Practical course M
2.1 Specific heat of solids

19. Dezember 2013

1 Introduction

In this experiment you will measure the specific heat c of KH_2PO_4 (KDP) in the temperature range from $77\,K$ to $300\,K$. Within this temperature range this material has a phase transition. Your task will be to analyse the temperature dependence of c and the phase transition. Moreover you will get to know two room temperature techniques for measuring the specific heat of solids, namely the relaxation and the heat pulse method.

2 Preparation

Before you start with the experiment, you should prepare the following basics:

- For the general theory about specific heat you should read the corresponding chapters, for example in the books of Becker[1] or Zemansky[2]. For the properties of phonons and their contribution to the heat capacity Kittel's book[3] will provide an excellent overview, and should not be missing in your preparation.

    - Definition of c, connection of c to the entropy and other thermodynamic potentials
    - Difference between c_p and c_V, What do you measure?
    - Classic model: the rule of Dulong and Petit
    - Acoustic/optical phonons and their dispersion relations
    - Einstein and Debye model; density of states $D(\omega)$, low- and high-temperature approximation

- Phase transitions

    - Orders of phase transitions with examples
    - Specific heat at phase transitions

- For information on the ferroelectricity of KDP you should read the corresponding parts of the publication of Jona and Shirane[4] about:

    - Specific heat and phase transition of KDP

- Structure of KDP and its connection to the phase transition
  - Role of the hydrogen bonds

- To get acquainted with the set-up and the basic principles of the measurement technique you should read and understand the publication of A. Junod[5]. Please note the differences to the actual set-up you will use and think about the changes for the quantitative analysis of the data! The differences are described in the section about the experimental procedure on the next page.

  - Basic set-up
  - What is meant by adiabatic/non-adiabatic? Which one are you going to you use and how is this realized in the set-up?
  - How can c be calculated from the measured quantities? Which quantities have to be measured in order to calculate c?
  - Basic principle of a PID temperature control [6]

During the main experiment you are supposed to get to know other methods for measuring the heat capacity of a solid, using a simple room temperature set-up. Therefore, please read about the principles and applications of the

- (semiadiabatic) heat pulse technique

- and the relaxation method

and work out how the specific heat can be calculated from the resulting data curves [7].

3 Experiment

3.1 Continuous method

In contrast to A. Junod's set-up, you will be using liquid nitrogen as a coolant instead of helium. Thus, the set-up only needs a simple Dewar vessel. The cylindrical adiabatic shield is heated by one heater only, so that there are four electrical connections in total: the sample temperature T_P, the sample heater H_P, the shield temperature T_S and the shield heater H_S. The sample heating power is set manually via a constant current. To heat the shield you will be using a 'Lakeshore' temperature controller that records both the sample temperature and the temperature of the adiabatic shield and controls the shield heater automatically via a PID-algorithm. The temperatures are measured with the help of two platin resistances. Thus, another main difference compared to A. Junod's set-up is that the measurement program directly saves the temperatures T_P and T_H by measuring the resistivity of the platin thermometers. In the columns of the output file the sample and shield temperature (in K), the time (in s), the heater voltage (in V), the heater current (in A) and once again the sample temperature (in Ω) are protocolled.
First evacuate the set-up. When the pressure has diminished below 10^{-4} mbar, you can begin with the filling of liquid nitrogen into the Dewar. After that, put an exchange gas into the sample chamber. (Why? What kind of gas?) About one
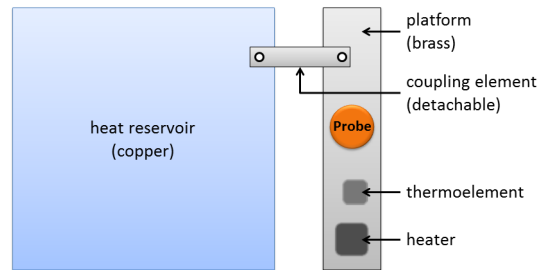
hour later the sample will be at 77 K and the sample chamber can be evacuated again before starting the measurement.

Now the measurement begins by switching on the sample heater. The heater has to be switched off several times during the measurement to check the background signal. (Where does this background signal come from?) Note again that the data acquisition and the temperature control is simplified in comparison to Junod's set-up. Use a rather low heater current (~ 6.5 mA) for the first temperature range up to the phase transition. After that you can use a higher current (~ 8.5 mA).

3.2 Heat pulse and relaxation method

Since the continuous temperature sweep from 77 K to room temperature takes quite long (approx. 4 h), the time can be used to get to know further methods for determining the specific heat of a solid. Therefor a room temperature model is available. Its set-up is shown in Figure 1.

The set-up is situated in an exsiccator, which is evacuated before carrying out the measurements (~ 1 mbar). Three gold-plated cylindrical pieces of copper, three pieces of lead and three pieces of aluminum are used as samples. The corresponding masses are listed below in paragraph 4.2. Your task is now to do measurements for different masses by using both the heat pulse and the relaxation technique and determine the specific heat of copper, lead and aluminum. Be careful when attaching and detaching the coupling element – the electric contacts, the heater and the thermoelement should not be damaged. The measurement software allows to set the heater current, the heating time, the waiting time before the heater is switched on and the follow-up time after the heating period. Play around with these values and try to find out the proper settings for each method. Moreover, for both cases the addenda has to be determined (What contributes to that?) by carrying out a measurement without any sample. The resistivity of the heating element is 1 kΩ.

Figure 1: Schematic set-up of the room temperature model used for the heat pulse and relaxation technique

4 Analysis

4.1 Continuous method

The sample temperature given by the Lakeshore temperature controller (first column in the output file) is calculated from the resistance of the sample thermometer (last column in the output file). After the conversion the data is internally smoothed to minimize a step-like behaviour. You can use directly the first column to calculate dT/dt. An additional smoothing of the derivative might be necessary.

Remember that 1 mole KDP contains $8\,N_A$ atoms. Your report should include the references of every picture and citation. Compare your results to the results in literature. Take care that the figures shown in your report are not too small – everything should be readable and reasonably scaled.

1. Find a reasonable fit function for the background signal and substract it from the data. Discuss what is causing the background and why you may substract it like this.

2. Calculate the specific heat c in units of $\frac{\text{J}}{\text{mole K}}$ of your sample in the temperature range from $77\,\text{K}$ to $300\,\text{K}$. The sample mass is $2.627\,\text{g}$. The addendum caused by the heater and thermometer are assumed to be negligible. Compare c with literature values.

3. Discuss the temperature dependence of c. Check the validity of Debye's T^3-law and the rule of Dulong and Petit. Make figures and discuss your results.

4. Extract the low-temperature results ($T < 77\,\text{K}$) from the work of Stephenson and Hooley (Table 1 and 2 in [8], attachment stephensondata.dat) and add them to your results for the specific heat of KDP. Try to model the behaviour of the specific heat (leaving out the phase transition) by adding up a Debye function with four Einstein modes:

$$f_{Einstein}(x) = 3N_A k_B \cdot \left(\frac{T_E}{x}\right)^2 \cdot \frac{\exp\left(\frac{T_E}{x}\right)}{\left(\exp\left(\frac{T_E}{x}\right) - 1\right)^2}$$

You can find the Debye function for a Debye temperature of $1\,\text{K}$ as debyefunktion1K.dat in the attached files. To choose a different Debye temperature, you have to scale the x-column in this file with the corresponding factor. For the choice of the Einstein temperatures T_E please note that the optical phonon spectrum of KDP mainly consists of two frequency regions, i.e. $70 - 430\,\text{K}$ for lattice modes and $450 - 1700\,\text{K}$ for internal modes of the phosphate group.

Explain why one acoustic and four optical modes are already a good approximation for the temperature dependence of the specific heat! How many modes would be necessary for a complete description? What Einstein temperatures are reasonable?

Note: In general there are – for p atoms per unit cell – 3 acoustic and 3p−3 optical modes; each one consisting of a longitudinal and two transversal

modes. But for the sake of simplicity we consider this 3 different parts as one contribution.

5. Discuss the phase transition. Compare the transition temperature with the literature. Calculate the entropy of the phase transition by integration. For this you need to substract the phononic background.

4.2 Heat pulse and relaxation method

Analyse the recorded curves and determine the specific heat of copper, aluminum and lead. Compare your results with literature values. Discuss how exact the two methods are and where possible problems lie. Consider also the following questions:

1. What do you have to take care of when adjusting the settings for the heating curve?

2. In which case is the semiadiabatic heat pulse technique (the relaxation method) more suited?

3. How important is the coupling element in both techniques?

The masses of the samples are:

	sample 1	sample 2	sample 3
Cu	1.3845 g	1.3838 g	1.3832 g
Al	0.1990 g	0.1994 g	0.2001 g
Pb	0.9256 g	0.9324 g	0.9254 g

5 Appendix

You should find the following files in this zip-file:

- M2.1[e].pdf (this tutorial)

- junod.pdf (reference [5])

- jonashirane.pdf (reference [4])

- pid.pdf (reference [6])

- breunig[e].pdf and breunig[d].pdf (reference [7])

- stephensonhooley.pdf (reference [8])

- debyefunktion1K.dat

- stephensondata.dat

Literatur

[1] R. Becker, *Theorie der Wärme*

[2] M.W. Zemansky, *Heat and Thermodynamics*

[3] C. Kittel, *Introduction to Solid State Physics*, Oldenbourg

[4] F. Jona and G. Shirane, *Ferroelectric Crystals*, Pergamon, 1962
     (jonashirane.pdf, in this zip-file)

[5] A. Junod, Journal of Physics; E12 (Physical Instruments), 945 (1979)
     (junod.pdf, in this zip-file)

[6] Some information concerning PID controllers
     (pid.pdf, in this zip-file)

[7] Techniques for determining the heat capacity;
     excerpt from O. Breunig's diploma thesis, 2011
     (breunig[e].pdf and breunig[d].pdf, in this zip-file)

[8] C. C. Stephenson and J.G. Hooley, *The Heat Capacity of Potassium Dihydrogen Phosphate from 15 to $300°K$*, 1944
     (stephensonhooley.pdf, in this zip-file)

[9] E. Fatuzzo, M.J. Merz, *Ferroelectrics*

Questionnaire for the M-practical course

Specific Heat of Solids

**Please fill in the form after you finished the experiment and discuss
the criticism with your tutor wherever applicable.**

The valuation is based on the german school mark system (1:best – 6:worst)

Semester: Winter 20___/___ Summer 20___

Abstention

Query 1:
How much did you learn from the experiment
in terms of concepts in physics as well as technical skills?

in physics   1 2 3 4 5 6   □ □ □ □ □ □   □

tech. skill   1 2 3 4 5 6   □ □ □ □ □ □   □

Query 2:
How do you rate the quality of the experimental equipment?

1 2 3 4 5 6   □ □ □ □ □ □   □

Query 3:
Is the experiment up-to-date with recent topics in physics?

1 2 3 4 5 6   □ □ □ □ □ □   □

Query 4:
What is the advance in your experimental skills?

1 2 3 4 5 6   □ □ □ □ □ □   □

Query 5:
Did you have fun carrying out the experiment?

1 2 3 4 5 6   □ □ □ □ □ □   □

Query 6:
Is the tutorial of the experiment explicit?

1 2 3 4 5 6   □ □ □ □ □ □   □

Query 7:
How much time did you invest in the preparation?

h

Query 8:
How do you assess the experiment in total?

1 2 3 4 5 6   □ □ □ □ □ □   □

study course: Master □   Teacher □

Comments and suggestions

Overall mark for your tutor   1 2 3 4 5 6
Name of your tutor: _____   □ □ □ □ □ □   □

Workplace:	**Operating instruction** *according § 20 GEFSTOFFV*	As at 5/2011 *Date:* 31.05.2011

Nitrogen, liquid, cryogenic

Kp.: -195.8 °C   Fp.: -210 °C rel.   Vapour density$_{(Air)}$= 1 : 0.97   Solubility (H_2O/20°): insoluble

Physical danger:
H202 Explosive; great hazard due to splitters and shards from explosion.
Cracks/scratches in the Dewar vessel may lead to spontaneous implosion! Explosion hazard due to a rise in pressure cause by evaporation of nitrogen.
H270 May cause or contribute to fire; oxidizing agent.
Condensation of oxygen into nitrogen is possible (the colour of the solution turns blue), this is an immediate danger to life. In such a case, let the nitrogen evapourate outside the building.

Dangers to health:
H 281 Contains cryogenic gas; may cause cryogenic burns or injury.
Depending on the duration of the contact, deep tissue destruction, frostbite, and severe eye damage may occur.
In high concentration, nitrogen leads to suffocation without warning!
Cool evaporating nitrogen has a density higher than air. Danger of suffocation by accumulation in low-lying closed rooms.

Attention

Safety instructions Prevention:
P271 Use only outdoor or in well-ventilated place.
P282 wear protective gloves / face protection shield / eye protection with cold insulation.
if necessary wear cryogenic safety gloves.
Technical measures : Liquid nitrogen should only be filled in dry and well-isolated Dewar vessel. Close the conainer such that the pressure in the container is balanced to ambient pressure or use overpressure relief valves.
Organizational measures:
Transport only specially suited nitrogen tanks or Cryogenic containers in elevators *without accompanying persons*.

Behaviour in case of danger: In case of massive gas release leave the room. Alert other people. Ventilate the room. Rescue injured persons in compliance with self-security.

First Aid

P361 Remove all contaminated clothes immediately.
Skin or eye contact:
P 315 Seek immediate medical advice/attention.
P 336 Warm frozen parts with lukewarm water. Do not rub the concerned area. Cover and keep the burned area sterile. Consult a physician.
Inhalation: High concentration may cause suffocation. Symptoms are loss of mobility and consciousness. Expose the victim to fresh air in compliance with self-security. Keep warm and calm. Consult a physician. If breathing stopped, begin artificial respiration.

Emergency number:

Emergency medical services: 01-112

Nearest hospital: 01-4792213 Evangelisches Krankenhaus,
                                                 Weyertal 76, 50931 Köln
Maintainance main building: 2200

Proper disposal
Let the nitrogen evaporate outside the building. Do not pour back liquid nitrogen into storage vessel.

*If necessary: * Specify location*	*(Signiture)*