Solids

1. Binding types
2. Crystal lattices
3. **Lattice vibrations**
4. Electrons in crystal lattices

Brillouin/Raman scattering

Solids: Lattice vibrations

- Vibrational modes and phonons
- Umklapp scattering
- Brillouin and Raman scattering
- Inelastic neutron scattering
- Heat capacity of the crystal lattice

Brillouin and Raman scattering 1

Brillouin and Raman scattering

Inelastic scattering of visible light due to lattice vibrations

- Elastic scattering of X-rays on a static crystal lattice:

  Laue condition $\boxed{\vec{k} - \vec{k}' = \vec{K}}$

- For visible light $\lambda \approx 400\,\mathrm{nm}$ to $600\,\mathrm{nm}$, i.e.

$$k = \frac{2\pi}{\lambda} \approx 10^7\,\mathrm{m}^{-1} \quad \text{to} \quad 1.6 \cdot 10^7\,\mathrm{m}^{-1}$$

- The length of the reciprocal lattice vectors is with $a \approx 3 \cdot 10^{-10}\,\mathrm{m}$, i.e.

$$K \approx \frac{2\pi}{a} = 2 \cdot 10^{10}\,\mathrm{m}^{-1} >> k \quad : \text{no reciprocal lattice vector is involved}$$

Brillouin and Raman scattering 1 Comment 1

The third lecture dealt with the scattering of X-rays on a static crystal lattice.

The energy of the incident and the scattered photon is the same and the Laue condition for elastic scattering results.

In this and the next section, the scattering on a dynamic crystal lattice is discussed.

Due to the lattice vibrations, the crystal lattice can transfer energy to the incident wave or withdraw energy from the incident wave.

Brillouin and Raman scattering describe the inelastic scattering of visible light on a crystal lattice.

Brillouin and Raman scattering 1 Comment 2

Since the wave numbers of visible light ($k \approx 10^7\,\mathrm{m}^{-1}$) are very small compared to the length of the reciprocal lattice vectors ($K \approx 10^{10}\,\mathrm{m}^{-1}$), no reciprocal lattice vector according to the Laue condition can be involved in the scattering of visible light, i.e. $\vec{K} = 0$ in the Laue condition.

Nevertheless, visible light is elastically scattered on crystal lattices.

The reason for this lies in statistical fluctuations in the density of the crystal lattice.

This type of scattering is called Rayleigh scattering.

Brillouin and Raman scattering 2

- **Brillouin scattering:** emission or absorption of an acoustic phonon
- **Raman scattering:** emission or absorption of an optical phonon

by a photon in the range of visible light

Emission of a phonon

$$\boxed{\begin{aligned} \hbar\vec{k} - \hbar\vec{k}' &= +\hbar\vec{q} \\ \hbar\omega(\vec{k}) - \hbar\omega(\vec{k}') &= +\hbar\omega(\vec{q}) \end{aligned}}$$

Absorption of a phonon

$$\boxed{\begin{aligned} \hbar\vec{k} - \hbar\vec{k}' &= -\hbar\vec{q} \\ \hbar\omega(\vec{k}) - \hbar\omega(\vec{k}') &= -\hbar\omega(\vec{q}) \end{aligned}}$$

Brillouin and Raman scattering 2 Comment

The inelastic scattering of light on a crystal lattice is usually described in the particle picture.

Photons scatter on the quantum particles of the lattice vibrations - the phonons.

The most important process is the emission or absorption of a phonon by a photon

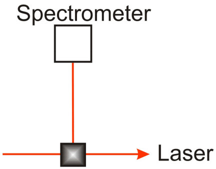
The equations outlined in red show the law of conservation of energy and momentum for these processes.

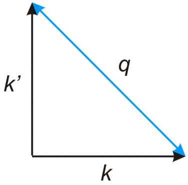
If a photon is involved in an acoustic branch, one speaks of Brillouin scattering.

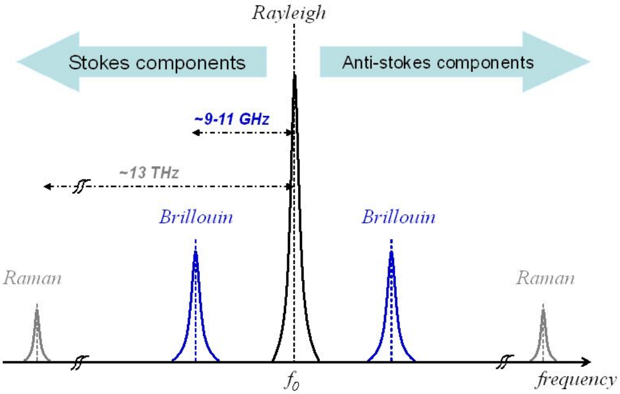
If a phonon is involved in an optical branch, one speaks of Raman scattering.

Chandrasekhara Venkata Raman was awarded the Nobel Prize in 1930 “for his work on the scattering of light and for the discovery of the effect named after him”

Brillouin and Raman scattering 3







Note: frequency of visible light is in the range between 500 and 750 THz

Brillouin and Raman scattering 3 Comment 1

The figure on the left shows the basic setup for measuring the light scattering on a crystal.

A laser beam penetrates the crystal and a small part of the light is scattered laterally and analyzed with a spectrometer or interferometer.

The vector diagram outlines the law of conservation of momentum for the scattering of a photon on a phonon.

If the vector $\vec{q}$ points to $\vec{k}'$, a phonon is absorbed.

If the vector $\vec{q}$ points to $\vec{k}$, then a phonon is emitted.

The right figure shows a schematic sketch of the expected experimental results.

Brillouin and Raman scattering 3 Comment 2

The central peak is the elastic scattering named after J.W. Rayleigh (1842-1919).

The peaks on the left side are named after Sir George Gabriel Stokes.

He discovered in 1852 that the wavelength of fluorescent light is larger than the wavelength of the exciting wave.

For comparison: the frequency of visible light is in the range between 500 and 750 THz (i.e. $5 \cdot 10^{14}$ to $7.5 \cdot 10^{14}$ Hz)

The frequency shift of the Brillouin peak is small and lies in the range of a few GHz, since the frequency of acoustic phonons approaches zero at the Γ point.

The frequency shift of the Raman peak is in the range of a few THz due to the higher frequency of optical phonons.

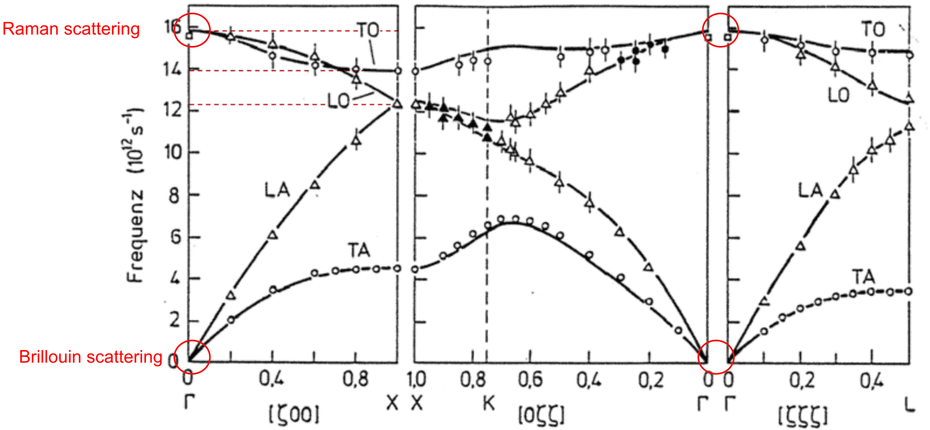
Brillouin and Raman scattering 3 Comment 3

The Stokes components correspond to the emission of a phonon by the incident photon.

The Anti-Stokes components correspond to the absorption of a phonon by the incident photon and the frequency is shifted to higher values.

Brillouin and Raman scattering 4

phonon dispersion of Silicon



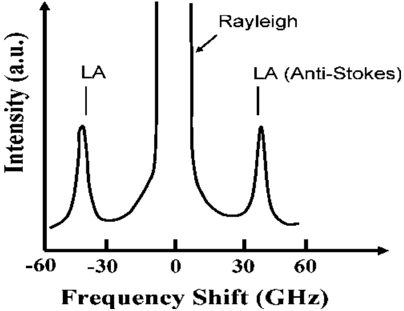
Brillouin and Raman scattering 4 Comment

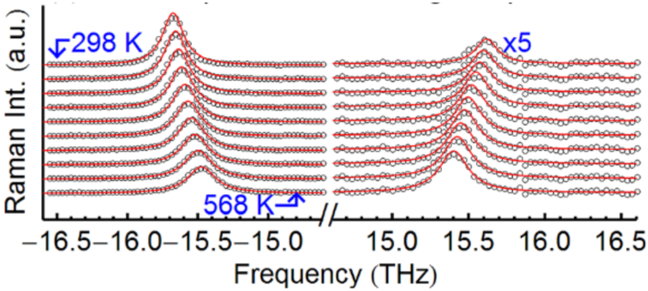
The figure shows the dispersion of the lattice vibrations in silicon.

The red circles show where in the dispersion spectrum of the lattice vibrations the phonons can be found that can be observed with Brillouin or Raman scattering.

Brillouin and Raman scattering 5

Brillouin and Raman scattering of Silicon





Brillouin and Raman scattering 5 Comment 1

The figure on the left shows an example of a Brillouin spectrum for silicon.

The shift depends on the momentum $\hbar\vec{q}$ of the phonon and the wavelength of the light used for the measurement.

The $\vec{q}$ vector of the phonon is determined by the geometry of the experiment.

The right figure shows the Raman scattering of Silicon.

The frequency shift is almost independent of the wavelength of the photon and the direction of the $\vec{q}$ vector of the phonon.

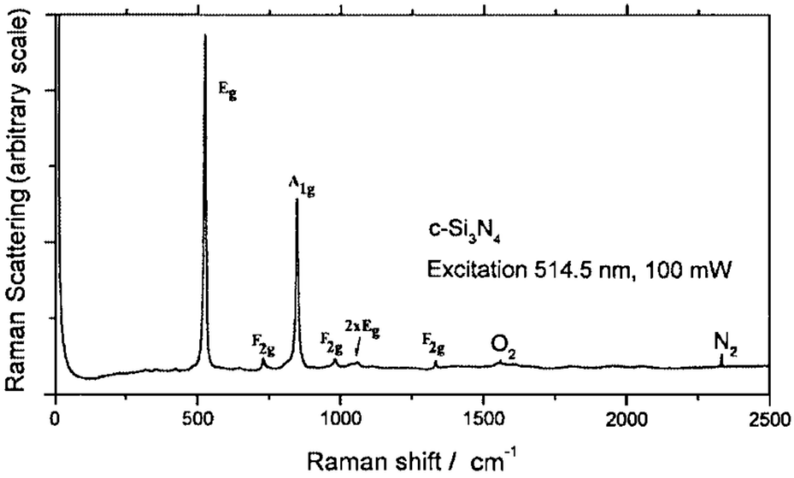
The Stokes line is much more intense than the Anti-Stokes line because only a few optical phonons are thermally excited, while many optical phonons can be excited or emitted by the oscillating electric field strength of the light wave.

Brillouin and Raman scattering 5 Comment 2

As the temperature rises, the Anti-Stokes line also becomes more intense.

The frequency of the Raman shift decreases with increasing temperature, suggesting that the lattice becomes softer with increasing temperature.

Brillouin and Raman scattering 6



Brillouin and Raman scattering 6 Comment

Since the Raman shift is independent of the wavelength of the incident photon, Raman scattering can be used to measure the vibrational frequencies of molecules and their surroundings.

The figure shows a measurement of cubic silicon nitride.

A multitude of different oscillation frequencies can be observed by measuring with one wavelength of light.

Alternatively, these vibrations would have to be observed directly during absorption or emission measurements.

Inelastic neutron scattering

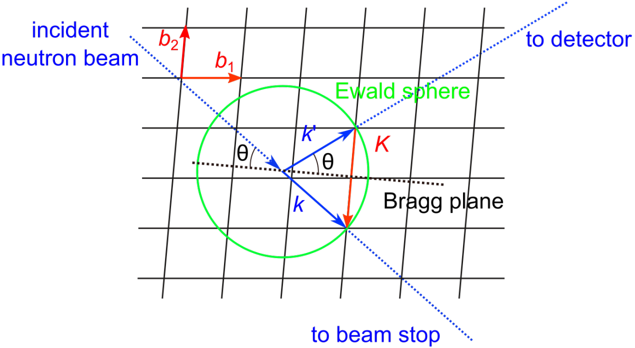
Solids: Lattice vibrations

- Vibrational modes and phonons
- Umklapp scattering
- Brillouin and Raman scattering
- Inelastic neutron scattering
- Heat capacity of the crystal lattice

Inelastic neutron scattering 1

For thermal neutrons and X-rays, the wavelength is smaller than the lattice parameters, i.e. $\lambda < a$ and $k > b$

Laue condition for elastic scattering $\boxed{\vec{k} - \vec{k}' = \vec{K}}$ or $\boxed{\vec{k} = \vec{k}' + \vec{K}}$



Inelastic neutron scattering 1 Comment 1

For thermal neutrons and X-rays, the wavelength is smaller than the dimensions of the primitive unit cell, i.e. $\lambda < |\vec{a}_{1,2,3}|$.

In the case of thermal neutrons, the kinetic energy is in the range of the thermal energy $k_\mathrm{B}T$.

The wave number k is therefore larger than the lattice parameters of the reciprocal lattice.

For elastic scattering, the Laue condition must be met.

If the Laue condition is interpreted as the law of conservation of momentum, the reciprocal lattice K denotes the momentum transfer to the crystal lattice.

No energy transfer is associated with this momentum transfer.

Inelastic neutron scattering 1 Comment 2

In classical mechanics, this corresponds to the elastic reflection of a rubber ball on a solid wall.

The figure illustrates the situation of elastic scattering of thermal neutrons and X-rays on a crystal lattice.

All reciprocal lattice points that lie on the surface of the Ewald sphere lead to an elastic scattering of the incident particles.

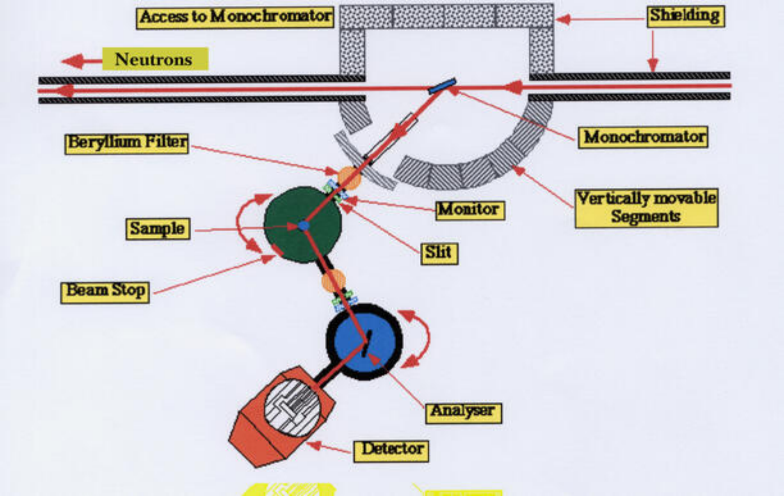
Inelastic neutron scattering 2

Triple axis neutron spectrometer

Inelastic neutron scattering 2 Comment

The classic setup for measuring the scattering of thermal neutrons on a crystal lattice is a three-axis neutron spectrometer.

Inelastic neutron scattering 3



Inelastic neutron scattering 3 Comment 1

The figure shows the experimental setup schematically.

Neutrons are created when ^{235}U decays or when other atomic nuclei are stimulated to decay by bombarding them with high-energy protons.

The high-energy neutrons are slowed down to thermal energy in a moderator (liquid water, H_2 or methane).

The wavelength of the neutrons is determined by the Bragg reflection on a crystal, the monochromator.

Monochromators are made from pyrolytic graphite, Si, Ge, Cu or magnetic alloys.

Magnetic monochromators are used to generate spin polarized neutrons for studying magnetic structures.

Inelastic neutron scattering 3 Comment 2

A berylium filter is used to remove spurious radiation, i.e. high energy neutrons or photons.

The number of incoming neutrons is measured with the monitor.

The monitor is a chamber filled with ^{3}He.

^{3}He efficiently captures neutrons and decays into a proton (^{1}H) and tritium (^{3}H) with an energy release of 0.76 MeV.

The number of protons and tritium nuclei produced in the chamber is a measure of the incident neutron flux.

The sample can be rotated.

Inelastic neutron scattering 3 Comment 3

The analyzer measures the energy of the scattered neutrons

For this purpose, the wavelength is measured by means of Bragg reflection on a second crystal.

In the detector, the incoming thermal neutrons are detected by an efficient capture reaction.

Suitable materials are ^{3}He, ^{6}Li, ^{10}B, ^{155}Gd, ^{157}Gd, and ^{235}U.

Inelastic neutron scattering 4

conservation laws:

momentum

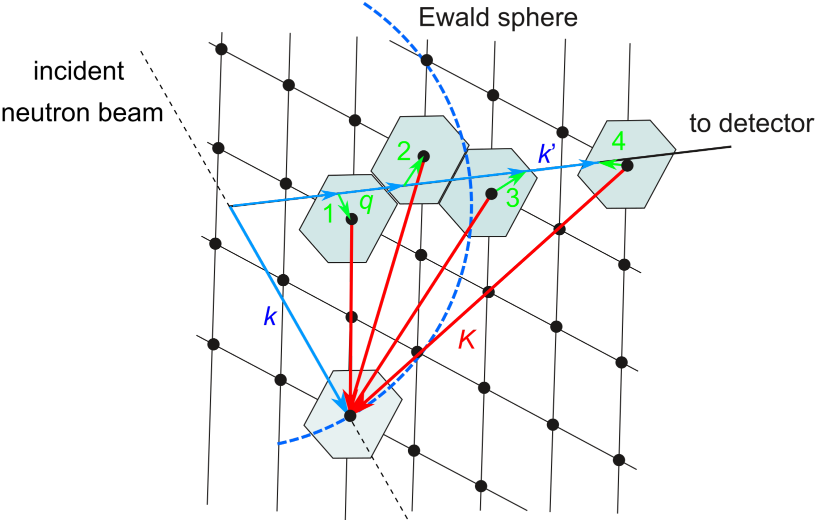
$$\boxed{\vec{k} - \vec{k}' = \vec{K} \pm \vec{q}}$$

energy

$$\boxed{E(\vec{k}) - E(\vec{k}') = \pm\hbar\omega(\vec{q})}$$

+: emission

−: absorption



Inelastic neutron scattering 4 Comment

The figure sketches the law of conservation of momentum for the case of inelastic scattering.

The black points show the reciprocal lattice.

The dashed line shows the Ewald sphere.

The vectors drawn in blue are the wave vectors of the incident and scattered neutrons.

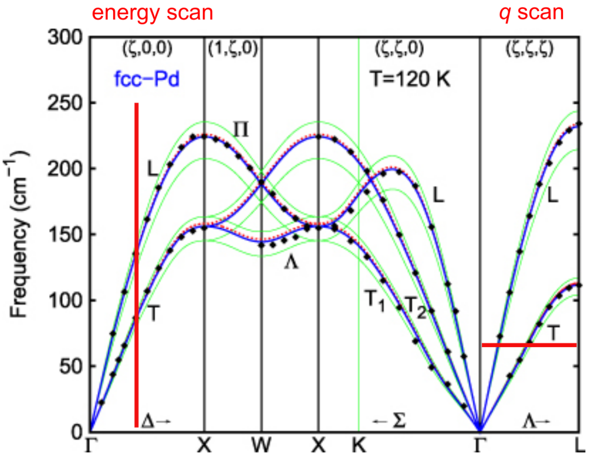
If the length of the wave vector of the scattered neutron is greater than the radius of the Ewald sphere, a phonon is absorbed ($E_{\mathrm{kin}} = \hbar^2 \vec{k}^2 / 2m_{\mathrm{n}}$).

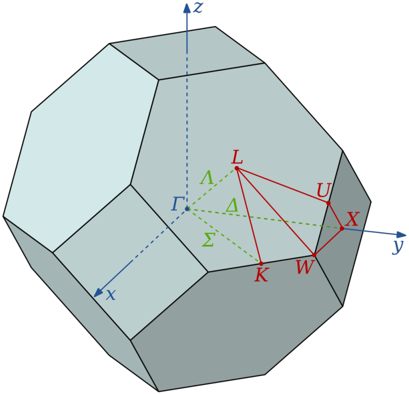
If the length of the wave vector is smaller than the radius of the Ewald sphere, a phonon is emitted.

The scattering events only take place, if in addition to conservation of momentum, the law of conservation of energy is also fulfilled.

Inelastic neutron scattering 5

measuring the dispersion branches of palladium





Inelastic neutron scattering 5 Comment

The figure once again shows the phonon dispersion of palladium as an example.

To measure this dispersion spectrum, one performs energy scans for a selected momentum.

This is indicated in the sketch by a red line for a selected momentum on the Δ-line connecting the Γ- and X-points.

Alternatively, a momentum scan can be carried out.

In the sketch, a red line indicates a momentum scan along the Λ-line connecting the Γ-point to the L-point

Inelastic neutron scattering 6

- momentum conservation law

$$\boxed{\vec{k} - \vec{k}' = \vec{K} \pm \vec{q}}$$

+: emission, −: absorption

- momentum transfer

$$\boxed{\vec{Q} = \vec{k} - \vec{k}'}$$

- momentum conservation law with momentum transfer

$$\underline{\vec{Q} = \vec{K} \pm \vec{q}}$$

- energy conservation law

$$\underline{E(\vec{k}) - E(\vec{k}') = \pm\hbar\omega(\vec{q})}$$

Inelastic neutron scattering 6 Comment

For the experiment it is important to consider the left and right sides of the law of conservation of momentum outlined in red.

The right side is determined by the reciprocal lattice vector $\vec{K}$ and the momentum to be measured $\vec{q}$.

The left side is the so-called momentum transfer $\vec{Q} = \vec{k} - \vec{k}\,'$.

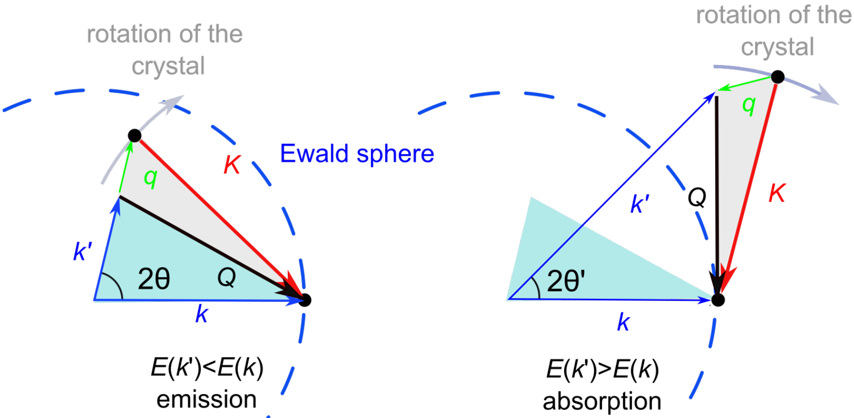
The momentum transfer is determined by the settings of the spectrometer.

The experimenter determines the scattering angle 2θ and the energy of the neutron to be detected, i.e. the length of the vector $\vec{k}\,'$.

Both 2θ and $|\vec{k}\,'|$ are varied until the law of conservation of energy is satisfied.

Inelastic neutron scattering 7: energy scan

$$\vec{Q} = \vec{k} - \vec{k}' \quad \text{and} \quad \vec{Q} = \vec{K} \pm \vec{q}$$



E(*k*')<*E*(*k*)
emission

E(*k*')>*E*(*k*)
absorption

Inelastic neutron scattering 7 Comment

The sketch illustrates the situation of an energy scan for the emission (left) and the absorption (right) of a phonon with momentum $\vec{q}$ at the reciprocal lattice vector $\vec{K}$.

To change the length of the vector $\vec{k}'$, the crystal must be rotated and the angle θ adjusted accordingly.

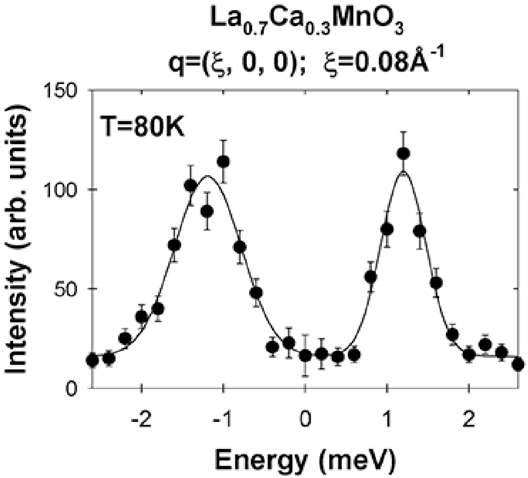
The gray triangle shows that the relative orientation of $\vec{q}$ and $\vec{K}$ is not changed, while the triangle spanned by $\vec{k}$ and $\vec{k}'$ is changed. This is highlighted by the blue triangle.

The sketch also illustrates the limits of neutron scattering.

If $|\vec{q}|$ is small, the scattering condition is satisfied near the Ewald sphere and the signal is dominated by the elastic scattering of the neutrons.

This is the range of Brillouin- and Raman-scattering.

Inelastic neutron scattering 8



Inelastic neutron scattering 8 Comment

The figure shows an example of such a measurement.

The left peak gives the emission and the right peak the absorption of a phonon with the wave vector $\vec{q} = (\xi = 0.08 \cdot 10^{10}\,\mathrm{m}^{-1}, 0, 0)$.

With neutrons, not only phonons but also magnetic excitations of the crystal lattice can be observed, since neutrons have a magnetic moment.

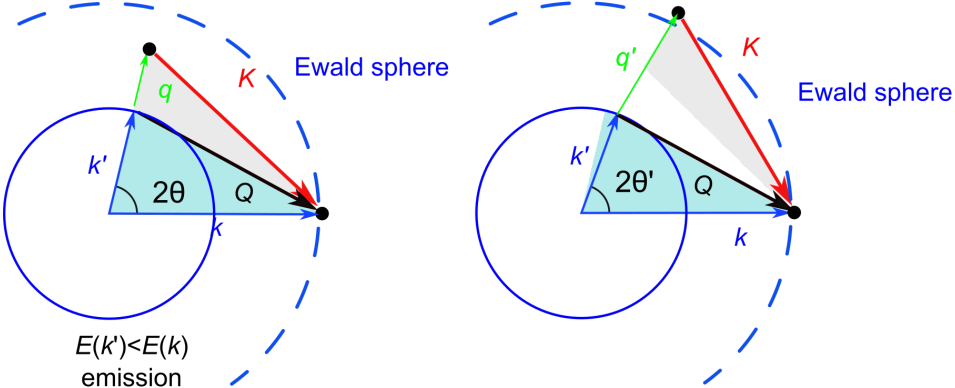
The quantum particles of magnetic excitations are called magnons in analogy to phonons and photons.

For example, waves can be excited in ordered magnetic structures (ferromagnets, antiferromagnets, etc.). These waves are called spin waves.

As with the lattice vibrations, the dispersion of the spin waves can be measured with neutrons.

Inelastic neutron scattering 9: *q*-scan

$\vec{Q} = \vec{k} - \vec{k}'$ and $\vec{Q} = \vec{K} \pm \vec{q}$



$E(k')<E(k)$
emission

Inelastic neutron scattering 9 Comment

The figure illustrates the situation of a q-scan.

The orientation of the crystal must be changed and the scattering angle 2θ adjusted accordingly. This is indicated by the blue triangle.

The gray triangle shows that the relative orientation between the vectors $\vec{q}$ and $\vec{K}$ is not changed. Only the length of $\vec{q}$ is varied.

Heat capacity

Solids: Lattice vibrations

- Vibrational modes and phonons
- Umklapp scattering
- Brillouin and Raman scattering
- Inelastic neutron scattering
- Heat capacity of the crystal lattice

Heat capacity of the crystal lattice 1

heat capacity

$$\boxed{C = \left.\frac{\partial E}{\partial T}\right|_{V\,or\,p}}$$

specific heat capacity: heat capacity per mass, molar amount etc.

Heat capacity of the crystal lattice 1 Comment 1

The heat capacity indicates the change in energy when the temperature varies.

In order to clearly define the heat capacity, the conditions under which the temperature change takes place must be specified.

For example, if the volume is kept constant, a crystal does not have to do any expansion work.

Usually a crystal expands when heated.

When the thermal expansion is suppressed, the elastic energy in the bonds greatly increases.

The thermal work of expansion is negligible compared to the elastic energy that is stored in the compressed bonds.

Heat capacity of the crystal lattice 1 Comment 2

Therefore the heat capacity of a crystal measured at constant pressure is smaller than the heat capacity measured at constant volume.

Usually, the heat capacity per mass of the crystal or the number of primitive unit cells of the crystal, etc. is measured.

This is known as the specific heat capacity.

In this section the heat capacity due to the vibrations of a crystal lattice is discussed.

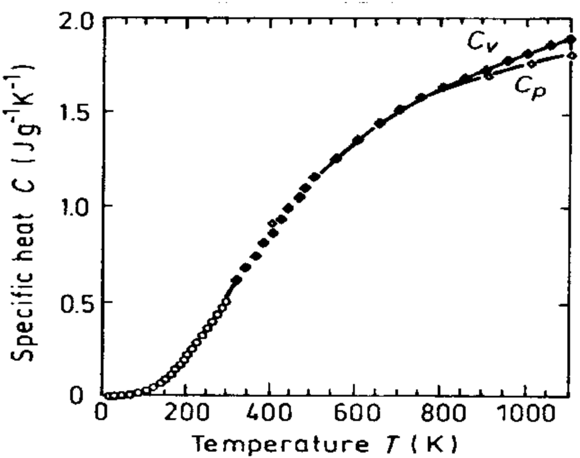
The quantization of the lattice oscillations is used below.

This allows a first approximation of the heat capacity.

But many effects are ignored (phonon-phonon scattering, thermal expansion, etc.) that are necessary for a complete description of heat capacity.

Heat capacity of the crystal lattice 2

specific heat capacity of diamond



Heat capacity of the crystal lattice 2 Comment

The figure shows the specific heat capacity of diamond.

The difference between measurements at constant volume and constant pressure is only noticeable at very high temperatures.

At zero temperature there are no phonons and the heat capacity disappears as the temperature approaches zero.

At high temperatures, the thermal capacity measured at constant pressure increases linearly due to the thermal expansion of the lattice.

If the heat capacity is measured at constant volume, i.e. the expansion of the solid is hindered, the elastic energy stored in the bonds increases the heat capacity at high temperatures.

Heat capacity of the crystal lattice 3

The Boltzmann factor gives the probability p_n that there are n phonons with the frequency ω and the wave vector $\vec{q}$.

$$p_n = \frac{1}{Z} \exp\left(-\frac{n\hbar\omega(\vec{q})}{k_B T}\right)$$

The average number $\bar{n}$ of phonons in thermal equilibrium with frequency ω and wave vector $\vec{q}$ is

$$\boxed{\bar{n} = \frac{1}{\exp(\hbar\omega(\vec{q})/k_B T) - 1}}$$

The average energy $\overline{E}$ of phonons in thermal equilibrium with frequency ω and wave vector $\vec{q}$ is

$$\boxed{\overline{E} = \frac{\hbar\omega(\vec{q})}{\exp(\hbar\omega(\vec{q})/k_B T) - 1}} = \bar{n}\hbar\omega(\vec{q})$$

Heat capacity of the crystal lattice 3 Comment 1

The thermal equilibrium of phonons can be described with the Boltzmann factor.

The probability that there are n phonons of a special phonon mode can be calculated with the Boltzmann factor of the line underlined in red.

In this formula, Z denotes the partition sum, i.e. the sum of all exponential functions $\exp(-n\hbar\omega/k_B T)$ starting with $n = 0$ to $n \to \infty$, i.e.

$$Z = \sum_{n=0}^{\infty} \exp(-\mathrm{n}\hbar\omega/k_\mathrm{B} T) = \frac{1}{(1 - \exp(-\hbar\omega/k_\mathrm{B} T))}$$

The average phonon number $\bar{n} = \sum_{n=0}^{\infty} n p_n$ can be calculated with the Boltzmann factor and is given by the first boxed equation.

Heat capacity of the crystal lattice 3 Comment 2

auxiliary calculation: with $x = \hbar\omega/k_\mathrm{B}T$ and $Z = \sum_{n=0}^{\infty} \exp(-nx)$

$$\frac{\partial Z}{\partial x} = -\sum_{n=0}^{\infty} n \exp(-nx) \quad \text{and} \quad \frac{1}{Z}\frac{\partial Z}{\partial x} = -\sum_{n=0}^{\infty} n p_n = \frac{1}{Z}\frac{\partial}{\partial x}\left(\frac{1}{1-e^{-x}}\right)$$

i.e.

$$\bar{n} = -\frac{1}{Z}\frac{\partial}{\partial x}\left(\frac{1}{1-e^{-x}}\right) = -(1-e^{-x})\frac{(-1)e^{-x}}{(1-e^{-x})^2} = \frac{1}{e^x - 1}$$

The mean energy of the phonon mode with $\vec{q}$ and $\omega(\vec{q})$ in thermal equilibrium is then $\overline{E} = \bar{n}\hbar\omega(\vec{q})$.

This is the second equation outlined in red.

Heat capacity of the crystal lattice 3

Comment 3

Note that the same formula occurs in Planck’s law of radiation.

This is not surprising, since both phonons and photons are bosons.

Photon-Photon interactions are negligible small and phonon-phonon interactions are ignored in the calculation.

Heat capacity of the crystal lattice 4

The total energy of the phonons in thermal equilibrium is

$$\boxed{E = \sum_{\vec{q}} \sum_{b} \frac{\hbar\omega_b(\vec{q})}{e^{\hbar\omega_b(\vec{q})/k_B T} - 1}}$$

the sum runs over all phonon modes, i.e. over all wave vectors $\vec{q}$ and phonon branches b

and

- the number of $\vec{q}$-modes is equal to the number of primitive unit cells of the lattice
- the number of branches b is equal to three times the number of atoms n within the primitive unit cell

Heat capacity of the crystal lattice 4 Comment

The total energy of the phonons in thermal equilibrium results from the sum of all phonon modes.

A phonon is characterized by its wave vector $\vec{q}$ and the phonon branch.

The number of different wave vectors $\vec{q}$ corresponds to the number of primitive unit cells that form the crystal lattice, and the number of phonon branches is determined by the number of atoms within the primitive unit cells.

There are three acoustical branches for the first atom and three optical branches for each additional atom.

Heat capacity of the crystal lattice 5

High temperatures:

- $k_B T >> \hbar\omega_{\max}$

$$e^{\hbar\omega_b(\vec{q})/k_B T} \to 1 + \frac{\hbar\omega_b(\vec{q})}{k_B T}$$

- $$E = \sum_{\vec{q}} \sum_{b} \frac{\hbar\omega_b(\vec{q})}{e^{\hbar\omega_b(\vec{q})/k_B T} - 1} \to \boxed{\sum_{\vec{q}} \sum_{b} k_B T = N\, 3\, n k_B T}$$

  N : number of primitive unit cells

  n : number of atoms in a primitive unit cell

- the heat capacity $C = \partial E/\partial T$ is (rule of Dulong-Petit 1819)

$$\boxed{C = 3nNk_B}$$

Heat capacity of the crystal lattice 5 Comment 1

The limit value of the heat capacity at high temperatures results from the Taylor expansion of the exponential function.

The total energy of the phonons at high temperatures is simply proportional to temperature T.

The heat capacity of phonons becomes constant at high temperatures when thermal expansion (measurements at constant pressure) or the change in force constants between atoms can be neglected (measurements at constant volume).

In other words: The heat capacity of phonons becomes constant at high temperatures as long as the bonds between the atoms are not influenced by the lattice vibrations.

Heat capacity of the crystal lattice 5 Comment 2

The heat capacity is proportional to the number of primitive unit cells N and the number of atoms within the primitive unit cell n.

This result corresponds to the rule of Dulong-Petit, which Pierre Louis Dulong and Alexis Thérèse Petit found in 1819 when investigating gases.

In 1907 Albert Einstein showed why this rule also applies to solids.

In 1900 Max Planck assumed that matter consists of quantized oscillators.

From this assumption he derived his famous radiation law.

In 1907 Albert Einstein applied the oscillator model to calculate the heat capacity of a solid.

Heat capacity of the crystal lattice 5 Comment 3

He assumed that the oscillators vibrate independently so that there is no dispersion of the vibration frequency.

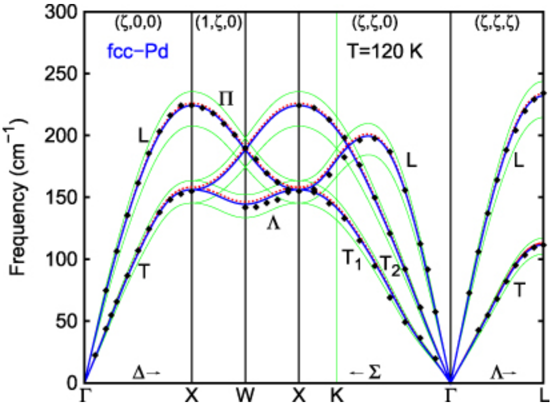
In the context of the Einstein model of heat capacity from 1907, $\omega(q)$ in the above formulae must be replaced by the constant frequency ω_E.

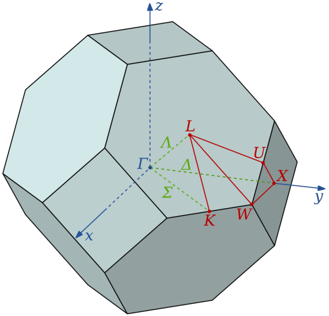
Einstein found the Dulong-Petit rule for solids, since neither the frequency nor the dispersion of the lattice vibrations at high temperatures contribute to the heat capacity.

This success in 1907 was a further indication that the quantization of energy is a general phenomenon of nature and is not limited to electromagnetic waves.

Heat capacity of the crystal lattice 6

High temperature limiting case of palladium:





$$T >> \frac{h\nu_{\mathrm{max}}}{\mathrm{k_B}} = \frac{4.14 \cdot 10^{-15}\,\mathrm{eVs} \cdot 220\,\mathrm{cm}^{-1} 3 \cdot 10^{10}\,\mathrm{cms}^{-1}}{8.617 \cdot 10^{-5}\,\mathrm{eVK}^{-1}} = 317\,\mathrm{K}$$

Heat capacity of the crystal lattice 6 Comment

The meaning of “high temperatues” is determined by the phonon dispersion of the lattice.

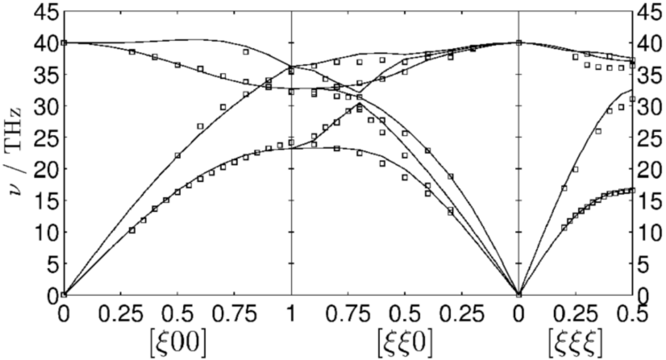
The figure shows the phonon dispersion of palladium.

The highest frequency is approximate $E/hc = 220\,\mathrm{cm}^{-1}$, i.e.
$\nu_{\mathrm{max}} = E/h = 220\,\mathrm{cm}^{-1} \cdot 3 \cdot 10^{10}\,\mathrm{cms}^{-1} = 6.6 \cdot 10^{12}\,\mathrm{Hz}$

Dividing $h\nu_{\mathrm{max}}$ by the Boltzmann constant results in a temperature of about 300 K.

Heat capacity of the crystal lattice 7

High temperature limiting case of diamond:



$$T >> \frac{h\nu_{\mathrm{max}}}{\mathrm{k_B}} = \frac{4.14 \cdot 10^{-15}\,\mathrm{eVs} \cdot {\color{blue}40 \cdot 10^{12}\,\mathrm{s}^{-1}}}{8.617 \cdot 10^{-5}\,\mathrm{eVK}^{-1}} = {\color{red}1926\,\mathrm{K}}$$

Heat capacity of the crystal lattice 7

Comment

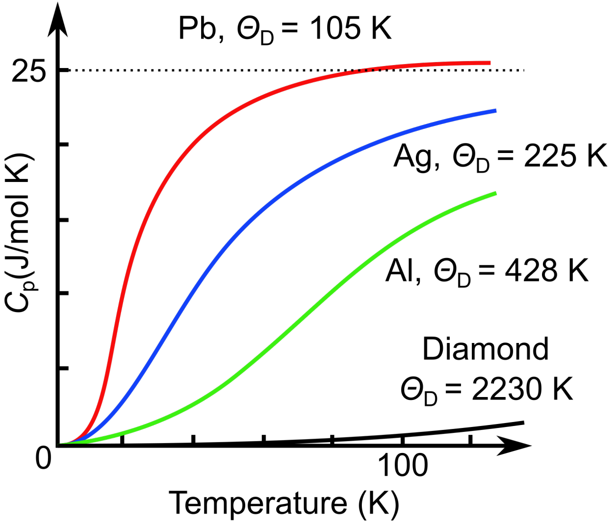
The figure shows the phonon dispersion of diamond.

Palladium and diamond both crystallize in an fcc lattice.

With diamond there are two atoms in the primitive unit cell, while with palladium there is only one atom.

Diamond’s highest phonon frequency of $40 \cdot 10^{12}$ Hz corresponds to a temperature of about 1900 K.

Heat capacity of the crystal lattice 8



Heat capacity of the crystal lattice 8 Comment 1

The figure compares the specific heat capacity of different crystalline substances.

The heat capacity refers to the molar amount of substances, i.e. the number of atoms measured in units of the Avogadro number ($6 \cdot 10^{23}\,\mathrm{mol}^{-1}$).

The limit case of high temperature is reached for lead (Pb) at much lower temperatures than e.g. for diamond.

A small calculation gives the value $3N_\mathrm{A}k_\mathrm{B} = 24.94\,\mathrm{Jmol}^{-1}\mathrm{K}^{-1}$.

The measurement of lead exceeds this value at about 90 K.

There are two reasons.

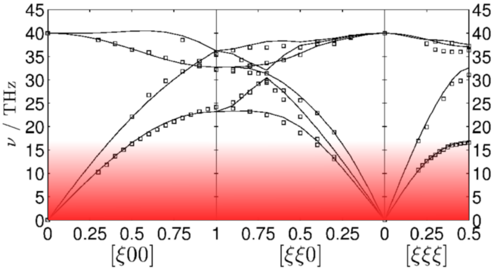
Heat capacity of the crystal lattice 8 Comment 2

On the one hand, the thermal expansion contributes to the heat capacity, on the other hand, in addition to the contribution of the lattice vibrations, there is also the contribution of the conduction electrons, which also increases proportionally to the temperature.

Θ_D denotes the Debye temperature, which is used to characterize the heat capacity of a solid.

Heat capacity of the crystal lattice 9

Low temperature:



- only the acoustic phonon branches can be excited
- the dispersion is linear for small phonon energy

$$\boxed{\omega(q) = c_s q}$$

Heat capacity of the crystal lattice 9 Comment 1

The figure shows once more the phonon dispersion of diamond.

The area marked in red shows the thermal activation of the phonon modes.

At low temperatures, only the acoustic branches of the dispersion of the lattice vibrations can be thermally activated.

The relationship between frequency and wave number is linear if the activated frequencies are not too high.

The equation outlined in red shows the linear relationship between the frequency and the wavenumber q of the phonons.

The constant of proportionality is the speed of sound in the crystal lattice, which of course depends on the polarization and the direction of propagation of the wave.

Heat capacity of the crystal lattice 9

Comment 2

The dispersion of the acoustic lattice vibrations in the vicinity of the Γ point is similar to the dispersion of the photons in a vacuum.

The speed of light must be replaced by the respective speed of sound.

Heat capacity of the crystal lattice 10

Photons: Stefan-Boltzmann law

$$\underline{P = A\sigma T^4}$$

Phonons at low temperatures

$$\underline{E \propto T^4}$$

heat capacity of a crystal lattice at low temperatures

$$\boxed{C \propto T^3}$$

Heat capacity of the crystal lattice 10 Comment 1

The linear phonon dispersion for small frequencies has an important effect on the heat capacity at low temperatures.

The Stefan-Boltzmann law is a consequence of the linear relation between the frequency and wave number of photons.

The Stefan-Boltzmann law states that the total radiation power in thermal equilibrium is proportional to T^4.

The total radiation power of a photon gas is proportional to the total energy of the photon gas.

Heat capacity of the crystal lattice 10 Comment 2

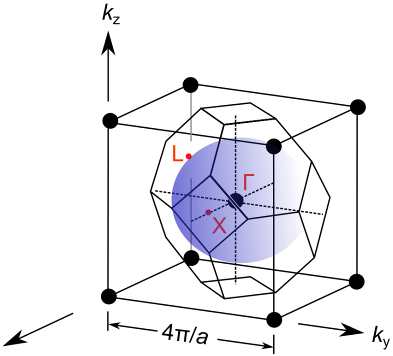
The same applies to a phonon gas if only the linear part of the phonon dispersion is thermally excited.

The total energy of the lattice vibrations is proportional to T^4 in this case and the heat capacity of a crystal lattice is therefore proportional to T^3 at low temperatures.

The T^3-law of the heat capacity at low temperatures due to the phonons is fundamental and usually dominates the heat capacity at low temperatures.

Heat capacity of the crystal lattice 11

Debye model (1912)



- replace the 1st Brillouin zone by a sphere
- the radius of the sphere $q_{\max}$ is determined by the condition

$$N = \frac{\frac{4}{3}\pi q_{\max}^3}{(2\pi)^3/V}$$

- the Debye temperature Θ_D is given by the highest phonon energy divided by Boltzmann's constant

$$\boxed{\Theta_D = \frac{\hbar c_s q_{max}}{k_B}} \quad \text{or} \quad \Theta_D = \frac{hc_s}{2k_B}\sqrt[3]{\frac{6}{\pi}\frac{N}{V}}$$

Heat capacity of the crystal lattice 11 Comment 1

The Einstein model of heat capacity from 1907 fails at low temperatures because the frequency of the lattice vibrations cannot be described by a fixed frequency ω_E.

In 1912 Peter Debye therefore proposed a model for calculating the heat capacity of the crystal lattice at low temperatures, which is based on the linear dispersion relation of sound waves.

The shape of the 1$^{\mathrm{st}}$ Brillouin zone does not matter at low temperatures, since lattice vibrations can only be excited near the Γ point. Therefore Peter Debye replaces the 1$^{\mathrm{st}}$ Brillouin zone with a simple sphere.

The sketch on the left illustrates this idea.

Heat capacity of the crystal lattice 11 Comment 2

The figure shows the cubic unit cell of the reciprocal lattice for an fcc lattice, the 1st Brillouin zone and the sphere of the Debye model drawn in blue.

The radius of the sphere q_{max} is determined by the requirement that the number of q-modes in the sphere is equal to the number of primitive unit cells in the crystal lattice, i.e. that the number of q-modes in the 1st Brillouin zone is equal to the number of q-modes enclosed by the sphere.

The formula underlined in red formulates this requirement.

The multiplication of the radius of the sphere q_{max} by an average speed of sound c_S gives the maximum phonon frequency of the Debye model ω_{max}.

The maximum energy of the Debye model is $\hbar\omega_{\mathrm{max}} = \hbar c_s q_{\mathrm{max}}$.

Heat capacity of the crystal lattice 11 Comment 3

The Debye temperature Θ_D is obtained by dividing the maximum energy by the Boltzmann constant.

The formula outlined in red gives the Debye temperature.

The Debye model describes the heat capacity only for temperatures that are much lower than the Debye temperature.

The Debye temperature is usually an experimental parameter that is determined by fitting the Debye model to measurements of heat capacity

$$C = Nk_B \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D} \right)^3 .$$

N denotes the number of primitive unit cells.

This formula is obtained by exploiting the equation on slide 4. The calculation can be found in many textbooks.

Heat capacity of the crystal lattice 12

diamond	2230 K
Si	645 K
Cr	610 K
Fe	470 K
Mo	450 K
Al	428 K
Ge	374 K

Table of Debye temperatures

Heat capacity of the crystal lattice 12

Comment

The table gives the Debye temperatures of some substances.

The harder the material, the higher the speed of sound and, accordingly, the Debye temperature.

Solids

1. Binding types
2. Crystal lattices
3. Lattice vibrations
4. Electrons in crystal lattices

Revision

Summary in Questions

1. Explain the difference between Brillouin and Raman scattering and give the typical frequency range of Brillouin and Raman spectra.
2. Sketch an experimental setup to measure Brillouin and Raman scattering.
3. Explain why Raman spectroscopy is widely used in chemistry.
4. Write down the law of conservation of energy for the absorption of a phonon by a neutron.
5. Write down the law of conservation of momentum for the absorption of a phonon by a neutron.
6. Calculate the molar specific heat capacity of a crystal lattice at high temperatures.
7. How does the heat capacity of the crystal lattice depend on temperature at low temperatures?
8. How is the Deby temperature Θ_D defined? How does Θ_D depend on the number of primitive unit cells and the speed of sound?