Inelastic Neutron Scattering and Applications

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A Short Course on Neutron Scattering in Earth Sciences
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An Outline

The Technique of Inelastic Neutron Scattering (INS)
  Double differential cross section
  Instruments: Triple-axis vs. TOF chopper spectrometers

Applications of INS in Earth Sciences
  Lattice dynamics: phonon dispersion & density of states
  Magnetic scattering: rare-earth energy levels structures

Examples:
  Xenotime (RPO$_4$)
  Spinels
  Nanostructured bone minerals (hydroxyapatite)

Resources: 🌐Web, 📡software, 📖text, 📚review
What is Inelastic Neutron Scattering (INS)? Scattering processes which involve energy and momentum exchange between the neutron & the scatterer.

The double differential cross section:

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{1}{N}\right) \frac{k_1}{k_0} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\langle k_{i\xi}\mid V \mid k_{0\xi_0}\rangle\right|^2 \delta(E + E_{\xi_0} - E_{\xi_1})$$

$$= \frac{k_1}{k_0} S(\bar{Q}, E).$$

The scattering function, $S(\bar{Q}, E)$, depending on coherent or incoherent scattering, is related to respectively the inter-particle or self-particle space-time correlation functions of the scatterer under study.
What Does an INS Instrument Do? 
Performs Accurate Measurements of $S(Q,E)$ in Absolute Units

In order to differentiate the net energy change for a scattering event, an *energy filter*, which selects neutrons with a narrow distribution of energies and/or spins over a collimated solid angle, has to be inserted in the incident or scattered beam, sometimes in both places.

- For fixed incident energy + variable scattered energies: *direct geometry*
- For variable incident energy + fixed scattered energy: *inverse geometry*
How to Define the Energy of a Neutron Beam? *Crystals & Choppers*

\[ \lambda = 2d_M \sin \theta_M \]
\[ \delta \lambda \sim \cos \theta_M \]
\[ \delta \lambda / \lambda \sim \cot \theta_M \]

highest resolution
=> limit the \( \Delta l \Delta t \) spread
=> time focusing techniques

*crystal (monochromator or analyzer)*

dl1 dt

time-of-flight

*chopper (velocity selector)*
How INS Instruments Work? **Triple-Axis Spectrometers**

Bertrand N. Brockhouse’s original TAS (1959)

How Does a Triple-Axis Spectrometers Work?

\[ \mathbf{Q} = \mathbf{k}_0 - \mathbf{k}_1 \]

\[ \mathbf{Q} = \mathbf{G} + \mathbf{q}; \quad q = \text{reduced wavevector} \]

Scattering Triangle
Conservation of momentum & energy
\[ \mathbf{Q} = \mathbf{k}_0 - \mathbf{k}_1 \]

\[ E = \hbar \omega = \frac{\hbar^2}{2m_n} \left( k_0^2 - k_1^2 \right) = E_0 - E_1 \]

Operation Modes:
Fixed \( E_0 \) or \( E_1 \)
May keep \( \mathbf{Q} \) or \( E \) constant
How to Measure Phonons Using a Triple-Axis Spectrometer?

\[
\frac{\partial^2 \sigma_{coh}}{\partial \Omega \partial E_1} \propto \frac{k_1}{k_0} \sum_{\bar{q}, j} |F(\bar{Q}, \bar{q}, j)|^2 \left[ n_j(\bar{q}) + \frac{1}{2} \pm \frac{1}{2} \right] \delta \left[ E_0 - E_1 \mp E(\bar{q}) \right] \delta \left[ k_0 - k_1 - \bar{G} - \bar{q} \right],
\]

\(F(\bar{Q}, \bar{q}, j)\) ≡ Inelastic structure factor for one-phonon coherent scattering

\[
= \sum_{\kappa} \left[ \frac{\hbar^2}{2m_\kappa E_j(\bar{q})} \right]^{1/2} b^\kappa e^{-W^\kappa(\bar{q})} e^{-i\bar{\Omega} \cdot \bar{x}^{(\kappa)}} \left[ \bar{Q} \cdot \bar{e}(\kappa; \bar{q}, j) \right]
\]

Transmission of a single slit - A triangle of $\Gamma_s$ in time

$$\Gamma_s = \sqrt{6} \frac{d}{2r\omega} \sigma_s(\beta),$$

$$\sigma_s^2(\beta) = \begin{cases} 
\frac{1}{10} \left( \frac{5 - 128\beta^4}{3 - 8\beta^2} \right), & \text{for } 0 \leq \beta \leq \frac{1}{4} \\
\frac{8}{5} \left( \sqrt{\beta} - \beta \right) \left( \frac{4 + \sqrt{\beta}}{2 + \sqrt{\beta}} \right), & \text{for } \frac{1}{4} \leq \beta \leq 1 \\
\text{undefined}, & \text{for } \beta \geq 1 
\end{cases}$$

$$\beta = \frac{r^2\omega}{d} \left( \frac{1}{v_{opt}^2} - \frac{1}{v} \right), \quad v_{opt} = 2\rho\omega.$$  

Transmission of a slit package - A trapezoid of an overall with $\Gamma$
**How Does a Chopper Spectrometers Work?**

Incident neutron velocity \( v_i \) defined by chopper phasing relative to \( t_0 \) (source emission time)

\[
\text{time at sample} \equiv t_s = \frac{l_1 + l_2}{v_i},
\]

A scattered neutron reaching a detector at \((l_3, \phi, \theta)\) at arrival time \( t \) has a final speed \( v_f \)

\[
v_f = \frac{l_3}{t - t_s}, \quad \text{then}
\]

\[
E = E_0 - E_i = \frac{m_n}{2} \left( v_i^2 - v_f^2 \right), \quad \text{and} \quad \vec{Q} = \frac{m_n}{\hbar} \left( \vec{v}_i - \vec{v}_f \right)
\]

\[
Q_x = \frac{m_n}{\hbar} \left( v_i - v_f \sin \theta \cos \phi \right),
\]

\[
Q_y = -\frac{m_n}{\hbar} v_f \sin \theta \sin \phi,
\]

\[
Q_z = -\frac{m_n}{\hbar} v_f \cos \phi.
\]

How to Measure Phonons/Magnons Using a Chopper Spectrometer?

\[ \vec{k}_0 \text{ is fixed by the chopper (direct geometry), } \vec{k}_i \text{ varies as shown for a detector at a scattering angle } \phi. \text{ In general, } \vec{Q} \text{ does not follow a symmetry direction in the reciprocal space for a crystal setting.} \]

If a chopper spectrometer is equipped with large detector banks covering a wide range of scattering angles, each detector locus will cut a dispersion surface at certain \( \vec{Q}, E \). The phonon dispersion can be reconstructed by resembling the proper data points from different detectors.

Applications of INS: 1. Lattice Dynamics of Minerals

Phonon Dispersion Relations

Phase velocity  \( v_p = \frac{\omega}{q} \)

Group velocity* \( v_g = \frac{d\omega}{dq} \)

As \( q \to 0 \),
acoustic branch:
\[ v_p = v_g = \sqrt{\frac{2K}{m_1 + m_2}} a = v_{\text{sound}} \]

optic branch:
\( v_g = 0 \)

⇒ non-propagating, localized mode

*The direction of group velocity is not parallel to the phonon wave vector in an isotropic medium.

* Born-von Kármán model with identical force constants from nearest-neighbor interaction

http://fermi.la.asu.edu/ccli/applets/phonon/phonon.html
Phonon Density of States (DOS), \( g(\omega) \)

\[ g(\omega)d\omega = \text{number of vibrational frequencies between } \omega \text{ and } \omega + d\omega \]

For \( r \) atomic constituents in \( N \) unit cells, total degrees of freedom is \( 3rN \),

\[ \int g(\omega)d\omega = \sum_i f_i(\omega)d\omega = 3rN \]

\( f_i(\omega) \) is the partial phonon DOS of atomic constituent \( i \)

Cutoff frequency

Phonon gap
Phonon DOS & Thermodynamic Properties

\[ F = U + \int \left[ \frac{1}{2} \hbar \omega + k_B T \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right] g(\omega) d\omega \]

\[ S = k_B \int \left[ (n + 1) \ln(n + 1) - n \ln(n) \right] g(\omega) d\omega, \quad n = \left( e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^{-1} \]

\[ C_V = k_B \int \left( \frac{\hbar \omega}{k_B T} \right)^2 \left( \frac{e^{\frac{\hbar \omega}{k_B T}}}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right)^2 g(\omega) d\omega \]

\[ P = -\frac{\partial F}{\partial V} = -\frac{\partial U}{\partial V} + \frac{1}{V_0} \sum_i \gamma_i \int (n + \frac{1}{2}) \hbar \omega g(\omega) d\omega = P_s - P_{\text{phonon}}, \quad \text{Mie-Gruneisen equation of state} \]

\[ \gamma_i = \frac{\partial \ln \omega_i}{\partial \ln V} = \text{Gruneisen parameter for the } i^{\text{th}} \text{ phonon mode} \]

\[ \alpha_V(T) = \frac{\partial V}{V \partial T} = \frac{1}{B V_0} \sum_i \gamma_i C_{V_i}(T) \approx \frac{1}{B V_0} - \gamma C_V(T) \]

Melting occurs at \( T_m \) above which \( P_{\text{phonon}} > P_s \)


Phonons & Mechanical Properties: The Continuum Limit

Returning to the example of a diatomic chain:
At long-wavelength ($q \rightarrow 0$) limit, lattice to continuum implies
elastic wave equation for the acoustic mode:
\[ \rho \frac{\partial^2 u}{\partial t^2} = Y \frac{\partial^2 u}{\partial x^2}, \quad \text{where} \]
\[ \rho = \frac{m_1 + m_2}{2a^3}, \quad \text{and} \quad Y = \frac{K}{a} = \text{Young's modulus} \]

For the optic mode, if atoms carry a charge $Q$, the polarization induced by an electric field $E$ is
\[ P = \left( \frac{Q^2}{2K - m\omega^2} + \chi \right) E \]
and the dielectric function is
\[ \varepsilon = 1 + \chi + \frac{Q^2}{2K - m\omega^2} \]
\[ \Rightarrow \text{resonance at} \quad \omega_0 = \sqrt{\frac{2K}{m}} \quad \text{in the infrared region.} \]

Likewise for elastic, electro-elastic, and electro-mechanical properties.

**Important References**

### Texts and Review Articles


### Bibliography & Compilation of Phonon Spectra

Prerequisite for Phonon Experiments Using INS

1. Prepare your samples: single crystals (the larger the better) for phonon dispersion and/or polycrystalline sample (the purer the better) for DOS measurements

2. Go to a reliable, high-flux neutron source, see for example
   [link: http://www.neutron.anl.gov/]

3. Gain access to a world-class neutron spectrometer: Triple-axis and/or chopper instrument

4. Check the neutron coherent scattering cross sections of the constituent elements, Beware of incoherent scattering and absorption/resonance. See, for example,
   [link: http://www.ncnr.nist.gov/resources/n-lengths/]

5. Better (necessary for single-crystal experiments) do a group theoretical analysis of the neutron spectrum for the crystal structure under study and develop an initial lattice dynamics model to calculate the inelastic structure factor. Software available, for example, [L. Warren and T. G. Worlton, "Improved version of group-theoretical analysis of lattice dynamics", Comp.Phys. Commu. 8 71-84 (1974) and J. L. Warren and T. G. Worlton, "Group-theoretical analysis of lattice vibrations", ibid, 3 88-117 (1972).
   [Collaborative Computational Project 5: http://www.ccp5.ac.uk/]

Incorporate as much as possible data from Raman, IR, Brillouin-scattering, ultrasonic measurements, etc.
**Monazite and Xenotime: Rare-Earth Orthophosphates $RPO_4^-$**

Key Collaborators:

J. C. Nipko, *Colorado State Univ.*
L. A. Boatner, *Oak Ridge National Lab.*
M. Loewenhaupt, *Tech. Univ. Dresden, Germany*
M. Braden, W. Reichardt, *Forschungszentrum Karlsruhe, Germany*

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**Chemistry**

High melting points (>2000°C)
Not attacked by water, organic solvents and common acids
Resistant to radiation damage
- High-temperature components, Medium for nuclear waste storage

**Optics**

High density, Mohr hardness ~5.5
Rare-earth activated luminescence
- Phosphors, Lasers, Scintillators

**Magnetism**

Antiferromagnetic phase transitions
Cooperative Jahn-Teller effects
Magnetoelectric effects
Rare-earth spin-lattice coupling
- Magnetic refrigerants, Sensors

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Zircon-type Structure of Nonmagnetic LuPO$_4$ Xenotime

Body-centered tetragonal structure $I4_1/amd$  \( Z=2 \)

36 phonon branches along each direction
**LuPO$_4$ Lattice Dynamics: Group Theoretical Analysis**

- LuPO$_4$ Crystal (D$_{4h}$)
- PO$_4^{3-}$ Site Symmetry (D$_{2d}$)
- Free PO$_4^{3-}$ Molecule (T$_d$)

**Energy (meV)**

- B$_1g$
- A$_2u$
- E$_g$
- A$_{1g}$
- E$_u$
- B$_{2g}$

**Description of Mode**
- antisymmetric P-O bond stretch
- symmetric P-O bond stretch
- antisymmetric O-P-O bond bend
- symmetric O-P-O bond bend
- translation-like or rotation-like
Single-Crystal, Triple-Axis Measurements of Phonon Dispersion Curves

LuPO$_4$ Room Temperature

- Neutron
- IR & Raman
- Shell-Model Calc.

Energy (meV)

- A$_1$
- A$_2$
- B$_1$
- B$_2$

Reduced Wavevector

Acoustic
- A$_{2u}$
- 17.8 meV
- B$_{1g}$
- 33.8 meV
- A$_{2u}$

- 39.6 meV
- B$_{1g}$
- 78.4 meV
- A$_{2u}$
- 85.1 meV
- B$_{1g}$

- 131.6 meV
- A$_{2u}$
- 131.7 meV
- B$_{1g}$

Example 1
Polycrystalline, Chopper Spectrometer TOF Measurements of Phonon DOS
**Magnetic INS: The Ground-State Wavefunction of a Magnetic Ion**

Magnetic Scattering

\[ S(Q, E) = \frac{(\gamma r_0)^2}{4} g_j^2 \left( 1 - e^{-\frac{E}{kT}} \right)^{-1} \chi''(Q, E, T) \]

\[ \propto f^2(Q) \sum_{i,j} e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \int_{-\infty}^{+\infty} dt e^{-\frac{iE_t}{\hbar}} \langle J_i^\alpha(0) J_j^\alpha(t) \rangle \]

Dipole Approximation of Crystal-Field Transitions of Non-interacting Rare-Earth Ions in a Crystalline Host

\[ S(Q, E) = f^2(Q) e^{-2W(Q)} \sum_{n,m} \frac{\exp(-E_n/kT)}{Z} \langle n|J_\perp|m \rangle^2 \delta(E_n - E_m - E) \]

**Excitation & de-excitation  Observed magnetic-scattering**

![Diagram](image)
Crystal-Field Excitation Spectra of \( \text{TbPO}_4 \)

Crystal Structure:
tetragonal zircon (I4\(_1\)/amd)
2 f.u./p.c.

R-ion site point-group symmetry:
\( D_{2d} \)

\( E_0 = 4 \text{ meV} \)
\( T = 4 \text{ K} \)

\( E_0 = 20 \text{ meV} \)

\( E_0 = 60 \text{ meV} \)

\( T_N = 2.2 \text{ K} \)

\( T_D = 2.3 \text{ K} \)

Tb sub-lattice
Crystal-Field Level Structure of TbPO$_4$: The Magnetic Properties

The magnetic INS measurement enables a characterization of the rare-earth ground- and excited states wavefunctions in terms of a handful of crystal-field parameters. The model can then be applied for calculations of the magnetic properties of the material, e.g., susceptibility and magnetic specific heat.

![Graph of TbPO$_4$ magnetic properties](image-url)

- $T_N$'s = 2.28 and 2.15 K
- Specific heat (J/mole K)
- $\chi$ (emu/mole)
Anomalous 4f-Electron Phonon Interaction in YbPO$_4$

The coupling of the Yb$^{3+}$ crystal-field states with the $E_g$ phonon is very strong, with strengths much larger than those of any previously reported systems such as CeAl$_2$, LnF$_3$, LiTbF$_4$ and Ln(OH)$_3$. The line widths change drastically with temperature.

$E_g$ crystal field state

Yb$^{3+}$ crystal field state

Example 1

The data suggest a large fluctuating component associated with the monopole term whereby coupling of the crystal field states, particularly the upper $\Gamma_6$ and $\Gamma_7$ doublets, with phonons of comparable strengths and energies. The coupling to the monopole term does not require the compatible symmetry of specific phonon modes (such as in the case for CeAl$_2$), and was observed throughout the Brillouin zone as long as the phonon energies and CF transition strengths are comparable.
**Spinels: From Gahnite (ZnAl₂O₄) to Nanostructured Li(H)Mn₂O₄ Adsorbent**

Approach:

Synthesis of novel n-MnO₂ adsorbents, electron microscopy (SEM, TEM), x-ray spectroscopy (EDX & XPS), chemical analysis (ICP) - H. Koyanaka, CRMD/CNRS, Orleans University, France

First-principle molecular-dynamics simulations - C. Fang, University of Uppsala, Sweden

INS - C.-K. Loong, Argonne, USA

The classic spinel structure:

(e.g., MgAl₂O₄) Cubic Fd3m, Z=2; 42 phonon branches


Where are the Hydrogen Atoms in HMn$_2$O$_4$?

A proton prefers the tetrahedral 8a cavity site but moves to one of the neighboring oxygen, breaking the local symmetry.

Fang & de Wijs (05)
Bone Minerals: Nanotechnology in Our Body

Apatite?
Evidence for the Lack of OH Ions in Bone Crystals as Compared to Hydroxyapatite (HAp) Ca_{10}(PO_4)_6(OH)_2

Approach:

Preparation of deproteinized bone apatite Crystals - M. J. Glimcher et al., *Harvard Medical School, USA*

Synthesis of hydroxyapatite powders, Fourier-transform infrared spectroscopy, chemical analysis - C. Rey, *CIAIMAT-ENSCT, Toulouse, France*

Proton solid-state NMR - Y. Wu, *Harvard Medical School, USA*

Neutron inelastic scattering & SANS - C.-K. Loong, *Argonne, USA*

Concluding Remarks

- INS is capable of accounting for the detailed atomic/molecular motions and electronic/magnetic excitations -- individual or collective -- within a many-body system (e.g., minerals).

- Since microscopic motions or excitations may occur in vastly different time and length scales, typically ps to ms and sub-nm to μm, the technique of INS necessitates an as wide as possible coverage in the energy ($E$) and wavevector ($Q$) space with good resolutions. *In situ* measurements under extreme sample environments (e.g., high T, high P) are highly desirable.

- INS is often flux-limited because of the weak intensity but this situation will be improved in the advent of new-generation high-flux neutron sources such as SNS.

- Interpretation of INS data can be a challenge facing experimentalists. Researchers nowadays have to apply methods of theoretical modeling and simulations that require high degree of sophistication and substantial amount of computing resources.

- Don’t worry, instrument scientists at neutron facilities will be glad to help you.