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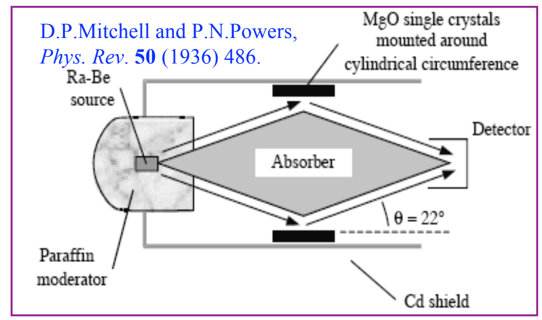
Inelastic Neutron Scattering and Applications

Chun Loong, IPNS



A Short Course on Neutron Scattering in Earth Sciences

Dec 7-8, 2006

Hilton Garden Inn, Emeryville, CA

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REVIEWS in MINERALOGY & GEOCHEMISTRY

GEOCHEMICAL SOCIETY 1955

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

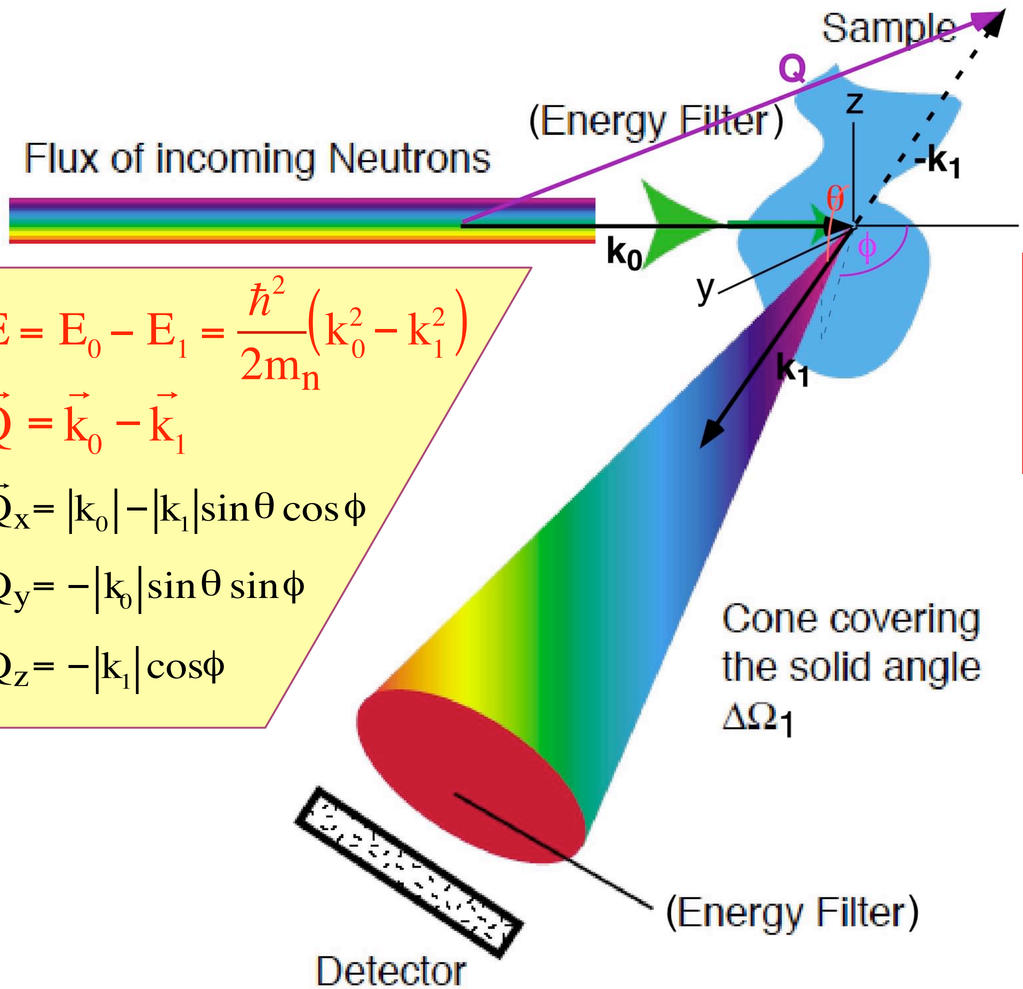
- Lattice dynamics: phonon dispersion & density of states
- Magnetic scattering: rare-earth energy levels structures

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



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

$$\vec{Q} = \vec{k}_0 - \vec{k}_1$$

$$\vec{Q}_x = |k_0| - |k_1|\sin\theta\cos\phi$$

$$Q_y = -|k_0|\sin\theta\sin\phi$$

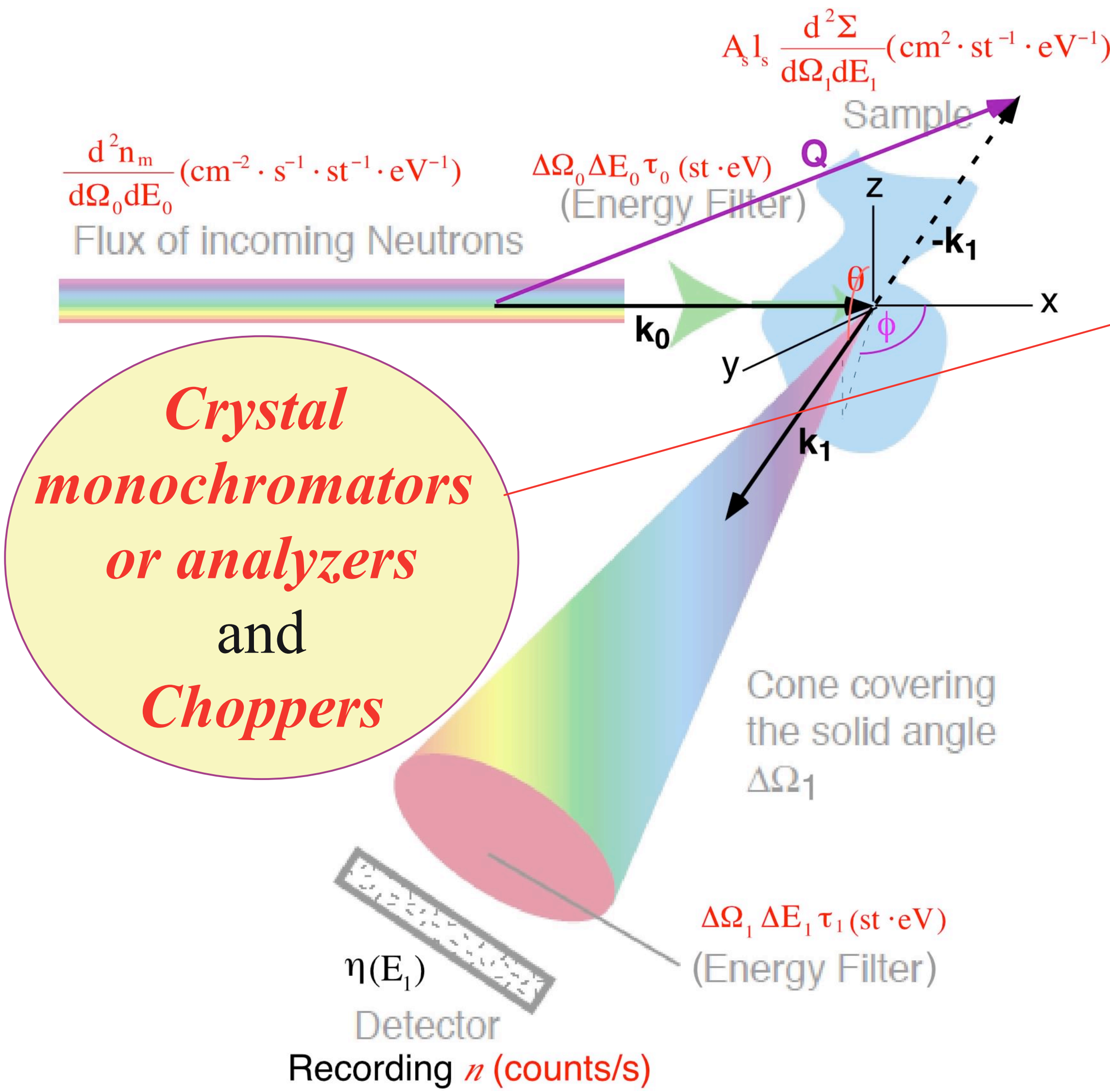
$$Q_z = -|k_1|\cos\phi$$

The goal is to measure precisely the ***double differential cross section*:**

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{1}{N}\right)\frac{k_1}{k_0}\left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\left\langle \vec{k}_1\xi_1 \middle| V \middle| \vec{k}_0\xi_0 \right\rangle\right|^2 \delta\left(E + E_{\xi_0} - E_{\xi_1}\right)$$
$$= \frac{k_1}{k_0} S\left(\vec{Q}, E\right),$$

The ***scattering function***, $S\left(\vec{Q},E\right)$, 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.

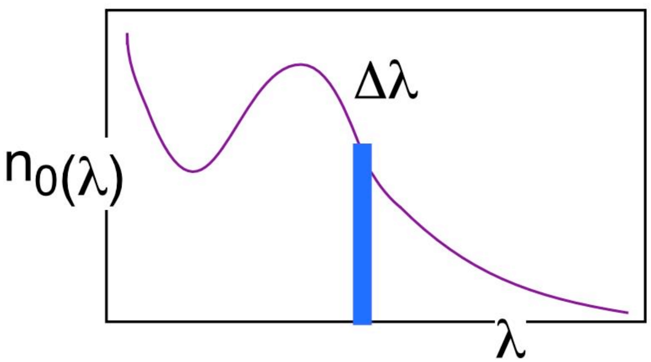
What Does an INS Instrument Do?
Performs Accurate Measurements of S(Q,E) in Absolute Units



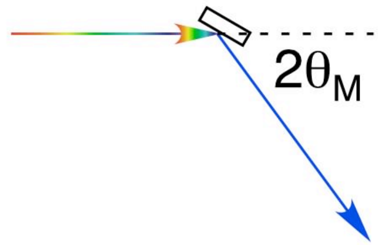
In order to differentiate the net energy change for a scattering event, an ***energy filter***, which selects neutrons with a narrow distribution of energies and/or spins over a collimated solid angle, has to be inserted in the incident or scattered beam, sometimes in both places.

- 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



crystal (monochromator
or analyzer)



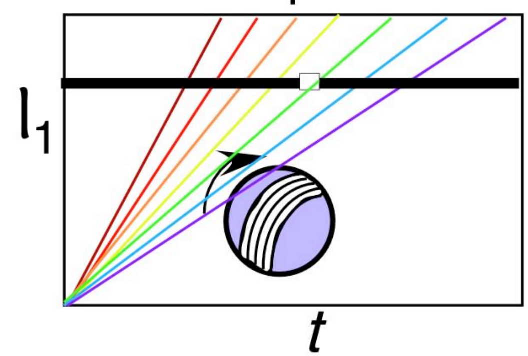
$\lambda = 2d_M \sin\theta_M$

$\delta\lambda \sim \cos\theta_M$

$\delta\lambda/\lambda \sim \cot\theta_M$

highest resolution
=> Backscattering

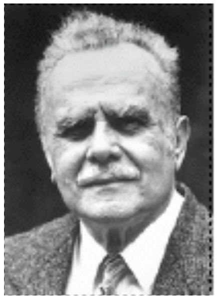
time-of-flight
Δl_1 Δt



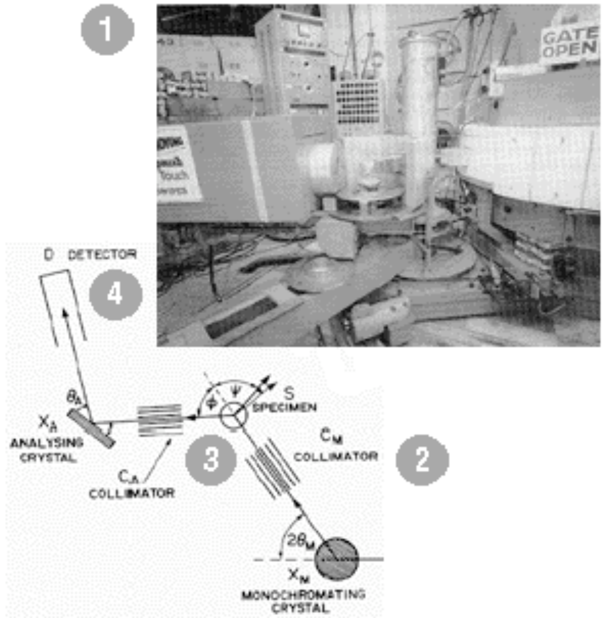
chopper
(velocity selector)

highest resolution
=> limit the Δl Δt spread
=> time focusing techniques

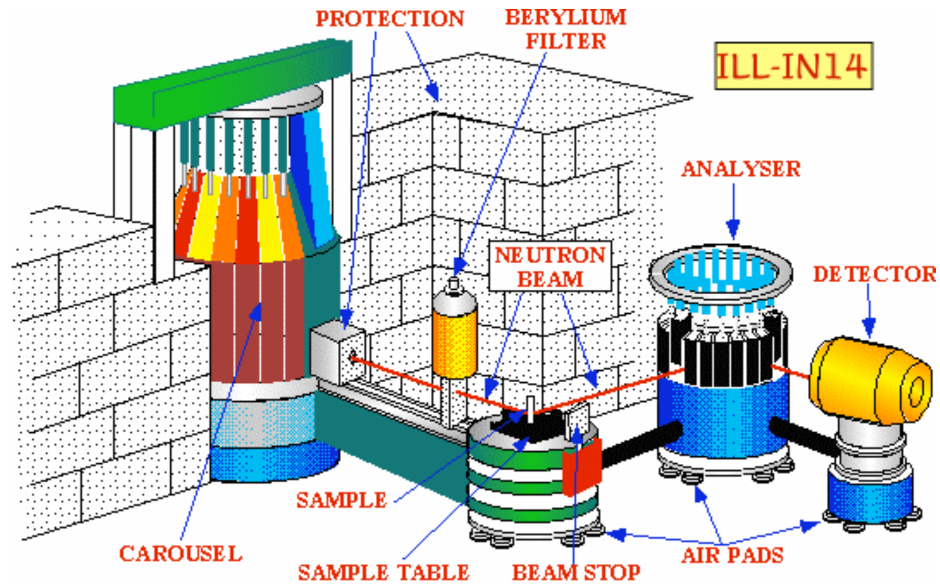
How INS Instruments Work? Triple-Axis Spectrometers

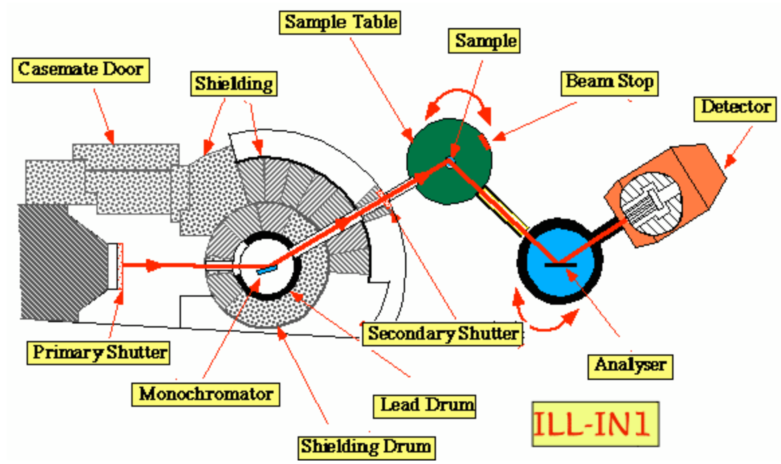


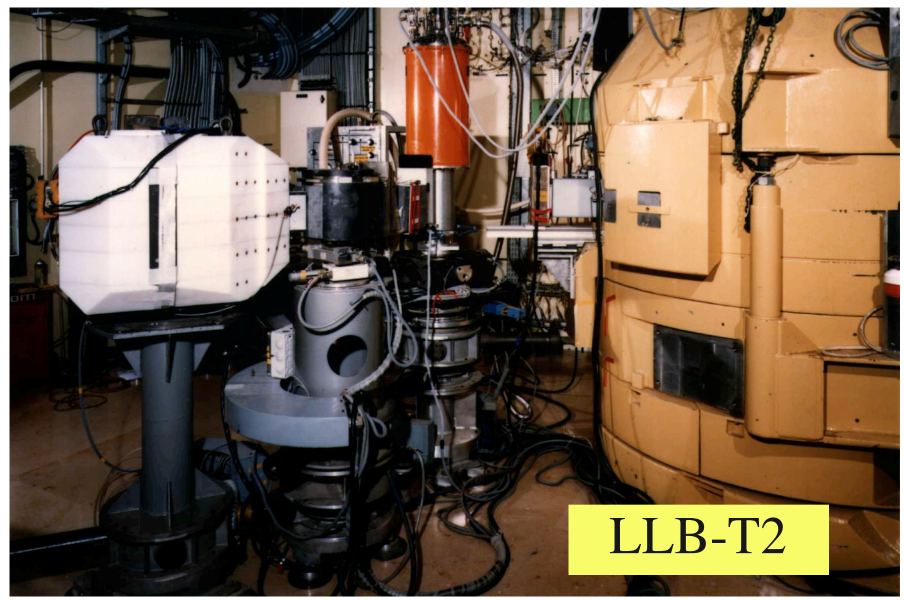
Bertrand N. Brockhouse's original TAS (1959)



http://www.nobel.se/physics/laureates/1994/index.html
http://www.science.ca/scientists/scientistprofile.php?pID=4 (3 of 4

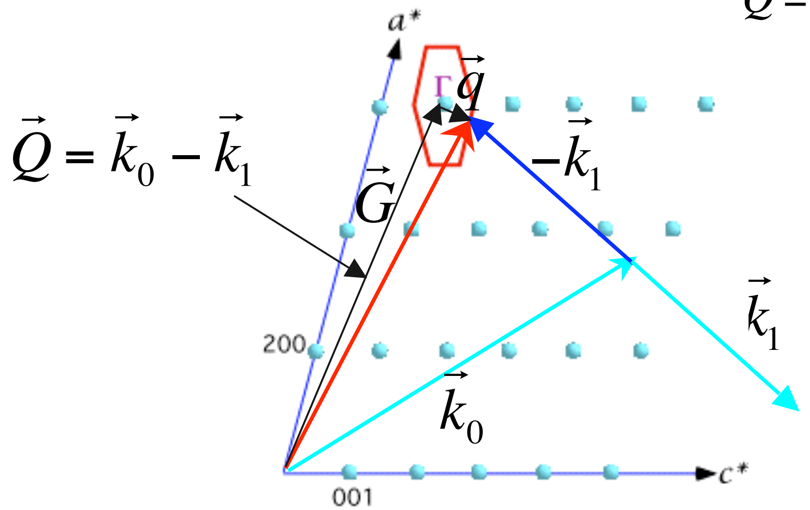






How Does a Triple-Axis Spectrometers Work?

$\vec{Q} = \vec{G} + \vec{q}; \quad q \equiv reduced \;\; wavevector$



Scattering Triangle

Conservation of momentum & energy

$$\vec{Q} = \vec{k}_0 - \vec{k}_1$$

$$E = \hbar\omega = \frac{\hbar^2}{2m_n}\left(\vec{k}_0^{\,2} - \vec{k}_1^{\,2}\right) = E_0 - E_1$$

Operation Modes:

Fixed E_0 or E_1

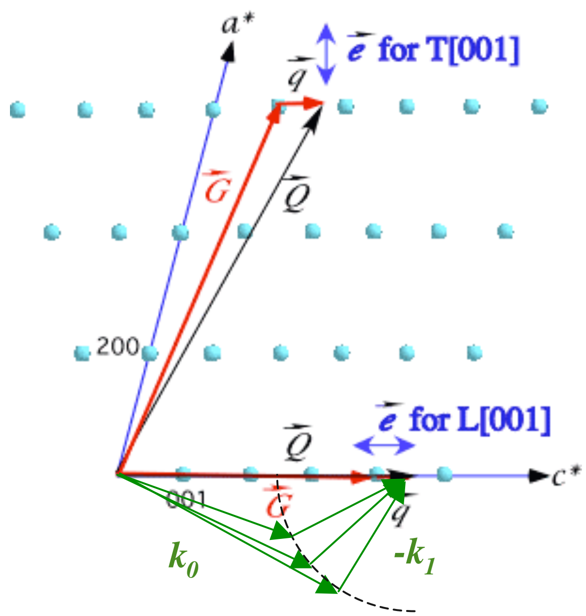
May keep $\boldsymbol{Q}$ or E constant

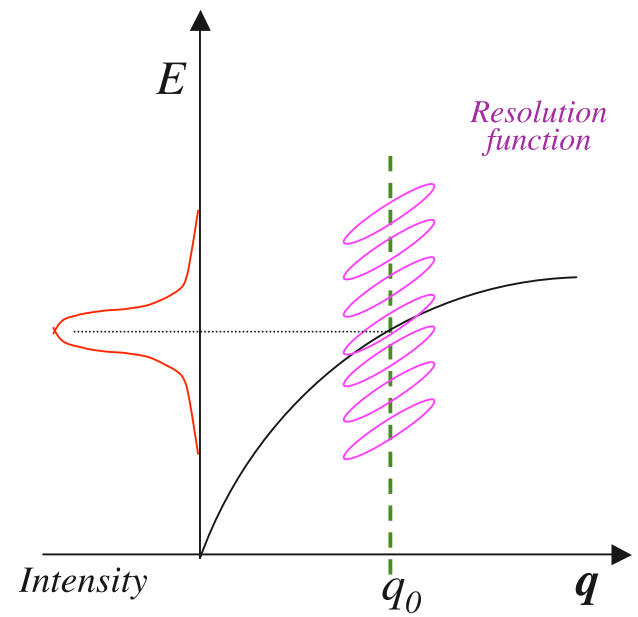
How to Measure Phonons Using a Triple-Axis Spectrometer?

$$\frac{\partial^2 \sigma^{coh}}{\partial\Omega\,\partial E_1} \propto \frac{k_1}{k_0} \sum_{\vec{q},j} \left| F(\vec{Q},\vec{q},j) \right|^2 \left[n_j(\vec{q}) + \tfrac{1}{2} \pm \tfrac{1}{2} \right] \delta\left[E_0 - E_1 \mp E(\vec{q}) \right] \delta\left[\vec{k}_0 - \vec{k}_1 - \vec{G} - \vec{q} \right],$$

$$F(\vec{Q},\vec{q},j) \equiv Inelastic\ \ structure\ \ factor\ \ for\ \ one-phonon\ \ coherent\ \ scattering$$

$$= \sum_{\kappa} \left[\frac{\hbar^2}{2m_\kappa E_j(\vec{q})} \right]^{1/2} b^{\kappa}_{coh} e^{-W_\kappa(\vec{Q})} e^{-i\vec{Q}\bullet\vec{x}(\kappa)} \left[\vec{Q} \bullet \vec{e}\left(\kappa;\vec{q},j\right) \right]$$



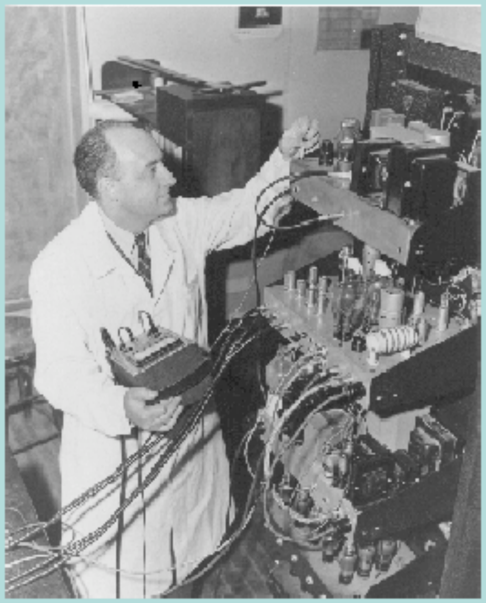


G. Shirane, S. M. Shapiro, & J. M. Tranquada, Neutron Scattering with a Triple-Axis Spectrometer: Basic Techniques (Cambridge, 2002).

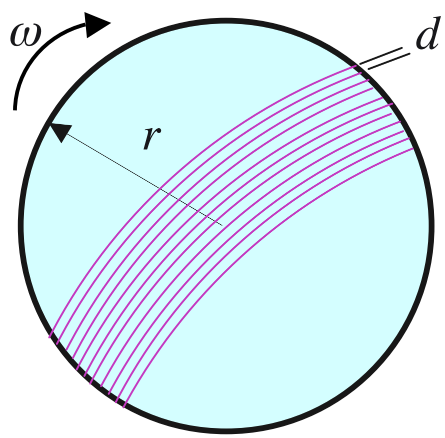
How INS Instruments Work? Chopper Spectrometers

E. Fermi, W. J. Strum, & R. G. Sachs, “A thermal neutron velocity selector and its application to the measurement of the cross section of boron”, *Phys. Rev.* **72,** 193 (1947).

http://www.anl.gov/OPA/logos20-1/fermi01.htm



Enrico Fermi works with an electronic control for a neutron chopper during his Argonne days.



Transmission of a single slit - A triangle of Γ_s in time

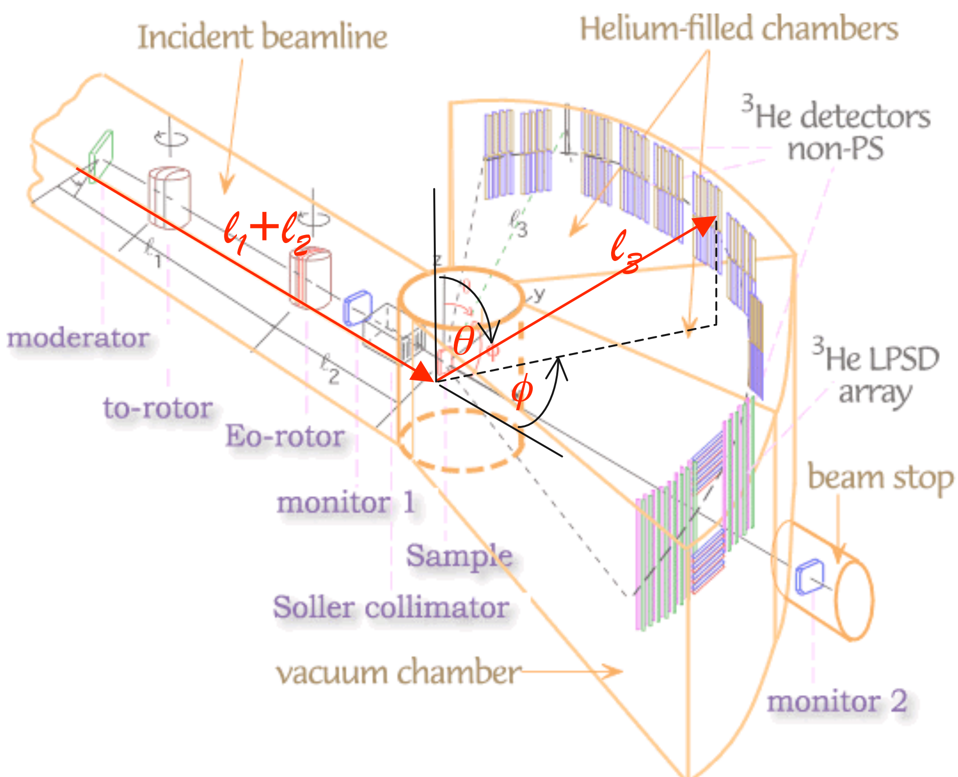
$$\Gamma_s = \sqrt{6}\,\frac{d}{2r\omega}\,\sigma_x(\beta),$$

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

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

Transmission of a slit package - A trapezoid of an overall with Γ

How Does a Chopper Spectrometers Work?



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

$$time \;\; at \;\; sample \equiv t_s = \frac{l_1 + l_2}{v_i},$$

A scattered neutron reaching a detector at (l_3, ϕ, θ) at arrival time t has a final speed v_f

$$v_f = \frac{l_3}{t - t_s}, \quad then$$

$$E = E_0 - E_1 = \frac{m_n}{2}\left(v_i^2 - v_f^2\right), \; and \;\; \vec{Q} = \frac{m_n}{\hbar}\left(\vec{v}_i - \vec{v}_f\right)$$

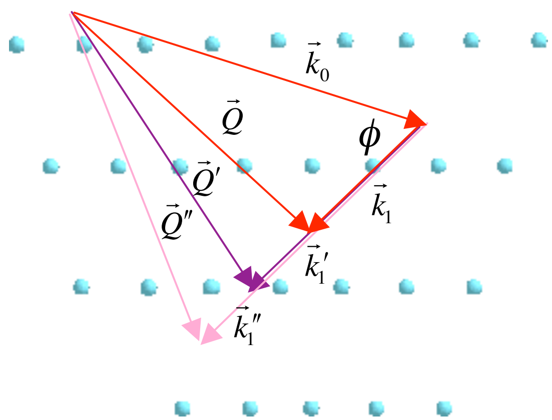
$$Q_x = \frac{m_n}{\hbar}\left(v_i - v_f \sin\theta\cos\phi\right),$$

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

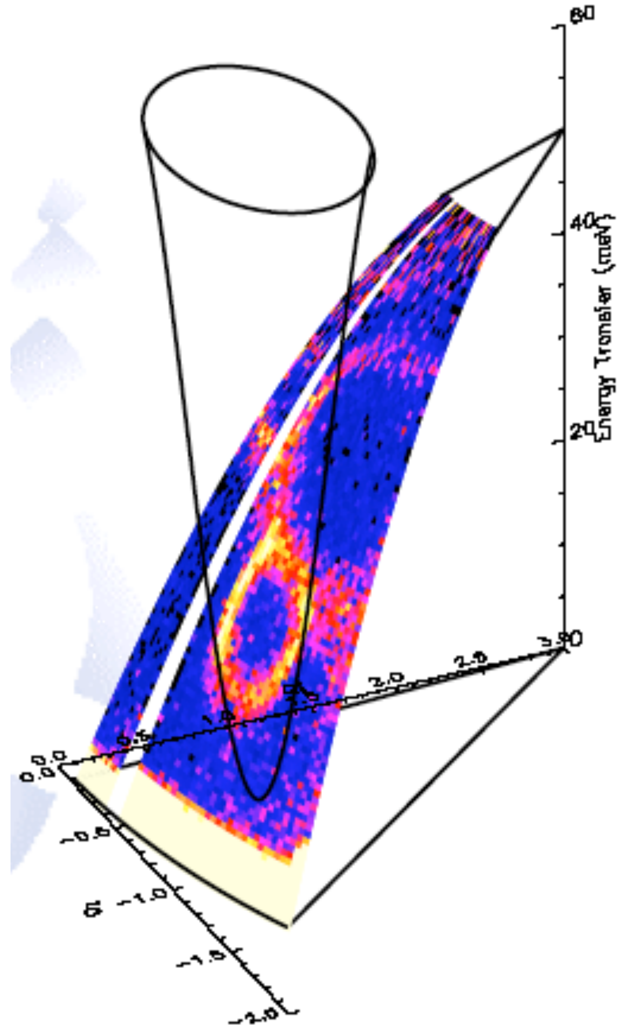
$$Q_z = -\frac{m_n}{\hbar} v_f \cos\phi.$$

C.-K. Loong, S. Ikeda, and J. M. Carpenter, "The resolution function of a pulsed-source neutron chopper spectrometer", *Nucl. Instrum. Methods* **A 260** 381-402 (1987).

How to Measure Phonons/Magnons Using a Chopper Spectrometer?



$\vec{k}_0$ is fixed by the chopper (direct geometry), $\vec{k}_1$ varies as shown for a detector at a scattering angle ϕ. In general, $\vec{Q}$ does not follow a symmetry direction in the reciprocal space for a crystal setting.

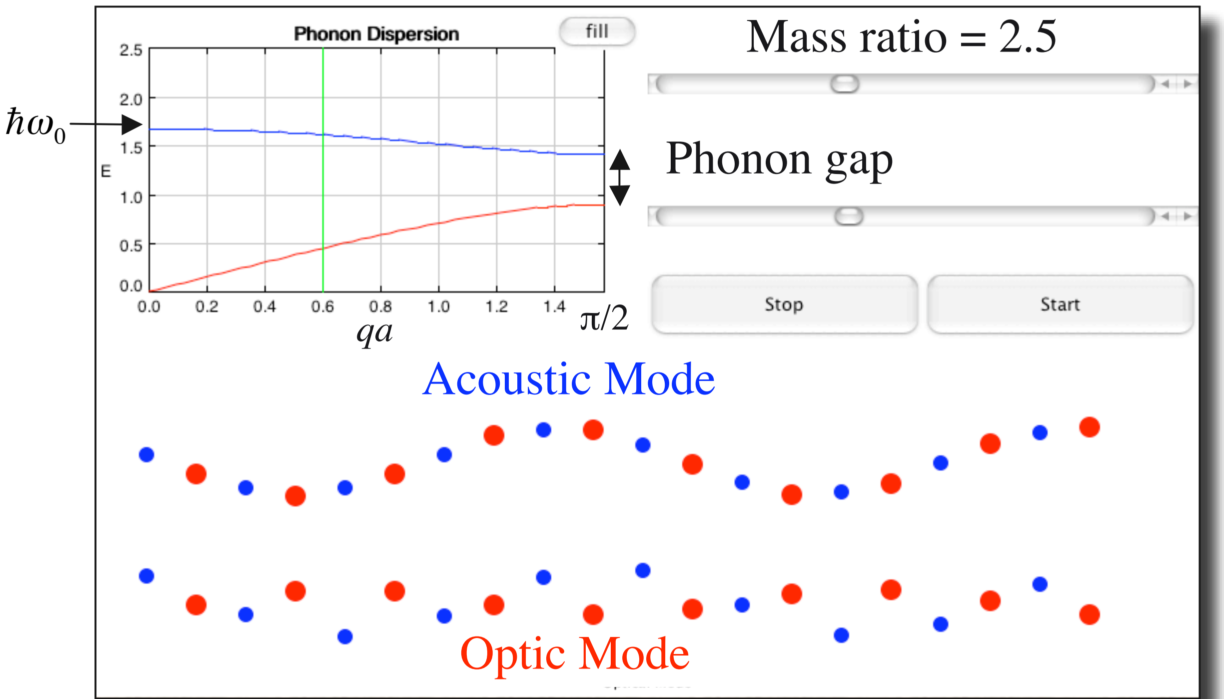


If a chopper spectrometer is equipped with large detector banks covering a wide range of scattering angles, each detector locus will cut a dispersion surface at certain $\vec{Q}, E$, The phonon dispersion can be reconstructed by resembling the proper data points from different detectors.

M. Arai, "Dynamic structure factor of non-crystalline and crystalline systems as revealed by MARI, a neutron chopper spectrometer", *Adv. Colloid Interface Sci.*, **71-72**, 209 (1997).

Applications of INS: 1. Lattice Dynamics of Minerals
Phonon Dispersion Relations

http://fermi.la.asu.edu/ccli/applets/phonon/phonon.html



Phase velocity $v_p = \omega / q$

Group velocity* $v_g = d\omega / dq$

£As $q \to 0$,
acoustic branch:

$$v_p = v_g = \sqrt{\frac{2K}{m_1 + m_2}}\, a = v_{sound}$$

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 Kámán model with identical force constants from nearest-neighbor interaction

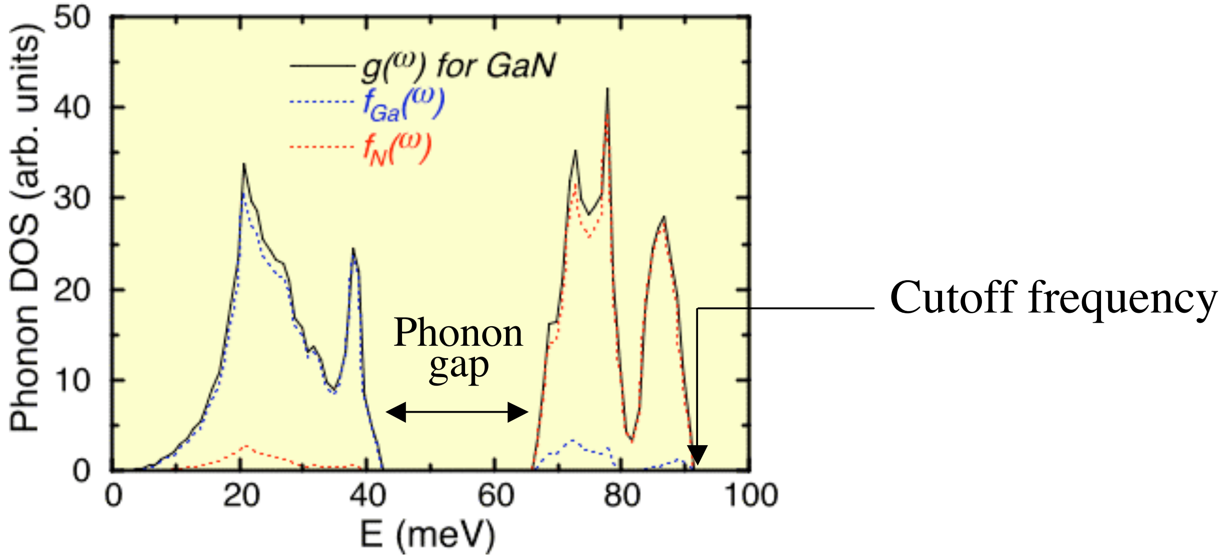
Phonon Density of States (DOS), $g(\omega)$

$$g(\omega)d\omega = number\ \ of\ \ vibrational\ \ frequencies\ \ between\ \ \omega\ \ and\ \ \omega + d\omega$$

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

$$\int g(\omega)d\omega = \int \sum_i^r f_i(\omega)d\omega = 3rN$$

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



Phonon DOS & Thermodynamic Properties

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

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

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

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial U}{\partial V} + \frac{1}{V_0}\sum \gamma_i \int \left(n + \tfrac{1}{2}\right)\hbar\omega g(\omega)d\omega = P_s - P_{phonon},$$ ***Mie-Gruneisen equation of state***

$$\gamma_i = \frac{\partial \ln\omega_i}{\partial \ln V} =$$ ***Gruneisen parameter for the i^th phonon mode***

$$\alpha_V(T) = \frac{\partial V}{V\partial T} = \frac{1}{BV_0}\sum_i \gamma_i C_{Vi}(T) \cong \frac{1}{BV_0}\bar{\gamma} C_V(T)$$

Melting occurs at T_m above which $P_{phonon} > P_s$

O. L. Anderson, Equations of State of Solids for Geophysics and Ceramic Science (Oxford University Press, New York, 1995).

A. Navrotsky, Physics and Chemistry of Earth Materials (Cambridge University Press, Cambridge, 1994).

Phonons & Mechanical Properties: The Continuum Limit

Returning to the example of a diatomic chain:

At long-wavelength *($q \to 0$)* limit, lattice to continuum implies elastic wave equation for the <u>acoustic mode</u>:

$$\rho \frac{\partial^2 u}{\partial t^2} = Y \frac{\partial^2 u}{\partial x^2}, \quad \textit{where}$$

$$\rho = \frac{m_1 + m_2}{2a^3}, \quad \textit{and} \quad Y = \frac{K}{a} = \textit{Young's modulus}$$

For the <u>optic mode</u>, 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

$$\varepsilon = 1 + \chi + \frac{Q^2}{2K - m\omega^2}$$

$\Rightarrow$ resonance at $\omega_0 = \sqrt{2K/m}$ in the infrared region.

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

A. Askar, <u>Lattice Dynamical Foundations of Continuum Theories</u> (World Scientific, Singapore, 1986).

Important References

Texts and Review Articles

- Spectroscopic Methods in Mineralogy and Geology, Ed. F. C. Hawthorne, Reviews in Mineralogy, Vol. 18 (Mineral. Soc. America 1988).
- P. Brüesch, Phonons: Theory and Experiments I-III (Springer-Verlag, Berlin, 1982, 1986, and 1987).
- Dynamical Properties of Solids, Ed., G. K. Horton and A. A. Maradudin, V. 1-7 (North-Holland 1974-1980)
- S. Chaplot et al.,"Inelastic neutron scattering and lattice dynamics of minerals", *Eur. J. Mineral.* **14**, 291 (2002), and R. Mittal et al., "Modeling of anomalous thermodynamic properties using lattice dynamics and inelastic neutron scattering", *Prog. Mat. Sci.* **51**, 211 (2006).
- E. Burkel, "Phonon spectroscopy by inelastic x-ray scattering", *Rep. Prog. Phys.* **63**, 171-232 (2000).

Bibliography & Compilation of Phonon Spectra

- Scattering of Thermal Neutrons, A Bibliography (1932-1974), Complied by A. Larose and J. Vanderwal (Plenum, New York 1974).
- H. Bilz and W. Kress, Phonon Dispersion Relations in Insulators (Springer-Verlag, Berlin, 1979).

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
   - 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,
   - 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).
   - Unisoft: http://134.76.68.210/Eckold/eckold.html,
   - Collaborative Computational Project 5: http://www.ccp5.ac.uk/

   Incorporate as much as possible data from Raman, IR, Brillouin-scattering, ultrasonic measurements, etc.

Example 1

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*

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

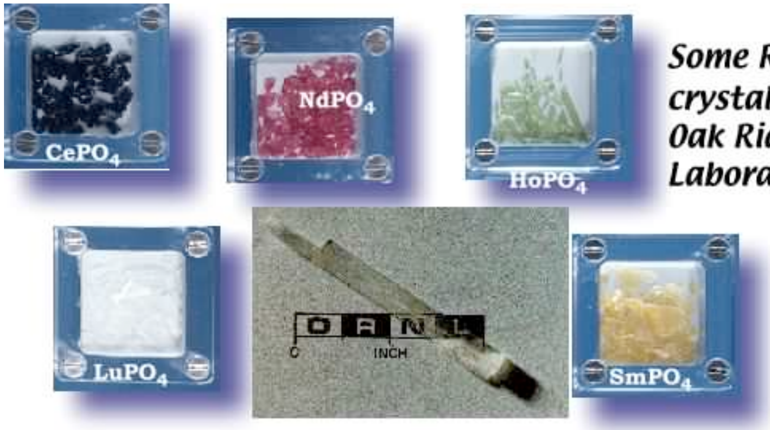
High density, Mohr hardness ~5.5
Rare-earth activated luminescence

- Phosphors, Lasers, Scintillators

Magnetism

Antiferromagnetic phase transitions
Cooperative Jahn-Teller effects
Magnetoelastic effects
Rare-earth spin-lattice coupling

- Magnetic refrigerants, Sensors

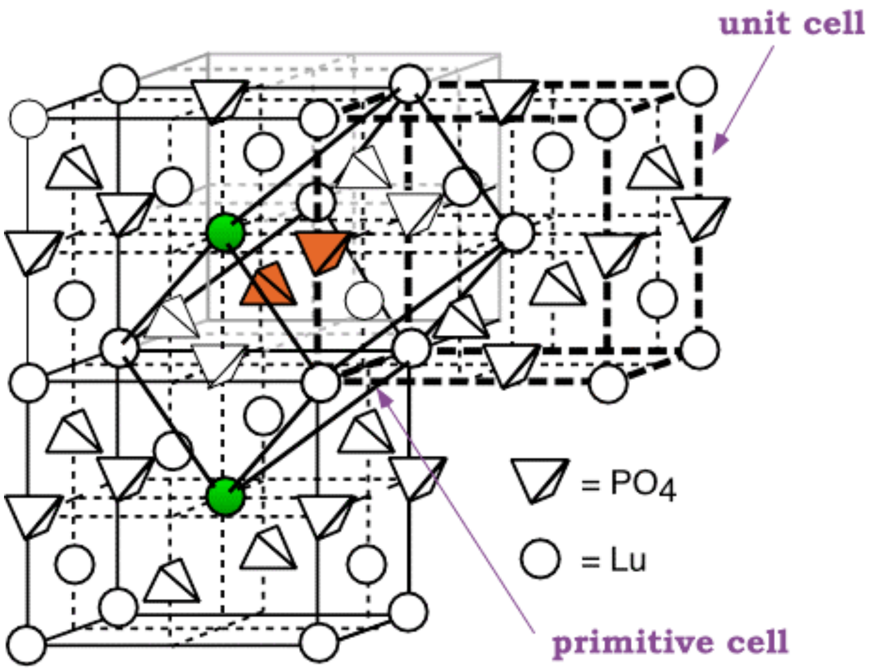


Some RPO_4 single crystals synthesized at Oak Ridge National Laboratory

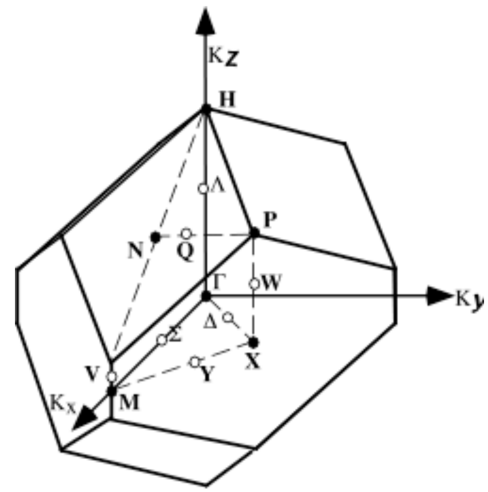
J. C. Nipko et al., *Phys. Rev.* **B 56** (18), 11584-11592 (1997), & C.-K. Loong et al, *Phys. Rev.* **B 60** (18), R12549-R12552 (1999).

Zircon-type Structure of Nonmagnetic $LuPO_4$ Xenotime

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

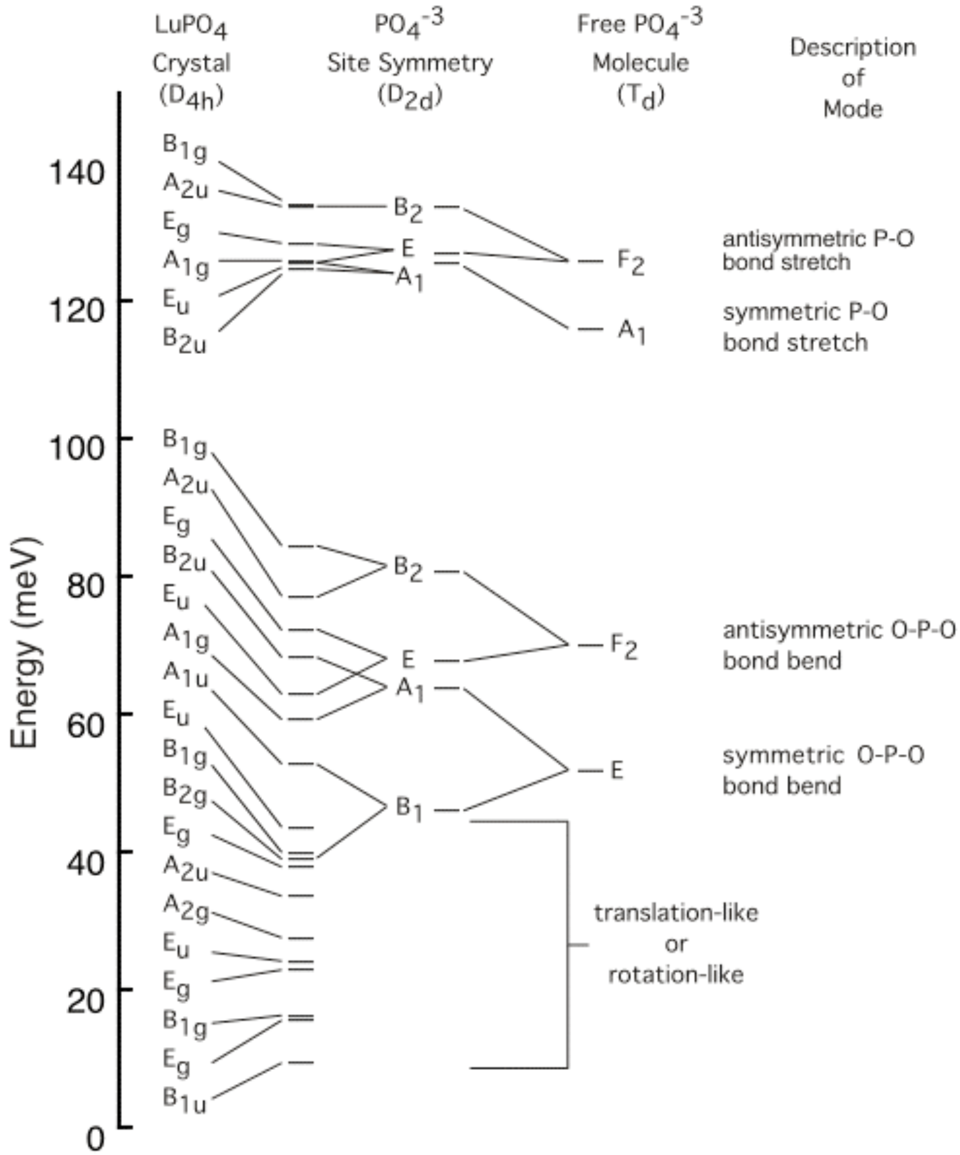


The Brillouin Zone



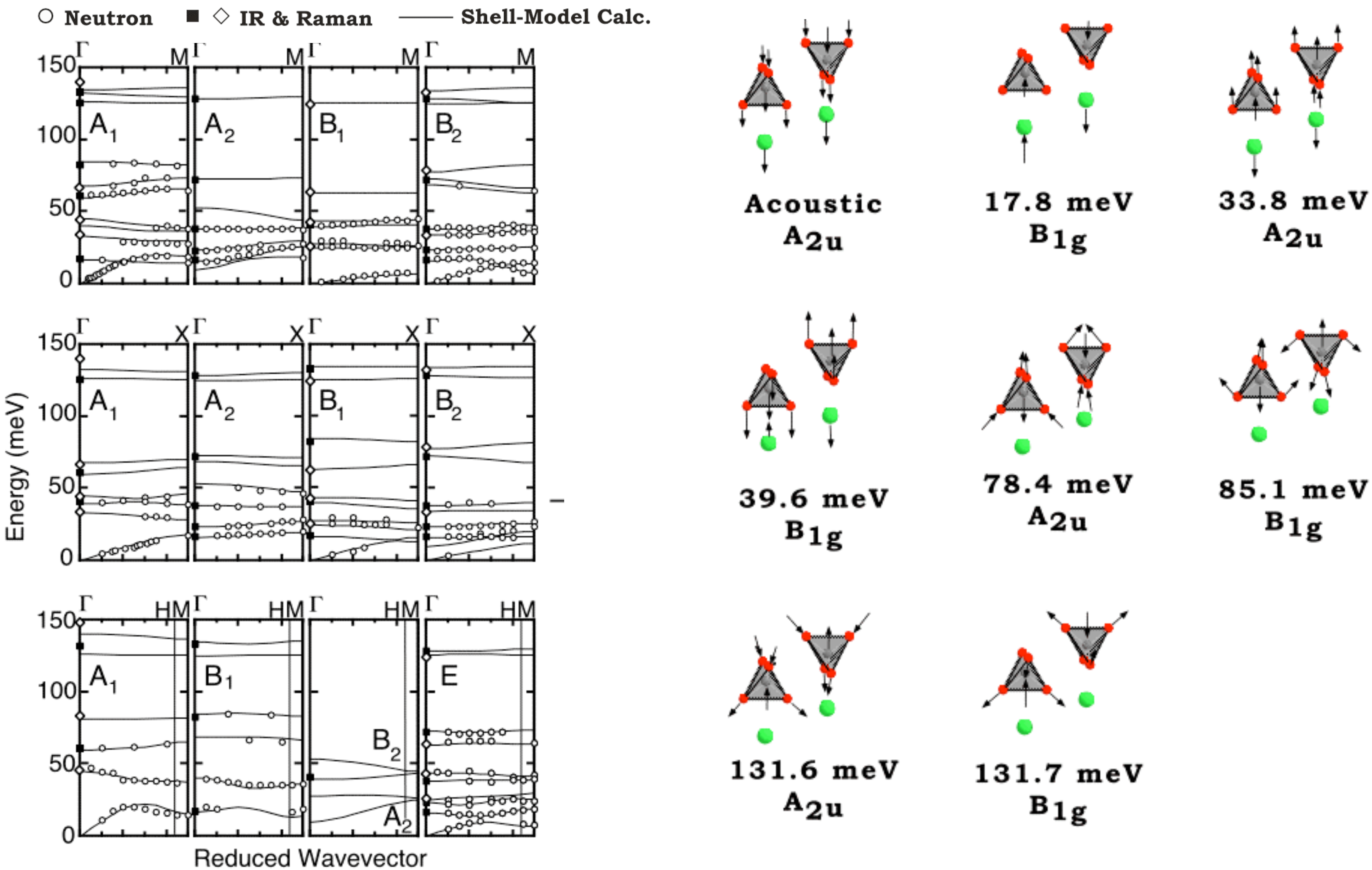
36 phonon branches along each direction

$LuPO_4$ Lattice Dynamics: Group Theoretical Analysis

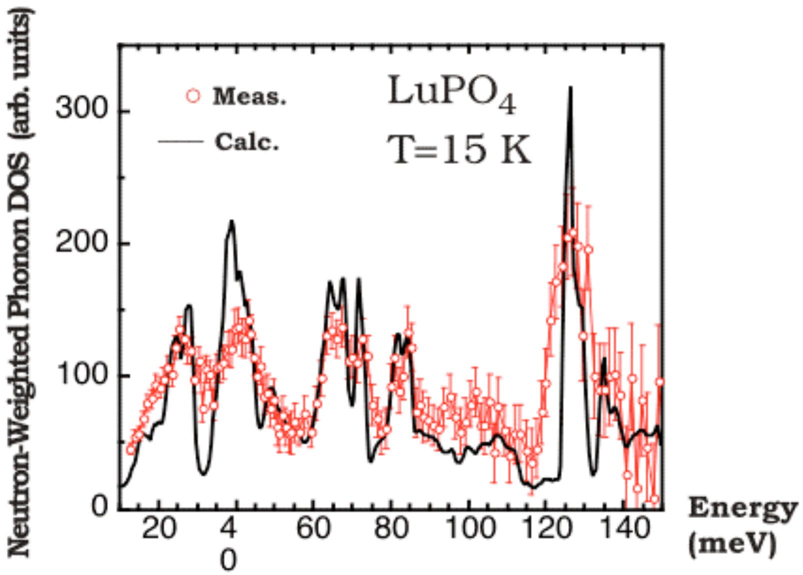


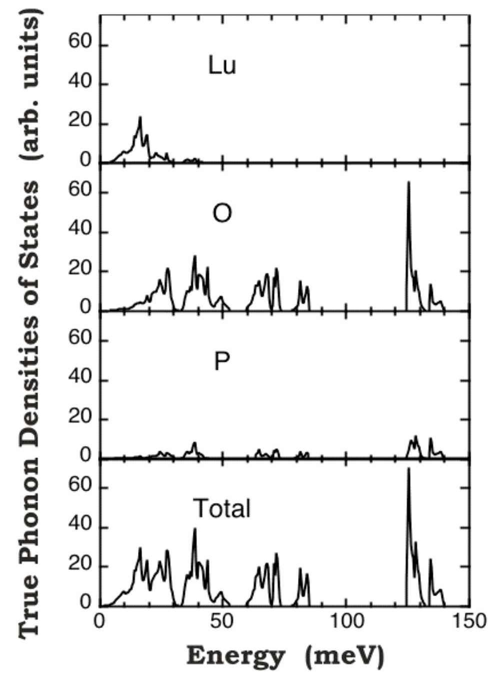
Single-Crystal, Triple-Axis Measurements of Phonon Dispersion Curves

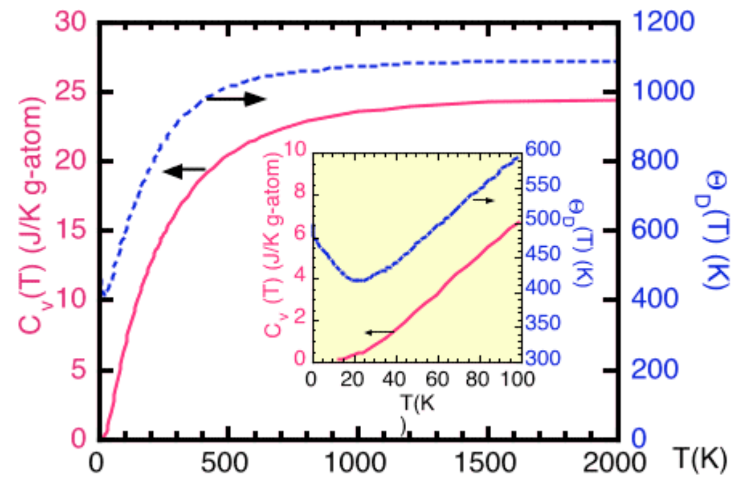
$LuPO_4$ Room Temperature



Polycrystalline, Chopper Spectrometer TOF Measurements of Phonon DOS







Magnetic INS: The Ground-State Wavefunction of a Magnetic Ion

Example 1

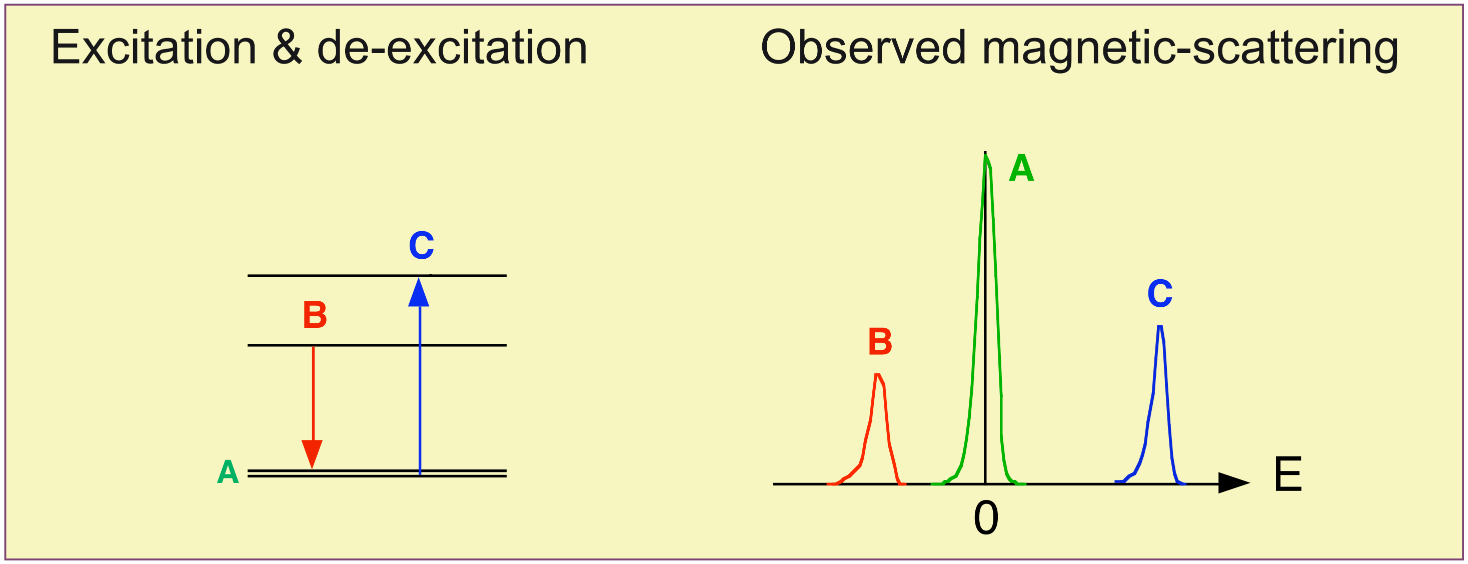
Magnetic Scattering

$$S(\mathbf{Q},E) = \frac{(\gamma r_0)^2}{4} g_J^2 \left(1 - e^{-E/kT}\right)^{-1} \chi''(\mathbf{Q},E,T)$$

$$\propto f^2(\mathbf{Q}) \sum_{i,j} e^{iq\bullet(R_i - R_j)} \int_{-\infty}^{+\infty} dt\, e^{-iEt/\hbar} \left\langle J_i^{\alpha}(0) J_j^{\alpha}(t) \right\rangle$$

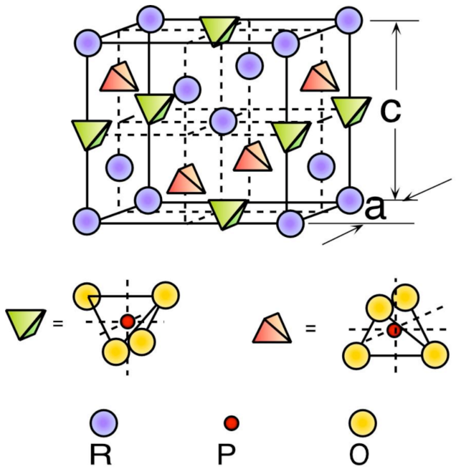
Dipole Approximation of Crystal-Field Transitions of Non-interacting Rare-Earth Ions in a Crystalline Host

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



Example 1

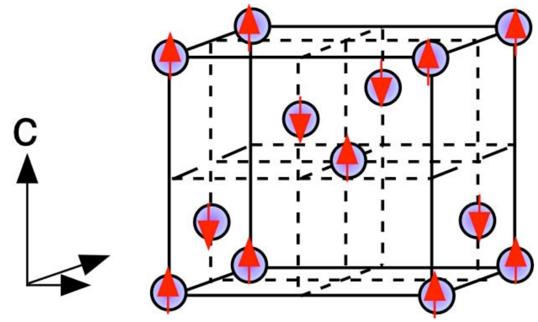
Crystal-Field Excitation Spectra of $TbPO_4$



Crystal Structure:
tetragonal zircon
($I4_1/amd$)
2 f.u./p.c.

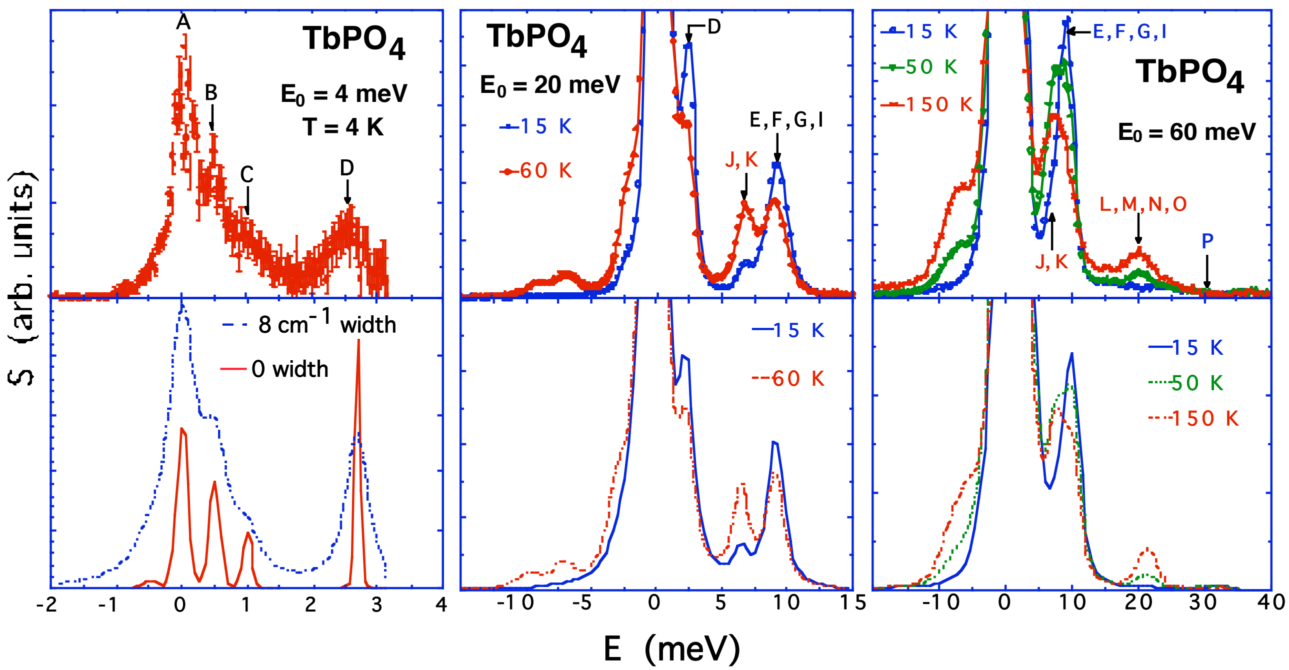
R-ion site point-group symmetry:
D_{2d}

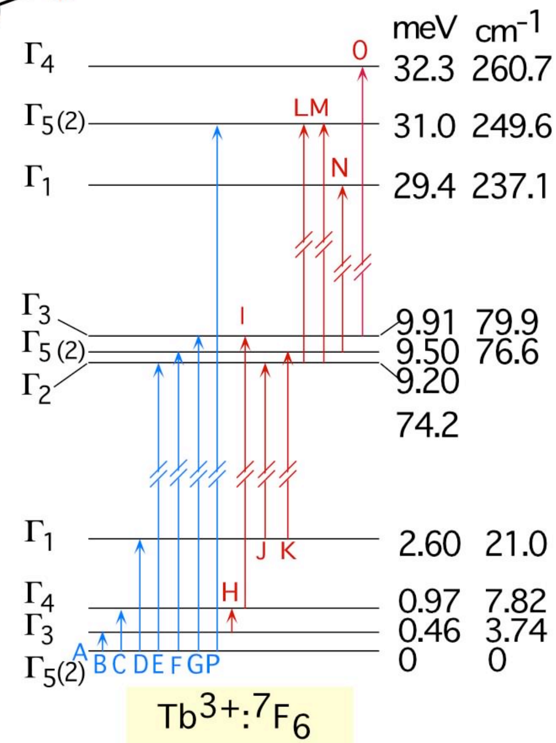
Tb sub-lattice



T_N=2.2K

T_D=2.3K

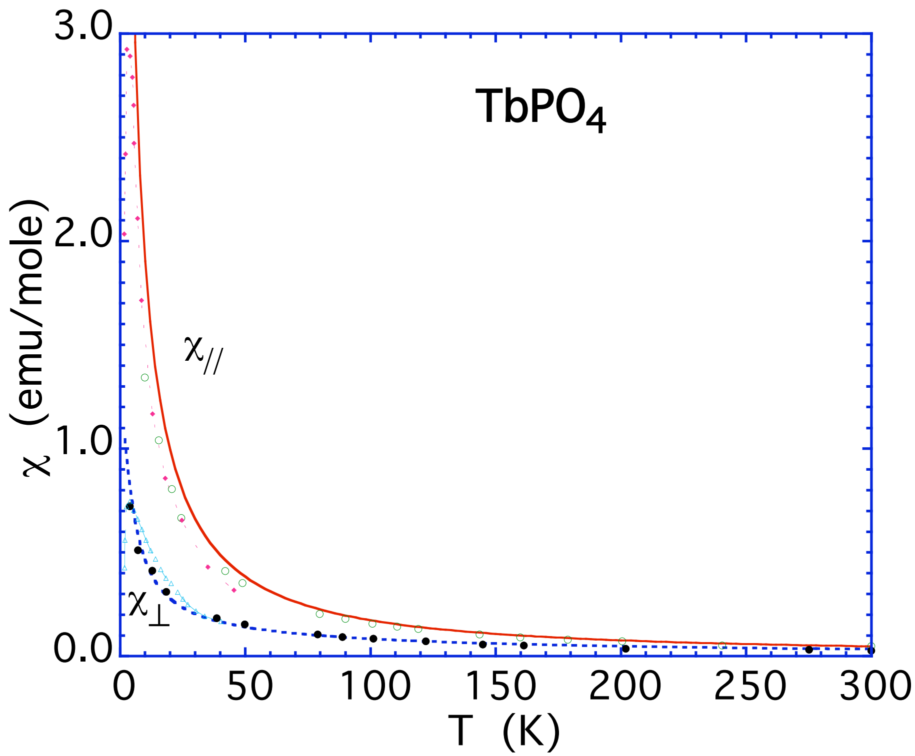


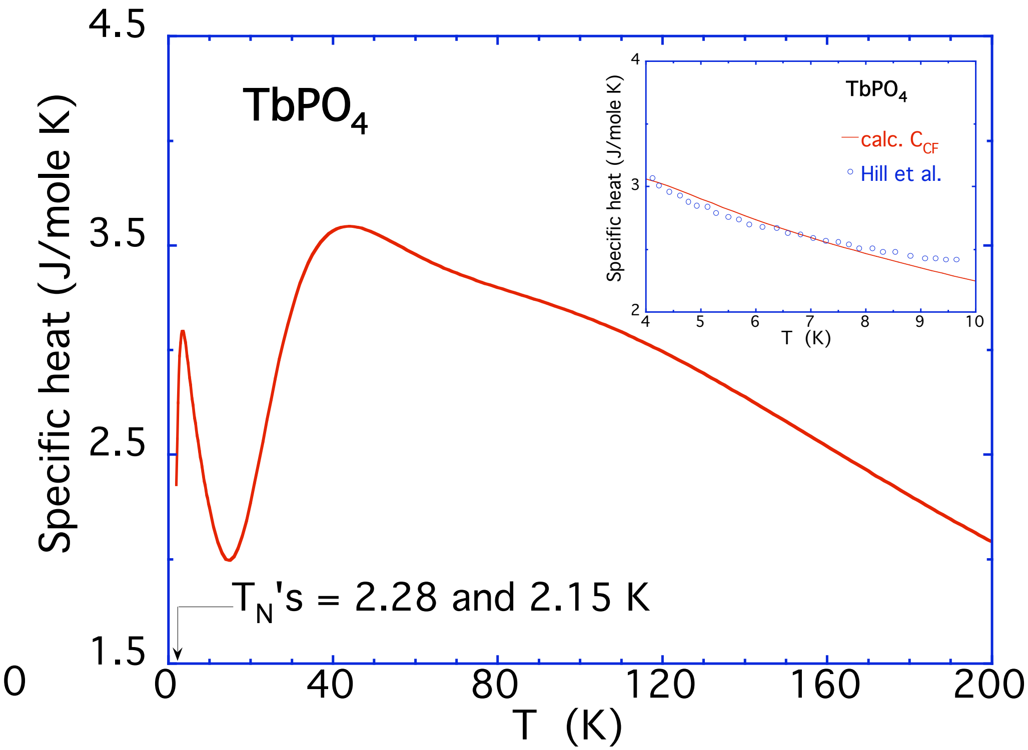


Crystal-Field Level Structure of $TbPO_4$: The Magnetic Properties

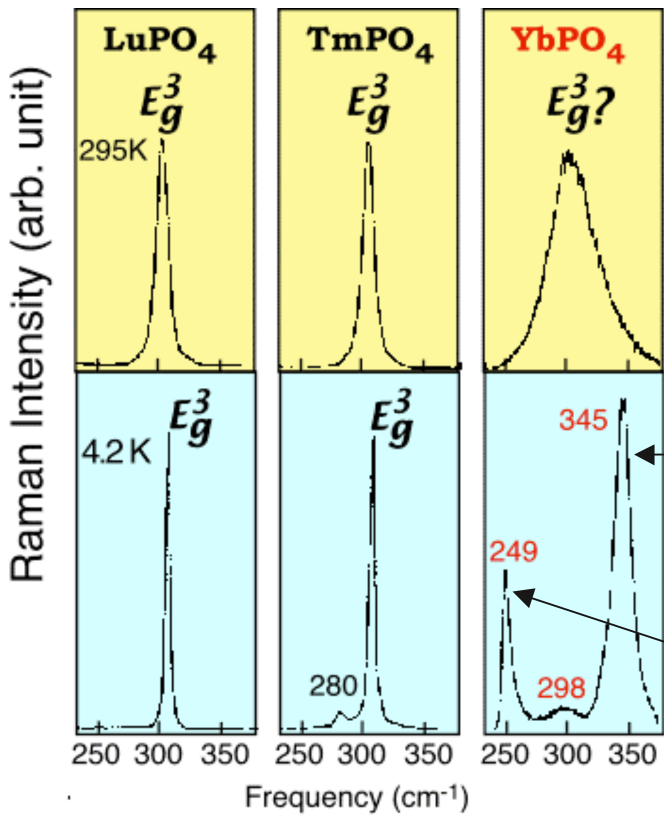
Example 1

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.





Anomalous 4f-Electron Phonon Interaction in $YbPO_4$

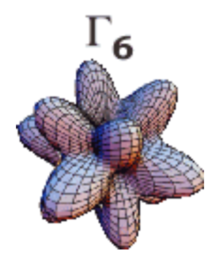


Becker *et al.* Phy. Rev. **B45**, 5027 1992)

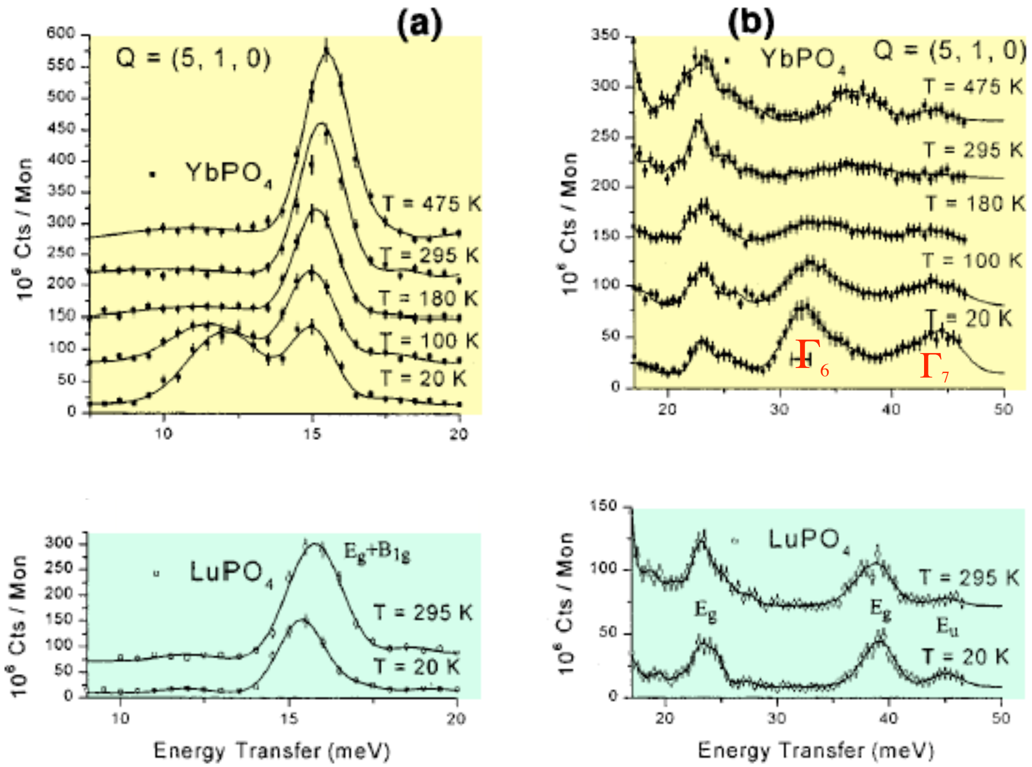
The coupling of the Yb^{3+} crystal-field states with the E_g phonon is very strong, with strengths much larger than those of any previously reported systems such as $CeAl_2$, LnF_3, $LiTbF_4$ and $Ln(OH)_3$. The line widths change drastically with temperature.

Yb^{3+} crystal field state

Yb^{3+} crystal field state



Dynamic Coupling of Crystal-Field and Phonon States in $YbPO_4$



The data suggest a large fluctuating component associated with the monopole term whereby coupling of the crystal field states, particularly the upper Γ_6 and Γ_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.

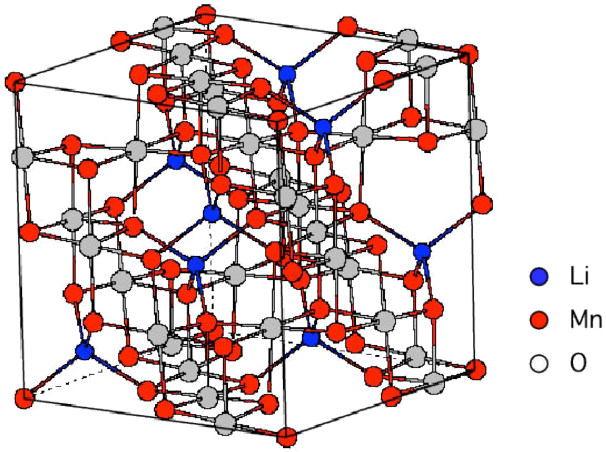
Spinels: From Gahnite ($ZnAl_2O_4$) to Nanostructured Li(H)Mn_2O_4 Adsorbent

Approach:

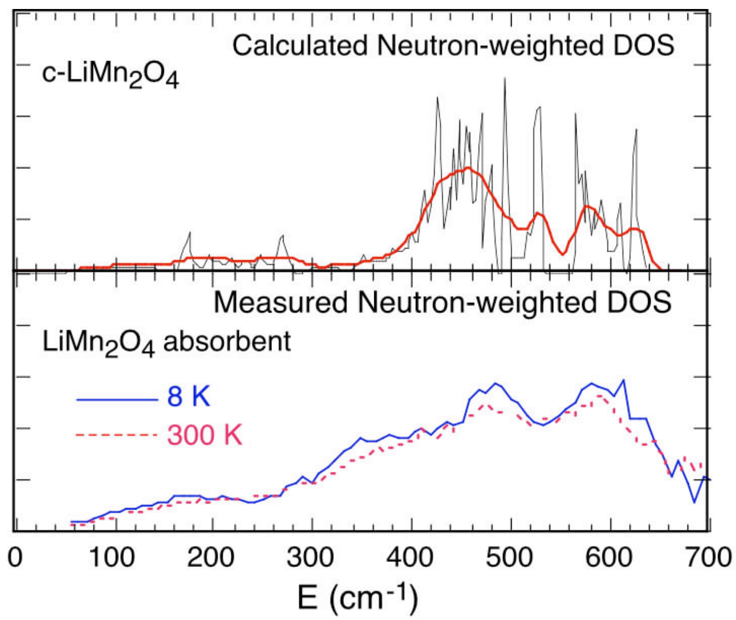
Synthesis of novel n-MnO_2 adsorbents, electron microscopy (SEM, TEM), x-ray spectroscopy (EDX & XPS), chemical analysis (ICP) - H. Koyanaka, *CRMD/CNRS, Orleans University, France*

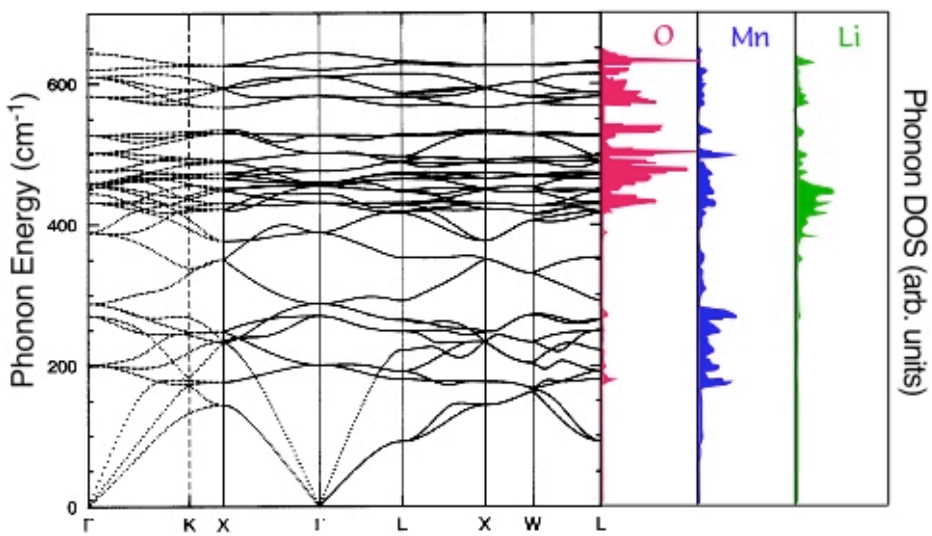
First-principle molecular-dynamics simulations - C. Fang, *University of Uppsala, Sweden*

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



The classic spinel structure: (e.g., $MgAl_2O_4$) Cubic *Fd3m*, Z=2; 42 phonon branches

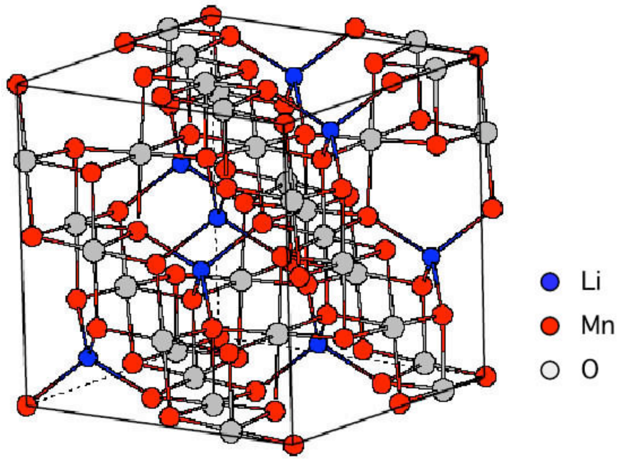


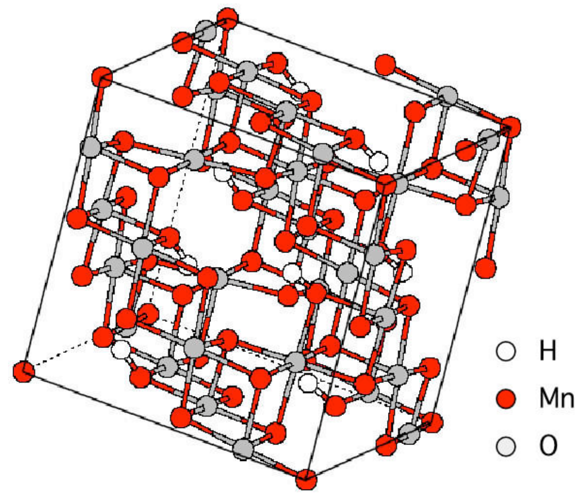


Koyanaka, Takeuchi, Loong, *Separ. Purif. Tech.* **43**, 9 (2005).
Loong & Koyanaka, *J. Neutron Res.* **13**, 15 (2005).

Example 2

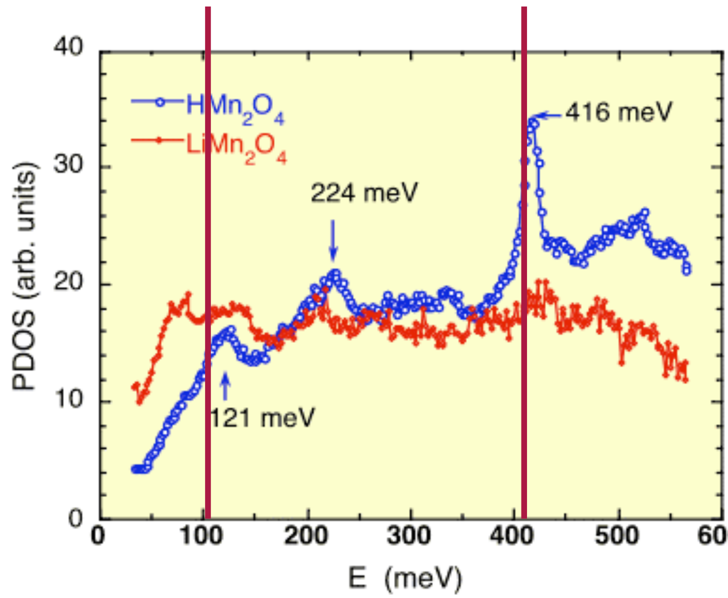
Where are the Hydrogen Atoms in HMn_2O_4?

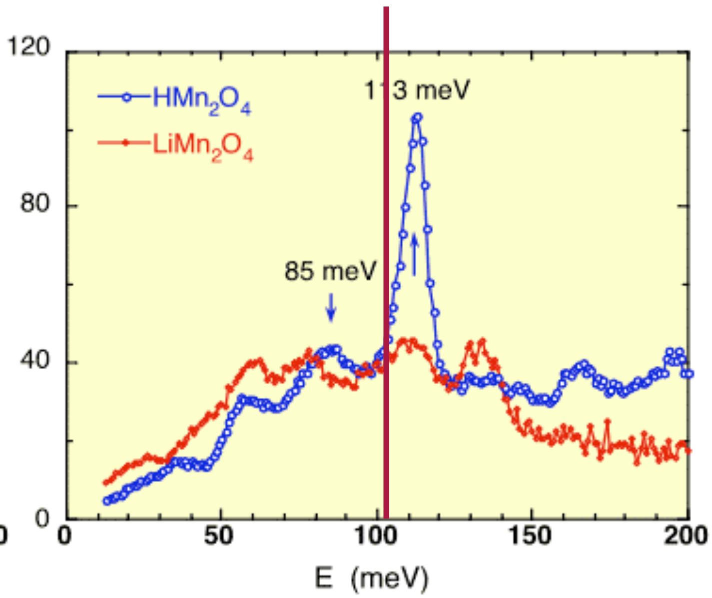




A proton prefers the tetrahedral 8a cavity site but moves to one of the neighboring oxygen, breaking the local symmetry

………. Fang & de Wijs (05)

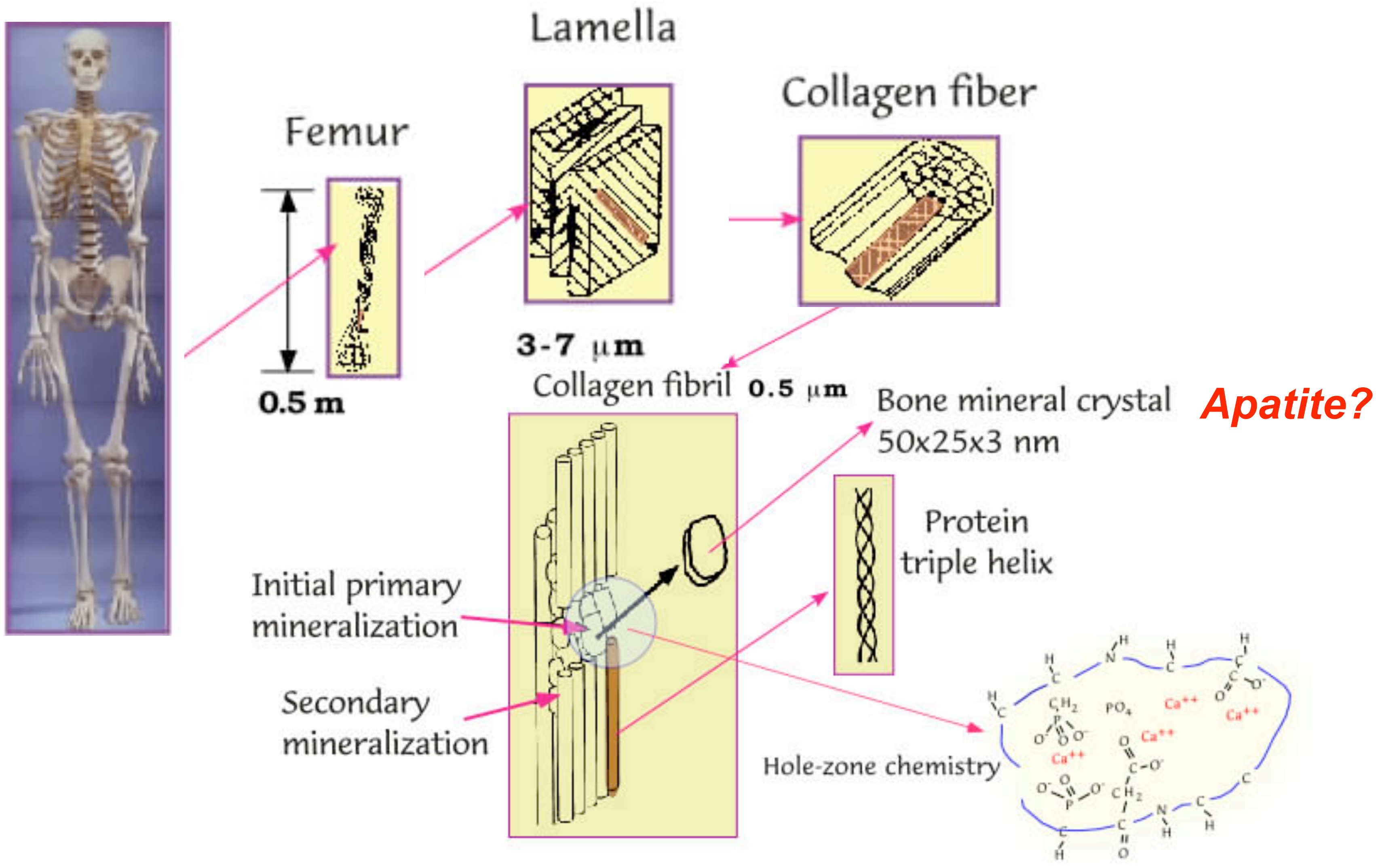




Ab initio calculation of H-vibrational frequencies

Bone Minerals: Nanotechnology in Our Body

Example 3



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

Example 3

Approach:

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

Children's Hospital Boston

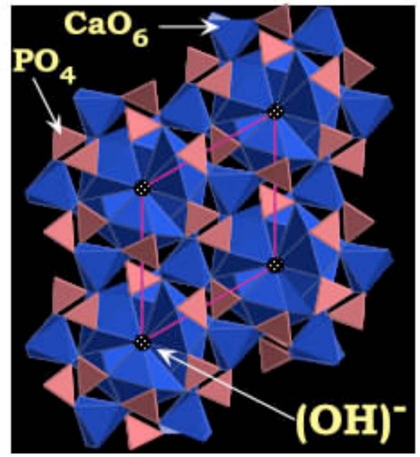
Synthesis of hydroxyapatite powders, Fourier-transform infrared spectroscopy, chemical analysis - C. Rey, *CIAIMAT-ENSCT, Toulouse, France*

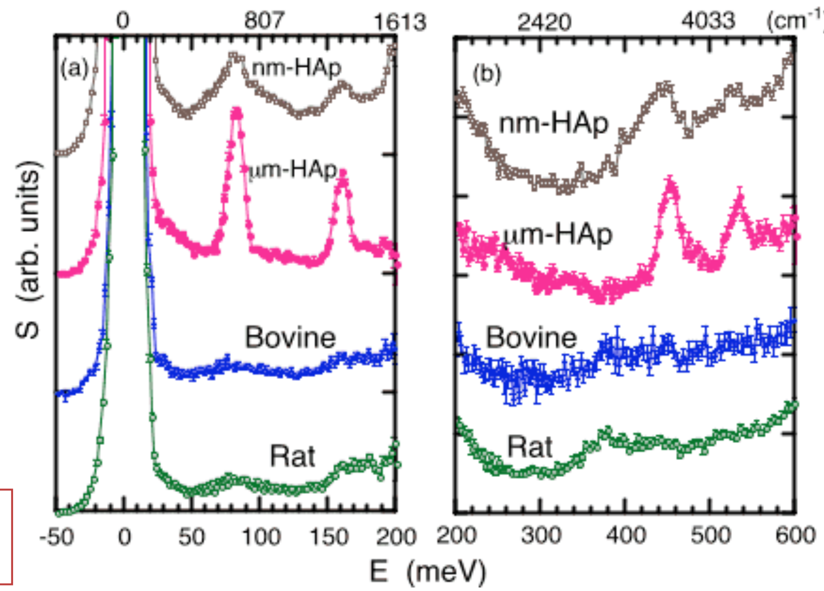
INP TOULOUSE

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

Children's Hospital Boston

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





Loong, Rey, Kuhn, Combes, Wu, Chen, and Glimcher, *Bone* **26**, 599 (2000).
Loong, Thiyagarajan, Kolesnikov, *Nanotech.* **15** S664 (2004).

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.