Molar heat capacity of copper

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Contents

1 Introduction

Goal of this experiment is the measurement of the temperature dependency of the heat capacity C_V at constant preassure and volume. The Debye temperature Θ_D will also be measured and compared to the theory value.

2 Theory

This section will give a brief overview of the theoretical framework needed to understand and interpret the following measurements. It will touch on the heat capacity C_V in the context of solid state physics and explain the differences between three main theoretical models, describing the same phenomenon. If not explicitly cited otherwise, this section will rely on the book "Festkörperphysik" [3].

2.1 Classical theory of the heat capacity

The molar heat capacity C_V, from now on referred to as heat capacity, is a thermodynamic variable describing the amount of heat ΔQ needed for a given temperature change of $1\,\mathrm{K}$. It is a material specific constant, which is different for different materials. The heat capacity is given by the relation

$$C_V = \left.\frac{\partial Q}{\partial T}\right|_{V,N} = \left.\frac{\partial U}{\partial T}\right|_{V,N} \tag{1}$$

where U is the solids inner energy. The heat capacity at constant preassure is given by

$$C_p = \left.\frac{\partial Q}{\partial T}\right|_{p,N} = \left.\frac{\partial H}{\partial T}\right|_{p,N} \tag{2}$$

where H is the enthalpy of the system. The relation $C_V \leq C_p$ is true for any system, as the system at constant preassure has to expand when applying an amount of heat ΔQ to it, thus doing more work ΔW which increases the heat capacity. C_V and C_p are fundamentally connected by the thermal expansion coefficient α and the compressibility κ in the relation

$$C_p - C_V = 9\alpha^2 \kappa V_0 \,, \tag{3}$$

where V_0 is the molar volume of the solid. To determine the heat capacity of a solid state body, we can approximate each atom in the solid as a harmonic oscillator, given by the Hamiltonian for a single atom in the solid

$$\mathcal{H}(\vec{p}, \vec{q}) = \frac{\vec{p}^2}{2m} + \frac{1}{2}k\vec{q}^2 \,. \tag{4}$$

Using the equipartition theorem

$$\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \rangle = k_B T \tag{5}$$

one can determine, that

$$U = \langle \mathcal{H} \rangle = \frac{1}{2} \sum_{i=1}^{3} \langle \frac{p_i^2}{m} \rangle + \langle kq_i^2 \rangle \tag{6}$$

$$= \frac{1}{2} \sum_{i=1}^{3} \langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \rangle + \langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \rangle \tag{7}$$

$$= 3k_B T \tag{8}$$

is the inner energy of a single Atom in a solid state body. By applying avogrados number N_A and using Equation 1, one can calculate the molar heat capacity of a solid state given by the doulong petite law

$$C_V = 3RT \tag{9}$$

2.2 Oscillation of the cristalline structure

In order to understand the heat capacity of a solid state body, one has to first understand the oscillations of its cristalline structure, which will be introduced in this subsection. The cristalline structure, when viewed from a purely mathematical perspective, becomes a set of vectors which are linear combinations of its basis vectors. This static view of a solid state body can be filled with motion when one imagines these vectors as springs, connecting each pair of neighbouring atoms in the lattice. The problem to be solved is then nothing more than the simple harmonic equations of motion every physicist has solved at least once in their live. This approach neglects the electrons contribution to the overall problem. The introduced springs are nothing more than a quadratic approximation of the more complex electromagnetic potential each atom experiences. If we assume the electrons to be significantly faster than the atomic nuclei, individual electromagnetic contributions of the electrons to the electromagnetic potential one atom experiences in the lattice can be neglected as a static background. This approach is known as the Born-Oppenheimer approximation and it allows us to approximate the electromagnetic potential in quadratic order, resulting in a harmonic potential which acts like a spring.
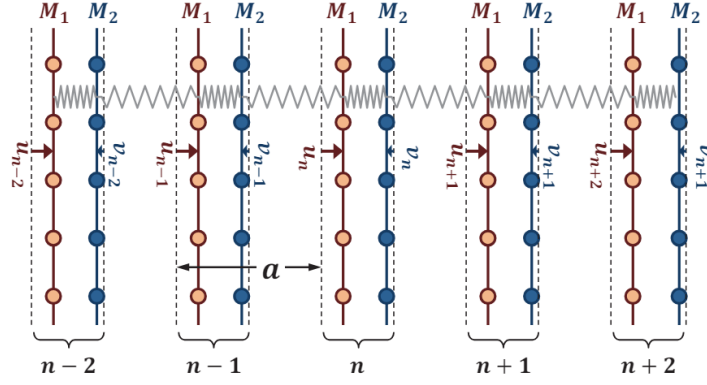
Figure 1: 2D lattice of 2 atoms with equal couplings f and different masses M_1 and M_2, [3].

The equations of motion for a 2D lattice of 2 Atoms with different masses M_1, M_2 and equal coupling f, see Figure 1, can then intuitively be written as

$$M_1 \frac{\mathrm{d}^2 u_n}{\mathrm{dt}^2} = f(v_n - u_n) + f(v_{n-1} - u_n) \tag{10}$$

$$M_2 \frac{\mathrm{d}^2 v_n}{\mathrm{dt}^2} = f(u_n - v_n) + f(u_{n+1} - v_n) \tag{11}$$

where u_n and v_n are the deflection function of each type of atom in a latice that can be seen in Figure 1. Solving the equations for one row of this simple case, results in two solutions for the frequencies of the lattice oscillations, which can be seen in Figure 2.
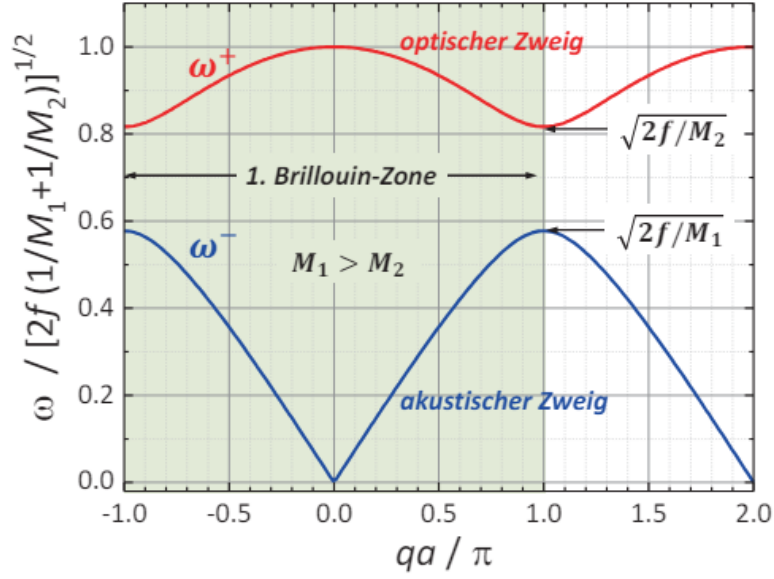
Figure 2: Dispersion relation for a 1D lattice of 2 atoms with different masses M_1, M_2 and equal coupling f, [3].

The upper branch of the dispersion relation in Figure 2 is called the optical branch and the lower branch is called the accoustic branch. The optical branch is a result of the different masses M_1 and M_2 and is not present in a lattice with one atomic basis. There are $3N$ branches in a $3D$ lattice of N different atoms, with $3N - 3$ accoustic branches and 3 optical branches, which are not dependent on the number of different atoms in the lattice. The different branches of the dispersion relation of a solid state body are often referred to as phonons, wich are quantized lattice vibration. Phonons are Bosons and follow the Bose-Einstein distribution given by

$$\langle n_{\mathrm{BE}} \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} .$$
(12)

2.3 Einstein model

The Einstein model approximates the heat capacity of a solid state body by assuming, that all phonons are of the same constant frequency ω_{E} called the Einstein frequency. The inner energy of one mol of the system under this assumption is then given by

$$U = 3N_A \hbar\omega_{\mathrm{E}} \left(\langle n_{\mathrm{BE}} \rangle + \frac{1}{2}\right) ,$$
(13)

using Equation 1 the heat capacity of the system is given by

$$C_V = 3N_A k_B \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left(\exp\left(\frac{\Theta_E}{T}\right) - 1\right)^2} ,$$
(14)

where $\Theta_E = \frac{\hbar\omega_E}{k_B}$ is the Einstein temperature. The Einstein approximation dominates at high temperatures and is a good approximation for the optical phonons in a solid state body. Because this experiment uses copper, which has a single atom basis, the Einstein model is not a good approximation in this case as there will be no optical phonons in the lattice.

2.4 Debye model

The Debye model postulates a linear dispersion relation for all $3N$ phonon branches with an upper frequency ω_D the Debye-frequency. The dispersion relation for each branch is given by $\omega = v_s \cdot k$, where v_s is the specific mode's speed of sound in the medium. Because copper is a single basis atom, it has 3 accoustic vibrational modes of which two are transversal and one is longitudinal. This results in a density of states

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

where v_s is a function of the transversal and longitudinal speeds of sound in the medium v_t and v_l, given by

$$v_s^3 = \frac{3v_l^3 v_t^3}{2v_l^3 + v_t^3}. \tag{16}$$

Given the integral

$$U = \int_0^{\omega_D} Z(\omega)\langle n_{BE}\rangle \mathrm{d}\omega, \tag{17}$$

The heat capacity can again easily be determined using Equation 1 resulting in an approximate solution for high and low temperatures to be

$$C_V = \begin{cases} \left(\frac{12\pi^2}{5}\right) N k_B \left(\frac{T}{\Theta_D}\right)^3 & \text{for } T \ll \Theta_D \\ \frac{3}{2} k_B T & \text{for } T \gg \Theta_D \end{cases}. \tag{18}$$

Θ_D is the Debye temperature which is given by the expression

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v_s}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}. \tag{19}$$

The Debye approximation is more accurate for smaller temperatures, which is where accoustic phonons dominate the heat propagation. It is thus the approximation which will be used in this experiment, as it fits the single atom basis of the copper cristalline structure.
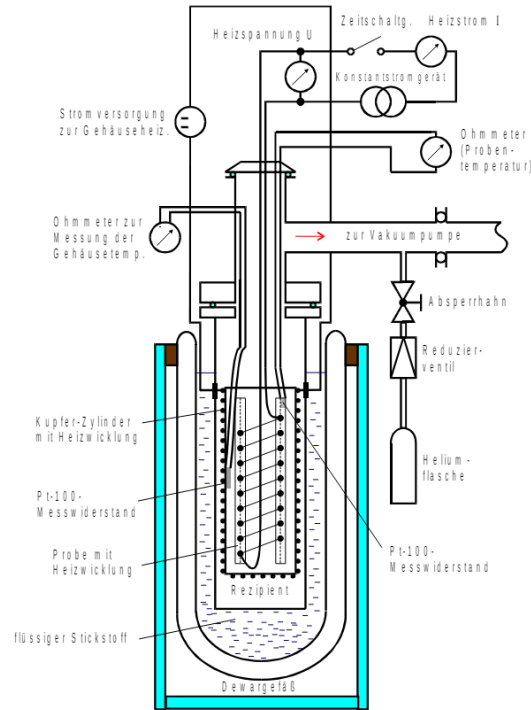
3 Experimental setup

Figure 3: Experimental setup for the measurement of the heat capacity of copper. [2]

Figure 3 shows the experimental setup needed to measure the heat capacity of copper. It consists of a devar vessel, in which liquid nitrogen is filled to cool the recipient chamber with the sample and its shell. The sample and shell are both heated and are both connected to a resistor for temperature measurements of both components. The recipient is connected to a vacuum pump and a helium tank and is air tight in order to be vacuumated or filled with helium. The temperature is measured indirectly, by measuring the resistors of both the shell and the sample using two ohm meters. The time can be stopped using a digital stop watch.

4 Execution

Before the measurement can take place, the recipient chamber has to be vacuumated. After the vacuum is established, the chamber is filled with helium, and the space between the recipient chamber and the devar vessel is filled with liquid nitrogen. Once a sample temperature of roughly $70\,\mathrm{K}$ is reached, the helium valve is closed and the helium is vacuumated out of the recipient vessel. The vacuum pump keeps running for the rest of the measurement. The current of the sample heater are then set to roughly $I_{Sa} = 155\,\mathrm{mA}$ and the corresponding voltage is read of a volt meter. The shell current is adjusted

manually to keep the shell and sample temperature equal. The timer is started and measures tabulated resistance ranges for the sample temperature resistor. For each time measurement, the current and voltage of the sample is written down as it tends to change during the experiment. This process is repeated until the sample temperature reaches 273,15 K.

5 Evaluation

The graphics and calculations shown in section 5 were created using the Python libraries Matplotlib [5], Scipy [9] and Numpy [4].

5.1 Calculations of the molar heat capacity at constant pressure

The heat capacity at constant pressure C_p is calculated using the formula

$$C_p = \frac{M}{m} \cdot \frac{\Delta E}{\Delta T} \tag{20}$$

where $M = 63{,}55\,\mathrm{g/mol}$ [7] is the molar mass of copper, $m = 0{,}342\,\mathrm{kg}$ [2] is the mass of the copper sample, $\Delta E = U \cdot I \cdot \Delta t$ is the energy supplied to the copper sample, $\Delta T = T_2 - T_1$ and Δt is the time interval in which the energy is supplied to change the temperature from T_1 to T_2.
Since the temperature is measured with heat dependent resistors, the temperature is calculated using the formula

$$T = 0.00134R^2 + 2.296R - 243.02 + 273.15.$$

For the measured values, an error of the last scale unit is applied which leads to the following uncertainties:

$$\delta U = \pm 0{,}01\,\mathrm{V},$$
$$\delta I = \pm 0{,}1\,\mathrm{mA},$$
$$\delta R = \pm 1\,\Omega,$$
$$\delta t = \pm 1\,\mathrm{s}.$$

Now one can calculate the heat capacity at constant pressure C_p for each measurement using Equation 20. The results are shown in Table 1.

Table 1: Measured values and calculated heat capacity at constant pressure C_p.

C_p (J/molK)	ΔT (K)	Δt (s)	I (mA)	U (V)
14.54 ± 4.75	10.23 ± 3.34	312	156.5	16.39
16.30 ± 5.43	10.09 ± 3.36	331	159.7	16.75
16.91 ± 5.69	10.02 ± 3.37	339	160.0	16.81
18.55 ± 6.29	9.99 ± 3.39	368	160.6	16.88
18.98 ± 6.47	9.99 ± 3.41	374	161.0	16.95
19.28 ± 6.60	9.99 ± 3.42	378	161.3	17.00
21.82 ± 7.51	9.99 ± 3.44	426	161.6	17.04
21.69 ± 7.50	9.98 ± 3.45	422	161.8	17.07
19.16 ± 6.66	9.98 ± 3.47	372	161.9	17.09
19.17 ± 6.69	9.97 ± 3.48	371	162.1	17.11
26.81 ± 9.41	9.97 ± 3.50	518	162.2	17.12
26.33 ± 9.28	9.96 ± 3.51	508	162.2	17.13
27.45 ± 9.73	9.96 ± 3.53	528	162.3	17.16
25.62 ± 9.13	9.95 ± 3.54	492	162.4	17.17
26.91 ± 9.61	9.96 ± 3.56	517	162.5	17.18
25.61 ± 9.15	10.01 ± 3.57	494	162.5	17.18
25.18 ± 8.99	10.05 ± 3.59	488	162.5	17.17
24.87 ± 8.93	10.04 ± 3.60	481	162.6	17.18
26.00 ± 9.36	10.06 ± 3.62	504	162.6	17.17

5.2 Calculations of the molar heat capacity at constant volume

The heat capacity at constant volume C_V can be calculated using thermodynamic relations. The heat capacity at constant pressure C_p and the coefficient of thermal expansion α are related to the heat capacity at constant volume C_V by Equation 3. The coefficient of thermal expansion α is given in the instruction manual [2] for the corresponding temperatures. The isothermal compressibility for copper is given by $\kappa = 140\,\text{GPa}$ [6] and the molar volume $V_0 = 7{,}11 \cdot 10^{-6}\,\text{m}^3/\text{mol}$ [1]. Plugging these values into Equation 3 and using the values for C_p from Table 1 one can calculate the heat capacity at constant volume C_V for each measurement. The results are shown in Table 2.

Table 2: C_p, α and calculated C_V for each measurement.

C_p (J/molK)	T (K)	α (1/MK)	C_V (J/molK)
14.54 ± 4.75	82.94 ± 2.36	8.50e-06	14.48 ± 4.75
16.30 ± 5.43	93.17 ± 2.37	9.75e-06	16.23 ± 5.42
16.91 ± 5.69	103.26 ± 2.38	1.07e-05	16.80 ± 5.69
18.55 ± 6.29	113.28 ± 2.39	1.15e-05	18.41 ± 6.29
18.98 ± 6.47	123.27 ± 2.40	1.21e-05	18.82 ± 6.47
19.28 ± 6.60	133.27 ± 2.41	1.27e-05	19.09 ± 6.60
21.82 ± 7.51	143.26 ± 2.42	1.32e-05	21.60 ± 7.51
21.69 ± 7.50	153.24 ± 2.44	1.36e-05	21.44 ± 7.50
19.16 ± 6.66	163.23 ± 2.45	1.39e-05	18.88 ± 6.66
19.17 ± 6.69	173.21 ± 2.46	1.43e-05	18.85 ± 6.69
26.81 ± 9.41	183.18 ± 2.47	1.45e-05	26.47 ± 9.41
26.33 ± 9.28	193.15 ± 2.48	1.48e-05	25.95 ± 9.28
27.45 ± 9.73	203.11 ± 2.49	1.50e-05	27.04 ± 9.72
25.62 ± 9.13	213.07 ± 2.50	1.52e-05	25.18 ± 9.12
26.91 ± 9.61	223.01 ± 2.51	1.54e-05	26.44 ± 9.61
25.61 ± 9.15	232.98 ± 2.52	1.56e-05	25.10 ± 9.14
25.18 ± 8.99	242.99 ± 2.53	1.58e-05	24.64 ± 8.99
24.87 ± 8.93	253.03 ± 2.54	1.59e-05	24.29 ± 8.92
26.00 ± 9.36	263.07 ± 2.55	1.61e-05	25.39 ± 9.35

5.3 Calculations of the Debye temperature

The Debye temperature θ_D is determined by using the given values for $\frac{\theta_D}{T}$ in the table in the instruction manual [2]. The Debye temperature is then calculated for each measurement below the temperature of 180 K by multiplying the given values with the corresponding temperature. After that, the weighted mean of the calculated Debye temperatures is calculated. The results are shown in Table 3. For the weighted mean the weights are calculated using the uncertainties of the calculated Debye temperatures so that the mean results in

$$\hat{x} = \frac{\sum_i \frac{x_i}{\sigma_i^2}}{\sum_i \frac{1}{\sigma_i^2}}.$$

Table 3: Calculated Debye temperatures for each measurement.

$\frac{\theta_D}{T}$	θ_D (K)	T (K)	C_V (J/molK)
3.5	290.29 ± 8.25	82.94 ± 2.36	14.48 ± 4.75
3.1	288.83 ± 7.34	93.17 ± 2.37	16.23 ± 5.42
2.9	299.45 ± 6.90	103.26 ± 2.38	16.80 ± 5.69
2.5	283.20 ± 5.98	113.28 ± 2.39	18.41 ± 6.29
2.4	295.86 ± 5.77	123.27 ± 2.40	18.82 ± 6.47
2.4	319.84 ± 5.79	133.27 ± 2.41	19.09 ± 6.60
1.7	243.53 ± 4.12	143.26 ± 2.42	21.60 ± 7.51
1.8	275.84 ± 4.38	153.24 ± 2.44	21.44 ± 7.50
2.4	391.74 ± 5.87	163.23 ± 2.45	18.88 ± 6.66
2.4	415.69 ± 5.90	173.21 ± 2.46	18.85 ± 6.69

Using the values from Table 3 the weighted mean of the Debye temperatures is calculated to be

$$\theta_D = 303.35 \pm 1.79 \text{K}.$$

The Debye temperature θ_D can also be calculated by theoretical considerations. Assuming that the Debye model is valid for the copper sample, the Debye temperature is approximated by Equation 19. Now assuming that v_s is given by Equation 16, where $v_l = 4,7 \cdot 10^3 \text{ m/s}$ and $v_t = 2,2 \cdot 10^3 \text{ m/s}$ [2] are the longitudinal and transversal sound velocities, respectively. The number of atoms per volume N is given by

$$N = \frac{N_A}{V} = \frac{N_A}{M} \cdot \frac{m}{V} = 3,25 \cdot 10^{24}.$$

V is the volume of copper and N_A is the Avogadro constant. Plugging these values into Equation 19 one can calculate the Debye temperature θ_D to be

$$\theta_D = 332.63 \text{K}.$$

6 Discussion

In the following, the percentage deviations are calculated with

$$\Delta = |\frac{exp - theo}{theo}| \cdot 100\%. \tag{21}$$

6.1 Heat capacity at constant pressure and constant volume

The heat capacity at constant pressure C_p and constant volume C_V has been calculated in subsection 5.1 and subsection 5.2. As expected, the heat capacity at constant pressure is higher than the heat capacity at constant volume. Expected is a T^3-dependence of the

heat capacity which cannot really be verified with the given data because the uncertainties in the initial values for the resistors are amplified by the calculation of the temperature and thus lead to a high uncertainty in the heat capacity. Furthermore, there are some outliers in the data which could be caused by a significant temperature difference between the shield and the copper sample. Even though it is tried to minimize this effect by constantly adjusting the power supply to heat the shield to the same temperature as the copper sample, it is not possible to completely eliminate this effect.

Only one reference value for the heat capacity at constant pressure could be found [8] at room temperature. The value is $C_p = 24{,}47\,\mathrm{J/molK}$ which is in the range of the measured values.

6.2 Debye temperature

The Debye temperature was calculated from the measured data aswell as from a theoretical point of view. The theoretical value is $\theta_D = 332{,}63\,\mathrm{K}$ and the from the measurement constructed value is $\theta_D = (303{,}35 \pm 1{,}79)\,\mathrm{K}$. The percentage deviation is calculated with Equation 21 and is $\Delta = 8{.}77\%$. The theoretical value is not within the uncertainty of the measured value. This could be caused by the effects mentioned in the previous section. Since the experimental value is in the range of the theoretical value, the Debye model can nevertheless be considered as valid for the copper sample.

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