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Molar heat capacity of copper

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1 Goal

In this experiment the specific heat capacity of copper as well as the debye temperature. Further the temperature dependence of the heat capacity will be compared to the theoretical predictions of the debye model.

2 Theory

There are 3 commonly used theories to describe the specific heat capacity. The classical approach, the Einstein model and the Debye model. Each approach will be explained in the following.

2.1 Classical predictions of the specific heat capacity

In classical thermodynamics, the expected kinetic energy of a particle can be expressed as

$$\langle u_i \rangle = \frac{1}{2} k_B T$$

per positional degree of freedom of the particle, with k_B being the Boltzmann constant and T being the temperature. In general a particle has 3 positional degrees of freedom so a mean energy of

$$\langle u_i \rangle = \frac{3}{2} k_B T.$$

According to the Virial theorem the mean potential energy and mean kinetic energy of a harmonic oscillator is the same. The specific heat capacity of a solid, consisting of N particles, is defined as

$$C_V = \frac{\delta U}{\delta T} = \frac{\delta 3 \cdot N k_B T}{\delta T} = 3 \cdot N k_B.$$

C_V in this case is the heat capacity with constant volume. For solids it is often easier to measure the heat capacity at constant pressure, or C_p , which is related to the former via

$$C_p - C_V = VT \frac{\alpha^2}{\beta}, \quad (1)$$

with V being the volume α the thermal expansion coefficient and β the compressibility.

2.2 Einstein model

In the Einstein model, the quantization of vibrational energies and frequencies of individual atoms in a solid is considered. It assumes that all oscillators vibrate at the same frequency ω , and their energies being multiples of $\hbar\omega$, where \hbar represents the reduced Planck's constant. The probability, $W(n)$, of an oscillator having an energy equal to $n\hbar\omega$ at a given temperature T is described by the Boltzmann distribution:

$$W(n) = \exp\left(-\frac{n\hbar\omega}{k_B T}\right)$$

The average energy per atom, $\langle u \rangle_{\text{Einstein}}$, is calculated by summing over all possible energies, $n\hbar\omega$, weighted by their respective probabilities, and dividing by the sum of all $W(n)$:

$$\langle u \rangle_{\text{Einstein}} = \frac{\sum_{n=0}^{\infty} n\hbar\omega W(n)}{\sum_{n=0}^{\infty} W(n)} = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

The molar heat capacity at constant volume, C_V , can be calculated by differentiating the average energy with respect to temperature, like in the classical case, resulting in

$$C_{V,\text{Einstein}} = \frac{3R\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2}.$$

For high temperatures it converges on the classical prediction of $3Nk_B$

2.3 Debye model

The Debye model takes into account the distribution of vibrational frequencies in a solid, rather than assuming a single frequency for all oscillators. It introduces a characteristic frequency called the Debye frequency, denoted as ω_D , which represents the maximum frequency of vibrations in the solid. The energy levels of the vibrational modes are quantized in units of $\hbar\omega$, and the Debye model considers an integration over all possible frequencies weighted by the density of states function, $D(\omega)$. The average energy per atom in the Debye model, $\langle u \rangle_{\text{Debye}}$, is given by:

$$\langle u \rangle_{\text{Debye}} = 9Nk_B T \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx$$

where $\Theta_D = \frac{\hbar\omega_D}{k_B}$ is the Debye temperature.

The molar heat capacity at constant volume, C_V , in the Debye model can be obtained by differentiating the average energy with respect to temperature:

$$C_{V,\text{Debye}} = 9R \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx$$

The Debye model provides a better description of the specific heat capacity of solids at low temperatures compared to the Einstein model. However, it also has limitations, such as assuming a linear sound velocity and neglecting anharmonicity effects.

3 Setup and Procedure

The experimental setup for determining the specific heat of copper is housed in a Dewar flask filled with liquid nitrogen to ensure the required temperature range for this experiment. Inside the Dewar flask is the copper sample, which is surrounded by heating

4 Analysis

The very first step is to convert the measured resistance R to temperature T . It is possible to do so according to the formula

$$T = 0,00134R^2 + 2,296R - 243,02. \quad (2)$$

The result is in celsius and by adding 273,15 K, it is converted to kelvin. The calculated temperature and other measured data are listed in Table 1. All the values that are required and to be determined for the heat capacities C_p and C_V will also be found in the mentioned table.

4.1 The Heat Capacity C_p of Copper

C_p is the heat capacity at a constant pressure and it is necessary for calculating the heat capacity at a constant volume C_V . So to calculate C_p , the following equation is used

$$C_p = \frac{MH}{m\Delta T} \quad (3)$$

where the heat added to the sample is defined as

$$H = I\Delta tU \quad (4)$$

while $M = 63,55 \frac{\text{g}}{\text{mol}}$ [3] being the molar mass of copper, $m = 342 \text{ g}$ [2] the sample mass and Δt the heating duration. ΔT is the difference of the temperature between two measurements.

4.2 The Specific Heat Capacity C_V of Copper

T [K]	70	80	90	100	110	120	130	140
$\alpha [10^{-6} \text{ grd}^{-1}]$	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
$\alpha [10^{-6} \text{ grd}^{-1}]$	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
$\alpha [10^{-6} \text{ grd}^{-1}]$	15,60	15,75	15,90	16,10	16,25	16,35	16,50	16,65

Abbildung 2: Linear expansion coefficient α of copper as a function of the temperature [2].

C_V is the heat capacity at a constant volume and it can be calculated with the correction formular

$$C_p - C_V = 9\alpha^2 \kappa V_0 T$$

that is depending on C_p , T , the bulk modulus $\kappa = 137 \cdot 10^9 \text{ Pa}$ [4], the molar volume V_0 and the linear expansion coefficient α of copper. The molar volume is given with the density of copper $\rho = 8,96 \frac{\text{g}}{\text{cm}^3}$ [4] by

$$V_0 = \frac{M}{\rho} = 7,092 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}.$$

The linear expansion coefficient is specified in the instructions for certain temperatures. But given that the measured values do not precisely match those provided in the given Table 2, an approximation can be obtained by performing a linear interpolation. According to the equation

$$\alpha(T_n) = \alpha_{i-1} + \frac{\alpha_i - \alpha_{i-1}}{T_i - T_{i-1}}(T_n - T_{i-1}),$$

α can be estimated. In Figure 3 the specific heat capacity is plotted against the temperature.

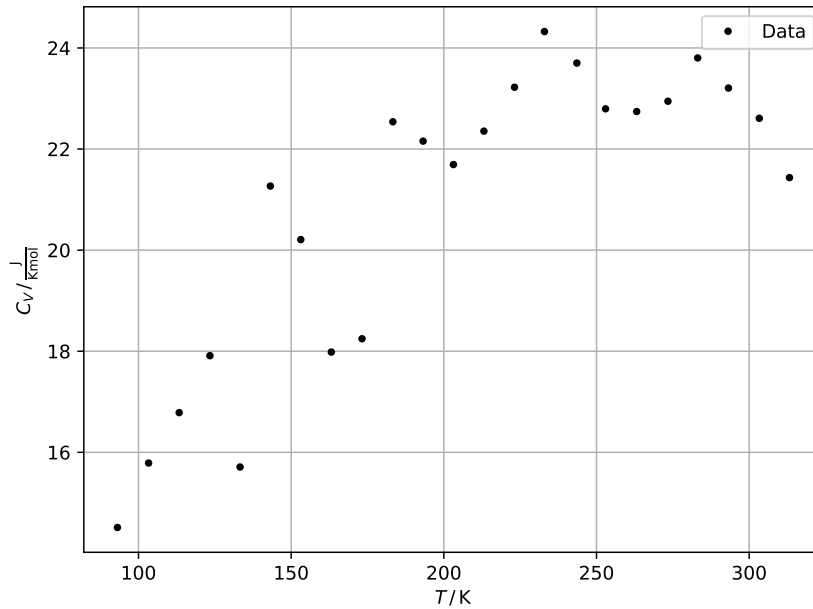


Abbildung 3: The specific heat capacity plotted against the temperature.

Tabelle 1: All measured and calculated datas.

t/s	$\Delta t/s$	U/V	I/mV	H/J	R_{sample}/Ω	T_{sample}/K	$\Delta T_{\text{sample}}/K$	$C_p/\frac{J}{molK}$	R_{shield}/Ω	T_{shield}/K	$\alpha/10^{-6}1/K$	$C_V/\frac{J}{molK}$
0	0	16,18	154,5	0	25,0	88,37	0	-	25,6	89,79	9,55	-
147,17	147,17	16,27	155,2	371,62	27,0	93,1	4,73	14,59	25,9	90,5	10,04	14,51
486,4	339,23	16,44	156,6	873,35	31,3	103,31	10,21	15,9	31,9	104,74	10,96	15,79
837,08	350,68	16,54	157,3	912,38	35,5	113,33	10,02	16,92	35,6	113,57	11,7	16,79
1211,36	374,28	16,6	157,6	979,18	39,7	123,39	10,07	18,07	40,0	124,11	12,29	17,91
1533,09	321,73	16,64	157,8	844,8	43,8	133,27	9,87	15,9	43,1	131,58	12,81	15,71
1968,79	435,7	16,66	158,0	1146,88	47,9	143,18	9,92	21,49	47,3	141,73	13,29	21,27
2384,24	415,45	16,69	158,2	1096,94	52,0	153,15	9,96	20,46	55,7	162,17	13,69	20,21
2756,08	371,84	16,71	158,3	983,59	56,1	163,15	10,01	18,26	62,5	178,86	14,01	17,98
3134,91	378,83	16,72	158,5	1003,94	60,2	173,21	10,05	18,56	60,6	174,19	14,33	18,25
3603,8	468,89	16,73	158,5	1243,36	64,3	183,3	10,1	22,88	64,9	184,78	14,58	22,54
4055,91	452,11	16,74	158,5	1199,58	68,3	193,2	9,89	22,53	68,3	193,2	14,81	22,16
4500,98	445,07	16,75	158,5	1181,61	72,3	203,14	9,94	22,09	71,9	202,14	15,03	21,69
4961,72	460,74	16,75	158,6	1223,98	76,3	213,12	9,98	22,79	77,2	215,37	15,26	22,35
5442,74	481,02	16,75	158,6	1277,85	80,3	223,14	10,02	23,69	80,6	223,89	15,46	23,22
5936,25	493,51	16,75	158,6	1311,03	84,2	232,95	9,81	24,82	81,5	226,15	15,64	24,32
6457,01	520,76	16,75	158,7	1384,3	88,4	243,57	10,61	24,23	88,5	243,82	15,8	23,7
6901,08	444,07	16,75	158,7	1180,44	92,1	252,96	9,39	23,36	92,1	252,96	15,96	22,8
7382,76	481,68	16,75	158,7	1280,41	96,1	263,15	10,19	23,34	96,1	263,15	16,15	22,74
7871,68	488,92	16,74	158,7	1298,88	100,1	273,39	10,24	23,58	100,8	275,18	16,28	22,95
8355,92	484,24	16,74	158,6	1285,64	103,9	283,15	9,76	24,47	103,4	281,86	16,4	23,8
8842,57	486,65	16,74	158,9	1294,48	107,8	293,21	10,06	23,91	107,1	291,4	16,55	23,21
9320,53	477,96	16,73	158,7	1269,01	111,7	303,31	10,1	23,34	111,7	303,31	16,65	22,61
9765,34	444,81	16,72	158,7	1180,29	115,5	313,19	9,88	22,19	117,6	318,67	16,65	21,44

4.3 The Debye Temperatur of Copper

In the next step the Debye temperature θ_D should be determined for the pairs of values (C_V, T) . Only the measured values up to 170 K are taken into account. Using the table in Figure 4, the experimental Debye temperature can be easily found.

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

Abbildung 4: The given table to determine the Debye temperature [2].

The quotient $\frac{\theta_D}{T}$ can be read by comparing the C_V values with the ones in the given table. Then the closest value is to be selected. The left column gives the digit before the comma and the line position indicates the first decimal place. Thus, it can be calculated by multiplying the quotient with the respective temperature for which C_V was calculated. Adjusted values and the Debye temperature are listed in Table 2.

Tabelle 2: Measured and calculated datas for the Debye temperature.

t/s	T/K	$C_V/\frac{J}{molK}$	$\frac{\theta_D}{T}$	θ_D/K
0	88,37	-	-	-
147,17	93,1	14,51	3,5	325,85
486,4	103,31	15,79	3,2	330,59
837,08	113,33	16,79	2,9	328,66
1211,36	123,39	17,91	2,8	345,49
1533,09	133,27	15,71	3,2	426,46
1968,79	143,18	21,27	1,8	257,72
2384,24	153,15	20,21	2,1	321,62
2756,08	163,15	17,98	2,7	440,51

Based on the equations

$$\bar{\theta}_D = \frac{1}{N} \sum_{k=1}^N \theta_{D,k}$$

and

$$\Delta\bar{\theta}_D = \sqrt{\frac{1}{N(N-1)} \sum_{k=1}^N (\theta_{D,k} - \bar{\theta}_D)^2}$$

the mean and standard deviation of the Debye temperature result in

$$\bar{\theta}_D = (347,11 \pm 55,6) \text{ K}.$$

4.4 The Theoretical Debye Temperatur and Frequency

To calculate the theoretical Debye frequency the following equation is required

$$\omega_D^3 = \frac{18\pi^2 N_A}{V_0} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{-1}.$$

With the Avogadro Constant $N_A = 6,022 \cdot 10^{23} \frac{1}{\text{mol}}$ [1], the phase velocity of a longitudinal wave $v_L = 4,7 \cdot 10^3 \text{ m/s}$ [2] and the phase velocity of a transversal wave $v_T = 2,26 \cdot 10^3 \text{ m/s}$ [2] the equation gives

$$\omega_D = 4,35 \cdot 10^{13} \text{ Hz}.$$

This allows to calculate the theoretical Debye temperature using the equation

$$\theta_D = \frac{\hbar \omega_D}{k_B}$$

with $\hbar = 6,63 \cdot 10^{-34} \text{ J s}$ [5] being the reduced Planck constant and $k_B = 1,38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$ [5] the Boltzmann constant. This results in

$$\theta_{D,\text{th}} = 332,18 \text{ K}$$

5 Discussion

In Figure 3 it can be seen that the shape approximaty matches with what is predicted by the Debye model. However, it is recognizable that there are obvious deviations probably caused by measurement errors and instrument inaccuracies. Further measurements would make the curve more precise. Aside from that, the theoretical

$$\theta_{D,\text{th}} = 332,18 \text{ K}$$

and the experimental Debye temperature

$$\bar{\theta}_{D,\text{exp}} = (347,11 \pm 55,6) \text{ K}.$$

was determined. According to the equation

$$\frac{|\bar{\theta}_{D,\text{exp}} - \theta_{D,\text{th}}|}{\theta_{D,\text{th}}} \cdot 100 \%,$$

the two results overlap and they have a deviation of 4,5 %. Another point to be mentioned is that the measurement setup is not completely isolated from external influences since the Dewar flask was open at the top resulting in thermal leakage. In addition, manual adjustments of the voltage had to be made so that the sample and the shield have similar temperatures which did not always work. For this reason, an appropriate suggestion for improvement is to adjust the voltage automatically. Therefore, overall it can be said that the Debye model is roughly confirmed with this experiment.

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Appendix

t	R_{sample} / Ω	$R_{H_{H_2}} / \Omega$	U / V	I / mA
0	25,0	25,6	16,18	154,5
2m 27,175	27,0	25,9	16,27	155,2
8m 06,405	31,3	31,9	16,44	156,6
13m 57,085	35,5	35,6	16,54	157,3
20m 11,365	39,7	40,0	16,60	157,6
25m 33,095	43,8	43,1	16,64	157,8
32m 48,795	47,9	47,3	16,66	158,0
39m 44,245	52,0	55,7	16,69	158,2
45m 56,085	56,1	62,5	16,71	158,3
52m 14,915	60,2	60,6	16,72	158,5
1h 0m 03,805	64,3	64,9	16,73	158,5
1h 07m 35,915	68,3	68,3	16,74	158,4
1h 15m 0,985	72,3	71,9	16,75	158,5
1h 22m 41,725	76,3	77,2	16,75	158,6
1h 30m 42,745	80,3	80,6	16,75	158,6
1h 38m 56,255	84,2	81,5	16,75	158,6
1h 47m 37,105	88,4	88,5	16,75	158,7
1h 55m 01,085	92,1	92,1	16,75	158,7
2h 03m 02,765	96,1	96,1	16,75	158,7
2h 11m 11,685	100,9	100,8	16,74	158,7
2h 19m 15,925	103,9	103,4	16,74	158,6
2h 27m 22,575	107,8	107,1	16,74	158,9
2h 35m 20,535	111,7	111,7	16,73	158,7
2h 42m 45,345	115,5	117,6	16,72	158,7