V47

Molar heat capacity

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Contents

1. Motivation

The aim of this experiment is to determine the specific heat capacity C of copper and its temperature dependence at low temperatures and room temperature. Therefore, the specific heat capacity at constant pressure C_p is measured and translated to the specific heat capacity at constant volume C_V. Different models to describe the temperature dependency are compared and experimentally tested. These are the classical model, the Einstein-Model and the Debye-Model. Furthermore, the *Debye Temperature* Θ_D is derived from the experiment's results and compared with the model's theoretical expectations.

2. Theory

The heat capacity of a material describes the amount of heat that is needed to increase the temperature of a certain amount of the material by $1\,\mathrm{K}$. In general, it can be calculated as

$$C = \frac{\delta Q}{\delta T}$$

where δQ is the input heat and δT the change in temperature. Most often the molar heat capacity c^{m} is used, but also the heat capacity per mass c^{mass} or the heat capacity per volume c^{vol} can be applied. As mentioned before, it is differentiated between heat capacity at constant volume C_V and constant pressure C_p. For C_V the equation

$$C_V = \left.\frac{\delta U}{\delta T}\right|_{\mathbf{V}} \tag{1}$$

can be used to calculate the heat capacity, where U is the internal energy of the system. Experimentally, it is often easier to measure the heat capacity

$$C_p = \left.\frac{\delta Q}{\delta T}\right|_{\mathbf{P}}$$

at constant pressure because most materials expand when heated. The deviation of C_p and C_V can be corrected using

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

where α_V is the volumetric expansion coefficient and B the so-called bulk module.

2.1. Classical Theory of Heat Capacity

In classical thermodynamics, the Equipartition theorem states that the thermal energy of a solid is evenly distributed on its degrees of freedom and every degree of freedom corresponds to $\frac{1}{2}k_B T$ of kinetic and potential energy respectively. k_B is the Boltzmann

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constant. Assuming a crystal of N unit cells (1 atom per cell), this results in a total internal energy of

$$U = U^{\text{eq}} + 3N \cdot 2\frac{1}{2}k_B T = U^{\text{eq}} + 3Nk_B T.$$

Using Equation 1 the heat capacity at constant volume reads

$$C_V = 3Nk_B.$$

For the molar heat capacity, the *Dulong-Petit* law

$$c_V^m = 3R \tag{3}$$

can be derived. Here $R = N_A k_B$ is the gas constant and N_A the Avogadro constant (number of atoms in $1\,\text{mol}$). The classical approach leads to a heat capacity that is material- and temperature independent. Experimental results however, show that at low temperatures, the heat capacity is proportional to T^3 and only approaches the classical value for C_V at higher temperatures. Also, a dependence on the material can be noticed in experiments. Quantum mechanical effects have to be taken into account to explain this behaviour.

2.2. The Einstein-Model

The Einstein-Approximation was the first theory to describe quantum dynamic effects on heat capacity. The approximation assumes the same frequency ω_{E} for all $3N$ oscillation modes of the system. Only energies of whole multiples of $\hbar\omega$ can be absorbed or emitted. With this approach

$$\langle U \rangle = 3N\hbar\omega_{\text{E}} \left(\frac{1}{2} + \frac{1}{\text{e}^{\hbar\omega_{\text{E}}/k_B T}} \right)$$

follows for the internal energy using the Bose-Einstein statistics. The heat capacity will be

$$C_V^{\text{E}} = 3Nk_B \left(\frac{\Theta_{\text{E}}}{T} \right)^2 \frac{\text{e}^{\Theta_{\text{E}}/T}}{(\text{e}^{\Theta_{\text{E}}/T} - 1)^2}, \tag{4}$$

where $\Theta_{\text{E}} = {}^{\hbar\omega_{\text{E}}}/k_B$ is the Einstein Temperature. The approximation for low and high temperatures

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

yields the correct result for high temperatures but does not follow the experimental dependency for the low temperature case. This is caused by the assumption that all atoms have the same frequency.

2.3. The Debye Model

A better approximation is given by the Debye Model, which introduces two fundamental assumptions: 1. All phonon branches are appoximated by three (acoustic) branches with

a linear dispersion relation $\omega_i = v_i q$. 2. The summation over all possible wave vectors q is replaced by an integration over the first Brillouin zone that can further be simplified to a spherical integration with radius q_D. Because of the requirement that N different states (per branch) have to be included in the sphere and using a volume of $(2\pi/L)^3$ per state, the wave vector reads $q_D = \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}}$. The Debye Frequency is $\omega_{D,i} = q_D v_i$ where v_i is the speed of sound of the i-th branch. The density of states can be written as

$$D_i(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v_i^3}.$$

Now the internal energy

$$U = \int_0^{\omega_D} \frac{D(\omega)}{\exp(\hbar\omega/k_B T) - 1}\, d\omega$$

can be calculated. Using the mean speed of sound v_S of the three phonon branches and substituting $x = \hbar v_S q/k_B T$, the heat capacity

$$C_V^D = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 \mathrm{e}^x}{(e^{-x} - 1)^2}\, dx \tag{5}$$

can be derived. This can be approximated as

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

for low and high temperatures respectively. This result includes the classical value for C_V at high temperatures, as well as the experimental observation of a T^3 dependency for low temperatures.

3. Experimental setup and measurement process

The apparatus to determine the heat capacity of copper can be seen in Figure 1. The copper sample can be found in the recipient, which is located in the middle of a Dewar container. It is surrounded by a heating coil that can be used to heat the sample while monitoring the input electric power. Another copper cylinder with a second heating coil is installed around the sample. This is needed to compensate the black body radiation from the sample and prevent heat conduction. The temperature of both copper pieces is measured using Pt-100 resistors connected to ohmmeters. Their resistance is a function of the temperature. The temperature in degrees Celsius can be calculated as

$$T(R) = 0.001\,34R^2 + 2.296R - 243.02 \tag{6}$$

with the resistor's value R in ohms. A vacuum pump is used to evacuate the recipient. The apparatus can be cooled by filling liquid nitrogen in the Dewar container. During this process, heilum is inserted into the recipient through a helium bottle that is also connected to the apparatus.
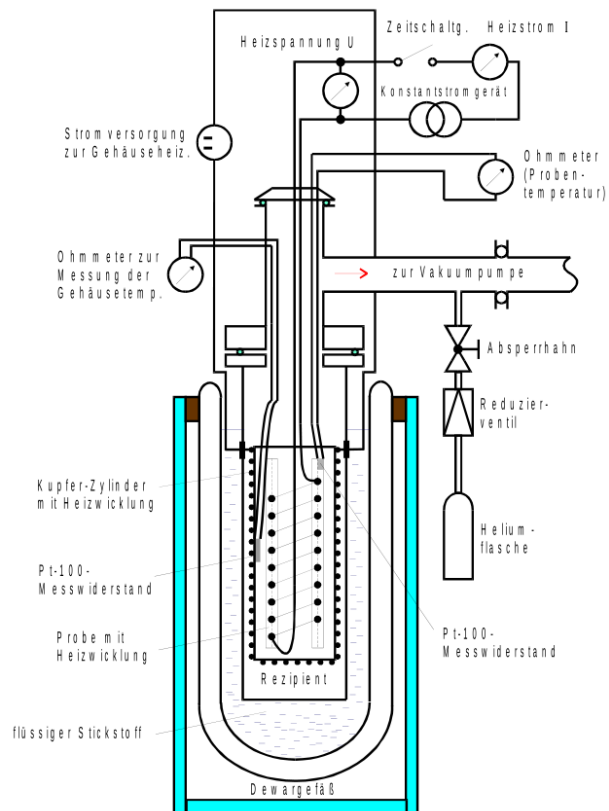
Figure 1: Experimental setup of the measurement of the heat capacity of copper [1].

3.1. Measurement process

First, the recipient is evacuated and filled with helium. Liquid nitrogen is poured into the Dewar container to cool the recipient. When a temperature of $80\,\mathrm{K}$ (i.e. $R = 22.6\,\mathrm{m\Omega}$) is reached, the vacuum pump is turned on to keep the experiment at a constant low pressure. The whole cooling process can take up to an hour. Now the apparatus is heated using the heating coils. The inner coil should be set to a current of approx. $160\,\mathrm{mA}$ while the outer coil has to be repeatedly adjusted to match the temperature of the inner coil. In steps of $7\,°\mathrm{C}$ to $11\,°\mathrm{C}$ the time interval, the sample temperature (resistance), as well as the current and voltage of the heating coil are noted. As a reference table 2 can be used to determine the resistances corresponding to the desired temperature intervals.

T[°C]	-200	-190	-180	-170	-160	-150	-140	-130	-120
R[Ω]	18,44	22,71	27,03	31,28	35,48	39,65	43,80	47,93	52,04
T[°C]	-110	-100	-90	-80	-70	-60	-50	-40	-30
R[Ω]	56,13	60,20	64,25	68,28	72,29	76,28	80,25	84,21	88,17
T[°C]	-20	-10	0	+10	+20	+30	+40		
R[Ω]	92,13	96,07	100	103,90	107,79	111,67	115,54		

Figure 2: Resistor values and corresponding temperatures [1].

The recorded data can be used to calculate the heat capacity at constant pressure C_p of copper.
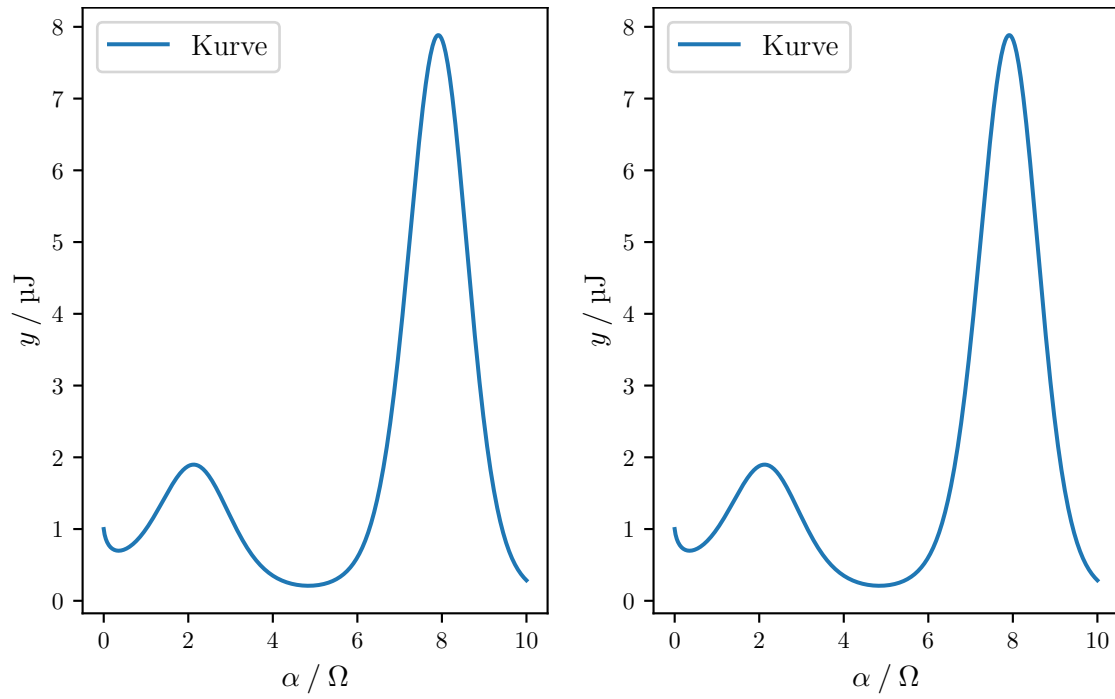
4. Auswertung

Siehe Figure 3!

Figure 3: Plot.

5. Diskussion

References

[1] *V47 - Temperaturabhängigkeit der Molwärme von Festkörpern.* TU Dortmund.

A. Anhang

A.1. Originaldaten