Measurement of excitations – phonons and magnons

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What are excitations?
What do they tell us about condensed matter?

- Forces between atoms: ionic or covalent crystals, metals, H-bonds
- Why structures are what they are: how (and when) do they melt?
- Elastic constants
- Bulk modulus & compressibility
- Thermal conductivity
- ....... and many more (also for magnetism)
Identify the length & time scales of your problem, choose the appropriate spectrometer(s) to achieve the measurements.
Phonons on a 1-D chain

\[ \omega_{ph} = 2 \sqrt{\frac{K}{M}} \left| \sin \left( \frac{k_{ph} a}{2} \right) \right| \]

Fig. 3. Dispersion curve for the \( L[001] \) modes in which the planes move as rigid units. The solid line is the best fitting (simple) sinc wave to the experimental points. The assignment of errors is discussed in the text.

Neutron inelastic scattering

Two equations are: \[ \vec{Q} = \vec{k}_i - \vec{k}_f \quad \hbar \omega = \Delta E = \hbar / (2 m_n) \left( k_i^2 - k_f^2 \right) \]

Elastic scattering has \( k_i = k_f \)

In terms of space-time correlation functions \textit{elastic} scattering measures at \( t = 0 \) the position of particles \( j \) and \( j' \)

\[
S(\vec{Q},0) \propto \sum_{jj'} \left\langle \exp[-i \vec{Q} \cdot \vec{R}_j(0)] x \exp[i \vec{Q} \cdot \vec{R}_{j'}(0)] \right\rangle
\]

We will now extend this to measure the correlation of particle \( j \) at \( t = 0 \) with particle \( j' \) at \( t = t \)

\[
S(\vec{Q},\omega) \propto \int_{-\infty}^{+\infty} \exp(-i \omega t) dt \sum_{jj'} \left\langle \exp[-i \vec{Q} \cdot \vec{R}_j(0)] x \exp[i \vec{Q} \cdot \vec{R}_{j'}(t)] \right\rangle
\]
In a crystal there is a periodic arrangement of atoms; we write this as $\vec{R}_l = \vec{l} + \vec{u}_l$ where $\vec{u}_l$ is the displacement of the atoms from their mean position $\vec{l}$.

The correlations between particles $l$ and $l'$ depends only on their vector difference $|\vec{l} - \vec{l}'|$ so the sum over $j$ and $j'$ is the same

$$\sum_{jj'} \left< \exp[-i\vec{Q} \cdot \vec{R}_j(0)] x \exp[i\vec{Q} \cdot \vec{R}_{j'}(t)] \right>$$

$$= N \sum_j \exp(i\vec{Q} \cdot \vec{l}_j) \left< \exp[-\vec{Q} \cdot \vec{u}_o(0)] x \exp[+\vec{Q} \cdot \vec{u}_j(t)] \right>$$

leading to:

$$S(\vec{Q}, \omega) \propto \sum_j \exp(i\vec{Q} \cdot \vec{l}_j) \int_{-\infty}^{+\infty} \exp(-i\omega t) dt \left< e^\vec{u} e^\vec{v} \right>$$

where $\sum_j \exp(i\vec{Q} \cdot \vec{l}_j)$ is the **elastic structure factor**.
\[ \langle e^U e^V \rangle \] where \[ U = -i \vec{Q} \cdot \vec{u}_o(0) \] and \[ V = +i \vec{Q} \cdot \vec{u}_j(t) \]

We assume the displacements are small and can be described in terms of an harmonic oscillator. Then we can use the identity

\[ \langle e^U e^V \rangle = e^{\langle U^2 \rangle} \langle UV \rangle \]

and note that \[ e^{\langle U^2 \rangle} \] is independent of \( t \)

This term is the Debye-Waller factor representing uncorrelated motions of the nuclei from their mean positions

\[ e^{\langle U^2 \rangle} = \left\langle \left[ \vec{Q} \cdot \vec{u}_o(0) \right]^2 \right\rangle = e^{-2W} \]

Finally

\[ e^{\langle UV \rangle} = 1 + \langle UV \rangle + \frac{1}{2} \langle UV \rangle^2 + \ldots \]

One phonon \hspace{1cm} two phonon
Final phonon cross section

\[
\left( \frac{d^2 \sigma}{d\Omega d\omega} \right) = \frac{\sigma_{coh}}{4\pi} \frac{k_f}{k_i} \frac{(2\pi)^3}{\nu_0} \frac{1}{2M} \exp(-2W)
\]

\[
x \sum_s \sum_\tau \frac{(\vec{Q} \cdot \hat{u}_s)^2}{\omega_s} \left( n_s + \frac{1}{2} \pm \frac{1}{2} \right) \delta(\omega \mp \omega_s) \delta(\vec{Q} \mp \vec{q} - \tau)
\]

Intensity \( \propto |Q|^2 \left( \vec{Q} \cdot \hat{u}_s \right)^2 \)

\( \propto \sigma_{coh} / \omega \)

\( \propto <n_s + 1/2 \pm 1/2> \) gives the population of phonon states.

There are more phonons at high T as phonons and magnons are bosons, no limit to population. \textbf{Detailed balance}

\( \propto \delta(\omega \mp \omega_s) \) gives Stokes and anti-Stokes lines

\( \propto \delta(\vec{Q} \mp \vec{q} - \tau) \) gives conservation of momentum for phonon of wavevector \( \vec{q} \); note \( |\vec{q}| = 2\pi / \lambda_{\text{phonon}} \)
Ways to measure excitations

- Triple axis spectrometer
- Time-of-flight chopper spectrometer

Special Instruments that have a more constrained energy or Q window

- Back-scattering spectrometer
- Spin-echo spectrometer
- Crystal-analyzer spectrometer
- Compton spectrometer
How do we measure these points?

- Momentum transfer \( \hat{h}Q = \hat{h}(k_i - k_f) \)

- Energy transfer \( \hat{h}\omega = E_i - E_f = \frac{\hbar^2}{2m} (k_i^2 - k_f^2) \)

\[ |Q|^2 = |k_i|^2 + |k_f|^2 - 2 |k_i||k_f|\cos (2\theta) \]
Techniques of the triple-axis spectroscopy

Focusing

scan direction

point by point scan to map out phonon dispersion curve

$E_i - E_f = n \omega$

$q$ fixed

$E_f$

$(q, \omega)$

two phonons measured

scan along a symmetry direction

locus of fixed incident energy $E_i$

reciprocal lattice of sample
Bertram N. Brockhouse

- Facts

Source: Atomic Energy of Canada Limited, Chalk River, Ontario (CC BY-NC-ND 2.0)

Note that the Be filter, which is used with cold neutrons, can either be before the sample (constant $k_i$) or after the sample (constant $k_f$).
The IN14 triple-axis spectrometer at the ILL
Phase transitions in solids

Dispersion relations of the $\Sigma_2$ soft mode and the $\Sigma_3$ acoustic mode in $K_2SeO_4$ plotted in an extended zone. Z.B. indicates the original zone boundary. The solid lines show the results of fitting force constant models to the data.

If one looks carefully at these data one can see that the initial “soft” point is not at $q = 2/3$, but rather at $q = 2/3 + \delta$

This is an example of an incommensurate phase transition, stabilised by higher-order terms in the Landau expansion.

Note the anomaly in the $a$ direction [100] and the incipient minimum of the $\Sigma_4$ mode. The other two directions are ‘normal’.

At low temperature the material transforms in a complex way, developing a charge-density wave.
In the BCS theory (1957) of s-wave superconductivity the lattice vibrations (phonons) mediate the attraction between electrons and form the Cooper pairs. Thus the measurements of phonons, in particular, the total phonon-density of states, is important to understand the overall mechanism of superconductivity.

Many phonon studies using neutrons have been done with this motivation.
An example of an electron-phonon interaction as measured by neutrons

Inelastic scattering from Nb$_3$Sn, $T_c = 18.3$ K.

For phonons with $E < 2 \Delta(T)$, where $\Delta(T)$ is the s/c energy gap, there is a loss of a damping mechanism as the low-energy electron states form Cooper pairs.

Notice how this phonon is much broader for $T > T_c$.

Axe & Shirane, PRL 30, 214 (1973)
Electron-phonon interaction in Nb$_3$Sn

Summary of line-widths as f(T)
Note that there is anisotropy in the damping mechanism. No measurable effect is observed along [100], but a large effect along [110]

No effect is observed for a phonon of $E = 8$ meV. This is above $2 \Delta(0)$.

The gap is well determined as $2 \Delta(0) = 7 \pm 1$ meV = $(4.4 \pm 0.6) k_B T_c$ in excellent agreement with the specific heat value of $4.8 k_B T_c$. 
FLAT CONE II

Top view

31 channels
75° angular range

sample

Side view

$k_f = 3 \text{ Å}^{-1}$

$k_f = 1.5 \text{ Å}^{-1}$
PZN-8%Pt relaxor

$\Delta E = 3 \text{ meV}$

$k_f = 3 \text{ Å}^{-1}$

IN20, July 2006

$t_{\text{exp}} = 23 \text{ sec}$

$t_{\text{tot}} = 5 \text{ hours}$

62 x 360 pixels
Chasing ghosts in reciprocal space—a novel inelastic neutron multiple scattering process

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Abstract

We have discovered that a recently reported weak excitation branch in the spin-Peierls material CuGeO\textsubscript{3} is in fact a ghost image of the primary magnetic excitation shifted in reciprocal space by a novel multiple scattering process. A model is developed that predicts the occurrence of such multiple scattering and accounts for the observations in CuGeO\textsubscript{3}. New ‘ghostons’ can occur when the magnetic unit cell is smaller than the structural, while mixing of intensities from different reciprocal space zones jeopardize accurate polarization analysis and the study of weak modes in general.

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Time-of-flight spectroscopy

Direct geometry:
- fix $k_i$ by chopper phasing
- scan through $k_f$ by time-of-flight

Distance

Sample chopper

Pulsed source

Time

from Ken Andersen
Constraints on Q and ΔE in inelastic scattering

Direct Geometry:

\[
\left( \frac{Q}{k_0} \right)^2 = 2 - \frac{E}{E_0} - 2\cos\phi \sqrt{1 - \frac{E}{E_0}}
\]

\[E = 2.072 \ k^2\]

\[\Delta E = 20 - 50 \text{ meV}\]
\[E_0 = 100 \text{ meV}, \ k_0 = 7 \ \text{Å}^{-1}\]
\[6 < Q < 8 \ \text{Å}^{-1}: \text{Res} \sim 3 \text{ meV}\]

\[\Delta E = 100 - 200 \text{ meV}\]
\[E_0 = 300 \text{ meV}, \ k_0 = 12 \ \text{Å}^{-1}\]
\[Q \sim 4 \ \text{Å}^{-1} \ \text{Res}: \sim 10 \text{ meV}\]
MERLIN chopper spectrometer at ISIS, RAL

Wide angle coverage, high intensity and moderate resolution direct chopper spectrometer

Also can run in special mode to allow more than one incident energy to be measured at same time
Phonons from \((\text{NH}_4)_2\text{SO}_4\) measured on MERLIN

Note these data are at ambient pressure; pressures up to several GPa were measured
Magnetic fluctuations in superconducting YBa$_2$Cu$_3$O$_{6+x}$

The excitations are incommensurate below $T_c$ even at high energies, in fact to 100 meV.

These data have be taken on the MAPS spectrometer at ISIS and show the great advantage of the multidetector system coupled to a pulsed source.

$E_i = 170$ meV; crystal 25 g. $T_c = 63$ K

Magnetic fluctuations in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

Although there are magnetic excitations over a wide range of energies near $(1/2 \ 1/2)$, they are by far the strongest at the resonant energy, in this case 34 meV, and below $T_c = 63 \text{ K}$

This is an integration so cannot show the incommensurate nature.

Magnetic fluctuations in superconducting YBa$_2$Cu$_3$O$_{6+x}$

What causes these excitations and are they related to the special superconductivity in these materials?

(1) Incipient spin-charge separation leading to “stripes”

(2) Electron-hole pair excitations governed by the underlying Fermi surface.

Many theories are presently trying to reproduce these effects. Together with photoemission (ARPES), these neutron scattering experiments are probably the most important set of data in the quest to understand high $T_c$ mechanism.
Inelastic X-ray scattering

Recall that a 1 Å x-ray beam has an energy of 12.4 keV – in case you missed it, that is 12.4 x $10^6$ meV.

Since we know that there are excitations at the eV level in solids, plasmons, inter-multiplet levels etc., these can be investigated with x-rays, and this resolution is relatively easy to achieve.

But to get to meV is clearly very hard. The solution comes from large perfect crystals developed by the semiconducting industry, and to rely on Backscattering techniques. There are only 3 such instruments in the world, at ESRF, APS (Argonne), and Spring-8 (Osaka).
ID28 IXS beamline at ESRF

Energy resolution decoupled from the energy transfer
Energy independent momentum transfer
Focusing capabilities

ΔE/E ≈ 10^{-8}

Si(9 9 9)
ΔE = 3 meV
E = 17.79 keV

Si(12 12 12)
ΔE = 1.5 meV
E = 23.72 keV

Δd/d = -α(T)ΔT
α = 2.58 × 10^{-6} at RT

Mirror (cylindrical-toroidal)
Pre-mono
Post-mono
KB focusing mirror
Sample
Detector
Spherical analyzers
Collimating Be lens
Undulators x3

80 m 70 m 50 m 40 m 30 m

Energy resolution decoupled from the energy transfer
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Δd/d = -α(T)ΔT
α = 2.58 × 10^{-6} at RT
Sample handling, cutting and surface preparation follows strict safety rules
Restricted scattering geometry due to the sample encapsulation

\[ \text{UO}_2: \quad \text{Mass} = 99000 \text{ mg} \]
\[ \text{NpO}_2: \quad \text{Mass} = 0.863 \text{ mg} \]
\[ \text{Activity} = 19.8 \text{ kBq} \]

Strong L$_3$ photo-absorption at working energies
\[ L_3(\text{Np}) = 17.610 \text{ keV}, \quad L_3(\text{U}) = 17.166 \text{ keV} \]
Sample quality affects the elastic line and prevents measurements at low energy

1\textsuperscript{st} Exp. at Si(999)
Crystal cut from large UO\textsubscript{2} sample
Bad crystal surface

2\textsuperscript{nd} Exp. at Si(999)
Single crystal grown by vapor transport
Slightly off-stoichiometric (T\textsubscript{N}=29.8K)

3\textsuperscript{rd} Exp. at Si(12 12 12)
Good quality single crystal.
Stoichiometric sample
T\textsubscript{N}=30.8K

L. PAOLASINI - 49èmes Journées des Actinides 2019
Inelastic scattering from thin films: phonons in irradiated UO$_2$ thin films

Thin films can be irradiated to make uniform damage up to a thickness of $\sim 4$ microns. Radiation using accelerated particles to simulate fission damage cannot penetrate $>20$ microns.
Experiments to compare phonons in pristine and irradiated UO$_2$ films of 300 nm

Phonons measured from 300 $\mu$g of material

Phonon energies same as measured in bulk and no change with irradiation, however extra diffuse scattering, and broader phonons, and some E or $q$ dependence of broadening. Consistent with 50% drop in thermal conductivity, $\kappa$. Cannot measure optic modes.

Neutrons are the probe of choice for phonons.

Many instruments at both reactors and pulsed sources are designed for such experiments and they can be used with both single crystals and polycrystalline samples. Be sure you know what you are looking for!

The crystals will have to be at least 100 mm$^3$

For exceptionally small samples (i.e. thin films) or high pressure, then you may want to consider inelastic x-ray scattering. (No magnetic excitations! RIXS?)