Chapter 4

Dynamics of Crystal-Atoms

Properties of solid state matter are driven by (a) the electron system and (b) the motion of atoms within the crystalline system. To some extend, it is possible to discuss the principle features of the electron and the atom system separately. This is motivated by the time scale of motion of electrons within the crystalline system which is much faster than the motion of atoms. As a consequence, electrons do see a more or less static potential environment formed by the atoms. Still, there are phenomena, which can only be understood in the interplay of electron-phonon (phonon = excitations of the atomic lattice) interaction, such as superconductivity and transport phenomena.

Today, we will therefore speak about the motion of atoms within the crystalline systems. The motion of atoms is responsible for the propagation of waves within the solid, thermal properties such as specific heat, thermal expansion, and thermal conductivity.

To study in full depth the entire system, one would have to calculate the motion of electrons within the potential of the atoms - and use the motion of electrons to calculate the potential for the motion of atoms and so one. This would be a mathematically rather complex system which is not easily solvable Instead, here we just assume that every atom is determined in its position by a potential Φ - and we try to find a general solution for the motion of atoms within this potential.

4.1 The atomic potential

Before we start the investigation of the physics, let us first introduce a scheme to uniquely address every single atom. Using the periodicity of the lattice system, we can define the position of every atom by its position within the unit cell and of the unit cell relative to an (arbitrarily chosen) origin. Thereby, the position $\vec{r}_\alpha$ denotes the relaxed position of the atom, i.e. in its potential minimum, and $u_{n\alpha i}$ the displacement of the atom in $(i = x, y, z)$ direction.

The total potential Φ of the entire crystal system is then developed in a Taylor development around the equilibrium position $\vec{r}_{n\alpha i}$:

$$\Phi(\vec{r}_{n\alpha i} + u_{n\alpha i}) = \Phi(\vec{r}_{n\alpha i}) + \frac{1}{2} \sum_{n\alpha i m\beta j} \frac{\partial^2 \Phi}{\partial \vec{r}_{n\alpha i} \partial \vec{r}_{m\beta j}} u_{n\alpha i} u_{m\beta j} \ldots.. \tag{4.1}$$

Note: the linear term with $u_{n\alpha i}$ does not appear. This is a consequence of the fact that we developed around the equilibrium position. The sum-indices n, m account for all unit cells, $\alpha\beta$ for all atoms within a cell, and i, j for all three space directions. For the beginning, all terms of higher order will be neglected. Therefore, the present simplification is called 'harmonic' approximation. But we have to remain aware that this

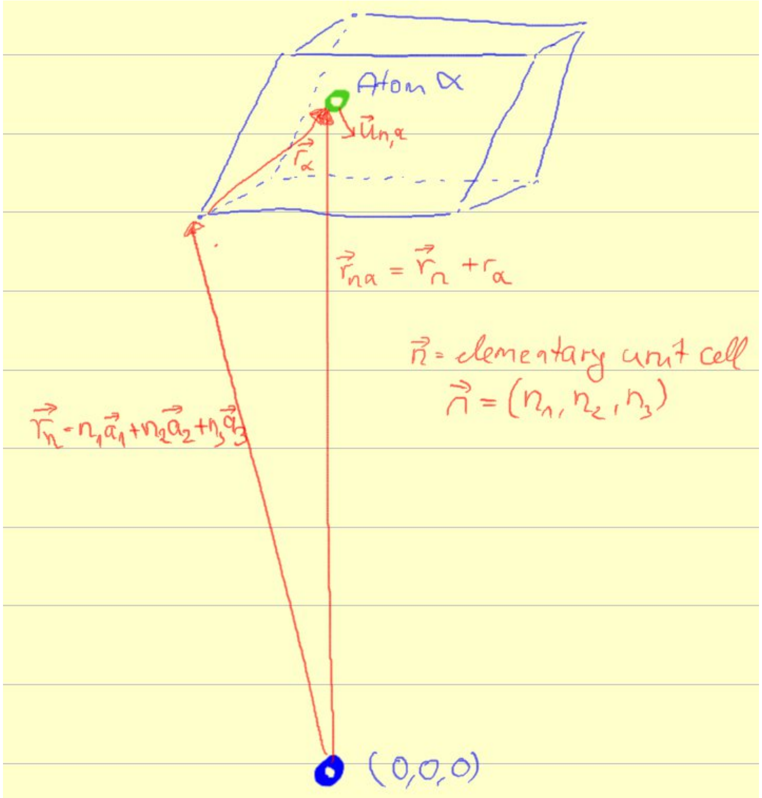

Figure 4.1: Definition of lattice vectors starting from an arbitrary lattice point (0,0,0). The lattice vector $\vec{r}_n$ points first to the respective unit cell and then to the position of the atom within the unit cell $\vec{r}_\alpha$. $\vec{u}_{n\alpha}$ denotes the displacement of the atom relative to its relaxed position.

is only an approximation and effects exists, which cannot be described by the harmonic approximation such as the thermal expansion of solid state matter.

The derivative of the potential

$$\frac{\partial^2 \Phi}{\partial \vec{r}_{n\alpha i} \partial \vec{r}_{m\beta j}} = \Phi_{n\alpha i}^{m\beta j} \tag{4.2}$$

is called coupling (or spring) constant. The entire system acts a large spring system but here it is an infinite system and each element is connected via a spring to each other element. $\Phi_{n\alpha i}^{m\beta j} \vec{u}_{m\beta j}$ is therefore the force which is acting on the atom α in the unit cell $\vec{n}$ in the direction j when the atom β in the unit cell m is displaced in the direction j by the amount of $\vec{u}_{m\beta j}$. We also have to note that the coupling constants have to obey the conditions of the underlying lattice (space anisotropy, translational invariance and point symmetry). The consequence of the translational invariance is, that not the specific position of atoms is relevant but only the distance between them:

$$\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j} \tag{4.3}$$

4.2 The Equation of Motion

As for all mass particles, the inertia of particle α with a mass M_α and the forces acting on the same particle must sum up to zero:

$$M_\alpha \ddot{u}_{n\alpha i} + \sum_{m\beta j} \Phi_{n\alpha i}^{m\beta j} u_{m\beta j} = 0 \tag{4.4}$$

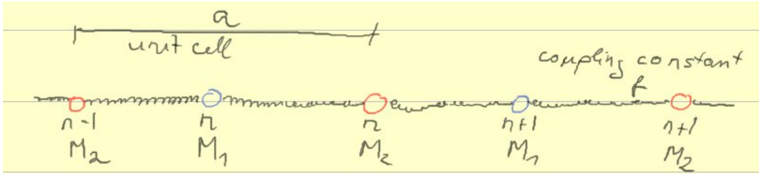

Figure 4.2: A two atomic linear chain: The unit cell of length a hosts two atoms of different masses (M_1 and M_2) with each atom connected to its neighbors via the coupling constant f.

That means, for a system of N unit cells and r atoms within each unit cell we get $3rN$ coupled differential equations, which describe the motion of the entire systems. Without further help or knowledge, this is a rather complicated set of equations to be solved. However, for a periodic system as a crystal, we can make a clever choice and choose a planar wave to describe the dislocation $u_{n\alpha i}$:

$$u_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\vec{q}) e^{i(\vec{q}\cdot\vec{r}_n - \omega t)}. \tag{4.5}$$

Different to a conventional wave, this wave is only defined at the lattice points $\vec{r}_n$! Introducing the plane wave assumption into eq. 4.3, we get:

$$-\omega^2 u_{\alpha i}(\vec{q}) + \sum_{bj}\sum_{m} \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi^{m\beta j}_{n\alpha i} e^{i\vec{q}\cdot(\vec{r}_m - \vec{r}_n)} u_{\beta j}(\vec{q}) = 0 \tag{4.6}$$

and

$$D^{\beta j}_{\alpha i}(\vec{q}) = \sum_{m} \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi^{m\beta j}_{n\alpha i} e^{i\vec{q}\cdot(\vec{r}_m - \vec{r}_n)} \quad \texttt{is called the dynamic matrix} \tag{4.7}$$

The resulting set of equations (invariance of translation !):

$$-\omega^2 u_{\alpha i}(\vec{q}) + \sum_{bj} D^{\beta j}_{\alpha i}(\vec{q}) u_{\beta j}(\vec{q}) = 0 \tag{4.8}$$

is a linear, homogeneous set of equations of the order of $3r$. Considering the case of a simple cubic system with only one atom per unit cell ($r = 1$) the previous equation reduces to one of the order of 3 !

A linear homogeneous set of equations has solutions (eigenvalue) only if the determinant is zero:

$$Det(D^{\beta j}_{\alpha i}(\vec{q}) - \omega^2 \vec{1}) = 0 \tag{4.9}$$

This equation has for every wave vector $\vec{q}$ exactly $3r$ different solutions for $\omega(\vec{q})$. $\omega(\vec{q})$ is the so called dispersion relation. The set of $3r$ solutions are called 'modes'. Instead of applying the developed formalism to a real crystal, we want first to study a more simple but very illustrative example, a linear two atomic chain.

4.3 The Linear Two-Atomic Chain

The linear two atomic chain has essentially no real application, as real systems are generally three dimensional. However, it is very instructive to 'see' the physics of lattice motions. We assume a chain of unit cells, each unit cell hosting two atoms of different mass (M_1 and M_2) (see Fig. 4.2). The distance between two atoms is a. I.e. α,$\beta = 1, 2$;

$i = x$ (and is therefore redundant). Further, we assume that we only have nearest neighbor interaction. Therefore, we can write the equation of motion the following way:

$$\begin{aligned} M_1\ddot{u}_{n1} + \Phi_{n1}^{n-1,2}u_{n-1,2} + \Phi_{n1}^{n1}u_{n1} + \Phi_{n1}^{n2}u_{n2} = 0 \\ M_2\ddot{u}_{n2} + \Phi_{n2}^{n1}u_{n1} + \Phi_{n2}^{n2}u_{n2} + \Phi_{n2}^{n+1,1}u_{n+1,1} = 0 \end{aligned} \tag{4.10}$$

The values of the remaining coupling constants are:

$$\begin{aligned} \Phi_{n1}^{n-1,2} = \Phi_{n1}^{n2} = \Phi_{n2}^{n1} = \Phi_{n2}^{n+1,1} = -f \\ \Phi_{n1}^{n1} = \Phi_{n2}^{n2} = +2f \end{aligned} \tag{4.11}$$

Therefore, we get:

$$\begin{aligned} M_1\ddot{u}_{n1} + f(-u_{n-1,2} + 2u_{n1} - u_{n2}) = 0 \\ M_2\ddot{u}_{n2} + f(-u_{n1} + 2u_{n2} - u_{n+1,1}) = 0 \end{aligned} \tag{4.12}$$

Using a planar wave of the previously introduced shape, we get:

$$u_{n\alpha} = \frac{1}{\sqrt{M_\alpha}}u_\alpha(q)e^{i(qan-\omega t)}. \tag{4.13}$$

Introducing eq. 4.13 into eq. 4.12 results in:

$$\begin{aligned} (\frac{2f}{M_1} - \omega^2)u_1 - f\frac{1}{\sqrt{M_1M_2}}(1+e^{-iqa})u_2 = 0 \\ -f\frac{1}{\sqrt{M_1M_2}}(1+e^{iqa})u_1 + (\frac{2f}{M_2} - \omega^2)u_2 = 0 \end{aligned} \tag{4.14}$$

and the dynamic matrix $D_{\alpha i}^{\beta j}(\vec{q})$ is:

$$\begin{pmatrix} \frac{2f}{M_1} & \frac{-f}{\sqrt{M_1M_2}}(1+e^{-iqa}) \\ \frac{-f}{\sqrt{M_1M_2}}(1+e^{iqa}) & \frac{2f}{M_2} \end{pmatrix} \tag{4.15}$$

As $D_{\alpha i}^{\beta j}(\vec{q}) = 0$ we get the following dispersion relation for ω:

$$\omega^2 = f\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm f\left[\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}sin^2\frac{qa}{2}\right]^{1/2} \tag{4.16}$$

Obviously, the dispersion relation is periodic in q with the periodicity of:

$$\frac{qa}{2} = \pi \texttt{ or } q = \frac{2\pi}{a} \tag{4.17}$$

. As we see, the periodicity distance is exactly the reciprocal lattice vector $\vec{G}$, which is valid for every kind of lattice. This is no surprise as $\vec{G}\cdot\vec{r}_n = 2\pi m$ and introduced into the definition of the dynamic matrix: $D_{\alpha i}^{\beta j}(\vec{q}) = D_{\alpha i}^{\beta j}(\vec{q}+\vec{G})$. The same holds for the dispersion relation:

$$\omega(\vec{q}) = \omega(\vec{q}+\vec{G}). \tag{4.18}$$

For symmetry reasons, also

$$\omega(-\vec{q}) = \omega(\vec{q}) \tag{4.19}$$

is valid.

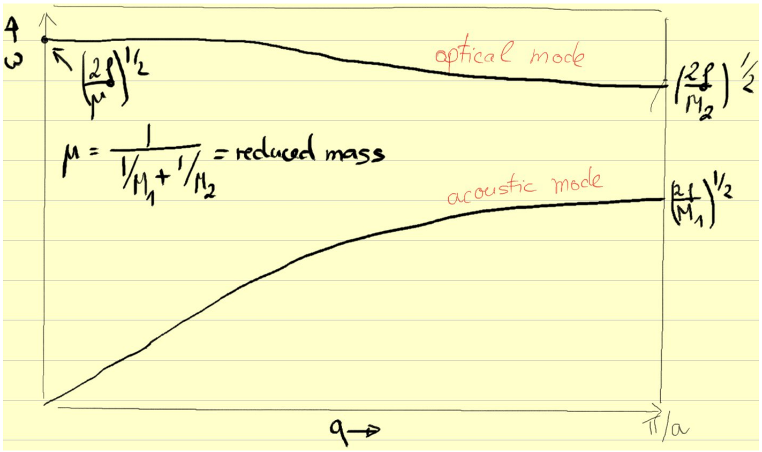

Figure 4.3:

Due to time invariance, incoming waves $u(\vec{q})$ and outgoing waves $u(-\vec{q})$ are equivalent and therefore their eigen-frequencies, see eq. 4.19. Therefore, the visualization of the dispersion relation as depicted in Fig. 4.3 can be restricted to the $\vec{q}$ range between $0 \leq q \leq G/2$. The point $G/2$ is sitting on the Brillouin boundary.

For the case of a linear chain, Fig. 4.3 presents the two modes of excitation for a system with $M_1 >> M_2$. The mode, which crosses the origin is called acoustic mode as it describes the dissipation less propagation of acoustic waves. Close to the origin, i.e. when $q \ll \pi/a$, $w \sim q$. The mode with an energy unequal zero at $q = 0$ is called optical mode. The reason for its name is given through the experimental observation that these modes are often observed by infrared or in the visible range. The interpretation of the optical mode in the dispersion relation at $q = 0$ and $q = \pi/a$ is straight forward. At $q = 0$ the displacement within each unit cell is identical: The sub lattices of heavy and light atoms are moving oppositely to each other and the system is reduced to a 2-mass system with a coupling constant of $2f$ and the reduced mass $1/\mu = 1/M_1 + 1/M_2$. At $q = \pi/a$ either the lattice formed of the heavy atoms or of the light atoms is fixed. Respectively, the frequencies are $(2f/M_2)^{1/2}$ and $(2f/M_1)^{1/2}$.

The two atomic linear lattice is explicitly instructive for the comparison with ionic crystals. In ionic systems, the lattice is formed by atoms which are oppositely charged. In that case, the optical mode describes the motion of anions relative to the cations, i.e. the motion of the lattice induces a electrical bipolar field which couples to external electro-magnetic fields and the mode is optically active.

For the discussed linear chain, we allowed only a displacement of atoms along the chain direction. Such kind of waves are called longitudinal waves. In the case of three dimensional crystals, we also have two further modes, so called transversal waves. Note: the distinction between longitudinal and transversal modes is only strict in specific crystal (symmetry) directions. In every other direction, we will find mixed states, respectively. Every crystal has three acoustic modes. For small values of q, i.e. long wave lengths, these waves correspond to the sound waves within the elasticity theory, which will be discussed later. For crystals with a one-atomic unit cell only acoustic modes exist. For every additional atom within the unit cell, three further optical modes appear (note: counting the atoms in the unit cell, one has to consider the smallest possible unit cell). For face centered cubic crystals (fcc), which is very common among metallic systems and which has only one atom per unit cell (see previous chapter), only acoustic modes can be observed. The same is valid for body-centered cubic (bcc).

(Note 1) We also have to note, that when we say that a crystal should have three acoustic modes we do not need to see three separate modes. Because of symmetry, the transversal modes along the [001] and [111] directions for cubic systems are entangled. The same can be observed for the diamond structure. However, in the diamond structure, which has two atoms within the unit cell, we observe instead optical modes.

(Note 2) All modes which have a frequency unequal zero at $q = 0$ are called optical modes. This is not automatically equivalent to be optically active ! In the case of the diamond lattice, at $q = 0$ the optical mode describes the motion of the two structurally identical fcc sub lattices relative to each other. This implies that the optical mode has no dipole moment and can therefore not interact with electro-magnetic waves.

In the case of the Zincblende structure of a salt, both fcc sub lattices are occupied by different atoms and the optical mode is indeed optically active.

(Note 3) The phase velocity is $c = \omega/k$ and the group velocity $v = \partial\omega/\partial k$. The group velocity corresponds to the speed of wave propagation. At $q = \pi/a$, we find that $v = \partial\omega/\partial k = 0$. That means, at the given q value no wave propagation can be observed. This is because at $q = \pi/a$ waves are Bragg reflected, i.e. the Laue condition as introduced earlier is fulfilled Instead of wave propagation, waves are reflected and standing waves ($v = 0$) emerge, i.e. constructive and destructive interference.

4.4 A brief overview on the last sections

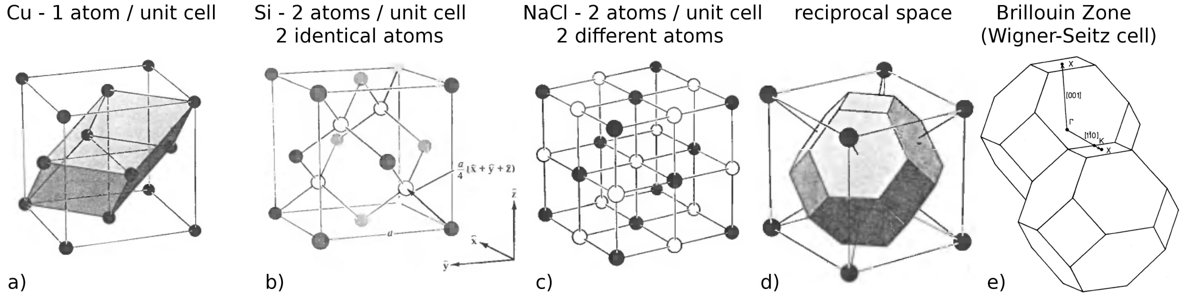

Figure 4.4: Crystal Structures of (a) Cu with one atomic basis, (b) Si with a two-atomic basis with two identical atoms, (c) NaCl with a two-atomic basis with two different atoms, (d) Image of the reciprocal lattice (which forms a bcc structure), and (e) the Wigner-Seitz cell of a bcc lattice with high symmetry points (Γ, ...) indicated.

For illustration (see Fig. 4.4), let us discuss three representative examples: Cu, Si, and NaCl which all condensate in a fcc structure. In Fig. 4.4(a), the conventional and a primitive unit cell of a Cu-fcc system are indicated. The primitive unit cell has 1 atom and the lattice vectors are $\vec{a_1}, \vec{a_2}, \vec{a_3}$. Respectively, for Si and NaCl we get the same unit cell, but the base of the Si-fcc system has two Si atoms, and the base of the NaCl-fcc system has one Na$^+$ and one Cl$^-$ ion.

In all cases, the Bravais lattice is formed by the same unit cell vectors $\vec{a_1}, \vec{a_2}, \vec{a_3}$. Whenever we are discussing material properties, which are related to the periodicity of the system, we have to consider the reciprocal vector $\vec{G}$ - as relevant for scattering or lattice waves. We can define 3 reciprocal unit vectors $\vec{g_1}, \vec{g_2}, \vec{g_3}$ with $\vec{g_1} = 2\pi\vec{a_2} \times \vec{a_3}/(\vec{a_a} \cdot (\vec{a_2} \times \vec{a_3}))$ and $\vec{g_2}$ and $\vec{g_3}$ obtained the same way. $\vec{G}$ is then: $\vec{G} = h\vec{g_1} + k\vec{g_2} + l\vec{g_3}$. The resulting reciprocal lattice is plotted in Fig. 4.4 (d) - which is for a fcc lattice a bcc lattice.

We can again define a unit cell as for the case of the real space lattice. Different to the real space case, where the conventional unit cell is the most common, in the

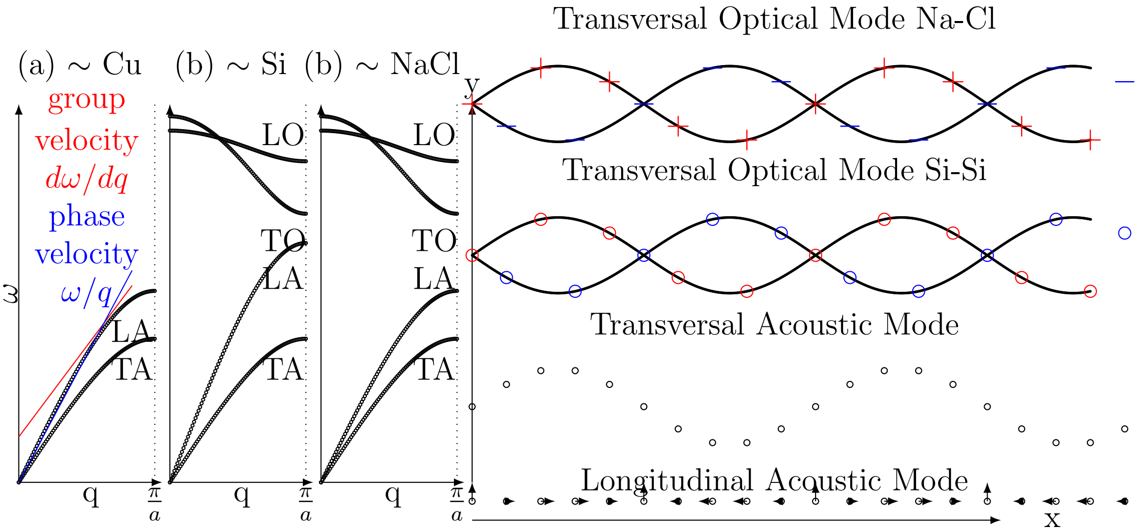

Figure 4.5: Schematic presentation of phonon modes for three different cases

reciprocal space the Wigner-Seitz cell is chosen. The Wigner-Seitz cell is the smallest possible unit cell AND has the full symmetry of the reciprocal lattice. Fig. 4.4 (d) and (e) demonstrate the Wigner-Seitz cell. It is constructed by first connecting the origin with every other lattice point - and draw a plane perpendicular to the interconnecting line. The space confined by all planes is called the Brillouin Zone (BZ) and the surface is called Brillouin Zone Boundary. High symmetry points of the Brillouin Zone are the defined, for example Γ represents the origin, K, X the central point of the face in the [001] and [1-10] direction.

Fig. 4.5 shows schematic representations of phonon dispersions for all three cases:

- Cu (fcc) ∼ linear atomic chain
  - 1 atom per unit cell (r = 1) ⇒ 3r phonon modes
  - 3 acoustical modes and 3 (r-1) = 0 optical modes
  - 1 longitudinal acoustic mode (LA) and 2 transversal acoustic modes (TA)
  - crystal has three equal directions ⇒ both TA are degenerate
- Si (fcc) ∼ linear 2 atomic chain
  - 2 atoms per unit cell (r = 2) ⇒ 3r phonon modes
  - 3 acoustical modes and 3 (r-1) = 3 optical modes
  - 1 longitudinal acoustic mode (LA) and 2 transversal acoustic modes (TA)
  - 1 longitudinal optical mode (LO) and 2 transversal optical modes (TO)
  - crystal has three equal directions ⇒ both TA and TO are degenerate
  - both atoms are identical ⇒ no dipole moment, optically inactive
- NaCl (fcc) ∼ linear 2 atomic chain
  - 2 atoms per unit cell (r = 2) ⇒ 3r phonon modes
  - 3 acoustical modes and 3 (r-1) = 3 optical modes
  - 1 longitudinal acoustic mode (LA) and 2 transversal acoustic modes (TA)
  - 1 longitudinal optical mode (LO) and 2 transversal optical modes (TO)

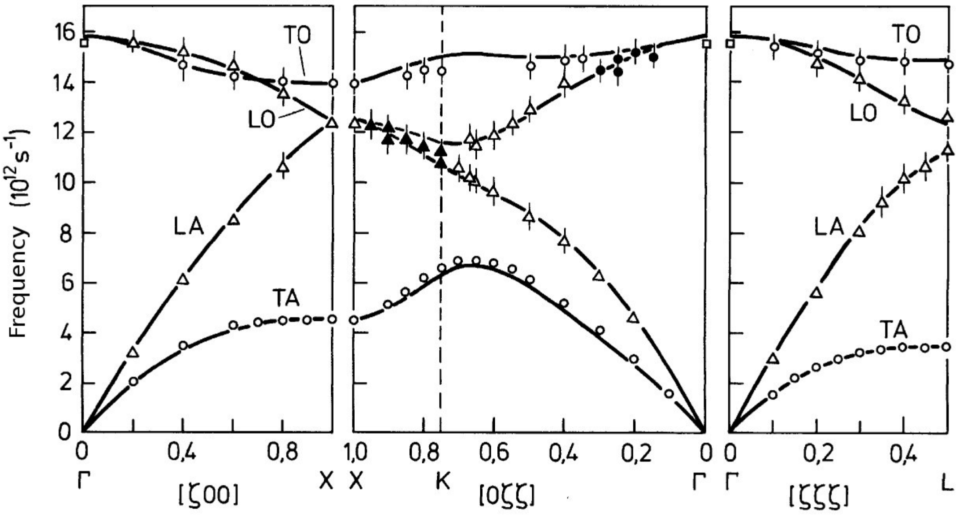

Figure 4.6: Phonon dispersion for Si as calculated - with experimental data from Neutron Scattering indicated by symbols.

- crystal has three equal directions ⇒ both TA and TO are degenerate
- both atoms are different ⇒ dipole moment, optically active

The description of the phonon dispersion by a two-atomic chain is certainly too simple. Therefore, Fig. 4.6 presents experimental (indicated by symbols) and theoretical (full lines) data as calculated for a Si fcc crystal. We see a pretty nice agreement between experimental and theoretical data. We can identify the different phonon modes (TA, LA, TO, LO) and see how the phonon dispersion evolves in 3 dimensions. In principle, one would have to consider the dispersion in the full 3 dimensional space. As the representation would be rather complex, one shows the dispersion along the directions between high symmetry points (see x-axis).

4.5 Peierls Transition

(This section will be written at a later time) The Peierls transition was first predicted in the 1930s by R. Peierls and later observed in real systems. In the last sections, we discussed linear atomic chains (with a two atomic base in the lecture and an one atomic base in the exercise). R. Peierls investigated further the physics of a linear, one atomic chain - including the electron system. He realized that a linear chain with a one atomic base and a half filled metallic electron band (which we will discuss later during the course) cannot be the ground state of the system. Instead, he predicted that at lower temperatures, a linear atomic chain with an one atomic base and lattice spacing a will transform into a linear chain with a two atomic base and lattice spacing $2a$. Following his calculations, a linear chain with an one atomic base has 3r modes, i.e. 2 TA and 1 LA. When it transforms into a linear chain with a two atomic base we have 6 modes, i.e. 2 TA, 1 LA, 2 TO, 1 LO, and a band gap between the optical and acoustical modes with the energy lowered for the acoustical mode and increased for the optical mode near $q = \pi/a$. The same process will occur for the electron system (which we did not yet introduce). In the case of a fully occupied band, we will loose more energy than we gain. However, for a half-filled system, we only gain energy due to lowering the fully occupied lower mode - but loose no energy as the upper mode is fully unoccupied.

4.6 Scattering at time-dependent objects: Phonon Spectroscopy

The solution of the equation of motion lead us to planar waves. Analogue to the wave-matter dualism in quantum physics, we might consider the planar waves as particles, so called phonons and ask to which extend these particles interact with other particles such as electron, neutrons or photons. We will therefore come back to the scattering process introduced in the previous chapter 3. Eq. 3.5 (see Notes) is the solution for scattering at a static system. We will now consider that the distribution of scattering centers ($\rho(\vec{r})$), as in the case of a time dependent displacement of atoms, is changing with time:

$$A \sim e^{-i\omega_0 t} \int_{particle} \rho(\vec{r}(t)) e^{-i\vec{K}\cdot\vec{r}} d\vec{r} \overset{(1)}{=} e^{-i\omega_0 t} \sum_{\vec{n}} e^{-i\vec{K}\cdot\vec{r_n}(t)} \overset{(2)}{=} \sum_{\vec{n}} e^{-i\vec{K}\cdot\vec{r_n}} e^{-i\vec{K}\cdot\vec{u_n}(t)} e^{-i\omega_0 t} \tag{4.20}$$

For simplicity, we assume that each atom is a point-like scattering center, set (1) $\rho(\vec{r}(t)) \propto \sum_{\vec{n}} \delta(\vec{r} - \vec{r}_n(t))$ and rewrite the position of the scattering centers under the usage of the previously introduced displacement u, i.e. (2) $\vec{r}_n(t) = \vec{r}_n + \vec{u}_n(t)$.

- For lecture : -

A can be Taylor developed for small displacements of u. Using a plane wave as a solution for u we get:

- For script: -

A can be Taylor developed for small displacements of u

$$A \propto \sum_{\vec{n}} e^{i(\vec{K}\cdot\vec{r_n}(t))} [1 - i\vec{K}\cdot\vec{u}_n(t) ...] e^{-i\omega_0 t} \tag{4.21}$$

Using a plane wave as a solution for u

$$\vec{u}_n(t) = \vec{u} \frac{1}{\sqrt{M}} e^{\pm i(\vec{q}\cdot\vec{r}_n - \omega(\vec{q})t)} \tag{4.22}$$

we get:

$$A_{inelastic} \propto \sum_{\vec{n}} e^{-i(\vec{K}\pm\vec{q})\cdot\vec{r}} i\vec{K}\cdot\vec{u} \frac{1}{\sqrt{M}} e^{-i(\omega_0 \pm \omega(\vec{q}))t} \tag{4.23}$$

We find that in the case of a motion of scattering centers, we get a second solution for the scattering amplitude. The incoming wave can interact with the crystal system and adsorb the energy of an excited phonon (+) or the incoming wave generates a phonon in the crystal ($-$). We also identify two conditions for such an elastic process, energy and momentum conservation:

$$\begin{aligned} \hbar\omega &= \hbar\omega_0 \pm \hbar\omega(\vec{q}) \\ \vec{k} - \vec{k}_0 \pm \vec{q} &= \vec{G} \end{aligned} \tag{4.24}$$

The process of creation or annihilation of phonon modes can be observed for all kind of wave-matter interactions. Very common techniques are Raman scattering (RLS) for optical modes and Brillouin scattering for acoustical modes (BLS) (note the interaction is through dipole transitions) to observe in an university laboratory phonons modes. Thereby, because of different energy ranges for BLS and RLS the setup for the detection of photons is different. But such optical experiments have a significant draw-back. Within the range of visible light the maximum possible transfer of momentum is limited by the momentum of light:

$$2k_0 = \frac{4\pi}{\lambda} \sim 2 \cdot 10^{-3} \mathring{A}^{-1} \tag{4.25}$$

Therefore, only a very small fraction of the reciprocal space (1/1000) can be probed and the measurement of the entire dispersion relation is not feasible. With x-rays it is possible to cover the entire reciprocal space using photons of the energy of 10 keV. However, the energy resolution is in the range of eV. Using a synchrotron source there exist possibilities to achieve higher energy resolution but the experimental requirements are challenging. Most efficient approach is to use thermal neutrons from a nuclear plant in the energy range of 0.1 - 1 eV.

4.7 Light Spectroscopy

Raman and Brillouin spectroscopy are important experiments in solid state physics to study elementary processes such as phonons, plasmons (many-electron excitations), ... The process of observation is achieved through inelastic light scattering as discussed in the previous section and obeys energy and momentum conservation:

$$\begin{aligned} \hbar\omega &= \hbar\omega_0 \pm \hbar\omega(\vec{q}) \\ \vec{k} - \vec{k}_0 &\pm \vec{q} = \vec{G} \end{aligned} \tag{4.26}$$

Thereby, ω_o and k_0 represent the incoming wave and ω and k the scattered waves. In the range of visible light, the maximum transmitted k momentum is small compared to the momentum of phonons, we only observe phonons at $q \sim 0$.

The process of interaction between excitation and photons goes through the polarizability of the valence electrons. The incoming light wave induces with its electrical field $\vec{E}$ a polarization $\vec{P}$ (which is described by the susceptibility tensor $\tilde{\chi}$).

$$\vec{P} = \epsilon_0 \tilde{\chi} \vec{E}_0 \text{ and } P_i = \epsilon_0 \sum_j \chi_{ij} E_{j0} \tag{4.27}$$

As the electrical field $\vec{E}$ modulates with time, also $\vec{P}$ does - and therefore, the system becomes a dipole-emitter. Described by the laws of electro-dynamics, the emitted energy density $\vec{S}$ is

$$\vec{S}(t) = \frac{\omega^4 P^2 sin^2\theta}{16\pi^2 \epsilon_0 r^2 c^3} \vec{s} \tag{4.28}$$

$\vec{S}$ is the Poynting vector, $\vec{s}$ the unit vector in observation direction, r the distance, θ the angle between the Polarization and the observation direction. The electrical susceptibility $\tilde{\chi}$ is now also a function of any kind of dipole inducing collective motions $X[\omega(\vec{q}), \vec{q}]$ such as phonons, plasmons, magnetic excitations (magnons). These collective motions $X[\omega(\vec{q}), \vec{q}]$ have to be treated as disturbances for $\tilde{\chi}$:

$$\tilde{\chi} = \tilde{\chi}^0 + \frac{\partial \tilde{\chi}}{\partial X} X \tag{4.29}$$

As we only have to consider the case $q \sim 0$, we can further simplify: $X = X_0 cos(\omega(\vec{q}t))$ and $\vec{E}_0 = \vec{E}_0 cos(\omega_o t)$ introduced into equation 4.27 gives:

$$\begin{aligned} \vec{P} &= \epsilon_0 \tilde{\chi}^0 \vec{E} cos(\omega_0 t) + \epsilon \frac{\partial \tilde{\chi}}{\partial X} X_0 \vec{E}_0 cos(\omega(\vec{q}t)) cos(\omega_0 t) \\ &= \epsilon_0 \tilde{\chi}^0 \vec{E} cos(\omega_0 t) + \frac{1}{2} \epsilon \frac{\partial \tilde{\chi}}{\partial X} X_0 \vec{E}_0 \{cos([\omega_0 + \omega(\vec{q})]t) + cos([\omega_0 - \omega(\vec{q})]t)\} \end{aligned} \tag{4.30}$$

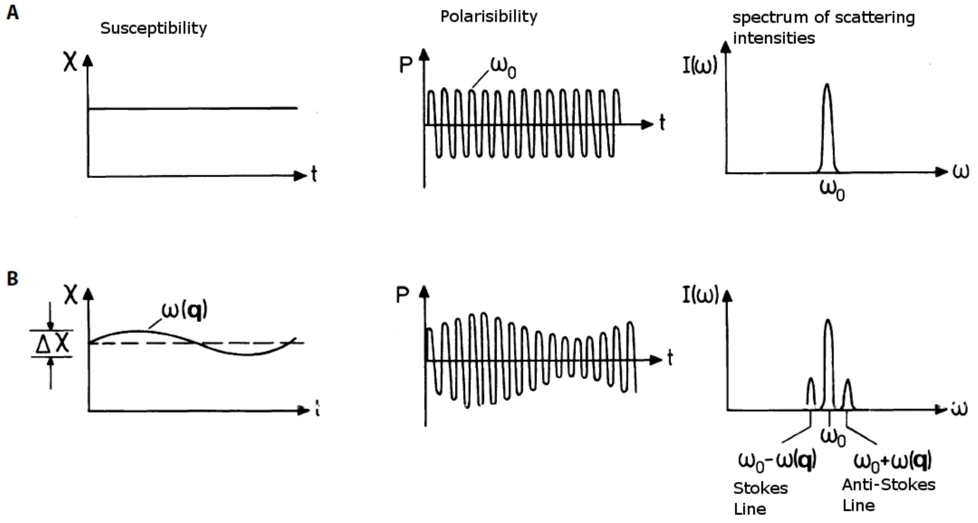

Figure 4.7: Schematics of Raman Scattering in the case of elastic scattering (A) and inelastic scattering (B)

The emitted waves have different contributions (see Fig. 4.7). At frequency ω_0 elastically scattered waves are reflected. These are called Rayleigh-Emission (Fig. 4.7A). But we also find two new additional features in the spectrum as soon as inelastic scattering is possible. These two features are called the Stokes-Line and the Anti-Stokes-Line (Fig. 4.7). The Stokes-Line ($-$) results from inelastic scattering and excitation of a mode (for example of a phonon mode). The Anti-Stokes-Line can be observed when the photon wave adsorbs during the scattering process energy through the de-excitation of a mode ($+$) as illustrated in Fig. 4.7B. Such a process can only occur as long as excited modes already exist in the sample. As the amount of excited modes is related to the temperature, the intensity of the Anti-Stokes line reduces drastically with reduction of temperature. Note: the cross-section for inelastic scattering is much lower than for elastic scattering, typically by a factor of 10^6.

Critical for the observation of Raman-lines (Stokes and Anti-Stokes) is that the differential of the susceptibility is unequal zero: $\frac{\partial \chi_{ij}}{\partial X}$ in the specific direction. That means, the presence of Raman-lines depends on the geometry of the system and the direction of observation. To illustrate this geometry related dependence, Fig. 4.8 presents experimental data for a Bi_2Se_3. Along the (trigonal) c-axis, the crystal is formed layer-wise of Se and Bi.

As illustrated in Fig. 4.8a the modes A^1_{1g}, E^2_g and A^2_{1g} have a changing dipole moment in the x and z direction. Whereas only the E^2_g mode has additional components in y direction. Therefore, along the z direction incoming light with a polarization parallel to the x axis will excite all modes. However, A^1_{1g} and A^2_{1g} will only emit radiation in x and z direction whereas E^2_g will also emit in y direction.

Note 1 Resonance-Raman-Scattering: A special experimental case is given when the energy of the incoming wave $\hbar\omega_0$ matches the energy of the phonons. Then, the efficiency of photon-phonon interaction goes into resonance and an amplification of the Raman intensity is the consequence.

Note 2 Light Source: From eq. 4.28 we see that the intensity of the scattered wave scales with ω^4 of the incoming wave. Therefore, to perform Raman experiments, one generally tries to use laser which are operated at low wavelengths.

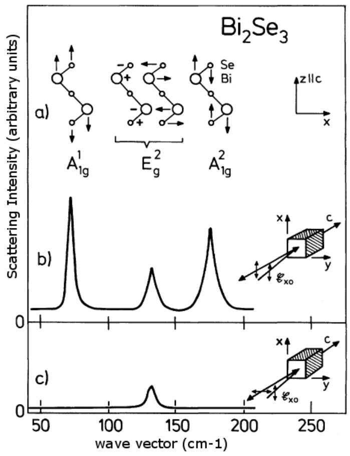

Figure 4.8: Raman spectra from Bi_2Se_3 in different geometries. (a) Three different phonon modes A^1_{1g}, E^2_g and A^2_{1g} are indicated. Vertical arrows indicate motion in z, horizontal arrows in x, and $+/-$ in y directions. Light scattering of photons propagating in z direction and polarization in x direction detects all three modes when (b) sensitive for x polarization whereas (c) with sensitivity for y polarization only the E^2_g is detectable.

4.8 elastic properties of crystals

So far, we studied the possibility of the motion of atoms. But for which purpose ? One reason is the coupling of electrons to the crystal lattice and therefore, we have to understand the lattice system to understand at a later stage the electronic properties. But the motion of atoms within the crystal does also determine the mechanical properties. We will not study these aspects in too great details but only give a brief and general look inside this aspect.

Let as assume a 3 dimensional cubic crystal with only nearest neighbor interaction with coupling constant f. In the same way as for the linear atomic chain, we derive an equation of motion:

$$M\ddot{u}_{n1} = f(u_{(n+1)1} - u_{n1}) - f(u_{n1} - u_{(n-1)1}) \tag{4.31}$$

The difference we can write as a differential (as long as the displacements are small):

$$\begin{aligned}(u_{(n+1)1} - u_{n1}) - (u_{n1} - u_{(n-1)1}) &= a\frac{\partial u_1}{\partial x_1}|_{x=(n+1/2)a} - a\frac{\partial u_1}{\partial x_1}|_{x=(n-1/2)a} \\ &= a^2\frac{\partial^2 u_1}{\partial x_1^2}|_{x=na}\end{aligned} \tag{4.32}$$

Introducing the material density $\rho = M/a^3$ we get:

$$\rho\ddot{u}_1 = c_{11}\frac{\partial^2 u_1}{\partial x_1^2} \tag{4.33}$$

with $c_{11} = f/a$ (called elastic module) and the speed of longitudinal waves $c_L = \sqrt{c_{11}/\rho}$.

The first derivative of u in respect of a direction defines the deformation, i.e. the deformation tensor ϵ_{ij}:

$$\epsilon_{ij} = \frac{\partial u_i}{\partial x_j}. \tag{4.34}$$

The deformation tensor describes the displacement of the lattice structure in direction j because of a force in direction i. The displacement can result in a rotation and volume extension.