Specific Heat

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1 Basics

1.1 The specific heat capacity of a solid state body

According to the first theorem of thermodynamics the change of the internal energy dU in a closed system is obtained by

$$dU = \delta Q + \delta W,$$
$$dU = TdS - pdV,$$

in which the following quantities occur:

- δQ: The heat, which is feed into or removed from the system and which can be expressed by the change of the entropy dS and temperature T of the system.

- δW: The work, which is done by the system and wich can be described by the change of volume dV and the pressure p in the system.

The quantities p, S, T and V are state variables of the system at this juncture.
Based on the first theorem of thermodynamics it is now possible to define the so-called heat capacity universally

$$C_X = \left(\frac{\partial Q}{\partial T}\right)_X$$

which is a measure for the change of heat due to the change of temperature.
Since state variables like the pressure p or volumen V are changed during a temperature change normally heat capacities are used in which one of these state variables is fixed. This is revealed by the index X. Thus it follows

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$
$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

Furthermore the so-called specific heat capacity c_X is introduced by obtaining the predefined heat capacity C_X considering the amount of substance n of the given substance and applying it to one mole:

$$c_x = \frac{C_X}{n} = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_X$$
$$\Rightarrow c_p = \frac{C_p}{n} = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_p$$
$$\Rightarrow c_V = \frac{C_V}{n} = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_V$$

The specific heat capacities c_p and c_V are connected with each other by the relation

$$R = c_V - c_p,$$

at which R is the universal gas constant.

In solid state bodies the difference between both heat capacities c_p and c_V is small hence the discrepency will be neglected in the future.

At last assuming that the Volumen is constant and therefore $dV = 0$ the specific heat can be described according to the internal energy U or rather the free energy $F = U - TS$ as:

$$c = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)$$

$$c = \frac{1}{n}\frac{dU}{dT}$$

$$c = -\frac{1}{n}T\left(\frac{d^2 F}{dT^2}\right)$$

1.2 The Debye-Model

For the debye-model it is assumed that the internal energy U and hence the heat capacity C of a cristall is mostly defined by the phonon oscillations and that for the energy of the phonon oscillations the assumption of N_A indepent harmonic oscillators is approximately correct, so that the interal energy U is given by:

$$U = \sum_{i=1}^{3N_A} \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1}$$

In cristals of macroscopic length the amount N_A is so large that the discrete oscillation values ω_i lay so close to each other that the sum can be approximately described by an integral

$$U = \int_0^{\omega_{max}} \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1} D(\omega)d\omega,$$

wherefore introducing the state density $D(\omega)$.

The state density $D(\omega)$ specifies the amount of frequencies ω laying in an intervall $[\omega, \omega + d\omega]$. To determine the state density $D(\omega)$ Debye assumed that in an isotropic continuum the dispersion of low frequencies is also valid for high frequencies. This in turns means that the dispersion is given by the the linear dispersion relation $\omega = c \cdot k$.

Using the condition that the total number of frequencies should not exceed $3 N_A$ in a three-dimensional cristal the maximum frequency ω_D can be obtained by the integral

$$\int_0^{\omega_D} D(\omega)d\omega = 3 N_A \quad .$$

The state density $D(\omega)$ is as follows

$$D(\omega) = \frac{9N_A}{\omega_D^3}\, \omega^2$$

$$\text{with} \qquad \omega_D = \sqrt{\frac{6\pi^2 N_A}{V}} \cdot v^3$$

in which v is the sonic speed. From the relation above it is clear that the state density rises quadratically with the frequency ω.

For this reason the internal energy U is given by

$$U = 9N_A \int_0^{\omega_D} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \frac{\omega^2}{\omega_D^3} d\omega$$

and the specific heat capacity c is given by

$$c = 9N_A k_B \int_0^{\omega_D} \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} \frac{\omega^2}{\omega_D^3} d\omega \quad .$$

Introducing the Debye temperature $\Theta_D = \frac{\hbar\omega_D}{k_B}$ and the parameter $x = \frac{\hbar\omega}{k_B T}$ the expression above can be written as:

$$c = 9N_A k_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

This integral is in general only numerical solvable, but it is possible to give exact results for some special cases:

In the case of a single atomic solid state body and high temperatures which means $T \gg \Theta_D$ the specific heat c is nearly constant and obeys the Dulong-Petit law:

$$c \approx 3N_A k_B$$

$$c \approx 25 \frac{J}{mol \cdot K}$$

In the case of a single atomic solid state body and low temperatures which means $T \ll \Theta_D$ the specific heat c is

$$c \approx 9N_A k_B \frac{4\pi^4}{15} \left(\frac{T}{\Theta_D}\right)^3 \quad ,$$

which means that the specific heat c is nearly proportional to T^3.

1.3 Phase transition

The analysed probe „Dysprosium" shows two critical temperatures.

Curie Temperature

First the *Curie temperature* $T_C = 85\text{K}$. Below this temperature Dysprosium is a ferromagnetic material which means that the magnetic domains are aligned and point into the same direction. Above the Curie temperature the material shows an antiferromagnetic behaviour. At the critical temperature T_C a phase transition takes place in the probe. It's an first order phase transition which means, that the derivation of the free energy F is not steady. Therfore the specific heat capacity has a divergence at T_C.

$$c = -\frac{1}{n} T \left(\frac{d^2 F}{dT^2} \right) \tag{1}$$

Energy feed into the material doesn't change the temperature of the material at this point.

Latent heat

Latent heat can be described as the amount of heat which can be feed into a body during a phase transition without a change of the body temperature.
The heat energy is used during the phase transition to change the inner structure of the body. For example, during the phase transition the magnetic properties of Dysprosium are changed by turning the spins of the electrons so that after the transition a new spin configuration with intrinsic higher energy exists. In the experiment we're going to measure the *latent heat*.

Neel temperature

A second phase transition is located, at the *Neel temperature* $T_N = 180\text{K}$. Above the Neel temperature Dyspoisum a paramagnetic behavior of the probe is observed.

This phase transition is an second order transition, which means that the heat capacity is discontinous at these critical temperatures. In the real experiment one can observe a heat capacity of the form:

$$C = \frac{A^\pm}{\alpha} |t|^{-\alpha} + Et + B \tag{2}$$

$$t = \frac{T - T_C}{T_C} \tag{3}$$

The factor $A^\pm$ is different below and above the critical temperature.

1.4 Magnetism

In these experiment two phase transition occur in which the magnetic properties of Dysprosium are changed.
Below the Curie-Temperature T_C Dysprosium is a ferromagnetic substance. Between the Curie-Temperature T_C and Neel-Temperature T_N Dysprosium has antiferromagnetic properties and over the Neel-Temperature T_N Dysprosium is a paramagnet.

1.4.1 Ferromagnetism

Due to exchange interaction ferromagnetic materials spontaneously divide into magnetic domains, the so-called Weiss domains. In a ferromagnetic material the spins in a domain are all parallel aligned and thus have a total magnetic moment.

But the total magnetic moment of the material is null when the material is in lowest energy configuration and unmagnetized because the spins of separate domains point in different directions and so their total magnetic moment cancels out.

When the material is totally magnetized the spins of all domains point in one direction and generate a large magnetic field with a lot of magnetostatic energy.

Even when the material is not fully magnetized the entropy of the ferromagnetic material is small because of the high structural order.

When the temperature increases this structural order becomes less likely and so causes the extinction of the ferromagnetic behavior above a specific temperature, the Curie-Temperature T_C.

1.4.2 Antiferromagnetism

In contrast to ferromagnetism the spins in the single domains are (nearly) anti-parallel aligned, so that no total outer magnetic field can be observed. Above a specific temperature, the Neel-Temperature T_N, the thermal energy is large enough to destroy the magnetic order and the material becomes paramagnetic.

1.4.3 Paramagnetism

Paramagnetic materials have no inner magnetic field unless an outer magnetic field exists. Under the influence of an outer magnetic field the spins in the paramagnetic material are so aligned that the material is magnetized and the outer magnetic field is extended by an temporary interior magnetic field. After the removal of the outer magnetic field the material becomes unmagnetized again.

1.4.4 Diamagnetism

Diamagnetic materials have no inner magnetic field unless an outer magnetic field exists. Under the influence of an outer magnetic field the spins in the diamagnetic material are so aligned that the material is magnetized and the outer magnetic field is extruded by an inverse-aligned temporary interior magnetic field. After the removal of the outer magnetic field the material becomes unmagnetized again.

2 Experiments

2.1 Scope of work

In this laboratory experiment the specific heat of Dysprosium at low temperatures shall be examined. The two phase transitions at the Curie-Temperature $T_C = 85\ K$ as well as the Neel-Temperatur $T_N = 180\ K$ are of special interest in this connection.
After the cooling-down of the cryostat the latent heat shall be determined in the first part of the experiment. In the next step the specific heat capacity shall be measured in the same temperature range. At last the specific heat shall be measured in the whole temperature range until the cryostat reaches ambient temperature.

2.2 Cooling-down of the sample

In a first step the sample and sample cup have to cooled below the Curie-Temperatur $T_C \approx 86\ K$ by using liquid nitrogen. For this reason the cryostat was evacuated with a sliding vane rotory pump so that the pressure p was below $p < 1\ mbar$. Next a small amount of helium gas was added so that the measured pressure was raised to $p \approx 25\ mbar$. According to the calibration of the pressure sensor for nitrogen the pressure of the helium gas in the cryostat corresponds to $p \approx 10\ mbar$. Due to improve the heat exchange the helium was added and the sample cup was put on the copper plate. After that step liquid nitrogen was added and the decrease of the temperature in the sample T_S and in the sample cup T_{SC} was monitored with a LabView-program.
When the sample reached a temperature $T_S \approx 77.5\ K$ the sample cup was raised from the copper plate and the helium was removed by using the sliding vane rotory pump.

2.3 Measurement of the latent heat

In this measurement the temperature of the sample T_S and the sample cup T_{SC} which was at first T_S, $T_{SC} \approx 77.5\ K$ was raised by using two heaters to determine the latent heat of the first phase transition at the Curie-Temperature T_C. The heat power of the sample heater was so adjusted that the sample and sample cup nearly had the same temperature while increasing their temperature. When the sample reached a temperature $T_S = 85\ K$ the adjusting process of the sample heater was stopped and the heating power of the sample remained constant at $P_S = (6.712 pm 0.1) \cdot 10^{-3}\ W$. The error was estimated out of the observed fluctuations.
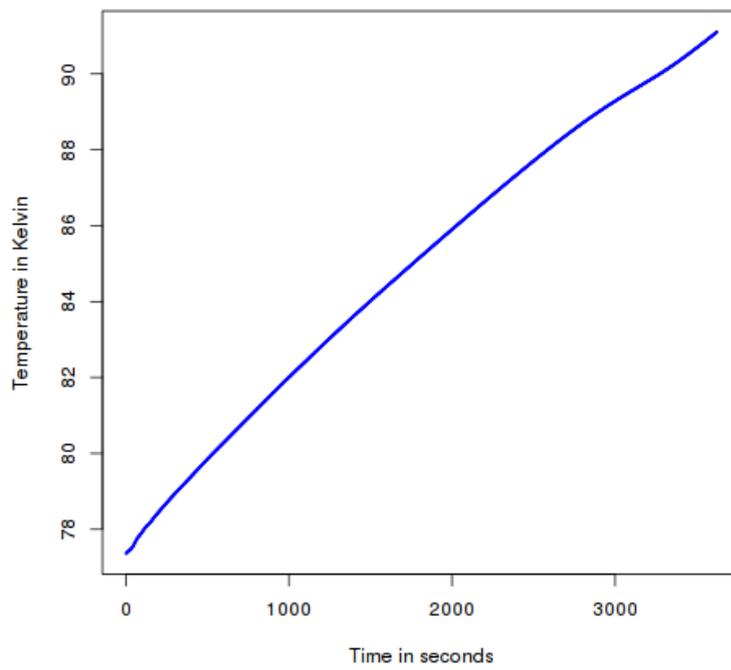The temperature curves for the sample and the sample cup are shown in figure 1.

Abbildung 1: Plot of entire mesured data - probe temperature over time

At a sample temperature $T_{S,1} = 87.6$ K the slope of the sample curve differed from the sample cup curve. This was a sign that the phase transition first order with the latent heat occured. In fact we would expect a sample curve with no slope but due to the low measurement time, high heating power and inhomogenous sample the phase transition occurs not in the full sample at the same resulting in a small slope of the temperature curve. At a sample temperature $T_{S,2} = 90.9$K the slope of the sample curve reached the same slope as the sample cup again. The phase transition has ended.

The temperatures $T_{S,1}$ and $T_{S,1}$ and were determined by fitting two straight lines to the sample curve in an interval $85 - 87$K below and $90.5 - 91$K above the phase transition. To the above fit we applied the constraint that the gradient above and below the phase transition are equal. The intersection points with a third fitted straight line between $87 - 90.5$K determine these temperatures as shown in figure 2.
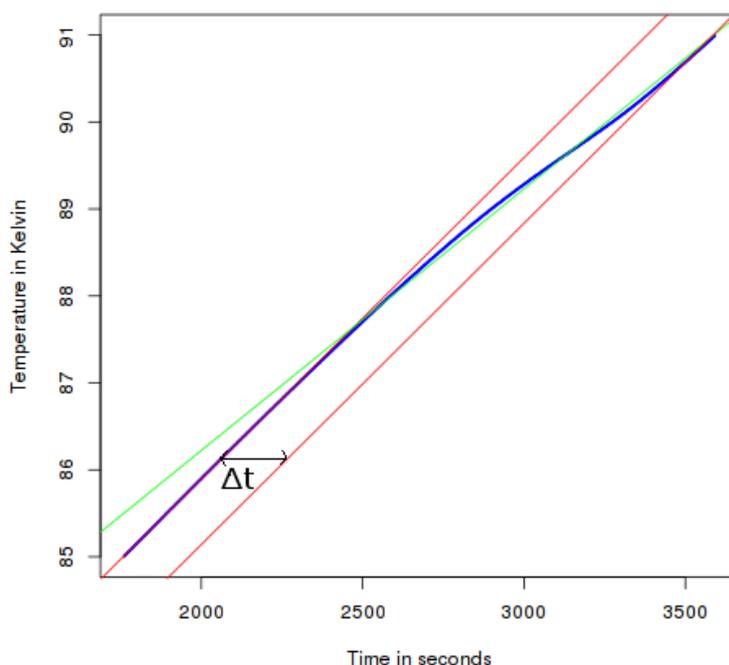

Abbildung 2: Three straight lines fitted in the intervalls **b**elow $85 - 87$K, **m**iddle $87 - 90.5$K and **a**bove $90.5 - 91$K.
$$b(t) = \left((78.51 \pm 0.0025) + (0.0037 \pm 1.2 \cdot 10^{-6}) \cdot t\right) \text{K}$$
$$m(t) = \left((80.21 \pm 0.02) + (3 \cdot 10^{-3} 6.9 \cdot 10^{-6}) \cdot t\right) \text{K}$$
$$a(t) = \left((77.75 \pm 0.0018) + (0.0037 \pm 1.2 \cdot 10^{-6}) \cdot t\right) \text{K}$$

By using the heat power of the sample heater P_S and the time difference between the two fits below and above the critical temperature $\Delta t = 204.6 \pm 0.8$ and the sample substance amount

$n = 0.0560 \, mole$ the latent heat Q_L was calculated:

$$Q_{L1} = \frac{P_S \cdot \Delta t}{n}$$

$$Q_{L1} = (24.5 \pm 0.4)\frac{\text{J}}{\text{mole}}$$

The error of the latent heat was calculated out of the standard errors of the fits. This error doesn't include systematic errors! Later the latent heat is calculated again with an independent method, the difference between this result and the below one, is a better estimation of the error. The curie temperature can be estimated as the mean of the two intersection points:

$$T_{C1} = (89.3 \pm 0.35)\text{K}$$

2.4 Measurement of the specific heat capacity

Before the start of this measurement the cryostat was cooled-down as written in section 2.2 again.

In this measurement the phase transition first order at Curie-Temperature T_C and the phase transition second order at Neel-Temperature T_N should examined by calculating the specific heat capacity for these transitions.

The measurement was started by starting the LabView-program for the specific heat. The program automatically adjusts the heating power of the sample cup so that the temperature of the sample cup T_{SC} nearly equals the temperature of the sample T_S while raising the temperature from approximately 78 Kelvin to ambient temperature.

Furthermore the program determines for every measurement step the temperature increase of the sample ΔT and the amount of heat Q_S which was feed into the sample. Due to the long required measurement time the measurement was conducted overnight and the measurement data was taken the next day.

The specific heat capacity at constant volume c_V is calculated by using the heat energy feeded in the sample Q_S, the substance amount of the sample n and the temperature increase ΔT:

$$c_V = \frac{1}{n}\frac{Q_S}{\Delta T}$$

As written in the basics we measured not the specific heat capacity at constant volume but at constant pressure however the discrepancy is negligible. The entire data is shown in figure 3.
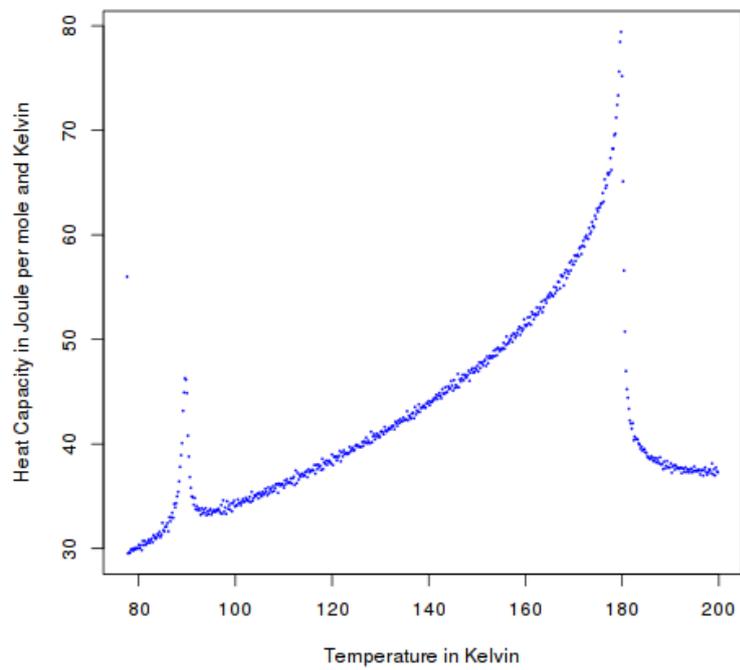
Abbildung 3: Plot of entire mesured data - heat capacity over probe temperature

As suspected there are two phase transitions identifiable by the two peaks in the heat capacity spectrum.

2.4.1 Latent heat out of the heat capacity measurement

The first one is the already observed phase transition at the curie temperature T_C. The position of the first peak can be used to estimate T_C:

$$T_{C2} = (89.6 \pm 0.2)\,\text{K}$$

The error was estimated out of the step size of the measurement, which was roughly 0.2K. Together with our above result we can caculate the mean T_C oberserved in the experiment:

$$T_C = 89.45 \pm 0.2\text{K}$$

This value doesn't match with the value calculated by Jayasuriya $T_C = (91.33 \pm 0.08)$K. In our result we only considered statistic errors, because the systematic errors of the thermometers, heating unit, etc... are unkown. The deviation from the result of Jayasuriya can be explained by these unconsidered systematic errors.

The integral under the first peak is equal to the latent heat. To calculate this integral, we fitted an straight line under the curve an adjusted the peak by substracting this regular straight increase.
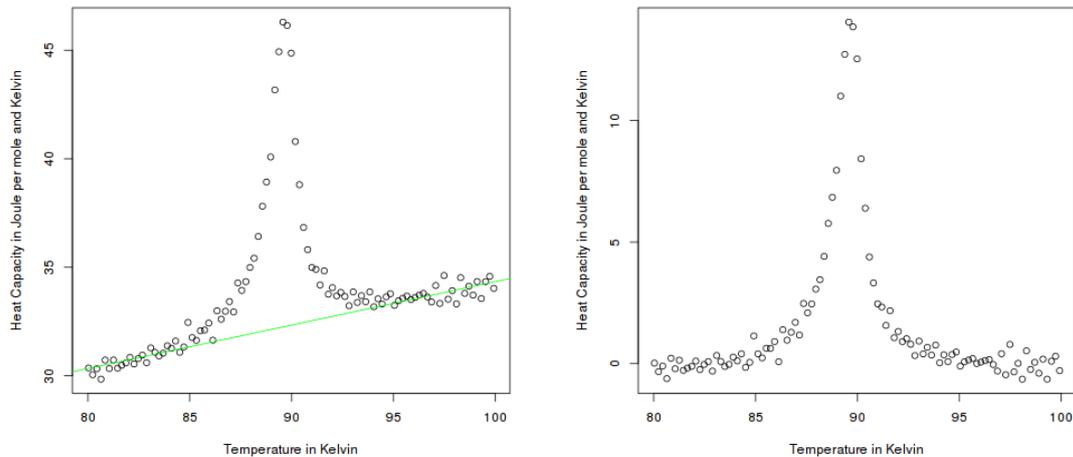
(a) With fitted straight line for regular increase

(b) Corrected by the regular increase – Integral under this curve is equal to the latent heat

Abbildung 4: Curie Peak – heat capacity over probe temperature

The integral under the corrected peak was calculated with an trapezium approximation:

$$Q_{L2} = 30.94 \frac{\text{J}}{\text{mole}}$$

There is no error available for this value. But with our above independent method for Q_L, we can roughly estimate the error with the difference of the two values. While our result for Q_L is the mean of the two observed values:

$$Q_L = (27.7 \pm 6.4)\frac{\text{J}}{\text{mole}}$$

This matchs with the value by Jayasuriya $T_C = (39.1 \pm 1.5)\frac{\text{J}}{\text{mole}}$ in an two sigma intervall. Jayasuriya obtained his result by 5 independent runs, so our result is not as bad as it seems to be.

2.4.2 Spin Entropy

According two the „Hundsche Regel" the 10 outer f-Elektrons of Dysposium first maximise their entire spins, than maximise the orbital momentum. Altogether we obtain an angular momentum of $J = 8$ of an dysposrium atom. The spin entropy can be calculated according to the „Vorbereitungsmappe" by:

$$S = R \cdot ln\,(2 \cdot J + 1) = 23.54\frac{\text{J}}{\text{moleK}} \qquad \text{with} \quad R = 8.31\frac{\text{J}}{\text{moleK}}$$

With the latent heat Q_L at the curie temperature T_C one can calulate the entropy increase at the first phase transition:

$$S_C = \frac{Q_L}{T_C} = (0.31 \pm 0.07)\frac{\text{J}}{\text{moleK}}$$

Hence we can infer that the first phase transition, is a transition between two states with a small entropy an therfore a high ordering. So the anti-ferromagnetic phase is only a little bit less ordered than the ferromagnetic state, compared to the whole spin entropy.

2.4.3 Neel temperature

The second phase transition from the antiferromagnetic phase into the paramagnetic phase takes place at the neel temperature T_N. As already described above, one can approximate the curve of the specific heat at the phase transition with an power law:

$$C = \frac{A^{\pm}}{\alpha}|t|^{-\alpha} + Et + B$$
$$t = \frac{T - T_N}{T_N}$$

The Neel temperature T_N can be obtained by the maximum of the heat capacity in the measurement:

$$T_N = (179.7 \pm 0.2)\text{K}$$

The error was estimated out of the step size of the measurement, which was roughly 0.2K. The value obtained by Jayasuriya is $T_N = 180.04\text{K}$ matchs in an two sigma intervall.
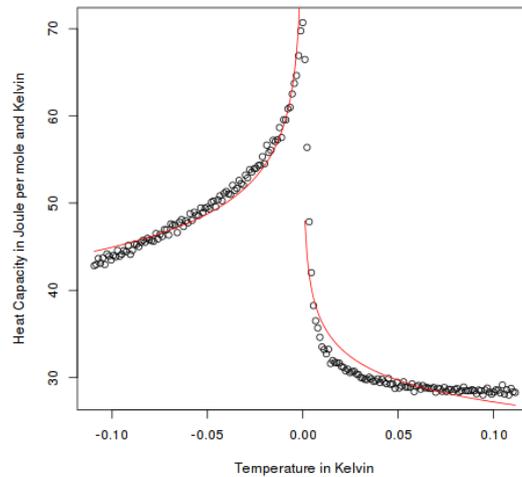
Abbildung 5: NeelPeak with fitted power law - heat capacity over critical temperature t

Left side	Right side
$\alpha = 0.117 \pm 0.0023$	$\alpha = 0.126 \pm 0.0065$
$A^- = 4.03 \pm 0.08$	$A^+ = 2.57 \pm 0.14$

The value obtained by Jayasuriya is $\alpha = 0.14 \pm 0.04$ matchs in an two sigma intervall, with the value of α on the right side of the neel temperature. We also see that the power law describes the curve well, because α on the left side, differs from the α on the right side by less than 8%.

2.4.4 Discussion of the specific heat curve

The entire specific heat curve is shown in figure 3. Besides the already discussed phase transitions at T_C and T_N we observe a linear increase in the heat capacity up to the neel temperature. At higher temperatures $T > T_N$ one can assume a constant heat capacity, according to the dulong-petit law. To test this assumption, we would need data beyond $T > 200$K. The above derived power law $c \sim T^3$ for low temperatures cannot be observed. Therfore we can infer that 77K is not smaller than the debye temperature T_D.

Literatur

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[Jayasuriya] K.D. Jayasuriya, S.J. Campbell und A.M. Stewart: Magnetic transitions in dysprosium: A specific-heat study, Physical Review B Volume 31 Number 9