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Heat capacity of copper

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Contents

1 Motivation

This lab is used to messure the heat capacity of copper. In this context, the Debey temperature and the Debey frequency are determined.

2 Theory

The molar heat capacity is defined by

$$C = \frac{\Delta Q}{\Delta T}. \tag{1}$$

It describes the proportion between the amount of heat Q to raise the tempreture T of a material. Regarding the first law of thermodynamics

$$\mathrm{d}Q = \mathrm{d}U + p\mathrm{d}V, \tag{2}$$

the variation of heat is dependend of the pressure p and the volume V. For experimental purposes it is beneficial to keep the pressure or the volume constant. The difference between these two cases is given by

$$C_p - C_V = TV\alpha_V^2 B. \tag{3}$$

T is the temperature, V the volume, α_V the expansion coefficient and B the bulk modulus. So this difference depends on properties of the respective material and the state of aggregation. Because of the small expansion coefficients of cristalls, the difference between the two heat capacities is neglectable. For experimental practicability, often the heat capacity by constant pressure is used.

2.1 Dulong-Petit

In the classical theory the heat capacity is constant and only depends on the number of degrees of freedom f of the system:

$$C = \frac{f}{2}R. \tag{4}$$

For a three dimensional cristall, every atom has three possible directions to oscillate. In average the atoms have the same kinetic and potential engergy of

$$E = \frac{1}{2}k_B T, \tag{5}$$

with k_B the Boltzman constant. So every atom has six degrees of freedom. Eventually the heat capacity results to

$$C = 3R, \tag{6}$$

where R is the gas constant. This result only holds for high temperatures. In contradiction experimental messurements by low temperatures are showing a T^3-proportionality. This law is only explainable with quantum effects.

2.2 Einstein model

To get a more precize describtion of the thermic behavior of cristalls, the model has to take quantum mechanics into account. Now the engergy of the osscilations are quantized. The Einstein model assumes a constant frequency $\omega = \omega_E$ for all atoms. This assumption is good to approximate a typical dispersionrelation for optical branches, which is shown in figure 1. The heat capacity results to

$$C_V^E = 3Nk_B \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2}, \tag{7}$$

where N is the number of particles, k_B is the Boltzman constant and $\Theta = \frac{\hbar\omega_E}{k_B}$ the Einstein temperature. For high temperatures this expression tends to the law of Dulong Petit. In the low temperature area the experimental result diverges from the theoretic predictions of this model. This is explainable with the assumption of constant frequencies, because for low temperatures most states not in the optical branches but in the accustical branches. To approximate these branches it needs a linear disperionrelation.

2.3 Debey model

Unlike the Einstein model the Debey model assumes a linear dispersionrelation with an maximal value ω_D, called the Debey frequency. The Debey frequency is defined by

$$\int_0^{\omega_D} Z(\omega)\mathrm{d}\omega = 3N_L, \tag{8}$$

with

$$Z(\omega) = \frac{L^3}{2\pi^2}\omega^2 \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3}\right) \tag{9}$$

as the spectral frequency distribution of the oscillators and N_L as the Loschmidt constant. v_{long} and v_{trans} are the respective phase velocities of the logitudinal- and transversal oscillations. To calculate ω_D, the equation (8) can be transformed into

$$\omega_D = \left[\frac{18\pi^2 N_L}{L^3}\left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3}\right)^{-1}\right]^{\frac{1}{3}}. \tag{10}$$

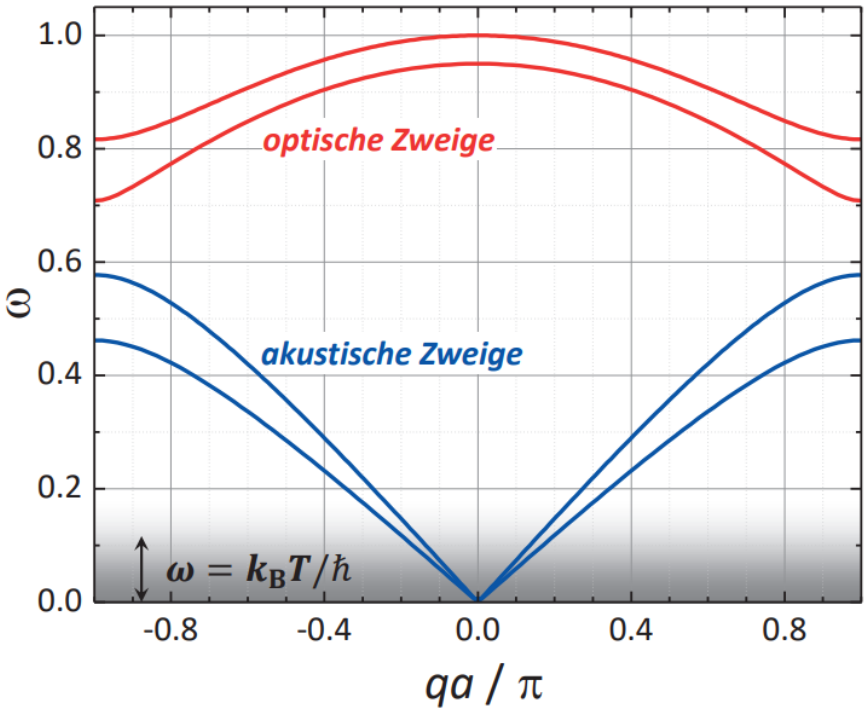

Figure 1: Typical disperion relations of an one atomic cristall. [4, S. 223]

In this model the heat capacity is given by the equation:

$$C_V^E = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2} \mathrm{d}x \tag{11}$$

$$= \begin{cases} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D}\right)^3, & T \gg \Theta_D \\ 3Nk_B, & T \ll \Theta_D \end{cases} \tag{12}$$

$\Theta_D = \frac{\hbar\omega_D}{k_B}$ is the Debey temperature and can be used to estimate the heat capacity for higher or lower temperatures. As equation (12) suggests the messured T^3-proportionality is given for low temperatures. Furthermore the limit of high temperatures matches the Dulong Petit law.

3 Execution

The used experimental setup is shown in figure 2. At first the recipient has to be evaccuated and filled with helium gas. The sample ($m = 342\,\mathrm{g}$) is surrounded by liquid nitrogen, to cool the sample to nearly $T = 80\,\mathrm{K}$. The liquid nitrogen is filled into a cryogenic storage dewar and stored there throughout the whole process. To heat up the copper to a specific temperature a heating coil with a adjustable engergy input is used. The added engergy depends on the current and the voltage. To reduce heat losses through other processes like radiation or convection, the recipient is kept at the same temperature as the sample. The temperature is messured indirectly by Pt-100-resistors. To calculate the temperatures the equation

$$T = 0.00134R^2 + 2.296R - 243.02 \tag{13}$$

is used. R is the messured resistance.

Starting by a temperature of $T = -180\,°\mathrm{C}$, the temperature is raised evenly up to $T = 20\,°\mathrm{C}$. The resistances - representive for the temperatures-, the time, the current and the voltage are messured and noted for every $10\,\mathrm{K}$ increment.

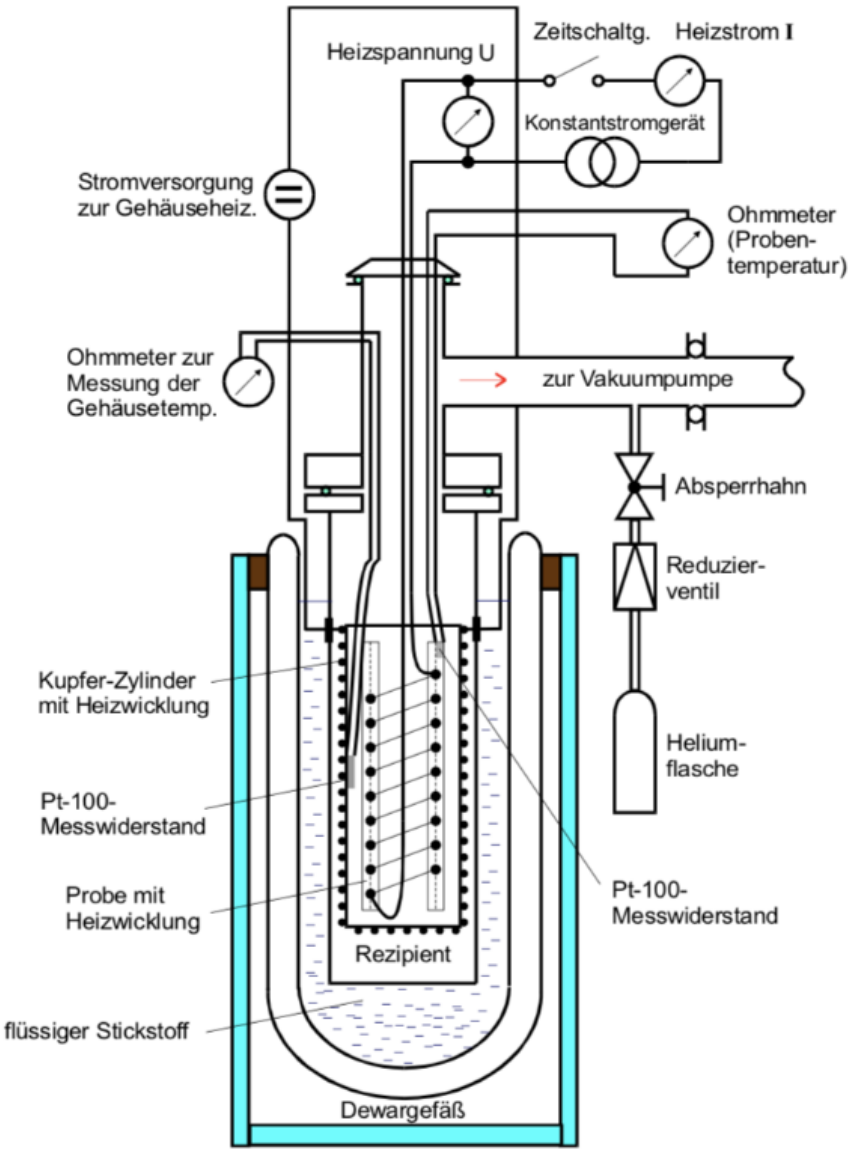

Figure 2: Experimental setup. [3]

4 Analysis

The following calculations are made with "Numpy" [10], "Uncertainties" [7], "Scipy" [6] and "Matplotlib" [5].

4.1 Fitting the linear expansion coefficient

For the following calculations the expansion coefficient is needed. For that purpose the data in table 5 is fittet with

$$\alpha = a\frac{1}{T} + b : \tag{14}$$

$$a = -873 \pm 4$$

$$b = 19.411 \pm 0.029$$

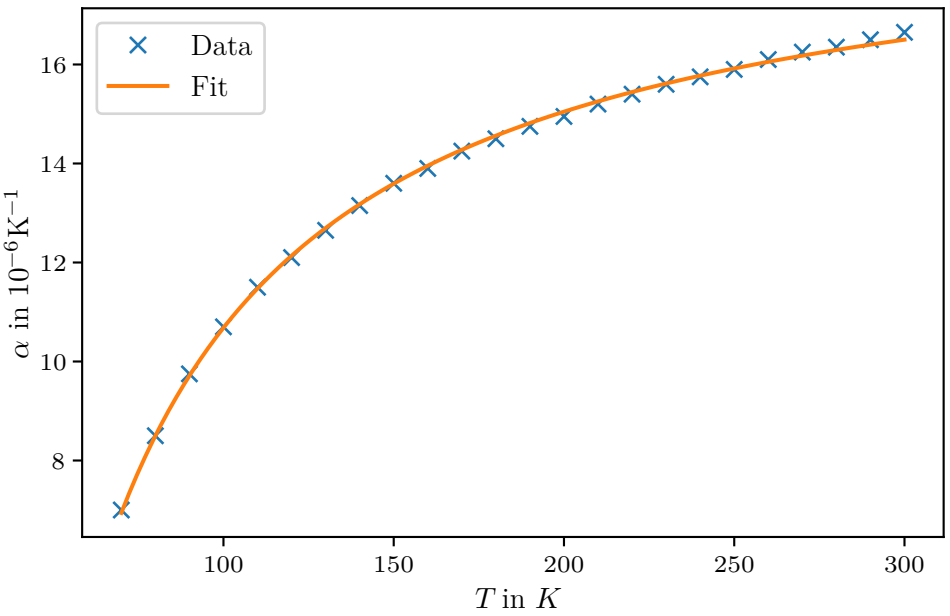

Figure 3: The expansion coefficient plottet against the temperature and the corresponding fit.

4.2 Calculating the molar heat capacity

For the calculation of the molar heat capacity the current I, voltage U , time t and resistance R are measured like described in section 3 (see Table 2).

The engergy the coppy receives is calculated by

$$E = U \cdot I \cdot \Delta t. \tag{15}$$

With (13) and the resistance R the temperature T is determined. The molar heat capacity for constant pressure ist calculated by

$$c_p = \frac{M}{m} \frac{E}{\Delta T}. \tag{16}$$

$M = 63{,}55\,\mathrm{g/mol}$ is the molar Mass and $m = 342\,\mathrm{g}$ [8][3]. The molar heat capacity for constant volume is calculated with

$$c_v = c_p - 9\alpha^2 \kappa V_0 \cdot T. \tag{17}$$

$\kappa = 140\mathrm{N/m^2}$ is the compression modulus [1] and $V_0 = V_0 = 7.11\mathrm{cm^3/mol}$ is the molar Volume [9]. The results are plottet in figure 4 and listet in table 3.

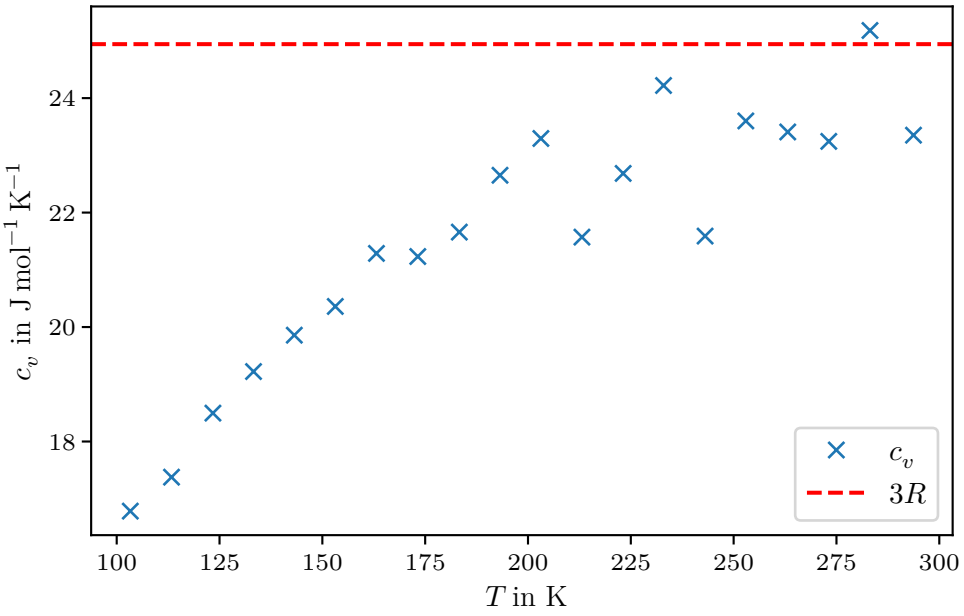

Figure 4: The heat capacity for constant volume c_v plottet against the temperature T.

4.3 Determining the Debye temperature

4.3.1 Empirically

With c_v and the table 6 $\frac{\Theta_D}{T}$ and Θ_D can be determined (see table 1). Then the mean and standard deviation is calculated:

$$\bar{\Theta}_D = (460 \pm 100)\text{K}$$

T in K	c_v in J/(mol K)	$\frac{\Theta_D}{T}$	Θ in K
103,3	16,78	4,6	475,2
113,3	17,38	4,7	532,6
123,4	18,50	4,9	604,6
133,3	19,22	3,5	466,4
143,2	19,86	3,6	515,5
153,1	20,36	2,0	306,3
163,2	21,29	2,1	342,6

Table 1: $c_v, \frac{\Theta_D}{T}$ and Θ_D for $T < 170$K.

4.3.2 Theoretically

The Debye temperature Θ_D can be calculated with (10). N_L and L^3 are replaced with

$$N_L = \frac{N_A \cdot m}{M} \quad \text{and} \quad L^3 = \frac{m}{\rho},$$

so that Θ_D can also be calculated with

$$\Theta_D = \frac{\hbar}{k_B} \left(\frac{18\pi^2 N_A \rho}{M} \left(v_l^{-3} + 2v_t^{-3} \right) \right)^{\frac{1}{3}} = 332.0\text{K} \tag{18}$$

for $\rho = 8.92\text{kg/cm}^3$ [9], $v_l = 4.7\text{km/s}$ and $v_t = 2.26\text{km/s}$ [3].

5 Discussion

The heat capacity can be calculated with the with the energy E and the temperature difference ΔT. The heat capacity is expected to not be greater than $3R$ (see (11)) In figure 4 one can see that this is true for the most part with the meassured data.

The Debye temperature Θ_D can be empirically determinted and calculated (see Chapter 4.3). Comparing these to the given value in literature $\Theta_{D,\text{lit}} = 345\text{K}$ [2], one gets the deviations :

$$\Theta_{D,\text{empirically}} = (460 \pm 100)\text{K} \quad \Delta = -0.34 \pm 0.28 = (-34 \pm 28)\%$$

$$\Theta_{D,\text{theoretically}} = 332.0\text{K} \quad \Delta = 0.038 = 3.8\%$$

with

$$\Delta = 1 - \frac{\Theta_D}{\Theta_{D,\text{lit}}}.$$

A possible explanation for the deviation of the empirically determined Debye temperature is, that the temperature of the reciepent and the shielding should be the same to avoid heat radiation loss, which is not given in this experiment, because the temperature of the shielding is controlled manually. Also there could be heat loss caused by convection, because the reciepent is not in a perfect vacuum.

6 Appendix

T [K]	70	80	90	100	110	120	130	140
α [10^{-6} grd^{-1}]	7,00	8,50	9,75	10,70	11,50	12,10	12,65	13,15
T [K]	150	160	170	180	190	200	210	220
α [10^{-6} grd^{-1}]	13,60	13,90	14,25	14,50	14,75	14,95	15,20	15,40
T [K]	230	240	250	260	270	280	290	300
α [10^{-6} grd^{-1}]	15,60	15,75	15,90	16,10	16,25	16,35	16,50	16,65

Figure 5: A table with the expansion coefficient dependent on the temperature [3].

t in s	$R_{\text{recipient}}$ in Ω	$R_{\text{shielding}}$ in Ω	I in mA	U in V
0	27.3	25.5	146.5	15.36
374	31.3	30.9	147.8	15.52
779	35.5	35.2	148.3	15.60
1209	39.7	39.5	148.8	15.66
1645	43.8	43.6	149.1	15.71
2096	47.9	48.2	149.3	15.74
2559	52.0	52.3	149.5	15.77
3044	56.1	56.1	149.7	15.79
3529	60.2	60.4	149.8	15.81
4025	64.3	64.7	149.9	15.83
4533	68.3	67.6	149.9	15.84
5057	72.3	72.8	150.0	15.85
5544	76.3	78.4	150.1	15.85
6058	80.3	79.8	150.1	15.86
6595	84.2	85.6	150.2	15.86
7088	88.2	88.3	150.2	15.86
7616	92.1	92.4	150.2	15.85
8155	96.1	95.9	150.3	15.85
8679	100.0	100.3	150.3	15.85
9249	103.9	104.3	150.3	15.85
9807	108.0	108.4	150.4	15.84

Table 2: The measured data for t, $R_{\text{recipient}}$,$R_{\text{shielding}}$, I and U.

T in K	c_p in J K/mol	c_v in J K/mol
103,3	16,7838135837253	16,7838135836141 ±0,0000000000010
113,3	17,377181029556994	17,3771810294178 ±0,0000000000011
123,4	18,49597821808551	18,4959782179173 ±0,0000000000012
133,3	19,222473319255368	19,2224733190579 ±0,0000000000013
143,2	19,857871916586102	19,8578719163587 ±0,0000000000014
153,1	20,35997052466634	20,3599705244084 ±0,0000000000015
163,2	21,286754832458026	21,2867548321691 ±0,0000000000016
173,2	21,23237293759968	21,2323729372792 ±0,0000000000017
183,3	21,658849381967833	21,6588493816154 ±0,0000000000018
193,2	22,651958634209254	22,6519586338254 ±0,0000000000019
203,1	23,294803442144367	23,2948034417287 ±0,0000000000020
213,1	21,57129628265861	21,5712962822108 ±0,0000000000021
223,1	22,684145329655074	22,6841453291749 ±0,0000000000021
233,0	24,22073896202113	24,2207389615091 ±0,0000000000022
243,1	21,589446126860107	21,5894461263152 ±0,0000000000023
253,0	23,60122013215889	23,6012201315816 ±0,0000000000024
263,2	23,408576448683668	23,4085764480731 ±0,0000000000025
273,1	23,24408456452845	23,2440845638851 ±0,0000000000026
283,1	25,18173424453668	25,1817342438604 ±0,0000000000027
293,7	23,352435895537067	23,3524358948259 ±0,0000000000028

Table 3: The results for c_p and c_v.

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 6: A table with $\frac{\Theta_D}{T}$ dependent on c_v [3].

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