IFES Report

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ABSTRACT

The goal of this report is to show the basic concepts of Solid-State Physics in general and especially for Calcium. In Chapter 1 we will talk about Crystal Structure and how it is described, chapter two will provide further informations about how to determine these structures. To get further insides in the topic of Solid-State Physics Chapter 3, we will discuss some of the models which are used to describe Atoms which are not at rest at their lattice site.

1 Introduction

he goal of this report is to show the basic concepts of Solid-State Physics in general and especially for Calcium. Calcium metal is used as a reducing agent in preparing other metals such as thorium and uranium. It is also used as an alloying agent for aluminium, beryllium, copper, lead and magnesium alloys. These use cases make a deeper understanding of solids states essential.

In the FIRST CHAPTER we will talk about the Chrystal Structures and how they are described. Most of the basic concepts will be shown directly by the example of calcium. The book *Elementary Solid State Physics* provided the necessary background information. In the SECOND CHAPTER we will talk about diffraction in this crystal, as by studying the diffraction pattern of a beam information about the structure of the crystal can be obtained. *Elementary Solid State Physics* [1] delivered insights in these concepts to get further information or different explanation to some topics, *Introduction to Solid State Physics* [2] was used in addition. In the first to parts, it is assumed that the Atoms stay at rest at their position. In reality this is not true as atoms oscillate arround their rest position. In CHAPTER 3 we will show some of these effecs.

2 Results

2.1 Chapter 1

First of all we need to identify in which structure calcium crystallizes. As it can be seen in Table 1, it crystallizes in a FCC-structure.

Table 1: Structures and Cell Dimensions of some Elements and Compounds, Elementary Solid State Physics [1], p. 18

Element or compound	Structure	a, Å	c, Å
Al	fcc	4.04	
Be	hcp	2.27	3.59
Ca	fcc	5.56	
C	Diamond	3.56	
Cr	bcc	2.88	
Co	hcp	2.51	4.07
Cu	fcc	3.61	
Ge	Diamond	5.65	
Au	fcc	4.07	
Fe	bcc	2.86	
Pt	fcc	3.92	
Si	Diamond	5.43	
Ag	fcc	4.08	
Na	bcc	4.28	
Zn	hcp	2.66	4.94
LiH	Sodium chloride	4.08	
NaCl	Sodium chloride	5.63	
AgBr	Sodium chloride	5.77	
MnO	Sodium chloride	4.43	
CsCl	Cesium chloride	4.11	
TlBr	Cesium chloride	3.97	
CuZn (β-brass)	Cesium chloride	2.94	
CuF	Zincblende	4.26	
AgI	Zincblende	6.47	
ZnS	Zincblende	5.41	
CdS	Zincblende	5.82	

FCC stands for *Face-centered cubic*, which means the Calcium crystal is built up uf cubes with atoms at each corner and an atom in the middle of each of the six cube planes. (As shown in Figure 1)

Unit Cell

The convential Unit Cell of a FCC lattice looks as follows:

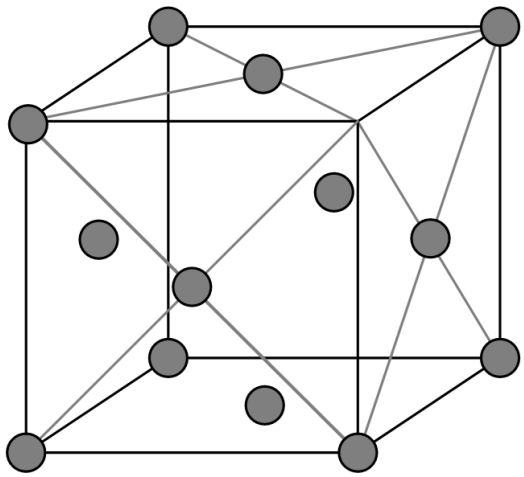

Figure 1: FCC-Lattice

Primitive Vectors

With the primitive vectors each point in a lattice can be represented by a linear combination of the three primitive vectors:

$$\mathbf{R} = n_1\vec{u} + n_2\vec{v} + n_3\vec{w}$$

It may be said, that the lattice is invariant under the group of all translations expressed by $\mathbf{R}$.

The three primitive vectors for the fcc lattice are shown in Figure 2 and specified below.

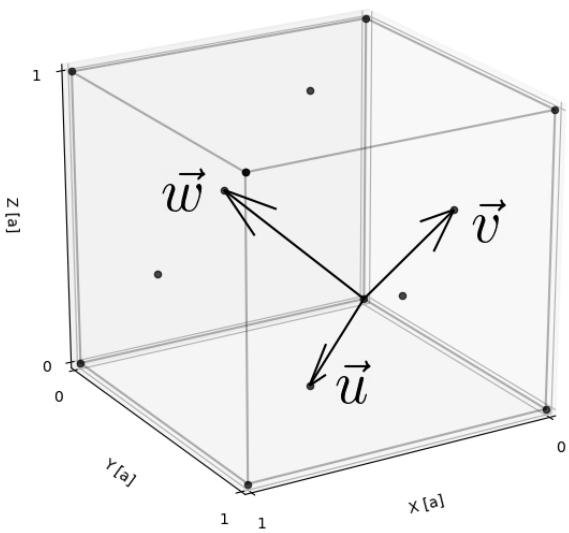

Figure 2: Primitive Vectors in a FCC-Lattice

$$\vec{u} = \frac{a}{2}\begin{pmatrix}1\\1\\0\end{pmatrix} \qquad \vec{v} = \frac{a}{2}\begin{pmatrix}0\\1\\1\end{pmatrix} \qquad \vec{w} = \frac{a}{2}\begin{pmatrix}1\\0\\1\end{pmatrix}$$

Whith these 3 base vectors a parallelepiped is given which is a primitive cell. The volume of the primitive cell can be calculated with the following formula

$$V_{PC} = |(\vec{u} \times \vec{v}) \cdot \vec{w}|$$

which equals (with $a = 5.56\,\mathring{A}$)

$$V_{PC} = \frac{a^3}{4} = 4.297 \cdot 10^{-30}\,m^3 = 4.297 \cdot 10^{-24}\,cm^3$$

Packaging Factor

The Packaging Factor can be calculated as the ratio between the volume of the atoms in the unit cell to the volume of the unit cell.

The volume of the unit cell can be calculated as:

$$V_{UC} = a^3$$

The unit cell containts 4 whole atoms. One eighth of a atomic sphere at each corner (8) and one half at each cube face (6).

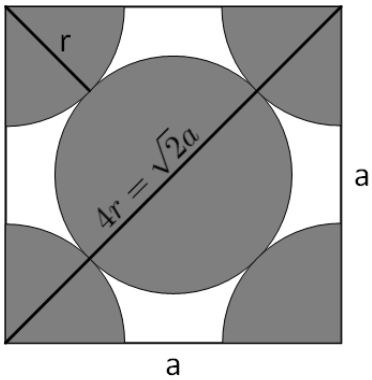

Figure 3: Relation between the atomic radius and the parameter a in a FFC

As Figure 3 shows the relationship between the parameter a and the radius of the atomic sphere is given as:

$$r = \frac{\sqrt{2}}{4}a$$

And further the volume of the sphere

$$V_{Atom} = \frac{4}{3}\pi r^3 = \frac{a^3\pi}{\sqrt{2^5}\cdot 3}$$

So the Atomic Packaging Factor APF can be calculated as ratio between the volume consumed by the atoms to the whole volume.

$$APF = \frac{4\cdot V_{Atom}}{V_{UC}} = \frac{\pi}{3\cdot\sqrt{2}} \approx 74\%$$

Density

The atomic mass of calcium is given as [3]:

$$m_{Ca} = 40.078\frac{g}{mol}$$

By dividing the mass of the four atoms of the fcc unit by the volume of the unit cell we get the density of Calcium.

$$\rho = \frac{4}{N_A}\cdot\frac{m_{Ca}}{V_{UC}} = 1.55\frac{g}{cm^3}$$

(110) Plane

To show that the plane contains reticular rows of atoms in the specified directions, we need to calculate the normal vektor $\vec{n}$ of the plane, which we get by inverting the Miller Indices

$$\vec{n} = (\frac{1}{h}, \frac{1}{k}, \frac{1}{l}) = (1,\ 1,\ 0)$$

By knowing that the dot product between to orthogonal vectors is zero, we can show that the three directions lay orthogonal to $\vec{n}$ and further so parallel to the (110) plane.

- [001]
  $\vec{v_1} = (0,\ 0,\ 1)$
  $\vec{n}\cdot\vec{v_1} = 1\cdot 0 + 1\cdot 0 + 0\cdot 1 = 0$
- $[1\bar{1}0]$
  $\vec{v_1} = (1,\ -1,\ 0)$
  $\vec{n}\cdot\vec{v_1} = 1\cdot 1 + 1\cdot(-1) + 0\cdot 0 = 0$
- $[\bar{1}11]$
  $\vec{v_1} = (-1,\ 1,\ 1)$
  $\vec{n}\cdot\vec{v_1} = 1\cdot(-1) + 1\cdot 1 + 0\cdot 1 = 0$

By knowing that the three directions lay inside or parallel to the plane, we showed that the plane contains reticular rows of atoms in the [001], $[1\bar{1}0]$ and $[\bar{1}11]$ directions.

Planes

In the following the planes $P1 : (0\bar{3}2)$ and $P2 : (\bar{1}21)$ are drawn inside the unit cell. The Miller-Indices of the planes corresbond to the following plane equations:

$$P1: \quad -\frac{1}{3}y + \frac{1}{2}z = 1$$

$$P2: \quad -x + \frac{1}{2}y + z = 1$$

With respect of the fact that all parallel planes have the same Miller-Indices the planes which were drawn are:

$$P1: \quad z = \frac{2}{3}y$$

$$P2: \quad z = x - \frac{1}{2}y$$

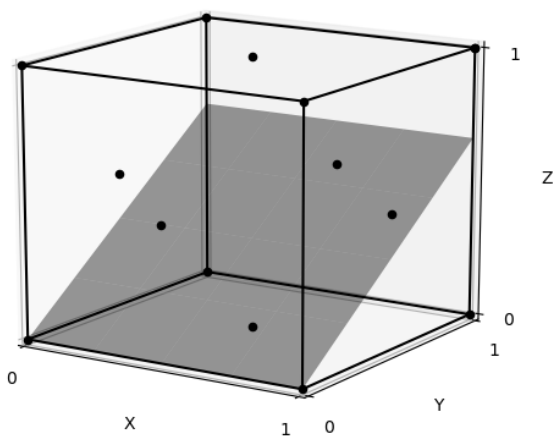

Figure 4: $(0\bar{3}2)$-Plane in a FCC-Lattice

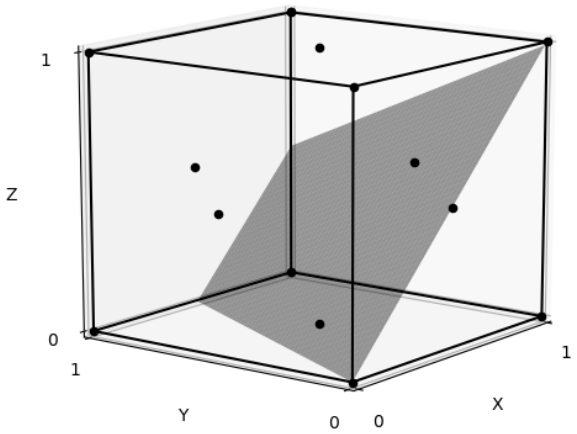

Figure 5: $(\bar{1}21)$-Plane in a FCC-Lattice

Linear Density [110]

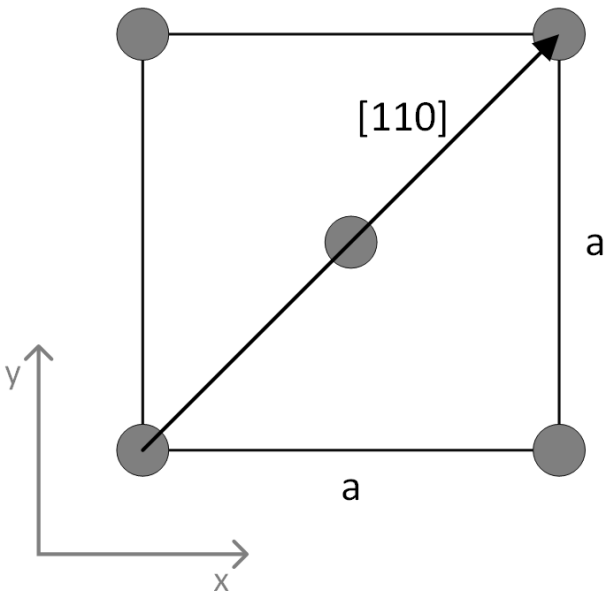

Figure 6: Linear Density of FCC in [110] Direction

?? shows the [110] direction in a FCC lattice. As you can see the [110] direction includes 2 atoms inside a length of $\sqrt{2}a$.

Therefore (with $a = 5.56\,\mathring{A}$)

$$\lambda = \frac{2\,Atoms}{\sqrt{2}a} = \frac{\sqrt{2}}{5.56}\frac{Atoms}{\mathring{A}}$$

Potential Energy

The potential energy between to adjacent ions can be represented by

$$E(r) = -\frac{A}{r} + \frac{B}{r^n} \tag{1}$$

To calculate the bonding energy $E_0 = E(r_0)$, which is a minimum of the function $E(r)$, the derivative has to equals zero. The negative derivative of the bonding energy equals the interatomic force.

$$F(r) = -\frac{\partial E(r)}{\partial r} = 0$$

$$-\frac{A}{r^2} + \frac{nB}{r^{n+1}} = 0$$

$$\Rightarrow r_0 = \left(\frac{A}{nB}\right)^{\frac{1}{n-1}}$$

By inserting the result for r_0 into Equation 1, the bonding energy E_0 in terms of A, B and n results as:

$$E_0 = E(r_0) = -\frac{A}{\left(\frac{A}{nB}\right)^{\frac{1}{n-1}}} + \frac{B}{\left(\frac{A}{nB}\right)^{\frac{n}{n-1}}}$$

2.2 Chapter 2

Geometric Structure Factor

The structure factor gives the amplitude of a scattered wave arising from the atoms with a single primitive cell.

$$\Phi_{\mathrm{k}} = \sum_j f_j(\mathrm{K}) e^{i\mathrm{K}\cdot\mathrm{d}} \tag{2}$$

For crystals composed of only one type of atom, it's common to split the structure factor into two parts:

$$\Phi_{\mathrm{k}} = f_j(K) S_{\mathrm{K}} \tag{3}$$

,where f_j is atomic form factor and S_{K} is geometric structure factor. Now let's focus on the second one.

$$S_{\mathrm{K}} = \sum_{j=1}^{n} e^{i\mathrm{Kd}} \tag{4}$$

For a perfect crystal the lattice gives the reciprocal lattice, which determines the positions (angles) of diffracted beams, and the basis gives the structure factor F_{hkl} which determines the amplitude and phase of the diffracted beams:

$$F_{hkl} = \sum_{j=1}^{N} f_j \mathrm{e}^{[-2\pi i(hx_j + ky_j + lz_j)]} \tag{5}$$

The FCC lattice is a Bravais lattice, and its Fourier transform is a body-centered cubic lattice. However to obtain F_{hkl} without this shortcut, consider an FCC crystal with one atom at each lattice point as a primitive or simple cubic with a basis of 4 atoms, at the origin $x_j, y_j, z_j = (0,0,0)$ and at the three adjacent face centers $x_j, y_j, z_j = \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(0, \frac{1}{2}, \frac{1}{2}\right)$ and $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$

$$F_{hkl} = \sum_{j=1}^{4} f_j \mathrm{e}^{[-2\pi i(hx_j + ky_j + lz_j)]} = f[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{h+l}]$$

with the result

$$F_{hkl} = \begin{cases} 4f, & h,k,l \text{ all even or all odd} \\ 0, & h,k,l \text{ mixed parity} \end{cases}$$

- lattice centering (translational operations derived from the lattice type)
- screw axes (symmetry axes that imply rotation and an additional translation)
- glide planes (mirror planes that imply reflection and an additional translation).

Diffraction Maximums

Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive

interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. Bragg's law, describes the condition on for the constructive interference to be at its strongest by formula:

$$2d_{hkl} \sin\theta = \lambda \tag{6}$$

We need to use the concept of the reciprocal lattice to evaluate the lattice structure factor S, which is involved in the x-ray scattering process. In equation:

$$S = G_{hkl} \tag{7}$$

The scattering vector s is equal to a reciprocal lattice vector.Also this implies that s is normal to the (hkl) crystal planes. For a cubic system we gave also a formula:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{8}$$

After few transformation we get:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + l^2 + k^2}}$$

Planes where we obtain a first 3 difraction maximums are following:

$$P_1 = (111) \qquad P_2 = (200) \qquad P_3 = (220)$$

We can calculate interplanar distances:

$$d_{hkl1} = \frac{5,58}{\sqrt{1^2 + 1^2 + 1^2}} = 3,23\text{Å}$$
$$d_{hkl2} = \frac{5,58}{\sqrt{2^2 + 0^2 + 0^2}} = 2,79\text{Å}$$
$$d_{hkl1} = \frac{5,58}{\sqrt{2^2 + 2^2 + 0^2}} = 1,98\text{Å}$$

$$sin\theta = \frac{\lambda}{2d}$$
$$\theta = \arcsin\frac{2d}{\lambda}$$

$$\theta_1 = 13,3^\circ \qquad \theta_2 = 15,7^\circ \qquad \theta_3 = 22,3^\circ$$

Reciprocal Lattice

In order to identify the reciprocal lattice we start by the calculating the reciprocal lattice vectors, which form a new set of basis vectors.

As in subsection 2.1 already explained the three primitive vectors of the fcc structure are:

$$\vec{u} = \frac{a}{2}\begin{pmatrix}1\\1\\0\end{pmatrix} \qquad \vec{v} = \frac{a}{2}\begin{pmatrix}0\\1\\1\end{pmatrix} \qquad \vec{w} = \frac{a}{2}\begin{pmatrix}1\\0\\1\end{pmatrix}$$

The new reciprocal lattice vectors are defined as:

$$\vec{u^*} = \frac{2\pi}{V_{PC}}(\vec{v} \times \vec{w}) \qquad \vec{v^*} = \frac{2\pi}{V_{PC}}(\vec{w} \times \vec{u}) \qquad \vec{w^*} = \frac{2\pi}{V_{PC}}(\vec{u} \times \vec{v}) \tag{9}$$

With V_{PC} the volume of the primitive cell given from subsection 2.1 as:

$$V_{PC} = \frac{a^3}{4}$$

The three vectors result in:

$$\vec{u^*} = \frac{2\pi}{a}\begin{pmatrix}1\\1\\-1\end{pmatrix} \qquad \vec{v^*} = \frac{2\pi}{a}\begin{pmatrix}-1\\1\\1\end{pmatrix} \qquad \vec{w^*} = \frac{2\pi}{a}\begin{pmatrix}1\\-1\\1\end{pmatrix}$$

Which represents the primitive translation vectors of a bcc lattice. Therefore the bcc lattice is the reciprocal lattice to the fcc lattice in which calcium crystallizes.

Eswald Sphere

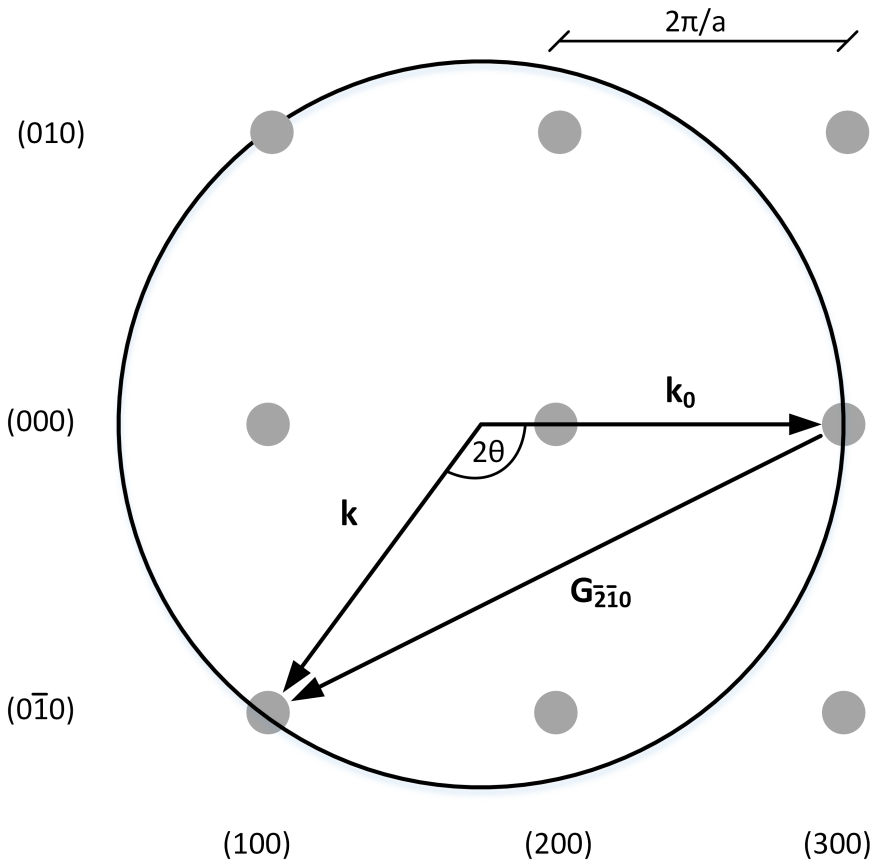

Figure 7: Ewald Sphere

$$\frac{G_{\overline{2}\overline{1}0}}{2a^*} = \frac{2k_0}{G_{\overline{2}\overline{1}0}} \qquad \Rightarrow k_0 = \frac{5a^*}{4} = \frac{5\pi}{2a}$$

As for the wavelength λ (with $a = 5.56\,\mathring{A}$):

$$\lambda = \frac{2\pi}{k_0} = \frac{4a}{5} = 4.45\,\mathring{A}$$

As for the angle 2θ follows

$$2\theta = 180^\circ - 2\cos^{-1}\left(\frac{G_{\overline{2}\overline{1}0}}{2k_0}\right) = 180^\circ - 2\cos^{-1}\left(\frac{\sqrt{5}}{10}\right) = 25.84^\circ$$

2.3 Chapter 3

Density of States (1D)

We start with the 1-D wave equation:

$$\frac{\partial^2 u}{\partial x^2} - \frac{\rho}{Y}\frac{\partial u}{\partial t} = 0$$

Which delivers a solution in the way of:
(The time depence is not needed for calculatiing the density of states)

$$u = Ae^{ikx} \tag{10}$$

By using the boundary conditions:

$$u(x = 0) = u(x = L)$$

We get:

$$e^{ikL} = 1$$

Due to Eulers-Equation we get for k

$$k = n\frac{2\pi}{L}$$

If you choose integer values for n and plot them along a k-axis, they form a one-dimensional mesh with a constants spacing $(2\pi/L)$ between the poins.

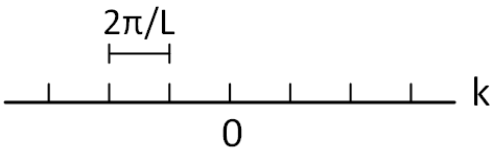

Figure 8: Allowed values of k

As we can see if L becomes large we get quasi-continous points for k. So the number of modes (points) in an interval dk in k-space equals:

$$\frac{L}{2\pi}dk$$

Using the dispersion relation we can find the number of modes in a frequency range $d\omega$, which lies within $(\omega, \omega + d\omega)$. This number is given as $(g\omega)d\omega$, with $g(w)$ defined as the density of states.

$$g(\omega)d\omega = \frac{L}{2\pi}dk$$

By solving for $g(\omega)$ and multipling with a factor of two. (Due to the fact that we have to include the modes lying the negative k-region)
We get:

$$g(\omega) = \frac{L}{\pi}\frac{1}{\frac{d\omega}{dk}} \tag{11}$$

By assuming that the dispersion in linear ($\omega = v_s k$) the density of states is

$$g(\omega) = \frac{L}{\pi}\frac{1}{v_s} \tag{12}$$

which is independet of ω

Density of States (3D)

Starting with the solution for the wave equation as same as in the 1-D case (Equation 10) we get:

$$u = Ae^{i(k_x x + k_y y + k_z z)} \tag{13}$$

By applying the same boundary conditions as in the 1-D case we get:

$$u = e^{i(k_x x + k_y y + k_z z)} = 1$$

$$(k_x,\, k_y,\, k_z) = (n\frac{2\pi}{L},\, m\frac{2\pi}{L},\, l\frac{2\pi}{L})$$

Each point in this k-space has a volume of $(2\pi/L)^3$. The number of modes that lie within a spherical shell with thikness dk with a radius k and a volume $4/3\pi k^3$, is given by:

$$\frac{d}{dk}(\frac{L}{2\pi})^3\frac{4}{3}\pi k^3 = (\frac{L}{2\pi})^3 4\pi k^2 dk$$

And so with $L^3 = V$:

$$g(\omega)d\omega = \frac{V}{2\pi^2}k^2 dk \quad \Rightarrow \quad g(\omega) = \frac{V}{2\pi^2}k^2\frac{dk}{d\omega}$$

By applying the linear dispersion relation, we get:

$$g(\omega) = \frac{V}{2\pi^2}\frac{\omega^2}{v_s^3} \tag{14}$$

As there are three different modes associated with the same value for q. (one longitudinal and 2 transversal modes). Equation 14 has to be multiplied by a factor of three to get the correct result.

$$g(\omega) = \frac{3V}{2\pi^2}\frac{\omega^2}{v_s^3} \tag{15}$$

Different to the 1-dimensional case the density of states in the 3-dimensional case is not a constant, rather increases as ω^2. This can be explained due to the fact that volume of the spherical shell increases with q^2 and as q is propotional to ω, the dependence on ω^2 can be explained.

Debye Frequency

In the Debye model the vibration frequency of the lattice covers a wide rang of values.

The total energy of the lattice is calculated by:

$$E = \int \bar{\epsilon}(\omega) g(\omega)\, d\omega \tag{16}$$

$g(\omega)$ ... density of states
$\bar{\epsilon}(\omega)$ ... energy of each mode

For various reasons a cutoff frequency is needed for example to not get infinit energys in Equation 16.

The upper cutoff frequency was defined, by requiring that the total number of modes included must be equal to the number of degrees of freedom for the entire solid.

$$\int_0^{\omega_D} g(\omega)\, d\omega = 3N_A \tag{17}$$

With inserting the Equation 14 into equation Equation 17 the integral can be solved and a expression for the Debye frequency w_D is obtained.

$$\int_0^{\omega_D} \frac{3V}{2\pi^2}\frac{\omega^2}{v_s^3}\, d\omega = \frac{3V}{2\pi^2}\frac{1}{v_s^3}\left[\omega\right]_0^{\omega_D} = \frac{V}{2\pi^2}\frac{\omega_D^3}{v_s^3}$$

$$\frac{V}{2\pi^2}\frac{\omega_D^3}{v_s^3} = 3N_A \qquad \Rightarrow w_D = (6\pi^2 n)^{\frac{1}{3}} v_s \text{ with } n = \frac{N_a}{V}$$

The debye frequency is proportinal to the 3rd root of the concentrations of the amtos n in the solid. This is simply explained by 3-dimensional q space.

Monoatomic 1D chain

We are going to consider elastic vibrations of the atomic network in classic terms. We assume that:

1. The average equilibrium position of each atom is placed at the Bravais network node.
2. Atomic deflections from equilibrium positions are small compared to the distances between atoms. This assumption leads to harmonic approximation allowing for simplification accounts
3. We will use the Born-Openhaimer adiabatic approximation: the velocities of electrons are on the order of $10^8 \frac{\mathrm{cm}}{\mathrm{s}}$, while the velocities of nuclei in atoms on the order of at most $10^5 \frac{\mathrm{cm}}{\mathrm{s}}$. When considering the motion of whole atoms or ions can therefore be assumed that electrons are always in their own ground state for a specific atom position.

If the waves propagate in a crystal with a regular structure the entire network planes move in phase, in direction or in parallel or perpendicular to the direction of the wave. After considering every of those statements the frequency of normal vibration modes $\omega(k)$ of modes with wave vector k (dispersion relationship) can be expressed by:

$$m\omega^2 = 4K \sin^2\left(\frac{ka}{2}\right) \tag{18}$$

So ω is (knwon as the dispersion relationship):

$$\omega = \sqrt{\frac{4K}{m}} \cdot |\sin\left(\frac{ka}{2}\right)| \tag{19}$$

The group velocity is defined as the partial derivative according to k.

$$v_G = \frac{\partial \omega}{\partial k} = \sqrt{\frac{K}{m}} a \cos\left(\frac{ka}{2}\right)$$

$$v_G(k=0) = \sqrt{\frac{K}{m}} a$$

$$v_G\left(k = -\frac{\pi}{a}\right) = v_G\left(k = \frac{\pi}{a}\right) = 0$$

The group velocities on the edge of the 1 Brillouin zone are zero, which means that we have a standing wave.

Disperision Relationship for Calcium

In subsection 2.1 we calculated the linear density λ for Calcium in the [110] direction as Figure 6 shows the [110] direction is the direction with the lowest distance between the atoms.

Therfore the parameter a in Equation 19 is given as the inverse of the linear density λ.

Another helpfull relationship is the following:

$$K = aY = \frac{Y}{\lambda} \tag{20}$$

Y ... Young's modulus

Elementary Solid State Physics [1], p. 91

The Youngs's modulus for calcium can be found in different literature [4] and is found to be:

$$Y_{Ca} = 20GPa$$

So for Calcium the dispersion relationship results in

$$\omega(k) = \sqrt{\frac{4Y_{Ca}}{m_{Ca}\lambda}} \cdot |\sin\left(\frac{k}{2\lambda}\right)| \tag{21}$$

with:

$Y_{Ca} = 20GPa$
$m_{Ca} = 40.078\,u$
$\lambda = \frac{\sqrt{2}}{5.56}\frac{1}{\mathring{A}}$

The resulting graph is shown in Figure 9.

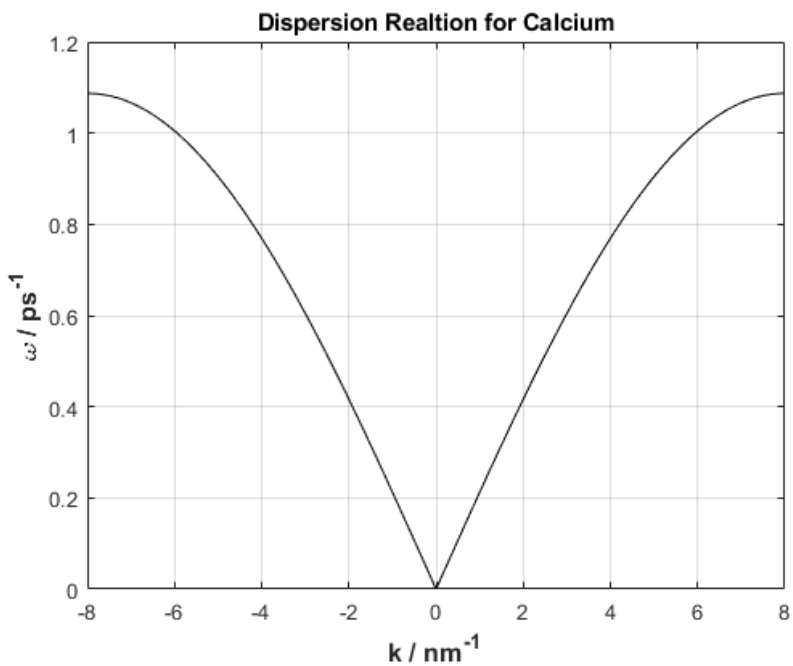

Figure 9: Disperision Realtion for Calcium

Experimental methodologies for determining the frequency of the lattice phonons

The phonon dispersion, which means the relationship between energy and momentum of the lattice vibrations can be investigated by inelastic neutron scattering and inelastic X-ray scattering. Small pulse phonons which means in the center of the Brillouin zone, can be detected by Raman, infrared spectroscopy or Brillouin scattering.

3 Conclusion

References

[1] M.A. Omar, *Elementary Solid State Physics: Principles and Applications*, Addison-Wesley, London, 1993.

[2] Charles Kittel, *Introduction to Solid State Physics*, 7th ed., Wiley, 1996

[3] Lenntech, *Chemical elements listed by atomic mass*, viewed 12 May 2020, *https://www.lenntech.com/periodic/mass/atomic-mass.htm*

[4] WebElements, *Calcium: physical properties*, viewed 13 May 2020, *https://www.webelements.com/calcium/physics.html*

List of Tables

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