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HOW TO MEASURE ROUTINELY SPECIFIC HEATS OF SOLIDS BELOW 150K?

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ABSTRACT

Advantages and disadvantages of adiabatic calorimeters (ADC) and differential scanning calorimeters (DSC) are compared in the temperature range between 100K and 200K. Recent experience with a plateform-type, easy to handle, low heat capacity and highly reproductible sample holder in an adiabatic calorimeter is reported. This sample holder which avoid most disadvantages of earlier adiabatic installations can be used to measure any type of sample: solid, liquid, powdered. The performance of the sample holder is illustrated by comparison of the heat capacities of phosphorous, sapphire and Duran-glass, measured by DSC and ADC from 100K to 200K.

INTRODUCTION

The specific heat is the key thermal property of solids which enable to calculate the basic thermochemical functions and to characterize phase transitions and reaction cinetics. In the temperature range above 120K thermal analysis has seen a rapid development in instrumentation and automatization, i.e. on line data registration and computation by application of recent progress in electronics and microcomputers. It is today standard practice to determine heat capacities above 120K by use of commercially available instruments, mostly scanning calorimeters (DSC). Accuracies of better than ±1% can be achieved [1]. Measurements below 100K, however, have been neglected somewhat in the past, due to technical difficulties and the time consuming procedure [2]. Naturally the application of microcomputers played an ever increasing role in setting up automatic low temperature calorimeters [3]. These calorimeters, however, have been designed mostly for special applications as for limited temperature ranges, for metallic samples etc.

It was our aim since many years to construct automatic, highly flexible, easy to handle low temperature calorimeters as a routine technique which enable to investigate the specific heat of any type of samples. Thus this report describes the heart of such an adiabatic calorimeter, the plateform-type sample holder [4], the recent experiences with this istallation, its flexibility and its performance which are demonstrated by measuring different samples between 100K and 200K and comparing the results to those received by DSC-measurements.

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COMPARISON OF DIFFERENTIAL SCANNING (DSC) AND ADIABATIC CALORIMETERS (ADC).

Table 1 presents a self explaining listing of advantages and disadvantages of the two types of currently used calorimeters in the temperature range from 100K to 200K: DSC and ADC. This temperature range is rather delicate for both methods due to the different type of heat exchange between sample and surrounding: exchange gas or radiation (see also table 1). The temperature of about 120K represents the lower limit of the commercial non-adiabatic DSC-apparatus as well as the upper limit of simple adiabatic instruments, working with only one adiabatic or isothermal shield. Therefore this temperature range is of special interest, because the accuracy of both methods can be compared and measurements with both types of calorimeters (ADC and DSC) enable to rule out systematic errors.

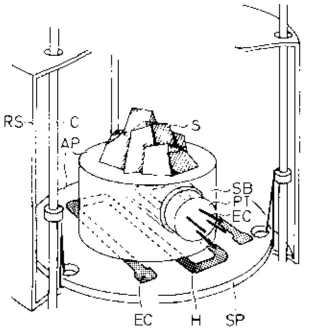

Fig.1 Plateform-type sample holder

C-support for sample holder
SP-sapphire plate
SB-sapphire bloc
S -sample
PT-Platinum thermometer
H -NiCr-heater
RS-radiation shield
EC-electrical connection
AP-Apiezon N grease

TABLE 1: COMPARISON OF ADVANTAGES AND DISADVANTAGES OF THE DSC.-AND ADC-METHOD

CHARACTERISTIC FEATURES OF	DSC	ADC
PRECISION	(1)-3%	0.1 - 1.5%
STABILITY OF CALIBRATION	REASONABLE	GOOD TO EXCELLENT
RESOLUTION FOR PHASE TRANSITION	VERY GOOD	REASONABLE
MEASURING TIME	HOURS	DAYS
SAMPLE MASS	1-50MG	50MG-GRAMMS
HANDLING	EASY	NOT EASY
AUTOMATIZATION	GOOD	GOOD
FLEXIBILITY	DEPENDING ON	PROBLEM
SYSTEMATIC ERRORS BY	CONDENSATION OF ICE/EXCHANGE GAS INFLUENCE/ DEPENDANCE ON HEATING RATE	BAD THERMAL CONDUCTIVITY OF SAMPLE/ UNCONTROLLED THERMAL RADIATION

EXPERIMENTAL

The fully automated process controll, data recording and analysing system to measure specific heats in the range 0.3 T 300K has been described in Ref. [3]. This calorimeter has not been designed to allow ultrahigh accuracy, i.e. 0.1%, rather than medium accuracy (0,5-1,5%), but the highest possible flexibility. The central part of the instrument - the plateform sample holder - has been also described in its technical details, recently [4]. Therefore only the most significant feature will be outlined here.

The sample holder (fig.1) consists of a sapphire disc (diameter ∅=20mm, thickness d=0,1mm) on which a NiCr heater of about 1KOhm has been evaporated. The Germanium or Platinum thermometric resistor is housed in a further Al_2O_3-block (∅=10mm, d=5mm) as illustrated in fig.1. The samples are deposited onto the Al_2O_3 block by applying a slight coat of Apiezon-N grease. We emphasize that the sample holder is a rigid installation in the calorimeter and its heat-capacity must not be measured separately for each unknown sample. In consequence this construction fulfils all requirements of a nearly perfect sample holder for adiabatic calorimetry:

(i) low heat capacity because of the high Debye temperature of Al_2O_3 *), allowing for measuring samples with a typical weight of 10-200mg

(ii) high reproducibility, guaranteed by the rigid installation. The change in heat capacity within 4 years during more than 100 experiments and 9 determinations of the sample holder heat capacity was less than 0,35%.

(iii) Easy handling and quick exchange of the samples (minutes) by locating the crystals onto the Al_2O_3 block.

(iv) Excellent thermal contact in general.

(v) Possibility to measure air sensitive samples or liquids. These samples are encapsulated into a bottle-like DURAN-glass-container which has a flat bottom. The container is placed on the plateform sample holder. Many experiments showed that the ratio of heat capacities of glass to sample usually amounts to a value of about 1:1. The holder has enhanced considerably the reliability of our calorimeter.

The DSC-measurements have been performed with a Perkin-Elmer DSC-2 instrument, which is controlled by an HP-9825 computer in order to measure entirely automatically heat capacities between 110K and 700K in succeeding intervals of 20K to 50K [7]. The use of the computer lead to a considerable time saving and increased the accuracy by a factor of 2 to 5 being 0.8% to 2% typically.

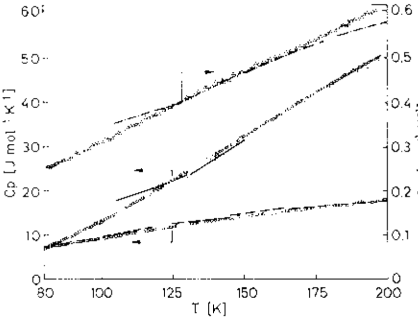

Fig.2 Heat capacities of:
DURAN-glass: ADC(△△△),DSC(—·—)
Sapphire: ADC(○○○),DSC(——)
literature(++)
Phosphorous: ADC(□□□),DSC(- - -)

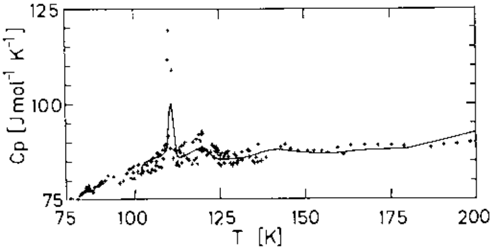

Fig.3 Specific heat of $TlGaSe_2$ near the ferroelectric transition
+++++++ ADC-measurement
——— DSC-data

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*) Very recently we have suppressed the sapphire block and how we use either evaporated Pt or Ge-exposed-elements (being only the inner tiny Ge-resistor without the metalhousing) as thermometer which are directly located on the sapphire disc beside of the heater. By this way the heat capacity was again reduced by a factor of 10.

RESULTS

Some typical results, taken with our ADC and DSC are plotted in fig.2. The data of amorphous phosphoros (powder pressed) show that both methods agree within 2%, no systematic errors occur. The agreement is even better for the Al_2O_3-data: the values of the literature and the two sets of experimental data coincide to better than 1%. However, there is a deviation below 120K of the heat capacity determined with the DSC. This systematic error often occurs in this temperature range and is attributed to inaccurate temperature calibration and influence of heat exchange gas in the DSC because the lowest calibration temperature was 128K (Hexafluorethane). The results for DURAN-glass illustrate problems in connection with adiabatic calorimetry: Above 150K a more precise shield control is needed: two adiabatic shields which follow the sample temperature within mk-differences instead of one isothermal shield. The DSC-data are the correct ones in the temperature range $130 < T \leq 200$K, but below 125K again a systematic error occurs. Fig.3 represents the specific heat of $TlGaSe_2$ near its ferroelectric transition point. These measurements illustrate impressively that sometimes one of both calorimetric methods should be preferred; in the present case the DSC. The large scattering of experimental data, measured by ADC is due to the very poor heat conductivity of $TlGaSe_2$ near 120K. The thermal relaxation time of the sample was about 30 min.

CONCLUSION

From our experiments with DSC and ADC we conclude that the performance of both methods in the considered temperature range are comparable and complementary. The overall precision of DSC is lower than that of ADC below 200K, it mostly provides adequate or higher precision (and more comfort) at measurements above 200K. On the other hand the measurement of small samples (mg) and former time consuming procedures are no longer a limitation for adiabatic calorimeters. ADC still is the only reliable method to determine heat capacities below 120K, whereas DSC-apparatus govern the region above 200K. It is well known to any calorimetrist that gratest caution has to be taken to avoid systematic errors. Therefore the intermediate range ($100 < T < 200$) offers a possibility to check both types of instruments, ADC and DSC. It remains a challenge for the future to develop reliable low temperature scanning calorimeters.

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