Thermodynamic and electronic properties of niobium at finite temperatures

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LITH-IFM-A-EX—15/3114—SE
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In the phonon dispersion relations, Kohn anomalies are experimentally observed to weaken with increased temperature, which is related to the superconducting properties of Nb. I include anharmonicity when I calculate the thermodynamic properties of Nb and relate this to the electronic structure.

In this thesis I show that anharmonicity can not be neglected when considering thermodynamic properties of Nb. I observe broadening in the electronic band structure with increasing temperature, correlated with the gradual weakening of the Kohn anomalies in the phonon dispersion relations. Kohn anomaly in the phonon dispersion relation can be observed at 300 K and is completely absent at 1200 K. The observation of the Kohn anomaly’s disappearance in the calculations is of great importance because it cannot be repeated by approaches that do not include anharmonic effects, meaning that properties that are directly related to phonon dispersion, like elastic constants, can be calculated more accurately with this approach.

**Nuclear properties**

Niobium has 47 neutrons and 72 protons. It has a natural isotopic abundance of 98.9% for Nb-93, 1.1% for Nb-95, and 0% for Nb-94. Niobium is a transition metal in group 5A of the periodic table, and it is hard, strong, and has a high melting point. It is used in various applications, such as in aerospace and nuclear power. The electronic configuration of niobium is [Kr] 4d^2 5s^1.
To my family
Abstract

Niobium (Nb) is a fascinating element, that when it is in a solid state has remarkable properties. This is believed to be a result of its electronic configuration that has partially filled 4d and 5s sub-shells. Nb has a melting temperature of 2750 K, a high strength at high temperature, and a good wear resistance. Because of these properties, Nb is used as material for components of rockets and jet engines, and for strengthening steel.

In the phonon dispersion relations, Kohn anomalies are experimentally observed to weaken with increased temperature, which is related to the superconducting properties of Nb. I include anharmonicity when I calculate the thermodynamic properties of Nb and relate this to the electronic structure.

In this thesis I show that anharmonicity can not be neglected when considering thermodynamic properties of Nb. I observe broadening in the electronic band structure with increasing temperature, correlated with the gradual weakening of the Kohn anomalies in the phonon dispersion relations. Kohn anomaly in the phonon dispersion relation can be observed at 300 K and is completely absent at 1200 K. The observation of the Kohn anomaly’s disappearance in the calculations is of great importance because it cannot be repeated by approaches that do not include anharmonic effects, meaning that properties that are directly related to phonon dispersion, like elastic constants, can be calculated more accurately with this approach.
Acknowledgements

I would first like to thank my supervisor Olle Hellman, for introducing me to the field and also for the opportunity he has given me. I also want to thank him for his help in this work. I also need to thank my other supervisor Nina Shuhumba for all the help she has given me. I am furthermore very thankful for the patience both my supervisors have had for me. I would also like to thank my examiner Sergey Simak, for letting me doing this thesis. I must also thank my family, for their support and reminding me that this is only a “job”. Finally, I want to thank my beer and rugby friends. You all made this possible.
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Chapter 1

Introduction

1.1 Background

Niobium (Nb) is an element widely known for its superconductive properties. Also, due to its temperature resistance, it is used as material for components in jet engines and rockets. This makes it interesting to calculate the thermodynamic properties for Nb at elevated temperatures. It is also interesting to relate the thermodynamics with the electronic properties at finite temperatures. It has been shown experimentally that the Kohn anomalies for acoustic transverse phonons and its superconducting properties are related [4]. The Kohn anomaly is a decrease in the frequency of phonons whose wave vectors connect two sheets of the Fermi surface [22]. The anomalies, or kinks, in the phonon dispersion relations for Nb have been noted from earlier experiments in a temperature range from 296 to 1030 K and their relation to the electron-phonon coupling has been discussed [37] [39, pp. 43-52] [42, 45, 46]. It has been shown that the Kohn anomaly weakens when the temperature is increased, especially between 296 to 700 K, and will not be observable at 1030 K [39, p. 45]. In this temperature range, the non-harmonic effects might be significant. It is my intention to include anharmonic effects in the discussion regarding the electron-phonon coupling and investigate its relation to the phonon dispersion and the electronic structure, see Chapter 4.

1.2 Purpose

The purpose of this thesis is to investigate non-harmonic effects on the thermodynamic properties of Nb and also if the anharmonicity can be related to the electron-phonon coupling.

1.3 Definition of problem

Thermal expansion, phonon dispersion relations, and phonon density of states which fully includes the anharmonic effect needs be obtained for finite tempera-
tures. The effect of anharmonicity on the phonon modes also needs to be described and compared with the effect of temperature on electronic structure at finite temperatures.
Chapter 2

Theory

2.1 First principles calculations

From one perspective, the most straightforward approach to make a model of a physical system is to use data from experiments and create an empirical model. This has the disadvantage of limited predictiveness: you can not get anything out you did not build into the model. An alternative is to simulate these systems “from scratch”, using fundamental physical laws. The physics of electrons and nuclei are governed by the Schrödinger equation. Explicitly solving this equation is prohibitively expensive, but with appropriate approximations accurate models can be constructed. This type of calculations are called first principles calculations.

2.2 Density functional theory

By solving the Schrödinger equation \[\hat{H}\Psi = E\Psi,\] where \(E\) is the energy of the state \(\Psi\), for a system consisting of \(N\) electrons and \(M\) nuclei where

\[
\Psi = \Psi(r_1, \ldots, r_N, r_{n1}, \ldots, r_{nM})
\]

is a wave function dependent of both of the sets \(\{r\}\) and \(\{r^n\}\), which are positions for the electrons and the nuclei. The wave function \(\Psi\) will be known, from which all the information that can be known of the system in that specific state will be accessible. The Hamiltonian takes the form

\[
\hat{H} = \hat{T}_{\text{nuc}} + \hat{T} + \hat{V}_{\text{nuc}} + \hat{V}_{\text{elec}} + \hat{V}_{\text{ext}}
\]

\[
= -\frac{\hbar^2}{2} \sum_i \frac{\nabla_i^2}{M_i} - \frac{\hbar^2}{2m_e} \sum_k \nabla_k^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|r_i - r_j|} + \frac{1}{2} \sum_{k \neq l} \frac{e^2}{|r_k - r_l|} - \sum_{j k} \frac{e Z_j}{|r_j - r_k|}.
\]

(2.3)
In (2.3), the term $\hat{T}_{\text{nuc}}$ is the kinetic energy of the nuclei, $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}_{\text{nuc}}$ is the Coulomb interaction between the nuclei, $\hat{V}_{\text{ee}}$ is the Coulomb interaction between the electrons, $\hat{V}_{\text{ext}}$ is the interaction between the electrons and the nuclei, and the hat above these terms denotes that they are operators for $\Psi$. The nuclei indices are noted as $i$ and $j$, the electron indices are noted as $k$ and $l$, $m_e$ is the electron mass, $M_i$ is the mass of nucleus $i$, $e$ is the elementary charge, and $Z_i$ is the elementary charge multiplied with the number of protons in nucleus $i$. For this expression, an exact solution can only be found for the simplest of systems. For real systems we need to introduce approximations. First we apply the Born-Oppenheimer approximation [8]. The assumption of this model is that the degrees of freedom of electrons and nuclei can be separated due to their difference in mass and velocity. The nuclei are then seen as a static point charges from the electrons point of view. The Hamiltonian will take a simpler form:

$$\hat{H}_e = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} = -\frac{\hbar^2}{2m_e} \sum_k \nabla^2_k + \frac{e^2}{2} \sum_{k \neq l} \frac{e^2}{|r_l - r_k|} - \sum_{jk} \frac{eZ_j}{|r_j - r_k|}. \quad (2.4)$$

The terms $\hat{T}$, $\hat{V}_{\text{ee}}$, and $\hat{V}_{\text{ext}}$ in (2.4) are the same as in (2.3). The Schrödinger equation, with this electronic Hamiltonian (2.4), is still unsolvable for a system consisting of more than a few atoms. The origin of complexity and the reason why the Schrödinger equation becomes intractable is the many-body problem that arise from that (2.4) is still dependent on the position of all the electrons. A step in the right direction to make this problem solvable was made by Hohenberg and Kohn in 1964, when they introduced density functional theory (DFT) [18]. As the name implies, DFT reformulates (2.4) to be dependent on the electron density. This results in a decrease of degrees of freedom from $3N$ to 3, with the electron degrees of freedom implicitly contained in the new expression. The theory can be expressed in two theorems:

**Theorem 1** The external potential $V_{\text{ext}}(r)$ is a functional dependent only of the ground state density of electrons $n_0(r)$. If two systems have the same ground state density $n_0^1(r) = n_0^2(r)$, but their external potentials are different $V_{\text{ext}}^1(r) \neq V_{\text{ext}}^2(r)$, the difference in potential must then be an arbitrary constant $V_{\text{ext}}^1(r) - V_{\text{ext}}^2(r) = \text{constant}$, for all $r$.

**Theorem 2** It exists a universal density functional $F_{\text{HK}}[n]$ that is valid for any number of electrons and any external potential $V_{\text{ext}}(r)$, that will minimize the total energy functional $E_{\text{tot}}[n]$ for the ground state density of the electrons $n_0(r)$.

The Hohenberg-Kohn (universal energy) functional can be expressed from these theorems as

$$F_{\text{HK}}[n] = E_{\text{tot}}[n] - \int dr V_{\text{ext}}(r)n(r), \quad (2.5)$$

and

$$F_{\text{HK}}[n] = T[n] + V_{\text{ee}}[n]. \quad (2.6)$$
2.2 Density functional theory

Where $T[n]$ is the kinetic energy and $V_{ee}[n]$ is the Coulomb potential energy for the electrons. From (2.5) and (2.6), the total energy functional can be expressed as

$$E_{\text{tot}}[n] = F_{\text{HK}}[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) = T[n] + V_{ee}[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$ (2.7)

This is still unsolvable because the explicit form of $F_{\text{HK}}[n]$ is unknown, but in 1965 Kohn and Sham presented the idea to replace the real electrons in the system with quasi-particles that are not interacting and retains the ground state density [23]. The universal energy functional can be written on the form

$$F_{\text{HK}} = T_s[n] + E_{\text{xc}}[n] + V_{ee}[n],$$ (2.8)

where $T_s[n]$ is the kinetic energy of non-interacting quasi-particles and $E_{\text{xc}}[n]$ is the collection of unknown terms called exchange and correlation. The total energy functional can now be expressed for the new system as

$$E_{\text{tot}}[n] = T_s[n] + E_{\text{xc}} + V_{ee}[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}).$$ (2.9)

Note that in (2.9) the form of $E_{\text{xc}}[n]$ is unknown and different approximations are used to estimate it. The simplest and the first suggestion of this approximation is presented also in the article of Kohn and Sham [23], called local density approximation (LDA) and has the form

$$E_{\text{xc}}[n] = \int \epsilon_{\text{xc}}[n(\mathbf{r})] n(\mathbf{r}) d\mathbf{r},$$ (2.10)

where $\epsilon_{\text{xc}}$ is the exchange-correlation energy of a uniform electron gas. Because the non interacting quasi-particles are fermions, the total wave function will be a single Slater determinant [47] consisting of a set of non interacting single particle orbitals $\psi_i(\mathbf{r})$ that will give the lowest energy solution to

$$\left\{ \frac{-\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}[n(\mathbf{r})] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}),$$ (2.11)

which is called the Kohn-Sham equations, where $\epsilon_i$ is the energy of the state for the orbital $\psi_i$, and

$$V_{\text{eff}}[n(\mathbf{r})] = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}),$$ (2.12)

where

$$V_{xc} = \frac{\partial E_{xc}[n(\mathbf{r})]}{\partial n(\mathbf{r})}.$$ (2.13)

The electron density can now be expressed as

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2.$$ (2.14)

Everything needed to calculate the total energy of the many-body system is now obtained.
2.3 Crystal lattice dynamics

Heat capacity and thermal expansion are thermal properties that are related to the increase of the amplitude of the atomic vibrations when the temperature is increased. To formalise this we start by considering an atom \( i \) positioned at \( \mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i \), where \( \mathbf{R}_i \) is the equilibrium position and \( \mathbf{u}_i \) is the fluctuation at any given time. The atoms move in a potential that is created from the interactions between all the nuclei and electrons, represented as the terms \( \hat{V}_{\text{nuc}} \), \( \hat{V}_{\text{elec}} \), and \( \hat{V}_{\text{ext}} \) in the Hamiltonian (2.3) for the the many-body Schrödinger equation (2.1). The Born-Oppenheimer approximation [8] makes it possible to write the total potential energy as a function of the positions of the atom’s nuclei

\[
U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N). \tag{2.15}
\]

To make the problem tractable, the expansion at the mean equilibrium positions of the atoms can be expressed in the following way using Taylor’s theorem:

\[
U = U_0 + \sum_{i} u_i^\alpha \frac{\partial U}{\partial u_i^\alpha} \bigg|_{u=0} + \frac{1}{2} \sum_{ij} u_i^\alpha u_j^\beta \frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta} \bigg|_{u=0} + \frac{1}{6} \sum_{ijk} u_i^\alpha u_j^\beta u_k^\gamma \frac{\partial^3 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} \bigg|_{u=0} + \cdots, \tag{2.16}
\]

where \( i, j, k \) are indices to the position of the atoms and \( \alpha, \beta, \gamma \) are Cartesian indices. The derivatives of the total potential energy are called force constant matrices and are denoted as

\[
\Phi_i^\alpha = \left. \frac{\partial U}{\partial u_i^\alpha} \right|_{u=0} = 0 \tag{2.17}
\]

\[
\Phi_{ij}^{\alpha\beta} = \left. \frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta} \right|_{u=0} \tag{2.18}
\]

\[
\Phi_{ijk}^{\alpha\beta\gamma} = \left. \frac{\partial^3 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} \right|_{u=0}. \tag{2.19}
\]

The value of the linear terms (2.17) is zero because they are the net forces acting on the atoms in the system in equilibrium [9, pp. 217-220]. The constant term in (2.16) is usually set to the equilibrium potential energy of the system, which is the energy that the system would have if all the nuclei where positioned at their mean equilibrium position. If only terms up to second order is considered, the expression of the total potential energy is the harmonic approximation. The Hamiltonian for the system can then be expressed as:

\[
\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2M_i} + \sum_{ij} \mathbf{u}_j \Phi_{ij} \mathbf{u}_i. \tag{2.20}
\]
2.3 Crystal lattice dynamics

The $p_i^2$ is the squared momentum and $M_i$ is the mass of atom $i$. The second term in (2.20) is a summation over pairs of global indices to the position of the atoms, which can be rewritten to a summation over pairs of indices in the unit cell if the system is assumed to have a periodic crystal structure. The atom at the global position $i$ and has the position $\mu$ in the unit cell will have $l$ vectors to the atoms at the global position $j$ that has the position $\nu$ in the unit cells of the system. This set of vectors is denotes as $\{R_{l}^{\mu\nu}\}$. With this, expression (2.20) can be expressed as

$$\hat{H} = \sum_{i\mu} \left( \frac{p_{i\mu}^2}{2M_{i\mu}} + \sum_{l,\nu} u_{\mu\nu} \Phi_{\mu\nu}(R_l^{\mu\nu}) u_{\nu l} \right).$$

(2.21)

Assuming that that the solid material consist of a large number of unit cells, the ratio between its surface and volume will be small and the effects of the boundary conditions (surface related effects) can be neglected [28]. The Hamiltonian (2.21) becomes independent of the global indices ($i$ and $j$) and the equation of motion for the atom at position $\mu$ in the unit cell can be written as

$$M_{\mu} \ddot{u}_{\mu} = -\sum_{\nu l} \Phi_{\mu\nu}(R_l^{\mu\nu}) u_{\nu l}.$$

(2.22)

This drastically reduces the number of coupled equations that needs to be solved. Because the Hamiltonian 2.21 is a sum of two terms that are on positive definite form, it is possible to transform the coordinates in a way that diagonalize the momentum operator, $\hat{p}$, and the position operator, $\hat{u}$, of the atoms [15, pp. 377-381] [21, pp. 28-29]. This canonical transformation is an expansion in the form of plane waves

$$\hat{u}_{\alpha}^{\mu} = \sum_{q,\nu} \sqrt{\frac{1}{2N\hbar}} e^{i\mu\nu(q)} e^{iq} \epsilon_{\mu\nu}(q) \left( \hat{a}_{q\nu} + \hat{a}_{q\nu}^\dagger \right)$$  

(2.23)

$$\hat{p}_{\alpha}^{\mu} = \sum_{q,\nu} \sqrt{\frac{1}{2N\hbar}} e^{i\mu\nu(q)} e^{iq} \epsilon_{\mu\nu}(q) \left( \hat{a}_{q\nu} + \hat{a}_{q\nu}^\dagger \right)$$  

(2.24)

and their inverses

$$\hat{a}_{q\nu} = \sum_{l,\mu} \sqrt{\frac{1}{2N\hbar}} e^{-iq} R_{l\mu}(q) \left( \hat{u}_{\mu\nu}^{\alpha} \sqrt{M_{\mu\nu}(q)} + i \frac{\hat{p}_{\nu\mu}^{\alpha}}{\sqrt{M_{\mu\nu}(q)}} \right)$$  

(2.25)

$$\hat{a}_{q\nu}^\dagger = \sum_{l,\mu} \sqrt{\frac{1}{2N\hbar}} e^{-iq} R_{l\mu}(q) \left( \hat{u}_{\mu\nu}^{\alpha} \sqrt{M_{\mu\nu}(q)} - i \frac{\hat{p}_{\nu\mu}^{\alpha}}{\sqrt{M_{\mu\nu}(q)}} \right).$$  

(2.26)

$N$ is the number of atoms in the system, $q$ is a vector in the first Brillouin zone (BZ), $\omega_s^2$ and $\epsilon_s$ are eigenvalues and eigenvectors of the dynamical matrix [31, pp. 16-18]

$$\omega_s^2(q)\epsilon_s(q) = \Phi(q)\epsilon_s(q)$$  

(2.27)
\[ \Phi(q) = \begin{pmatrix} \Phi_{11}(q) & \cdots & \Phi_{1N_{uc}}(q) \\ \vdots & \ddots & \vdots \\ \Phi_{N_{uc}1}(q) & \cdots & \Phi_{N_{uc}N_{uc}}(q) \end{pmatrix} \quad (2.28) \]

with
\[ \Phi_{\mu\nu}(q) = \sum_l e^{iq \cdot R_l} \frac{\Phi_{\mu\nu}(R_l)}{\sqrt{M_\mu M_\nu}} \quad (2.29) \]

where \( N_{uc} \) is the number of atoms in the unit cell and both \( M_\mu \) and \( M_\nu \) are the masses of the atoms at position \( \mu \) and \( \nu \) in the unit cell. The eigenvalues \( \omega_s^2 \) will have multiple values for every \( q \). The number of values of \( \omega_s \) is \( 3N_{uc} \), and the separated values are called modes and are denoted as \( s \). The frequencies \( \omega_s \) as a function of reciprocal vectors \( q \) are known as dispersion relations. If the orthonormality relations for \( \hat{u} \) and \( \hat{p} \) hold, it becomes clear that \( \hat{a}_s^\dagger q_s \) and \( \hat{a}_q s \) define annihilation and creation operators for a quantum mechanical harmonic oscillator.

With these operators, the Hamiltonian can be expressed on the simple form
\[ \hat{H} = \sum_{q\omega} \hbar \omega_s(q) \left( \hat{a}_s^\dagger q_s \hat{a}_q s + \frac{1}{2} \right) \quad (2.30) \]

which is a sum of uncoupled harmonic oscillators. The bosonic quasi-particles that are related to the creation and annihilation operators in (2.30) are phonons. These can be defined as quantized crystal lattice vibrations. The partition function for one phonon will be
\[ Z_s = \sum_{n=0}^{\infty} e^{-\frac{n+\frac{1}{2}}{n^2}} \hbar \omega_s(q) = \frac{1 - e^{-\frac{\hbar \omega_s(q)}{k_B T}}}{1 - e^{-\frac{\hbar \omega_s(q)}{k_B T}}} \quad (2.31) \]

the total partition function will therefore be
\[ Z = \prod_{q\omega} e^{-\frac{\hbar \omega_s(q)}{2k_B T}} \frac{1 - e^{-\frac{\hbar \omega_s(q)}{k_B T}}}{1 - e^{-\frac{\hbar \omega_s(q)}{k_B T}}} \quad (2.32) \]

From the total partition function, Helmholtz free energy can be expressed as
\[ F = -k_B T \ln Z = \sum_{q\omega} \frac{\hbar \omega_s(q)}{2} + k_B T \ln \left( 1 - \exp \left( -\frac{\hbar \omega_s(q)}{k_B T} \right) \right) \]
\[ = \int_0^{\infty} g(\omega) \frac{\hbar \omega}{2} + g(\omega)k_B T \ln \left( 1 - \exp \left( -\frac{\hbar \omega}{k_B T} \right) \right) d\omega, \quad (2.33) \]

where \( g(\omega) \) is the phonon density of states and is given by
\[ g(\omega) = \sum_s \int_{uZ} \frac{\delta(\omega - \omega_s(q))}{2\pi^3} dq. \quad (2.34) \]
2.4 Anharmonicity

The quasi-harmonic approximation is the harmonic approximation where the force constant matrix depends on the volume \([1]\). Applied to a series of volumes, one obtains the Helmholtz free energy from which the Gibbs free energy can be mapped out from by using

\[
G = F + PV
\]  
(2.35)

where the pressure \(P\) is obtained from

\[
\frac{\partial F}{\partial V} \bigg|_T = -P, \tag{2.36}
\]

The volume as a function of pressure and temperature is calculated from the the Gibbs free energy by

\[
\frac{\partial G}{\partial P} \bigg|_T = V. \tag{2.37}
\]

From which the volumetric thermal expansion can be derived from as

\[
\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T} \bigg|_P. \tag{2.38}
\]

2.4 Anharmonicity

Until now, phonons have been considered independent, but in reality they interact. By also considering terms of higher order than two in the Taylor expansion of the total potential energy (2.16), these interactions are included. The Hamiltonian (2.21) will then not be a sum of two terms of quadratic form like in Section 2.3, and can therefore not be diagonalized. But by adding a complex frequency dependent self-energy, \(\Sigma = \Delta + i\Gamma\), that represents that \(q\) is not a good quantum number in the cases when force constant matrices of higher order than 2 are included. The Schrödinger equation still can be solved as an eigenvalue problem. This will give the lineshape (or one-phonon cross section) \([11]\)

\[
\sigma_s(q, \Omega) \propto \frac{\omega_s(q)\Gamma_s(q, \Omega)}{[\Omega^2 - \omega_s^2(q) - 2\omega_s(q)\Delta_s(q, \Omega)]^2 + 4\omega_s^2(q)\Gamma_s^2(q, \Omega)}. \tag{2.39}
\]

where \(\Omega\) is the frequency of a matter wave of a particle with no electric charge, called dispersion frequency and is defined as \(\Omega = E/\hbar. E\) is the probe energy of the incident particle that will have the likelihood \(\sigma_s(q, \Omega)\) to interact with the phonon described by \(q\) and \(s\). If the real and imaginary parts are set to be constant with energy, then \(\Delta\) is the shift of \(\omega\) and \(\Gamma\) is the broadening of the phonon lineshapes, and (2.39) reduces to a Lorentzian function with a full width half maximum of \(\Gamma\) centered at \(\omega + \Delta\). To describe interacting phonons we need to keep higher order terms in the expansion in (2.16). Keeping terms up to third order, the lowest order of perturbation theory is used to evaluate \(\Gamma_s(q, \Omega)\) and \(\Delta_s(q, \Omega)\). They can
be written as [11, 30]

\[
\Gamma_s(q, \Omega) = \sum_{s' s''} \frac{\hbar \pi}{16} \frac{V}{(2\pi)^3} \iiint_{BZ} |\Psi_{ss' s''}(q, q', q'')|^2 \\
\times \Delta(q, q', q'')(n_s(q') + n_{s''}(q'') + 1)\delta(\Omega - \omega_s(q') - \omega_{s''}(q'')) \\
+ 2(n_s(q') - n_{s''}(q''))\delta(\Omega - \omega_s(q') + \omega_{s''}(q'')) \ \! dq' dq''.
\] (2.40)

The \( \Delta(q, q', q'') \) function ensures that \( q + q' + q'' = K \), and the three phonon element is

\[
\Psi_{ss' s''}(q, q', q'') = \sum_{ijk\alpha\beta\gamma} \frac{e^{\alpha i}(q) e^{\beta j}(q') e^{\gamma k}(q'')}{\sqrt{m_i m_j m_k}} \sqrt{\omega_i(q) \omega_j(q') \omega_k(q'')} \Psi_{ij k} e^{iq \cdot r_i}. \] (2.41)

And the real part is gained from a Kramers-Kronig (Hilbert) transformation of \( \Gamma \)

\[
\Delta_s(q, \Omega) = \mathcal{H}(\Gamma_s(q, \Omega)) = \frac{1}{\pi} \int \frac{\Gamma_s(q, \omega)}{\omega_s(q) - \Omega} d\omega_s(q). \] (2.42)

This can be described as when we have an unperturbed phonon, it will be represented as a single peak in the frequency domain, see a) in Figure 2.1, that would be a single point if it was plotted against \( q \). When the temperature is finite, the frequency of the phonon will shift by \( \Delta \) and also broaden by \( \Gamma \), see b) in Figure 2.1. If the lineshapes are plotted versus momentum \( q \), you get the broadened phonon dispersions, usually denoted as \( S(q, E) \) or the phonon spectral function, see c) in Figure 2.1.

2.5 Molecular dynamics

To generate detailed data regarding the movements of the atoms in a system at a finite temperature, molecular dynamics (MD) is a suitable method. The basis of this method is to determine the interatomic forces, to solve the equation of motion for every atom in the system, and for a number of discrete steps propagate the equations of motion. The classical way to calculate the interatomic forces is from empirical force fields [2, pp. 71-78]. The method used in this thesis is Born-Oppenheimer molecular dynamics (BOMD). Here, the Born-Oppenheimer approximation [8] is used, but instead of seeing it as the nuclei are fixed from the electrons point of view, from the nuclei perspective it can be considered as classical particles moving in a potential generated by the electrons, under the condition that the electron relaxation time is sufficiently small, which is usually the case. Because of the sufficient short relaxation time, the system can be considered to be in equilibrium. If the Hellmann-Feynmann theorem [14] is applied

\[
\frac{dU}{d\lambda} = \langle \Psi | \frac{d}{d\lambda} \hat{H} | \Psi \rangle,
\] (2.43)

where \( \lambda \) is any parameter specifying the positions of the nuclei, \( U \) is the potential, \( \Psi \) is the wavefunction, and \( \hat{H} \) is the Hamiltonian for the system. The force \( f_i \) can
Figure 2.1. Theoretical graphic description of a) a phonon, b) the effect of finite temperature on a phonon, and c) the anharmonic effect on a phonon in the time and the frequency domain. Note that the finite temperature effects will only shift the frequency of the phonon while the anharmonic effect will make a single phonon contain multiple frequencies.
be calculated for every atom $i$ as

$$f_i = -\frac{dE}{d\lambda_i}, \quad (2.44)$$

where $\lambda_i$ is specifying the position for atom $i$. The classical equations of motions can be expressed as

$$\dot{r}_i = \frac{p_i}{M_i}, \quad (2.45)$$
$$\dot{p}_i = f_i. \quad (2.46)$$

These simple equations are $6N$ coupled differential equations that are solved iteratively. This can be done by using the velocity Verlet algorithm [48]:

$$r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 \quad (2.47)$$
$$\dot{r}_i(t + \Delta t) = \dot{r}_i(t) + \frac{\ddot{r}_i(t) + \ddot{r}_i(t + \Delta t)}{2} \Delta t. \quad (2.48)$$

In (2.47) and (2.48), the forces are calculated from DFT, the initial positions and velocities are given, and the system is propagated from time $t$ to $t + \Delta t$. The procedure is repeated for a sufficient number of time steps until statistics and properties of interest are obtained. However, this will give a system dependent on the number of particles, the volume, and the energy. The ensemble will be microcanonical, also called NVE. The thermal effect becomes difficult to evaluate because the temperature does not have a parameter in this ensemble, it would be much more suitable to have a canonical ensemble, dependent on the number of atoms, the volume of the system, and the temperature, also called NVT. To go from the microcanonical to the canonical ensemble a thermostat is needed. In this work the Nosé-Hoover thermostat is used [38, 19, 20], where the equation of motion is coupled to an external system with a fictitious mass and the Hamiltonian for the system has an additional degree of freedom that include the effect of temperature on the momentum in the system.

### 2.6 Temperature dependent effective potential

The temperature dependent effective potential method (TDEP) [16, 17] enables calculation of temperature dependent force constants, which are of interest because at finite temperature, the effective potential felt by the ions might be different than at 0K. The method is based on fitting the the forces from a model Hamiltonian to the forces from a set of samples from the appropriate phase space (PS) where the fitting parameter are the force constants. Constraining the TDEP formalism to the second orders gives the following model Hamiltonian:

$$\hat{H} = U_0 + \sum_i \frac{p_i^2}{2M_i} + \frac{1}{2} \sum_{ij} u_{ij} \Phi_{ij} u_i. \quad (2.49)$$
2.7 Unfolding band structures

Note that the model Hamiltonian can be easily extended to arbitrary order, but for simplicity we illustrate the formalism with a second order model. In (2.49), $U_0$ includes the terms not included by the model, $p_i$ is the momentum, $M_i$ is the mass, $u_i$ is the displacement from the mean position of the nucleus $i$, and $\Phi$ is the force constant matrix calculated from

$$
\min_{\Phi} \Delta t = \frac{1}{N_t} \sum_{t} |f_{t}^{PS} - f_{t}^{TDEP}|^2 = \frac{1}{N_t} \sum_{t} |f_{t}^{PS} - \Phi u_{t}^{PS}|^2
$$

$$
= \frac{1}{N_t} \|(f_{t}^{PS} \ldots f_{N_t}^{PS}) - \Phi (u_{1}^{PS} \ldots u_{N_t}^{PS})\|^2 .
$$

In (2.50), $\{f_{t}^{PS}\}$ are the forces, $\{u_{t}^{PS}\}$ the displacements of the atoms in the phase space sample, and $t$ denotes the sample index. The phase space samples can be obtained by e.g. BOMD. The purpose of this method is that the fitted model will include all orders of anharmonicity and electron-phonon coupling, renormalized into the model Hamiltonian of choice, and thereby be more accurate than the quasi-harmonic approximation. $U_0$ in (2.49) is calculated as a correction term between the phonon contribution to the potential energy in the model and the potential energy of the temperature dependent simulation, which will make itself temperature dependent

$$
U_0 = \left\langle U_{PS}(t) - \sum_{ij\alpha\beta} \frac{1}{2} \Phi_{ij}^{\alpha\beta} u_i^{\alpha}(t) u_j^{\beta}(t) \right\rangle ,
$$

where $ij$ are global indices, $\alpha\beta$ are Cartesian indices, and $\Phi_{ij}^{\alpha\beta}$ is the force constant matrix. The model fitted to the simulations is of finite order, $U_0$ will therefore approximate all terms that can not be included. The free energy can then be expressed as a summation of $U_0$ and the free energy phonon contribution calculated with (2.33) as

$$
F_{TDEP} = U_0 + F_{phonon} .
$$

2.7 Unfolding band structures

The phonon dispersion relations and the electronic band structure gives specific information regarding the thermodynamic and electronic transport properties of a crystal. When the effect of temperature is added, the lines of these will become phonon spectral functions, also called lineshapes. For the phonon dispersions this can be obtained from the self-energy as a function of $q$, see Section 2.4, but for the electronic band structure it becomes trickier. If the electronic band structure would be directly measured from a system, the result would be a configuration average over all possible ionic states. Sampling all these configurations would be practically impossible, but in molecular dynamics (MD), the ergodic principle is applied which is that the configuration average can be replaced with a time average. This results in an electron band structure for the whole system is obtained as a function of time for BOMD. However, it would be more convenient to represent it
as an electron band structure for the primitive cell with broadened lines. Because
the supercell in BOMD can be represented as a repetition of the primitive cell, a
band unfolding technique can be applied. It will generate the primitive cell Bloch
characters from the eigenstates of the supercell [12, 33, 41, 49, 51] from the BOMD.
The idea is that for every wave vector \( \mathbf{K} \) in the supercell Brillouin zone there is
\( N_{\text{unfold}} \equiv \Omega_{\text{PCBZ}}/\Omega_{\text{SCBZ}} \) wave vectors \( \mathbf{k}_i \) in the primitive cell Brillouin zone where
\( i = 1, 2, 3, \ldots, N_{\text{unfold}} \). \( \Omega_{\text{PCBZ}} \) and \( \Omega_{\text{SCBZ}} \) are the volumes for the primitive cell
Brillouin zone and the supercell Brillouin zone. An unfolding vector \( \mathbf{G}_{\mathbf{k}_i \rightarrow \mathbf{K}} \) is
said to unfold \( \mathbf{K} \) onto \( \mathbf{k}_i \) with the relation
\[
\mathbf{k}_i = \mathbf{K} + \mathbf{G}_{\mathbf{k}_i \rightarrow \mathbf{K}} .
\]
(2.53)
The folding vector \( \mathbf{G}_{\mathbf{k} \rightarrow \mathbf{K}} \) is said to fold \( \mathbf{k} \) into \( \mathbf{K} \) with the relation
\[
\mathbf{K} = \mathbf{k} - \mathbf{G}_{\mathbf{k} \rightarrow \mathbf{K}} .
\]
(2.54)
Because of the periodicity of both the primitive cell and the supercell, \( \mathbf{k} \) and \( \mathbf{K} \)
are good quantum numbers, and the Schrödinger equation can be solved for these
two systems
\[
\hat{H}_{\text{crystal}} |\mathbf{K} m\rangle = E_m |\mathbf{K} m\rangle \quad \text{(2.55)}
\]
\[
\hat{H}_{\text{crystal}} |\mathbf{k} n\rangle = E_n |\mathbf{k} n\rangle . \quad \text{(2.56)}
\]
In (2.55) and (2.56), \( \hat{H}_{\text{crystal}} \) is some crystal Hamiltonian, \( |\mathbf{K} m\rangle \) and \( |\mathbf{k} n\rangle \) are the spinor eigenvectors for the electrons described by the wave vector and orbit
(also called band index) \( \mathbf{K} \) and \( m \) for the supercell and \( \mathbf{k} \) and \( n \) for the primitive
cell. \( E \) is the energy of the electron in the state described by a wave vector and
a band index. Because of the fold and unfolding relations ((2.53) and (2.54)) the
eigenvector of the supercell can be expressed as a linear combination of the the
eigenvectors of the unit cell [12, 41, 49]:
\[
|\mathbf{K} m\rangle = \sum_{i=1}^{N_{\text{unfold}}} \sum_{n} a(\mathbf{k}_i, n; \mathbf{K}, m) |\mathbf{k}_i n\rangle .
\]
(2.57)
To create a spectral function from the \( |\mathbf{K} m\rangle \), the probability of finding a set of
\( |\mathbf{k}_i n\rangle \) that contributes to the state \( |\mathbf{K} m\rangle \) is needed. This is obtained by projecting
the \( |\mathbf{K} m\rangle \) on all Bloch states \( |\mathbf{k}_i n\rangle \). This is called the spectral weight and can be
expressed as [41, 49]
\[
P_{\mathbf{K} m}(\mathbf{k}_i) = \sum_{n} |\langle \mathbf{K} m | \mathbf{k}_i n \rangle|^2 = \sum_{g \in \text{PCRC}} |C_{\mathbf{K} m}(g + \mathbf{k}_i - \mathbf{K})|^2 ,
\]
(2.58)
where \( C_{\mathbf{K} m}(g + \mathbf{k}_i - \mathbf{K}) \) is the amplitude of the wave in the supercell Brillouin
zone. Expression (2.58) is equivalent with the fraction of Bloch characters that is
presented when the energy is the same for \( |\mathbf{K} m\rangle \) and \( |\mathbf{k}_i m\rangle \) [12, 49]. The energies
\( E \) are obtained from (2.55) and (2.56). The spectral function can be expressed as
\[
A(\mathbf{k}_i, E) = \sum_{m} P_{\mathbf{K} m}(\mathbf{k}_i) \delta(E_m - E) \quad \text{(2.59)}
\]
where \( E \) is a continuous variable [41, 51].
2.8 Phase space sampling

BOMD is inherently classical, meaning that for temperatures below the Debye temperature, important quantum effects will not be treated correctly. To make quantum mechanical calculations of the potential energy, a stochastic approach can be used. To sample phase space according to the appropriate Bose-Einstein statistics one can use the phonon dispersions [13]. To obtain sample points in phase space corresponding to a canonical ensemble, the inverses of (2.23) will give the following expression for the displacements of the atoms in the system and their momentum [13]:

\[ u_i = \sum_s \frac{e_i^s c_s}{\sqrt{M_i}} \sqrt{-2 \ln \xi_1 e^{i2\pi \xi_2}} \]
\[ p_i = M_i \dot{u}_i , \]

where \( u_i \) is the displacement from the mean position, \( p_i \) is the momentum, \( e_i^s \) is the polarization vector for the dynamical matrix, \( M_i \) is the mass for the nucleus \( i \), \( s \) is the mode, \( \xi_1 \) and \( \xi_2 \) are uniformly distributed variables with values between 0 and 1, and the variable \( c_s \) is described quantum mechanically as

\[ c_{\text{quantum}}^s = \sqrt{\frac{\hbar \coth(\hbar \omega_s / 2 k_B T)}{2 \omega_s}} , \]

and classically (in the \( k_B T \gg \hbar \omega_D \) limit, where \( \omega_D \) is the Debye frequency) as

\[ c_{\text{classic}}^s = \sqrt{\frac{k_B T}{\omega_s^2}} . \]

In these expressions ((2.62) and (2.63)), the amplitude \( c_s \) is the thermal mean amplitude of mode \( s \), \( \omega_s \) is the frequency for the mode \( s \), and the Box-Muller transform \( (\sqrt{-2 \ln \xi_1 \exp(i2\pi \xi_2)} \) in (2.60)) ensures a normal distribution around these values. This procedure is called the method of West and Estreicher [50].
Chapter 3

Computational details

All the simulations in this thesis were carried out with the projector augmented wave (PAW) method [6, 25], implemented in the Vienna Ab-initio Simulation Package (VASP) [24, 26, 27]. The Monkhorst-Pack scheme [36] was used to sample the Brillouin zone.

3.1 Choice of exchange-correlation functional and PAW-potential

To select the exchange-correlation functional that gives the equilibrium lattice parameter closest to the experimental values I performed 0 K unit cell calculations. The unit cell was sampled with a $32 \times 32 \times 32$ k-point grid and a 400 eV plane-wave energy cutoff. The electron energy at every k-point was interpolated with the tetrahedron method with Blöchl corrections [7]. The calculations were performed for 9 volumes in a range of 14.89 and 21.43 Å$^3$/atom, PAW-potentials with the valence 11 and 13, and different exchange-correlations (local density approximation (LDA) [23], generalized gradient method (PBE) [40], and AM05 [3, 32]) for each pseudopotential. The PAW-potential with a valence of 11 treats the electrons from the sub-shell $4p$ as valence electrons and the PAW-potential with the valance of 13 treats the electrons from the sub-shells $4s$ and $4p$ as valence electron, the remaining electrons below these are treated as parts of the nucleus. For every combination of PAW-potential and exchange-correlations we calculate the equation of state fitted with Birch-Murnaghan function [5], see Figure 3.1, given by

$$
E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V}{V_0} \right)^{\frac{3}{2}} - 1 \right]^3 B'_0 + \left[ \left( \frac{V}{V_0} \right)^{\frac{3}{2}} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V}{V_0} \right)^{\frac{3}{2}} \right] \right\},
$$

(3.1)

where $E(V)$ is the total energy of the system as a function of the volume at 0 K, $E_0$ and $V_0$ are the energy and volume at equilibrium, $B_0$ is the bulk modulus.
3.1 Lattice parameter \([a]\) (Å)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.4</td>
</tr>
<tr>
<td>0.5</td>
</tr>
</tbody>
</table>

- LDA 11 valence electrons
- LDA 13 valence electrons
- PBE 11 valence electrons
- PBE 13 valence electrons
- AM05 11 valence electrons
- AM05 13 valence electrons

3.2 Calculation of Helmholtz free energy

The following calculations were all preformed with a volume grid (3.135, 3.238, 3.335, 3.427, and 3.513 Å). To calculate Helmholtz free energy at 0 K, the small displacement method [1] was used. A \(6 \times 6 \times 6\) supercell was sampled with a \(3 \times 3 \times 3\) k-point grid. The plane wave energy cutoff was 600 eV. The smearing of the electron energy was preformed with the Methfessel-Paxton method of first order [34] and the width of the smearing was set to be the product of the temperature and the Boltzmann constant. To calculate Helmholtz free energy for

\[ B_0 = -V \frac{\partial P}{\partial V} \bigg|_{P=0} \quad (3.2) \]

\[ B'_0 = \frac{\partial B}{\partial P} \bigg|_{P=0} \quad (3.3) \]

where \(P\) is the pressure and \(V\) is the volume. PAW-sv potential with PBE exchange-correlation functional gives the equilibrium lattice parameter 3.3092 Å closest to the experimental value 3.3026 Å [43]. Therefore I use these settings when I calculate Helmholtz free energy from first principles in the following section.
the temperatures (300, 1200, 2000, and 2700) K, first a molecular dynamics (MD) simulation was first performed for every temperature with a $6 \times 6 \times 6$ supercell, and a $1 \times 1 \times 1$ k-point grid. The plane-wave energy cutoff was 600 eV, the smearing of the electron energy was performed with the Methfessel-Paxton method of first order with a width of the smearing equal to the temperature multiplied with the Boltzmann constant. The mean simulation time was 156 fs, the time step was 1 fs, and the the Nosé-Hoover thermostat was used. TDEP with a model Hamiltonian constrained to the second order (theory in Section 2.6) was used to calculate the force constants matrices from these MD simulations and the phase space was sampled from the force constants by using the theory in Section 2.8. This phase space sample consisted of 30 configurations for every point in the temperature-volume grid. From these 30 configurations Helmholtz free energy was calculated by using TDEP. The configurations were sampled with a $3 \times 3 \times 3$ k-points grid, 600 eV was used as plan-wave cutoff, and the Methfessel-Paxton method of first order was used with a smearing equal to the product of the Temperature and the Boltzmann constant.

3.3 Calculation of phonons including the effect of thermal expansion and unfolding electron band spectrum

To calculate the phonon dispersions that includes the effect of thermal expansion, the volume as a function of temperature was first determined by using (2.35), (2.36), and (2.37) on Helmholtz free energy for the temperatures (0, 300, 1200, 2000, and 2700) K and volumes (3.135, 3.238, 3.335, 3.427, and 3.513) Å. The phase space was then sampled for every volume calculated for a specific temperature. I generated 10 configurations for every temperature and calculated the phonon dispersion by using TDEP as in earlier calculations. The configurations where sampled with a $3 \times 3 \times 3$ k-points grid, a 600 eV plan-wave cutoff, and the Methfessel-Paxton method of first order was used with a smearing width that was set to 0.1 eV if the temperature multiplied with the Boltzmann constant did not exceed this value, if it did, the smearing width was set to the product of the Boltzmann constant and the temperature. To calculate the phonon spectral function I calculated the force constant matrices as I did for the phonon dispersions with the modification that the model Hamiltonian used in TDEP included both the second and the third order force constants. Theory from Section 2.4 was then used to plot the phonon spectral function. The electron band structures was also unfolded for these configurations by applying theory from Section 2.7.
Chapter 4

Results and Discussion

The central quantity when discussing the thermodynamic properties is the Gibbs free energy:

\[ G(P, T) = U - TS + PV. \]  

(4.1)

In the TDEP formalism, this is written as

\[ G_{\text{TDEP}}(P, T) = U_0 - TS_{\text{vib}} - TS_{\text{el}} + PV, \]  

(4.2)

where \( U_0 \) is the renormalized quasi-particle baseline, \( S_{\text{vib}} \) is the vibrational entropy, and \( S_{\text{el}} \) is the electronic entropy. The vibrational entropy is evaluated from phonon density of state at appropriate pressure and implicitly contains renormalized anharmonicity to all orders. I would like to compare this with the quasi-harmonic approximation where the vibrational entropy only depends on the volume, and the anharmonicity is absent:

\[ G_{\text{QH}}(P, T) = U - TS_{\text{vib}} - TS_{\text{el}} + PV. \]  

(4.3)

The theoretical used methods, static DFT calculations, Born-Oppenheimer molecular dynamics, and the phase space sampling described in Section 2.8, uses constant volume and temperature: a canonical ensemble. The first step is to transform Helmholtz free energy to Gibbs free energy via

\[ P(V, T) = -\frac{\partial F}{\partial V} \bigg|_T. \]  

(4.4)

If the \( P = 0 \) isobar is followed, the volume is obtained as a function of temperature. This is a central quantity for the thermodynamic properties and it will enter the phonons, the entropy, and the electronic structure. It is also experimentally accessible. In Figure 4.1 the values obtained from the quasi-harmonic approximation is compared with those obtained from TDEP. From Figure 4.1 we conclude that anharmonicity certainly influences thermal expansion, and the anharmonic values are closer to the experimental than the quasi-harmonic. Having obtained
Results and Discussion

1. Thermal expansion, I proceed to calculate the Gibbs free energy, and related quantities such as total entropy and isobaric heat capacity:

\[ S(P, T) = -\frac{\partial G}{\partial T} \bigg|_P \]  

(4.5)

and

\[ C_p(P, T) = T\frac{\partial^2 G}{\partial T^2} \bigg|_P \]  

(4.6)

This is illustrated in Figure 4.2, where we once again see that the anharmonic TDEP calculations reproduce experimental values well, and the quasi-harmonic values deviate from the experimental at higher temperatures. If we look at the phonon dispersions in Figure 4.3 we see where the quasi-harmonic approximation fails. The TDEP phonon dispersions reproduce both the low and high temperature dispersions accurately. The quasi-harmonic dispersions on the other hand do not. The kink close to \( \Gamma \) in the \( \Gamma-H \) direction should disappear with temperature, as seen in experiment. The quasi-harmonic dispersions retain this kink at all temperatures. This raises the question of what causes the kink to disappear. A traditional approach to go beyond the quasi-harmonic approximation is to introduce phonon-phonon-interactions via perturbation theory, as described in Section 2.4. We see in Figure 4.4 that this is not sufficient. What we can conclude is that the kinks are not related to, or affected by thermal expansion or phonon-phonon-interactions.

Figure 4.1. Thermal expansion for Nb obtained from the quasi-harmonic approximation (QH) and TDEP. The experimental values are from Ref. [35].
This is reassuring, since [22] it is known that the Kohn anomalies occur when the phonon wave vector $q$ coincide with a nesting vector connecting sheets of the Fermi surface. We attempt to quantify this by comparing the unfolded electronic band structure, as described in Section 2.7, to the fully temperature dependent TDEP spectral functions. This can be seen in Figure 4.5. In the left hand panels we have the phonon spectral function as a function of temperature, and in the right hand panels are the unfolded electronic spectral functions. We see clearly, that as temperature increases the kinks in the phonon spectra straighten out. This is correlated with increased smearing in the electronic spectral functions. This smearing is in addition to the Fermi-smearing effect of temperature, this is the thermal dis-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a): Gibbs free energy at $P = 0$. (b): Total entropy. (c): Isobaric heat capacity. The graphs in (a) to (c) are obtained for Nb from the quasi-harmonic approximation (QH) and TDEP. Experimental data 1 and Experimental data 2 in (c) are from Ref. [10, 29].}
\end{figure}
order induced smearing. The smearing of the electronic states will lead to a diffuse Fermi surface. At 0 K, there is a collection of nesting vectors connecting sheets of the surface. The surface is sharp, and the nesting vectors are clearly defined. As temperature increase, the Fermi surface gets smeared out, and the nesting vectors will be convoluted with this smearing, and as a result the Kohn-anomalies become less pronounced, to eventually disappear altogether.

\[ \text{Figure 4.3.} \quad \text{Phonon dispersion relations for Nb obtained from the quasi-harmonic approximation and TDEP. The experimental values for 300 K is from Ref. [42] and for 1030 K Ref. [39, p. 46].} \]
Figure 4.4. (a): Spectral function for the quasi-harmonic approximation. (b): Spectral function for TDEP. Both (a) and (b) are for Nb at 1200 K with the phonon-phonon-interactions added by using perturbation theory as described in Section 2.4. Note that by adding phonon-phonon-interactions to the quasi-harmonic approximation the disappearance of the kinks with increasing temperature can not be reproduced.
Figure 4.5. (a) to (d): Spectral functions of Nb at different temperatures. (e) to (h): Unfolded electron band structures at different temperatures. Note the correlation between the kinks in the spectral functions and the smearing in the electron band structures.
Chapter 5

Conclusions

By using TDEP on a sufficient large canonical ensemble, sampled from phase space by using the method of West and Estreicher, we have proven that the disappearance of Kohn anomalies with increased temperature can be calculated for Nb. We have also shown that the result from these calculations correlates to experimental data better than the results from the quasi-harmonic approximation. A correlation between the smearing of the electronic structure and how pronounced the kinks are in the spectral functions has also been noted.

5.1 Future work

It is my intention to continue with investigate how the Fermi surface is dependent of the temperature and the behaviour of the elastic constants for Nb. I will also expand this work to include zirconium (Zr) and the rest of the refractory metals.
Bibliography


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