Physikalisches Fortgeschrittenenpraktikum

Spezifische Wärme

– Auswertung –

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1 latent heat of dysprosium at 1st order phase transition

After measuring the temperature around the first phase transition (around 88 K) as well as the specific heat from 77 K up to 200 K, we now want to determine the latent heat of the analysed dysprosium.

1.1 latent heat from temperature course

Let's first have a look at the overall temperature course we measured in the first place (see figure 1). Here we see that the temperature of the cup does not show the expected linear course, which is why we will not use this data. Instead, we will only use the temperature curve of the sample, where we can distinguish the phase transition somewhere around 88 K, where the curve flattens for a while before steepening up again to the former slope.

We fitted two straights to this data, one before and one after the phase transition range:

$$g_1(t) = at + b \qquad g_2(t) = ct + d \tag{1}$$

This yielded figure (2) and the following results:

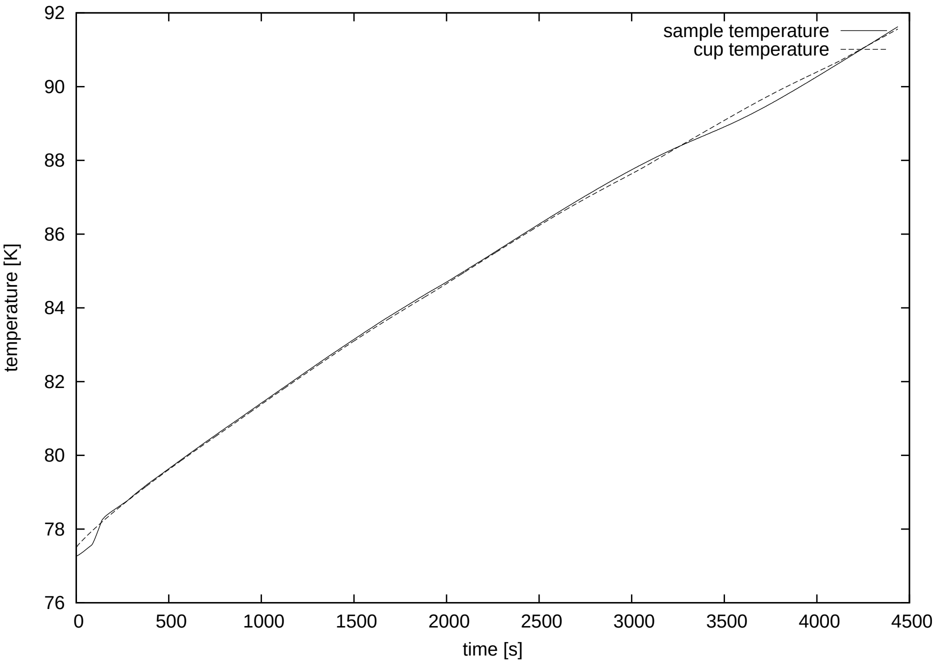

Figure 1: temperature course of dysprosium

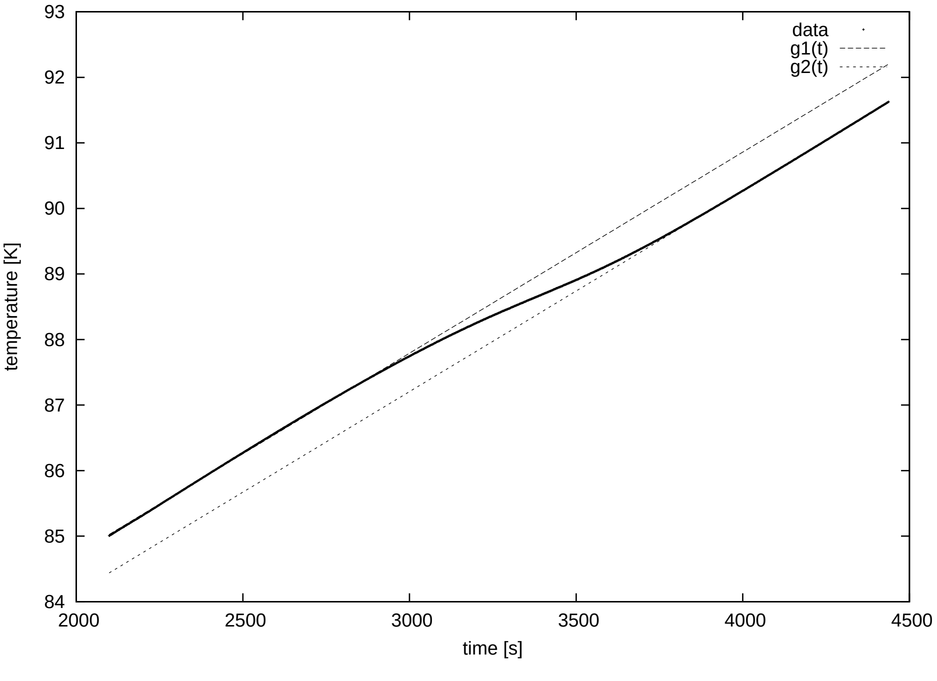

Figure 2: temperature course of dysprosium around the first phase transition with linear fits before and after the transition area

$$a = 0,0030686 \pm 2,762 \cdot 10^{-6} \qquad b = 78,5852 \pm 0,00709$$
$$c = 0,0030693 \pm 1,614 \cdot 10^{-6} \qquad d = 77,9975 \pm 0,006655$$

As we can see, the slopes of g_1 and g_2 are almost exactly the same.

To determine the latent heat, we first need to know the duration of the phase transition, which we get by subtracting the roots of the two straights. To minimize errors resulting from the different slopes, we did not choose the root but the time at which both functions reach 88 K, obtaining

$$\Delta t = \frac{88-d}{c} - \frac{88-b}{a} = 190,81\text{ s} . \tag{2}$$

The standard deviations of our fitting parameters a to d will propagate with this calculation; thus we will apply Gauss' law of error propagation, obtaining the standard deviation of Δt:

$$\Delta t = (190,81 \pm 4,54)\text{s} = 190,81\text{ s} \pm 2,38\% \tag{3}$$

Knowing the constant heat power P and the molar mass n of our sample, we can easily calculate the latent heat

$$Q_L = \frac{P \cdot \Delta t}{n} , \tag{4}$$

where $P = (5,648 \pm 0,02) \cdot 10^{-3}\text{W}$ and $n = 0,056$ mol.

For the systematic error, we assume $\Delta P = 0,02 \cdot 10^{-3}\text{W} = 0,35\%$ for the heating power P, while we neglect the error of the molar mass. Thus, the percental error of Q_L equals the percental error of P.

This leads us to our first result for the latent heat of the first phase transition of dysprosium:

$$\mathbf{Q_L} = (\mathbf{19,24 \pm 0,0681})\text{J/mol} = \mathbf{19,24}\text{J/mol} \pm \mathbf{0,35}\% \tag{5}$$

1.2 latent heat from specific heat

Next, we want to determine the latent heat a second time, now from the course of the specific heat we measured in a second run, obtaining figure (3). We can clearly see the peak around 88 K, marking the phase transition we're interested in. With the definition of specific heat

$$c = \frac{\partial Q}{\partial T} \tag{6}$$

we see that the area under the peak is the very latent heat we are searching for. In an ideal case, this peak is a delta function $\delta(T_C)$ which is blurred due to relatively fast heating of the sample.

We fit the following function to the peak:

$$c(T) = aT + b + \frac{cd}{d^2 + (T-e)^2} \tag{7}$$

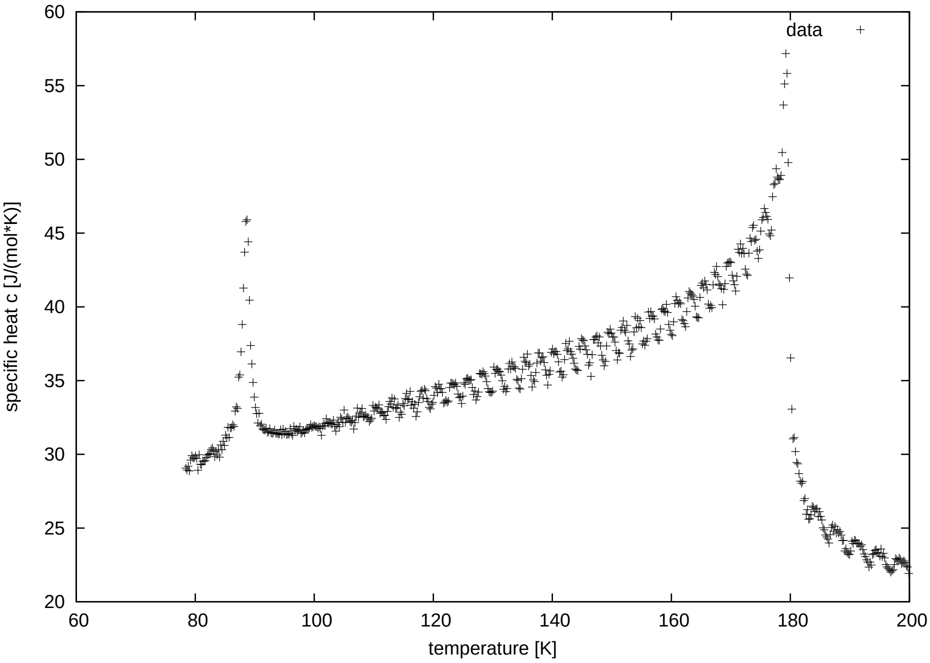

Figure 3: course of specific heat of dysprosium with two phase transition peaks

where $aT + b$ represents the linear part of the curve the peak "sits on". For the peak itself, we expect a divergent behaviour of the specific heat around the Curié temperature, which is why we use a rational function here. Furthermore, the ideal behaviour is only valid in the limit of $d \to 0$, where the function behaves like a delta function. By using a non-vanishing d, we can describe the sharpness of the peak. We obtain the following results (figure 4):

$$\begin{aligned} a &= 0,1095 \pm 0,00176 = 0,1095 \pm 1,61\% \\ b &= 20,791 \pm 0,2014 = 20,791 \pm 0,97\% \\ c &= 11,329 \pm 0,244 = 11,329 \pm 2,16\% \\ d &= 0,72542 \pm 0,0202 = 0,72542 \pm 2,78\% \\ e &= 88,571 \pm 0,0129 = 88,571 \pm 0,0146\% \end{aligned}$$

The last fit parameter e also corresponds to the Curié temperature T_C.

To calculate the latent heat Q_L, we cut off the linear part of the function and integrate only over the peak itself. As integration limits we choose 78 K and 100 K, where the function is almost linear again. We obtain

$$Q_L = \int_{78\,\mathrm{K}}^{100\,\mathrm{K}} dT \frac{cd}{d^2 + (T-e)^2} = c \cdot \arctan\left(\frac{2T-2e}{2d}\right)\Bigg|_{78\,\mathrm{K}}^{100\,\mathrm{K}} \approx 33,65\ \mathrm{J/mol}\ . \qquad (8)$$

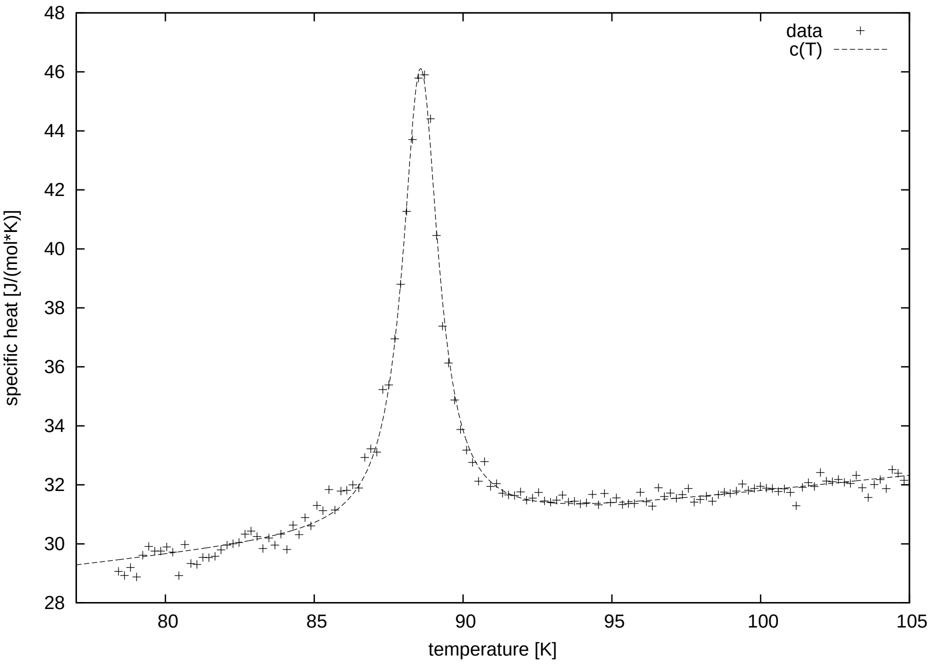

Figure 4: function fitted to phase transition peak of first order

To calculate the error of Q_L, we again have to apply Gauss' law of error propagation, this time to our arctan-function, obtaining our second result for the latent heat:

$$\mathbf{Q_L} = (\mathbf{33,65 \pm 0,219})\,\mathrm{J/mol} = \mathbf{33,65}\,\mathrm{J/mol} \pm \mathbf{2,19}\% \tag{9}$$

1.3 entropy of the phase transition

To calculate the entropy of the analyzed phase transition, we have a look at how entropy is defined:

$$dS = \frac{\delta Q}{T} \tag{10}$$

With δQ being the applied heat and T being the absolute temperature. In our case, we can substitue δQ by the latent heat Q_L, while T equals the Curié temperature where the phase transition happens, in our case $T_C = 88,57\,\mathrm{K}$. Thus, we get

$$\Delta S = \frac{Q_L}{T_C} \qquad \sigma_{\Delta S} = \sqrt{\sigma_{Q_L}^2 \cdot \left(\frac{1}{T_C}\right)^2 + \sigma_{T_C}^2 \cdot \left(-\frac{Q_L}{T_C^2}\right)^2} \tag{11}$$

and

$$\Delta S_T = 0,217 \pm 0,00077\,\mathrm{J/molK} \qquad \Delta S_c = 0,38 + 0,0025\,\mathrm{J/molK}\ , \tag{12}$$

where ΔS_T is the entropy based on the latent heat $Q_L = 19,24\,\mathrm{J}$ derived from the temperature course, while ΔS_c is the entropy based on the latent heat $Q_L = 33,65\,\mathrm{J}$ derived from the course of the specific heat.

In comparison we calculate the spin entropy

$$S = R\,\ln(2J+1)\ , \tag{13}$$

where $R = k_B \cdot N_A$ is the gas constant. The total electronic angular momentum $J = L + S$ equals 8 for our case: Dysprosium has the electronic configuration $[Xe]4f^{10}6s^2$, from which the 10 4f-electrons are responsible for the magnetic characteristics. According to Hund's rules, seven of those will have "spin up", while their angular momenta sum up to zero. The other three will have "spin down", yielding an angular momentum of $L = 3+2+1$ and a total spin of $S = 7/2 - 3/2 = 2$. Thus we obtain $J = 8$ and can calculate the spin entropy:

$$S = R\,\ln(17) \approx 23{,}557\,\mathrm{J/molK} \tag{14}$$

The huge difference between our calculated entropy and the spin entropy can be explained quite easily: The spin entropy describes the transition from an ordered state to a totally disordered state, while we calculated the entropy of the transition from ferromagnetism to the slightly more disordered antiferromagnetism. While there obviously is an increment of entropy, the antiferromagnetic state is not completely disordered and thus the transition cannot be described with spin entropy.

1.4 discussion of results

Summarizing, we have two results for the latent heat of dysprosium at the first phase transition:

- Out of the temperature course: $Q_L = 19{,}24\,\mathrm{J/mol}$
- Out of the specific heat course: $Q_L = 33{,}65\,\mathrm{J/mol}$

To us the first measurement seemed not so accurate, for the interval where the phase transition took place was hard to define precisely, which is why we rate the second result higher.

In addition we want to compare our results with those of K. D. Jayasuriya, whose measurements were far more detailed and precise compared to what we were able to do, yielding the following latent heat:

$$\begin{aligned} Q_L &= 39{,}1\,\mathrm{J/mol} \qquad \text{(single crystal)} \\ Q_L &= 35\,\mathrm{J/mol} \qquad \text{(polycristalline sample)} \end{aligned}$$

Here we see that our second result matches the literatic values quite well, boosting our assumption that our first measurement was not too accurate. Assuming that our second measurement was accurate, we can also take the guess that our dysprosium sample was a polycristalline one.

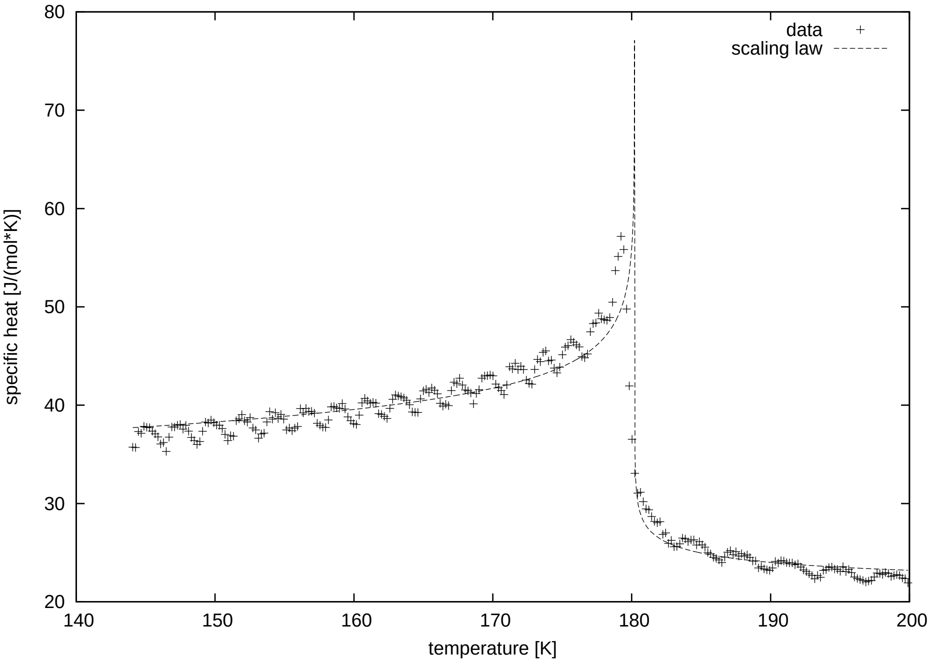

Figure 5: scaling law applied to our specific heat data

2 2nd order phase transition at Néel temperature

2.1 Critical exponent and Néel temperature

The behaviour of the specific heat around the Néel temperature can be described by a scaling law of the form

$$C(t) = \frac{A^{\pm}}{\alpha}\,|t|^{-\alpha} + Et + B \tag{15}$$

where $t = \frac{T-T_N}{T_N}$ is called the *reduced temperature*. As $E = 2{,}63\frac{\mathrm{J}}{\mathrm{molK}}$ and $B = 8{,}716\frac{\mathrm{J}}{\mathrm{molK}}$ are given for $|t| < 0{,}2$, we use data in that region to fit the scaling law curve (assuming $T_N \approx 180\mathrm{K}$, this yields a range from 144K to 216K). Figure 5 shows the resulting curve.

The fit parameters result in the following values:

$$\begin{aligned}
A^- &= (2{,}33909 \pm 0{,}06947)\,\mathrm{J/molK} = 2{,}33909\mathrm{J/molK} \pm 2{,}97\% \\
A^+ &= (1{,}06447 \pm 0{,}03196)\,\mathrm{J/molK} = 1{,}06447\mathrm{J/molK} \pm 3{,}002\% \\
\alpha &= (\mathbf{0{,}0918011 \pm 0{,}003636}) = \mathbf{0{,}0918011 \pm 3{,}96}\% \\
\mathbf{T_N} &= (\mathbf{180{,}214 \pm 0{,}01666})\,\mathrm{K} = \mathbf{180{,}214}\mathrm{K} \pm \mathbf{0{,}009246}\%
\end{aligned}$$

2.2 Discussion

K. D. Jayasuriya et al. have found $T_N = (179{,}90 \pm 0{,}18)\,\mathrm{K}$ and $\alpha = 0{,}14 \pm 0{,}05$ (for a polycristalline sample). We notice the far greater errors of the literatic values which denotes that there is at least one remarkable systematic error source we did not cover.

Unfortunately, the measurement already ended at 200K. However, the course beyond the Néel temperature seems to continue with a negative slope. We'd expect it to become positive again in the non-critical region.

Also, the peak of the fitted curve does not match the measured data. We assume this is because otherwise the regions before and after the Néel temperature would not match our data as good as it does. The fitting algorithm had to find a tradeoff. Concluding, the actual Néel temperature might as well be a bit lower than our result $T_N = (180{,}21 \pm 0{,}01)\,\mathrm{K}$.

3 Course of specific heat curve

The general course of $C(T)$ (see figure 1) shows two phase transitions at roughly 88,5K and 180K which show up as peaks in the specific heat. This means that energy fed to the system is not (only) used for increasing temperature, but instead to accomplish a (magnetic) phase transition.

Ideally, we would see sharp peaks in specific heat, but due to a relatively high warming rate and due to the fact that different parts of the sample might have different temperatures we observe finite values over a broader temperature region.

Since the first transition is one of first order, after Curié temperature the the specific heat goes down to the same value as before. On the other hand however, it shows a discontinuity at Néel temperature which indicates that the second transition is of second order.

Another thing to note is that in non-critical regions, the specific heat is slightly oscillating. We assume this is mainly because of non-vanishing thermal conduction between the sample and the cup. The *LABVIEW* program tries to keep the two values synchronized, but it overdrives a bit as the reaction of sample or cup in response to heating is quite slow.