D403026:

Advanced methods of solids characterization

K4 Determination of heat capacity of powder samples with low thermal conductivity

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Development of new laboratory tasks for the DSP course D403026 "Advanced methods for solids characterization" and their translation into the English language

Content

1 Introduction

The PPMS is primarily intended for single crystal measurements only. Powder samples tend to have low thermal conductivity, resulting in long measurement times and less accurate results. In addition, powder samples may be contaminated with the device. It is therefore necessary to ensure that the powder sample is held together and that heat is better passed through it.

Several methodologies for measuring powder samples have been developed in the literature to address both of these problems:

A. mixing the sample with apiezone
   - high measurement uncertainty

B. compressing the sample into a tablet
   - poor heat transfer
   - volatile samples may evaporate and contaminate the instrument

C. pour the sample into an aluminium DSC pans
   - poor heat transfer
   - slow measurement

D. pressing of the sample in copper or aluminium foil
   - complex sample preparation

E. compressing the sample into a tablet and then placing it in an aluminium pan together with Apiezon N
   - slow measurement

F. compressing the copper foil sample into a tablet and placing it in an aluminium pan together with Apiezon N
   - slow measurement
   - high uncertainty of measurement when deducting contributions
   - complex sample preparation

All of these methodologies are described in detail in Mahnel et al.[1]

After a critical evaluation and extensive testing, we decided to use the D method for measuring conventional low volatile powder samples, namely copper foil molding, since copper is a reliable measured substance (used as a standard) with good thermal conductivity.

The measurement itself is equivalent to the measurement of a single crystal sample (described in K0: Determination of heat capacity by PPMS), therefore it is explained very briefly in this manual.

The evaluation of the measured data differs slightly from the usual procedure for a single crystal sample, as we have to subtract the contribution of the copper foil to the total measured thermal capacity.

[1] Mahnel T.; Pokorný V.; Fulem M.; Sedmidubský D.; Růžička K., *Measurement of low-temperature heat capacity by relaxation technique: Calorimeter performance testing and heat capacity of benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene*, J. Chem. Thermo. 142 (2020) 105964.

2 Sample Preparation

During the entire sample preparation process, gloves should be worn to prevent sample contamination. In addition, we will need our sample, copper foil, scissors, tweezers, specimen transfer aids (depending on sample stickiness, different aids, see Figure 2.1), vial described by sample name and preparation date, mold and drill (see Figure 2.2, they are at the press), a workbook ("PPMS") and stationery.

Figure 2.1: Aids for pouring the sample

Figure 2.2: Mold and drill

First, take the copper foil and cut out a square about 1 - 1.5 cm from it (see Figure 2.3 on the left). To save material, cut the strip from the foil and cut it into 3 equal parts (see Figure 2.3 on the right). We store the unused squares in the vial next to the press (which is prepared for this purpose). We carefully weigh the copper square on the microbalance (laboratory G01 in building A). Weighing weights should not touch, allow contactless opening.

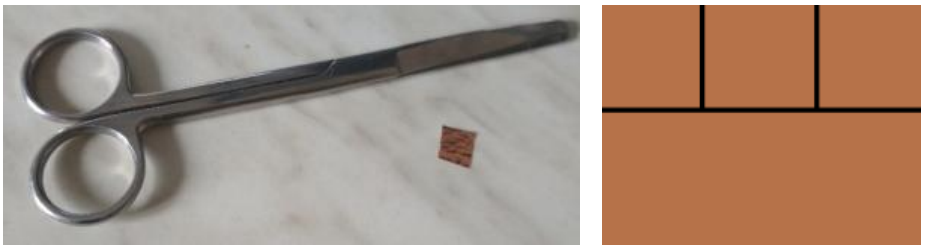

Figure 2.3: Square cut out of copper foil

Using a drill and a brass mold, turn the weighed copper square into a sample cup (see Figure 2.4). Place the square on the mold and drill it gently (so as not to break). We take the copper foil with the drill bit and align the corners of the square with a twisting motion. We try to have the same layer everywhere and no sharp edges anywhere (they could cause tearing of the foil during pressing). Insert the resulting cup back into the mold (again we have to be careful of puncture) and remove the drill bit.

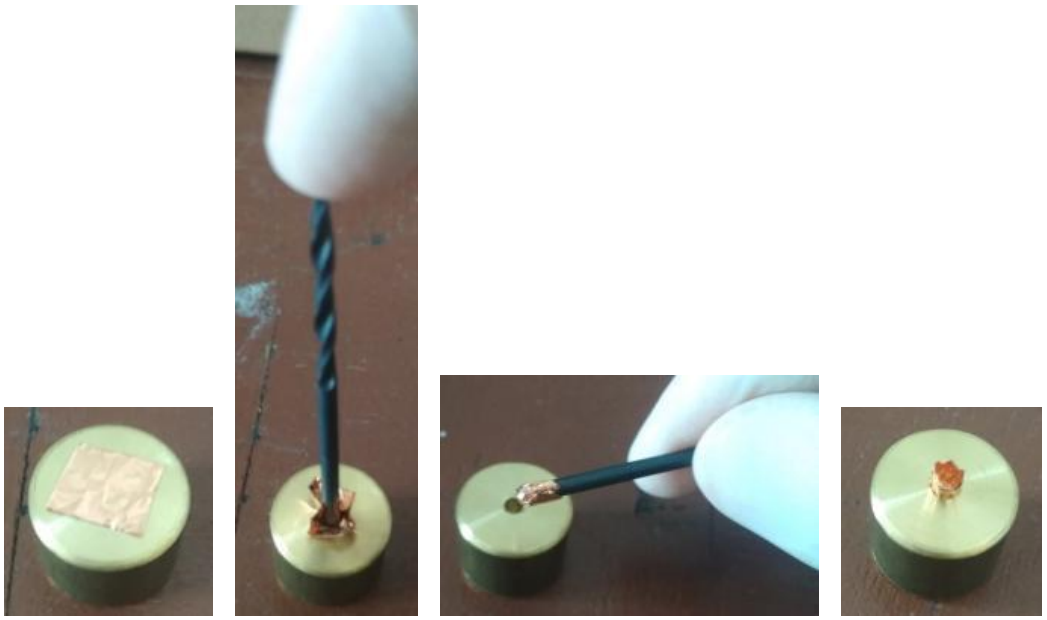

Figure 2.4: Preparation of copper foil cup

Fill the cup with as much sample as possible but still close to the top so that no sample could be spilled (Figure 2.5). Close the cup by hand, or we can help with tweezers (twist the end). Check that the sample does not spill somewhere and weigh the sample dish on the microbalance. Subtracting the first weighing weight from the second weighs the sample weight.

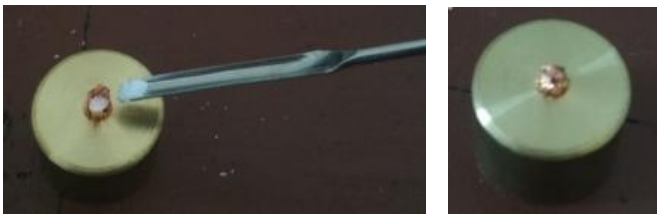

Figure 2.5: Filling the cup with sample

Now we move on to pressing. First, check the cleanness of the mold. If there are any remnants of copper inside, it is enough to scrape them with a metal tool (for example, by pouring the sample into a copper cup). If there is any powder inside, the mold must be washed with solvents (acetone, toluene, petroleum ether) and dried. When the mold is clean, we can start pressing. Insert the roller into the middle part of the mold and attach the lower (with shorter rod) and upper part. The glossy surface of the stick must face the sample. The joined mold is shown in Figure 2.6.

Figure 2.6: Combined mold

Carefully put the mold with the sample into the press. The mold should be centered (according to the circles at the bottom of the press), as the upper part of the press is on the joint and could bend during pressing (see Figure 2.7). Pull the press manually as far as it will go.

Figure 2.7: Press mold correctly (left) and wrong (right) inserted into the press

Now by pumping the bar on the right side of the press, we will increase the pressure. The pressure only increases when the locking bar on the left side of the press is turned to the right (see Figure 2.8). When the bar turns to the left, the pressure is immediately reduced.

Figure 2.8: Press locking bar

According to the manufacturer, the mold should withstand 1.5 T (15 kN), but for sure we should not exceed 10 kN or just slightly (see Figure 2.9). Repeat this step at least three times to ensure that the sample is pressed evenly (with each press we can increase the pressure a little, but never exceed 15 kN!).

Figure 2.9: Pressure gauge at the press with recommended pressure values

Loosen the press, remove the mold, remove the lower part (sometimes it is necessary to twist it a little to loosen it) and replace it with a transparent ("extrusion") piece. Then return the mold to the press. Now it is enough to tighten by hand and the resulting tablet is pushed into the transparent part. Remove the mold from the press again, remove the middle part and push the tablet out of the transparent piece using the upper part of the pressing mold (see Figure 2.10).

Figure 2.10: Extrusion of a tablet from a compression mold

Remove the protruding bits of copper foil and weigh the tablet on microbalance. During molding, a part of the copper foil is lost, either falling off or remaining on the mold walls (see Figure 2.11). Usually about 0.5 - 1 mg of copper is lost. The final weight of copper in the tablet is calculated according to the formula: weight of copper = 1. weighing (copper foil) + 3. weighing (sample tablet with copper surface) - 2. weighing (copper cup with sample).

Figure 2.11: Made sample tablet and dropped pieces of copper

3 Thermal Capacity Measurement

The measurement of the thermal capacity of the powdered sample itself is equivalent to the measurement of a single crystal sample, which is described in „K0 Determination of heat capacity by PPMS“.

Again, the measurement consists of two experiments - a blank (addenda) with vacuum grease (apiezon N) and an experiment with an added sample that is glued to the platform using fat.

When specifying the file name, it is convenient to include the weight of the sample itself and the copper foil, or the molar weight of the sample (for example, 2031-cp-L-HIS (Mw119_1192) _11_245mg (19_436mgCu) -300-2_puck1676.dat).

In the window for entering sample information (Figure 4.22 in „K0 Determination of heat capacity by PPMS“) we should fill in “1” in all windows, as the software does not count on the measurement of samples containing more substances.

4 Evolution of Measured Data

The evaluation of the measured data is described in detail in the manual „K0 Determination of heat capacity by PPMS“, including evaluation of samples in copper foil, therefore the procedure is repeated here very briefly.

First we use ExportData.exe (QdPpms\Tools\) to export the measured data. We'll need Pressure (Torr), Sample Temp (Kelvin), Samp HC (μJ/K), Samp HC Err (μJ/K), Addenda HC (μJ/K), Fit Deviation (ChiSquare), and Sample Coupling (Percent). Choose “Destination File Format” for “Tab Delimited” and “Headers” for “Column Headers”.

Run the program PPMSeval.exe (we need the MATLAB compiler runtime to run it), select the exported file and select the option “Sample in copper foil”. Enter the weights of copper and sample and the molar mass of the sample. Then the program creates a .RES file containing the evaluated molar heat capacity of our powder sample.

5 Protocol

Described in „K0 Determination of heat capacity by PPMS“.