

Specific heat

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Abstract

Phase transitions, for example transitions between energetically different magnetic configurations of a solid, cause discontinuities in the course of its specific heat due to the warmth energy pushing forward the transition instead of increasing the temperature of the specimen, as it is the case in first order transitions for example. Another behaviour occurs at transitions of second order, where the course of the specific heat diverges at the critical temperature.

This experiment consists of cooling down a specimen of Dysprosium and heating it up again while determining the electrically deposited amount of energy. In this element two phase transitions of different orders occur at both the Curie and the Neel temperature.

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1 Preparation

1.1 Thermodynamic fundamentals

1.1.1 Specific heat

Definition

The term “specific heat” denotes the linear response of the internal energy under changes in temperature. In order to properly define such an answer coefficient, either pressure p or volume V has to be held constant. Thus we define

$$c_p = \left. \frac{\partial U}{\partial T} \right|_p, \quad c_v = \left. \frac{\partial U}{\partial T} \right|_V.$$

The difference in c_p and c_v is

$$c_p - c_v = T \cdot \alpha^2 \cdot k,$$

where α is the coefficient of thermal expansion and k is the inverse of the isothermal compressibility. Generally one does not need to consider the difference in specific heats when dealing with a solid, therefore we will use $c_v = c_p = c$ from now on.

Phonons

Above temperatures of ~ 10 K the internal energy of a solid is mostly given by the energies of the phonons:

$$U = \sum_{i=1}^{3N} \hbar \omega_i \cdot n(\omega_i) = \int d\omega \nu(\omega) \hbar \omega \cdot n(\omega), \quad (1.1)$$

where $n(\omega)$ is the Bose Einstein statistic and $\nu(\omega)$ is the density of states. Using the Debye approximation $\omega = v \cdot k$ (v = velocity of sound, k = wave vector) $\forall k \in 1^{\text{st}}$ Brioullin Zone and the normalization condition $\int_0^{\omega_D} \nu(\omega) \stackrel{!}{=} 3N$ for the density of states, we find

$$\nu(\omega) = \frac{9N}{\omega_D^3} \omega^2, \quad (1.2)$$

where $\omega_D = v^3 \sqrt{\frac{6\pi^2 N}{V}}$ is the Debye frequency. Plugging (1.2) in (1.1) we find

$$U = 9N \int_0^{\omega_D} d\omega \frac{\hbar \omega^3}{\omega_D^3 (\exp(\frac{\hbar \omega}{k_B T}) - 1)},$$

which is equivalent to

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

If we define the Debye Temperature $\theta_D = \frac{\hbar \omega_D}{k_B}$ and the dimesionless parameter $x = \frac{\hbar \omega}{k_B T}$ we can write the above in the following way:

$$c = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \underbrace{\int_0^{\theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}}_{\text{can be evaluated numerically}}. \quad (1.3)$$

Now let us consider two limits:

a. $T \gg \theta_D$

For high temperatures (1.3) becomes the Dulong-Petit law of a constant specific heat regardless of the kind of solid:

$$c_{DP} = 3Nk_B \approx 25 \frac{\text{J}}{\text{mol} \cdot \text{K}} \Big|_{N=N_A}.$$

The physical interpretation of a constant specific heat is that at such high temperatures all phononic modes are excited. Therefore no new degrees of freedom are available with rising temperature, which, when combined with the equipartition principle, explains the constancy of specific heat.

b. $T \ll \theta_D$

At low temperatures the integral in (1.3) becomes approximately constant and has the numerical value of $\frac{4\pi^2}{15}$. This leads to a temperature dependency of

$$c = 9Nk_B \left(\frac{T}{\theta_D} \right)^3.$$

The specific heat rises strongly with temperature, as more and more phononic modes are excited and the equipartition principle dictates that the energy is distributed among more and more degrees of freedom.

Below $T = 10 \text{ K}$ the conductive electrons add another term to the specific heat which is linear in temperature.

1.1.2 Phase transitions

Thermodynamically, phase transitions occur, wherever a derivative of the free energy is discontinuous. Orders of phase transitions are defined to match the derivative that in which the discontinuity appears, so a phase transition of 1st order occurs when the first derivative of the free energy is discontinuous.

In nature, only first and second orders of phase transitions occur. Both can be examined and categorized by the behaviour of specific heat at the critical temperature. As specific heat is connected with derivatives of free energy by

$$c = -\frac{1}{T} \frac{\partial^2 G}{\partial T^2},$$

phase transitions show typical behaviours in temperature dependency of specific heat.

First order transitions carry a latent heat, an amount of energy that does not contribute to heating the specimen. Instead, it pushes onward the phase transition. Usually the specific heat differs on both sides of the transition point. Therefore a phase transition of first order can be identified by a discontinuity within a plot of specific heat over temperature. Another way to discern one is by finding a plateau in a heating curve, i.e. an amount of time in which the temperature of the specimen did not increase despite constant heating. Using the second method, the latent heat linked with the phase transition can be quantified.

In contrast to those of first order, second order transitions do not carry a latent heat. Specific heat diverges at the critical temperature. The divergence can be quantified approximately by

$$c = (A^\pm/\alpha)|t|^{-\alpha} + Et + B, \quad (1.4)$$

where α is the critical exponent and the coefficient $A^\pm$ is different for temperatures above and below the critical temperature T_C . In addition we introduced the “reduced temperature” $t = \frac{T-T_C}{T_C}$. Both, the critical exponent α and the critical temperature T_C can be determined by a double logarithmical plot of specific heat over temperature, after the noncritical behaviour $Et+B$ has been subtracted out.

1.1.3 Dysprosium

In this experiment we will examine Dysprosium, a lanthanoid. In pure form Dysprosium presents a hexagonal crystal structure. It exhibits two magnetic phase transitions: One from the paramagnetic high temperature phase to a helical antiferromagnetic phase, in which all magnetic moments of a crystallographic plane are aligned, but, in contrast to ferromagnetic structures, at a fixed angle to neighbouring planes. This phase transition occurs at the “Neel temperature” of $T_N \approx 180$ K. It is a phase transition of second order, i.e. a phase transition with a divergence in specific heat. The other magnetic phase transition is from the antiferromagnetic phase to a regular ferromagnetic phase at the Curie temperature of $T_C = 90$ K, being a first order transition. Therefore we expect a latent heat at the Curie temperature.

1.2 Experiment

In this experiment, we will record a heating curve of Dysprosium in order to examine its magnetic phase transitions at the Curie temperature $T_C = 90$ K and the Neel temperature $T_N = 180$ K. Experimental difficulties arise in measuring the temperature of the specimen whilst keeping it isolated from further heating by the environment.

1.2.1 Measurement

Cooling

To isolate the Dysprosium specimen from undesired environmental effects, it is suspended from three nylon cords within an evacuated screening jar. In order to cool the jar down to 77 K, boiling temperature of nitrogen, the cryostat is equipped with a copper floor, from which the jar can be lifted for controlled heating. Putting the jar down on the floor establishes the necessary thermal contact for cooling. Another possibility to establish thermal contact is to fill the surrounding dewar with a small amount of gas and reevacuating it afterwards.

Heating

In order to controlledly heat the specimen, the screening jar is provided with an electrical heater. Before heating, the jar is of course lifted from the copper floor. The energy used to heat can then be determined by a simple measurement of current and voltage of the heating circuit. We easily find the amount of energy used to heat by

$$\Delta Q = \sum_{i=1}^n U_i \cdot I_i \cdot (t_i - t_{i-1}) \quad (1.5)$$

using discrete points of time t_i where the measurements take place.

Measurement of specimen temperature

Specimen temperature is recorded by measuring the resistance of a thin platinum wire fixed on the specimen. Within the temperature range of this experiment, its resistance can well be assumed to be proportional to temperature.

1.2.2 Tasks

For most of our tasks a prepared LABVIEW program exists. We still have to define the parameters though.

Cooling down the cryostat

The first task is cooling down the cryostat. In order to do so, we evacuate it and refill it with an exchange gas, allowing easier dissipation of heat from inside the dewar. Temperature is controlled via a LABVIEW program. As soon as temperature inside has reached less than 80 K we are ready for the first measurements after we lifted the screening jar and pumped out exchange gases.

Measurement of latent heat

Since the phase transition from ferromagnetic to helically antiferromagnetic phases is exhibited at 90 K we reheat the specimen up to 87 K. This allows us to find proper heating rates for both the specimen and the jar, in order to keep them on the same temperature as they are heated. From 87 K on we heat with a constant low heating rate, where values of 2 mW have shown good results, in order to quantize latent heat at Dysprosium's Curie temperature.

Measurement of specific heat close to T_C

Again, we are to calibrate heating power and an idle time in order to find values that allow proper examination of specific heat around T_C . We measure specific heat precisely until a few Kelvin above the leap we expect at $T_C = 90$ K.

Measurement of specific heat up to room temperature

We recool our specimen below the phase transition and re-calibrate the measurement. Afterwards we leave it to the LABVIEW program to perform measurements up to 250 K.

1.2.3 Evaluation of the data

In the evaluation we will determine latent heat at Dysprosium's first order phase transition by

1. temperature progression during constant heating power. During phase transition a graph of temperature over time is expected to show a plateau of constant temperature. Latent heat can then be calculated as the amount of heat that did not increase temperature, i.e. time the temperature stayed constant times heating rate.
2. measured specific heat. At a phase transition of first order specific heat diverges. Latent heat can be calculated as the area below the peak at T_C .

As a reference value we will compare our results to the work of Jayasuriya et al.

Secondly we will determine the Entropy related to this phase transition by

$$\Delta S = \frac{\Delta Q}{T},$$

where ΔQ is the determined latent heat. As a comparison value we take spin entropy which, since this phase transition occurs in $4f$ -orbitals, is

$$\Delta S_{\text{spin}} = R \ln(2J + 1) = R \ln(17) = 23.6 \frac{\text{J}}{\text{K} \cdot \text{mol}}.$$

Concerning the second order phase transition in Dysprosium at a Neel temperature of $T_N \approx 180 \text{ K}$, we will determine the precise Neel temperature and critical exponent. Again the work of Jayasuriya et al. will provide a reference value.

2 Evaluation

2.1 Methods and programs used

- All numerical values are rounded to the first significant (= non-zero) digit of the statistical error on the value. Errors are given with respect to that digit, except for cases in which that digit would be a “1”. In those cases the two first significant digits are given and the error is considered to be with respect to the two last digits of the given value. Example: 3.948872 ± 0.04213 would be rounded to 3.95 ± 0.04 and represented as 3.95 ± 4 , whereas 3.948872 ± 0.01542 would be rounded to 3.949 ± 0.015 and represented as 3.949 ± 15 .
- All plots and fits are done with GNU PLOT
- All numerical integrations are performed via MATHEMATICA’s online interface, available at <http://www.wolframalpha.com>.

2.2 The first order phase transition at T_C

The amount of latent heat bound in a first order phase transition can be determined in two ways, both of which we will employ, comparing the results afterwards.

2.2.1 Calculation from the heating curve

We recorded the heating curve of Dysprosium, starting from 78 K up to 91 K. However temperatures ranging from 78 K up to 85 K were used to adjust the heating parameters of our sample. This was done by aligning the heating curve of the specimen to the surrounding jar’s, which was equipped with its own heating circuit, to minimize additional, unaccounted for heating through heat radiation. The experimental challenge consisted in adjusting the digital rotary buttons of LABVIEW with a precision of a single pixel on screen – which was not even precise enough for aligning the two heating curves properly – without the possibility to simply enter numerical values for the heating currents. Our experiences in playing ego shooters were absolutely useful for this task.

From 85 K to 91 K the actual experiment was conducted, using a heating power of $P = 6.97$ mW. One second of heating therefore corresponds to $\delta Q = P \cdot \delta t = 6.97 \text{ mW} \cdot 1 \text{ s} = 6.97$ mJ. The heating curve, as well as the low and high temperature asymptotic behaviour, are shown in figure 2.1, where deposited warmth has been arbitrarily chosen to be zero at 2000 seconds after the experiment started. The fit parameters of the asymptotes are detailed in table 2.1¹. It can clearly be seen, that the slope of both lines are close to each other, so that they can be assumed to be parallel for the purposes of this experiment. Additionally, we would like to point out how well linearity fits temperature behaviour in the respective reigns, as can be seen in the extremely small standard errors.

We read from figure 2.1 that the phase transition started at 86.5 K and was completed at 90 K. Taking the median value of starting and endpoint, we obtain a Curie temperature of 88.25 K,

Table 2.1: *Fitting parameters of high- and low-temperature asymptotes*

Reign	Slope (in $\frac{\text{K}}{\text{s}}$)	Offset in K	Range of data used to fit
Low-temperature	0.5039 ± 3	$85.3006 \pm 4\text{K}$	85 K - 87 K
High-temperature	0.4854 ± 3	$84.788 \pm 3\text{K}$	89.87 K - 90.77 K
Median	0.4946 ± 3	$85.0443 \pm 4\text{K}$	

¹Errors are in respect to the last digit given

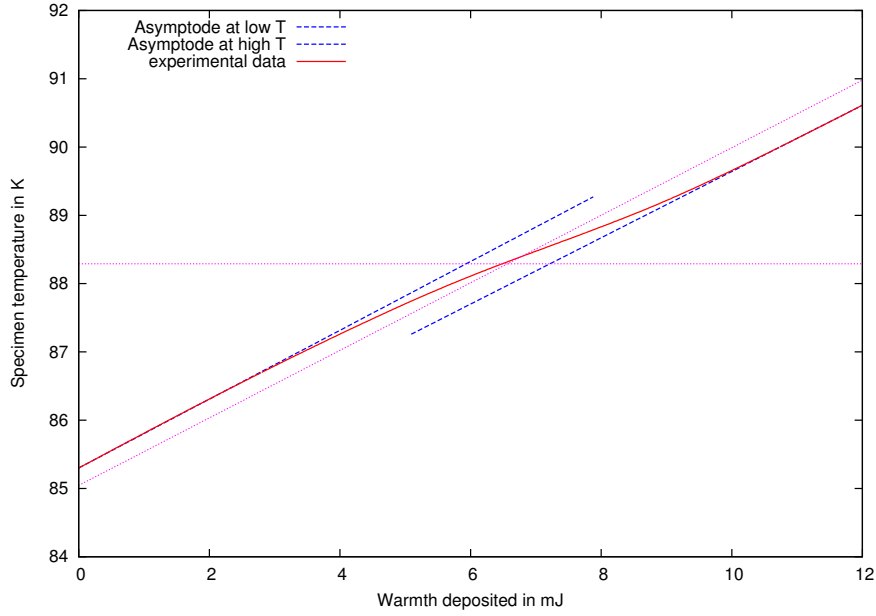


Figure 2.1: Temperature curve (drawn in red) with asymptotic behaviour (blue)

however such a method is coarse and contains large errors due to unaccurate interpretation of starting and ending points of the phase transition. Thus, we applied a second method of finding the Curie temperature assuming that the phase transition aligns symmetrically to the asymptotes: We drew the experimental data corrected by the median of the asymptotes and checked where the resulting curve passes zero. Thus we determined the amount of heat, at which the process was half finished. Now we assume the Curie temperature to be the temperature the median gives at this amount of heat. This second method yields a Curie temperature of 88.290 ± 0.002 K. The median of the asymptotes and a horizontal line at this temperature are drawn in figure 2.1.

The horizontal line drawn at the Curie temperature can be used to determine the latent heat of this phase transition. It's portion between the asymptotes can be interpreted as an idealized temperature course, the portion's length thereby amounting to the latent heat we want to determine. We easily find it's intersections with the asymptotes and calculate their difference to be: $\Delta Q = 1.28 \pm 0.01$ J. This has to set into relation with the amount of Dysprosium, 0.0560 mol. We obtain a final result for the latent heat of Dysprosium $Q = 22.86 \pm 0.18 \frac{\text{J}}{\text{mol}}$

Sources of Error

Theoretically, one would expect the heating curve to form a horizontal plateau in a plot like figure 2.1. The gradual shift from one asymptote to the other originates from fast heating. By heating more rapidly than the sample can install thermal equilibrium within itself, the phase transition was performed at different times in different parts of the specimen.

2.2.2 Calculation from measuring specific heat

A second method to determine latent heat is to determine the area of the divergence in specific heat at the phase transition. For this calculation, data ranging from 85 K to 91 K have been evaluated, just as above. In order to determine the best estimate for the peak's area, we used

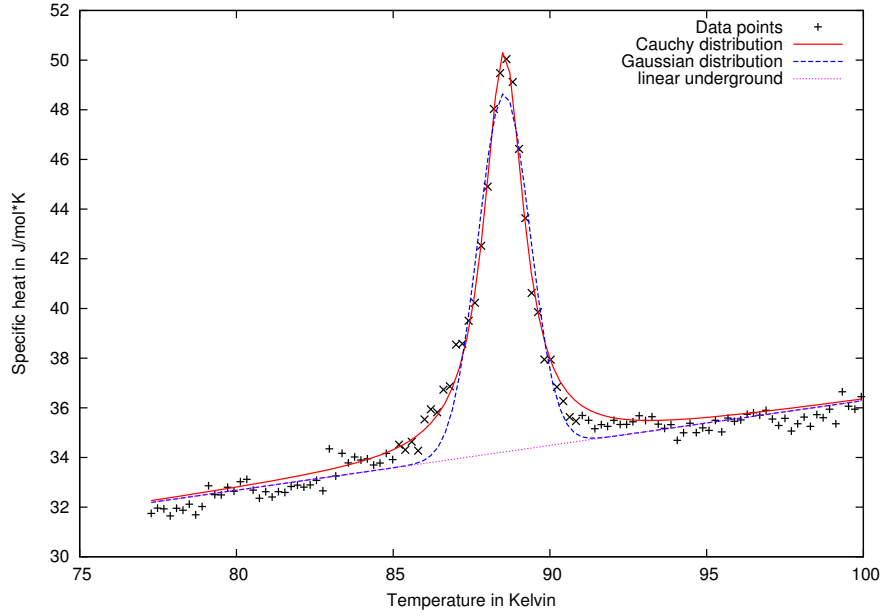


Figure 2.2: Specific heat in the vicinity of T_C

both, Gauss and Cauchy distribution functions to fit into our data. Before fitting those functions, we did a linear fit on the data surrounding the peak in order to exclude the noncritical behaviour. The Cauchy distribution is to be preferred, as becomes obvious in figure 2.2. Its peak lies at $T_C = 88.53 \pm 0.02$ K.

The latent heat to be determined is the area between the Cauchy distribution curve and the linear underground. Using MATHEMATICA, we obtain a value of $37.32 \frac{\text{J}}{\text{mol}}$, a value that fits the experiment of Jayasuriya et al. very well. Since the integration was performed numerically the influence of errors in the fitting parameters on the final value cannot be determined easily.

2.2.3 Entropy

The entropy related to this phase transition can be calculated using $\Delta S = \Delta Q/T$, where in our case we will use the Curie temperature as T . This gives the following results:

$$\Delta S = \frac{22.86 \pm 0.18}{88.290 \pm 0.002 \text{ K} \cdot \text{mol}} \frac{\text{J}}{\text{K} \cdot \text{mol}} = 0.259 \pm 0.002 \frac{\text{J}}{\text{K} \cdot \text{mol}} \quad \text{through temperature course}$$

$$\Delta S = \frac{37.32}{88.53 \pm 0.02 \text{ K} \cdot \text{mol}} \frac{\text{J}}{\text{K} \cdot \text{mol}} = 0.422 \frac{\text{J}}{\text{K} \cdot \text{mol}} \quad \text{through specific heat course}$$

Both values are small in comparison to the theoretical value for $4f$ -orbital spin entropy. The main reason for this is that spin entropy as calculated above considers the transition into a completely disordered state, whereas the actual phase transition encountered conveys Dysprosium from one ordered state into another.

2.2.4 Comparison of results

Our results gained through different methods differ significantly. Only the Curie temperature T_C is similar in both measurements. However latent heat calculated from the temperature course is

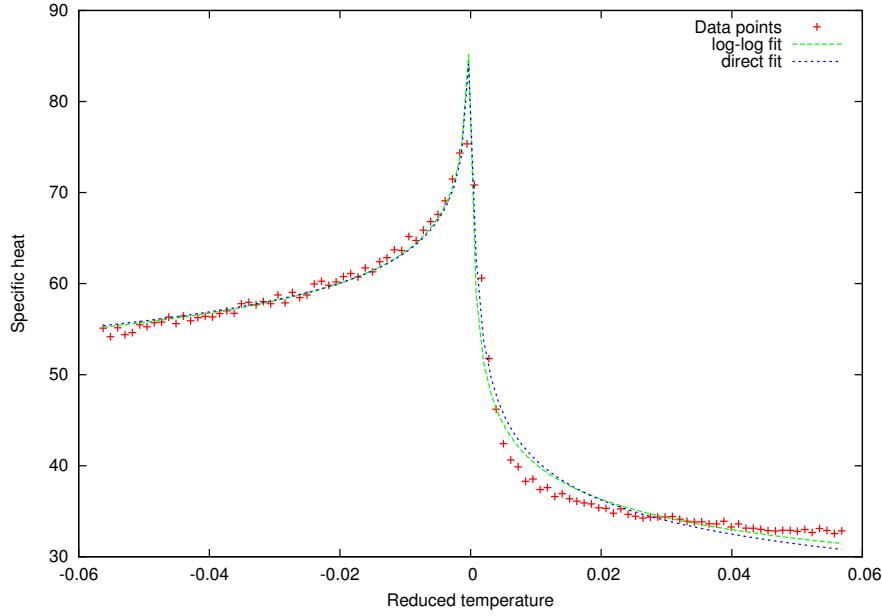


Figure 2.3: Specific heat at the Neel temperature

way smaller than the literature value found in the paper by Jayasuriya et al. on the same topic. Main source of error in this part of the experiment is the fast heating, as explained above. To achieve better results the experiment should be rerun with a slower heating rate, allowing more precise determination of starting and ending points and transition temperature.

Comparing the latent heat obtained from specific heat course, we are in good agreement with Jayasuriya et al. Our result lies within one standard deviation of their's, unfortunately we were unable to calculate a variation on our result. Curie Temperature, as determined by Jayasuriya et al. is about 2 K higher than the value we found, one probable reason for the discrepancy being uncorrect gauging of our thermometer, since we neither controlled the gauge nor did we perform an experiment allowing us to independently determine a gauge from the results. Spin entropy, as calculated from specific heat course, matches the literature value of $0.428 \pm 0.001 \frac{\text{J}}{\text{K}\cdot\text{mol}}$ roughly, better results could be obtained by either slowing the heating process down, taking more data points, or rerunning the experiment for the same reason.

2.3 The second order phase transition at T_N

For the second order phase transition at the Neel temperature, we assume a power-law dependency as shown in equation (1.4). We determined the Neel temperature graphically, or rather directly from the data, by taking the arithmetic average of the peak value (which we attributed to the rising branch, as fit results and graphs suggested) and its successor, achieving a value of $T_N = 179.68 \pm 0.05 \text{ K}$, where the uncertainty is considered to be one half of the data point's distance.

In order to find the proper parameters for the power law, we did both, a log-log fit as well as a direct fit with an exponential function, each for both branches of the peak separately after subtracting the noncritical linear behaviour. The results can be seen in figure 2.3. Any values

Table 2.2: *Coefficients of the plots concerning the second order phase transition*

Temperature range	Function	Kind of fit	Coefficients	
$T < T_N$	$f = a \cdot t + b/a$	log-log	$a = -0.093 \pm 2$	$b = -0.334 \pm 7$
	$h = r/s \cdot t ^s$	direct	$s = -0.090 \pm 2$	$r = -3.25 \pm 5$
$T > T_N$	$g = c \cdot t + d/c$	log-log	$c = -0.190 \pm 8$	$d = -0.488 \pm 14$
	$i = q/p \cdot t ^p$	direct	$p = -0.215 \pm 7$	$q = -2.55 \pm 2$

obtained through fitting are depicted in table 2.2, where the first row of coefficients² are the critical exponentials.

The values we obtained do not confirm $\alpha^- = \alpha^+$, but instead they vary by a factor of two. This is not surprising, however, since Jayasuriya et al. needed another diverging term in the power law in order to achieve $\alpha^+ = \alpha^-$. Still, the specific heat course follows a power law, as can be seen by the small errors and the good alignment of the curves to the data points, as seen in figure 2.3

2.4 Discussion of specific heat course

The results of the previous sections allow us to describe the specific heat course of Dysprosium through a set of phenomenologically found fits:

- In the vicinity of the first order phase transition at $T_C = 88.29$ K a Cauchy distribution matches the experimental data very well, as can clearly be seen in figure 2.2.
- For the second order phase transition at $T_N = 179.68$ K we apply a modified power law, that uses different critical exponentials on each side of the phase transition. Again, the functions align well to the results, becoming clear when looking at figure 2.3.
- In general, we considered a linear “basic progression” of specific heat while fitting the respective functions. This is, naturally, allowed in approximation. However, the nicety, with which the line fitted for the noncritical behaviour in section 2.2.2 matches large parts of the data from the antiferromagnetic reign, suggests that a linear dependency on temperature exists indeed. Therefore, we seem to have measured in an intermediate region, in terms of the limits in equation (1.3).

²errors are with respect to the last digit(s) given