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THE CONSTRUCTION OF A SENSITIVE MICROCALORIMETER

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SUMMARY

The construction of a small differential calorimeter with a temperature range between 273 K to 373 K is described. The calorimeter is power compensated with adiabatic surroundings. The sample volume is 2 ml. In the most sensitive mode the noise level is below 0.4 microwatt. The α-β phase transition in paradichlorobenzene is used to demonstrate its performance.

INTRODUCTION

We wanted to construct a small microcalorimeter with a high sensitivity for measuring phase transitions in binary solid solutions. The apparatus to be described uses most of the electronic equipment of our adiabatic calorimeters (ref. 1), so not always the most economical solution may be chosen.

CONSTRUCTION

The apparatus is depicted in figure 1. The sample and the reference holder (a and b) are clamped to a peltier element (Melcor type FCO-6-66-06).
Both holders are equipped with two heaters, one of each heaters is connected in series to deliver the basic heating power. The other heaters are used to compensate the difference in energy needed to keep the holders at the same temperature. The holders are connected to two thin-walled stainless steel tubes. Holes in these tubes are used for the feed-through of the wiring. The adiabatic shield (c) is also connected to these tubes. The temperature difference between this shield and the holders is detected by a double thermocouple (copper-constantan). At the bottom of this shield a 100 ohm platinum thermometer is placed. The second shield is also connected to the tubes, a single thermocouple detects the temperature difference between the shield. The tubes rest on the cooling block (G), cooling of this block can be achieved by circulating cold nitrogen gas through it. A third shield (E), also equipped with a heater can be used to keep the environment constant. A radiation shield (F), resting on teflon spacers surrounds the whole system. The outer can is evacuated with an oil-diffusion pump.

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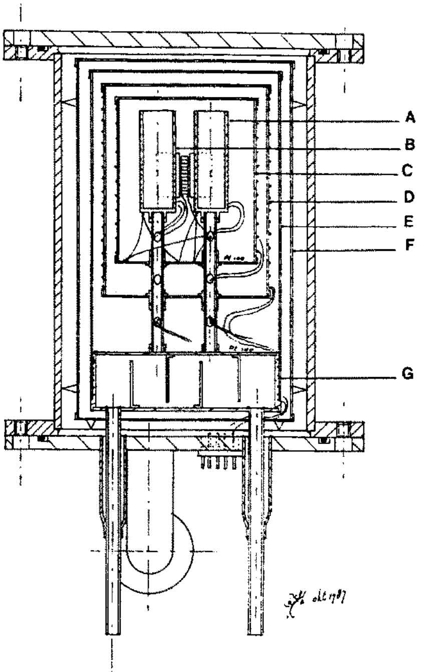

Fig. 1. The microcalorimeter. (a) and (b) sample cup holders. (c) First adiabatic shield. (d) Second shield. (e) Cooling shield. (F) Radiation shield. (G) Cooling block.

Electronics and regulation

The first shield is regulated at the same temperature as the holders. The thermocouple signal is amplified using a Keithley 135 amplifier. The output of the amplifier is sampled with a 12 bit A/D convertor, an Apple microcomputer collects these data and calculates

$$D/A = [p.(A/D\text{-setpoint}) + I.\Sigma\ (A/D\text{-setpoint})]^{\frac{1}{2}}$$

in which

D/A = analog signal made by a 12 bit D/A convertor used to set the current
A/D = value read from the A/D convertor
p = proportional factor
I = integral factor

The second shield is regulated in the same way, its temperature is kept about one degree below the first shield. For the basic heating power a 0-40 mA constant current source is used. The on-off switch is controlled by the measuring computer (a HP 9816). Two ten turn 1000 ohm potentiometers are connected parallel to the heater. This allows for compensating differences in heat capacity between the vessels. The temperature is measured with an ASL F17 resistance bridge. The signal of the peltier element is measured with a Keithley 148 nanovoltmeter. The output of the nanovoltmeter is read into the measuring computer with a digital voltmeter. The current used to compensate the difference in temperature between the holders is proportional to the square root of a proportional factor times the temperature difference. Depending on the sign of the temperature difference the current is switched to the left or to the right holder. A Keithley 220 programmable current source is used .

Vessels

The measuring vessels are made of gold plated copper. In the neck of the vessels a sharp stainless steel rim is soldered. A gold plate is pressed against this rim to assure vacuum tightness. The maximum sample volume is 2 ml.

RESULTS

The noise level of the measurements depends on the setting of the amplification factor, the signal of the peltier element can easily be regulated to within 0.1 microvolt, resulting in a noise level below 0.4 microwatt. In figures 2 and 3 a few examples of the α-β phase transition in para-dichlorobenzene are given. The sample mass was 0.12 grams. Figure 2 gives the transition of the freshly prepared compound, the preparation was done by zone-levelling (ref. 2).

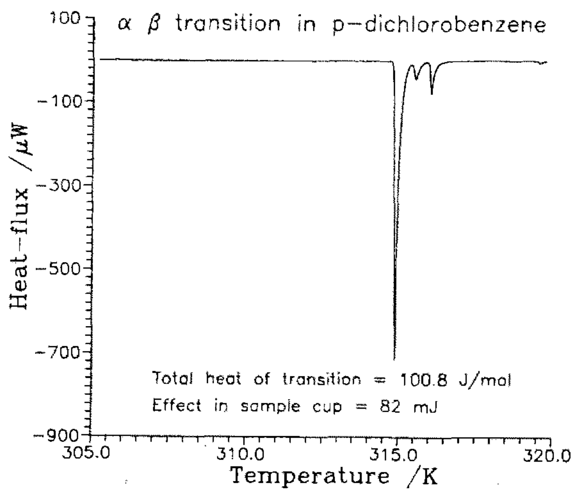

Figure 2

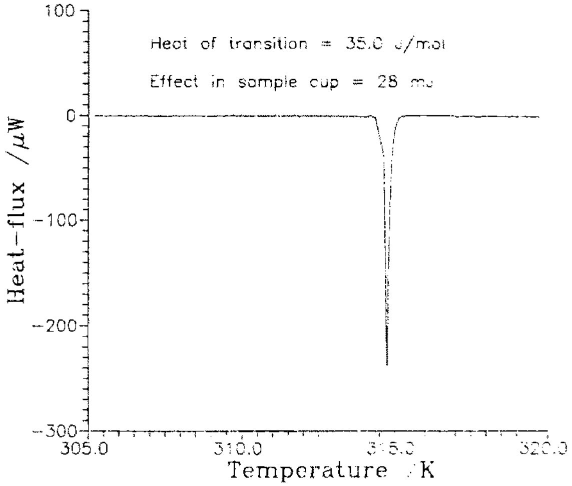

Figure 3

Figure 3 gives the transition in the same sample after it has been heated to 320 K once and was kept at 290 K for 3 days. In this case only a part of the sample has returned to the α phase.

CONCLUSION

The described apparatus is very well suited for measuring small heat effects. Its construction is relatively simple and the operation is easy.

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