Solids

1. Types of binding
2. Crystal lattices
3. Lattice vibrations
4. Electrons in crystal lattices

Solids: Lattice vibrations

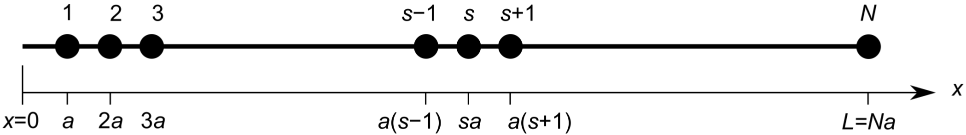
- Vibrational modes and phonons
- Umklapp scattering
- Brillouin- and Raman-scattering
- Inelastic neutron scattering
- Heat capacity of the crystal lattice

Monatomic chain

Vibrational modes and phonons

- Monatomic chain of atoms
- Crystal with one atom per primitive unit cell
- Diatomic chain of atoms
- Crystal with *n* atoms per primitive unit cell
- Phonons and Crystal momentum

Monatomic chain of atoms1



atoms oscillate around their equilibrium positions

(laufendeWelleundreflektierteWelle.mp4)

Monatomic chain of atoms 1 Comment

The sketch shows a chain of N equal atoms.

The distance between the atoms is the lattice parameter a of the one-dimensional lattice.

The rest position of the atoms is indicated by the index s starting with $s = 1$ up to $s = N$.

The video of a chain of coupled pendulums can serve as a model for the atoms of a crystal lattice.

Atoms of a solid can swing around their equilibrium positions, similar to the pendulums in the model.

And as with the model of the coupled pendulums, waves can propagate in a crystal lattice.

Monatomic chain of atoms 2

the shift of the atoms from their equilibrium positions is described by the vector $\vec{u}(x)$, i.e.

$$\boxed{\vec{u}(x) = \vec{u}_0 \exp i(kx - \omega(k)t)}$$

Newton's equation of motion

$$\underline{m\ddot{\vec{u}}(sa) = D\{\vec{u}(a(s+1)) - \vec{u}(sa)\} + D\{\vec{u}(a(s-1)) - \vec{u}(sa)\}}$$

gives the angular frequency

$$\boxed{\omega(k) = 2\sqrt{\frac{D}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|}$$

- one longitudinal mode $\vec{u}_0 \parallel x$-axis
- two transversal modes $\vec{u}_0 \perp x$-axis

Monatomic chain of atoms 2 Comment 1

The displacement of the atoms from their equilibrium positions can be described by the vector $\vec{u}(x)$.

The video shows that waves can propagate on a chain of coupled pendulums.

Waves can also propagate on a chain of atoms that can exert forces on one another.

The motion of the atoms is determined by Newton’s equation of motion.

The wave function $\vec{u}(x)$ outlined in red is a reasonable ansatz to solving Newton’s equation of motion.

In a chain of atoms, two forces act on the mass of an atom.

One force on the right and one on the left of the atom.

Monatomic chain of atoms 2 Comment 2

The first curly bracket indicates the force on the right and the second curly bracket indicates the force on the left.

If the displacement of the atoms from equilibrium is not too big, then the force is proportional to the difference in the displacement vectors.

If a harmonic wave is used as the solution, the formula outlined in red results for the relationship between the angular frequency of the wave and the wave number.

$$\begin{aligned}
-m\omega^2 u(sa) &= Du(sa)\{(\exp(ika)-1)+(\exp(-iak)-1)\} \\
&= Du(sa)\{\exp(ika/2)\cdot 2i\sin(ka/2)+\exp(-ika/2)\cdot(-2i)\sin(ka/2)\} \\
&= Du(sa)(-4)\sin^2(ka/2)
\end{aligned}$$

In general, the constant of proportionality D of the force depends on the direction of the displacement vectors.

Monatomic chain of atoms 2 Comment 3

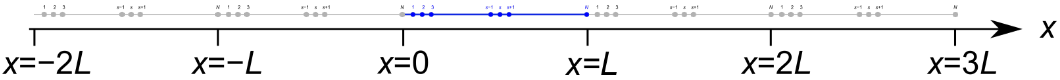
There is a longitudinal mode and two transverse modes.

The angular frequencies of the longitudinal and transverse modes are usually different.

Monatomic chain of atoms 3

- harmonic waves have no starting and no end point and describe not a finite chain

Periodic boundary conditions:



$$\underline{\vec{u}(sa) = \vec{u}(sa+L)}$$

the allowed wave numbers are

$$k_n L = 2\pi n \quad \text{and} \quad \boxed{k_n = \frac{2\pi}{L} n}$$

Monatomic chain of atoms 3 Comment 1

Harmonic waves are infinite and have no start and end point.

Therefore harmonic waves are not directly suitable to describe the properties of a finite chain or a finite crystal.

The video shows that the reflection creates standing waves at the end points of the chain.

In macroscopic systems, however, there are no standing waves, since the undisturbed propagation of the waves is hindered by scattering events.

So-called periodic boundary conditions are used to solve the problem.

The figure illustrates the approach.

Monatomic chain of atoms 3 Comment 2

The finite chain (or crystal in three dimensions) is formally repeated infinitely often, so that a virtual infinite chain with the period L is created.

Now it is required that every chain segment with the length L behaves in exactly the same way.

The formula underlined in red is the mathematical formulation of this requirement.

A Fourier series expansion can be used to describe a general periodic function with the period L.

Only those harmonic waves contribute to the Fourier series expansion that satisfy the condition $k_n L = 2\pi n$ with n $= \pm 1, \pm 2, \ldots$.

Monatomic chain of atoms 3 Comment 3

Only a discrete set of wave numbers is necessary to describe a general periodic function with the period L.

The general behavior of a finite chain of length L can be described by harmonic waves if the wave numbers are restricted to this set.

Monatomic chain of atoms 4

the largest possible wave length on the chain is

$$\lambda = L \quad \rightarrow \quad \boxed{|k| \geq \frac{2\pi}{L}}$$

the smallest possible wave length on the chain is $\lambda \geq 2a$

$$\rightarrow \quad \boxed{-\frac{\pi}{a} \leq k_n \leq \frac{\pi}{a}}$$

The number of different wave numbers k_n equals the number of atoms N

$$\boxed{\frac{\frac{2\pi}{a}}{\frac{2\pi}{L}} = \frac{L}{a} = N}$$

Monatomic chain of atoms 4 Comment

The smallest absolute value of the wave number is $k_1 = 2\pi/L$, i.e. the largest possible wavelength on the chain is $\lambda = L$.

The smallest wavelength on a chain with the lattice parameter a is $\lambda = 2a$.

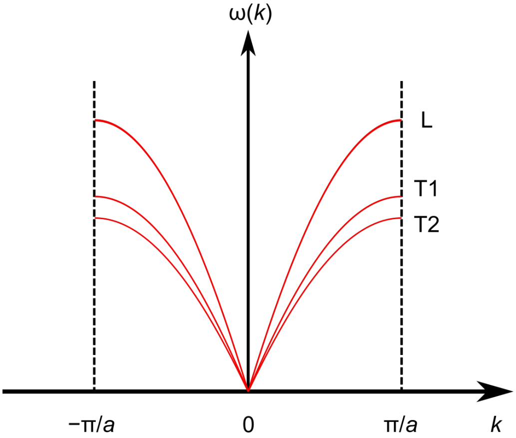
A shorter wavelength cannot be resolved with the distance a of the atoms.

Therefore, the wave number can be restricted to the range given by the second inequality outlined in red.

The range of these wave numbers divided by $2\pi/L$ gives the total number of wave numbers in this range.

This number is equal to the number of atoms in the chain.

Monatomic chain of atoms 5



Monatomic chain of atoms 5 Comment

The sketch summarizes the results.

There are three branches of dispersion for the oscillations of the chain: one longitudinal mode and two transversal modes.

The wave numbers are limited to the range between $-\pi/a$ and $+\pi/a$.

The total number of oscillation modes is $3N$ due to the three polarization directions.

N denotes the number of atoms in the chain.

One atom in V_{cell}

Vibrational modes and phonons

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Crystal with one atom per primitive unit cell 1

- The waves can propagate in three dimensions, i.e. $k \to \vec{k}$
- The range $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ for the chain has to be generalized

$$\boxed{\vec{k} \in 1^{\text{st}} \text{ Brillouin zone}}$$

- The volume of a $\vec{k}$-mode is $\left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$
- the volume of the 1st Brillouin zone is $V_{1^{\text{st}}\,\text{BZ}} = \frac{(2\pi)^3}{V_{Cell}}$
- the number of $\vec{k}$-modes is N

$$\boxed{N = \frac{V_{1^{\text{st}}\,\text{BZ}}}{(2\pi)^3/V} = \frac{V}{V_{Cell}}}$$

i.e. number of primitive unit cells within the crystal

Crystal with one atom per primitive unit cell 1 Comment 1

If the vibrations of the atoms are considered in a three-dimensional crystal lattice, then the wave number must be generalized to the wave vector $\vec{k}$ and the wave number interval $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ to the 1st Brillouin zone.

The periodic boundary condition is now applied in all three spatial directions, which works most easily with a cube-shaped sample.

The difference between the wave numbers of a chain of $\frac{2\pi}{L}$ generalizes to $\left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$.

That is the volume that each wave vector can occupy in k-space.

Crystal with one atom per primitive unit cell 1 Comment 2

Periodic boundary conditions can only be used if the surface of a crystal does not affect the properties of the crystal, i.e. that due to the reflection of the waves on the surface of the crystal, no standing waves may form that extend over the entire crystal.

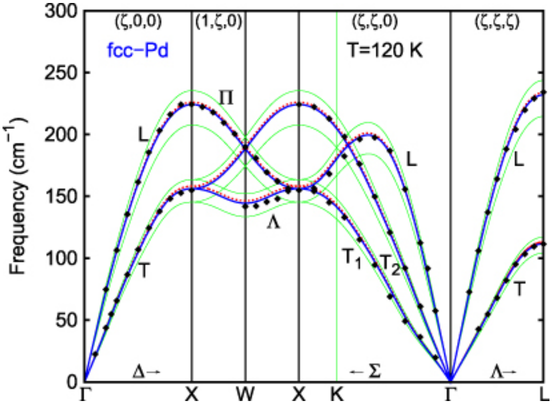
But if the surface of a crystal has no influence, one can abandon the assumption of a cube-shaped sample with the edge length L and replace L^3 with the volume V of a sample of any shape.

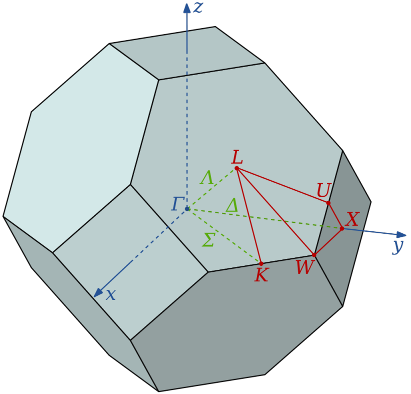
The number of different wave vectors results from dividing the volume of the 1st Brillouin zone by the volume that a wave vector can occupy.

The number of different wave vectors is equal to the number of primitive unit cells in the crystal lattice.

Crystal with one atom per primitive unit cell 2

dispersion branches of palladium





Crystal with one atom per primitive unit cell 2 Comment 1

In a crystal lattice it is not possible to plot the frequency of the lattice vibrations for all wave vectors.

One has to restrict oneself to certain characteristic wave vectors.

The figure shows the procedure using palladium (Atomic number (Z) 46, [Kr]$4d^{10}$) as an example.

Palladium crystallizes in an fcc lattice.

The figure on the right shows the 1st Brillouin zone of the fcc lattice.

The dispersion of the lattice vibrations is shown in the figure on the left along certain directions.

Crystal with one atom per primitive unit cell 2 Comment 2

If one starts on the left side of the figure, the wave vector points along a coordinate axis of the cubic unit cell (compare the figure on slide ”Reciprocal lattice 7” of the last lecture).

The direction is denoted by Δ and the frequency of the lattice oscillations is plotted for all wave vectors between Γ and X.

Along the coordinate axes there is a longitudinal mode and two transversal modes of the same frequency.

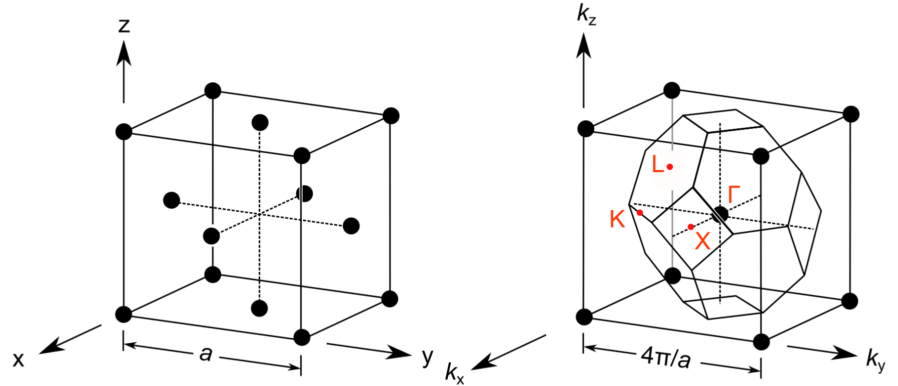
The frequency of the two transverse modes is the same, since the coordinate axes are four-fold axes of symmetry of the cube.

In the next column, the wave vectors end on the connecting line between points X and W.

Reciprocal lattice 7

Notice

The reciprocal lattice of an fcc lattice is a bcc lattice!



Crystal with one atom per primitive unit cell 2 Comment 3

For this orientation of the wave vectors, the frequencies of the two transverse modes are no longer the same.

On the right side of the figure, the wave vector lies on the connecting line Σ between Γ and K and on the connecting line Λ between Γ and L.

The line Σ denotes a twofold axis of symmetry that goes through one edge of the cubic unit cell.

The frequency of the two transverse modes is different.

The Λ line denotes a six-fold axis of symmetry that corresponds to the diagonals of the cubic unit cell.

Crystal with one atom per primitive unit cell 2 Comment 4

The frequencies of the two transverse modes are the same for this highly symmetrical direction.

The frequency of the longitudinal modes is always greater than the frequency of the transverse modes.

The force constant is consequently greater when the atoms swing directly towards one another than when they move to the side.

Finally, it makes sense to think about the temperature, which corresponds to an energy of $E/hc = 220\,\text{cm}^{-1}$.

$$E/k_B = \frac{4.14 \cdot 10^{-15}\,\text{eVs}\, 3 \cdot 10^{10}\,\text{cms}^{-1}\, 220\,\text{cm}^{-1}}{8.617 \cdot 10^{-5}\,\text{eVK}^{-1}} = 317\,\text{K}$$

This means that all lattice vibrations are excited at room temperature.

Diatomic chain

Vibrational modes and phonons

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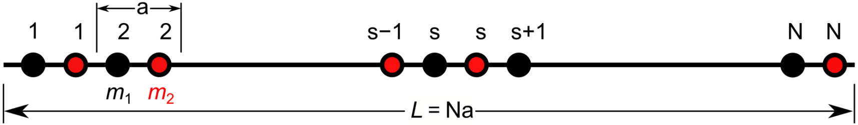
- Crystal with *n* atoms per primitive unit cell
- Phonons and Crystal momentum

Diatomic chain of atoms 1



the solution are harmonic waves

$$\vec{u}(x) = \vec{u}_0 \exp i(kx - \omega(k)t) \qquad \text{and} \qquad \vec{v}(x) = \vec{v}_0 \exp i(kx - \omega(k)t)$$

Newton's equation of motion

$$\boxed{\begin{aligned} m_1\ddot{u}(sa) &= D\{v(sa) - u(sa)\} \qquad\quad + D\{v((s-1)a) - u(sa)\} \\ m_2\ddot{v}(sa) &= D\{u((s+1)a) - v(sa)\} + D\{u(sa) - v(sa)\} \end{aligned}}$$

Diatomic chain of atoms 1 Comment 1

The figure shows a linear chain with two atoms in the primitive unit cell.

The lattice parameter is a.

The shift from the equilibrium position is $\vec{u}$ for the atoms with the mass m_1 and $\vec{v}$ for the atoms with the mass m_2.

The movement of the atoms around their equilibrium position is a harmonic oscillation which, due to the coupling of the atoms, leads to a wave that can propagate along the chain.

Newton’s equation of motion does not contain the absolute coordinates of the atoms, but only the positions of the primitive unit cells.

The reason for this is that the force with which the atoms act on each other is simply proportional to the displacement of the atoms from their equilibrium position.

Diatomic chain of atoms 1 Comment 2

As with the monatomic chain, the force depends on the direction of vibration of the atoms.

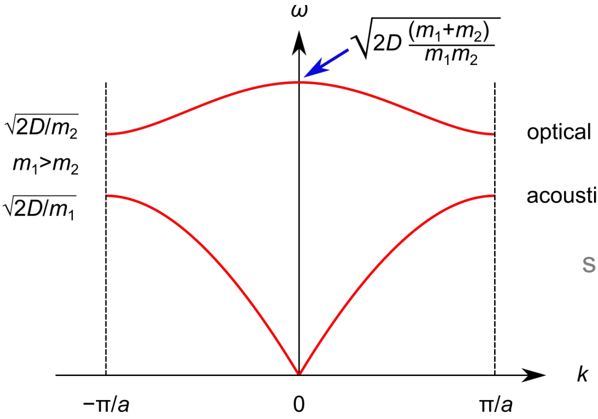
There are three main directions of vibration (L, i.e. longitudinal, T1 and T2, i.e. transversal 1 and 2), for which Newton's equations of motion can be solved independently of each other.

The equations of motion outlined in red correspond to one main directions of vibration.

The shifts correspond to this polarization direction, so that the vector arrows can be omitted.

The force constant generally has three different values for the three directions of polarization.

Diatomic chain of atoms 2



shift of the atoms in the unit cell at $x = sa$

$$u(sa) = u_{0,\text{branch}}(k)e^{i(k\cdot sa-\omega_{\text{branch}}(k)t)}$$

$$v(sa) = v_{0,\text{branch}}(k)e^{i(k\cdot sa-\omega_{\text{branch}}(k)t)}$$

Diatomic chain of atoms 2 Comment 1

The figure shows the dispersion relation of the diatomic chain, i.e. the solution of Newton's equation of motion for one direction of polarization, with the force constant D and $m_1 > m_2$.

The absolute positions of the atoms do not enter Newton's equation of motion, and the shift u and v are determined by the localization of the primitive unit cell, i.e. $x = sa$.

The formulas outlined in red explicitly show the solution of Newton's equations of motion for the two atoms within the primitive unit cell.

The amplitudes of the waves for the two types of atoms $u_{0,\text{branch}}$ and $v_{0,\text{branch}}$ depend on the wave number k and the dispersion branch.

Diatomic chain of atoms 2 Comment 2

As with the monatomic chain, the periodic boundary conditions can be applied and the corresponding results obtained for the monatomic chain remain valid.

The distance between two neighboring wave numbers is $2\pi/L$ and $\omega(k)$ is again shown in the range between $-\pi/a$ and $+\pi/a$.

The number of different wave numbers k_n between $-\pi/a$ and $+\pi/a$ corresponds to the number of primitive unit cells.

The figure shows the so-called acoustic branch and the optical branch of the dispersion of the lattice vibrations.

The acoustic branch begins with $\omega \propto k$ for $k \to 0$, as we know it for sound waves in a gas.

Diatomic chain of atoms 2

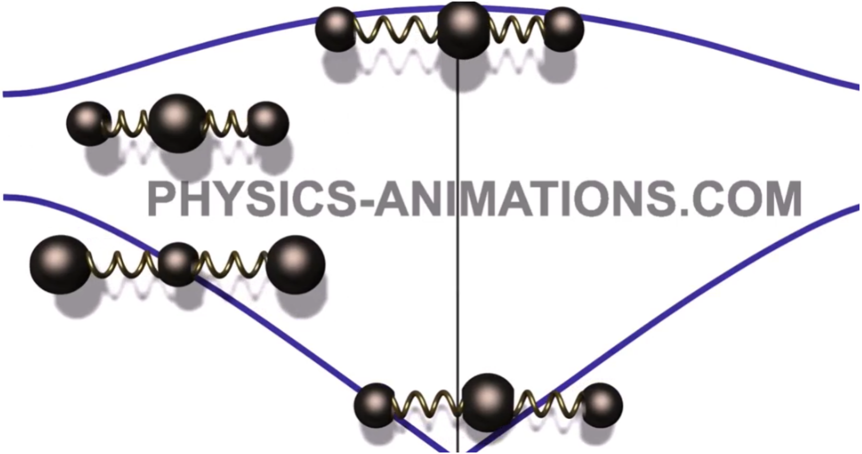
Comment 3

Both atoms in the primitive unit cell vibrate in the same direction.

At higher oscillation frequencies, an optical branch lies above the acoustic branch.

This branch is known as the optical branch because the atoms vibrate against each other, which in ionic crystals such as sodium chloride leads to oscillating electrical dipoles that can absorb and emit electromagnetic waves.

Diatomic chain of atoms 3



(Kette.mp4)

Diatomic chain of atoms 3 Comment 1

The animation shows the movement of the atoms for both branches for $k = 0$ and $k = \pi/a$.

For $k = 0$ all atoms in all primitive unit cells vibrate with the same phase.

In the acoustic branch the amplitudes $u_{0,\text{acoustic}}(k \to 0)$ and $v_{0,\text{acoustic}}(k \to 0)$ have the same sign and the atoms vibrate in the same direction.

In the optical branch the amplitudes have opposite signs, i.e. $u_{0,\text{optical}}(k \to 0) = -v_{0,\text{optical}}(k \to 0)$, and the atoms vibrate against each other.

At the borders of the first Brillouin zone, i.e. for $k = \pm\pi/a$, the sign of the oscillation between neighboring unit cells changes because of $e^{i(ksa)} = e^{i\pi s}$.

Diatomic chain of atoms 3

Comment 2

In the acoustic branch the smaller masses $m_2 < m_1$ are at rest, i.e. $v_{0,\text{acoustic}}(k = \pm\pi/a) = 0$, and the heavier masses m_1 swing against the smaller masses m_2.

In the optical branch the smaller masses m_2 oscillate, i.e. $v_{0,\text{optical}}(k = \pm\pi/a) \neq 0$, whereas the heavier mass m_1 is at rest.

The frequency of the vibration is consequently higher.

n atoms in V_{cell}

Vibrational modes and phonons

- Monatomic chain of atoms
- Crystal with one atom per primitive unit cell
- Diatomic chain of atoms
- Crystal with *n* atoms per primitive unit cell
- Phonons and Crystal momentum

Crystal with n atoms per primitive unit cell 1

Rules

- The number of different $\vec{k}$ vectors in the 1st Brillouin zone corresponds to the number of primitive unit cells that make up the crystal
- For one atom per primitive unit cell there are three acoustic branches (LA, TA1, and TA2)
- For each additional atom in the primitive unit cell there are three optical branches (LO, TO1, and TO2)

Crystal with *n* atoms per primitive unit cell 1 Comment

This page summarizes the rules for a crystal.

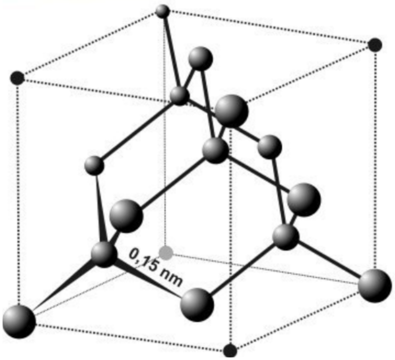
Except for the last rule, all rules for a crystal with *n* atoms per primitive unit cell agree with the rules for crystals with only one atom in the primitive unit cell.

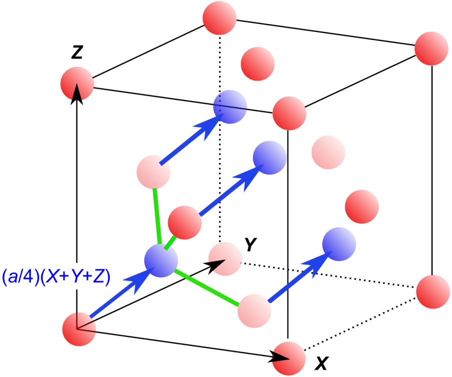
For example, if there are two atoms in the primitive unit cell, there are three acoustic branches and three optical branches.

If there are three atoms in the primitive unit cell, there are three acoustic branches and six optical branches, and so on.

Crystal with *n* atoms per primitive unit cell 2

Cubic unit cell of Silicon





Crystal with *n* atoms per primitive unit cell 2 Comment

The figures show the cubic unit cell of the diamond structure again.

The diamond structure is an fcc lattice with two atoms per primitive unit cell.

In the figure on the right, one atom of the primitive unit cell is highlighted in red and the other in blue.

The two atoms are shifted against each other by the vector $(X + Y + Z)(a/4)$ along the space diagonal of the cubic cell.

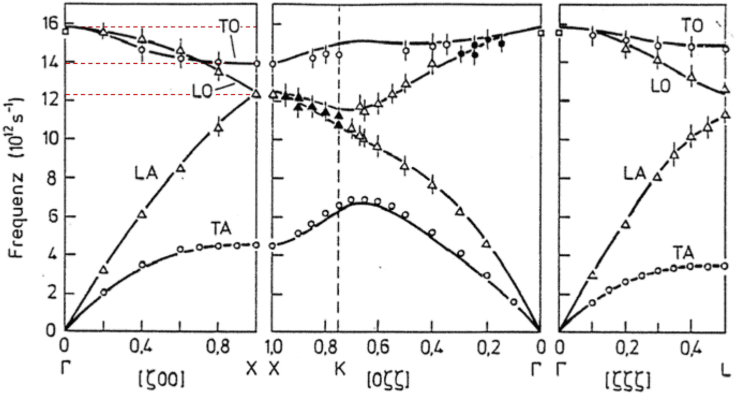
This results in a tetrahedral environment for each atom, which corresponds to the geometry of a sp^3 hybrid orbital.

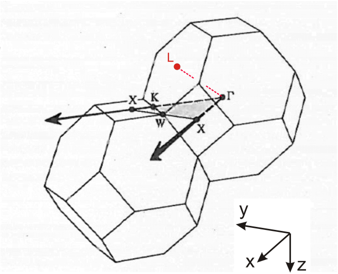
The tetrahedra are indicated by the vectors drawn in blue and the green lines.

The next page shows the dispersion branches of the lattice vibrations for silicon. Like carbon and germanium, silicon crystallizes in the diamond structure.

Crystal with n atoms per primitive unit cell 3

dispersion branches of the lattice vibrations for silicon





Crystal with *n* atoms per primitive unit cell 3 Comment 1

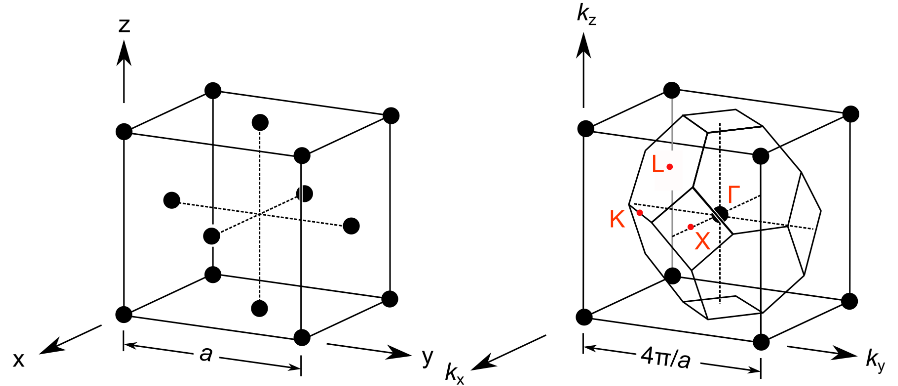
The left figure shows the dispersion branches of the lattice vibrations for silicon measured by neutron diffraction.

The right figure shows two neighboring 1^{st} Brillouin zones of the fcc lattice and it is good to remember a page from the last lecture, which I show here again:

Reciprocal lattice 7

Notice

The reciprocal lattice of an fcc lattice is a bcc lattice!



Crystal with *n* atoms per primitive unit cell 3 Comment 2

The dispersion of the lattice vibrations is measured in selected directions of the lattice.

The left figure shows the path from $\Gamma \rightarrow$ X.

The middle figure shows the way from $\Gamma \rightarrow$ K $\rightarrow$ X.

The right figure shows the path from $\Gamma \rightarrow$ L.

The vectors $[\zeta, \zeta, \zeta]$ etc. indicate the wave vectors which refer to the 1^{st} Brillouin zone.

For the directions of propagation $[\zeta, 0, 0]$ and $[\zeta, \zeta, \zeta]$ it is to be expected that the frequencies of TA1 and TA2 and TO1 and TO2 polarization are identical.

Crystal with *n* atoms per primitive unit cell 3 Comment 2

For the directions of propagation $[\zeta, \zeta, 0]$, a splitting of the dispersion for the polarizations TA1 and TA2 as well as TO1 and TO2 is to be expected.

This splitting was shown, for example, by measuring the lattice vibrations for palladium.

These splittings are not resolved in the measurement shown and are obviously small.

The path $\Gamma \rightarrow$ K $\rightarrow$ X leaves the 1st Brillouin zone.

In the next section I will explain what happens when the boundary of the 1st Brillouin zone is crossed.

Crystal with n atoms per primitive unit cell 3 Comment 3

Finally, it makes sense to think about the temperature, which corresponds to an energy of $E/h = 16 \cdot 10^{12}\,\text{Hz}$.

$$E/k_B = \frac{4.14 \cdot 10^{-15}\,\text{eVs}\,16 \cdot 10^{12}\,\text{s}^{-1}}{8.617 \cdot 10^{-5}\,\text{eVK}^{-1}} = 769\,\text{K}$$

Phonons and Crystal momentum

Vibrational modes and phonons

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Phonons and Crystal momentum 1

- Quantum particles form the waves of the lattice vibrations
- In analogy to electromagnetic waves, the quantum particles of the lattice vibrations are called phonons

de Broglie and Planck $\boxed{\vec{p} = \hbar\vec{q} \quad \text{and} \quad E(\vec{q}) = \hbar\omega(\vec{q})}$

Phonons and Crystal momentum 1 Comment 1

It is not difficult to set up the Schrödinger equation of the lattice vibrations.

The Hamiltonian contains the kinetic energy and potential energy of the atoms.

The solution of the Schrödinger equation can be found in many textbooks and cannot be discussed here because this is not a lecture on mathematical physics.

Therefore, the following remarks will have to suffice.

First, remember the harmonic oscillator discussed in the 12th lecture.

The energy of the oscillator is quantized according to $E = \hbar\omega(\frac{1}{2} + n)$.

The zero-point energy of the ground state is $E = \hbar\omega\frac{1}{2}$, since the particle cannot be at rest due to the uncertainty relation.

The energy increases in quanta of $E = \hbar\omega$, and the frequency ω is given by the solution of Newton's equation of motion $\omega = \sqrt{D/m}$.

Phonons and Crystal momentum 1 Comment 2

When harmonic waves are used to solve Newton's equation of motion for the lattice vibrations, the originally coupled equations decouple into an equation for each branch (acoustic or optical) and polarization mode.

The same thing happens with the Schrödinger equation, which reduces to the Schrödinger equation of the harmonic oscillator for each branch (acoustic or optical) and each polarization mode.

The energy of each mode increases in steps of $E = \hbar\omega(\vec{q})$, where $\omega(\vec{q})$ is given by the solution of Newton's equation of motion.

The excitation energy is characterized by the quantum number n, the branch (acoutic or optical), the polarization and the wave vector $\vec{q}$.

Phonons and Crystal momentum 1 Comment 3

The relation between the wave vector $\vec{q}$ and the momentum $\vec{p} = \hbar\vec{q}$ is a fundamental feature of the Schrödinger equation and expressed by the definition of the momentum operator $\hat{\vec{p}} = -i\hbar\nabla$.

Therefore, the excitation energy of the lattice vibrations is also characterized by a momentum $\vec{p} = \hbar\vec{q}$.

An excitation that is characterized by the energy $E = \hbar\omega(\vec{q})$ and the momentum $\vec{p} = \hbar\vec{q}$ is called a particle.

The particles of the lattice vibrations are called ‘phonons’.

It was clear from the start that the lattice oscillations were quantized.

The quantization of the lattice vibration was a model for the quantization of other waves - especially of electromagnetic waves.

Phonons and Crystal momentum 1 Comment 4

Detecting the quantum particles of electromagnetic waves was possible because the energy of the photons can be large and easy to measure.

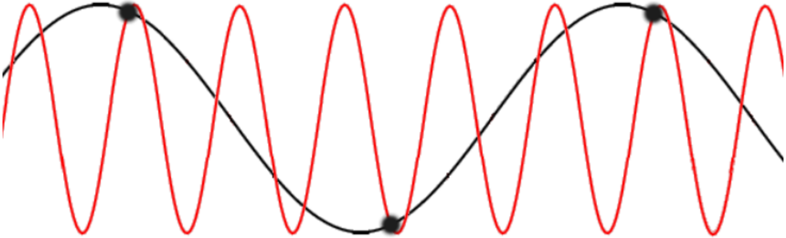
In contrast, the energy of the phonons is very small and lies in the range of thermal energies.

Therefore, it was only with the methods of modern nanophysics that it was possible to detect phonons directly and to experimentally demonstrate the quantization of lattice vibrations.

The formulas outlined in red summarize the quantization of lattice vibrations, which is completely analogous to the quantization of electromagnetic waves.

Phonons and Crystal momentum2

Crystal momentum



(Crystalmomentum.mp4)

Notice!

the same oscillation of the atoms results for $\vec{q} + \vec{K}$

Phonons and Crystal momentum 2 Comment 1

The wave vector of phonons is usually denoted by $\vec{q}$ and the q-vectors are restricted to the 1st Brillouin zone.

However, the movement of atoms can be described by very different wavelengths and wave vectors.

The animation shows that the same movement of the atoms is described by a wave with the wavelength $\lambda = 2a$ and a wave with the smaller wavelength $\lambda = 2a/5$.

The wave number corresponding to the long wavelength (black line) is included in the 1st Brillouin zone, while the wave number corresponding to the short wavelength (red line) is not included in the 1st Brillouin zone.

Phonons and Crystal momentum 2 Comment 2

In a crystal lattice the motion of the atoms does not change if a reciprocal lattice vector $\vec{K}$ is added to the wave vector $\vec{q}$.

note:

$$\exp(i\vec{q}\vec{R}) = \exp(i(\vec{q} + \vec{K})\vec{R})$$

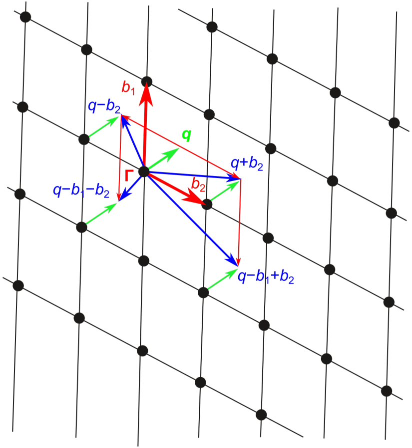
The waves of the lattice vibrations are determined by the vectors of the Bravais lattice $\vec{R}$ not by the precise position of the atoms. For a simple example, compare Newton’s equations of the diatomic chain (Diatomic chain of atoms 1).

It is the displacement from the equilibrium positions that, together with the force constant D, determines the force between the atoms and not the absolute position of the atoms within the primitive unit cell.

Phonons and Crystal momentum 2 Comment 3

In the animation the wave number of the black wave is $q = \pi/a$. A basis vector of the one-dimensional reciprocal lattice has the length $K = 2\pi/a$. Therefore, $q + 2K = 5\pi/\mathrm{a}$ and the corresponding wavelength is $\lambda = 2a/5$.

Phonons and Crystal momentum 3



- All waves with the wave vectors $\vec{q}+\vec{K}$ describe the same lattice oscillation
- The energy $\hbar\omega(\vec{q})$ of a phonon is periodic in the reciprocal lattice, i.e.

$$\boxed{\omega(\vec{q})=\omega(\vec{q}+\vec{K})}$$

- The momentum $\hbar\vec{K}$ can always be added to the momentum of a phonon without changing the momentum of the phonon
- The momentum of a phonon $\hbar\vec{q}$ is sometimes called a crystal momentum or quasimomentum.

Phonons and Crystal momentum 3 Comment 1

The sketch illustrates this result for the case of a two-dimensional reciprocal lattice.

The green vector $\vec{q}$ show the wave vector of a phonon.

By adding reciprocal lattice vectors, the blue wave vectors are obtained.

These wave vectors all point in different directions, although these waves all describe the same motion of the atoms caused by the phonons with wave vector $\vec{q}$.

A reciprocal lattice vector can be added to the wave vector of a phonon without changing the momentum and the energy of the phonon.

All points of the reciprocal lattice are equivalent and can be chosen for the Γ-point.

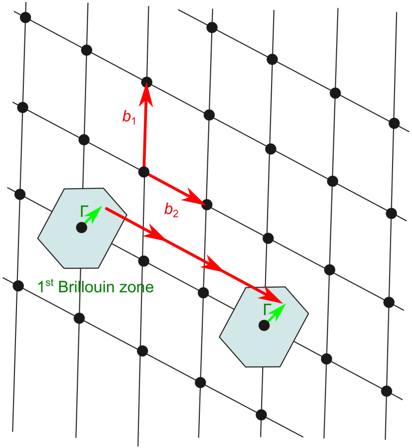
Phonons and Crystal momentum 3 Comment 2

This is indicated by the various green vectors of the sketch.

Because of this property, the momentum of a phonon $\hbar\vec{q}$ is sometimes called crystal momentum or quasi-momentum, since it differs from Newton's definition of momentum.

The energy of the phonons is therefore a periodic function in the reciprocal lattice.

Phonons and Crystal momentum 4



Phonons and Crystal momentum 4 Comment

The periodicity of the energy of a phonon in the reciprocal lattice can be easily formulated by the equation $\hbar\omega(\vec{q}) = \hbar\omega(\vec{q} + \vec{K})$.

Because of the translation invariance of the crystal lattice, the momentum of a phonon does not change when $\hbar\vec{K}$ is added.

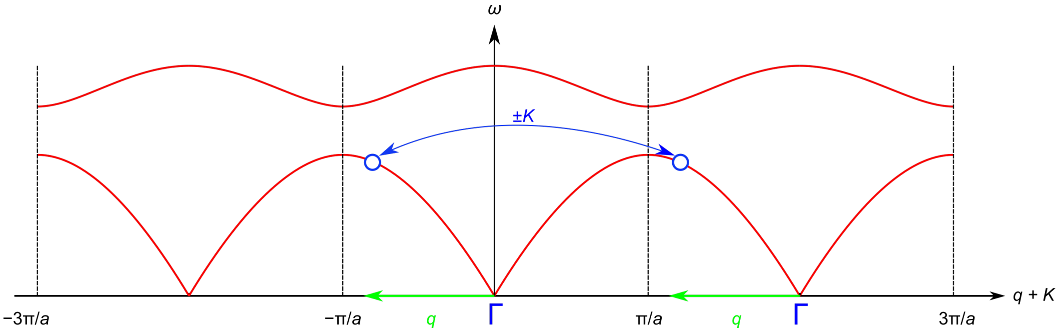
This fact cannot be expressed by an equation since $\vec{q}$ and $\vec{q} + \vec{K}$ are different vectors.

The sketch shows the consequence of the translation invariance of a crystal lattice for the momentum of a phonon $\hbar\vec{q}$.

Each Γ point in the reciprocal lattice is as good as any other.

Phonons and Crystal momentum 5

Consequence of translation invariance for the phonons of a diatomic chain



Phonons and Crystal momentum 5 Comment

The sketch shows the consequences of translation invariance for the phonons of a diatomic chain.

The red lines show the periodic frequency change in the reciprocal lattice for the acoustic and optical phonons.

The blue circles mark two wave numbers that are connected by adding a reciprocal lattice vector (i.e. by adding $\pm 2\pi/a$).

The green arrows mark the momentum of the phonon.

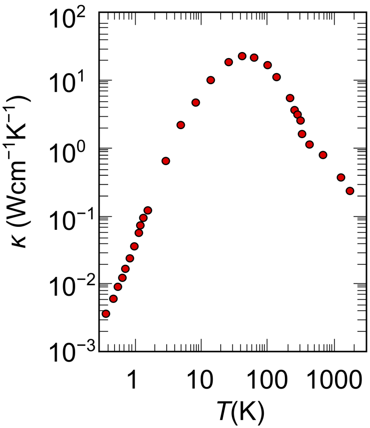
Umklapp scattering

Solids: Lattice vibrations

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

Umklapp scattering 1

thermal conductivity of silicon



thermal conductivity

$$\boxed{\vec{j} = -\kappa \nabla T}$$

- energy flow $\vec{j}$
- temperature gradient ∇T

Umklapp scattering 1 Comment

The figure shows the thermal conductivity of silicon.

The formula outlined in red gives the definition of thermal conductivity.

When a temperature gradient is applied to a crystal, energy flows from the warm side to the cold side, i.e. in the opposite direction to the temperature gradient.

The energy flow $\vec{j}$ is the energy density e times the energy flow velocity, i.e. $\vec{j} = e\vec{v}$ and $e = \partial E/\partial V$.

The energy flow is measured in W/m^2.

If the temperature difference is not too great, the energy flow $\vec{j}$ is proportional to the temperature gradient ∇T.

The constant of proportionality κ is the thermal conductivity.

Umklapp scattering 2

- If there are no conduction electrons, the thermal energy is transported exclusively by phonons from areas of higher to lower temperature
- The flow of energy due to a temperature gradient is proportional to and opposite to the temperature gradient

$$\boxed{\vec{j} = -\kappa \nabla T}$$

- Phonons are necessary for the transport of thermal energy. Therefore

$$\boxed{\kappa \rightarrow 0 \quad \text{if} \quad T \rightarrow 0}$$

- Phonons are scattered on impurities and grain-boundaries
  → the transport of thermal energy is diffusive

Umklapp scattering 2 Comment 1

Silicon is a semiconductor, i.e. a very poor conductor with a small thermally activated conductivity.

The transport of thermal energy is dominated by the excitation of phonons.

Since more phonons are excited on the warm side of the sample than on the cold side, there is a net phonon flow from the warm to the cold side.

The phonons do not propagate undisturbed through the crystal lattice, but are scattered at impurities and imperfections in the crystal lattice, so that the energy transport through phonons has a diffusive character.

Umklapp scattering 2 Comment 2

Since the number of phonons decreases with decreasing temperature, it is plausible that the thermal conductivity decreases with decreasing temperature.

However, the thermal conductivity of silicon does not increase steadily with increasing temperature.

The thermal conductivity reaches a maximum at temperatures around 50 K and then decreases with increasing temperature.

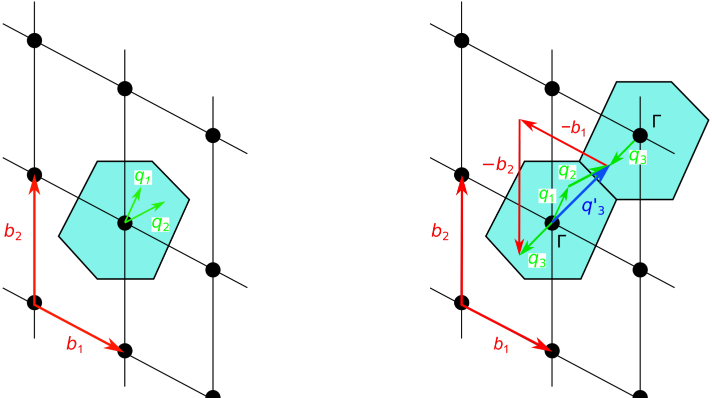
The reason for the maximum is that at higher temperatures the phonons are not only scattered from lattice defects, but also from the lattice vibrations themselves.

Although the law of conservation of energy prevents most phonon-phonon scattering processes, phonon-phonon scattering becomes more and more important with increasing temperature.

Umklapp scattering 3

phonon-phonon scattering at high temperatures

$$\hbar\omega(\vec{q}_1) + \hbar\omega(\vec{q}_2) = \hbar\omega(\vec{q}_3) \qquad \text{and} \qquad \vec{q}_1 + \vec{q}_2 + \vec{K} = \vec{q}_3$$



Umklapp scattering 3

Comment 1

The first formula gives the energy conservation law for the collision of two phonons that merge to a single new phonon.

The total energy before and after the scattering event must be the same.

The second formula gives the law of conservation of momentum, which in a crystal lattice can also contain a vector of the reciprocal lattice.

Since the momentum of a phonon is a crystal momentum, any vector of the reciprocal lattice can be added without changing the momentum of the phonon.

The figure shows the addition of the momenta of two phonons.

Umklapp scattering 3 Comment 2

The addition of $\vec{q}_1$ and $\vec{q}_2$ results in the blue vector $\vec{q}_3'$, the tip of which protrudes into the neighboring Brillouin zone.

The addition of the reciprocal lattice vector $\vec{K} = -\vec{b}_1 - \vec{b}_2$ brings the momentum of the phonon $\vec{q}_3'$ in the neighboring Brillouin zone back into the original Brillouin zone.

The momentum of the associated phonon is $\vec{q}_3$, which points exactly in the opposite direction to $\vec{q}_3'$.

After this scattering event, the energy flows in the opposite direction.

Such scattering events are the reason that the thermal conductivity decreases at higher temperatures after the maximum.

Umklapp scattering 3

Comment 3

This explanation was given by Rudolf Peierls in 1929.

Peierls wrote, ”…I used the German term Umklapp (flip-over) and this rather ugly word has remained in use….”

The umklapp scattering obviously hinders the transport of thermal energy and therefore leads to a reduction in thermal conductivity at high temperatures.

Although Rudolf Peierls was not awarded the Nobel Prize, he is very famous.

E.g. the building housing the sub-department of Theoretical Physics at the University of Oxford is formally named the Sir Rudolf Peierls Centre for Theoretical Physics.

Revision

Summary in Questions 1

1. Use Newton's equation of motion to calculate the dispersion relation for a monatomic chain.
2. Explain the periodic boundary condition.
3. Write down the different wave numbers of a monatomic chain with N atoms of length L when periodic boundary conditions are used.
4. How many different wave numbers are then in interval $\pm\pi/a$?
5. Sketch the dispersion spectrum of a monatomic chain.
6. Sketch the dispersion spectrum of a diatomic chain.
7. Describe the difference between the acoustic and the optical branches of the dispersion spectrum of the lattice vibrations.

Summary in Questions 2

8. What determines the number of acoustic and optical branches of the dispersion spectrum of the lattice vibrations?

9. The interval $\pm\pi/a$ is generalized to the 1st Brillouin zone for three dimensional crystal lattices. How many different wave vectors are there in the 1st Brillouin zone if periodic boundary conditions are used?

10. The momentum of the phonon $\hbar\vec{q}$ is a crystal or quasi momentum. What is the difference to the usual Newtonian momentum?

11. What is umklapp scattering?

12. What is the experimental evidence that there is umklapp scattering?