University of Ulm
Institute for Micro- and Nanomaterials

Lab
„Materials Science“

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Group 9: Adelheid Grob & Brook Esseye

Lab D: Phase Transitions
lab on May, 24 2007

1 Introduction

The goal of this experiment is to verify the phase diagram of a lead-tin-alloy. That means finding out the temperature at which the state changes between liquid and solid at certain compositions. It is expected that at these characteristic temperatures the free enthalpy changes.

To measure this enthalpy we use the method of Calorimetry with a DSC (Differential Scanning Calorimetry). The DSC we used in this lab is capable to do measurement in a range from -140°C up to 700 °C.

The DSC works in principle in the following way: There are two ovens, which are exactly equal. Both of them have platinumbonds at the bottom, with which the characteristic restistance is measured. The characteristic resistance is temperature dependent, that means by measuring the resistance, the temperature of the bonds can be calculated.

Now in one of the ovens the probe is inserted, while the other one is kept empty. What our DSC is doing now, is to measure the power difference between the two ovens while heating. This difference is equal to the heat flow. Because we have a controlled heating, which is done by a heating program and can be as well a linear heating or a more complex heating, we've got a well-known temperature value and a measured heat flow value.

What we measure are peaks in the heat flow at certain temperatures. If the peak begins with a positive slope, we know that it results from an endothermal reaction, if it has a negative slope the reaction is exothermal.

The area a peak covers can be used to calculate the enthalpy with the formula:
area $= K\Delta Hm$, K being a callibration constant.

First of all we have to calibrate the DSC, that means we have to measure once in the desired temperature range with two empty ovens to get a baseline of the measured power, which has to be subtracted from the later measured curves. The baseline we measured was about 20 mW.

The probes are weighted and the encapsulated. As we want to figure out the phase diagram at a constant pressure, it is necessary to make a small hole in the cap of the bin, so that pressure can be equalized.

2 Measurements

2.1 First Probe

The first probe we used, has had a weight of 29.4 mg and contained of 12 At% of Sn. The heating programm heated the system linearly with 20°K/min. The range was from 50°C to 350°C.

The plot below (Fig. 1) shows the results we got with the first sample.

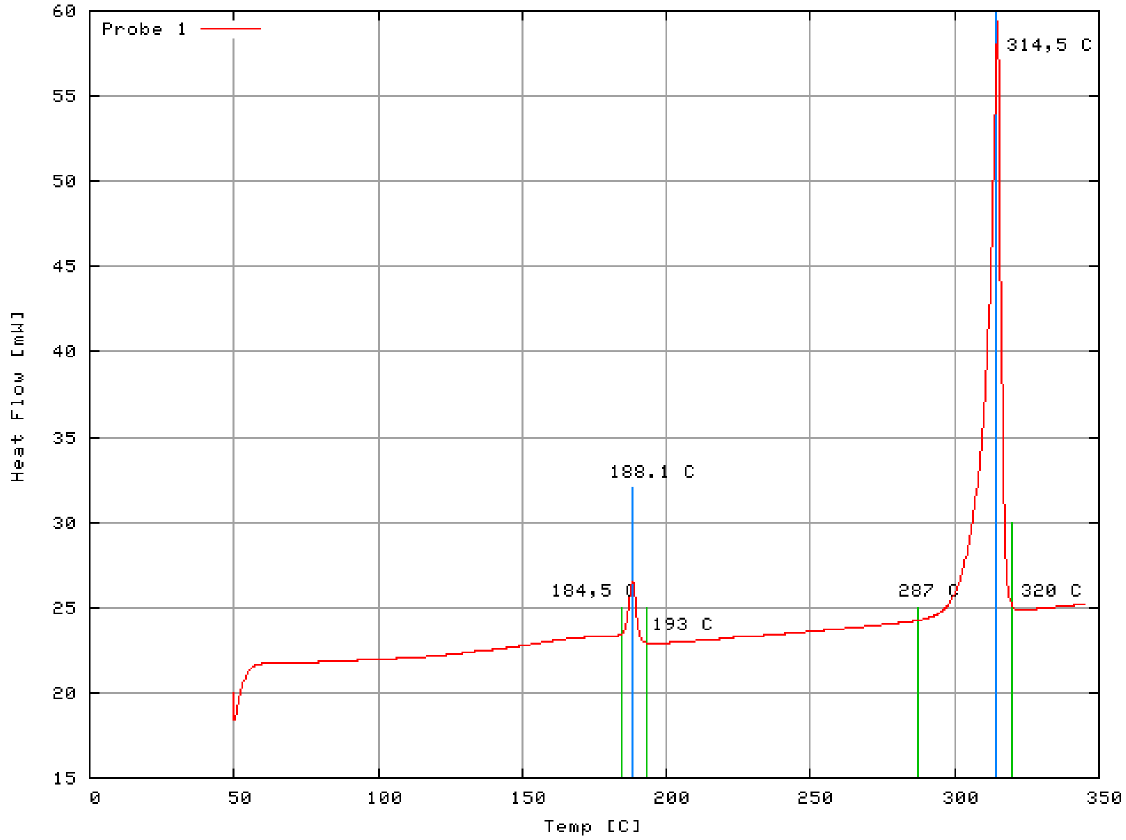

Fig. 1: Plotted results of Probe 1

As you can see, there are two peaks, one at 188.1°C and the other at 314.5°C. So we can assume, that in both points there is a heat flow. By taking a look on the given PbSn-Phase Diagram, we can see, that we'd expect only one peak at about 310°C, where the liquid phase begins.

The melting began in our measurement at about 287°C and was finished at nearly 320°C. This is quite in the expected range.

The peak area of the interesting (second) peak is 27.59 J/g.

The other peak is due to the effect of kinetics. That means, that we don't start with a equilibrium in the solid phases. So by increasing temperature the solibility of tin in lead increases and at the eutetic temperature a melting begins to get the equilibrium between Pb-atoms and Sn-Atoms.

To lower this effect it is possible to heat the sample, cool it down, heat it again and so on, so that the two materials get mixed in a better way. If you do this long enough, only the peak remains which corresponds to a real phase transition.

2.2 Second Probe

The second probe we took a look at, weighted 20.1 mg and consisted of 20 At% Sn. We heated it in a range from 50°C up to 340°C in steps of 20°K/Min.

First we got nearly the same result as in probe one, that means two peaks, one at nearly 185°C and the other at about 290°C.

To find out, which point is a real phase transition and which one is due to kinetics, we went on as described above: we heated the probe at 180°C and cooled it and heated it again and so on. As we perform this some time, the first peak nearly disappeared, that means we have reached a state of equilibrium.

The remaining peak can be seen in the following plot.

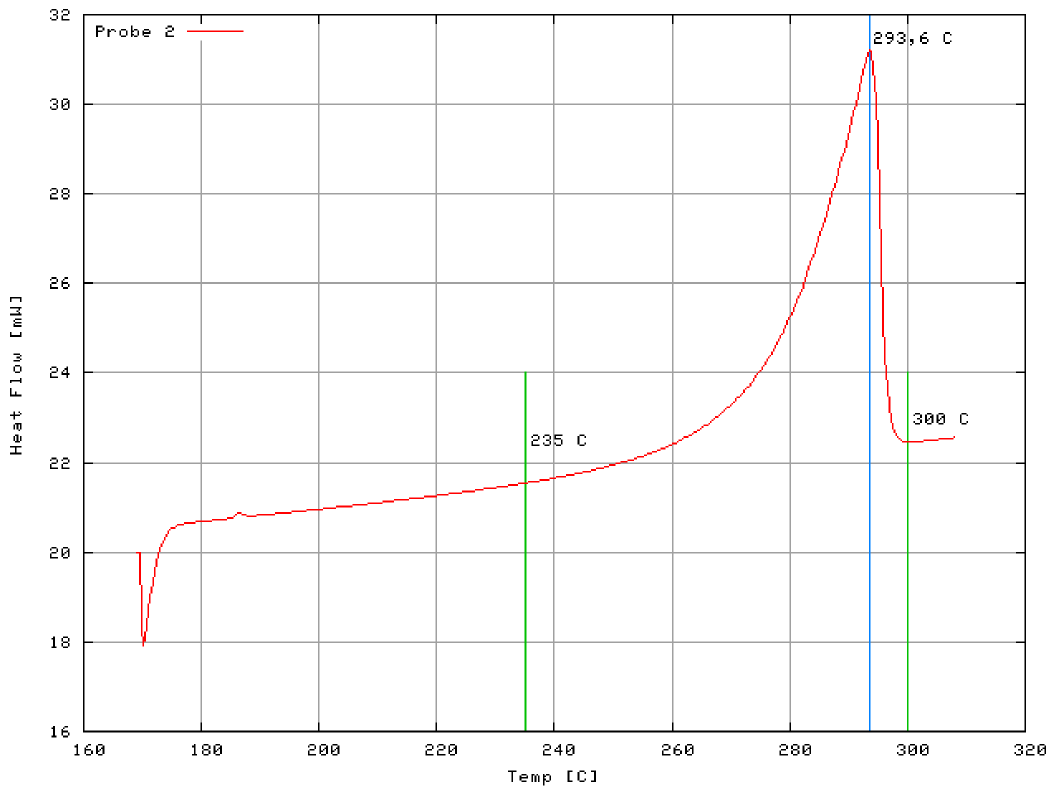

Fig. 2: Plotted results of probe 2

Looking in the given phase diagram we can find a value of 290°C for the transition from solid to liquid. This value can be found in our measured graph, too. The melting begins at nearly 235°C, has its peak at 293.6°C and ends at 300°C. This value corresponds very good to our looked-up value.

We also measured the area covered by this peak as 19 J/g.

2.3 Third Probe

The third sample we put in, contained 32 At% Sn and had a weight of 16.1 mg. We heated it in a range from 100 to 300°C in steps of 20°K/min.

The resulting plot is the following:

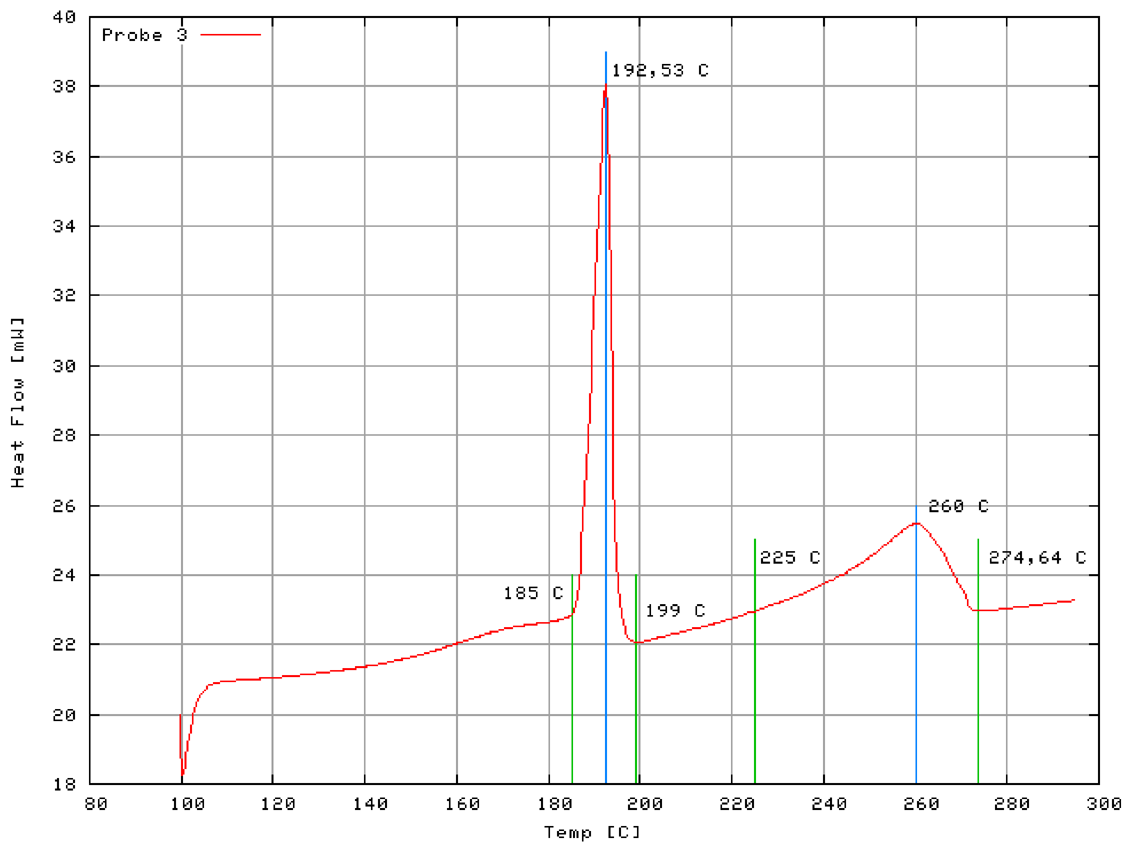

Fig. 3: Plotted result of probe 3

As you can see, the same phenomema as described in ?? occurs: a second peak appears due to kinetics.

The peak we have to consider is the second one. It begins at nearly 225°C, has its peak at 260°C and ends at 274.64°C. The area which is covered by the peak is 13.6169 J/g.

A look in the PbSn-Phase Diagram tells us, that the border between solid and liquid at 32 At% Sn is at 275°C, which is very close to our measured value.

2.4 Fourth Probe

The forth sample we examined weighted 53.2 mg and consisted of 55 At% Sn. Again, we measured in a range from 100°C up to 300°C in steps of 20°K/min.

We got the following graph as a result:

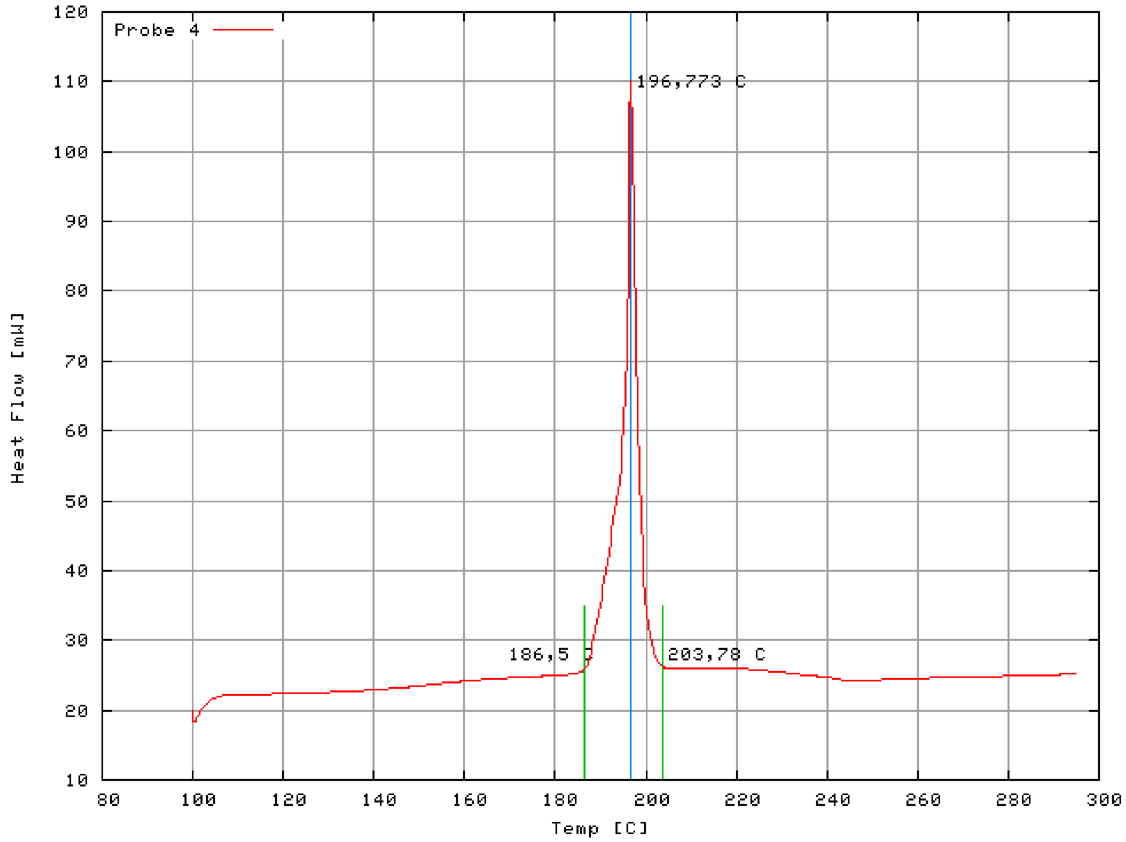

Fig. 4: Plotted result of probe 4

We can see the peak is beginning at 186.5°C and ending at 203.78°C. Its maximum is at 196.77°C. The measured area of the peak is 62,775 J/g.

This peak again is near the eutectid temperature, so we can consider it again as an effect due to kinetics.

To find out the point of phase transitions we have to take a deeper look at the area beyond the eutectid temperature.

By doing this, we can see, that the curve decreases a bit, that means, that another reaction has to occur here.

The minimum lies at 245.4°C, this point is the Liquidus, that means the point where all material is in a liquid state.

So by looking in the phase diagram again we can find the Liquidus at 235°C, which is nearly what we measured.

Perhaps our probe contained a bit more than 55 At% of Sn, that would explain the small deviation.

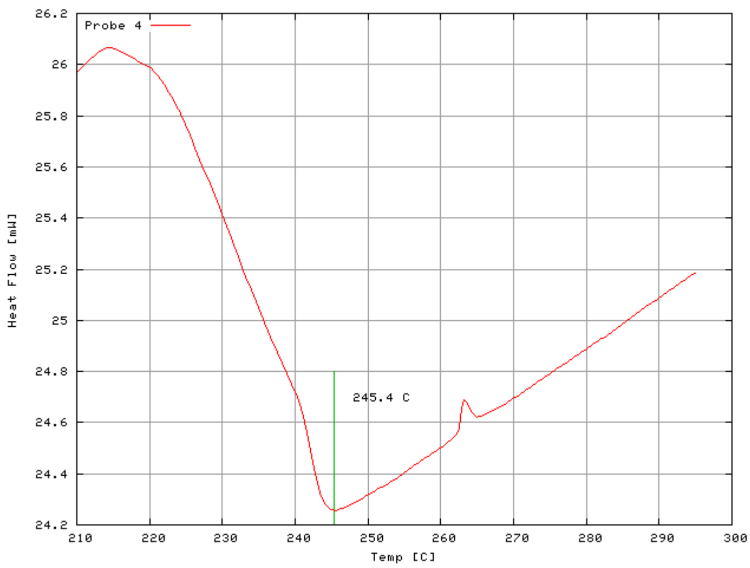

Fig. 5: liquidus of probe 4

2.5 Fifth Probe

The fifth probe weighted 22.7 mg and contained 73.9 At% Sn, that means this probe is the eutectid one. By the first measurement the melting began at 186°C and ended at ca. 200°C. The area covered was 59.57 J/g. As we can see in the first plot the peak is buckling a bit at the beginning. This is caused at the point the specimen is changing its shape and is due to the effect that the melted material does not wet the complete bottom of the oven.

As we would expect at the eutectid point a very sharp peak, we try to get the first measured peak sharper by annealing the probe.

We made smaller steps in heating (10°K/min) and heated the probe to 160°C, stayed at this temperature for a minute and heated then up to 193°C. We repeat this step with even smaller steps (5°K/min). As we can see in the plots Fig. 7 and Fig. 8

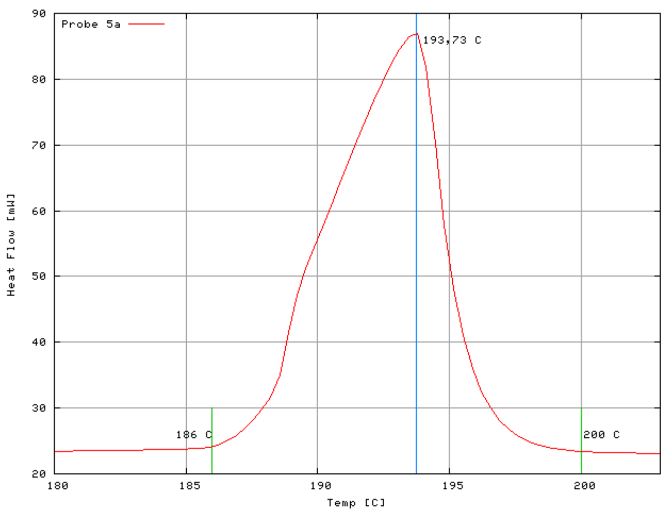

Fig. 6: plot of the first measurement

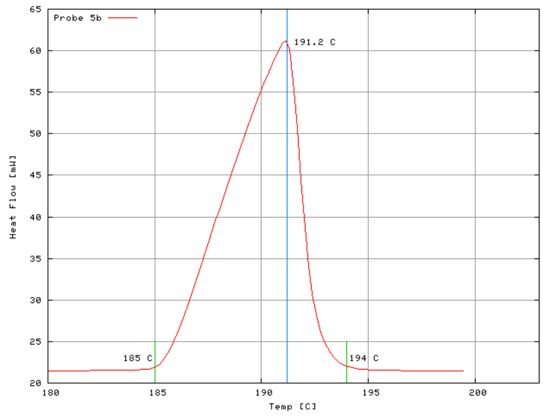

Fig. 7: plot of the second measurement

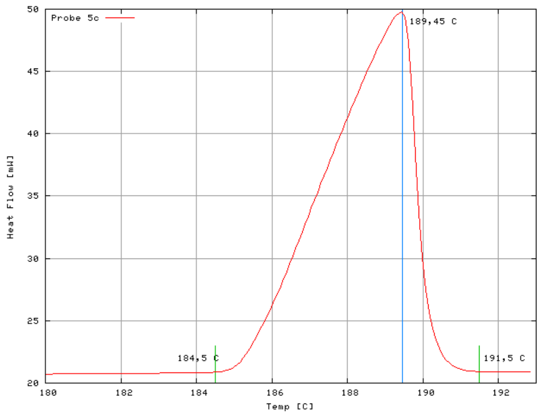

Fig. 8: plot of the third measurement

the peak is getting smaller and sharper.

Due to the fact, that it takes a certain time until the thermal signal arrives, you can't get the peak as sharp as you want.

All results you can see in Fig. 9.

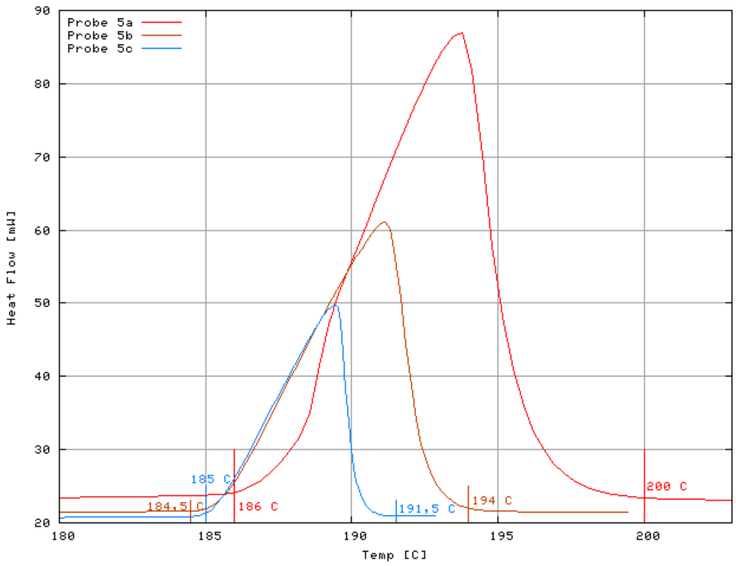

Fig. 9: plot of all results

2.6 Sixth Probe6

The last probe we examined contained of 82 At% Sn and had a weight of 23.4 mg. That means we are in the hypereutectic region. Again we heated the probe from 180°C up to 220°C in steps of 20°K/min.

The result we got by measuring is depicted in Fig. 10.

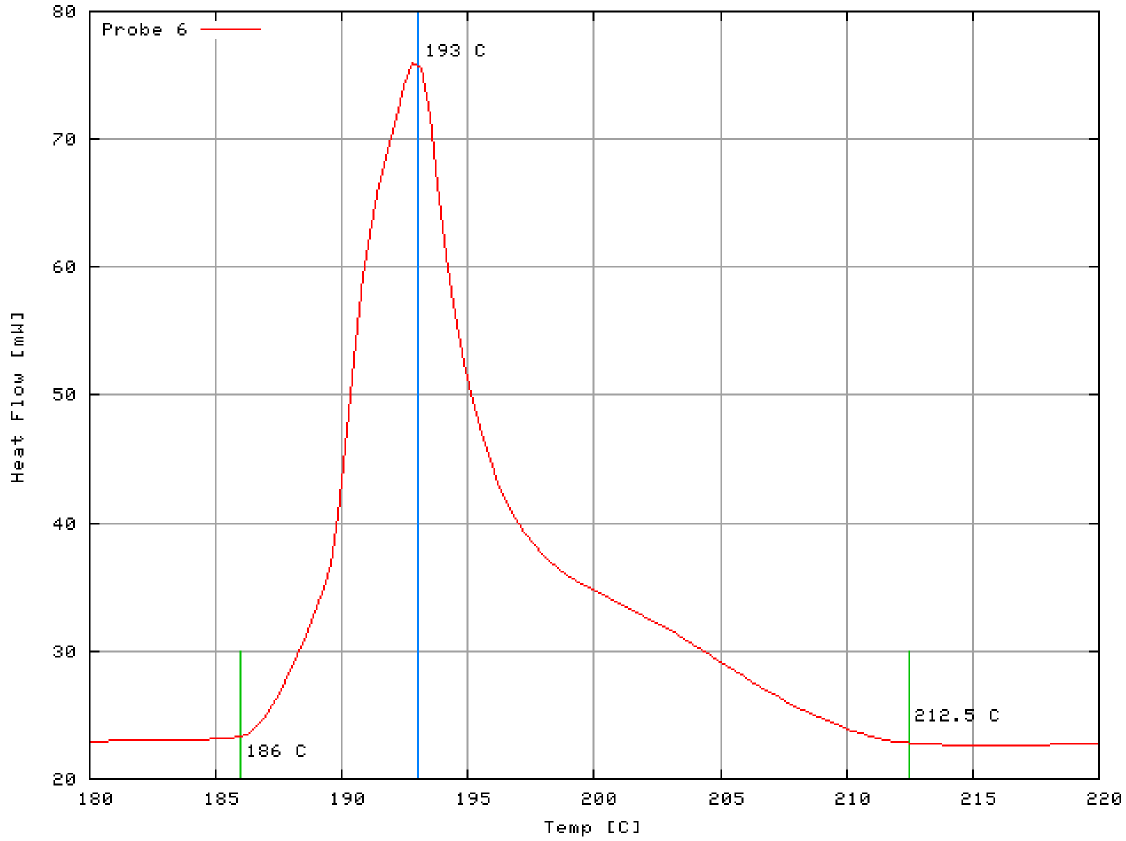

Fig. 10: plot of the measurement of the sixth probe

As you can see, you can't determine where the peak ends which is due the kinetics at nearly the eutectid temperature and where the melting sets in.

The area covered by both peaks is 71.54 J/g. The Liquidus is at 212°C.

A look in the phase diagram of PbSn gives as a Liquidus at nearly 200°C. That means our measurement is in the right region.

3 Additional Tasks

3.1 Characteristic Temperature as a function of composition

We had to do a plot of the characteristic temperatures as a function of the composition.

For the plot we took the temperature, where the melting sets in, where it has reached its maximum and where it ended.

By doing so, we got the following result:

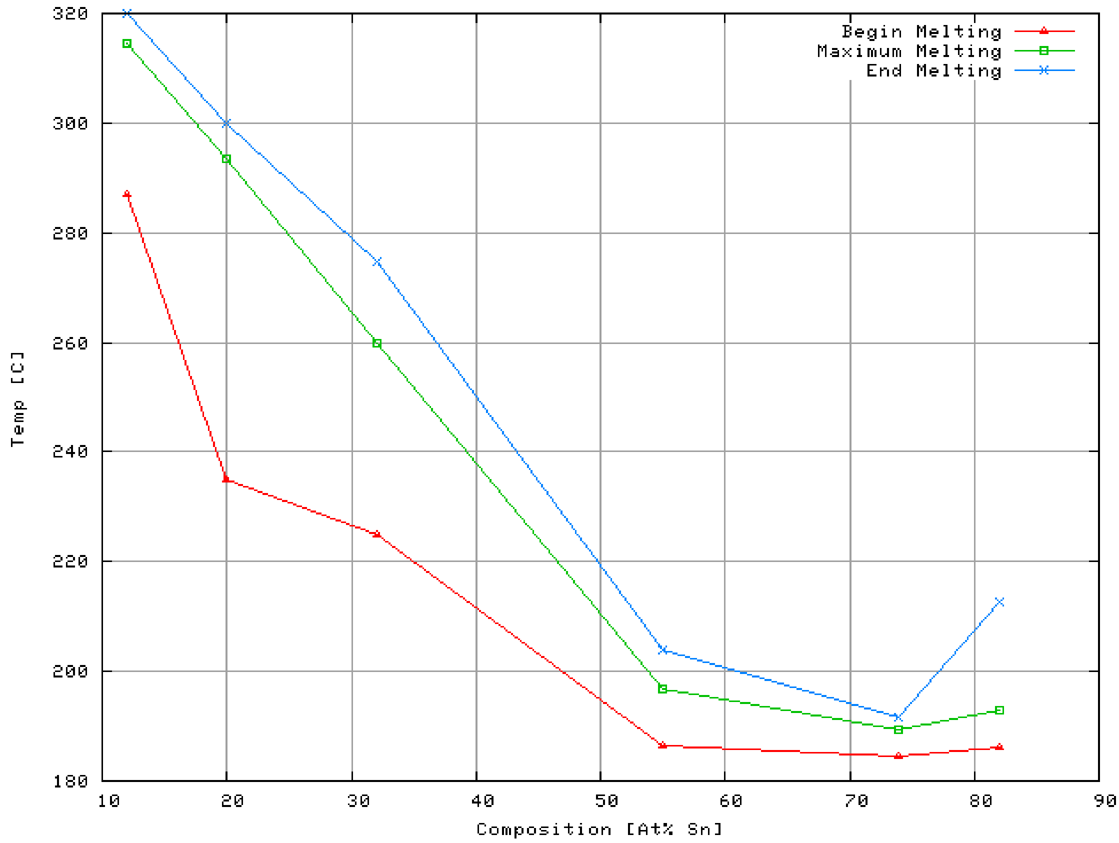

Fig. 11: plot of the characteristic temperature over the composition

We can see that the melting temperature decreases the higher the atomic percentage of Sn gets. This is what we expected, as the melting point of pure Sn is much lower than the one of pure Pb: the melting point of pure Sn lies at 231°C and the one of pure Pb at 327.5°C.

3.2 Enthalpy of fusion as a function of composition

Another plot we were asked to do is a plot of the enthalpy of fusion as a function of composition.

Doing the plot we got the following results:

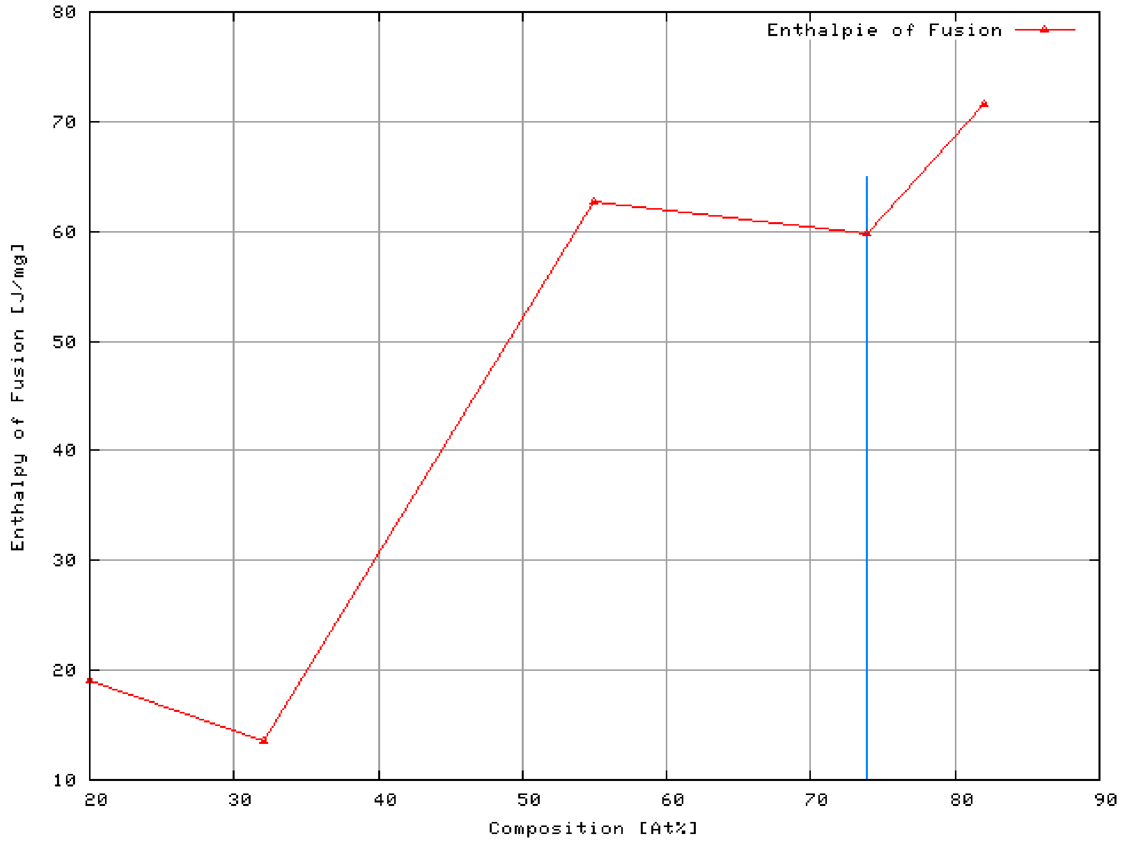

Fig. 12: plot of the enthalpy of fusion over the composition

This plot differs a lot from the one we expected (fig. 13). First the results are quite in the right region: the enthalpy of fusion gets more as the composition approaches the eutectid point.

But after the eutectid point the enthalpy of fusion doesn't get smaller! This may be due the fact that in the last measurement we didn't anneal the probe and therefore enthalpy which is from kinectic effects is contained in the measured area.

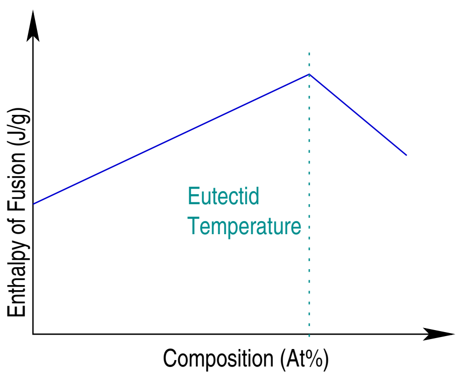

Fig. 13: expected graph

3.3 Melting Points of different materials

We found the melting points of the given materials as following:

Element	Melting Point
Pb	327°C
Au	1063°C
Fe	1535°C
Re	3180°C
W	3410°C

We suggest that the melting point depends also on the following aspects:

- **Bulk and Youngs Modulus** In higher the Bulk/Youngs Modulus is, the higher would we expect the melting temperature, because the material is “harder“, that means the changes in the volumina are not so high at high Bulk/Youngs Modulus.
- **Debye Temperature** The higher the Debye Temperature is, the higher should be the melting point.
- **Lattice Errors** A material which has a lot of Lattice Errors, especially imperfections, the lower would we expect its melting point.
- **Lattice Parameter**