

V47 - Molwärme von Cu

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1 Goals

In this experiment the temperature dependent specific heat capacity for copper is to be determined to proof the validity of the Debye model.

2 Theory

As mentioned in chapter 1, we want to understand the nature of the specific heat capacity of Copper. This requires an understanding of the underlying effects, that influence the heat capacity. But it is more important to first understand what the heat capacity is. The Theory of the heat capacity will be discussed first in a calssical approach and then in a qunantized approach.

2.1 Heat Capacity

The heat capacity is defined as the amount of energy, which is needed to heat a body by 1 K. That means the heat capacity is an amount of heat per temperature. The general formula is given by the equation 2.1, in which dQ is the needed amount of heat and dT is the temperature change.

$$C = \frac{dQ}{dT} \quad (2.1)$$

This definition of heat capacity leads to a sample-size dependent quantity. Thus meaning a definition per mol, per mass or per volume is more informative. The definition per mol is named “molar heat capacity”. The definition per mass and per volume is called “specific heat capacity”. They are distinguished via an index. To understand where the specific heat capacity is coming from, it is needed to approach this with thermodynamics. The first law of thermodynamics describes the energy balance of a system.

$$dE = dQ + dW = TdS - pdV \quad (2.2)$$

In equation 2.2 it can be seen, that $\delta W = 0$ for a constant volume, because $dV = 0$. Applying this information to equation 2.1 it yields that for constant volume the specific heat capacity can be described by the following equation 2.3.

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V \quad (2.3)$$

To get the specific heat capacity for a constant pressure, we have to apply an legendre transformation to the energy. This transformation leads to the enthalpy H given by equation 2.4. The enthalpy H is, similar to the inner energy E , a measure of energy in an thermodynamic system.

$$dH(S, p, N) = dE(S, V, N) + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp \quad (2.4)$$

Using $p = \text{const}$ this equation yields $dH = dQ$. Adding this to the definition of the specific heat capacity results in equations 2.5 describing the specific heat capacity with a fitting thermodynamic state functions.

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V, \quad C_p = \left. \frac{\partial H}{\partial T} \right|_p \quad (2.5)$$

The specific heat capacity for constant pressure can also be calculated by equation 2.6. This equation is a more practical way of calculating the heat capacity. In this equation E is the added energy of the system, which is described in chapter 3, M the molar mass, m the mass of a sample and ΔT is the raise in temperature.

$$C_p = \frac{ME}{m\Delta T} \quad (2.6)$$

2.2 Comparisson of C_V and C_p

From measurements it is known, that C_V and C_p differ to some extend. The reason for this is, that for a constant pressure p the volume V of the sample changes, thus work has to be put into the deformation of the solid. This creates a loss of energy that does not exist for a constant volume. This is an isentropic process, therefore the adiabat equation is valid. The isentropic constant, which is given by $\kappa = \frac{C_p}{C_V}$, describes the ratio of the two specific heat capacities. It can be approximated by equation 2.7, in which f is the amount of dof.

$$\kappa = \frac{f + 2}{f} \quad (2.7)$$

For a solid in a classical approach(6 dof), this yields an ratio $\kappa = \frac{4}{3}$. This ratio is larger than one, therefore $C_p > C_V$. This difference in these two seemingly similar quantities, not at all random. More so it is tightly embedded in thermodynamic theory. At this point the derivation of the correction formula is not shown. The correction formula is given by equation 2.8.

$$C_p - C_V = 9\alpha^2 \kappa V_0 T \quad (2.8)$$

α being the thermal expansion coefficient, κ the bulk modulus, V_0 the molar volume and T the temperature.

2.3 Classical Theory of the Heat Capacity

In section 2.1 the formula for the specific heat capacity with constant volume was derived. Thus C_V is dependent on the inner energy of a system. To calculate the inner energy it is of interest to understand what defines or gives an solid state sample inner enregy. The answer is lattice vibrations. For each of the three directions in space, there

are two possible vibration modes. Thus having a three dimensional sample, there are six degrees of freedom (“dof”). To compare this an ideal gas has three (kinetic) dof.

The equipartition theorem states, that every dof has an energy of $\frac{1}{2}k_B T$. k_B is the boltzmann-constant and T the temperature. With this it is possible to calculate the “classical” inner energy of an sample as shown in equation 2.9.

$$E = N'_{\text{dof}} N_{\text{atoms}} \frac{1}{2} k_B T = \frac{6}{2} N k_B T = 3N k_B T \quad (2.9)$$

Now the specific heat capacity can be calculated using equation 2.3, which results in 2.10.

$$C_V = 3N k_B \quad (2.10)$$

This is the “Law of Dulong-Petit”, which describes the classical limit of the specific heat capacity. Note, that the calssical limit is not dependent on the temperature.

2.4 Experimental partially falsification of the Law of Dulong-Petit

Now that we have a model for the temperature-depence of the specific heat capacity, we can compare the model to measured data, to evaluate the theoretical model. For this a temperature measurement of the heat capacity is needed. In Figure 2.1 we can see, that C_p is not constant in temperature. From this follows, that C_V is also not constant in temperature, since the difference between C_p and C_V is small in a solid.

From the measurement, we can see that the classical limit, which means for high temperatures, the Dulong-Petit law is valid. Small deviations come due to anharmonic effects dominating for higher T . But the significant perception is, that for low temperatures $C_V \propto T^3$. Therefore “new physics” must be the explanation. With the idea of qunantization of classically continuous phenomena a new idea for the calculation of the inner energy in a solid state system came up.

2.5 Quantummechanical Theory of the Heat Capacity

Now we want to look at the quantized nature of lattice vibrations, so called *Phonons*. Even so the Dulong-Petit model cannot describe the heat capacity for low temperatures, the approach over the energy of lattice vibrations is not incorrect. We can describe the vibrations not as classcial oscillators, but as quantummechanical oscillators. Therefore the states in the low temperature regime are quantized, because $\hbar\omega \gg k_B T$. With this idea we can describe the solid state as an system of $3N$ harmonic oscillators. To calculate the inner energy of such a system we can use Bose-Einstein-statistics. The inner energy in the low temperature regime is fundamentally dependent on the phonon dispersion. In a solid state system there are always $3N - 3$ optical modes and 3 acoustic modes. The common dispersion relation of phonons is shown in Figure 2.2.

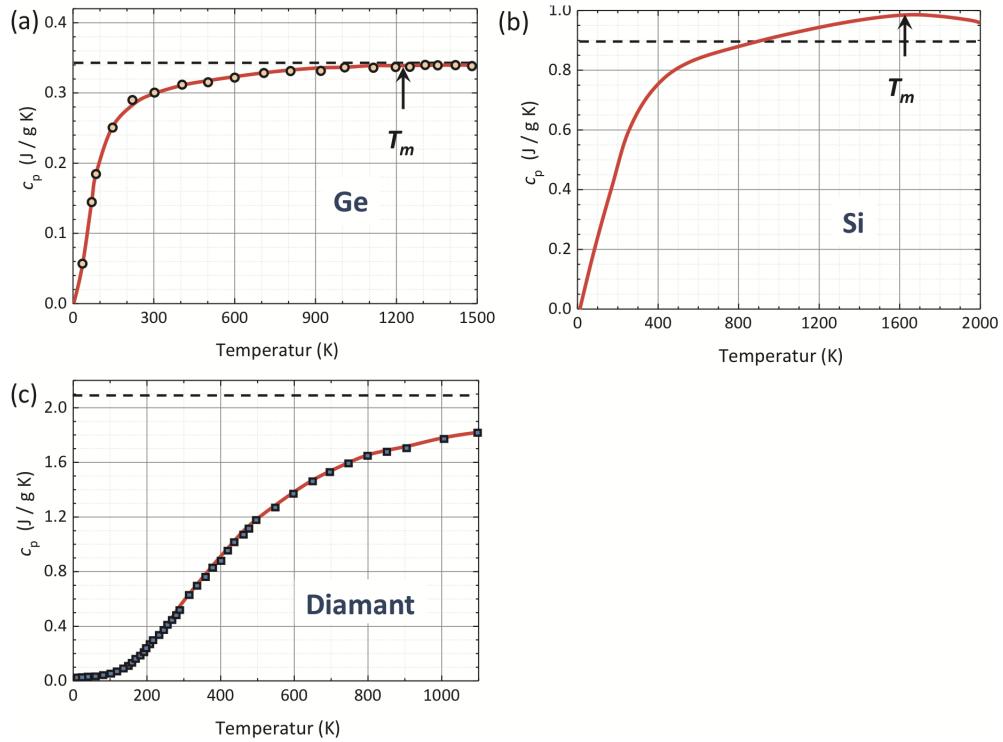


Figure 2.1: In this figure we can see the temperature-dependence of the specific heat capacity C_p for different solids. [1]

The general approach to calculate the inner energy of this system would be using $D(E)dE = Z(\vec{k})d^3k$ and integrating over the energy to get the inner energy. But calculating this without approximations is not possible.

There are two common approximations to calculate the inner energy of a solid. The “Einstein-Approximation” and the “Debye-Approximation”.

2.6 Einstein Approximation

The Einstein Approximation is based in the simple idea, that all the $3N$ phonon modes of the lattice have the same constant frequency ω_E . This means, that we have state density given by equation 2.11.

$$D(\omega) = 3N\delta(\omega - \omega_E) \quad (2.11)$$

With this state density we can calculate the inner energy with the before mentioned approach, which yields $\langle E \rangle = 3N\hbar\omega_E(\frac{1}{2} + \frac{1}{e^{\hbar\omega_E/k_B T} - 1})$. From this we can calculate the specific heat capacity with equation 2.5. To make so solution easier we define the “Einstein-temperature” $\Theta_E = \frac{\hbar\omega}{k_B}$. The specific heat capacity calculated using the Einstein-Approach results in equation 2.12.

$$C_V^E = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1 \right)^2} \quad (2.12)$$

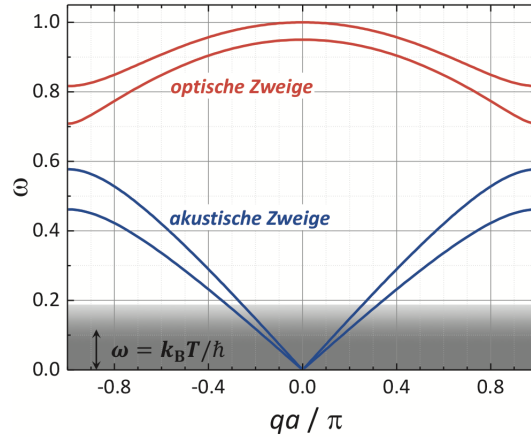


Figure 2.2: In this figure we can see the phonon dispersionrelation for acoustic and optical modes. [1]

From equation 2.12 we can discuss the high and low temperature limits. These are given by the following equation.

$$C_V^E = \begin{cases} 3Nk_B \left(\frac{\Theta_E}{T}\right)^2 e^{\frac{\Theta_E}{T}} & \text{for } T \ll \Theta_E \\ 3Nk_B & \text{for } T \gg \Theta_E \end{cases}$$

In the first case we see, that in this approximation we get an strong drop of the heat capacity for low temperatures. From measurements we know, that the heat capacity follows an T^3 proportionality, which is not the result. But in general this is an better description of the nature than Dulong-Petit. As for the other case, which is the *calssical limit*, we optain the Law of Dulong-Petit. This shows, that even with this strong approximation we still get a better result than the classical approach.

2.7 Debye-Approximation

The Debye-Approximation has the idea to look at the low temperature limit, because this is where the classcial theory deviates from the measurement. In the low temperature regime the occupation of optical phonon modes is low. Due to that it is a good approximation to just use the 3 acoustic phonon modes. The dispersion of acoustic phonons is proportional to $|\sin x|$. For small temperatures the argument of the sinus is very small. Due to the small angle approximation it is valid to assume a linear dispersion for acoustic phonons. Also the sum over all wavevectors can go over to an integral og the first Brillouin-Zone. This is the Debye Approximation. Due to the finiteness of a solid we can define a cutoff frequency w_{D} which is given by equation 2.13.

$$\int_0^{w_D} D(\omega) d\omega = 3N_L \quad (2.13)$$

In this equation N_L is the Loschmidt-constant. We can calculate the state density $D(\omega)$ using the approach with the linear dispersion. We know, that the state density in frequency domain is given by equation 2.14.

$$Z(\omega)d\omega = \frac{V}{2\pi^2}\omega^2 \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{long}}^3} \right) \quad (2.14)$$

Since we only look at the longitudinal(acoustic) modes we can rewrite equation 2.14 using the Debye frequency ω_D . This formula is shown in equation 2.15.

$$Z(\omega)d\omega = \frac{9N_L}{\omega_D^3}\omega^2 d\omega \quad (2.15)$$

With this state density we can calculate the energy of the solid and by deriving that for the temperature we can obtain the heat capacity in the Debye-model. It is shown in equation 2.16.

$$C_V^D = \frac{\partial}{\partial T} \frac{9N_L}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} \quad (2.16)$$

From this equation we can discuss the two limits. The formula for each limit is shown in equation 2.17. We see, that the debye approximation results in an $\propto T^3$, which describes the nature very good. Also the classical limit is the Dulong-Petits law.

$$C_V^D = \begin{cases} \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D} \right)^3 & \text{for } T \ll \Theta_D \\ 3N k_B & \text{for } T \gg \Theta_D \end{cases} \quad (2.17)$$

The upper equation is defined in units of $\frac{T}{\Theta_D}$. It is in units of the debye-temperatur, which is defined in equation 2.18.

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \quad (2.18)$$

It is a material specific value, characterizing its thermodynamic quantities.

2.8 Comparison of the Debye and Einstein Model

Both the Einstein and Debye-model use simple approximations to calculate the specific heat capacity. As seen in Figure 2.3 the Debye model describes the nature better than Einstein, but for the extent of the approximations Einstein made both models have their own advantage for the low temperature regime. For high temperatures both models are equal. Figure 2.3 also shows the heat capacity for an free electron gas. A metal, such as copper, can be described using the free electron gas. Therefore we can see, that effects of the electron gas only play a role in the very low temperature regime.

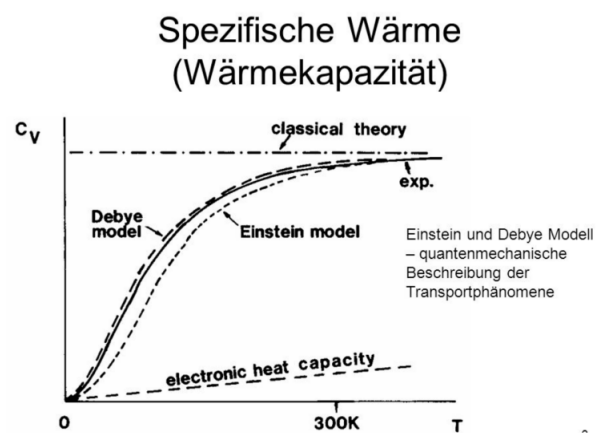


Figure 2.3: In this figure we can see the function of the heat capacity for classical calculation and in the Einstein/Debye model.

3 Experiment

3.1 Experimental setup

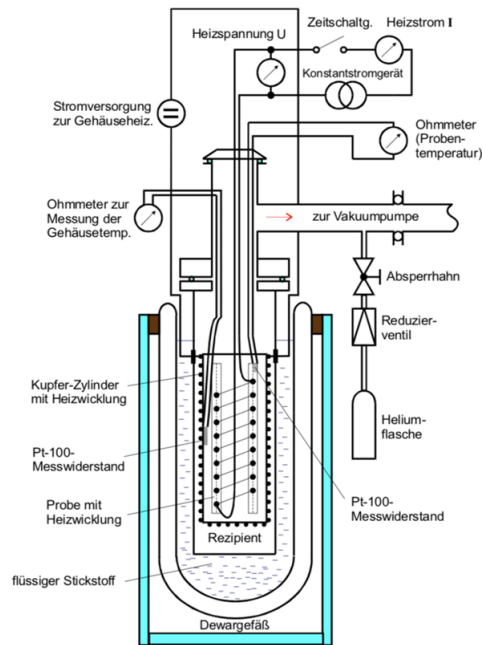


Figure 3.1: This figure shows the used experimental setup. [3]

Figure 3.1 shows the experimental setup that is used. To measure the wanted temperature dependent effects on the heat capacity, very low temperatures have to be achieved. the copper sample which is to be analyzed is inside another copper shielding, which itself is within a recipient. This recipient is sealed tightly, so there is no air exchange between the sample and the surrounding area. It again is located inside another vessel - a Dewar vessel.

The recipient is connected to two valves, which lead to a vacuum pump and a helium container. To heat sample and copper shielding independently, both have their own heating coil which can be controlled via a chosen heating voltage and current. The heat of the sample and copper shielding are measured with a Pt-100 measuring resistor, which has a temperature dependent resistance. The amount of resistance is measured with an ohmmeter and the corresponding temperature calculated with [eq:resistance].

3.2 Experimental execution

At the beginning the sample has to be cooled down to 80 K. To do this, the recipient has to be evacuated and filled with helium. To further help with the cooling process and stop the recipient from getting heated from the outside, the Dewar vessel is carefully filled with liquid nitrogen. This is done with a pair of safety gloves and a hopper. This process takes up to an hour.

When 80 K is reached, the valve to the helium container is closed up and the vacuum pump is started again to evacuate the recipient to minimize heat loss through the air molecules.

As soon as the recipient is fully evacuated the measuring process will start. The heating coils are turned on and the value for the heating voltage and current for the sample are chosen to be 16.56 V and 157.6 mA. The heating voltage and current for the shielding are constantly adjusted, so the temperature of the shielding matches the one of the sample. This way heat loss through convection is also minimized. Further heating loss through cable attachments (conduction) and radiation cannot be stopped, but are assumed to be very minor and will not be taken into account.

Every time the temperature has risen by approximately 7 to 11 K, the heating time, the heating voltage and current of the sample and the exact resistance are noted. Every measurement takes between 5 and 8 minutes. This is repeated until the sample has reached a temperature of 300 K.

4 Analysis

4.1 Heat capacity C_p of copper

To calculate the heat capacity at constant volume later, the heat capacity at constant pressure has to be determined from the measurements first. To do this Equation 2.6 is needed.

The variable H describes the heat which is being applied to the sample. This observable cannot be measured directly, but can be calculated with

$$H = I \cdot \Delta t \cdot U, \quad (4.1)$$

where I is the heating current of the probe, U the heating voltage and Δt the duration of the heating. Table 4.1 shows the taken measurements of those observables and the calculated amount of heat supplied.

The amount of temperature the sample has risen by is calculated with

$$T = 0.00134 \cdot R^2 + 2.296 \cdot R - 243.02. \quad (4.2)$$

The corresponding values for the ΔT are found in Table 4.2. The $M = 63.546 \frac{\text{g}}{\text{mol}}$ [2] is the molecular mass of copper and $m = 342 \text{ g}$ [3] is the mass of the sample.

The calculated values for the heat capacity at constant pressure are also found in Table 4.2.

4.2 Specific heat capacity C_V of copper

The specific heat capacity at constant volume is given by a correction term in Equation 2.8. C_V is the wanted specific heat capacity at constant volume, C_p is the heat capacity at constant pressure, which was determined earlier in Table 4.2, $\kappa = 140 \times 10^9 \text{ Pa}$ [2] is the bulk modulus, $V_0 = \frac{M}{\rho} = 7.092 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}$ [2] the molar volume, T the temperature and α the linear thermal expansion coefficient, which is given in a table in [3]. Since the values measured are not exactly those given in the besaid table, an estimation via the equation

$$\alpha(T) = \frac{\alpha_i - \alpha_{i-1}}{T_i - T_{i-1}} (T - T_{i-1}) + \alpha_{i-1} \quad (4.3)$$

was performed. The results of α and C_V can be seen in Table 4.3. In addition figure ?? shows the measured temperature dependence of the specific heat capacity for constant volume.

Δt	U_{sample}/V	I_{sample}/mA	H/J
0	16.56	157.6	-
135	16.56	157.6	352.33
173	16.78	160.2	465.05
328	17.03	162.2	906.02
351	17.15	163.2	982.41
341	17.24	163.7	962.37
385	17.32	164.3	1095.59
372	17.37	164.6	1063.59
415	17.42	165.0	1192.83
452	17.45	165.2	1302.99
337	17.48	165.4	974.33
431	17.50	165.6	1249.04
458	17.52	165.7	1329.60
380	17.53	165.8	1104.46
433	17.54	166.0	1260.74
447	17.56	166.0	1302.99
516	17.56	166.2	1505.93
406	17.56	166.2	1184.89
471	17.57	166.4	1377.04
464	17.57	166.4	1356.57
449	17.57	166.4	1312.72
449	17.57	166.5	1313.51
486	17.57	166.5	1421.75
426	17.56	166.6	1246.26

Table 4.1: Measurements of the heating voltage, current and time for the sample and the results for the supplied heat.

$R_{sample}/k\Omega$	T_{sample}/K	$\Delta T_{sample}/K$	$C_P/\frac{J}{molK}$	$R_{shield}/k\Omega$	T_{shield}/K
0.0234	84.59	-	-	0.023	83.41
0.0250	88.37	3.78	17.33	0.0235	84.83
0.0270	93.10	4.73	18.26	0.0252	88.84
0.0311	102.83	9.73	17.29	0.0313	103.31
0.0354	113.09	10.26	17.79	0.0349	111.89
0.0395	122.91	9.83	18.19	0.0391	121.95
0.0438	133.27	10.35	19.66	0.0437	133.02
0.0477	142.70	9.43	20.95	0.0488	145.37
0.0520	153.15	10.45	21.21	0.0520	153.15
0.0567	164.62	11.48	21.09	0.0559	162.66
0.0600	172.71	8.09	22.37	0.0590	170.26
0.0642	183.06	10.34	22.44	0.0653	185.77
0.0685	193.69	10.64	23.22	0.0681	192.70
0.0720	202.39	8.69	23.60	0.0702	197.91
0.0760	212.37	9.98	23.48	0.0754	210.87
0.0801	222.64	10.27	23.57	0.0789	219.63
0.0847	234.21	11.58	24.17	0.0835	231.19
0.0881	242.81	8.59	25.62	0.0878	242.05
0.0921	252.96	10.15	25.21	0.0913	250.92
0.0961	263.15	10.19	24.73	0.0963	263.66
0.1000	273.13	9.98	24.44	0.1007	274.93
0.1039	283.15	10.02	24.36	0.1037	282.64
0.1080	293.73	10.58	24.97	0.1081	293.99
0.1118	303.57	9.84	23.552	0.1122	304.61

Table 4.2: Measurements of the temperature, resistance and results for the heat capacity at constant pressure.

T/K	$\alpha/10^{-6}\frac{1}{K}$	$C_V/\frac{J}{molK}$	T/K	$\alpha/10^{-6}\frac{1}{K}$	$C_V/\frac{J}{molK}$
84.59	9.074	-	193.69	14.8	22.85
88.37	9.55	17.26	202.39	15.01	23.20
93.10	10.04	18.18	212.37	15.25	23.04
102.83	10.93	17.19	222.64	15.45	23.10
113.09	11.69	17.66	234.21	15.66	23.66
122.91	12.26	18.04	242.81	15.79	25.09
133.27	12.81	19.47	252.96	15.96	24.64
142.70	13.27	20.73	263.15	16.15	24.13
153.15	13.69	20.96	273.13	16.28	23.81
164.62	14.06	20.81	283.15	16.39	23.68
172.71	14.32	22.06	293.73	16.56	24.27
183.06	14.58	22.09	303.57	16.70	22.78

Table 4.3: Calculated values for the linear thermal expansion coefficient and the specific heat capacity at constant volume.

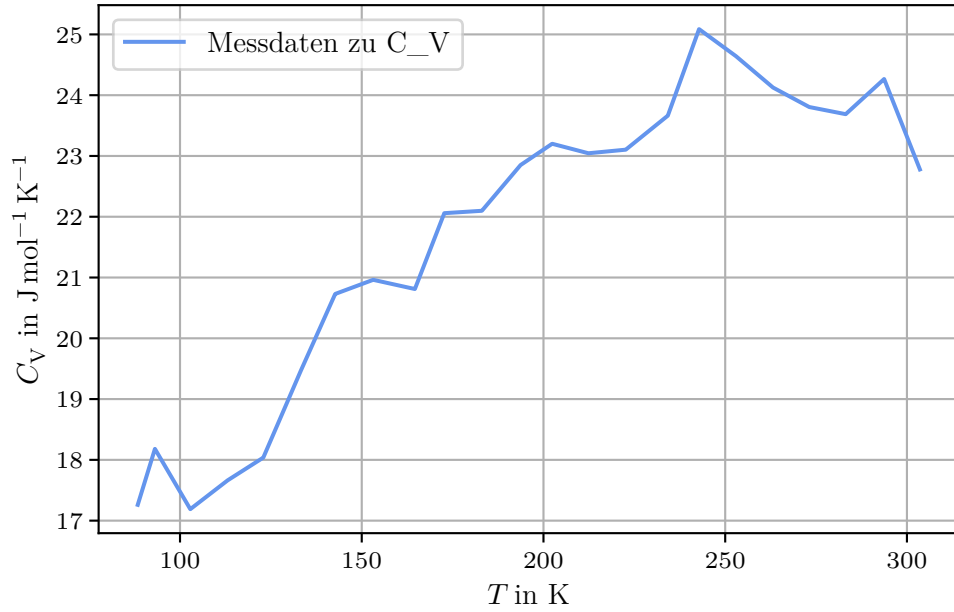


Figure 4.1: Specific heat capacity C_V dependet on the temperature.

4.3 The Debye temperature of copper

To determine the debye temperature θ_D of the sample, Figure 4.2 is needed. It yields the value for $\frac{\theta_D}{T}$ for a certain C_V . The result is then multiplied by the temperature the C_V was calculated for. This gives the debye temperature θ_D . The values can be seen in Table 4.4.

The mean and error of the debye temperature is

$$\theta_D = 288.67 \pm 8.62 \text{ K}. \quad (4.4)$$

T/K	$C_V/\frac{\text{J}}{\text{molK}}$	$\frac{\theta_D}{T}$	θ_D/K
84.59	-	-	-
88.37	17.26	2.8	247.43
93.10	18.18	2.6	242.06
102.83	17.19	2.8	287.93
113.09	17.66	2.7	305.34
122.91	18.04	2.6	319.57
133.27	19.47	2.3	306.51
142.70	20.73	2.0	285.39
153.15	20.96	1.9	290.98
164.62	20.81	1.9	312.78

Table 4.4: Calculated values for the Debye temperature.

Θ_D/T	0	1	2	3	4	5	6	7	8	9
0	24,9430	24,9310	24,8930	24,8310	24,7450	24,6340	24,5000	24,3430	24,1630	23,9610
1	23,7390	23,4970	23,2360	22,9560	22,6600	22,3480	22,0210	21,6800	21,3270	20,9630
2	20,5880	20,2050	19,8140	19,4160	19,0120	18,6040	18,1920	17,7780	17,3630	16,9470
3	16,5310	16,1170	15,7040	15,2940	14,8870	14,4840	14,0860	13,6930	13,3050	12,9230
4	12,5480	12,1790	11,8170	11,4620	11,1150	10,7750	10,4440	10,1190	9,8030	9,4950
5	9,1950	8,9030	8,6190	8,3420	8,0740	7,8140	7,5610	7,3160	7,0780	6,8480
6	6,6250	6,4090	6,2000	5,9980	5,8030	5,6140	5,4310	5,2550	5,0840	4,9195
7	4,7606	4,6071	4,4590	4,3160	4,1781	4,0450	3,9166	3,7927	3,6732	3,5580
8	3,4468	3,3396	3,2362	3,1365	3,0403	2,9476	2,8581	2,7718	2,6886	2,6083
9	2,5309	2,4562	2,3841	2,3146	2,2475	2,1828	2,1203	2,0599	2,0017	1,9455
10	1,8912	1,8388	1,7882	1,7393	1,6920	1,6464	1,6022	1,5596	1,5184	1,4785
11	1,4400	1,4027	1,3667	1,3318	1,2980	1,2654	1,2337	1,2031	1,1735	1,1448
12	1,1170	1,0900	1,0639	1,0386	1,0141	0,9903	0,9672	0,9449	0,9232	0,9021
13	0,8817	0,8618	0,8426	0,8239	0,8058	0,7881	0,7710	0,7544	0,7382	0,7225
14	0,7072	0,6923	0,6779	0,6638	0,6502	0,6368	0,6239	0,6113	0,5990	0,5871
15	0,5755	0,5641	0,5531	0,5424	0,5319	0,5210	0,5117	0,5020	0,4926	0,4834

Figure 4.2: This is a table to calculate the debye temperature.

4.4 Theoretical calculation of Debye-frequency and the Debye-temperature

The theoretical value of the debye-frequency can be calculated using equation 4.5.

$$\omega_D^3 = \frac{18\pi^2 N_A}{V_0} \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3} \right)^{-1} \quad (4.5)$$

This equation derives from equation 2.14, by calculating the density state function $Z(\omega)$. In this equation v_{long} is the longitudinal phase velocity and v_{trans} is the transversal phase velocity[3]. $N_A = 6.022 \times 10^{23}$ 1/mol is the *Avogadro constant* and V_0 the molar volume of the sample. The theoretical value of the debye-frequency is $\omega_D = 4.35 \times 10^{13}$ 1/s. From this the debye-temperature can be calculated using equation 2.18. With the boltzmann constant this results in $\Theta_D = 332.18$ K

5 Discussion

The calculated specific heat capacity at constant volume plotted against the temperature roughly yields what is expected from the Debye model. Big uncertainties and measurement outliers would lose importance if more data would be taken. This could fix the shape of the plot and could validify the Debye model.

The Debye temperature calculated with the measurement data is $\theta_{D,exp} = 288.67 \pm 8.62 \text{ K}$ while the theoretically calculated Debye temperature is $\theta_{D,theo} = 332,18 \text{ K}$. Therefore those two values do not overlap and the Debye model cannot be validated. Possible reasons why measurement data is faulty, would be that the heat loss, which was assumed to be rather small, is actually influencing the data to a significant amount. A better isolation and an automated heat controller could make the results better.

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Appendix