

Powder inelastic scattering analysis

Phonons in aluminium

In non-magnetic polycrystalline materials inelastic excitations normally are produced by the creation/absorption of phonons in the crystal. Phonon scattering will therefore occur when the neutrons have the right energy and momentum for the phonons to be created or absorbed according to the conservation laws

$$\hbar\mathbf{Q} = \hbar(\mathbf{k}_{ph} + \mathbf{G})$$

$$\hbar\omega_n = \hbar\omega_{ph}$$

Taken as a snapshot in time, a phonon looks like a static sinusoidal lattice distortion

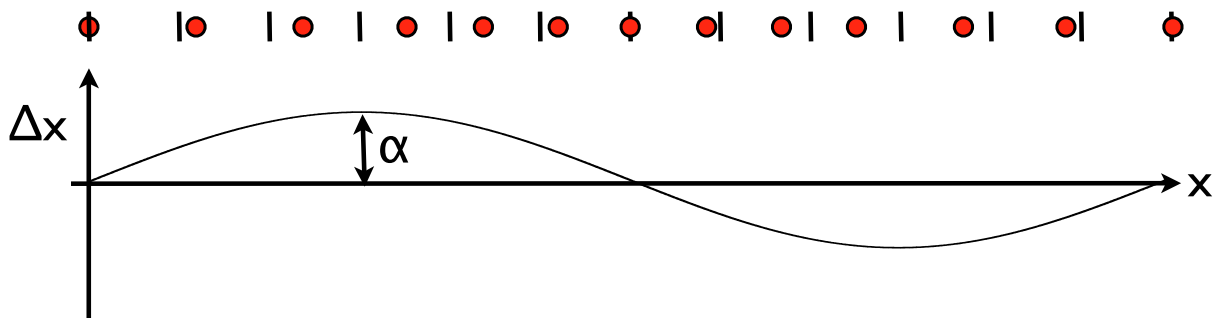


Figure 1: Atoms displaced sinusoidally from their equilibrium positions at a single point of time

According to Fig. 1 the position of the n^{th} nucleus is $x_n = nd + \alpha \sin(k_{ph}nd)$

$$\begin{aligned} \text{Therefore the neutron cross-section will be } \frac{d\sigma}{d\Omega} &= \left| \sum b_n \exp(i\mathbf{Q}\cdot\mathbf{r}_n) \right|^2 \\ &= \left| \sum_n b_n \exp \{iQ(nd + \alpha \sin(k_{ph}nd))\} \right|^2 \end{aligned}$$

Expanding the exponential term assuming that the lattice displacements are small:

we get

$$\frac{d\sigma}{d\Omega} = \left| \sum_n b_n [1 + iQ\alpha \sin(k_{ph}nd)] \exp(iQnd) \right|^2$$

The first term $\left| \sum_n b_n \exp(iQnd) \right|^2$ peaks at the normal Bragg peak positions, $Q = m \left(\frac{2\pi}{d} \right)$ (m integer)

whereas the second term $\left| \sum_n b_n Q \alpha [\exp \{i(Q + k_{ph})nd\} - \exp \{i(Q - k_{ph})nd\}] \right|^2$

peaks at positions given by $Q = m \left(\frac{2\pi}{d} \right) \pm k_{ph}$ with intensity $\propto \bar{b}^2 Q^2 \alpha^2$

Phonons are, of course, dynamic sinusoidal lattice distortions, but the cross-section for the phonon is the same as for the static case, with the additional constraint of energy conservation.

i.e peaks in $\frac{\partial^2 \sigma}{\partial \Omega \partial E}$ when $\hbar \mathbf{Q} = \hbar(\mathbf{k}_{ph} + \mathbf{G})$ and $\hbar \omega_n = \hbar \omega_{ph}$ with intensity $\propto \bar{b}^2 Q^2 \alpha^2 \propto \frac{\bar{b}^2 Q^2}{\omega_{ph}}$

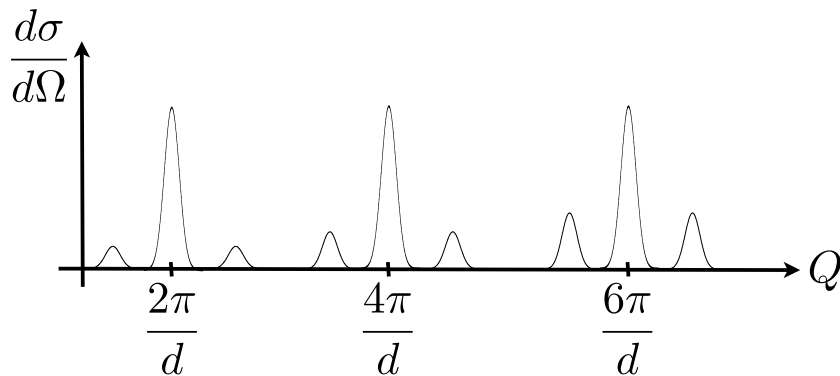
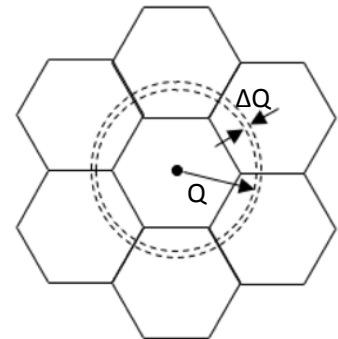
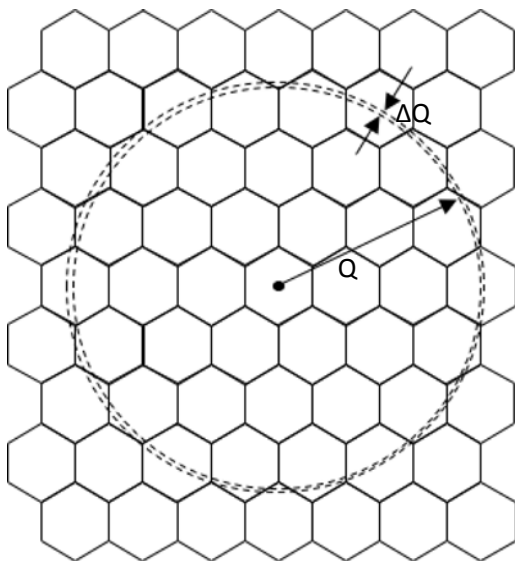


Figure 2. Cross-section for "static" phonon with given k_{ph}

In a polycrystalline sample, we measure the direction average of the phonons cross-section over all space. That means we sum over all the scattering at the same modulus of the wavevector, Q , between Q and $Q+\Delta Q$.



At small values of momentum transfer the powder average

samples a small region of reciprocal space and coherent effects can be seen clearly. But at large momentum transfers the powder average samples almost the whole Brillouin zone (see below) and coherent effects are lost. At high momentum transfers the incoherent and coherent cross-sections become the same. Typically a phonon measurement in a polycrystal will involve an

average of the scattering over a wide angular range, and since the scattering intensity at low momentum transfers is small the average is dominated by the high-Q data. In these circumstances it is common to assume that there is no difference between the coherent and incoherent scattering; this is the ***incoherent approximation***.

Often what is needed is the generalized phonon density-of-states (GDOS) $Z(\omega)$. This is related to the inelastic cross-section via the relation

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)^{inel} = N \frac{k'}{k} \frac{\sigma}{8\pi M} Q^2 \exp\{-2W(\mathbf{Q})\} \frac{Z(\omega)}{\omega} \{n(\omega) + 1\}$$

where $n(\omega)$ is the Bose-factor $\{\exp(\hbar\omega/kT) - 1\}^{-1}$, $\exp\{-2W(\mathbf{Q})\}$ is the Debye Waller factor and the other symbols have their usual meanings.

$Z(\omega)$ represents the dynamical properties of the systems *without probe-bias*. That is, it's a characteristic of the material, and not how it was measured. It is generally the GDOS with is compared with theoretical calculations.

Questions

- 1) Read the MARI aluminium data into Mantid, and reduce using *Pyslice*
- 2) Extract a constant energy cut of the elastic line, and using the positions of the Bragg peaks, verify that the sample is aluminium
- 3) Examine the inelastic data as a function of Q and ω – look for the transverse and longitudinal phonons
- 4) Convert the data to a GDOS – using the algorithm supplied in Mantid – or on your own!
- 5) In the Debye approximation (constant phonon velocity in each direction) the low-energy part of the GDOS should be parabolic up to the Debye cutoff. Fit a parabola to the low-E data, thereby extracting the velocity of sound, c , for aluminium using the relation

$$Z(\omega) \simeq \frac{3\omega^2}{2\pi^2 c^3}$$

Data for aluminium

Structure: fcc
 Lattice constant: 4.03 Å
 Debye-Waller factor: $W(\mathbf{Q}) = 0.13 Q^2$

Crystal Field Excitations in PrAl₃

Rare earth ions such as Pr commonly carry a magnetic moment due to the gradual filling up of the 4f electron shell across the rare-earth series.

The magnetic rare-earth ions in solids can undergo many types of magnetic interaction with their surroundings – but these are broadly classified as either *single ion interactions* or *two-ion interactions*. Single ion interactions act independently at each rare-earth ion site, whereas the two-ion interactions act between pairs of ions (e.g. magnetic exchange interactions).

PrAl₃ is a *Van Vleck paramagnet*. This sort of paramagnetism is characterised by a flat magnetic susceptibility at low temperatures brought about due to the varying statistical occupancy of closely spaced multiplets (see J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, 1932, p. 226). Pr interactions in PrAl₃ are dominated by single ion crystal field interactions. These are Coulomb interactions between the charge density at the rare-earth ion site and the symmetry of the local electric field produced by the neighbouring ions. These interactions generally lift the degeneracy of the 2J+1 states of a particular electronic state multiplet, such that different orientations of the charge distribution carry different energies. These orientations in space are characterised by the quantum numbers m_j representing the space quantisation of the electronic state.

Question

- 1) The rare-earth Pr ions in PrAl₃ are in the Pr³⁺ ground state, which leaves 2 4f electrons in the f-shell. Using Hund's rules, find L, S and J of Pr³⁺ and hence write down the term value, and the expected degeneracy of the ground-state multiplet.

Neutrons are capable of exciting transitions between the energy levels split by the crystal field. This is due to the fact that under some circumstances neutrons scatter from magnetic fields associated with the unpaired f-electrons while flipping the neutron spin. Neutrons are spin-1/2 so only have a choice of two wavefunctions $|+1/2\rangle$ and $|-1/2\rangle$. If a neutron “flips” (changes from the $|+1/2\rangle$ to $|-1/2\rangle$ state or vice versa) then in order to conserve angular momentum, the ionic state must change by $\Delta m_j = \pm 1$. This is the crystal field level transition selection rule for neutrons.

So what do we expect to see in a neutron scattering experiment from PrAl₃? Transitions between allowed crystal field levels will appear as peaks in the inelastic neutron scattering spectra at energies equal to the spacing between the split CF levels. The form of the CF levels is calculable using so-called *point charge approximation* or *ligand field approximation* techniques. The precise energies of the CF energy levels in general have to be characterised by experiment – including by neutron scattering. Figure 3 shows the CF scheme for PrAl₃.

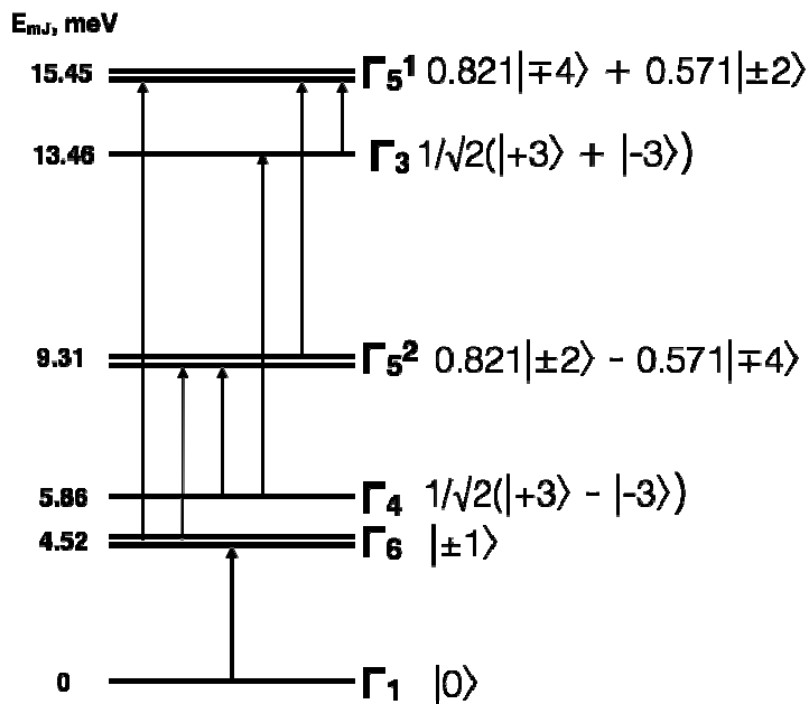


Figure 3: The CF level scheme for PrAl_3 . The selection rules allow for only one transition from the ground state to an excited state. Further transitions from excited states are allowed, as shown.

Pr3Al Questions

Load and Reduce the data

- 1) Read in the first run (#1) using the Reduction tab of *PySlice* - Select "autoEi" and "background subtractor" [sic]
- 2) Display the data using the Visualisation tab of *PySlice*.
- 3) Describe the excitations you see.
- 4) Try various levels of smoothing - does this help the visualisation?
- 5) Do the same for the second run (#2)

Inspection of the data

- 1) Take a constant Q cut of the two data sets at low momentum transfers. You'll need to take quite a wide strip in Q to maximise the statistics.
- 2) Plot these Q-cuts on top of one another - how do they compare. Note their major differences.
- 3) Taking a constant energy transfer cut of the two data sets at the elastic line, decide whether the sample is magnetically ordered.

- 4) What do you notice when you plot the difference between the elastic line cuts.

Data analysis

- 1) Using the first data set (#1) find the intensities and positions of the largest peak at around 4.5 meV (on both the negative (energy gain) and positive (energy loss) sides.
- 2) Using the *Law of detailed balance* calculate the temperature of the sample?
- 3) Take a constant E cut of the excitations you see. Which ones are magnetic (crystal field excitations) and which are nuclear, and why?
- 4) An approximation of the magnetic form factor of Pr³⁺ is $F(Q) = \exp(-aQ^b)$ with $a=0.0268$ and $b=1.775$. Check that the Q-dependence of the intensity in the largest excitation peak is well described by the square of this form factor. What does this tell you?
- 5) Read in the low temperature run you did on MARI. Check that the temperature of this is where it should be.
- 6) What's different about this data compared with the high temperature data set (#1)?
- 7) Assign the peaks to the CF scheme shown in figure 3. Why do most of the peaks disappear?