Solids

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

Solids: Lattice vibrations

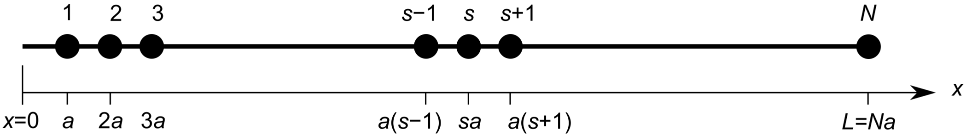
- Vibrational modes and phonons
- Brillouin- and Raman-scattering
- Inelastic neutron scattering
- Heat capacity of the crystal lattice
- Umklapp scattering

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

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 pendulum, 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 functions $\vec{u}(x)$ are a reasonable approach 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.

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

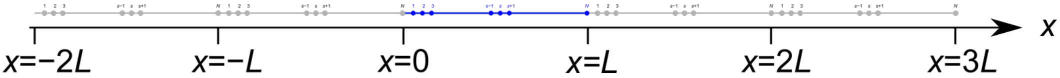
There is a longitudinal mode and two transverse modes.

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 wavenumbers 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 plane 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

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

(Crystalmomentum.mp4)

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 $\lambda = 2a$.

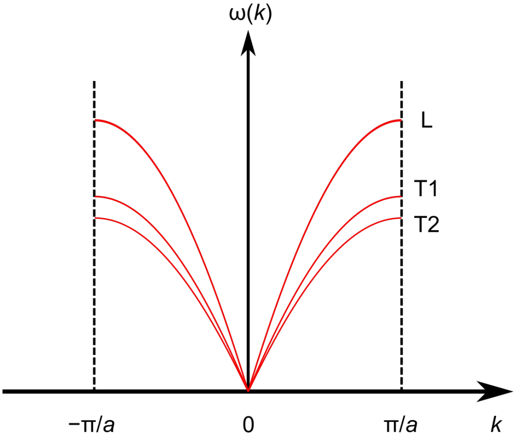
A shorter wavelength cannot be resolved with the distance a of the atoms.

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

The range of these wavenumbers divided by $2\pi/L$ gives the total number of wavenumbers 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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- Diatomic chain of atoms
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- Phonons

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 wavenumber must be generalized to the wave vector $\vec{k}$ and the wavenumber 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.

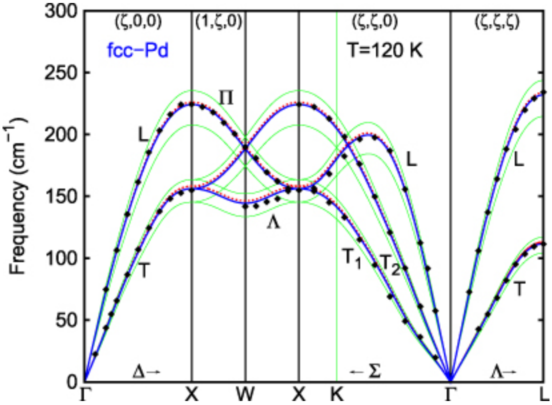
But if the surface of a crystal has no influence, one can abandon the assumption of a cube-shaped sample with the edge length L and replace L^3 with the volume V of a sample of any shape.

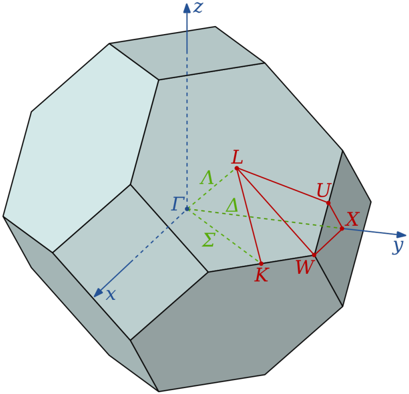
The number of different wave vectors results from dividing the volume of the 1st Brillouin zone by the volume that a wave vector can occupy.

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 1$^{\text{st}}$ 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.

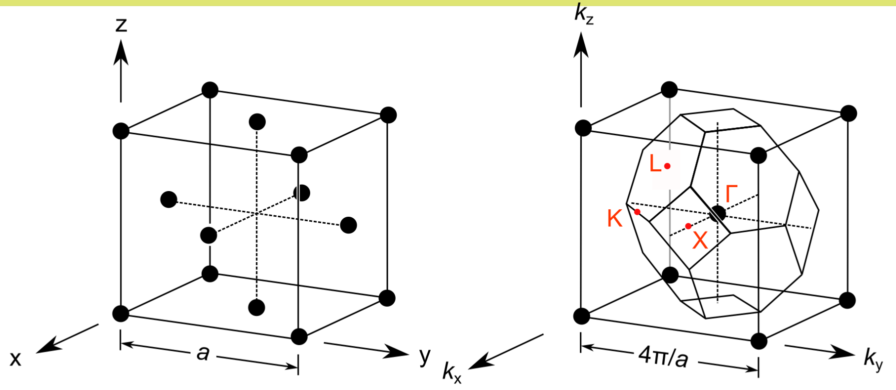
The frequency of the two transverse modes is the same, since the coordinate axes are four-fold axes of symmetry of the cube.

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 $E/hc = 220\,\text{cm}^{-1}$.

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

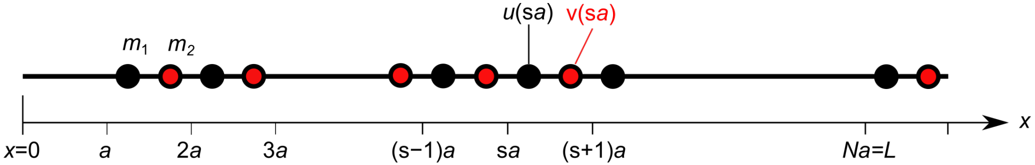
This means that all lattice vibrations are excited at room temperature.

Diatomic chain

Vibrational modes and phonons

- 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

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

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

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.

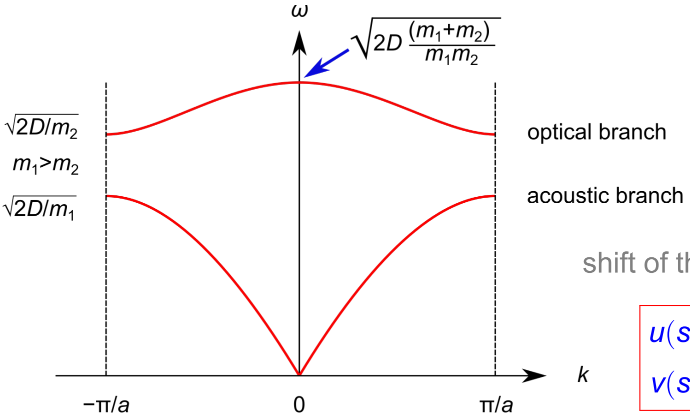
There are three main directions of vibration (L, i.e. longitudinal, T1, and T2, i.e. transversal 1 and 2), for which Newton’s equations of motion can be solved independently of each other.

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 $x = sa$

$$\boxed{\begin{aligned} u(sa) &= u_{0,\text{branch}}(k)e^{i(k\cdot sa-\omega_B(k)t)} \\ v(sa) &= v_{0,\text{branch}}(k)e^{i(k\cdot sa-\omega_B(k)t)} \end{aligned}}$$

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.

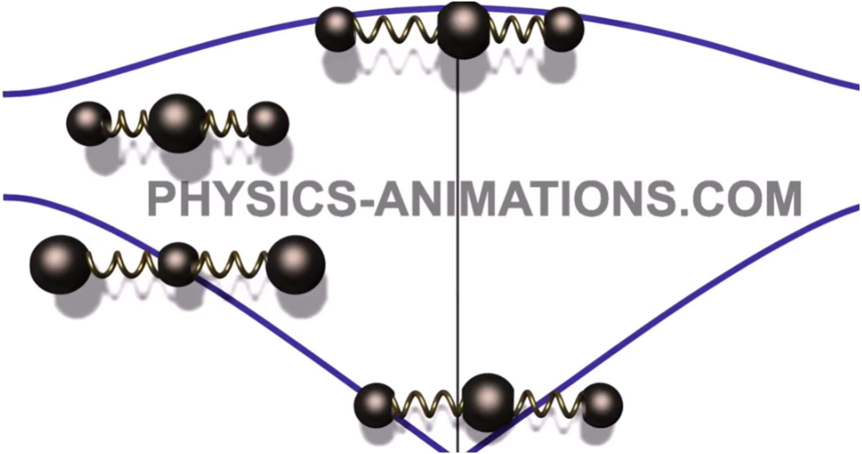
Diatomic chain of atoms 2 Comment 3

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.

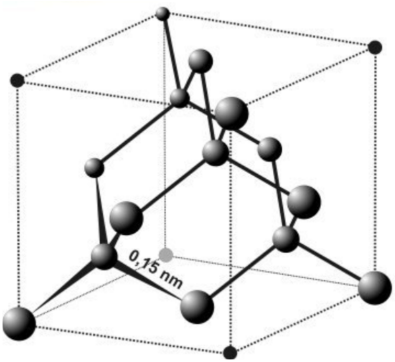
Except for the last rule, all rules for a crystal with *n* atoms per primitive unit cell agree with the rules for crystals with only one atom in the primitive unit cell.

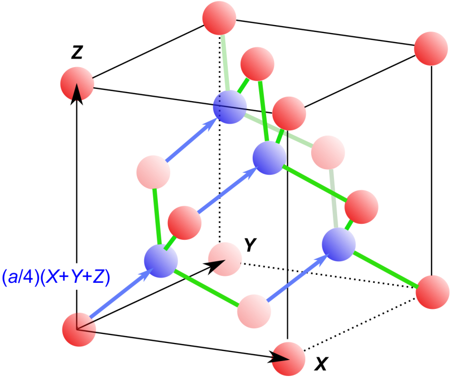
For example, if there are two atoms in the primitive unit cell, there are three acoustic branches and three optical branches.

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.

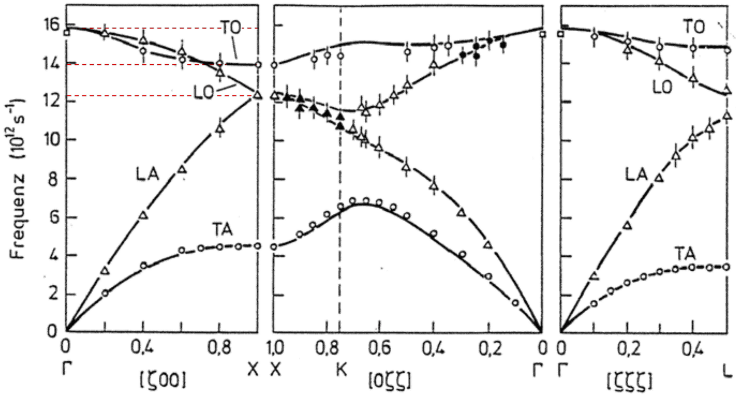
This results in a tetrahedral environment for each atom, which corresponds to the geometry of a sp^3 hybrid orbital.

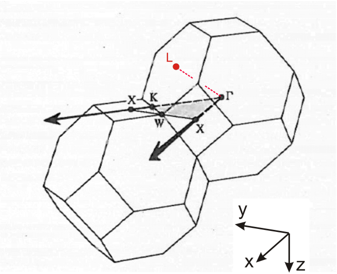
The tetrahedra are indicated by the vectors drawn in blue and the green lines.

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

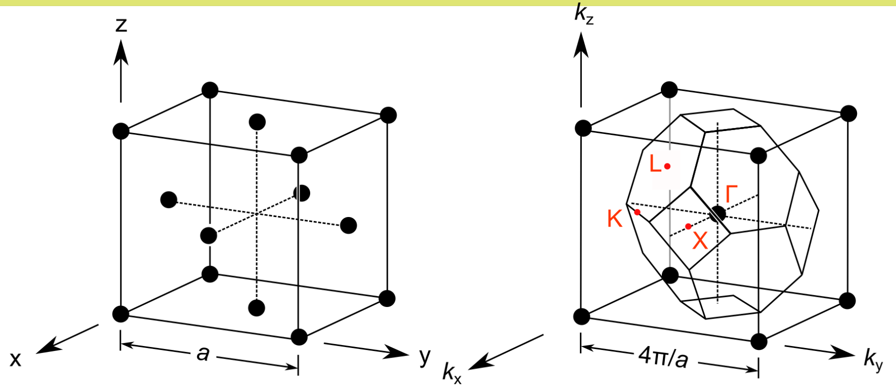
The left figure shows the dispersion branches of the lattice vibrations for silicon measured by neutron diffraction.

The right figure shows two neighboring 1st 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 1st 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 $\Gamma \to \mathrm{K} \to \mathrm{X}$ 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 $E/h = 16 \cdot 10^{12}\,\text{Hz}$.

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

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 wavenumbers of a monatomic chain with N atoms of length L when periodic boundary conditions are used.
4. How many different wavenumbers 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?