i}{kT} \right) \left| \langle \psi_f | \mu_\perp | \psi_i \rangle \right|^2 \]

INS Spectrum

Density Matrix Method

EPR Spectrum

Timescale \( \times 10^{-9} \)
Theoretical INS Spectra. Orthorhombic Strain and 10Dq Diminish with Increasing Temperature
Theoretical and Experimental Cr-O bond lengths

![Graph showing bond lengths versus temperature for Cr-O(7), Cr-O(8), and Cr-O(9). The graph includes curves for theoretical and experimental data.]
5.

Theoretical EPR Spectra as a Function of Temperature: Fast Inter-State Relaxation

\[ \nu = 285 \text{ GHz} \]
Spin-Hamiltonian Parameters of the System Depend on the Experimental Technique Used to Determine Them
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Exchange Coupling in Molecular Clusters

Case Studies

1. \([(\text{NH}_3)_5\text{Cr(OH)}\text{Cr(NH}_3)_5]\text{Cl}_5 \cdot 3\text{H}_2\text{O}\)
2. \([\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]\)
3. \(\text{MnMoO}_4\)

INS has played a pivotal role in the elucidation of exchange interactions in molecular clusters. The variation of the energies and intensities of the transitions with Q, provides a wealth of information that cannot be obtained with other techniques.
Acid Rhodo Complex
Bis-μ-hydroxo-pentamine chromium(III)

\[ H_{\text{ex}} = -2J_{ab} S_a \cdot S_b \]

E

\[ \begin{align*}
3 & \quad -12J_{ab} \\
2 & \quad -6J_{ab} \\
1 & \quad -2J_{ab} \\
S = 0 & \quad 0 
\end{align*} \]

W.E. Hatfield et al. 1973
1. \begin{align*}
[(\text{ND}_3)_5\text{Cr(OD)Cr(ND}_3)_5]\text{Cl}_5 \cdot \text{D}_2\text{O} \\
\text{Inelastic Neutron Scattering}
\end{align*}

3-ax, $\lambda = 2.34 \, \text{Å}$

$E$

\begin{align*}
3 & \quad - 12 J_{ab} - \frac{18}{2} J_{ab} \\
2 & \quad - 6 J_{ab} - \frac{27}{2} J_{ab} \\
1 & \quad - 2 J_{ab} - \frac{13}{2} J_{ab}
\end{align*}

$S = 0$

$E_{\text{ex}} = - 2 J_{ab} S_a \cdot S_b + J_{ab} (S_a \cdot S_b)^2$

\begin{align*}
- 2 J_{ab} &= 3.84 \pm 0.12 \, \text{meV} \\
+ J_{ab} &= 0.021 \pm 0.023 \, \text{meV}
\end{align*}

Oscillatory behaviour due to interference effects, which are a direct product of metal-metal distance in the cluster

2. **Paramagnetism, Superparamagnetism, and Ferromagnetism**

- **Paramagnet**
  - $H = 0$
  - $H \rightarrow$
  - $H = 0$

- **Superparamagnet**
  - $H = 0$
  - $H \rightarrow$
  - $H = 0$

- **Ferromagnet**
  - $H = 0$
  - $H \rightarrow$
  - $H = 0$
2. Single Molecule Magnets (SMMs)

- Molecular Clusters with Large Spin Ground States and Ising Type Anisotropy
- Slow Relaxation of the Magnetisation at Low Temperatures
- Intermediate Behaviour Between Classical and Quantum Magnets
The Prototype SMM $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$
The Prototype SMM \([\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]\)

\[\{\text{Mn}_{12}\text{O}_{12}\}\text{ core}\]

8 \(\text{Mn}^{\text{III}}\)  \(S = 2\)
4 \(\text{Mn}^{\text{IV}}\)  \(S = 3/2\)

\[\Rightarrow \ S = 10\]

2. Energy Barrier to Magnetisation Relaxation

Barrier height:
\[ \Delta = S^2 |D| \]
(integer \( S \))

\[ Mn_{12}: \quad S = 10 \]

\[ D \sim -0.5 \text{ cm}^{-1} \]

\[ \Delta = 50 \text{ cm}^{-1} \]
2. Slow Magnetisation Relaxation

At low temperature...
2. **Resonant Quantum Tunnelling**

\( H = 0 \)

\( H \neq 0 \)

\( H = \frac{nD}{g\mu_B} \)

Magnetisation hysteresis loops steps due to quantum tunnelling through the energy barrier

2. Magnetic Relaxation

Thermally Activated Relaxation
Arrhenius Expression: $\tau = \tau_0 \exp (\Delta/kT)$

Quantum Mechanical Tunnelling
2. **Mn$_{12}$ - Acetate**

**Inelastic Neutron Scattering**

**Instrument IN5 (ILL), l = 5.9 Å**

Roland Bircher and Hansueli Güdel, Unpublished Results

2. \[
[Mn_{12}O_{12}(OCH_3COO)_{16}(H_2O)_4] \\
\cdot 2CH_3COOH \cdot 4H_2O
\]

\[
H_{\text{ZFS}} = D \left(S_Z^2 - \frac{1}{3} S(S+1)\right) + B_0^4 \cdot O_0^4 + B_4^4 \cdot O_4^4
\]

\[
O_0^4 = 35S_Z^4 - (30S(S+1) - 25)S_Z^2 + 3S^2(S+1)^2 - 6S(S+1)
\]

\[
O_4^4 = \frac{1}{2} \left(S_+^4 + S_-^4\right)
\]

\[D = -0.457(2) \text{ cm}^{-1}\]

\[B_0^4 = -2.33(4) \times 10^{-5} \text{ cm}^{-1}\]

\[B_4^4 = \pm 3.0(5) \times 10^{-5} \text{ cm}^{-1}\]
INS Study of MnMoO$_4$

- Edge-sharing Mn(II)O$_6$ octahedra $\rightarrow$ tetramers
- Tetramers are connected by Mo(VI)O$_4$ tetrahedra

Exchange pathways:
- within tetramers: $\text{Mn-O-Mn}$
- between tetramers: $\text{Mn-O-Mo-O-Mn}$

- Ferromagnetic alignment of the spins within the clusters.
- Antiferromagnetic ordering of the clusters at 10.7 K.
3.

TOF INS Spectrum of MnMoO$_4$

- instrument: FOCUS at PSI
- incident wavelength: 4.75 Å
- temperature: 1.5 K
  → 4 peaks on neutron energy loss side

3.

Exchange Interactions of MnMoO₄

Isotropic quantum mechanical model for the intracluster interactions

\[ \hat{H} = -2 \sum J_{ij} S_i \cdot S_j \]

J = 0.4 cm\(^{-1}\), J' = -0.15 cm\(^{-1}\)
S = 10 Ground state

Molecular Field model for the intercluster interaction

Molecular Field at Cluster: 
\[ g\mu_B H_{\text{mol}} = -2J_{\text{inter}} \langle S_{\text{cluster}} \rangle z \]

where \( z \) = number of neighbours on opposite sublattice

\[ J_{\text{inter}} = -0.036 \text{ cm}^{-1} \] (average intercluster interaction)
3. Variation in Energies as a Function of Q

Measured spectra along (h0h):
Peak positions and intensities vary as a function of the scattering vector $Q \Rightarrow$ spin wave dispersion.
Dispersion curves along \((h \ 0 \ h)\)

Dispersion revelations contain detailed information on the inter-cluster exchange interactions.

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Ground State Zero-Field-Splitting of non-Kramers Ions
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