

Praktikum Moderne Physik

Versuchsprotokoll:

Spezifische Wärme

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1 Introduction

In this experiment the heat capacity of the rare earth dysprosium at low temperatures shall be measured. In particular, the behaviour of the heat capacity around the curie temperature $T_C = 90$ K shall be analysed.

1.1 The Debye- and Sommerfeld-Model of Heat Capacity

The heat capacity C is defined as the derivation of heat Q in respect to temperature T of a material:

$$C = \frac{\partial Q}{\partial T} \quad (1.1)$$

For a constant volume of the examined material, the intrinsic energy U is the same as the heat Q , because:

$$dU = \delta Q + \delta W = \delta Q + p \underbrace{dV}_{=0} = \delta Q \quad (1.2)$$

So the heat capacity for a constant volume can be written as a derivation of the intrinsic energy with respect to the temperature:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (1.3)$$

In the case of the solid Dysprosium, the experiment is not perfectly done under constant volume, but due to the low expansion coefficient of solids, the resulting error is negligible.

The intrinsic energy of a solid has two components, the contribution of electrons and of phonons (lattice vibration).

To calculate the intrinsic energy component of the phonons, all phonon energies have to be summed up. As phonons are bosons, they obey the Bose-Einstein distribution. So the intrinsic energy is:

$$U_{ph} = \sum_{i=1}^{3N_A} \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1} \quad (1.4)$$

The factor 3 arises from the 3 dimensions. Transforming this sum into an integral, it has to be multiplied by the density of states $z(\omega)$:

$$U_{ph} = \int_{\omega} \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1} z(\omega) d\omega \quad (1.5)$$

Here Debye used an approximation. In order to calculate the density of states in dependence of the frequency ω , he used the linear dispersion relation $\omega = c \cdot q$, with q as the wave vector of the phonons. This is actually only valid for low energy acoustic phonons. Then he cut up the allowed frequency at a certain value, the Debye-frequency which can be put into relation to the sound velocity. Finally, the intrinsic energy becomes:

$$U_{ph} = 9N_A \int_0^{\omega_D} \left(\frac{\hbar\omega_i}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega_i}{k_B T}}}{\left(e^{\frac{\hbar\omega_i}{k_B T}} - 1 \right)^2} \cdot \frac{\omega^2}{\omega_D^2} d\omega \quad (1.6)$$

The heat capacity then becomes:

$$C_{ph,V} = 9N_A k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad \theta_D = \frac{\hbar\omega_D}{k_B} \quad x = \frac{\hbar\omega}{k_B T} \quad (1.7)$$

θ_D is called the Debye-temperature. This leads to following results:

$$c_{ph,V} \propto T^3 \quad \text{for } T \ll \theta_D \quad (1.8)$$

$$c_{ph,V} = \text{const.} = 3N_A k_B \quad \text{for } T \gg \theta_D \quad (1.9)$$

In the case of this experiment, the formula for low temperatures is more important.

The electronic heat capacity can be calculated via an “enlargement” of the Fermi-Dirac distribution at the Fermi energy. In this calculation, the density of states of electrons can be approximated by a Taylor expansion series. The first non-vanishing contribution is of second order. In Sommerfeld’s approximation, he exactly only used this second order term to calculate the heat capacity contribution of electrons. As the intrinsic energy is of second order in temperature, the heat capacity is of first order. The neglect of the following terms is reasonable because the number of thermally excited electrons is proportional to $\frac{T}{T_F}$, and T_F is very high. In conclusion, the heat capacity contributions of electrons is:

$$c_{el} \propto \frac{T}{T_F} \quad (1.10)$$

It is only important for materials with very low temperature and can be neglected in the case of the experiments done here.

1.2 Magnetic Phase Transitions of Dysprosium

The behaviour of the heat capacity described above are for non-magnetic materials. In magnetic materials (ferromagnetic or anti-ferromagnetic), there are magnetic phase transitions which break the symmetry of the former isotropic material. The magnetisation of the rare-earth dysprosium arises from the indirect RKKY exchange interaction via the two 6s electrons which leads to an anti-ferromagnetic order below the Néel temperature of $T_N = 180$ K and a ferromagnetic order below the Curie temperature $T_C = 90$ K.

The existence of those two phase transition temperatures can be explained by the oscillating behaviour of the exchange integral J_{RKKY} of RKKY interactions in dependence of the distance of 4f-electrons of the magnetic atoms. This distance decreases with lower temperature so that the sign of the exchange interaction switches from negative (anti-ferromagnetic) to positive (ferromagnetic) at the Curie temperature.

Experimentally, the behaviour of the specific heat of Dysprosium around the second phase transition at the Néel-temperature can be determined as:

$$c = \frac{A^\pm}{\alpha} |t|^{-\alpha} + Et + B \quad t = \frac{T - T_N}{T_N} \quad (1.11)$$

t is also called the “critical temperature” and α the “critical exponent”.

2 Experimental Setup

The sample is situated in an evacuated box. The box itself was hung into a cryostat which can be cooled down by liquid nitrogen. The bottom of the cryostat is made of copper. If the box is put on the bottom, it cools down very fast by the nitrogen. To cool down the sample inside the box, the exchange gas helium can be filled into the box to transfer the coldness from the box into the sample. The box also works as a heat shield for the sample to minimize the radiant heat exchange. In the ideal case, the radiance of the sample and the radiance of the box compensate each other. A schematic picture of the whole device can be found in the instructions for this experiment.

After the cool-down of both sample and box, the box can be removed from the bottom again in order to loosen the contact to the cryostat. The helium exchange gas then can also be removed by an diffusion vacuum pump. There are two electric heaters and temperature sensors at the sample and the box which can be controlled separately. As there are no contacts and also not exchange particles between the box and the sample, almost no heat exchange occur. There are some clips between the cryostat and the box in order to stabilise the box mechanically and in order to have still a possibility of a small heat transfer between the box and the cryostat if the heater heats to fast and the box need to be cooled.

The aim of this experiment is to measure a dependence of the supplied heat energy by the heaters and the temperature of the sample. To have an equilibrium of the radiant energy, it was attempted to adapt the temperature of the box to the temperature of the sample. In the first measurement, the examination of the latent heat of dysprosium at the Curie-temperature, this was done manually with rotary knobs of LabView. But for the measurement of the specific heat capacity of a spectrum to get the critical parameters at the Néel-temperature which took several hours, this job was done automatically by LabView itself.

3 Measurement of lateral heat

3.1 Through Temperature Curve at T_C

For the measurement of the lateral heat of Dysprosium at the Curie temperature T_C the sample was cooled down to 77 K. Then the exchange gas helium was removed and both box and sample were heated with constant power. The temperatures of these two were measured over time and are shown in Figure 1. At the beginning, the heating power of box and sample were adjusted to an equal

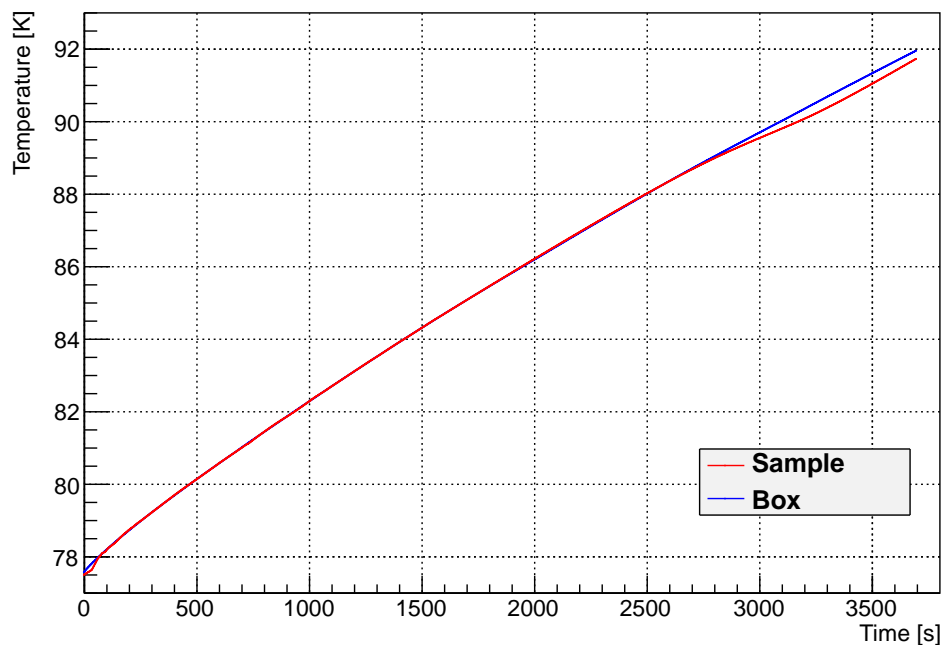


Figure 1: Temperature of box and dysprosium sample over time.

increase of temperature. At the critical temperature T_C a phase transition can be observed. Figure 2 on the next page shows this region in detail.

To calculate the latent heat, two lines had been fitted to the temperature profile of the sample, one before the phase transition and one after. Because of the non-linear temperature profile in the first plot, these two lines are not exactly parallel. So we decided to take the distance of these lines at a temperature of 89.5 K, which seemed to be in the middle of the visible phase transition in the plot. With an error of this assumption of 1 K and the resulting errors of the fitting procedure used in an Gaussian error propagation we get a time difference of

$$\Delta t = (185.5 \pm 16.7) \text{ s}$$

With a constant heating power of 6.781 mW this leads to an energy difference of the phase transition of $(1.26 \pm 0.12) \text{ J}$. So the sample with a mass of $5.6 \cdot 10^{-2} \text{ mol}$ has a latent heat at the first phase transition of

$$(22.46 \pm 2.02) \text{ J/mol}$$

which is equivalent to $(0.138 \pm 0.013) \text{ J/g}$.

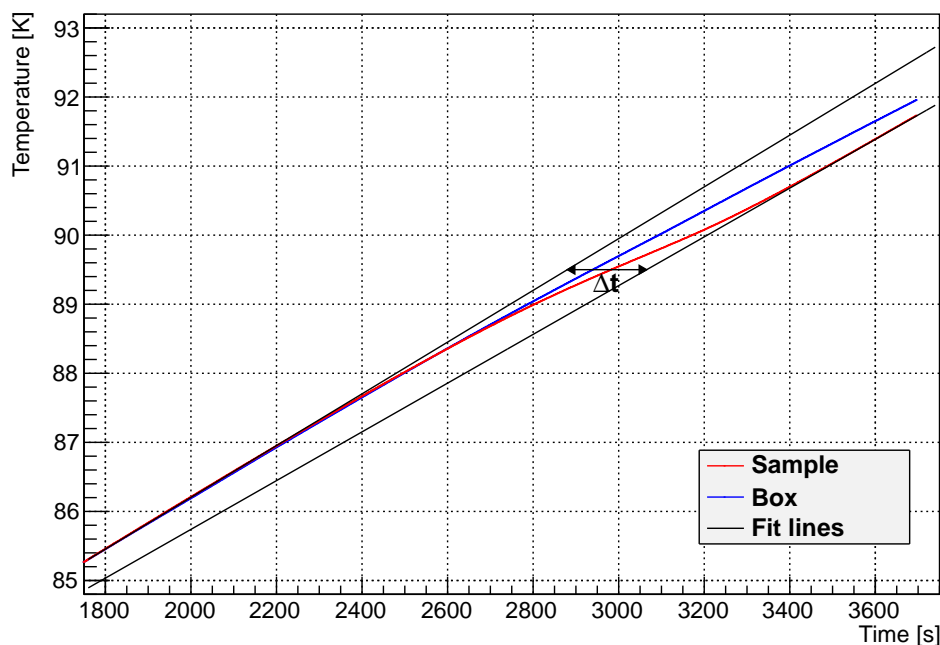


Figure 2: Temperature of box and dysprosium sample over time.

Fit parameters: Two lines with $y = m_i \cdot x + c_i$

$$m_1 = (0.0037456 \pm 0.0000013) \text{ K/s} \quad \text{and} \quad c_1 = (78.713 \pm 0.003) \text{ K}$$

$$m_2 = (0.0035289 \pm 0.0000022) \text{ K/s} \quad \text{and} \quad c_2 = (78.682 \pm 0.008) \text{ K}$$

3.2 Through Specific Heat

For this measurement, the specific heat was measured over the temperature of the sample by measuring its temperature and the heating power. This curve can be seen in Figure 3 on the following page.

The latent heat of the first phase transition can be gained by integrating the peak of this phase transition. For this purpose, a Breit-Wigner distribution with a linear background has been fitted to

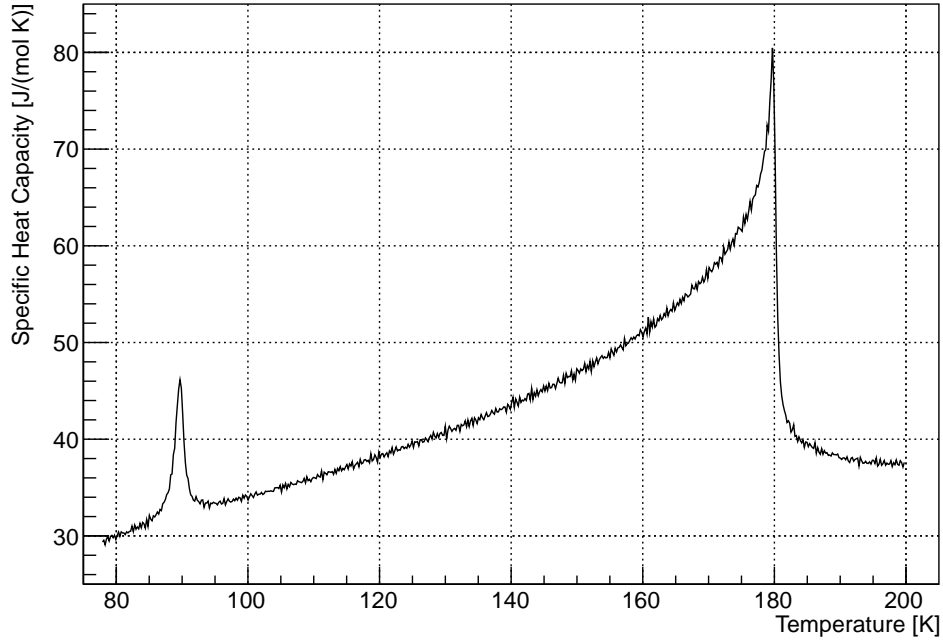


Figure 3: Specific heat of dysprosium over temperature. The two phase transitions at the Curie temperature (left) and at the Néel temperature (right) can be seen.

these data points, as seen in Figure 4 on the next page. Then this Breit-Wigner distribution without the background was integrated from 80 K to 100 K, which is equivalent to the lateral heat of

$$\int_{80 \text{ K}}^{100 \text{ K}} \frac{s}{2\pi} \cdot \frac{\Gamma}{(x - \mu)^2 + \frac{1}{4}\Gamma^2} dx = \boxed{(33.65 \pm 0.51) \text{ J/mol}}$$

These two values differ very much. The first one might be very inaccurate because of the linear fits combined with the non-linear behaviour of the curve and because of the quite short measuring time. The second value seems to be more accurate, because measurement time was much longer and the value was determined from a fitted function.

But the literature value of $93.1 \pm 1.5 \text{ J/mol}$ still is much higher, maybe because of a much longer measurement time.

3.3 Entropy

The entropy can be calculated through the definition of thermal energy $\delta Q = T dS$. So we get for the entropy based on the temperature curve for a Curie temperature of $T_C = 90 \text{ K}$:

$$\Delta S = 0.2496 \frac{\text{J}}{\text{mol K}}$$

And for the entropy based on the specific heat curve:

$$\Delta S = 0.3739 \frac{\text{J}}{\text{mol K}}$$

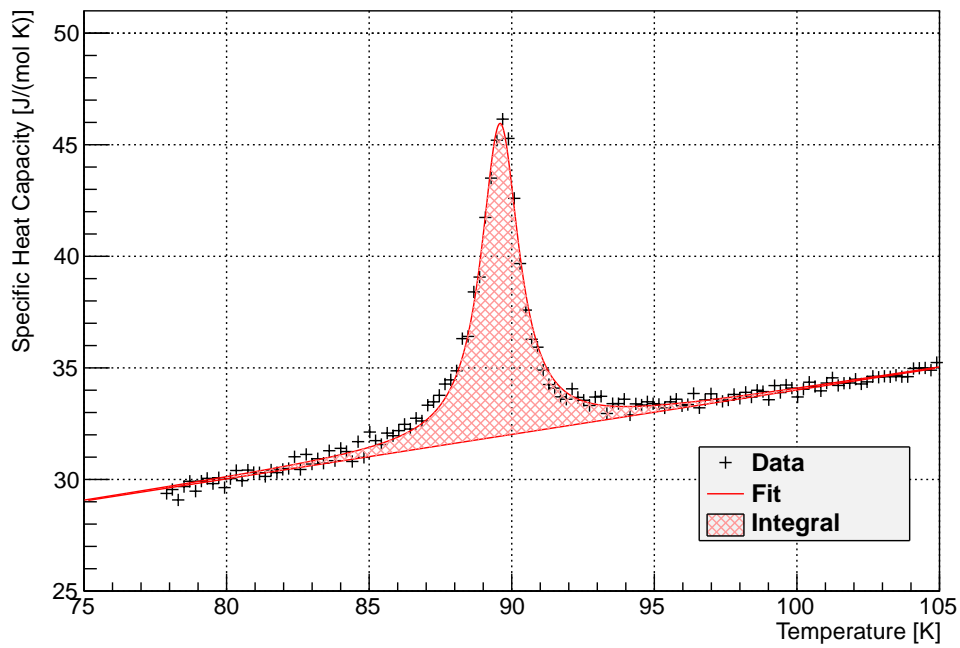


Figure 4: Specific heat of dysprosium over temperature, first peak in detail.

Fit parameters: $y(x) = m \cdot x + c + \frac{s}{2\pi} \cdot \frac{\Gamma}{(x-\mu)^2 + \frac{1}{4}\Gamma^2}$ with

$$m = (0.1991 \pm 0.0035) \frac{\text{J}}{\text{mol K}^2}$$

$$c = (14.10 \pm 0.33) \frac{\text{J}}{\text{mol K}}$$

$$s = (35.46 \pm 0.56) \frac{\text{J}}{\text{mol}}$$

$$\Gamma = (1.610 \pm 0.033) \text{ K}$$

$$\mu = (89.59 \pm 0.02) \text{ K}$$

For comparison with the spin entropy, the total angular momentum L and the total spin S had to be calculated. Dysprosium has an electron configuration of $[\text{Xe}]4f^{10}6s^2$. Therefore the angular momentum of the 7 electrons in the first half of the 4f-shell sum up to zero. So the momentum of the remaining 3 electrons sums up to $L = 3 + 2 + 1 = 6$. Additionally, these 3 remaining electrons compensate the spin of 3 electrons in the first half of this shell, which results in a total spin defined by the remaining 4 electrons of $S = 4 \cdot \frac{1}{2} = 2$. So the total momentum of the dysprosium sample is $J = L + S = 6 + 2 = 8$. Therewith the spin entropy can be calculated to

$$S = R \ln(2J + 1) = 8.314 \frac{\text{J}}{\text{molK}} \cdot \ln(17) = 23.55 \frac{\text{J}}{\text{molK}}$$

This entropy is the entropy the system receives when it transfers from the helical antiferromagnetic state to the unmagnetic isotropic state. During this phase transition, it is obvious that much more entropy gets into the system than during the phase transition from the ferromagnetic state to the antiferromagnetic state at Curie temperature which was calculated before. So actually, there is not a big difference between the entropy of the magnetic states, but between the isotropic and the magnetic states.

4 Critical Exponent and Neél temperature

For the determination of the critical exponent α and the Neél temperature T_N , a function

$$C(T) = \frac{A^\pm}{\alpha} \left| \frac{T - T_N}{T_N} \right|^{-\alpha} + E \cdot \frac{T - T_N}{T_N} + B \quad (4.1)$$

described by scale laws has been fitted to the data values of the right phase transition, as seen in Figure 5 on the facing page. In this function, A^+ is for $T > T_N$ and A^- for $T < T_N$ and the given parameters $E = 25 \frac{\text{J}}{\text{molK}}$ and $B = 16 \frac{\text{J}}{\text{molK}}$ are fixed. Resulting from the fit we get a value for the critical exponent of

$$\alpha = 0.138 \pm 0.002$$

and for the Neél temperature we get

$$T_N = (180.097 \pm 0.002) \text{ K}$$

Compared to the literature values of $\alpha = 0.14 \pm 0.05$ and of $T_N = (179.90 \pm 0.18) \text{ K}$, our results are quite good. Maybe they could be improved by a longer measurement time. As can be seen in our results, the scale law matches quite well to the measured values. Before reaching the critical temperature T_N , the curve follows the exponential regime which can be got by using Landau-theory of phase-transitions. Then, at the critical temperature, there is a jump of the free energy which results also in a discontinuity of the specific heat as its proportional to the second derivation of the free energy after the temperature. After this transition, the material shows a linear, but almost constant behaviour of the specific heat. In this quite high-temperature regime where the material is isotropic. The specific heat should be just before reaching its constant value along with Einstein's model.

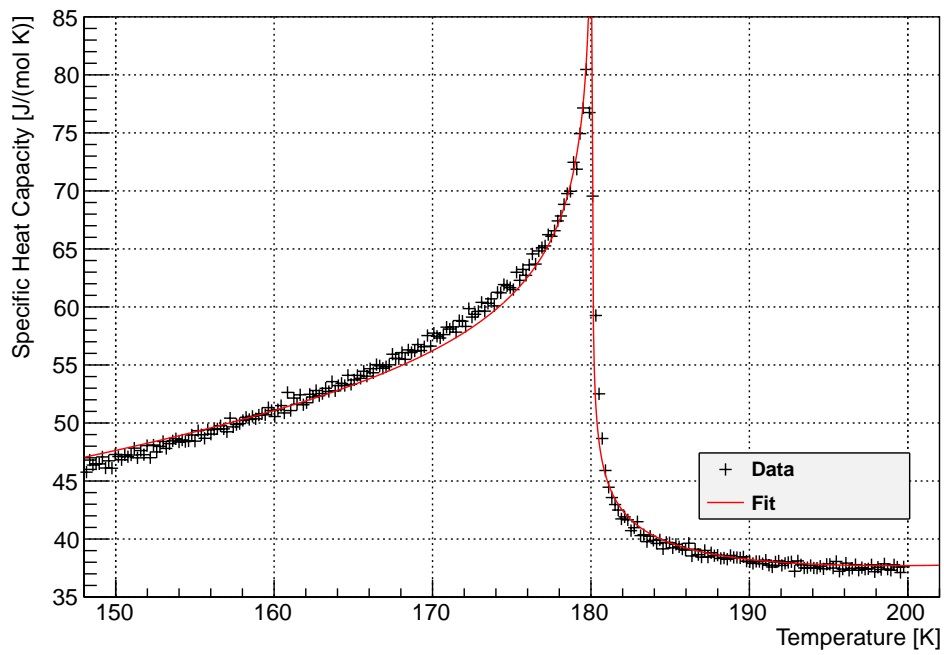


Figure 5: Specific heat of dysprosium over temperature, first peak in detail.

Fit parameters to Equation (4.1) on the preceding page:

$$A^+ = (1.93 \pm 0.02) \frac{\text{J}}{\text{mol K}}$$

$$A^- = (3.86 \pm 0.03) \frac{\text{J}}{\text{mol K}}$$

$$\alpha = 0.138 \pm 0.002$$

$$T_N = (180.097 \pm 0.002) \text{ K}$$