

BAKKELAUREATSARBEIT

Sommerfeld expansion for various metals

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October 12, 2010

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1 Introduction

Many physical properties of a solid body are partly or fully determined by electrons. Nearly everyone knows that they transport charge and energy. But there are many more things they are responsible for. In a solid body, properties depend on lattice dynamics (phonons) and on the electronic band structure (electrons). Both parts contribute to different properties, as for instance the thermodynamic properties. Some properties are only dependent on the electronic structure such as magnetism, the chemical potential or if the solid is a metal, a semimetal or an insulator.

If the electronic structure of a solid is known, it is possible to calculate the electronic part. Often integrals like equation (1) are needed to calculate a property. One can try to solve the integral but this is most of the time very complicated or not possible. Another way is to use the Sommerfeld expansion. It was Arnold Sommerfeld, as the name suggests who invented this expansion. The main advantage of the Sommerfeld-expansion is, that it's yielding to rather easy mathematical expressions with the use of an approximation in (1). The approximation is nearly exact at low temperatures, which means in this case low in respect to the Fermi-energy. This means a few 100 degrees Kelvin which is basically the range of interest. A precise derivative and the reason for this can be seen under 2.

So this expansion is a powerful tool to gather information about properties of a solid. Even if the results are only approximate, one should get a better understanding how a property is reacting if the temperature is changed.

It has to be mentioned that all density of states (DOS) are numerically calculated and not experimentally determined. The reason for this is, that in the experiment always measurement uncertainties occur. The formula for the Sommerfeld expansion needs either the density of states or the slope of the DOS at the Fermi energy. This is a problem when experimental data is used. For one reason, the uncertainty changes the slope of the DOS and for the other the value at the Fermi energy is changed. One can look in [6] to see this. So this work is also going to take a closer look at numerically calculated DOS and which results they are delivering with the Sommerfeld expansion. This Bachelor work tries to take a closer look on the advantages and disadvantages of this approximation and how this could be used in solid state physics.

2 The Sommerfeld expansion

Before we start with the mathematical derivative of the Sommerfeld expansion, we should take a closer look at the idea behind it. Some properties of a metal can be calculated with an integral of the following form.

$$I = \int_0^{\infty} g(E) \cdot f(E) dE \quad (1)$$

This integral consists of one part with the Fermi-Dirac distribution and one part of some function of energy. If we now make a integration by parts (see equation (2)) we obtain the derivative of the Fermi-Dirac distribution, which is sharply peaked around the Fermi energy. Figure 1 shows this graphically.

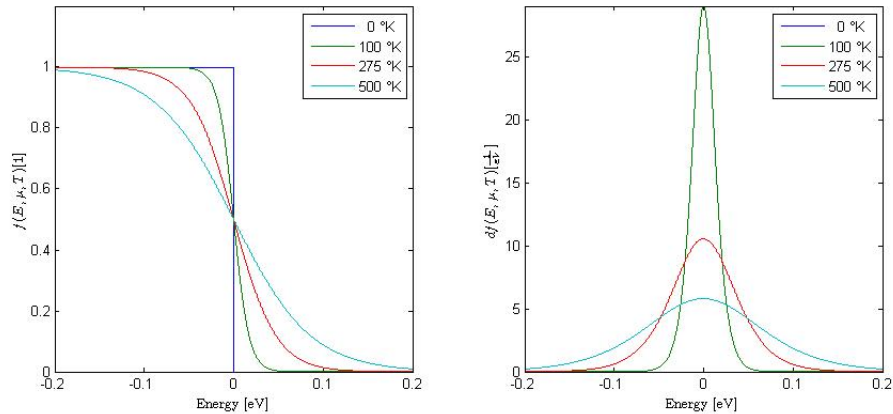


Figure 1: **left:** The Fermi-dirac distribution for a few temperatures T **right:** The derivative of the Fermi-dirac distribution for the same temperatures.

In the figures above it's easy to see that the derivative of the Fermi Dirac distribution is only nonzero in a region around a few k_bT of the Fermi energy. This means that only the electrons around the Fermi energy are contributing to the different properties. This is easy to understand, because it is not possible for a lower lying electron to jump to a higher energy level, because this is already occupied. Lower lying electrons can only jump over the Fermi energy when the thermal energy is high enough. So low thermal energies means a sharp peak of the derivative of the Fermi Dirac distribution. Hence for low thermal energies (up to a few 100°K) we can expand the whole integral

around E_F and we will get a good approximation of the integral. This means we expand the integral (1) in a Taylor series which is done in the following part. First of all, we show the Sommerfeld expansion in a general case. All off the following equations and mathematical derivatives are also in [3].

We start with (1)

$$I = \int_0^{\infty} g(E) \cdot f(E) dE$$

We can use partial integration. This yields to (2).

$$I = G(0) \cdot f(0) - G(\infty) \cdot f(\infty) - \int_0^{\infty} G(E) \cdot \frac{d(f(E))}{dE} dE \quad (2)$$

where $G(E) = \int_0^E g(E') dE'$. and the first two parts are zero because $f(\infty)$ has to be zero and $G(0)$ is also zero by definition.

If we consider the negative derivative of the Fermi function, we see that it is sharply peaked around the Fermi energy (see Figure 1). This means that only a narrow interval (usually around a few $k_B T$) is contributing to the integral. So it doesn't matter when we expand the integration interval to $-\infty$ and ∞ . This helps us to calculate integrals as in (4).

The next step is to expand $G(E)$ around μ . This yields to (3)

$$G(E) = G(\mu) + (E - \mu) \cdot \left(\frac{d(G(E))}{d(E)} \right)_{E=\mu} + \frac{1}{2} \cdot (E - \mu)^2 \cdot \left(\frac{d^2(G(E))}{d(E)^2} \right)_{E=\mu} \dots \quad (3)$$

The combination of (2) and (3) yields to (4):

$$I = G(\mu) \cdot \int_{-\infty}^{\infty} \left(-\frac{d(f(E))}{dE} \right) dE + G'(\mu) \cdot \int_{-\infty}^{\infty} (E - \mu) \cdot \left(-\frac{d(f(E))}{dE} \right) dE \dots \quad (4)$$

Since $\frac{d(f(E))}{d(E)}$ is even in $E - \mu$ the odd terms vanish in (4)

and $\int_{-\infty}^{\infty} -\frac{d(f(E))}{dE} = 1$. This leaves us with:

$$I = G(\mu) + \sum_{n=1}^{\infty} \frac{1}{2n!} \cdot \left(\frac{d^{2n}(G(E))}{d(E)^{2n}} \right)_{E=\mu} \cdot \int_{-\infty}^{\infty} (E - \mu)^{2n} \cdot \left(-\frac{df(E)}{dE} \right) dE \quad (5)$$

To solve the integral in (5) we make use of (6) without mathematical derivative. (if needed see [3])

$$c_{2n} = \int_{-\infty}^{\infty} \frac{x^{2n}}{2n!} \cdot \left(-\frac{d}{dx} \frac{1}{e^x - 1} \right) dx = 2 \cdot \sum_{l=1}^{\infty} \frac{(-1)^{l+1}}{l^{2n}} = 2(1 - 2^{1-2n})\zeta(2n) \quad (6)$$

Combining (5) and (6) yields to:

$$I = G(\mu) + \sum_{n=1}^{\infty} c_{2n} \cdot (k_B T)^{2n} \cdot \left. \frac{d^{2n}(G(E))}{dE^{2n}} \right|_{E=\mu} \quad (7)$$

This is the Sommerfeld expansion. If we consider that $g(E) = \int_{-\infty}^{\infty} G(E) dE$ equation (7) yields the final Sommerfeld expansion for different $g(E)$:

$$I = G(\mu) + \sum_{n=1}^{\infty} c_{2n} \cdot (k_B T)^{2n} \cdot \left. \frac{d^{2n-1}(g(E))}{dE^{2n-1}} \right|_{E=\mu} \quad (8)$$

3 Derivative of different thermodynamic properties

3.1 The chemical potential

We start with the Sommerfeld expansion for the electron density

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE \quad (9)$$

With the Sommerfeld expansion we get:

$$n = \int_{-\infty}^{\mu} D(E) dE + \frac{\pi^2}{6} \cdot (k_B \cdot T)^2 \cdot \left. \frac{d(D(E))}{dE} \right|_{E=\mu} + O((k_B \cdot T)^4) \quad (10)$$

The term of order $O((k_b \cdot T)^4)$ is very small and can therefore be neglected. This is also true for all following expansions. Since the chemical potential differs very little from its $T = 0$ value E_F , we can expand the first integral in (10) into a Taylor series around E_F .

$$\int_{-\infty}^{\mu} D(E) dE = \int_{-\infty}^{E_F} D(E) dE + (\mu - E_F) \cdot D(E_F) \quad (11)$$

The first integrand in equation (11) is the electron density at $T = 0$.

$$n = n(T = 0) + (\mu - E_F) \cdot D(E_F) + \frac{\pi^2}{6} \cdot (k_B \cdot T)^2 \cdot D'(\mu) \quad (12)$$

For low temperatures the electron density can be taken to be constant. So $n = n(T = 0)$. Because the chemical potential differs very little from its zero temperature value, we can simplify equation (12) to :

$$\mu = E_F - \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot \frac{D'(E_F)}{D(E_F)} = E_F - \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot \left. \frac{d \ln(D(E))}{dE} \right|_{E=E_F} \quad (13)$$

This is the Sommerfeld expansion for the chemical potential. When T goes to zero the chemical potential goes to E_F as it should be. The behaviour is of quadratic order and is a good approximation to a few hundred degrees Kelvin.

3.2 The internal energy and specific heat

As we know the internal energy is given by:

$$u = \int_{-\infty}^{\infty} ED(E)f(E) dE \quad (14)$$

We use equ.(8) and set $g(E) = ED(E)$ and obtain:

$$u = \int_{-\infty}^{\mu} E \cdot D(E) dE + \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot \left. \frac{dg(E)}{dE} \right|_{E=\mu} = \int_{-\infty}^{\mu} E \cdot D(E) dE + \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot (D(\mu) - \mu D(\mu)) \quad (15)$$

Again we expand the integral around E_F and for low temperatures where μ is about E_F , we get:

$$u = \int_{-\infty}^{E_F} E \cdot D(E) dE + (\mu - E_F) \cdot E_F \cdot D(E_F) + \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot \left(D(E_F) - E_F D'(E_F) \right) \quad (16)$$

If we use (13), we get for the internal energy the equation:

$$u = \int_0^{E_F} E D(E) DE + \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot D(E_F) \quad (17)$$

This is the Sommerfeld expansion for the internal energy. With this equation the specific heat is easy to calculate and yields:

$$c_V = \left(\frac{du}{dT} \right)_{V=const} = \frac{\pi^2}{3} \cdot k_B^2 T \cdot D(E_F) \quad (18)$$

So the electronic specific heat of a metal is linear with the temperature. To get the whole specific heat of a metal one has to calculate also the phononic part (see [2, 1]). The electronic part can be written as $c_{Vel} = \gamma \cdot T$, where γ is the so called Sommerfeld coefficient. Under 4.3 these coefficients are calculated for a few metals and compared to experimental data.

3.3 Entropy and the Helmholtz free energy

The entropy can be easily calculated, if we take the thermodynamic relation for the specific heat $c_V = \frac{1}{V} \cdot \frac{\partial Q_{rev}}{\partial T}$ and use the thermodynamic equation for the entropy.

$$s = \frac{1}{V} \cdot \int_0^T \frac{\partial Q_{rev}}{T} = \frac{1}{V} \cdot \int_0^T \frac{C_V}{T'} dT' = \frac{\pi^2}{3} \cdot k_B^2 T \cdot D(E_F) \quad (19)$$

So in this approximation the entropy is equal to the specific heat. This result can also be obtained by starting with the grand canonical sum of statistic thermodynamics and applying the Sommerfeld expansion to it (see [3]).

The Helmholtz free energy is now easy to calculate since only the entropy and the internal energy have to be known.

$$f = u - Ts = u(T=0) - \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot D(E_F) \quad (20)$$

3.4 Pauli paramagnetism and Landau magnetism

This part deals with the magnetic properties of a metal and how the electrons affects these properties. If we take a look at the properties of electrons we already know that they are carriers of a charge, but they also have an intrinsic spin. This spin is inducing a magnetic field. So it should be expected that the DOS is closely related to the magnetic properties. The derivative of the formulas in table 1 doesn't need the Sommerfeld expansion but it shows that also these properties are only dependent on the density of states. The derivative of the formulas is complicated and is therefore not done in this work. A good derivative is given in [3].

We start with the Pauli magnetism which is a paramagnetic effect. Since only two spin directions are possible, there are two densities of states. One with spin up and one with spin down. If a magnetic field is applied, electrons with a parallel spin move up in energy and electrons with an anti parallel spin move down in energy. Hence this would mean, that one sort of electrons occupies higher energies. This is not thermal equilibrium, so there has to be a mechanism where the electrons with spin up move to levels below them. Since only spin down levels are free the electron has to give up some of its momentum and make a spin flip because of the Pauli principle. The momentum change is done by transferring some of the momentum to the lattice. With the fact that the energy shift depends only on the spin quantum and not on the momentum of the electron, following equation can be derived.

$$\chi_{Pauli} = \frac{1}{4} \cdot \mu_0 \cdot (g_e \mu_B)^2 \cdot D(E_F) \quad (21)$$

Another sort of magnetism is the Landau diamagnetism which is a diamagnetic effect. Diamagnetic means that if an external field is applied the diamagnetic material is going in the lower field direction. An external field is affecting the orbital movement and is therefore changing the magnetic dipole moment of the atom. The effect can only be described quantum mechanical and leads to equation (22).

$$\chi_{Landau} = -\frac{1}{3} \cdot \chi_{Pauli} = -\frac{1}{12} \cdot \mu_0 \cdot (g_e \mu_B)^2 \cdot D(E_F) \quad (22)$$

In both equations only the zero temperature value has been taken. The quadratic correction in temperature can be derived with the Sommerfeld expansion "but this correction does not have any practical importance in

most metals.” ([3] p.45). So the quadratic term isn’t needed. Since there is no temperature dependence the magnetism plots are missing in figure 7.

3.5 Summary

Name	Formula	Sommerfeld expansion
chemical potential μ	$\int_0^\infty D(E) \cdot f(E) d(E)$	$\mu = E_F - \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot \frac{D'(E_F)}{D(E_F)}$
internal energy u	$\int_{-\infty}^\infty E D(E) f(E) dE$	$u(T = 0) + \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot D(E_F)$
specific heat c_V	$\left(\frac{du}{dT} \right)_{V=const}$	$\frac{\pi^2}{3} \cdot k_B^2 T \cdot D(E_F)$
Entropy s	$\int_0^T \frac{c_V}{T'} dT'$	$\frac{\pi^2}{3} \cdot k_B^2 T \cdot D(E_F)$
Helmholtz free energy f	$u - Ts$	$u(T = 0) - \frac{\pi^2}{6} \cdot (k_B T)^2 \cdot D(E_F)$
Pauli magnetism χ_{Pauli}	—	$\frac{1}{4} \cdot \mu_o \cdot (g_e \mu_B)^2 \cdot D(E_F)$
Landau magnetism χ_{Landau}	—	$-\frac{1}{12} \cdot \mu_0 \cdot (g_e \mu_B)^2 \cdot D(E_F)$

Table 1: The properties and the obtained formulas with Sommerfeld expansion. Only terms up to second order of temperature were taken. This is in most cases a good enough approximation

4 Application of the Sommerfeld expansion

This section deals with the Sommerfeld expansion applied on some common metals. It should show the strengths and weaknesses of this expansion and how it can be applied to a given density of states. First of all it should be mentioned that all in this document used DOS are numerically calculated and therefore based on a theoretical model. This is, as mentioned in the introduction due to a experimental problem. Methods as PES and IPES can only show the DOS either below or above the Fermi energy. You can see a short description of these methods under 5.

4.1 DOS and Wien2k

The program to produce the numerical calculated DOS is WIEN2k¹. According to the information I got from Prof. Dr. Karlheinz Schwarz the program uses 2 methods to produce the Density of States. One is, to take large quantity of k points in the Brillouin zone of the crystal and calculate for each k -point the energy. Then the program counts all the energy-values in an interval of δE and plots the DOS as a histogram. This method isn't good to calculate the derivative and is therefore not used. The second method is the tetrahedron method. This method splits the Brillouin zone in tetrahedrons and calculates for each tetrahedron the contributions to the DOS by interpolating the energy for the four corner points analytically. This more precise method can be used to get the derivative. An example for a DOS calculated by WIEN2k can be seen in figure 2. The green line is the free electron model. (see Ref. [7])

¹Inst. f. Material Chemistry, TU Vienna P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz.

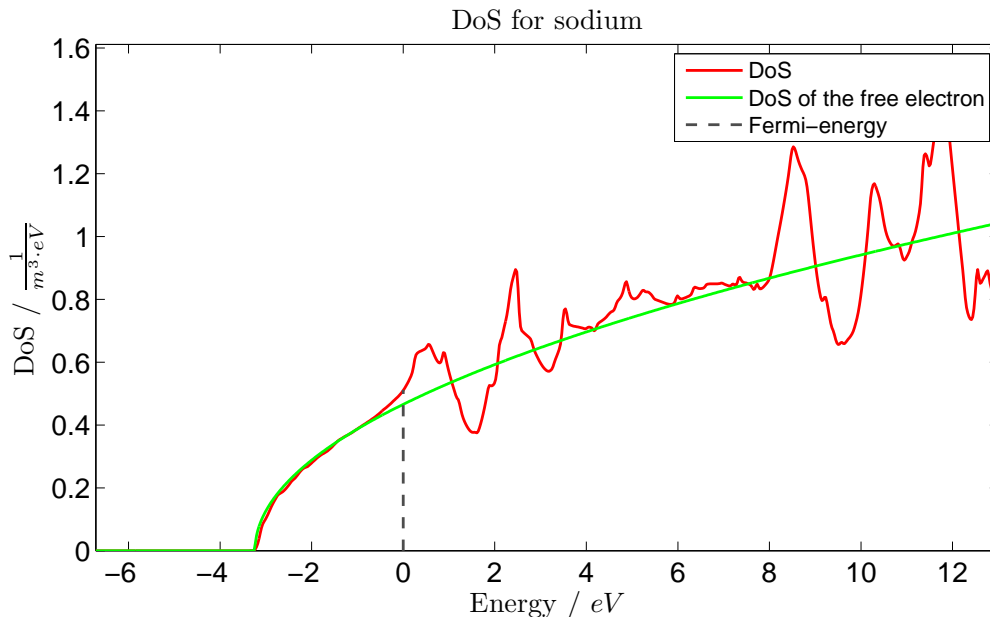


Figure 2: The Density of States calculated for sodium by WIEN2k. The high peaks are van Hove Singularities. See also 6

4.1.1 Results for different amount of used k-points

As already mentioned, the program uses a quantity of k-points and calculates the corresponding energy to each point. It is obvious, that the result depends on the chosen amount of k-points. More k-points in the Brillouin zone should lead to a more accurate result. It is now a question to find a compromise between needed computation time and accuracy. To see, how this is important for calculations with the Sommerfeld expansion a closer look was taken, how different amounts of k-points affect the calculation result. Figure 3 shows two different calculations with 5000 k points and 100000 k points. Both calculations show the correct valence of three electrons. Although the Shape of the DoS is roughly the same, the Sommerfeld-expansion would lead to complete different results. This is in order of the much bigger oscillations of the DoS from 5000 k points. So this is a problem and shows that the sommerfeld expansion is highly dependent on the accuracy of the DoS, especially around the Fermi energy.

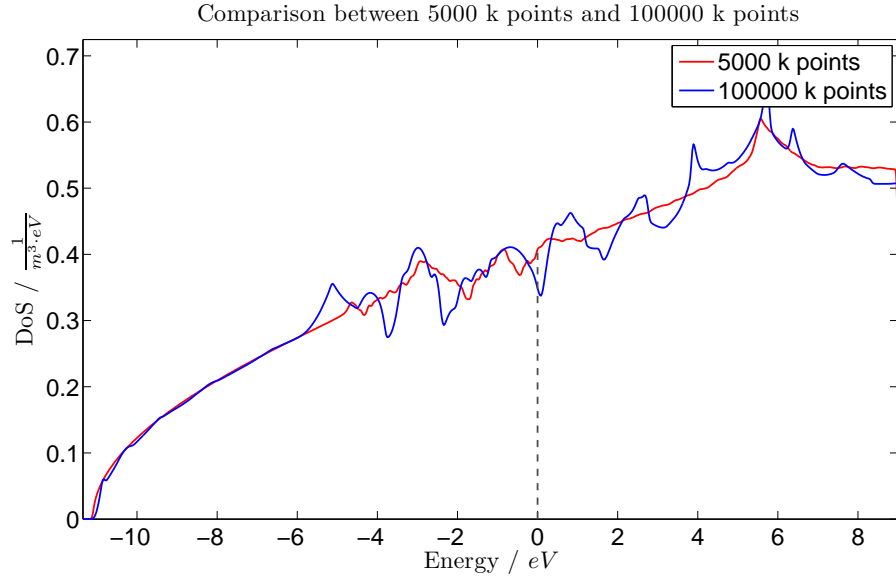


Figure 3: 2 different calculations for the metal Aluminum.

4.2 The program for the Sommerfeld expansion

All plots and calculations were performed by a self-written matlab program. The program uses the calculated DOS to determine the derivatives at the Fermi energy to calculate and plot the different thermodynamic properties seen in table 1. The program is written for a certain type of data file which is produced by WIEN2k. If another data file is used the program has to be modified. Since the program isn't very complex this should be no problem for anyone. A documentation and description of the program is in the code. The code can be seen in the appendix.

4.2.1 Important points for the calculation

There are certain points to be considered when calculating the properties. An important point is the error of each calculated data point. Unfortunately it was not possible for me to get the information how this error should look like. Since it is not the goal of this work to get deeper into the calculation program wien2k, there wouldn't be an error analysis in the calculation of the different properties. If someone takes a closer look at figure 2, he can see

that there are high peaks at certain energies. These peaks are the result of the following relationship: $D(E) = \int_{S_n(\epsilon)} \frac{1}{4\pi^3 \cdot |\Delta E(\mathbf{k})|} dS$ (see Ref. [1] page 144) So if the gradient of the energy band goes to zero the integral diverges.

It can be shown that in three dimensions such singularities are integrable, yielding finite values for $D(E)$. However they result in divergences of the slope $\frac{dD(E)}{dE}$. These are known as van Hove singularities (Ashcroft & Mermin, 1976, p.145)

So if the Fermi energy is near or in the worst case at these singularities the calculation cannot be performed with the Sommerfeld expansion. There is a method to smooth out these singularities by applying a Gaussian broadening to the DOS. This is ok, if the results are compared to experimental data, since in experiments there is a natural smoothing of the DOS due to measurement resolution. But if someone thinks about it, this method cannot be applied to these calculations because it's changing the slope of the curves. Nonetheless there is a small broadening to get rid of numerical fluctuations. This decision was made with Prof. Dr. Heinrich Sorman who performed the calculations for me and figure 4 shows how different broadenings are affecting the slope.

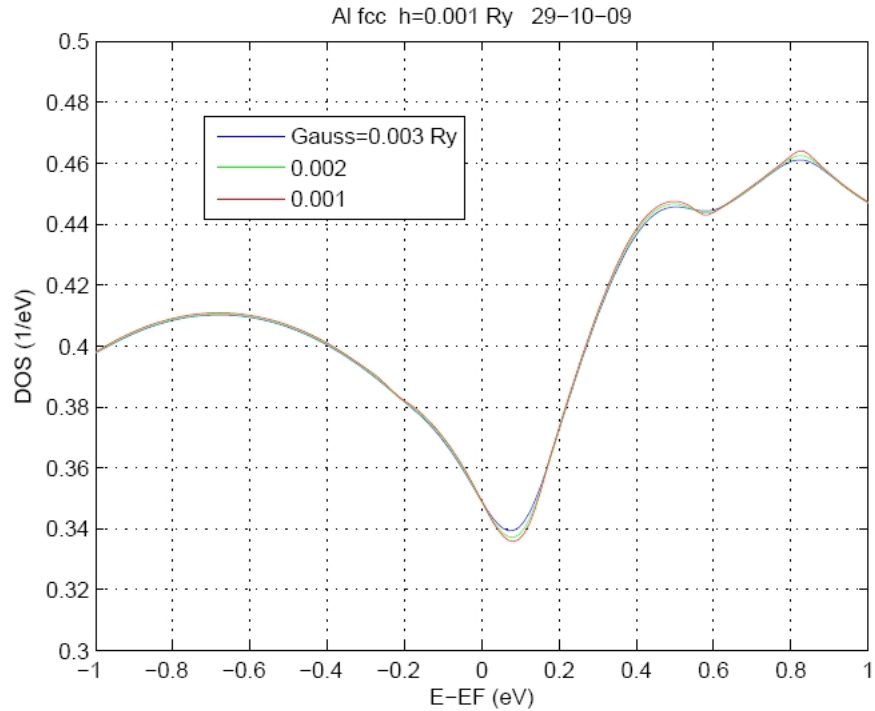


Figure 4: The same DOS of aluminum 3 times with different gaussian broadening. It is plotted around the Fermi energy.

Figure 4 shows how the Gaussian broadening is changing the slope of the curve. In this particular case it shows, that at the Fermi energy there is nearly no effect but if you go elsewhere that there is one on the slope. Hence this should be considered before starting a calculation. For this calculations the effects are small enough to be neglected. So it wasn't tested for each metal. It should only show that it could affect the calculation.

4.3 Results

The calculation has been performed for a few metals. Each metal delivers a number of plots for the internal energy, the specific heat,... etc. All of these plots can be generated with the Matlab program. Here only the values and the derivatives of the DOS at E_F are shown in table 2, so someone can use

them and calculate all the properties with the formulas in table 1. For one chosen metal the plots are shown in figure 7.

Metal	$D(E_F)[\frac{1}{Jm^3}]$	$\frac{dD(E)}{dE}\Big _{E=E_F} [\frac{1}{J^2m^3}]$	$n[\frac{1}{cm^3}]$	$Valence_{(calculated)}$
THUNGSTEN	3,21E+47	4,30E+99	7,60E+23	6,0
GOLD	1,03E+47	4,73E+98	6,48E+23	11,0
PLATINUM	8,21E+47	-2,76E+100	6,62E+23	10,0
ALUMINUM	1,31E+47	1,33E+97	1,810E+29	3,0
COPPER	1,52E+47	-2,08E+97	9,303E+29	11,0
POTASSIUM	7,42E+46	5,34E+97	1,397E+28	1,0
LITHIUM	1,56E+47	5,31E+98	4,734E+28	1,0
SODIUM	8,41E+46	4,27E+98	2,656E+28	1,0
VANADIUM	9,93E+47	3,99E+100	3,652E+29	5,1

Table 2: The numerical evaluated DOS and derivative of the DOS at the Fermi energy. The electron density n is given per cubic centimetre and once per unit cell which is the valence of the metal.

Table 2 shows the right valences of the metal. Since the program changes units of the DOS in order to calculate the properties, this is a good way to compare if the transformation to other units and the DOS is correct. With these values other properties (see table 1) can be calculated. Figure 7 gives an example for Na. A very useful and comparable result is the Sommerfeld coefficient which can be seen in table 3. The magnetic susceptibility can be seen in table 4 and figure 5 shows the different values in respect to the atomic number Z .

Metal	$\gamma^{calc}[\frac{J}{(K^2*m^3)}]$	$\gamma^{exp}[\frac{J}{(K^2*m^3)}]$	$\gamma^{calc}[\frac{mJ}{(molK^2)}]$	$\gamma^{exp}[\frac{mJ}{(molK^2)}]$
THUNGSTEN	200,99	136,12	1,92	1,30
GOLD	64,74	71,43	0,66	0,73
PLATINUM	514,78	735,14	4,76	6,80
ALUMINUM	82,20	135,09	0,82	1,35
COPPER	95,11	97,55	0,68	0,69
POTASSIUM	46,55	45,75	2,12	2,08
LITHIUM	97,96	124,46	1,28	1,63
SODIUM	52,73	58,22	1,25	1,38
VANADIUM	622,84	1110,60	5,21	9,29

Table 3: Calculated und experimental values for the Sommerfeld coefficient. Experimental values are from [2]

The calculated values with the Sommerfeld expansion are very good for the alkali metals. Other metals than the s-band dominated alkali metals show differences which could be due to the more complicated structure of the bands at the Fermi energy. This is easy to see, if the value of the calculated Sommerfeld coefficient of aluminum is considered. The value is significant to low. In ([2] p.164) table 6.2 shows that the value of the free electron model is $\gamma = 0.912 \frac{mJ}{mol \cdot K^2}$. So the free electron value is closer to the experimental value than the calculated one. All other calculations except vandanium are showing better results than the free electron model. That the value of aluminum is lying below can also be seen in figure 6 a). The density of states at the Fermi energy lies below. Why the value is lying below of the free electron value couldn't be determined by myself. The programm Wien2k should deliver very precise values for the Fermi energy and the DOS seems to be correct since the valence is correct. So the reason for this isn'r really clear. It could also be an error in the experimental value. The result for vandanium cannot be interpreted in respect to the free electron model since there is no value in table 6.2 in ([2] p.164). Copper is interesting because it is a transition metal and showing a very good calculated value. The reason for this is easy to see in figure 6 b). Copper shows at the Fermi energy again a s-electron like behaviour. The more peaky d-bands which are way more critical for small differences in the Fermi energy are lying below.

Table 4 shows the magnetic properties.

Metal	$\chi_m^{exp} [\frac{m^3}{kg}]$	$\chi_m^{calc} [\frac{m^3}{kg}]$	$\chi_V^{exp} [1]$	$\chi_V^{calc}[1]$
THUNGSTEN	4,59E-09	1,20E-09	8,84E-05	2,31E-05
GOLD	-1,78E-09	3,86E-10	3,44E-05	7,45E-06
PLATINUM	1,22E-08	2,81E-09	2,57E-04	5,93E-05
ALUMINUM	7,80E-09	3,51E-09	2,11E-05	9,47E-06
COPPER	-1,08E-09	1,23E-09	-9,63E-06	1,10E-05
POTASSIUM	6,70E-09	6,23E-09	5,76E-06	5,36E-06
LITHIUM	6,30E-09	2,13E-08	3,34E-06	1,13E-05
SODIUM	6,40E-09	6,26E-09	6,21E-06	6,07E-06
VANADIUM	6,28E-08	1,18E-08	3,82E-04	7,17E-05

Table 4: Calculated und experimental values for the mass susceptibilty and the volume susceptibility. Experimental values are from [14].

The calculation of the different susceptibility doesn't show the same results as the Sommerfeld coefficient. Also for an alkali metal the value could be very bad in respect to the experimentally determined. You can see this for example in table 4 for lithium. The reason for this is, that magnetism isn't so easy to describe and that it is more complicated than the simple models suggest. This is true also for other simple models (see [8]). The problem is that these models aren't taking into account that there is also an electron electron interaction which has an affect on the magnetic properties. On the other hand there are also really pretty results as for example for potassium. Also this fact isn't easy to explain and I'm also not sure why the expansion is obtaining good results for potassium but it is probably depending on many parameters.

If one is only interested on an overview over the magnetic properties and the specific heat one can look at figure 5 where the density of states at the Fermi energy , the magnetic susceptibility and the Sommerfeld coefficient is plotted for different elements. If table 1 is considered one sees that the specific heat, the entropy and the magnetic properties are proportional to the DOS at the Fermi energy. This means figure 5 shows the crude relations between different metals. A high DOS at the Fermi energy means a high magnetic sucseptibility and a high sommerfeld coefficient which can be seen in table 3 and figure 5. The experimentally determined values show with little differences to the calculated ones the same relations between the different elements. This shows again that the values calculated with the Sommerfeld expansion may not be exactly correct but they show about the right relation

to each other. This should mean that, if one knows the magnetic susceptibility of aluminum he knows by looking at figure 5 that vanadium is going to have a much bigger value. For the magnetic properties there has also to be considered if the metal is para- or diamagnetic.

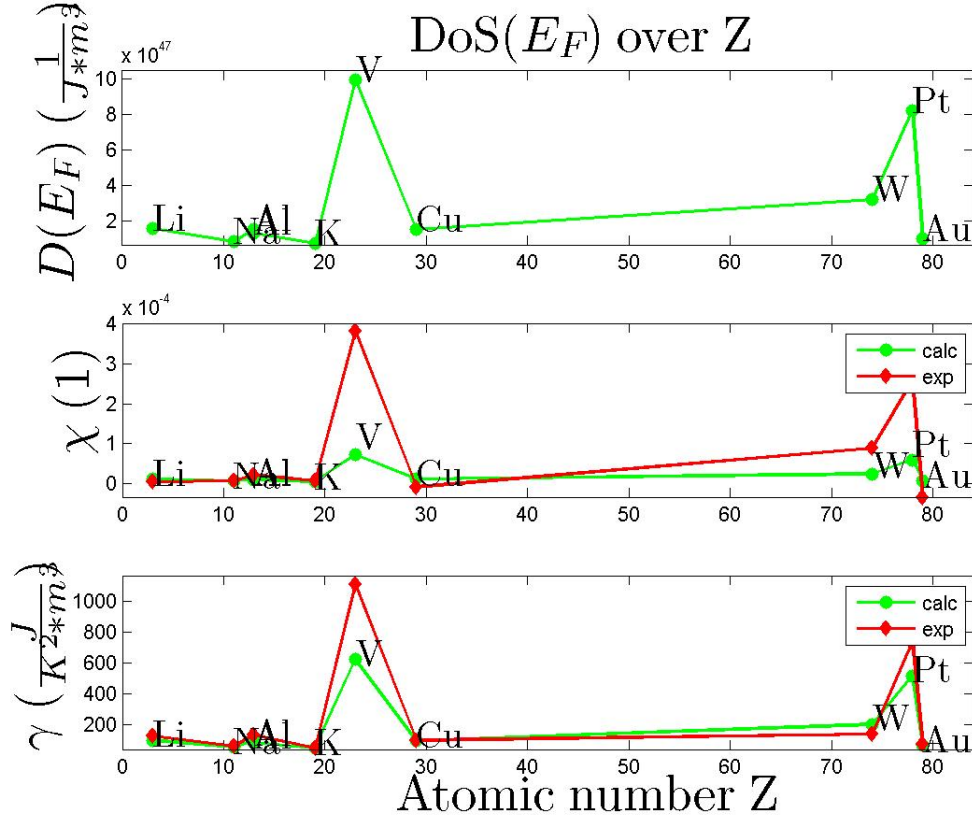
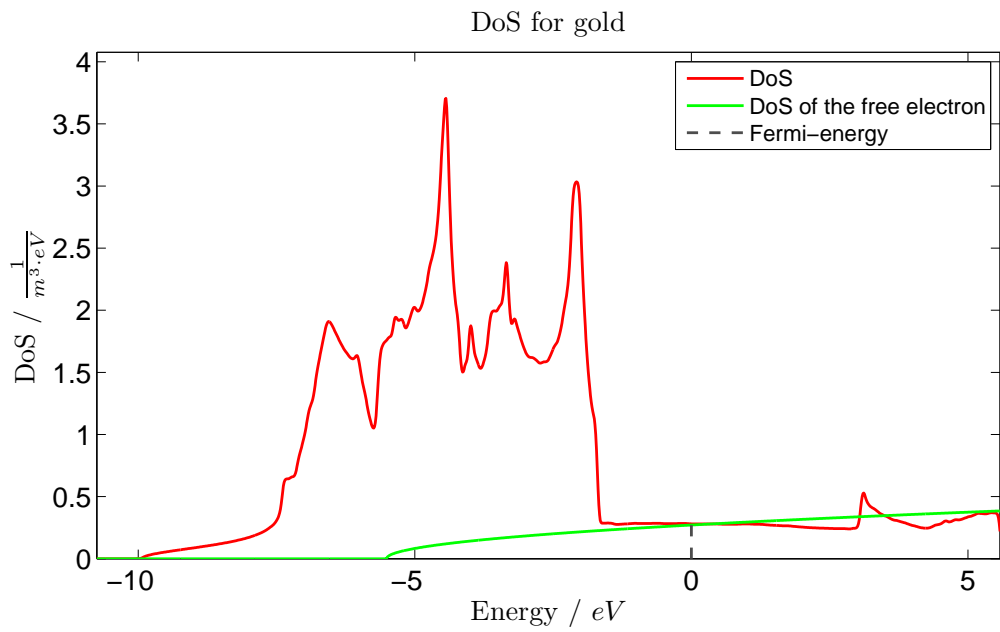
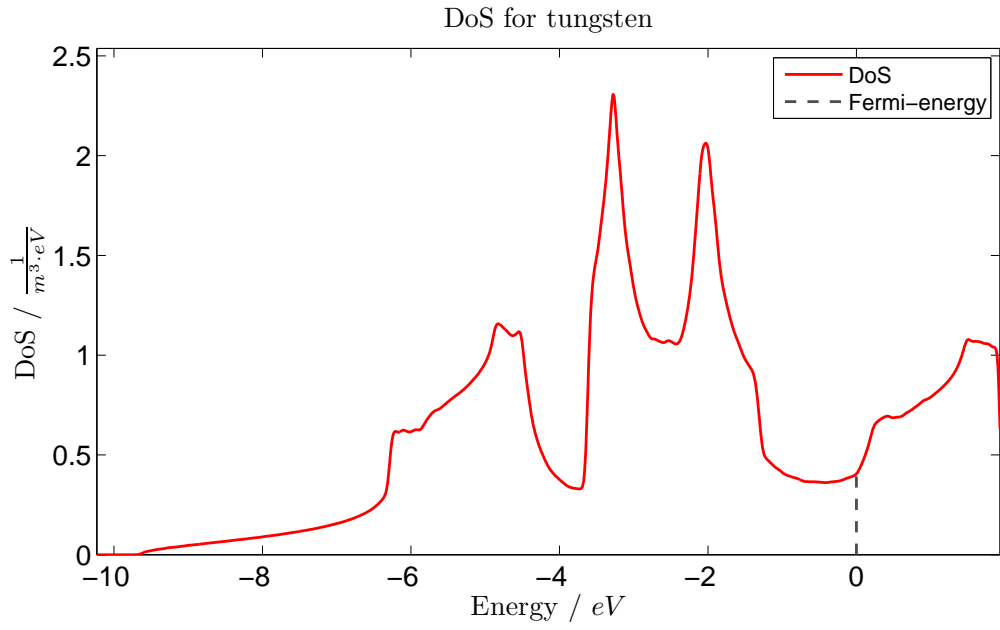
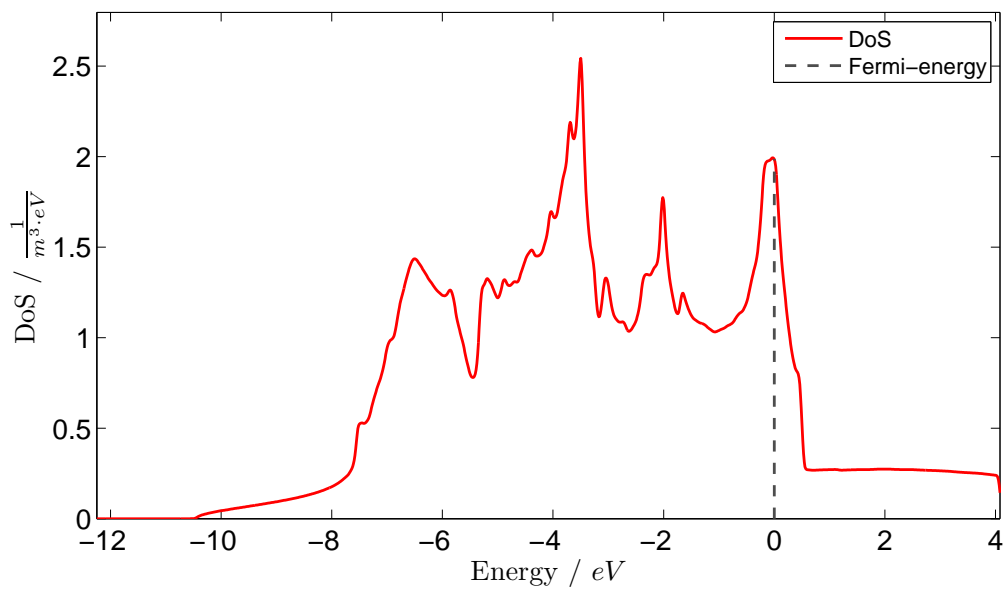


Figure 5: The Density of states at the Fermi energy, the magnetic susceptibility and the sommerfeld coefficient in respect to the atomic number Z. A big value of $D(E_F)$ corresponds with a high sommerfeld coefficient and high magnetic susceptibility.

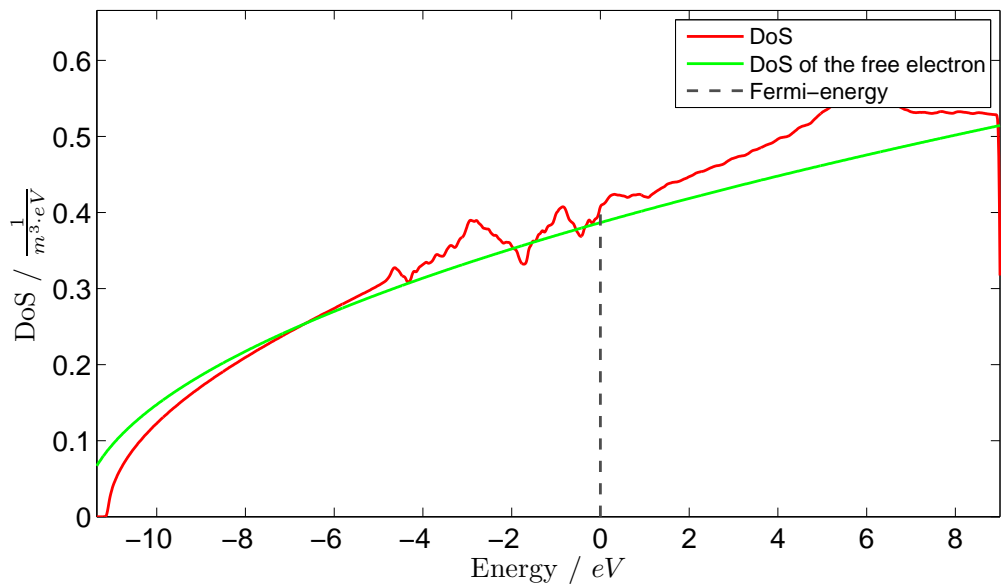
All calculated band structures are shown in the following figure. The values and formulas for the calculation of the free electron model (green line) can be seen in [7] or [1]. Figure 7 shows the results for Na.



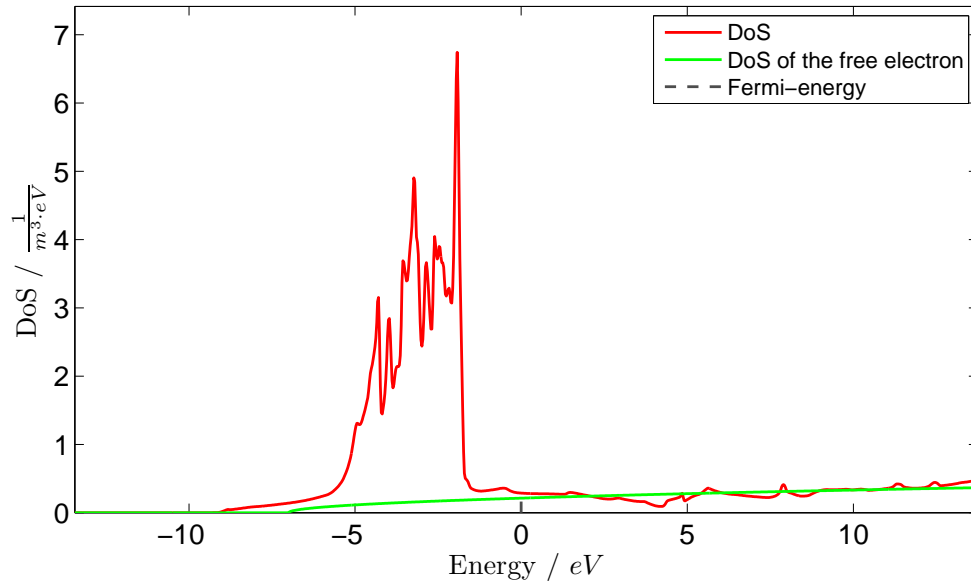
DoS for platinum



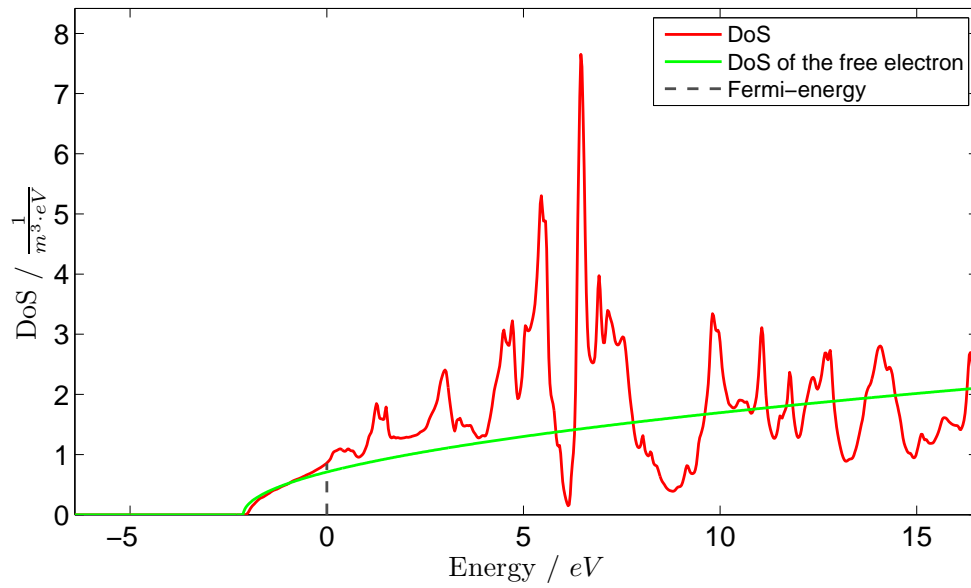
DoS for aluminum



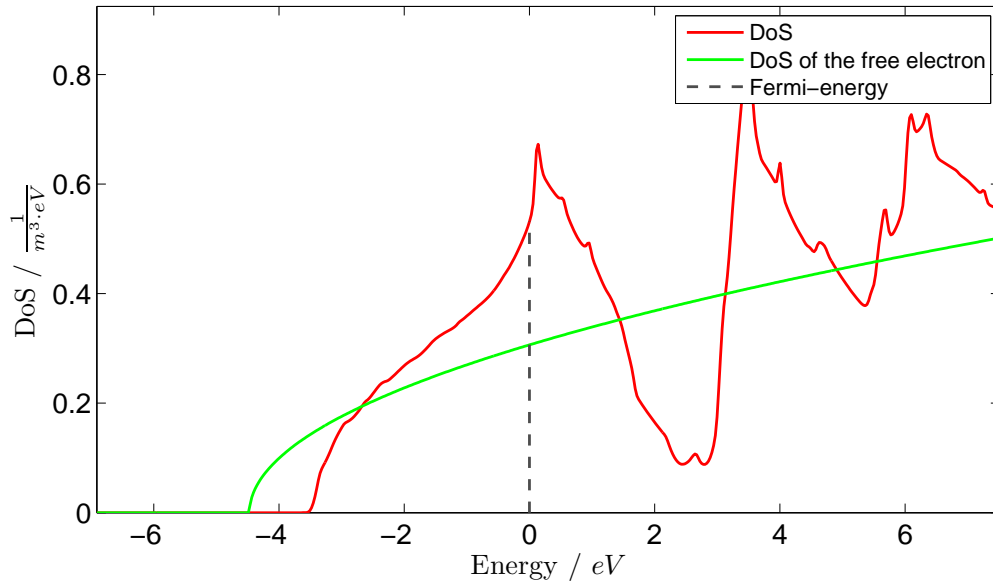
DoS for copper



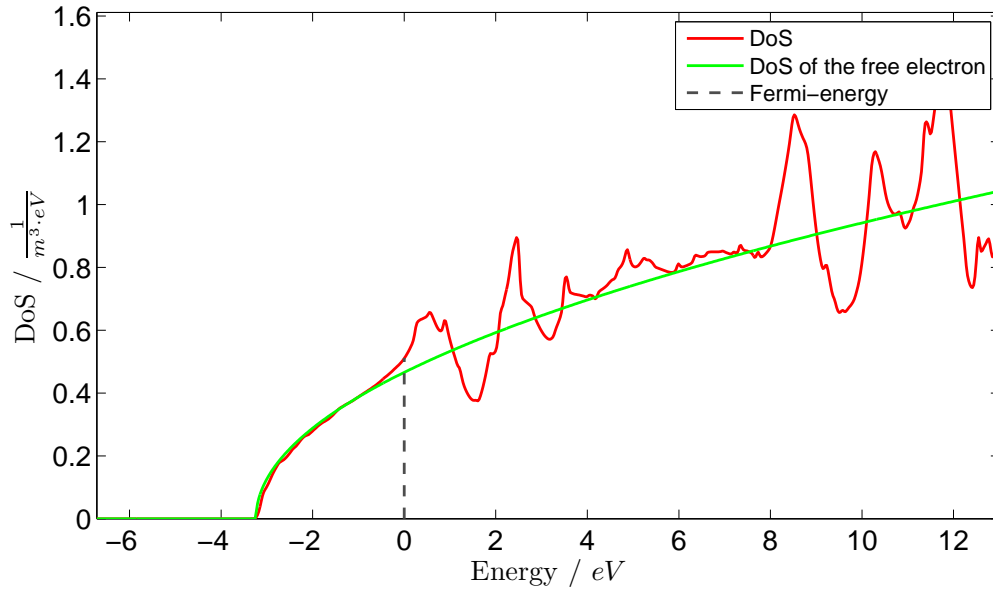
DoS for potassium



DoS for lithium



DoS for sodium



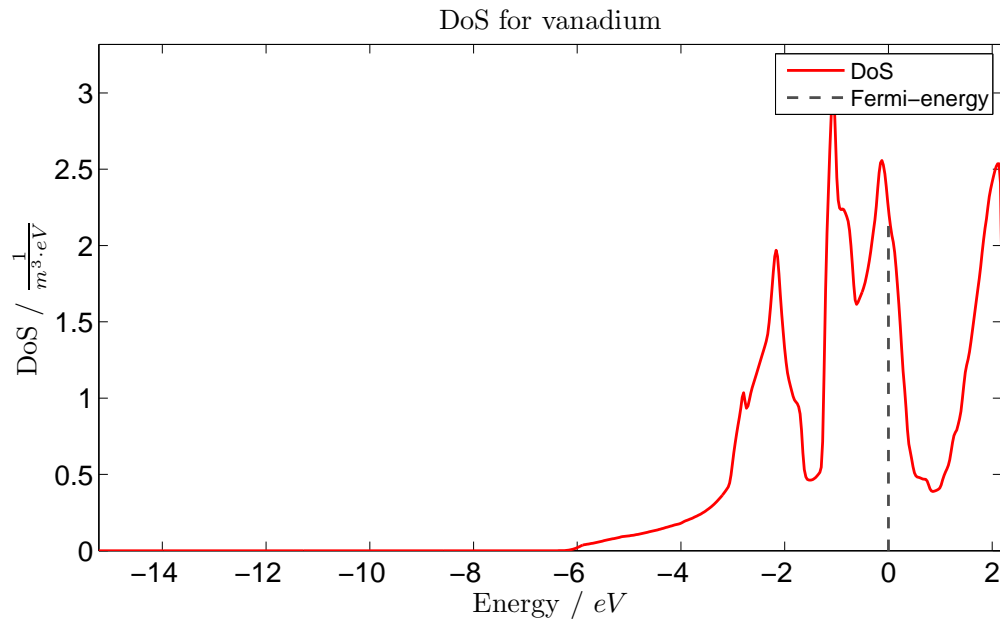


Figure 6: All by Wien 2k calculated density of states

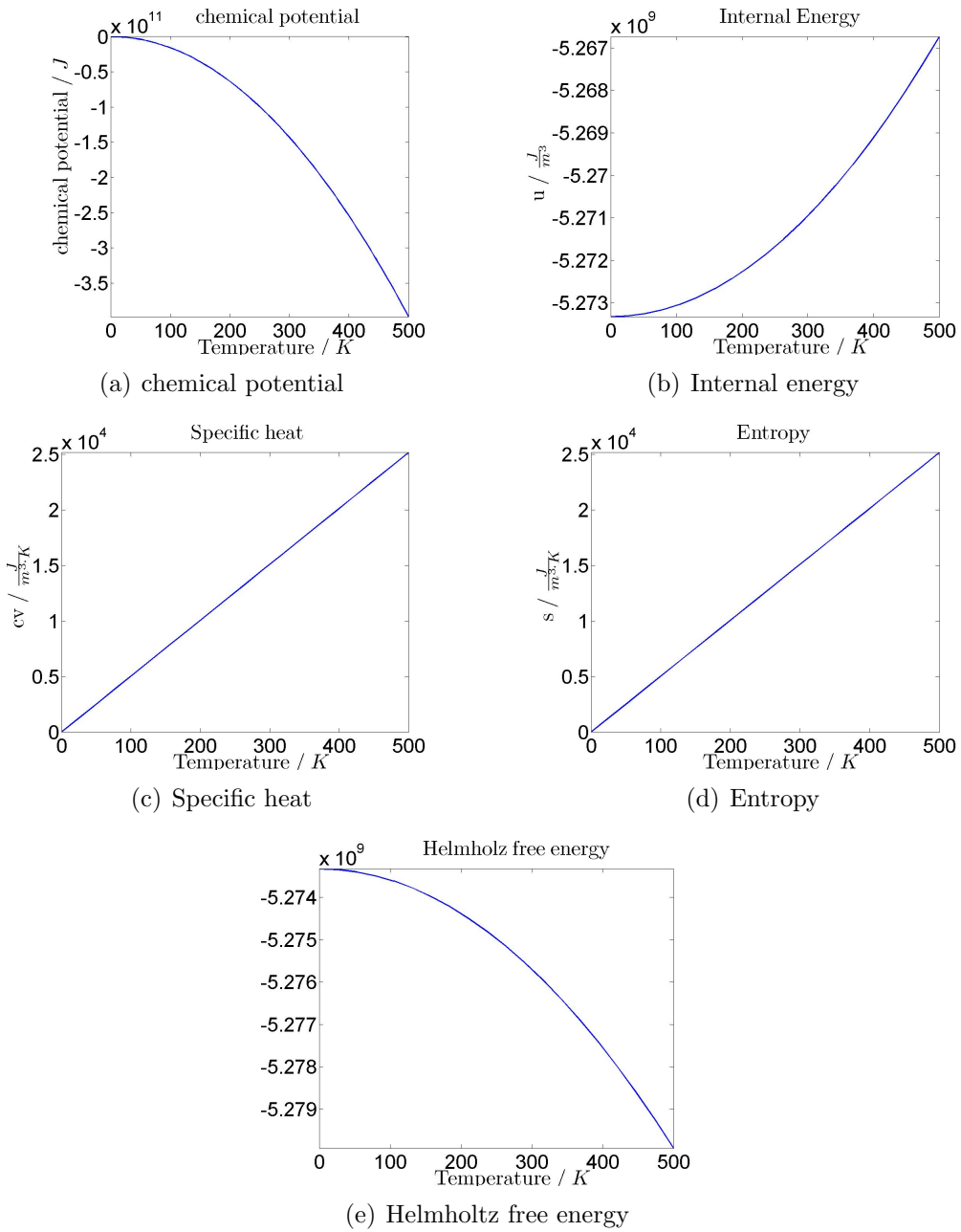


Figure 7: All calculated thermodynamic properties for sodium

5 Experimental Methods to evaluate the DOS

5.1 PES

PES or Photoemission spectroscopy is a method to gather information about a solid such as electronic structure or chemical composition. Which property should be analyzed depends on the chosen PES method. The three main types of PES are UPS, XPS and ARPES. There are many other special types of PES but all of them are based on the same physical principle, the outer photoelectric effect. This photoelectric effect was discovered by Heinrich Rudolf Hertz and Wilhelm Ludwig Franz Hallwachs in the 19. Century and later described by Albert Einstein. They found out, that if a metal is illuminated by light a current is flowing when a electrical field is present. The amount of current is not dependent on the intensity, but on the frequency of the light. This discovery led to the understanding of light as photons. The incoming photon with the energy $h \cdot \nu$ hits an electron in the solid and is loosing the whole energy to the electron which is excited to a higher state or if the energy is high enough, the electron can leave the metal. The difference of the photon energy and the bounding energy of the electron and work function is the kinetic energy of the electron. Hence this energy can give information about the electronic structure of a metal. To determine the DOS only UPS and ARPES are used. XPS is used for chemical analysis. XPS uses energies which are sufficient to excite core electrons. This core levels are characteristic for each element and are therefore used for chemical analysis. UPS is ultraviolet photo electron emission and is described below. ARPES is angle resolved photo emission spectroscopy and can also give information about the momentum of the electron and hence also the dispersion relationship or the Fermi surface can be measured (see [9]).

5.2 UPS

UPS as the name suggest uses ultraviolet light to excite electrons in the metal. The energy is in about the range of the valence electrons and delivers therefore only information about the valence band structure. Mostly a He gas lamp is used because of the very sharp spectral lines. This leads to a energy resolution about 10^{-3} eV. The energy filtering is made with a hemispherical electron analyzer as shown in figure 8.

5.3 ARPES

Angle resolved PES can also obtain information about the dispersion relationship and the Fermi surface. Hence this method is one of the most important to get information about electronic structuring in solids. The principle is similar to UPS or other PES methods. The only difference is that also the angle of the photo electrons is measured (see figure 8). Since the k value is dependent on different directions in the crystal, this gives information about the dispersion relationship of the electrons. (a better explanation can be seen in [5])

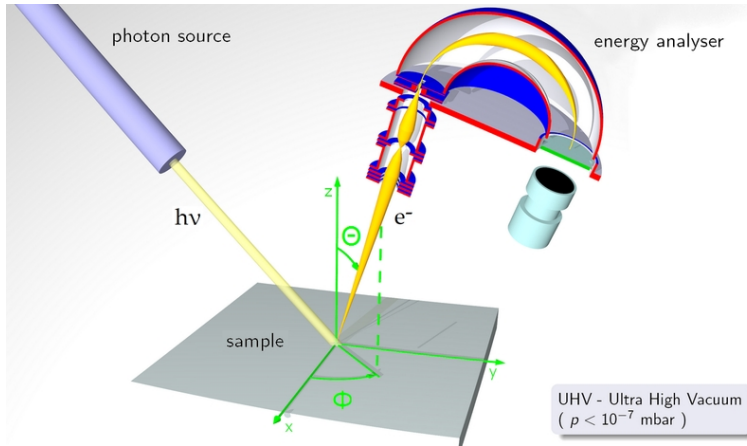


Figure 8: Schematic picture of the ARPES method. [9]

To get a good angle and energy resolution the electronic lenses of the analyzer have to be prepared for a very small angle. That means that only electrons from a small dihedral angle can go into the analyzer. Today resolutions of 0,2 degree and 1-2 meV are possible (see Ref. [9]).

5.4 IPES or BIS [6, 9]

Inverse Photoemission spectroscopy or Bremstrahlung isochromat spectroscopy is the inverse process of the photoemission spectroscopy. Here a beam of electrons is directed on the sample surface instead of photons. The electron penetrates into the bulk and couples with some probability into an unoccupied state of the bulk. The coupled electron can now go to lower states by radiating energy or by nonradiative decay through inelastic electron-electron

scattering. These two processes are in competition with each other. If the electron decays by radiating light the emitted photon is carrying information about the unoccupied state. So it is now possible to get information about the unoccupied states by analysing the photon energy and hence the density of states above the Fermi energy can be measured.

6 Conclusion

It turns out that the Sommerfeld expansion is a very easy way to calculate properties, because the formulas are very simple and easy to derive. The approximation should be really good for temperatures of a few hundred degrees Kelvin. One disadvantage is that the model is only considering the electronic part. So the property which is sometimes dependent on both parts shows only the electronic behaviour which makes it difficult to get experimental data on this property. In nature it is not always easy to separate the electronic part from the phononic. Nevertheless the expansion can show what a property, which is almost fully dependent on the electronic part, is going to do if the temperature is changed. This is helping to understand the property of the metal even if the result is not absolutely correct. Another problem is that the Sommerfeld expansion is not really applicable on experimental data. The reason is easy. For the expansion either the slope or the value of the DOS at the Fermi energy is needed. An experimentally evaluated DOS has measurement uncertainties which are changing the slope and probably also the value at the Fermi energy. So only numerically calculated DOS can be used. One goal of the work was to look how good such calculated DOS are to calculate properties like in table 1. In the case of the Sommerfeld coefficient, experimental data could be found for all calculated metals. These values are listed and compared in table 3. The alkali metals are showing a good correlation with the experimental data. The transition metals are except for copper not so good. Aluminium as a non transition metal is also showing a difference in the calculated value. As section refkpoints shows, is the calculation sensitive on how many k-points are considered. This may be the reason for this discrepancy in the case of Aluminum. There may be also another reason for this but since the calculations were performed external it was not possible for the author to take a closer look on this. This is valid for all DOS calculations in this work. Additionally, metals with a peaky DOS around the Fermi energy are much more prone to calculation errors. Espe-

cially transition metals are often showing a peaky DOS in this region. Except for Copper which is interesting, because it is a transition metal but it shows a very good value for the Sommerfeld coefficient. Copper is showing *s*-band like behaviour which is probably the reason for the very good value of the calculated Sommerfeld coefficient. Vanadium is also showing a value which is not very good. The reason is probably again the peakier *d*-band structure. The magnetic properties in table 4 are showing a little bit different results. There are also bad values for alkali metals. This is probably so because the magnetic properties of a metal aren't so easy to describe. But if you look at figure 5 you see that most values are about the same and that the crude relations are true. For example the calculated value of vanadium is bigger than aluminium and so on. All in all the Sommerfeld expansion is a good model to calculate properties for the alkali metals and to show how different properties relate to each other.

Acknowledgments

I want to thank my advisor Univ.-Prof. Ph.D. Peter Hadley for his support during the work. I also thank Prof. Dr. Karlheinz Schwarz for his assistance with density of States calculations and the program Wien2k. I also gratefully acknowledge that also Univ. Prof. Dr. Heinrich Sorman has performed the DOS calculations for me and that he helped me with some problems.

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A Matlabprogram

The following program can be used to calculate all properties except the magnetic properties. The basis for these calculations is the Density of states file. These files are generated with Wien 2k. If someone has another data file the program `fun_load_data.m` has to be changed. The documentation of the code is in the code.

A.1 function sommerfeldexpansion (main)

```
% Sommerfeld Expansion
% Thomas Ganner
% Bachelor-Work
% 24.11.2009 (Sormann-Version)
```

```
function sommerfeldexpansion
```

```
clear
```

Important:

Always use row vectors All calculation is in SI except for the DOS plots (in eV)!!!

physical constants

```
const = struct;
const.bohr = 52.9177e-12; %[m]
const.q_e = 1.60217733e-19; %[As]
const.m_e = 9.1093879e-31; %[kg]
const.h_quer = 1.054571628e-34; %[Js]
const.kb_J = 1.380658e-23; %[J/K]
const.kb_eV = 1.380658e-23/1.60217733e-19; %[eV/K]
```


Get data

```
%+++++
% This part is responsible for loading all the data-files
% into the program. Only files with *.DOS ending are
% considered. For other data files the function
% fun_loaddata_mod has to be changed.
%+++++

cd 'E:\uni\6.semester\bak\density of states data';
A = dir('*.DOS'); %get all files with ending *.DOS
B = struct2cell(A); %change A from struct to cell.
der_table_element = zeros(size(B,2),12); % element
der_table_DOS = zeros(size(B,2),1); %D(Ef)
der_table_dDOS = zeros(size(B,2),1); %dD(E)/dE E = Ef

for i =1:size(B,2); %This loop performs the calculations
    % for each data file

        filename = A(i).name; %get filename
        filename = filename(1:end-4); %delete the ending *.DOS
% +++++
% fun_loaddata_mod loads the data files with ending *.DOS.
% contains 5 columns. only the first 2 are necessary for
% the calculations. the Energy, DOS_all is the overall
% density of states (s,d,f..band together)
        [Energy,DOS_all,V_uc,element{i}] = fun_loaddata_mod(...
        'E:\uni\6.semester\bak\density of states data',...
        A(i).name,const.bohr);
%+++++
% Here all the values are changed in SI einheiten
        eVEnergy = Energy.';
        Energy = (Energy*const.q_e).';
        eVDOS = DOS_all;
        DOS = (DOS_all./(V_uc*const.q_e)).';
        [Fermi_Energy,position_Ef] = min(abs(Energy));
% get the Fermi Energy. usually the data from the
% simulation contains no value with exactly zero. So the
```

```

% closest value is searched. Later after the spline
% the Fermi energy is set to exactly zero.
%+++++

% For the expansion the derivative of g... is needed at
% the Fermi energy. To get the derivative a spline
% interpolation is made around the Fermienergy which
% is set to zero.

%+++++
%Make sure that the point E = 0 = Ef is in the vector
ptsp = 5; %points to spline
get_points_minusEtozero = ...
    linspace(eVEnergy(position_Ef-ptsp),0,100);
get_points_minusEtozero = ...
    get_points_minusEtozero(1:(end-1));
%otherwise there would be 2 zero points in the vector
get_points_zerotoE = ...
    linspace(0,eVEnergy(position_Ef+ptsp),100);

%+++++
%This part performs the spline interpolation. This is
%needed to calculate the derivative. The spline
%interpolation is chosen because no statistical data
%is available.
Energy_spline_vector = ...
    [get_points_minusEtozero,get_points_zerotoE];
%Make a vector for the spline interpolation
position_around_Ef = position_Ef-ptsp:1:position_Ef+ptsp;
% 2*ptsp points around Ef are splined. There is no need
%for more since only the derivative at the Fermi
%Energy is of interest.
%+++++

%perform the spline
splined_DOS = spline(eVEnergy(position_around_Ef)...
    ,eVDOS(position_around_Ef),Energy_spline_vector);

```

```

splined_DOS_J = spline(Energy(position_around_Ef)...
    ,DOS(position_around_Ef),Energy_spline_vector);

%+++++++free electron model+++++++
% here the free electron model is calculated.
% This is possible if the Fermi energy of the free
% model is known. The file Fermief.xls contains this
% information.

DOS_f = free_electr(V_uc,const.h_quer,Fermi_Energy...
    ,const.m_e,Energy,char(element{i}),const.q_e);

% Here a directory is created where all the plots
% for a certain DOS are saved
cd 'E:\uni\6.semester\bak\plots';
mkdir(filename);
cddir = ['E:\uni\6.semester\bak\plots\' ,filename];
cd(cddir);

%+++++++
% Plot the density of states in units of eV. A line
% is also plotted at the Fermi Energy.
plot1 = figure('name','DOS'); % plot
plot(eVEnergy,eVDOS,'r-','LineWidth',1.5);
hold on;
plot(eVEnergy,DOS_f*const.q_e,'g','LineWidth',1.5);
%'color',[90/265,90/265,140/265]
line([0,0],[0,eVDOS(position_Ef)],'color'...
    ,[0.3,0.3,0.3],'LineStyle','--','linewidth',1.5);
title(['Density of States for ',char(element{i})]...
    , 'fontsize',20);
ylabel('DOS [eV-1'],'fontsize',20);
xlabel('Energy [eV]','fontsize',20);
axistext;
if ~isnan(DOS_f)
    l = legend('DOS','DOS of the free electron',...
        'Fermi-energy');

```

```

else
    l = legend('DOS', 'Fermi-energy');
end
set(l, 'fontsize', 12);
print(plot1, '-djpeg', [filename, '_DOS']);
saveas(plot1, [filename, '.m']);      %save the plot
%+++++

close DOS % The plot is saved an therefore closed

%+++++
% All the derivatives are calculated
d_g = diff(splined_DOS_J); % g...D(E)
d_E = diff(Energy_spline_vector);
d_2_g = diff(diff(splined_DOS));
%d_E_2zw = d_E.^2;
%d_E_2 = d_E_2zw(1:(end-1));
%d2gtodE2 = d_2_g./d_E_2; %second derivative
dgtodE = d_g./d_E; % first derivative
dgtodE_at_Ef(1) = 1/2*(dgtodE(98)+dgtodE(99)); % mean
%d2gtodE2_at_Ef(1) = 1/2*(d2gtodE2(97)+d2gtodE2(98));

% save the element, the DOS and the derivative of the
% DOS into a array (at the E_F)
der_table_element(i, 1:size(filename, 2)) = filename(1:end);
der_table_DOS(i) = DOS(position_Ef);
der_table_dDOS(i) = dgtodE_at_Ef(1);

%+++++
% this is the calculation for the chemical potential.
% This is needed for all other calculations

mu_sf = @(T) -pi^2/6.*(const.kb_J.*T).^2*...
    dgtodE_at_Ef(1)/DOS(position_Ef);
T = linspace(0, 500, 100);
mu_calc = mu_sf(T);

```

```

%+++++
% plot for the chemical potential (in SI)

plot2 = figure('name','mu');
plot(T,mu_calc,'b','LineWidth',1.5);
xlabel('Temperature / Å°K','fontsize',20);
ylabel('chemical potential / J','fontsize',20);
title('chemical potential','fontsize',20);
axistext;
mu_range = [min(mu_calc),max(mu_calc)];
axis([min(T),max(T),mu_range]);
print(plot2,'-djpeg',[filename,'_mu']);

close mu

% Sommerfeld expansion for the internal energy,specific
%heat,entropy and helmholz free energy.

%+++++
% Variate Fermienergy. The reason is to look how small
% changes in the Fermi energy are affecting the different
% properties. To see how this is working in detail see
% the function SommerFeld_ucvsf_Efvar
deltapEf = 5;
DOS_Ef = [DOS(position_Ef),DOS(position_Ef+deltapEf),...
          DOS(position_Ef-deltapEf)];
%+++++

% This function calculates the rest of the properties.
% The value sf_c is the sommerfeld coefficient
[u,cv,sf_c(i,:),s,f,T] = SommerFeld_ucvsf_Efvar...
    (DOS.*Energy,Energy,position_Ef,DOS_Ef,const.kb_J);

%+++++plot internal energy+++++
plot3 = figure('Name','Inten');
plot(T,u,'b','LineWidth',1.5);
title('Internal Energy','fontsize',20);

```

```

xlabel('Temperture /  $\hat{\text{A}}^\circ\text{K}$ ','fontsize',20);
ylabel('u / [J/m3'],'fontsize',20);
axistext;
print(plot3,'-djpeg',[filename,'_u']);
close Inten

%+++++++plot specific heat+++++++
plot4 = figure('Name','Spheat');
plot(T,cv,'b','LineWidth',1.5);
title('Specific heat','fontsize',20);
xlabel('Temperture /  $\hat{\text{A}}^\circ\text{K}$ ','fontsize',20);
ylabel('cv / [J/(m3  $\hat{\text{A}}^\circ\text{K}$ )]','fontsize',20);
axistext;
print(plot4,'-djpeg',[filename,'_cv']);
close Spheat

%+++++++plot entropy+++++++
plot5 = figure('Name','Entropy');
plot(T,s,'b','LineWidth',1.5);
title('Entropy','fontsize',20);
xlabel('Temperture /  $\hat{\text{A}}^\circ\text{K}$ ','fontsize',20);
ylabel('s / [J/(m3* $\hat{\text{A}}^\circ\text{K}$ )]','fontsize',20);
axistext;
print(plot5,'-djpeg',[filename,'_s']);
close Entropy

%+++++++plot helmholz free energy+++++++
plot6 = figure('Name','gfenergy');
plot(T,f,'b','LineWidth',1.5);
title('Helmholz free energy','fontsize',20);
xlabel('Temperture /  $\hat{\text{A}}^\circ\text{K}$ ','fontsize',20);
ylabel('f / [J/m3'],'fontsize',20);
axistext;
print(plot6,'-djpeg',[filename,'_f']);
close gfenergy

%+++++++calculate the density of electrons+++++
Fermi_function = @(E,T) 1./(1+exp((E)./(const.kb_J.*T)));

```

```

H = DOS.*Fermi_function(Energy,0);
n(i) = sum(DOS(1:position_Ef),2).*(Energy(2)-Energy(1));
n(i) = n(i)/1e6;
%+++++
% all variables are deleted expect the following e.g ^B
clear('-regexp','[^B,^A,^const,^der_table_element,...
    '^der_table_DOS_dDOS,^sf_c,^n,^element]*');
end

%+++++
%save the derivatives and the DOS at the Fermi Energy
txtfilename = 'table.txt';
fin = fopen(txtfilename,'w');
for i = 1:size(der_table_element,1);
    fprintf(fin,'%s \t %1.3e \t %1.3e \t %1.3e \n',...
        char(element{i}),der_table_DOS(i),...
        der_table_dDOS(i),n(i));
end
fprintf(fin,'\n\n\n');
for i = 1:size(der_table_element,1);
    fprintf(fin,'%s \t %1.3f \t %1.3f \t %1.3f \n',...
        char(der_table_element(i,1:end)),sf_c(i,1),...
        sf_c(i,2),sf_c(i,3));
end
fclose(fin);
%+++++
end

function axistext
set(gca,'fontsize',20);
end

function [DOS_free] = free_electr(V_uc,hquer,...
    Ef,mass_e,Energy,element,qe)
cd 'E:\uni\6.semester\bak\plots';
%+++++
% Fermi Energys of the free electron model
% (from Ashcroft & Mermin) saved in Fermiief.xls

```

```

[Fermifree,name] = xlsread('Fermief.xls');
namelog = strcmp(element,name);
if ~any(namelog)
    DOS_free = nan;
    return
end
Ef_free = Fermifree(namelog);

Energy_new = Energy+Ef_free*qe;

DOS_free = 2*heaviside(Energy_new).*V_uc./(4*pi.^2).*...
    (2.*mass_e./hquer.^2).^ (3./2).*sqrt(Energy_new);
end

```

A.2 function fun_loaddata_mod (load DOS files)

% This function loads files from the type *.DOS. These files
% generated by the program Wien2k. For other files this
% function has to be modified.

```

function [Energy,DOS_all,V_uc,element] = ...
    fun_loaddata_mod(dir,file,bohr)
cd(dir)
[Energy,DOS_all] = textread(file,'%f %f %*f %*f %*f %*f',...
    'headerlines',4);
[dummy,element,lattice,a_bohr,unit] = ...
    textread(file,'%s %s %s %s %s',1);
clear dummy;
a_bohr = a_bohr{1}(3:end);
a_bohr = str2num(a_bohr)*bohr;
switch char(lattice)
    case {'fcc'}
        V_uc = a_bohr^3/4;
    case {'bcc'}
        V_uc = a_bohr^3/2;
end

```


A.3 function SommerFeld_ucvsf_Efvar (calculate properties)

```
function [u,cv,sommef_coeff,s,f,T] = SommerFeld_ucvsf_Efvar...
    (g_u,E,position_Ef,DOS_Ef,kb)
% This function calculates the internal energy, the specific
% heat, the entropy and the helmholz free energy. The function
% needs the function for the sommerfeld expansion
% (for the internal energy. All the other values can be
% calculated from this one.), the Energy, the Density of
% States at the Fermi surface and the bolzman consant.
% To see a precise derivative of the different values see
% the documentation.
T = linspace(0,500,20);
dE = E(2)-E(1);
u_T_0 = sum(g_u(1:position_Ef),2).*dE; %This is the internal
% energy at temperature T=0ÅK
u = u_T_0 + pi.^2./6.*(kb.*T).^2.*DOS_Ef(1);
for i=1:numel(DOS_Ef)
    cv = pi.^2./3.*kb^2.*T.*DOS_Ef(i);
    sommef_coeff(i) = cv(2)./T(2);
end
s = cv;
f = 2*u_T_0-u;
```