ELSEVIER

Thermochimica Acta 304/305 (1997) 1–26

thermochimica
acta

Review

Classical temperature-modulated calorimetry: A review

Eberhard Gmelin*

Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Heisenbergstrasse 1, Germany

Received 10 November 1996; accepted 24 February 1997

Abstract

The historical, methodological and technical development and the applications of temperature-modulated calorimetry (also known as AC calorimetry) are reviewed over the last three decades, up to about 1992. Modulation calorimetry (MC) is compared with other calorimetric methods. Particular emphasis is given to temperature scanning and frequency-dependent heat capacity experiments. Recent advances in MC, in particular the combination of differential scanning calorimetry (DSC) and modulation technique – the temperature-modulated DSC (TMDSC) – is discussed in view of measured dynamic specific heat. The theoretical models worked out before 1990 are briefly described. The limiting boundary conditions for dynamic calorimetry are critically discussed. Some selections of experimental setups for MC, selected among about 200 citations given here, exemplify by their characteristic experimental parameters the broad variety of existing possibilities to carry out temperature-modulated calorimetric experiments. © 1997 Elsevier Science B.V.

Keywords: AC calorimetry; DSC; Dynamic calorimetry; Heat capacity measurement; Modulation calorimetry; Review

1. Introduction

In the last three decades, precision and resolution of calorimetric methods increased significantly by the application of improved non-adiabatic and/or dynamical methods, as AC calorimetry [1–3] – which we call by the following more appropriate term *temperature-modulated calorimetry* (TMC), differential scanning calorimetry [4,5], heat-pulse (or relaxation-time) calorimetry [6,7], continuous heating calorimetry (DSC) [8,9] and the revived 3ω method [10], introduced by Corbino in 1910 [11]. The recent application of *temperature modulation* to differential scanning calorimetry (DSC) resulted in the construction of the temperature-modulated scanning calorimeter (TMDSC) [12]. This had a profound impact on the technical development of both DSC and TMC equipment, on the underlying theoretical background of these *dynamic* instruments as well as on the physics and chemistry of the measured values, e.g. dynamic heat capacity and related kinetic mechanisms.

Modulation calorimetry, better known to physicists as AC calorimetry, was introduced in 1968 by Sullivan and Seidel [1,13,14] and Handler et al. [2], simultaneously. Today, it is a well-established, reliable and widely used – now 'classical' – calorimetric method particularly suited for the investigation of small samples and good caloric resolution at all temperatures. The method is theoretically well understood ([1,5, 15–22]; for more Refs. see Table 5). It has been set up in widely different types of experimental arrange-

---

*Corresponding author. Tel.: +49 711/689 1366; fax: +49 711/689 1010; e-mail: gmelin@tilux.mpi-stuttgart.mpg.de.

PII S0040-6031(97)00126-3

ment (see Section 4) and used at very low ($T < 1$ K) and very high temperatures (up to 3600 K) as well, including linear temperature scanning, measurement of frequency-dependent heat capacities ([5,10,16,21–30]; see also Table 5) and time dependence of specific heat [10,31–34]. However, in most experiments, the information from the phase of the temperature signal was not utilized. The frequency dependence of the heat capacity was scarcely studied over more than one-and-a-half decades and the frequency range remained usually restricted to the (1–10) Hz range. On the other hand, *differential scanning calorimetry* is widely used in physics, chemistry and material science in the temperature range from 100 to ≈2000 K. It is accepted as a useful tool for the investigation of chemical reactions, phase transitions, a source of thermodynamic data and for establishing phase diagrams. Since they are commercially available, the instruments are widely used in industrial research and production control. In recent years, the theory of DSC and its understanding progressed considerably [35–39], and some shortcomings were understood and can be accounted for or compensated today [36–39]. The combination of DSC and TMC techniques, however, led to some confusion and misunderstanding in the last three years with respect to the interpretation of data gained with TMDSC. Although TMC and DSC by themselves are understood rather well in most details of heat flow and internal thermal relaxation times, it turned out that the simultaneous effects of temperature scanning *and* periodic heating/cooling are not described sufficiently by the present models. The essential implication of TMDSC originates from the fact that, besides the temperature-dependent heat capacity, the frequency dependence of heat capacity becomes involved. Hence, any type of relaxation phenomenon, being intrinsic to the sample studied and/or characteristic of the calorimetric cell used (heat resistances), influences the experimental results. TMDSC should, strictly speaking, be called spectrometry. It enables measurement of $C(T,\omega)$, the *dynamic* heat capacity that is as a function of *temperature and frequency*. This feature, at first glance, appears surprising since heat capacity is in general considered to be a static thermodynamic quantity. More drastically, it can be expressed as follows: thermodynamically non-equilibrium properties can be studied with temperature scanning methods at various scanning rates. This situation necessitates recalling the concept of dynamic heat capacity and considering how the heat capacity depends on the time scale of the experiment. Similar to the concept of treating real and imaginary parts of physical parameters, e.g. impedance, susceptibility, dielectric constant, sound velocity or optical absorption, the specific heat displays real and imaginary contributions. Indeed, the mathematical fundamentals of dynamic/complex heat capacity are already described in literature [40,41]. It is referred, in analogy to the mechanical modulus (stress/strain ratio), to the general response theory in order to extend the definition of the static specific heat to a dynamic one. There is, however, an essential difference between the imaginary part of heat capacity and the imaginary part of other physical properties. The latter are normally related to dissipation processes. That is generally not true for heat capacity, because heat is not converted to other forms of energy. Whenever, an imaginary term exists, the entropy increases. However, for heat capacity phenomena, the phonon system acts usually as a thermodynamic heat reservoir, and during storage and loss of heat by samples, the intrinsic relaxation phenomena remain in most cases reversible when averaged over a sufficiently long time (i.e. chemical reaction are excluded). The reader may find more details on that tricky problem in the contributions by Donth et al. [46], Jeong [47], Schawe [48] and Wunderlich et al. [45].

In this paper, as foundation for the discussions in the IV Lähnwitz Seminar, and to arrive at a better understanding of TMDSC, the historical, methodological and technical developments of MC are traced, the particularities outlined and future prospects discussed. Section 2 of this review describes the fundamentals of modulation calorimetry and outlines its historical development. In Section 3, MC is compared to other classical calorimetric methods and advantages and disadvantages of MC are listed. The present knowledge on modelling MC and the critical boundary condition for application of MC is discussed in Section 4. Then, in Section 5, we refer to a selection of typical methodological and experimental arrangements, described in the literature. Finally, we conclude with a summary of the critical parameters and conditions for MC and TMDSC and outline possible future developments and requirements.

It is a necessary, to draw attention here to the many expressions and abbreviations used for *temperature* modulated calorimetry, e.g. alternating-current (ac, or AC), alternating-heating/cooling, periodic, oscillatory-, undulatory-heating method, etc. that will lead, in future, almost to confusion. As one example, the frequency of heating could increase linearly in an isothermal experiment; the result: frequency-modulated calorimetry. Therefore, according to the results of discussions during the present workshop, we use the term 'temperature-modulated' calorimetry or TMDSC; by analogy, it is proposed to use power-modulated, frequency-modulated, thermal-radiation modulated calorimetry, etc.

Finally, the author notes that this review was consciously restricted to the development of MC before the appearance of a commercial TMDSC instrument in 1992 [12]. Also, it does not include details on the so-called 3ω-method that is described in detail in Refs. [10,47].

2. Fundamentals and history of temperature modulated calorimetry

2.1. Historical

The first measurements of specific heat, by the modulation method, were performed by Corbino in 1910/11 [11]. Corbino developed the theory and indicated how to use the resistance of electrically conducting samples to determine the temperature oscillations. He detected oscillations of the resistance either by passing an additional alternating current, the frequency of which was equal to that of the temperature oscillations, or by recording the amplitude of the third harmonic signal. The latter method is the basis of the so-called '3ω method', which today finds rapidly increasing application, also due to the recent development of TMDSC and increased interest in complex heat capacity.

The basic and characteristic steps of the historical development of TMC are compiled in Table 1. Remarkable advancement was then made in the beginning of the sixties. The progress achieved, from 1960 to 1965, by Rosenthal [49], and Filippov and Yuchak [50], refer to the high-temperature range, where metallic or refractory samples were investigated and the (oscillating) sample temperature was detected by measuring the sample resistance or the sample's thermal emission. In 1962, Kraftmakher developed AC calorimetry and measured heat capacities of metals up to 3600 K [51]; subsequently, in 1981, applying also 'high' frequencies ($> 10^5$ Hz) [52]. Unfortunately, the comprehensive work of the Russian groups in the field of high-temperature TMC is less well known [see Ref. [5] for further references].

Table 1
Important steps in the historical development of modulation calorimetry

Year	Subject	Authors	Ref.
1910	General theory of principle of 3ω method	Corbino	[11]
1911	First application of third-harmonic principle	Corbino	[11]
1922	Use of thermionic current oscillations	Smith and Bigler	[89]
1960	Development of third harmonic (3ω) method	Rosenthal	[49]
1962	Bridge circuit for wire sample at $T > 1200°C$	Kraftmakher	[51]
1963	Application of photodetectors	Loewenthal	[90]
1965	Heating by electron bombardment	Filippov and Yuchak	[91]
1966	Modulated resistive-heating and low-temperature experiments	Sullivan and Seidel	[1]
1967	Modulated light-heating	Handler et al.	[2]
1974	High-pressure calorimetry	Bonilla and Garland	[59]
1979	Improvement of light-modulated method, measuring of thermal diffusion coefficient	Hatta/Ikeda and Ishikawa	[21,92]
1981	High-frequency relaxation ($> 10^5$ Hz)	Kraftmakher	[93]
1986	Specific heat spectrometer	Birge/Dixon	[23–25]
1989	Ultra-small sample measurement ($< 100\,\mu g$)	Graebner/Inderhees	[19,170]
1991	Temperature-modulated DSC (TMDSC)	Reading, Elliot and Hill	[12]

A landmark in the TMC history was the new method introduced by Sullivan and Seidel, and Mapother et al. in 1966/67, subsequently called *AC calorimetry* [1,2,13,14]. Using external light or resistive heating with the sample on a sample support, the method enables one to determine the heat capacity of any type of sample if certain restrictions concerning thermal relaxation times are kept in mind. Some of the numerous, and very different installations, as described in the following years in the literature, will be briefly characterized in Section 5. Among those are applications to measure heat capacities – near phase transition with high-caloric and high-temperature resolution ($<10^{-5}$) [21,30,53–58,65,67–70], at high pressures by Bonilla and Garland and others [18,53,56,59–63], in high magnetic fields [13,19, 30,63,68], with extremely small samples (25 μg) by Graebner [19] and also other groups [65–67,71–73], the thermal diffusivity measurements (on thin films by periodic heating) [20–22,74], experiments in noisy environment [68] and experiments with extremely small scanning rates (< 0.1 K/h) [67,70,75]. The method followed the pioneering experiments on the frequency-dependent heat capacity by Birge and Nagel [8,23,24], and Dixon [25] using the 3ω method that has now been further developed [10,76–79]. The interesting development of TMC technologies in the seventies and eighties culminated in 1991 when the TMC principle was transferred to the widely used DSC instruments that led to the present rapidly progressing development of commercial TMDSC equipment [12].

2.2. Principles of classical temperature-modulation methods

While looking at traditional modulation calorimetry, one quickly stumbles upon a clue for the difference between AC calorimetry and TMDSCs: The former is directly related to quasi-adiabatic calorimetry, the latter is a heat-flow instrument. Thus, in the AC-type arrangement, the oscillating temperature (or enthalpy), monitored at the calorimeter cell (sample/sample-holder/heater/thermometer assembly), is thermally directly related to the periodic heat input into the cell. According to Fig. 1, the thermal resistance R_B is rather high and the thermal-relaxation time τ_B of the calorimetric cell is mostly of the order of a few minutes or an hour. The measurement is carried out under *quasi-adiabatic* conditions. In contrast, in the DSC-type instrument, the temperature oscillation in the calorimetric cell itself is produced indirectly: The cell is attached to a heat reservoir, whose temperature oscillates and the oscillating heat flow – from the reservoir to the cell – is registered by a thermometer, which gives an indication of the transferred enthalpy. The latter case corresponds to the TMDSC operational mode. As seen in Fig. 1, R_B is rather low, with τ_B being of the order of a few seconds and the thermometer is located along the thermal link R_B. The measurement is performed under *isoperibol* (i.e. non-adiabatic) condition. The difference between the two types of dynamic calorimeter does not show up if the heat capacity is purely static; however, it generates significant differences in the time dependences of the temperature amplitude as well as in the phase behaviour when the heat capacity is complex, i.e. possesses an imaginary contribution. The calorimeters described below are all of the 'AC' type. The 'DSC' type calorimeters are discussed in Refs. [12,42–45,48].

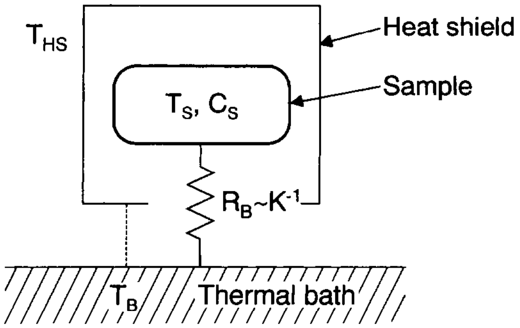

Fig. 1. Principle arrangement for a calorimetric measuring cell. T_B – temperatures of thermal bath; T_{HS} – heat shield; T_S – sample; K_B – thermal link with conductance (or R_B – thermal resistance), respectively: and C_S – sample heat capacity.

Modulation calorimetry consists in generating a periodic oscillation of power $P(t)$ with the frequency 2ω that heats the sample (having a heat capacity, C_S) and in recording the resulting temperature oscillations $T_{AC}(t)$ as a function of time. The measured temperature oscillates with the same period and an amplitude $\Delta T_{AC}(t)$ around a mean temperature T_M. A phase shift ϕ develops between $P(t)$ and $T_{AC}(t)$ due to the finite thermal resistance R_B (or thermal conductance K_B) between the sample/sample-support ensemble and its surrounding (thermal bath, T_B and the heat shield, T_{HS}, and the general situation: $T_B \approx T_{HS}$). The principle of such a calorimeter is shown in Fig. 1. The basic relations for a modulation calorimeter result from the following common equation that describes in its simplest form any calorimetric system as shown in Fig. 1:

$$P(t) = C_s(\mathrm{d}T/\mathrm{d}t) + K_B(T_S - T_B) \qquad (1)$$

If one drives the heater with a current $I = I_0 \cos \omega t$, then Joule heating occurs at a frequency 2ω at the heater. Eq. (1) then modifies to:

$$P(t) = P_{AC}e^{i2\omega t} = i2\omega C_S \Delta T^*(t) e^{i2\omega t} + K_B \Delta T^*(t) e^{i2\omega t} \qquad (2)$$

The solution $\Delta T(t)$ can be written as:

$$\Delta T_{AC}(t) \equiv \Delta T^* e^{i\omega t} = |\Delta T^*| e^{i\phi} e^{i\omega t} \qquad (3)$$

where ΔT^* denotes the complex amplitude of the oscillations. Introducing the complex heat capacity as $C_S^* = C' - iC''$, the real and imaginary parts of heat capacity, the temperature oscillations and the phase shift (between power and temperature) are given by the following four equations:

$$C' = -(P_{AC}/2\omega|\Delta T^*|)\sin\phi \qquad (4)$$

$$C'' = (P_{AC}/2\omega|\Delta T^*|)\cos\phi - K_B/2\omega \qquad (5)$$

$$|\Delta T^*| \equiv P_{AC}/[(2\omega C_S)^2 + K_B^2]^{1/2} \text{ with } K_B = [P_{AC}/|\Delta T^*|]\cos\phi \qquad (6)$$

$$\phi = \mathrm{arctg}\,\{2\omega C_S/K_B\} \qquad (7)$$

These formulas simplify to the oft-cited equations when dealing with a purely static heat capacity, since in that case $C'' = 0$.

For this simplified system (Fig. 1 and Eqs. (1) and (2)), we must assume that the thermometer is connected to the sample without a thermal resistance and that the mean temperature, amplitude of temperature oscillation and phase shift are the same throughout the sample. We note, that the modulation method requires a heat loss by heat conduction to the thermal bath over R_B (or equivalently, K_B) or by radiative heat to cool the sample after a half-period of heating. As a consequence:

(i) MC can never operate under strictly adiabatic conditions and there always exists a heat flow from the sample to the thermal bath through R_B; and
(ii) if R_B is chosen such that $R_B \gg C_S$, then Eq. (6) yields $\Delta T_{AC} \approx P_{AC}/\omega C_S$ and the phase approaches the value $\phi = -(\pi/2)$. These are the usual working conditions of a traditional AC calorimeter and the system works under quasi-adiabatic conditions.

For all other cases, we must account for heat losses and phase shifts between input power and sample temperature. Therefore, we have to use the full formulas given in Eqs. (6) and (7).

Finally, according to Eqs. (1)–(7), the oscillations are automatically superimposed by a linear temperature increase, given by $\Delta T_{DC} = P_{AC}R_B/2$. An additional DC power is often applied for scanning experiments.

In the general case, Eqs. (4)–(7) contain three items of information: the heat capacity C_S and, as in all classical calorimetric measurements, the heat conductance K_B, and eventually sample-intrinsic stored energy that is released with a characteristic thermal-relaxation time τ_I (what is equivalent to a heat production or in some cases to a heat absorption *inside* the sample). This leads to a complex heat capacity, i.e. a C'' term. It is obvious that the frequency used constitutes yet another variable parameter in the experiment. *Measured heat capacities, therefore, are forced to depend on temperature and frequency in any modulation-type experiment.* This may even be the case when no sample-specific relaxation mechanism occurs inside the sample itself: there always exist other thermal relaxations in a caloric cell resulting from the various experimental arrangements; as for example, from frequency-dependent thermal resistance between the different components of the cell. The result – the response of the sample to heat input – depends on the experimental time scale and its relationship to intrinsic relaxation phenomena. Therefore, more than in all other calorimeters, the relationship between the various relaxation times of the modulation experiment are of crucial importance to enable well-defined and acceptable results:

(i) the external relaxation time, τ_B, that characterizes the thermal relaxation between sample and its surroundings, given by $\tau_B = C_S/K_B$;

(ii) the internal relaxation time, $\tau_S = C_S/\kappa_S$ (κ_S being the thermal conductivity of the sample), describing the internal equilibrium of the sample that usually includes the heater and the thermometer; and
(iii) τ_I, which is the characteristic relaxation time for any sample-intrinsic relaxation process.

As a rule, good heat capacity experiments are carried out when the derivative of the amplitude of the heating-power-induced oscillations $d(\Delta T_{AC})/dt$ is much larger than the change in absolute temperature $d(\delta T_{DC})/dt$ (per unit time) that occurs during one period because of heat loss across the thermal link R_B or due to scanning (Fig. 1):

$$d(\delta T_{DC})/dt \leq 0.01 d(\Delta T_{AC})/dt$$

is required. Otherwise, the amplitude ΔT_{AC} will not correctly display the related heat capacity C_S.

The periodic heating of the sample and the temperature monitoring can be done in different ways that, according to the chosen combination, offer a multitude of experimental arrangements:

- Direct Joule heating, with either AC- or DC-current passing through the sample or an external heater being attached to the sample during a given period of time, periodic heating by alternately chopped light absorption (contact-free heating), electron bombardment, inductive heating of metallic samples, etc.
- Various resistance thermometers (for the different temperature ranges), thermocouples, diodes, pyrometers, etc.

We note that, in contrast to other calorimetric methods, in the TMC the sample can be located in vacuum or in exchange gas. AC calorimetry is, apart from DSC instruments, the only caloric method for which a commercial instrument has successfully been introduced in the market [80].

Evidently, modulation is not restricted to sinusoidal oscillations but can have any other waveform, e.g. rectangular or triangular wave forms have been used [60,70,81]. Modulation was also induced indirectly to the sample by giving a modulated power to the heat shield [82].

A modification of the TMC technique – the *3ω-method* – is based on the original work by Corbino [11]. Later, Rosenthal [49] and Filippov [50] used the bridge technique to measure third harmonic signals. Smith applied the method to measure frequency-dependent heat capacity of Ge [83]. In 1986/87 Birge and Nagel reported in detail on dynamic heat capacity experiments using this method [23,24]. Their experiment allowed to measure the dynamic specific heat over a wide frequency range, (1–3) kHz, for the first time. In the meantime, the frequency range has been extended to the (1–10) kHz range. The setup may be regarded as a thermal spectrometer and is schematically shown in Fig. 2. The experiment relies on heat diffusion from an infinitely long and thin plate heater of width *d* on the surface of a semi-infinite medium, realized by immersing the heater (evaporated on the bottom plate) in a liquid or, alternately, deposits it on a solid sample [23,24,78]. The technique exploits the fact that the solution of the heat diffusion equation has the simplest form in one dimension near a heater with simple geometry [84], when the thermometer and heater are identical in that arrangement. Thus, the source of limited frequency range, the fact that heater and thermometer are separated, is eliminated. In this type of experiment, the *same* thin-film metal resistor-element is used as both *heater and thermometer*. Thus, the restriction imposed by finite size of the sample is removed. The frequency range is limited by the geometry of the heater. The solution for the heat-diffusion equation (planar infinite long strip on a semi-infinite surface) is given by Carslaw and Jaeger [84] and is described in full length in Ref. [47]. The result says that the amplitude of the temperature change at the surface $T(x, y = 0)$, resulting from a power input to the heater, decays exponentially in the y-direction with

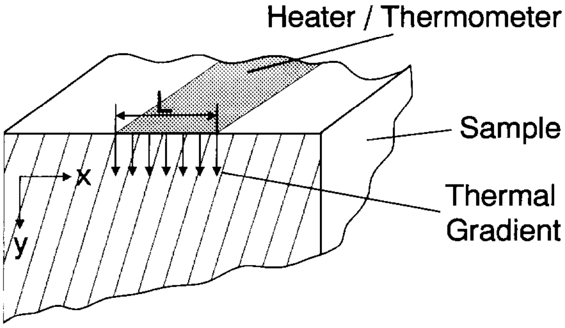

Fig. 2. Schematic view of a calorimeter for measuring with the 3ω-method.

the characteristic thermal length λ_{th}:

$$\lambda_{\mathrm{th}} \equiv (\kappa\omega C_{\mathrm{S}})^{1/2} = (D/2\pi)^{1/2} \tag{8}$$

where κ and D are the heat conductivity and the thermal diffusivity of the material of the semi-infinite sample. The two cases $d \ll \lambda_{\mathrm{th}}$ and $d \gg \lambda_{\mathrm{th}}$ may be investigated. The case, $d \ll \lambda_{\mathrm{th}}$, which is not discussed here, allows to determine the heat conductivity alone. The other case, $d \gg \lambda_{\mathrm{th}}$, is the common experimental condition encountered. The temperature oscillation is obtained as [84]:

$$\Delta T_{\mathrm{AC}} \equiv (P\lambda_{\mathrm{th}}/d\kappa) = [(P/d)/(2\omega C_{\mathrm{S}}\kappa)^{1/2}]\mathrm{e}^{-\mathrm{i}\pi/4} \tag{9}$$

The resulting temperature oscillations are proportional to the power input per unit area and related to *the product of heat capacity and thermal conductivity*. Provided κ is known, the dynamic heat capacity can be obtained from Eq. (9).

In order to create temperature oscillations, a current $I = I_0 \cos\omega t$ is passed across the heater and produces a heat flux with frequency 2ω:

$$P(t) = P_{\mathrm{AC}}\mathrm{e}^{i2\omega t} \tag{10}$$

from the heater into the sample. The DC component of $P(t)$ establishes a time-dependent gradient in the y-direction in the sample. Since the resistance of the heater has a temperature coefficient α, its resistance $R(t)$ and the resulting voltage drop $V(t)$ also oscillate:

$$R(t) = R_{\mathrm{DC}}[1 + \alpha|\Delta T_{\mathrm{AC}}|\cos(2\omega t + \phi) \tag{11}$$

and

$$\begin{aligned} V(t) \equiv I(t)R(t) &= I_0 R_{\mathrm{DC}} \cos(\omega t) \\ &+ (I_0 R_{\mathrm{DC}}/2)\alpha|\Delta T_{\mathrm{AC}}|[\cos(\omega t + \phi) \\ &+ \cos(3\omega t + \phi)] \end{aligned} \tag{12}$$

In Eq. (12), it is the third term that contains the essential information, namely ΔT_{AC} with a frequency 3ω. Although the 3ω signal is relatively small compared to the first two terms (oscillating with ω); it is not mixed and it allows registering the temperature amplitude and phase shift, and it can be well separated by the lock-in technique. For more experimental details, the reader is referred to Refs. [10,23,47,78,79].

Due to the low mass of the heater, acting simultaneously as generator and detector, the 'external' relaxation time of the calorimetric system can be held at an extremely short value in comparison with other calorimetric arrangements. The basic limitation that must be respected is that the thermal wavelength λ_{th} should be much longer than the thickness d and much shorter than the shortest lateral dimension L of the heater:

$$L \gg \lambda_{\mathrm{th}} \gg d \tag{13}$$

where λ_{th} is given by Eq. (8). One can satisfy this condition, e.g. with $d = 10^{-5}$ cm, $L = 1$ cm, for the frequency range from a few mHz to kHz. For this reason, the 3ω method – and its variations – have experienced a widespread revival. It is the method *best suited to measure the frequency dependence* of the heat capacity over a relatively wide frequency range.

There are only a few experiments using the TM principle for the determination of thermal diffusivity D so far [20,21,26,74,85–88,95,96]. Howling et al. [86] measured D on centimeter-sized metal rods in the temperature range of liquid helium. The decay of the temperature oscillations was detected on two different positions along the rod. Plate-like samples (thickness (0.1–1) mm) have been measured by light irradiation using the AC calorimetric method. D was obtained from the observation of the phase difference of the temperature oscillations, or from the phase shifts and temperature amplitudes at the front and rear surfaces. Measurements of D parallel to a thin plate were reported by Salamon et al. [87]. In these diffusion measurements, a part of the sample was shadowed by a mask and the diffusivity was determined from the oscillating temperature amplitude observed both at an unmasked and a masked point. An advanced modification of this experiment was developed by Hatta in 1985 [74]. The arrangement is schematically shown in Fig. 3. Light energy $P = P_{\mathrm{AC}}\,\mathrm{e}^{i\omega t}$ (for $x < 0$) is supplied uniformly to the unmasked left side portion of the plate-like sample with thickness d ($50\,\mu\mathrm{m} < d < 300\,\mu\mathrm{m}$), whereas the right side is shadowed by a movable mask. The periodic heat, absorbed by the sample, propagates one-dimensionally, along the x-direction in the sample into the shadowed region (to the heat sink on the right side). The resulting temperature oscillations ΔT_{AC} are detected behind the masked area by an appropriate thermometer, e.g. a thermocouple. It is assumed that

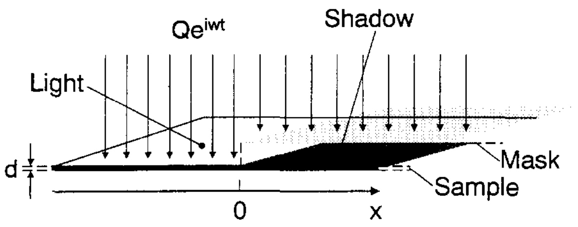

Fig. 3. Schematic view of light modulated measurement of thermal diffusivity. Sample thickness is *d*.

no temperature gradient perpendicular to the sample plane occurs. Thermal diffusivity is calculated from the solution of the one-dimensional heat diffusion equation with the given boundary conditions for $x > 0$ [84]:

$$\Delta T_{\mathrm{AC}}(x) = [P_{\mathrm{AC}}/2(i\omega cd + K'_{\mathrm{B}})]\exp\{[(i\omega cd + K'_{\mathrm{B}})/\kappa d]^{1/2}x\} \quad \text{for } x > 0 \qquad (14)$$

where c is the heat capacity per unit volume, d the thickness of the sample and κ its heat conductivity; K'_{B} denotes the heat conductance from the sample to the thermal bath (on the right side in Fig. 3). The external relaxation time is given by: $\tau_{\mathrm{B}} = cd/K'_{\mathrm{B}}$. Eq. (14) simplifies to:

$$\Delta T_{\mathrm{AC}}(x) = [P_{\mathrm{AC}}/2\omega cd]\exp\{-\kappa x - i(\kappa x + \pi/2)\} \qquad (15)$$

when the conditions $\omega\tau_{\mathrm{B}} \ll 1$, $D = \kappa/c$, and $\kappa = (\omega/2D)^{1/2}$ are introduced. The condition

$$\kappa d = d(\omega/2D)^{1/2} \ll 1 \text{ and } \omega\tau_{\mathrm{B}} \ll 1 \qquad (16)$$

must be fulfilled for a correct measurement to be performed.

The method is related to the thermal wave techniques. Obviously, the amplitude as well as the phase change in Eq. (14) changes as a function of ω and x. This enables determination of the thermal conductivity κ and the diffusivity D along the x-direction from a *measurement of the x dependence of the temperature amplitude*. Equally, *a measurement of the dependence of the amplitude or the phase yields the value of D* [74,94–111].

Besides the measurement of heat conductivity or diffusivity, the method described can alternately serve to find heat capacities according to the AC method described before: the unmasked part constitutes the sample, the masked part is the thermal link. Simultaneous determinations of heat capacity and thermal diffusivity were also performed [87,99–103,105–107].

All the TM techniques described here – AC calorimetry, 3ω method, light-modulated diffusion experiment – are well-suited for computer-controlled automated measurements.

In the last two years, because of the appearance of commercial TMDSC's, the broad know-how of traditional AC calorimetry was rapidly combined with DSC technique [29,101–108]. That had an enormous impact on the investigation of dynamic heat capacity phenomena and technological progress, like better temperature and caloric resolutions, application of light-modulation to DSC, shorter calorimeter time constants (compared to commercial DSC), simultaneous measurement of heat capacity by DSC and AC calorimetry using the same apparatus including linear temperature scanning [30,87,101,103,104,109] and the combination of TMC and relaxation time (non-adiabatic step heating) techniques [106]. It is interesting to note that the intensified research on dynamic heat capacity – and new technological accomplishment – today has been initiated by 'TMDSC' although all the ingredients for measuring $C(T,\omega)$ were available for more than one decade. It seems that physicists did not take enough care to exploit the *phase information and the potential of classical AC calorimetry*. Vice-versa, few chemists, in particular, very few TA-scientists followed the calorimeter development in other fields of science, e.g. low-temperature calorimetry where high-precision differential experiments enable to achieve an accuracy of 0.02% on milligram samples [8,9,186–190]. More work must be done to transfer the knowledge on that topic from the various areas of science to the field of thermal analysis. The most recent development clearly also suggests that TMDSC is a bad solution for the determination of $C(T,\omega)$. The methods and arrangements of traditional TMC, in particular the low-temperature installations and the 3ω method, are much more suited to expand the frequency range for any $C(T,\omega)$ studies.

2.3. Application of TMC

An external heater together with resistance thermometers or heating by light absorption and temperature detection by thermocouple have been used, with advantage, in the low-temperature range ($T < 300\,\mathrm{K}$), whereas resistive sample heating and pyrometric temperature registration were applied above 1500 K. Modulation calorimetry, in comparison with other calorimetric methods, has been performed over the largest temperature range, from 40 mK to 3600 K [5,51,72,112]. TMC was also carried out with frequencies as low as a few mHz up to 10 kHz. However, the number of published reviews on modulation calorimetry remained rather scarce, presumably, because of the large amount of constructions reported, either for a special temperature range in case of certain physical phenomena such as phase transitions, for a particular type of samples, e.g. thin films, or for certain materials. Nevertheless, most of the basic knowledge is contained in the reviews on calorimetry [4,5,47,51,111,113–118] and is, to a great extent, identical for all calorimetric methods. In the three decades of using TMC, more than 200 papers have been published on TMC-technology and the number of contributions dealing with results from TMC measurements will go far beyond 1000.

TMC is only a narrow area of the broad field of thermal analysis, but we should be aware that it is also *only one technique among other modulation techniques* currently applied in physics of thermophysical data when a higher resolution is required. Modulation is frequently used to measure thermal dilatation [119,120], electrical resistance [51,121], thermoelectric power [56,122–124] and other quantities [5,51,124]. Here, one has to discriminate between *modulation* methods (as explained before) and *derivative* methods where the derivative of a physical (or chemical) quantity with respect to another parameter is measured, e.g. change of heat capacity with magnetic field, $\mathrm{d}C_\mathrm{S}/\mathrm{dB}$. The information obtained from modulation experiments comprise the amplitude signal and the phase signal whereas simple derivative technique only yields higher resolution.

As will be shown in the next section, TMC fulfills most of the requirements of a reliable, powerfulness and economical calorimeter for modern materials science: *Very small samples required, very high relative temperature resolution achievable, possibilities of automation and short measuring times.* For that reason, in the last 20 years, hardly any phenomena in specific heat [64] have been studied with TMC, particularly phase transitions:

- phase transitions of ferri-, ferro- and antiferromagnetic, ferro- and ferri-electric, superconducting materials, spin-glasses, structural transition in solids, liquids, liquid crystals and biological substances, also critical behaviour, etc.; and
- heat capacity of metals, semiconductors, insulators, inorganic and organic solids and liquids, binary alloys, single- and polycrystalline materials, powders, and biological material.

Two reviews have appeared concerning the use of MC for studying phase transitions [55,67]. An extended overview on MC is given in Ref. [5].

Nevertheless, it remains a significant potential to be explored in future: The phase information, which is of particular interest in non-equilibrium thermodynamics, kinetically hindered processes, melting phenomena, thermal hysteresis, incommensurate phases and glassy-type transitions. Dynamic heat capacity is one subject that has been of great theoretical interest for a long time. The recent technological progress in TMC renewed that interest and, with modern electronics now, opens new ways to investigate frequency-dependent heat capacity and to study the product of heat capacity and thermal conductivity.

3. Comparison of TMC with other calorimetric methods

In this section we compare the most frequently used calorimetric methods with temperature-modulated calorimetry to point out the advantages and disadvantages of TMC, to evaluate its optimized application and to find out its limitations.

3.1. Calorimetric methods – a comparison

The principal arrangement of any type of calorimeter is that shown in Fig. 1. It may work in thermal equilibrium (called ‘static’) or non-equilibrium, mostly in the scanning mode (named ‘dynamic’). The often used and best known calorimeters work as isothermal, adiabatic (Nernst-type) or isoperibol (i.e. quasi-adiabatic) step heating systems, as continuous heating (or cooling), temperature modulation,

Table 2
Classification of calorimetric measuring methods [a]

Thermodynamic classification	isothermal $R_B = 0$	isothermal $R_B \neq 0$	quasi-adiabatic $R_B \approx 0$	adiabatic $R_B = \infty$
Thermal shield control:	$T_S = T_{SH}$	$T_{SH} = \text{const}$ $T_S = T_{SH}(t)$ $T_{SH} = T_{SH}(t)$	$T_{SH} = \text{const}$ $T_S = T_S(t)$ $T_{SH} = T_{SH}(t)$	$T_{SH} = T_{SH}(t)$
Detection of caloric signal				
Compensation of measuring effect by phase transition or thermoelectrically	1, 2	2		2
Measurement of time-dependent temperature change		2, *3S*	4S, *6*, *7*, *8*	2, 5S, *6*
Measurement of local-spatial temperature difference		*9T– 11T*		
Measurement of frequency- or time-dependent heat capacity		*11*	*7*, *8*	5

[a] The different types of calorimetric methods are labelled by 1 to 11:
(1) –Isothermal ice calorimeter type; (2) – Mixing or dilution calorimeter; (3) – Relaxation time calorimeter (PHC); (4) – Quasi-adiabatic calorimeter (QAC); (5) – Adiabatic (Nernst-type) calorimeter (ADC); (6) – Continuous heating (scanning) calorimeter (CHC); (7) – Temperature-modulated calorimeter (TMC); (8) – Third harmonic method (THC); (9) – Differential scanning calorimeter (DSC); (10) – Differential thermal analysis (DTA); (11) – Temperature-modulated DSC (TMDSC).

1. S denotes: Stepwise-heating required.
2. T denotes: Twin arrangement of caloric cells.
3. Italic lettering denotes: Scanning mode possible.

pulse-heating methods, with the 3ω method or as differential thermal analysis instrument. In all types of calorimeters, the surrounding (thermal shield) can create either adiabatic, isoperibol or isothermal conditions for the calorimeter cell. The calorimetric methods are classified in Table 2 according to the given thermal boundary conditions (isothermal, isoperibol or adiabatic) and the way how the thermal event is detected. The calorimeters may be further divided in stepwise-heating (denoted in Table 2 as ‘S’) and temperature-scanning type instruments (labelled by italic lettering in Table 2). A further division is made in single sample/sample-support and double (twin-type) arrangements (labelled ‘T’). Twin devices are used when reference samples are required for determining the caloric signal qualitatively, e.g. DSC. The class of isoperibol and quasi-adiabatic calorimeters can also work at constant temperatures in order to observe the change in C_S under the influence of an external parameter, e.g. pressure, magnetic field.

In Table 2, the transition from one method to the next one is always smooth. The external relaxation time τ_B is decisive for the method applied, i.e. the manner in which the heat shield is controlled and the heat transfer between shield and the sample/sample-holder assembly takes place (heat conduction, heat of radiation, exchange gas). The heat-shield temperature T_{hs} may: (i) be held constant as an isothermal shield; (ii) follow the sample temperature adiabatically or with a temperature difference between shield and sample (isoperibol); or, conversely (iii) the sample follows the shield temperature adiabatically or isoperibolically. Moreover, in former times every calorimeter was especially designed to a specific measuring-method or purpose. Today, thanks to modern computers and high-quality and flexible electronics, their use enables running on the same calorimeter-hardware, with the same sample/sample-holder and heat-shield assembly, *different software* that permits us to work the calorimeter according to the various methods. Also, a certain method with various shield-control operations, e.g. Nernst step-heating, pulse-heating or temperature modulation with isothermal or adiabatic thermal shield, can be chosen [9].

The *adiabatic* (*Nernst type*) *calorimetry* (ADC) [113–118] – we refer in the following, again to Fig. 1 – is today often carried out as quasi-adiabatic method with an isothermal shield at low temperatures (below 20 K) and an adiabatic-shield control above

Table 3
Table of characteristic parameters of the most common type of calorimeters [c]

Parameter	ADC	QAC	TMC	PHC	CHC	DSC	TMDSC	THC
Inaccuracy, absolute(%)	< 0.1–1	0.5–2	2–5	2–5	0.7–5	2–10	2–10	2–20
Inaccuracy, relative (%)	< 0.1–0.5	0.1–1	0.01	1–3	0.3–5	0.5–5	0.5–5	< 1–5
Temperature-resolution (%)	+	+	++	+	++	+	+	++
Sample mass (mg)	> 5000	10–500	1–100	50–500	50–1000	10–100	10–100	< 0.1–1000
Temperature-range (K)	all	all	0.3–300	all	15–300	> 100	> 100	all
Measuring time	week	days	days	days	hours	hours	hours	hours
Flexibility [b]	+	++	+	+	+	++	+	–
Heat-transfer control [b]	—	++	+	—	+	–	–	++
Thermal equilibrium. [b]	—	++	++	+	+	–	— [a]	+ [a]

[a] Always to be checked.

[b] + – reasonable good; ++ – very good; – less good; and — bad performance with respect to the indicated property.

[c] Remarks:
ADC (Adiabatic calculation) – highest absolute accuracy.
TMC (Temperature modulated calculation) – best relative resolution for temperature and caloric signal.
PHC (Pulse-heating calculation) – well suited for low temperature and non adiabatic conditions.
CHC (Continuous heating calculation) – high resolution, good absolute accuracy and suited for small samples.
DSC (Differential scanning calculation) – moderate precision and suitable for measuring small samples.
TMDSC (Temperature-modulated DSC) – similar to DSC, but provides additional information on complex heat capacity available.

$(R_{\mathrm{B}} \approx \infty)$. The Nernst method modifies into a *pulse-heating calorimeter* (PHC) [6,7,112–114,118] under strong non-adiabatic (isoperibol) conditions $(R_{\mathrm{B}} \cong 0)$. Pulse-heating is realized at constant temperature or as a scanning method [7,124]; also scanning during cooling is possible. The *continuous heating method* (CHC) [8,9,114,115] allows heating and cooling under adiabatic or isoperibol conditions where, in the latter case, the sample may follow a time-dependent shield drift or the shield follows the sample (for more references, see [9]). The number of modifications described in the literature is manifold. The various forms of temperature-modulated calorimeters have been discussed in the previous chapter. They can be regarded as working with quasi-adiabatic condition $(R_{\mathrm{B}} \approx \infty)$. Measurement at constant temperature by varying, as for example, an external parameter (magnetic field or pressure) or scanning – heating or cooling – is applicable without problems. The TMC technology offers the broadest spectrum of variability as is noticeable from Table 2. Heat-flow instruments – DSC and TMDSC, also differential thermal analyses (DTA) instruments – represent a further class of calorimeters that work under strong non-adiabatic/isoperibolic conditions $(R_{\mathrm{B}} \cong 0)$ [4,35,36,39].

In Table 3, the calorimetric methods are compared by listing typical values for their characteristic performance parameters (inaccuracy, temperature resolution, sample mass needed, etc.). An evaluation of this table shows that the highest absolute precision is almost reached with proper adiabatic calorimetry. TMC and CHC offer the best relative resolution with respect to temperature and caloric value which is very important for the investigation of narrow phase transitions. Isoperibol conditions or modulation methods like PHC and TMC are best suited for low and very low temperatures (extremely low heat capacity) what is identical to the requirement for ultra-low mass measurements. Shortest measuring times over a large temperature range are achieved with DSC and CHC. The most frequently used calorimeter is the DSC that provides only moderate accuracy [(1–5)%] and must be carefully calibrated [38,39,125,126]. However, DSC's requires only small masses (mg-range). Presumably, the largest technical advance in recent years was reached with CHC that gives a remarkably good absolute precision, requires small samples (mg-range) and allows short measuring times, e.g. one day from (4–300) K [8,9]. As mentioned before, the 3ω method presumably is in a new stage of development and offers the most interesting advantages to study complex heat capacity.

The condition for *thermal equilibrium* is most important for many studies and for the interpretation of the data found. It is best guaranteed with adiabatic calorimetry and becomes more difficult to hold when going from ADC to TMC and further on to PHC, CHC and finally to TMDSC and DSC, since in that line the used scanning speeds are increased to have sufficient caloric sensitivity.

TMDSC adds additional information to the heat capacity measurements, namely that of the frequency dependence, and therefore, for correct data interpretation, more and precise information is required on the various dependences of the result on the experimental parameters used: Scanning rate, temperature amplitude on sample, sample support, sample mass and position in the cell, pressure and flow rate of purge gas, calibration factor, on the phase shift, as well as frequency dependences, etc. [38]. We note that in long-time relaxation phenomena – with relaxation times in the range of minutes to hours – the adiabatic calorimetry can deliver reliable results on the frequency dependence of the heat capacity. In summary, the complexity of TMC requires much more careful testing and calibration of the experimental installation and caution with data treatment.

3.2. *Advantages and disadvantages of temperature-modulated calorimetry*

What are the advantages and disadvantages of TMC in comparison to the other calorimetric methods? To answer this question, a deeper evaluation of the individual methods is necessary besides the information given in Tables 2 and 3. Such an analysis yields the following conclusions:

Advantages:

- Dynamic measurements under quasi-adiabatic conditions are possible over a very wide temperature range (50-mK to 3600 K).
- Correction or extensive avoidance of any type of heat loss, when the oscillation period is chosen short enough.
- Extremely high relative caloric sensitivity and high-temperature resolution ($<0.001\%$).
- Experiments with small and ultra-small samples (mg and μg range).
- Best suited for studying samples under extreme external conditions as high pressure, high magnetic and electric fields, also very low temperatures.
- Appropriate for sweep runs (scanning) in heating and cooling modes.
- Short measuring time compared to other calorimetric methods.
- Information on sample-specific relaxation phenomena.
- Study of frequency-, pressure-, magnetic field dependences under isothermal condition.
- Possibility to apply selective amplifiers (also use in mechanically or electrically noisy environment).

Disadvantages:

- Moderate absolute precision, error range (1–10)%, which may be removed by combination with other calorimetric methods, possibly on the same calorimeter stage.
- Very difficult, or even impossible, for the determination of latent heats, first-order phase transitions and hysteresis phenomena, see e.g. Refs. [29,99,103,105,108].
- Strong and limiting boundary conditions for the relaxation times.
- Large variety of partially very complex experimental accomplishments, often with insufficient description of details, which render it difficult to properly evaluate the results.

In summary, TMC (including 3ω method) offers several technical modifications that are permanently improved. Similar to all other isoperibol systems, TMC calls for very careful and stringent testing of the behaviour and limits of the different calorimeter parameters – temperature dependence of relaxation times, differences between true and measured (indicated) temperature, influences of frequency, phase-shift, etc. Although the theoretical background for some TMC arrangements is not yet fully worked out, TMC has great potential for new and surprising developments in the future. What is known on the theoretical basis and the critical boundary conditions for TMC are discussed now in the next section.

4. Theoretical knowledge and critical boundary conditions

The model shown in Fig. 1 and expressed by Eqs. (1) and (7) describes insufficiently the true temperature vs. time behaviour of the different components of a TMC setup in practice. The model is too simple; by far, it does not include the multiple ways of heat flow in a realistic calorimeter model. Correct modelling, primarily, requires a well-defined separation of *sample-intrinsic relaxation process* on the one hand, and *instrument-induced relaxations* on the other. Secondly, the detected temperature oscillations of the sample can originate from a heat flux into the sample (case of TMDSC) or from heating the sample directly by an optical or a resistive heater (case of classical TMC). Here, we treat only the latter case. TMDSC is described in more detail in papers in this issue as well as in Refs. [42–45].

The most important problem which arises when treating TMC mathematically, is to evaluate the *internal* thermal equilibrium times for the sample/support/thermometer/heater assembly and its frequency dependence, both of which are controlled by the heat capacities involved and the interlinking thermal resistances. It turns out that the appropriate choice of the frequency window, in which the calorimeter operates, is decisive for the dynamic behaviour of the calorimeter and thus for the reliability of the measurement. These thermal parameters – heat capacities and heat resistances – are dependent on the temperature. Consequently, the frequency dependent behaviour of amplitude and phase shift change with temperature. In addition, the thermal resistance between the sample and its support (including the thermometric sensor) may vary markedly from one measurement to the next and thereby strongly influence the result obtained. A very good and reproducible thermal link between the sample and sample-support is indispensable.

Various models, sometimes in great detail, have been discussed in the literature [1,5,15,17,26,29,57,61,67,74,95,96,101,127–129]. Here, we skip the detailed mathematical descriptions in favour of presenting a rough outline and demonstrating the core-conclusions. Three diagrams of different possible calorimetric arrangements for a TMC are shown in Figs. 4 and 5. Fig. 4(a) and (b) refer to classical TMC, Fig. 5 models TMDSC. The measuring systems are essentially characterized by internal and external relaxation times by which the internal one mostly is composed of the different contributions resulting from the sample itself, the thermometer, the heater and the sample support. The analyses are made in analogy to electrical networks.

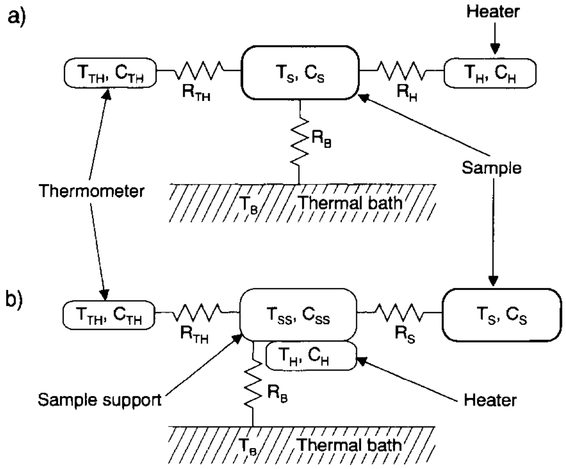

Fig. 4. Schematic arrangement of a temperature-modulated (AC) calorimeter. (a) – without sample support; and (b) – including sample support. T_i and C_i denote, respectively, the temperatures and heat capacities of the sample, sample-support, heater and thermometer, labelled by the indices i = S, SS, H, and Th. T_B is the temperature of the thermal bath, R_B represents the thermal resistances to the component labelled with the corresponding indices.

The simplest model, in which the influence of thermal resistance between heater and sample, thermometer and sample, has been treated by Sullivan and Seidel (see Fig. 4(a)) [1]. In that experiment, the sample used had a large mass and the contribution of the sample support could be neglected. Subsequently, this arrangement has been discussed and re-described in many papers and it is, therefore, only briefly described here. The following assumptions are made in this model:

- The temperature variations are taken sufficiently small so that the various heat capacities and thermal resistance may be considered as constant.
- It is also assumed that the temperature of the thermal bath is constant or varying very slowly so that $\delta T \ll \Delta T_{AC}$.
- Furthermore, as assumed in other models, the heat capacity of the thermal resistance is set equal to zero, thermometer and heater (later, also the sample support) itself have an infinite heat conductivity

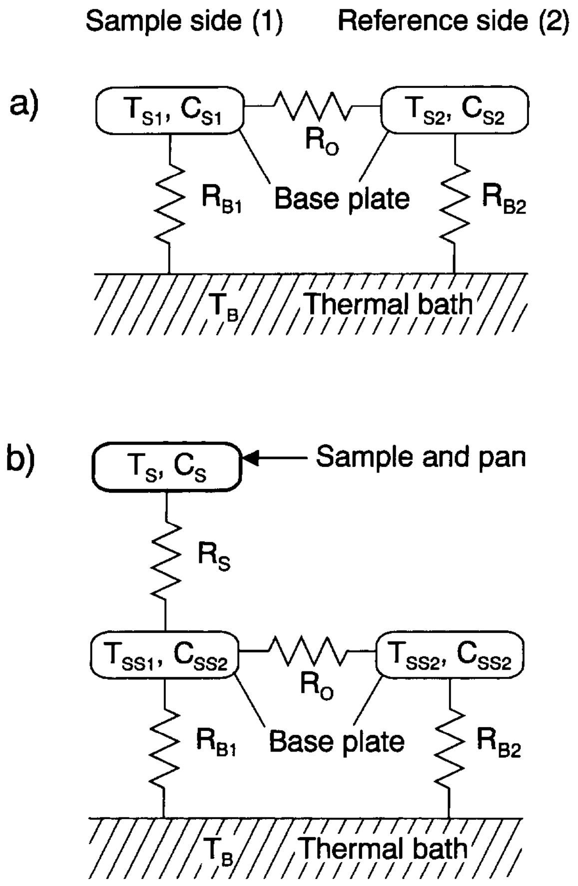

Fig. 5. Schematic arrangement for differential scanning (DSC) or temperature-modulated differential scanning (TMDSC) calorimeters. Labelling is identical to Fig. 4.

and does not develop any temperature gradient inside.

After writing down the thermal equations for the system, the steady state solution for the temperature oscillations, generated in the heater at the rate $P = P_{AC}(1 + \cos t)$ and monitored at the thermometer TAC consists of three terms – the constant bath temperature T_B, a DC term T_{DC} and a modulation contribution T_{AC} including the phase shift:

$$T = T_B + T_{DC} + T_{AC} = T_B + P_{AC}R_B + (FP_{AC}/\omega C)\cos(\omega t + \phi) \qquad (17)$$

where

$$C = C_S + C_{Th} + C_H \qquad (17a)$$

and $F = f(X_i)$, is a complex function of the heat capacities, heat conductivities, thermal relaxation times (defined as $\tau_i = C_iR_i$, with $i = \mathrm{S, Th, H}$) of the sample, thermometer and heater, of the sample-to-bath relaxation time ($\tau_B = C_{RB}$) and the frequency. The full formula is given by Eq. (3) in Ref. [1]. If:

(i) the heat capacities of the addenda (heater, thermometer) are much smaller than that of the sample, $C_S \gg C_{th}, C_H$;
(ii) the addenda reach thermal equilibrium with a time constant much less than the inverse of the temperature-oscillation frequency ω, more specifically when $\omega^2(\tau_{Th}^2 + \tau_H^2) \ll 1$; and
(iii) the frequency is much larger than the inverse of the sample-to-bath thermal relaxation time, $\omega\tau_B \gg 1$,

then F in the third term in Eq. (17) simplifies and yields:

$$T = T_B + P_{AC}R_B + \{[P_{AC}/(\omega C)][1 + (\omega\tau_B)^{-2} + \omega^2(\tau_{TH}^2 + \tau_H^2)]^{-1/2}]\}\cos(\omega t + \phi) \qquad (18)$$

$$\phi = \arcsin\{1 + [(\omega\tau_B)^{-1} - \omega(\tau_{th} + \tau_H)]^2\}^{-1/2} \qquad (19)$$

τ_B characterizes the period needed for the caloric cell to reach thermal equilibrium with the bath and is often denoted as external relaxation time τ_{ext}. The contributions of τ_{th} and τ_H are often taken together and defined as the internal relaxation time τ_{int}. That is the characteristic time constant for the calorimetric platform itself to reach thermal equilibrium. The thermal equilibrium inside the sample, however, may be different and depend on the thermal conductivity κ_S of the material investigated and the amount of mass used. The equilibrium is characterized by τ_{INT}. The condition $\tau_{INT} \approx \tau_{int} > \tau_{th}, \tau_H$ should hold.

The most important problem of dynamic calorimetry is how to guarantee spatial temperature homogeneity in the sample itself. In Refs. [1,65], the influence of the finite sample conductivity and influence of sample size, respectively, have been discussed. Taking a slab-shaped sample with cross-sectional area A_S and thickness l_S (with the thermometer attached on one side and the heater linked on the other according Fig. 4(a)), the size of T_{AC} (oscillatory part of temperature) becomes:

$$T_{\mathrm{AC}}(1_{\mathrm{S}},t) = [P_{\mathrm{AC}}/\omega C_{\mathrm{S}}] \cdot [1 + (\omega\tau_{\mathrm{B}})^{-2} + (\omega\tau_{\mathrm{INT}})^{2} + (21_{\mathrm{S}}K_{\mathrm{B}}/3A_{\mathrm{S}}\kappa_{\mathrm{S}})]^{1/2} \tag{20}$$

where τ_{INT} is given by

$$\tau_{\mathrm{INT}} = (l_{\mathrm{S}})^{2}/D(90)^{1/2} \tag{21}$$

The finite sample size and thermal conductivity result in one correction term τ_{INT} of the same form as the terms arising from the thermal resistance sample-to-heater and sample-to-thermometer (τ_{int}). However, there also exists a frequency-independent correction of the form $(2l_{\mathrm{S}}K_{\mathrm{B}}/3A_{\mathrm{S}}\kappa_{\mathrm{S}}) = 2K_{\mathrm{B}}/3\kappa_{\mathrm{S}}$. At low temperatures, this term is very much smaller than that given in Eq. (21) and therefore negligible. However, this term is no more negligible at higher temperatures and/or for samples with poor heat conductivity κ_{S}. The thickness of the sample slab must then be decreased correspondingly.

The magnitudes of the temperature oscillations show directly the heat capacity

$$\Delta T_{\mathrm{AC}} = P_{\mathrm{AC}}/[\omega(C_{\mathrm{S}} + C_{\mathrm{H}} + C_{\mathrm{th}})] \tag{22}$$

with the phase approaching $\phi = -\pi/2$, when

$$\tau_{\mathrm{ext}} > 100\tau_{\mathrm{int}} \text{ and } \tau_{\mathrm{ext}}/10 > 1/\omega > 10\tau_{\mathrm{int}}. \tag{23}$$

These boundary conditions are rather stringent and not always easy to fulfill. From the model, the most critical boundary condition, namely the internal thermal relaxation time of the sample, becomes understandable. The sample thickness l_{S} is most crucial with respect to τ_{INT}. It should remain below the required minimum size so that:

$$\tau_{\mathrm{INT}} = [\omega l_{\mathrm{S}}^{2}/(\kappa_{\mathrm{S}}(90)^{1/2)}] \ll 1 \tag{24}$$

The appropriate choice of frequency range is crucial for the reliability of the measurement. As the conditions given in Eqs. (23) and (24) are frequency-dependent, a study of the frequency dependent behaviour of the TMC cell is required before a heat capacity experiment. In addition, the value of the thermal links, in particular that of R_{B} (τ_{B}) vary markedly with temperature for most of the materials used for that purpose. The relevant and admissible frequency window, then shifts as a function of temperature and the phase signal is modified. A final check is to look at the proper modulation of both temperatures (heat flow) and sample temperature, e.g. by observing the relevant Lissajous figures [44]. In general, there exists a window of frequencies for which Eq. (22) is valid with $\phi = -90^{\circ}$ and where the conditions given in Eqs. (23) and (24) are fulfilled.

A more realistic model of a TMC includes the effect of a *finite thermal resistance between the sample and the sample-support*. A detailed analysis of this problem is shown schematically in Fig. 4(b). The thermometer and heater are attached to the sample support and a thermal resistance R_{S} exists between sample and support (addenda). The heater, in practice, is deposited as a thin film resistance on the sample-platform and thus the thermal resistance between the support and the heater becomes negligible. The situation is more complex in twin arrangements as displayed in Fig. 5(a), the simplest schematics of a DSC. A heat flow between both sample supports, along R_0 in Fig. 5(a), is unavoidable. Introduction of a thermal resistance R_{S} between the sample and the support, as displayed in Fig. 5(b), again yields a more realistic description of the twin-type (or differential) calorimeter. The mathematical solution of this network gives even more complicated results than those discussed in the following for the arrangement shown in Fig. 4(b).

The configuration schematized in Fig. 4(b) has been discussed by Velichkov [15]. If the power dissipated in the heater is given again by $P = P_{\mathrm{AC}}(1 + \cos\omega t)$, in analogy to the above given description, the modulation term of the temperature indicated at the thermometer is as follows [15]:

$$T = T_{\mathrm{B}} + T_{\mathrm{DC}} + \Delta T_{\mathrm{AC}}\cos(\omega t + \phi) \text{ with}$$

$$T_{\mathrm{AC}} = [P_{\mathrm{AC}}R_{\mathrm{B}}(1 + (\omega\tau_{S})^{1/2}\cos(\omega\tau + \phi)] \times [(1 - a^{2}\omega^{2})^{2} + b^{2}\omega^{2}]^{-1/2} \tag{25}$$

$$\phi = -\arcsin\{(1 - a\omega^{2} + \tau_{\mathrm{S}}b\omega^{2})[(1 - a\omega^{2} + \tau_{\mathrm{S}}b\omega)^{2} + \omega^{2}(b - \tau_{\mathrm{S}} + \tau_{\mathrm{S}}a\omega^{2})^{2}]^{-1/2}\} \tag{26}$$

where $$a = \tau_{\mathrm{B}}\tau_{1} + \tau_{\mathrm{B}}\tau_{\mathrm{S}} +_{\mathrm{S}} \tau_{\mathrm{th}} + \tau_{\mathrm{th}}R_{\mathrm{B}}C_{\mathrm{SS}}R_{\mathrm{B}}C_{\mathrm{th}} \tag{27}$$

and $$b = \tau_{\mathrm{B}} + \tau_{\mathrm{TH}} + \tau_{\mathrm{S}} + R_{\mathrm{B}}C_{\mathrm{TH}} + R_{\mathrm{B}}C_{\mathrm{S}} + \omega^{2}\tau_{B}\tau_{\mathrm{th}}\tau_{\mathrm{S}} \tag{28}$$

Inspection of these formulae show that the range of frequency and thermal resistances R_B, R_S and R_{th} for which Eq. (22) is valid is very narrow or does not exist. A minimum value of R_B is required to guarantee adiabatic condition. Similarly R_{th} and R_S must remain below certain values, otherwise the temperature monitored is wrong or the sample gets thermally disconnected from the sample-holder; in the worst case, the heat capacity of the holder alone is measured. The frequency window for which $\phi = -\pi/2$ is the most restricting parameter.

The complex situation is illustrated by model calculations which are shown in Figs. 6 and 7. The curves shown are calculated with commercially available software (MAPLE V). We use Eqs. (25)–(28) for the model displayed in Fig. 4(a) with $C_S \equiv C_{SS} = 1\,\mathrm{J/MolK}$, $C_{Th} = 0.2\,\mathrm{J/MolK}$, $P_{AC} = 50\,\mathrm{mW}$; the resistances R_i are given in mK/W. The left side diagrams show the product $\omega\Delta T_{AC}\,(C_S + C_{CC})$ vs. different thermal resistance R_i and/or frequency ω; the right side diagrams give the phase ϕ as a function of R_i and ω (Note that ϕ is given in radians; $\pi/2 \approx 1.57$);

(i) *Perfect thermal coupling of thermometer* ($R_{th} = 0$) *and finite thermal resistance of the sample to sample-support* ($R_S = 0.1$): The result is shown in Fig. 6 (upper part). The amplitude $\omega\Delta T_{AC}$ increases with increasing R_B to a constant value, $\omega\Delta T_{AC} = 0.23$, that corresponds to reaching adiabatic condition (for $R_B \geq 3$). However, $\omega\Delta T_{AC} \equiv C^{-1} = \mathrm{const.}$ holds only for the shadowed area ($R_B > 3$ and $\omega < 3$). Beyond a certain frequency, the sample that is poorly attached to the support, begins to lag behind the temperature oscillations of the support and, at sufficiently high frequencies, it does not influence T_{AC} any more. The relaxation time of the sample/support assembly is $\tau_S = R_S C_S = 0.1$ s, corresponding to $\omega = 10$. Here, for $\omega > 3$, the value of $\omega\Delta T_{AC}$ increases linearly (thick line in the diagram) which indicates that the sample smoothly decouples from the support; the measured heat capacity $C = C_S + C_{SS}$ apparently drops down. Correspondingly (right side diagram) the phase approaches, but does not reach $-90°$ ($= -1.57$). The conditions implied from R_B, R_S and ω to hold the phase near -1.57 are much more stringent: Only $\phi = -1.4$ (instead 1.57) is reached for the most favourable case with $\omega \approx 2$ and $R_B = 5$ (right side in Fig. 6).

(ii) *Perfect thermal coupling of sample* ($R_S = 0$) *and finite thermal resistance to the thermometer* ($0 < R_{Th} < 2$) *and* $R_B = 3$: The result is displayed in the lower part of Fig. 6. Correct heat capacity is measured for the conditions given in the shadowed area of the $\omega\Delta T_{AC}$ (left side) and ϕ diagram (right side) and along the line $R_{Th} = 0$. The finite thermal contact of the thermometer is reflected on $\omega\Delta T_{AC}$ so that beyond a certain frequency $\omega\Delta T_{AC}$ (here $1 < \omega < 5$ on ω-scale and/or $0 < R_{Th} < 0.5$ on the thermal resistance scale) falls off faster than $T_{AC} = 1/\omega$. The amplitude $\omega\Delta T_{AC}$ drops also for a given frequency (e.g. $\omega = 20$, thick line in diagram) when R_{Th} is increased, and the drop is the faster, the higher the frequency is. At the same time, the phase shifts smoothly from $-90°$ (shadowed area with -1.57 in the phase diagram) along the R_{Th} and ω scale to nearly $-180°$ (-3.14, e.g. see near $R_{Th} = 2, \omega = 20$). At very low ω, T_{AC} drops because a considerable part of power P is lost to the thermal bath by R_B. Correspondingly the phase falls from $-90°$ to zero. At high frequencies, the thermal resistance R_{Th} and R_S limit the transmission of power to the sample and/or heater, respectively.

(iii) *Finite thermal resistance to the sample* ($R_S = 0.1$) *and to the thermometer* ($0 < R_{Th} < 2$) *with* $R_B = 3$: The result is given in the upper diagrams in Fig. 7. The conditions are identical to case (ii) discussed before; however, now the sample-to-support relaxation time is not zero but $\tau_S = 0.1$ s. The differences between Fig. 6 (lower part diagrams) and Fig. 7 are obvious: The amplitude $\omega\Delta T_{AC}$ is correct for $0 < \omega < 2$ when $R_{Th} = 0$, then $\omega\Delta T_{AC} = 0.23$. The increase of $\omega\Delta T_{AC}$ with ω, along the R_{Th} scale, manifests the thermal decoupling of the sample; the decrease of $\omega\Delta T_{AC}$ along the R_{Th} scale – that of the thermometer. The situation is reflected in the phase behaviour shown in the right side diagram. The combined effect of finite thermal linkage of sample ($0 < R_S 1$) and thermometer ($0 < R_{Th} < 2$) is presented again in a different form in Fig. 7 (lower part diagrams), for the fixed parameters $\omega = 5$ and $R_B = 3$. In the $\omega\Delta T_{AC}$ diagram (left) the thermal decoupling of the sample with increasing R_S is easily seen when $R_{Th} = 0$: $\omega\Delta T_{AC}$ doubles its value from 0.23 to ca. 0.4 for R_S rising from 0 to 1 (see the two shadowed areas, connected by the thick line, in the diagram); the amplitude $\omega\Delta T_{AC}$ approaches zero when the thermal

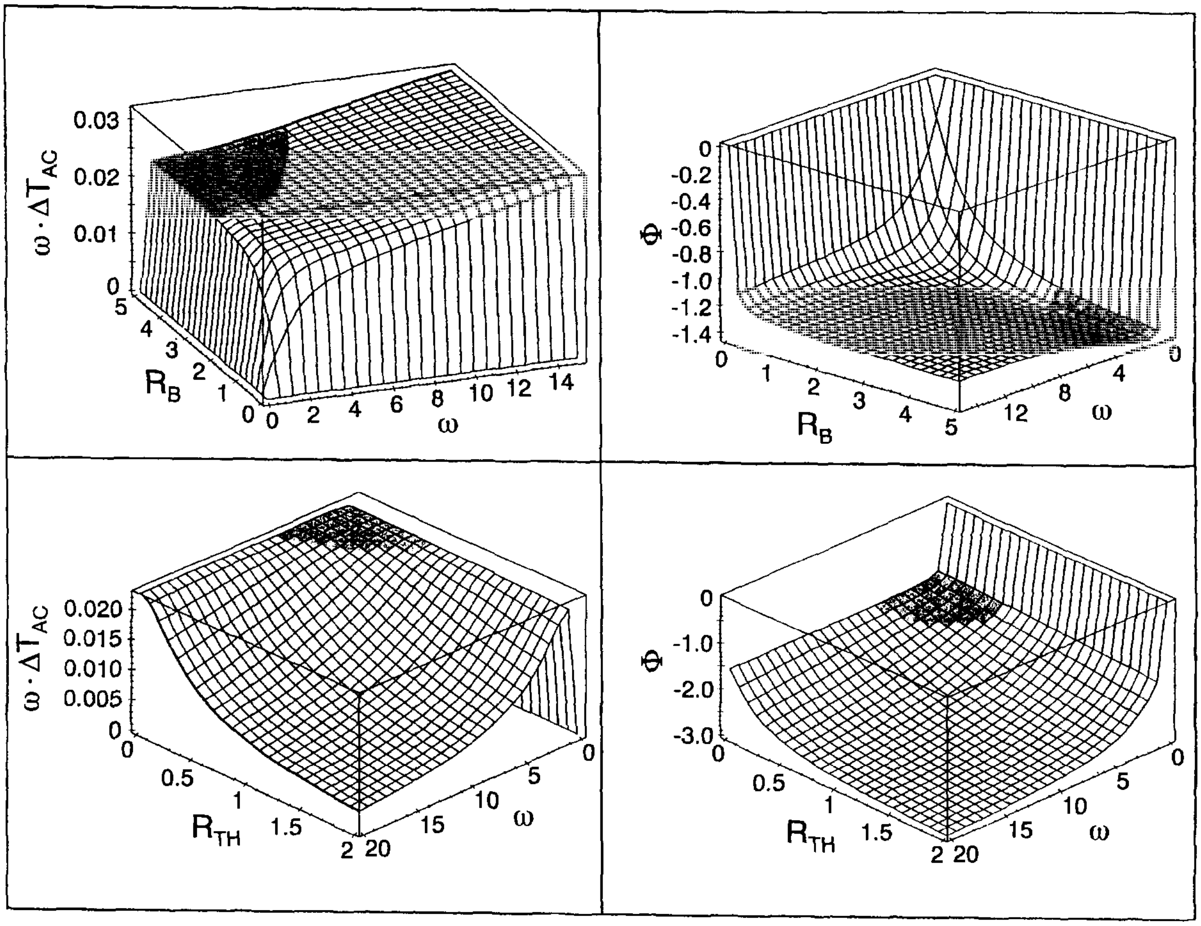

Fig. 6. Amplitude multiplied with frequency ωT_{AC} (left side in K s^{-1}) and phase shift ϕ (right side, in radians) as a function of the various thermal resistances R_{TH}, R_{B} and R_{S}, calculated according to Eqs. (25)–(28) for the calorimeter system shown schematically in Fig. 4(b). For detailed discussion, see text. The values used for the calculations are, for the heat capacities (in J/g K), always: $C_{\mathrm{S}} \equiv C_{\mathrm{SS}} = 1$, $C_{\mathrm{th}} = 0.2$; for the thermal resistances (in mK/W) the following holds: upper part (ideal thermal coupling of thermometer) – $0 < R_{\mathrm{B}} < 5$, $R_{\mathrm{S}} = 0.1$, $R_{\mathrm{Th}} = 0$ and $0 < \omega < 15$ lower part (ideal thermal coupling of sample) – $R_{\mathrm{B}} = 3$, $R_{\mathrm{S}} = 0$, $0 < 2$ and $0 < \omega < 15$. Note that the correct heat capacity is measured for a phase shift of −90° which corresponds to a phase shift value of $\phi = -1.57$ in the diagrams shown.

resistance to the thermometer is increased. The corresponding phase behaviour is given in the right side diagram, and does not show a larger region where $\phi = -1.57$, allowing correct heat capacity experiments.

Case (iii) shows that the thermal resistances and frequency may influence the temperature and phase signals in a complex way. If characteristic frequencies (of the various $1/\tau_i$) coincide, the effects can mask the influence of one another because their influence on amplitude and phase may be opposite, e.g. in Fig. 7 (lower diagrams) a correct phase $-\pi/2$ can be found in the diagram of the phase, but the corresponding ΔT_{AC} would be wrong; conversely, the phase that belongs to the correct amplitude $\omega\Delta T_{\mathrm{AC}} = 0.23$ is not $-\pi/2$.

The results of this rather simple model explain why it is highly recommended to examine stringently the frequency behaviour of the calorimeter in question, empty and with sample loaded, with respect to phase and amplitude, and that the amplitude and phase-shift behaviour may be complex even in simple cases. For

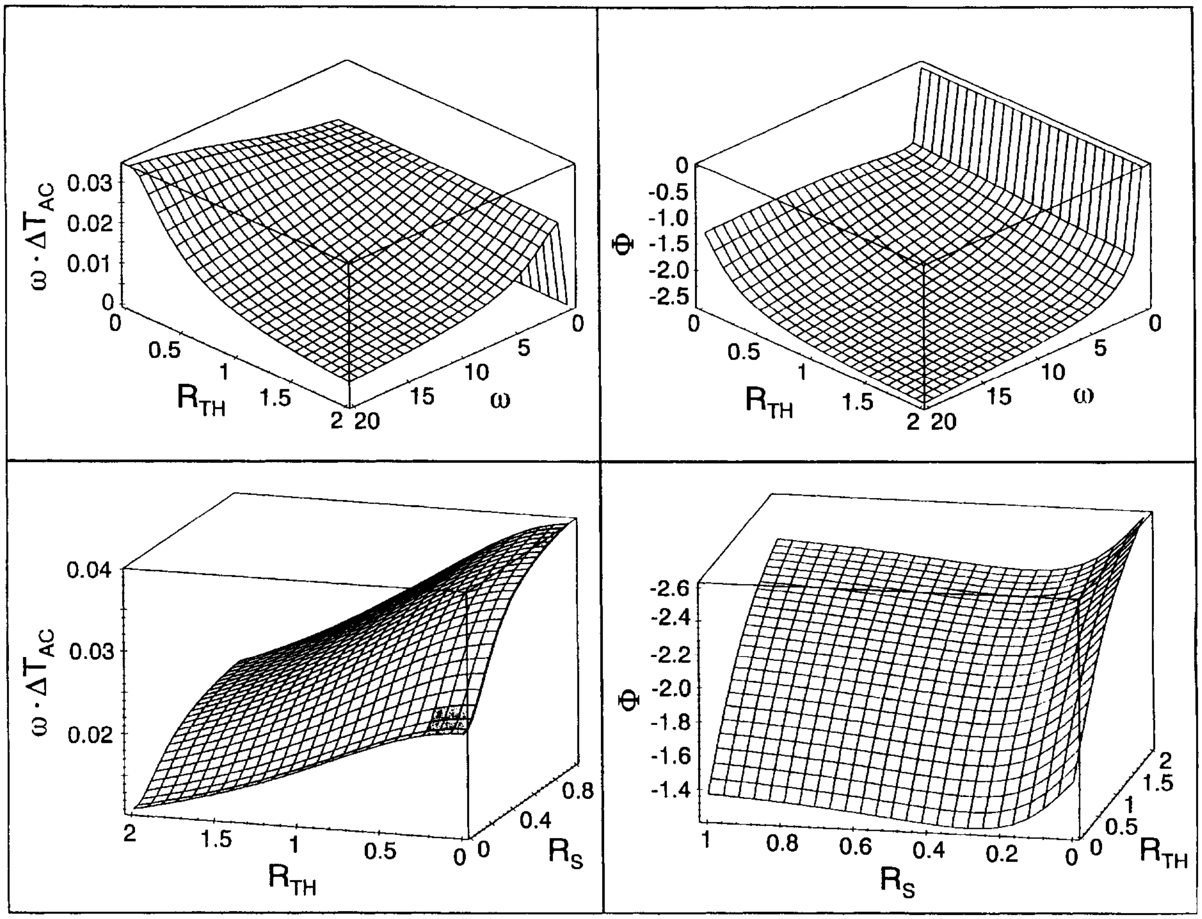

Fig. 7. Caption and units are identical with Fig. 6. The values used for the thermal resistances are: upper part (finite thermal resistances) – $R_B = 3$, $R_S = 0.1$, $0 < R_{Th} < 2$ and $0 < \omega < 15$; lower part (finite thermal resistances) – $R_B = 3$, $0 < R_S < 1$, $0 < R_{Th} < 2$ and $\omega = 5$.

dynamic heat capacity experiments, however, the frequency dependences may interfere with the sample-intrinsic relaxation processes and, hence, render again more complicated the separation of the various relaxation times or the data interpretation, respectively. A knowledge of the ω-dependence of the instruments is indispensable.

It is another interesting result of Velichkov's analysis [15] that heat capacity determination may be performed also under the condition that $\omega\tau_{ext} < 10$. For the validity of Eqs. (22) and (23), $\omega\tau_{ext} > 10$, must hold and it is required that the calorimeter works under quasi-adiabatic condition (influence of R_B is negligible). The condition $\omega\tau_{ext} > 10$ sets a lower limit for the applicable frequency. When $\omega\tau_{ext} < 10$, the thermal resistance R_B significantly influences T_{AC}; however, that influence can be determined exactly in a simple way. If $R_{Th} \sim R_S \sim 0$, then from Eq. (25), with $\tau_B = R_{BC}$ and C being defined by Eq. (7), it follows that:

$$\begin{aligned}\Delta T_{AC} &\equiv [P_{AC}R_B]/[1+(\omega\tau_{ext})^2]^{1/2}\\ &= T_{DC}[1+(\omega\tau_{ext})^2]^{1/2}\end{aligned} \tag{29}$$

$$\begin{aligned}\phi &\equiv -\arccos\{(1+(\omega\tau_{ext})^2)^{-1/2}\}\\ &= \arccos\{\Delta T_{AC}/T_{DC}\}\end{aligned} \tag{30}$$

by use of $T_{DC} = P_{AC}R_B$. Thus the resulting ΔT_{AC} is corrected by a term involving sin ϕ only:

$$C = (P_{\mathrm{AC}}/\omega\Delta T_{\mathrm{AC}})[1 - (\Delta T_{\mathrm{AC}}/T_{\mathrm{DC}})^2]^{1/2} = (P_{\mathrm{AC}}/\omega\Delta T_{\mathrm{AC}})\sin\phi \tag{31}$$

The outlined analysis changes only by constant factors when periodic excitations other than sinusoidal waveforms are used [70,81] or asymmetric heating occurs due to the pulse shape of the laser beam used [131]. The application of different non-sinusoidal waveforms lead, in general, only to a constant prefactor (≈ 1) to the given formulae.

The effect of heat leakage from the sample into the electrical wires and the influence of the ratio of sample size (or heat capacity, respectively) to measuring wires were discussed. The indicated temperature oscillations (e.g. of a thermocouple) are disturbed close to the region where the thermometer is attached to the sample [132]. Other effects may occur that deteriorate the measurement and lead to incorrect results, e.g. radiation losses of the thermometer, asymmetries of the caloric cell, influence of the position of the sample on the support, thermal contact of the thermometric sensor [37,38,130,132,188].

4.1. *Requirements and limiting conditions for correct and reliable TMC experiments*

To perform reliable and correct TMC measurements, the following requirements must be fulfilled:

- Test the frequency dependence of the empty system by plotting $(P/\Delta T)$ vs. ω.
- Determine the thermal constant of the calorimeter τ_{B} by measuring $\Delta T_{\mathrm{DC}} = (P_{\mathrm{DC}}/K_{\mathrm{B}})$ when a constant power is applied to the calorimeter.
- Adiabatic conditions (with respect sample) are valid if: $\tau_{\mathrm{int}} = L^2/(90)^{0.5} \cdot D \ll \omega^{-1} \ll \tau_{\mathrm{ext}}$. The sample thickness must remain below the limit given by $d \ll (\omega D)^{1/2}$, so that a uniform temperature distribution is guaranteed across the sample.
- The heat capacity can be calculated in a straightforward manner from Eq. (22) when the phase shift remains small: $\tan\phi > 10$ or $\sin\phi < 0.005$.
- For a temperature-sweep experiment, the scanning rate β must remain much smaller than the modulation-induced periodic temperature changes $dT : \beta = (\delta T/\mathrm{d}t) < (\mathrm{d}T/\mathrm{d}t)$,
- The temperature amplitude applied should remain always smaller than 10^{-3} of the absolute temperature,
- In the case of investigation of dynamic heat capacity – or the separation of real and imaginary part – it is recommended to establish the isothermal frequency dependence of the loaded and empty calorimeter at various temperatures. Also, the amplitude and phase shift of the calorimetric cell should be monitored permanently, e.g. by displaying the corresponding Lissajous figures [44,45].
- Remember whether heat capacity or enthalpy are being measured.

Obviously, most of the inconsistencies reported in the literature and most of problems with TMC originate from the low thermal diffusivity of the sample. Therefore, a careful check and control of the influence of the relevant sample parameters – dependence on mass, thickness, frequency, thermal coupling (to the sample support) – on the result is mandatory in TMC as in DSC experiments [38]. When part of the sample does not experience the modulation imposed, the measured heat capacity decreases; as soon as the thermal resistance in the sample–support–thermometer assembly increases, the phase shifts also changes the temperature amplitude. Such effects may occur, in particular, while measuring phase transitions when, due to the strong variation of the heat capacity in the transition region, the thermal diffusivity drops down or sample specific phonon scattering mechanisms become activated, e.g. phonon-spin disorder scattering.

This short overview on modelling TMC systems illustrates that a detailed and realistic theoretical description of the components acting in a calorimeter under modulating operation become complex. Modelling becomes even more complicated when (i) differential arrangements, as shown in Fig. 5, are used, and (ii) heat-flow instruments ($R_{\mathrm{B}} \leq R_{\mathrm{S}}$) are modelled [42–48,133]. *It would be of great help – and contribute to clarify the scientific problems studied – if the commercial instrumentation available now, could be equipped with permanent amplitude and phase monitoring and with isothermal frequency sweep facilities.*

Table 4
Selected overview on characteristic parameters of some temperature-modulated calorimeters

Year	Authors/[reference]	T-range (K)	Scan (K/min)	f (Hz)	ΔT (K)	$\mathrm{d}T/T$	$\mathrm{d}C/C$ absolute	$\mathrm{d}C/C$ relative	Sample (mg)	Special conditions and remarks
1967	Handler et al. [2]	≈ 600	(+)[a]	26	0.01	0.0005	—	0.5	25 μm foil	Heating by modulated light source
1968	Sullivan and Seidel [1]	1–4	(+)[a]	10	0.003	0.0002	0.02	0.1	86	Low temperature and magnetic field
1971	Connolly et al. [130]	0.06	no	0.05	?	0.01	?	0.004	8	Magnetic field/Ni-Curie point
1971	Hemstead and Mochel [54]	1–4	—	0.05	0.0001	0.0001	0.02	10^{-4}	~1.500	Critical exponents/thermal equilibrium
1972	Manuel et al. [17]	0.3–4	—	—	—	—	—	—	—	Very low temperatures
1979	Eichler and Gey [18]	1–10	no	120	0.005	0.001	0.03	0.01	50–100	High pressure
1981	Kämpf et al. [72]	0.05–10	(+)[a]	10	$<10^{-4}$	—	0.05	0.001	0.3	Thin film, prepared in situ
1982	Suzuki et al. [71]	0.3–4	(+)[a]	>200	—	0.002	0.05	0.002	—	B-field sweep, pJ-resolution
1983	Imaizumi et al. [85]	270–400	2	1–2	0.02	mK	—	0.002	100 μm	Biological material
1984	Gast and Jakobs [22]	300–800	no	1–5	0.1	—	0.05	0.002	—	Computation of phase signal
1985	Garland [67]	ca. 300	$<10^{-4}$	0.03	0.005	mK	0.02	$<10^{-4}$	50–100	Pressure/liquid crystals
1986	Birge and Nagel [23]	90–350	10^{-3}	0.01–3000	—	<0.1	mK	—	—	100 Specific heat spectrometer
1988	Yao and Hatta [111]	300	(+)[a]	1	—	mK	0.01	0.004	1 μl	Liquid in stainless steel tube
1989	Graebner [19]	2–300	(+)[a]	0.07–2	—	mK	0.1	0.0001	0.003(!)	High-magnetic field
1989	Kenny and Richards [65]	2–100	—	150–500	—	0.001	—	0.025	—	UHV/absorbed gas
1991	Gee et al. [66]	300–400	(+)[a]	35	—	mK	—	0.0001	20×10^{-6}	Free standing films
1993	Bednarz et al. [57]	300	0.003	—	$<10^{-5}$	<mK	0.002	—	20	High resolution experiment
1994	Castro and Puertolas [70]	300–550	10^{-5}	30–60	0.05–0.3	<mK	5	0.001	ca.10	Liquid crystals, scan 1 mK/h

[a] Scanning experiments performed without more specification.

5. Performance of select experimental equipment

Far more than 200 experimental arrangements have been described in the literature since 1968. Each displays particular features, technical details and the experimental equipment are often constructed for a special purpose such as temperature range, type of sample, etc. Their performances, regarding absolute accuracy or relative resolution, temperature or caloric resolution are also very different. It would be good to find these equipments listed in one comparative table but this would require more space than available here. Instead, we conduct a random walk through the literature of the last 25 years and pick-up some installations that constitute particular progress and give a rather detailed description of the experiment. That illustrates the broad scope of different experimental implementations performed over the years. The apparatus selected are listed in Table 4 in historical order together with their most characteristic parameters. Except for this collection, the author abstains from discussing further details and refers to the list of classified references presented in Table 5, and to other contributions in this volume. The literature survey, given in Table 5, should enable the reader to go into more details.

The temperature range covered by TMC today ranges from 50 mK to 3600 K, nearly over five decades in temperature. The frequency ranges from mHz to a few kHz, and covers in a few experiments only 2 to 2.5 decades, whereas in ultrasound and thermoelastic experiments the frequency can be changed by 16 orders of magnitude. For TMC, the relative resolution, in temperature as well as in energy, are among the best achieved in calorimetry. Resolution up to 10^{-5}, or better have been reported whereas the absolute accuracy is limited: the error amounts typically to (1–10)%. The ultimate energies measured with TMC (at low temperatures) are in the pico-Joule range [1,19,65] and must be compared with the measurement of changes of reaction energy detected with a modified atomic-force microscope where 10^{-18} J has been measured ([134]; for more information on this field see, e.g. Ref. [191]). The installations listed in Table 4 also include some cases in which the sample is submitted to extreme external conditions like high magnetic field or high pressure. Most of the experiments are performed in the scanning mode. Shortly after the pioneering work of Sullivan and Seidel, the frequency dependence of the heat capacity was sometimes studied (see Table 5). As mentioned in Section 1, the samples investigated by TMC include any of the chemical and physical properties with particular emphasis on small samples and thin films.

6. Summary

The review given here shows the great variety of *temperature-modulated calorimeters* that was designed during the last three decades. There is no standard technique available, rather the experiments consist of very differently and individually constructed facilities. That is, at the same time, an advantage and a disadvantage: The variety and creativity have pushed forward the technical development and have enhanced the wish to understand deficiencies on the one hand, but have hindered a modelling in deep that could be generally applicable, on the other. The appearance of commercial TMDSC has made understanding and modelling of TMC calorimeters a challenge and will, in future, certainly promote significantly our understanding of the additional information gained from TMC experiments at various frequencies. TMC, including the 3ω method, turns out to be the most suitable tool to study dynamic heat capacity and, in this context, certain relaxation phenomena like melting, phase transitions (e.g. glass transition), incommensurability, magnetic or dielectric domains, etc., may be better understood in future.

For nearly thirty years, TMC was performed preferentially as a quasi-adiabatic experiment with a constant phase shift of 90°, to measure 'static' heat capacities. Now, opening the frequency/time scale for calorimetry by broader application of TMDSC, it must become a routine to: (i) calibrate the DSC instruments used by recommended standard procedures and materials; (ii) describe the properties of the caloric cell properly with respect to frequency dependence and the various thermal relaxation times; (iii) indicate the limits where strong phase shifts occur indicating deviation from quasi-adiabatic state or non-stationary conditions in the experimental run; and (iv) display and reference continuously any variation of phase (with the measurement of the temperature amplitude) during the measurement. Thus, presumably, we are at

Table 5
Survey on the literature for temperature-modulated calorimetry

Techniques	Literature
Overviews	[4,5,35,36,47,51,52,55,64,70,93,113–118]
on AC calorimetry	[5,35,51,55,67,97,109,111,118]
Theory	[1,5,7,15–24,26,29,42–45,57,61,67,74,95,96,100,101,113,127–130]
dynamic specific heat	[40–44,46–48,152] and Refs. in [48]
Modulated sample heating	
resistive (Joule heating)	[1,13,14,18,19,22–25,27–29,31,53,54,56,60,65,71,72,81,88,107,130,132,135,138,141,150–152,174,176,178,179,181]
light	[2,21,26,30,62,66,70,71,74,80,85,87,94–98,100,107,130,131,145,153,165,182]
direct resistive heating	[3,5,16,50,51,93,136]
elctron bombardement	[5,50,136]
inductive heating	[51,155]
Detection of temperature oscillations	
resistance thermometer	[1,13,14,17–19,22,24,25,30,31,53,54,56,65,68,88,70,72,101,135,139–142,152,174,178,181]
thermocouple	[2,20,21,26,60–62,66,73,74,80,87,98,99,130,131,137,138]
photoelectric detector	[5] (refs. therein),[90,113,156]
Temperature range	
low temperature	[1,6,7,9,10,17–19,31–34,62,63,65–68,71,72,78,80,87,97,100,112,114,117,131,132,137–139, 142–144,147,150–152,157,174,176,177,179–187]
ambient temperature	[2,16,21,26,27,53,56–59,67,70,74,79,85,88,89,95,96,100,130,135,140,141,144–146,148–160, 165,179–181]
External conditions for sample	
high magnetic field	[1,13,19,30,63,68,98,101,130,152,177,178,189]
high pressure	[18,53,56,59–63,67,149]
Measured physical parameter [a] (without static specific heat)	
thermal conductivity	[102,110,135,139,162,172]
thermal diffusion	[20,21,74,85–88,94–102,148,157,162–164,172]
phase dependence	[10,22–30,79,107,127,166–169]
frequency dependence	[5,10,16,21–30,55,60,78,79,83,88,127,156,173,184]
time dependence	[28,31–34,108]
Special arrangements for	
high precision calorimetry	[9,21,26,34,53–58,65,67–70,108,160,167,170,171,183,186]
specific heat spectroscopy	[10,23–25,27,29,66,83,85,166]
simultanous methods	[30,87,101–103,105–107,109,172]
very small samples	[7,19,65–67,71–73,78,98,108,110,118,173–175]
high frequency	[5,51]
biological materials	[27,85,106,166,183,185]
3ω method	[10,11,23,24,46,47,76–79,107]
detoriating effects	[37,38,95,101,103,109,130,132,161,188]

[a] Dynamic specific heat is included in 'phase-dependence' and 'frequency-dependence'.

the beginning of an exciting new development that I would call heat-capacity spectrometers where additional information as complex heat capacity becomes available. On the other hand, one has to admit that many complex thermal properties in the so-called materials are based mainly on instrumental and not on materials-intrinsic properties. Such instruments do not facilitate measurements or save time: in contrast, the supplementary information supplied requires more measuring time and delivers more complex results. Full advantage of the new information is taken when: (i) in addition to the temperature scale, the frequency scale is also fully scanned, as for instance, isothermal frequency scanning, eventually at different (frequency) scanning rates, and (ii) during data computation the different experimental relaxation times (including internal sample relaxation characterized by its diffusivity) and sample intrinsic relaxation time (e.g. stored energy) are determined and scrutinized. The instrumental development should emphasize equipment with large frequency range, smaller temperature-modulation amplitude and the possibility of isothermal frequency sweeps. Simultaneous experiments and combination of the various calorimetric methods on the same measuring cell are advantageous and will receive increased attention to have both, highest caloric resolution and absolute precision even when repeated measurement on the sample with different methods are required. In fact, the present construction of all the commercial DSC instruments is most unsuitable as heat spectrometer. The expansion of the frequency range, according to the present knowledge may be possible only by further developing, simplifying and improving the performance of the 3ω method.

Acknowledgements

The author thanks R. Stitzinger for performing the model calculations, W.Schnelle and G. Rangarajan for many valuable comments and gratefully acknowledges many interesting and clarifying discussions with the colleagues who participated at IV. Lähnwitz seminar.

References

[1] P.F. Sullivan and G. Seidel, Phys. Rev., 173 (1968) 679.
[2] P. Handler, D.E. Mapother and M. Rayl, Phys. Rev. Lett., 19 (1967) 356.
[3] Y.A. Kraftmakher, Zh. Prikl. Mekh. and Tekh. Fiz., 5 (1962) 176.
[4] W. Hemminger and G. Höhne, Grundlagen der Kalorimetrie, Verlag Chemie, Weinheim, 1979.
[5] Y.A. Kraftmakher, Modulation Calorimetry, in: K.D. Maglic, A. Cezairliyan and V.E. Peletsky (Eds.), Compendium of Thermophysical Property Measurement Methods, Vol.1, Plenum Press, New York, 1984, Chap. 1, pp. 591–641; ibid Vol.2, Chap.14, pp. 409–436.
[6] R. Bachmann, F.J. DiSalvo, Jr., T.H. Geballe, R.L. Greene, R.E. Howard, C.N. King, H.C. Kirsh, K.N. Lee, R.E. Schwall, H.U. Thomas and R.B. Zubeck, Rev. Sci. Instrum., 43 (1972) 205; Ya.A. Kraftmakher, High Temp. High Pressure, 24 (1992) 433.
[7] U. Rahm and E. Gmelin, J. Therm. Anal., 38 (1992) 335.
[8] A. Junod, J. Phys. E: Sci. Instrum., 12 (1979) 945; A. Junod, E. Bonjour, R. Calemzuczuk, J.Y. Henry, J. Muller, G. Triscone and J.C. Vallier, Physica C, 211 (1993) 304.
[9] W. Schnelle and E. Gmelin, Thermochim. Acta., 269/270 (1995) 27.
[10] D.H. Jung, T.W. Kwon, D.J. Bae, I.K. Moon, Y.H. Jeong, Measurement Science and Technology, 3 (1992) 475; Y.H. Jeong, D.J. Bae, T.W. Kwon and I.K. Moon, J. Appl. Phys., 70 (1991) 6166.
[11] O.M. Corbino, Phys. Z., 12 (1911) 292; *ibid* Phys. Z., 11 (1910) 413.
[12] M. Reading, D. Elliott and V.L. Hill, J. Therm. Anal., 40 (1993) 949; S.R. Sauerbrunn, B.S. Crowe and M. Reading, Polym. Mater. Sci. Eng., 68 (1993) 269; P.S. Gill, S.R. Sauerbrunn and M. Reading, J. Therm. Anal., 40 (1993) 931.; W.J. Sichina, Am. Lab. (Shelton, Conn.), 25 (1993) 26.
[13] P.F. Sullivan and G. Seidel, Phys. Lett., 25A (1967) 229.
[14] P.F. Sullivan and G. Seidel, Ann. Acad. Sci. Fennicae, 210 (1966) 58.
[15] I.V. Velichkov, Cryogenics, 32 (1992) 285.
[16] Ya.A. Kraftmakher and V.L. Tonaevskii, Phys. Stat. Sol. (a), 9 (1972) 573.
[17] P. Manuel, H. Niedoba and J.J. Veyssié, Rev. Physique Appliquée, 7 (1972) 8.
[18] A. Eichler and W. Gey, Rev. Sci. Instrum., 50 (1979) 1445.
[19] J.E. Graebner, Rev. Sci. Instrum., 60 (1989) 1123.
[20] I. Hatta, H. Yao, R. Kato and A. Maesono, Jpn. J. Appl. Phys., 29 (1990) 2851.
[21] I. Hatta and A. Ikushima, J. Phys. Chem. Solids, 34 (1973) 57.
[22] Th. Gast and H. Jakobs, Thermochim. Acta, 72 (1984) 71.
[23] N.O. Birge and S.R. Nagel, Rev. Sci. Instrum., 58 (1987) 1964.
[24] N.O. Birge, Phys. Rev., B 34 (1986) 1631.
[25] P.K. Dixon, Phys. Rev., B 42 (1990) 8179.
[26] I. Hatta and A. Ikushima, Phys. Lett., 37A (1971) 207.
[27] H. Yao, H. Nagano, Y. Kawase and K. Ema, Biochimica et Biophysica Acta, 1212 (1994) 73.
[28] R.B. Phelps, J.T. Brimingham and P.L. Richards, J. Low Temp. Phys., 92 (1993) 107.
[29] Y. Saruyama, J. Therm. Anal., 38 (1992) 1827.
[30] L.J. Schowalter, M.B. Salamon, C.C. Tsuei and R.A. Craven, Solid State Commun., 24 (1977) 525.

[31] H. Tietje, M. v.Schickfus and E. Gmelin, Z. Phys. B – Condensed Matter., 64 (1986) 95, and further refs. therein.
[32] J. Zimmermann, Cryogenics, 24 (1984) 27.
[33] M.T. Loponen, R.C. Dynes, V. Narayanamurti and J. Garno, Phys. Rev., B 25 (1982) 1161.
[34] M. Meissner and K. Spitzmann, Phys. Rev. Lett., 46 (1981) 265.
[35] B. Wunderlich, Thermal Analysis, Academic Press, San Diego, 1990.
[36] G.W.H. Höhne, W. Hemminger and H.-J. Flammersheim, Differential Scanning Calorimetry, Springer, Berlin, 1996.
[37] G.W.H. Höhne and J.E.K. Schawe, Thermochim. Acta, 229 (1993) 27; G.W.H. Höhne, J. Therm. Anal., 37 (1991) 1987; G.W.H. Höhne and E. Glöggler, Thermochim. Acta, 151 (1989) 295.
[38] E. Gmelin and St.M. Sarge, J. Appl. Chem., 67 (1995) 1789.
[39] M.J. Richardson, The application of differential scanning calorimetry to the measurement of specific heat, in: K.D. Maglic, A. Cezairliyan, V.E. Peletsky (Eds.), Compendium of Thermophysical Property Measurement Methods, Vol.2, Plenum Press, New York, 1984, Chap. 18, p. 518.
[40] M. Fixmann, J. Chem. Phys., 33 (1960) 1363; *ibid* 36 (1962) 1961; R.A. Ferell and J.K. Bhattacharjee, Phys. Rev., A 31 (1985) 1788.
[41] K.F. Herzfeld and F.O. Rice, Phys. Rev., 31 (1928) 691.
[42] J.E.K. Schawe, Thermochim. Acta, 261 (1995) 1; 261 (1995) 183.
[43] J.E.K. Schawe, Thermochim. Acta, 271 (1996) 127.
[44] B. Wunderlich, this issue.
[45] B. Wunderlich, A. Boller, I. Okazaki and S. Kreitmeier, Thermochim. Acta, (1996); B. Wunderlich, Y. Yin and A. Boller, Thermochim. Acta, 238 (1994) 277; A. Boller, C. Schick and B. Wunderlich, Thermochim. Acta, 266 (1995) 97; A. Boller, Y. Jin, and B. Wunderlich, J. Therm. Anal., 42 (1994) 307.
[46] H. Donth et al., this volume.
[47] Y.H. Jeong, this volume.
[48] J.E.K. Schawe, this volume.
[49] L.A. Rosenthal, Rev. Sci. Instrum., 32 (1961) 1033.
[50] L.P. Filippov, Inzh. Fiz. Zh., 3 (1960) 121.
[51] Ya.A. Kraftmakher, High Temp. High Pressure, 24 (1992) 433.
[52] Ya.A. Kraftmakher, High Temp. High Pressure, 5 (1973) 645.
[53] J.E. Smaardyk and J.M. Mochel, Rev. Sci. Instrum., 49 (1978) 988; B. Kasting, K.J. Lushington and C.W. Garland, Phys. Rev., B 22 (1980) 321; K.J. Lushington, G.B. Kasting and C.W. Garland, Phys. Rev., B 22 (1980) 2569.
[54] R.D. Hemstead and J.M. Mochel, Phys. Rev., 7 (1973) 287.
[55] I. Hatta and A.J. Ikushima, Jpn. J. Appl. Phys., 20 (1981) 1995.
[56] C.W. Garland, G.B. Kasting and Lushington, Phys. Rev. Lett., 43 (1979) 1420..
[57] G. Bednarz, B. Millier and M.A. White, Rev. Sci. Instrum., 63 (1992) 3944.
[58] G. Bednarz, D.J.W. Geldart and M.A. White, Phys. Rev., B47 (1993) 14247.
[59] A. Bonilla and C.W. Garland, J. Phys. Chem. Solids, 35 (1974) 871.
[60] X.C. Jin, P.H. Hor, M.K. Wu and C.W. Chu, Rev. Sci. Instrum., 55 (1984) 993.
[61] J.D. Baloga and C.W. Garland, Rev. Sci. Instrum., 48 (1977) 105.
[62] S. Stokka and V. Samulionis, Phys. Stat. Sol. (a), 67 (1981) K89; S. Stokka and K. Fossheim, J. Phys. E: Sci. Instrum., 15 (1982) 123.
[63] X. Chen, A.S. Perel, J.S. Brooks, R.P. Guertin and D.G. Hinks, J. Appl. Phys., 73 (1993) 1886.
[64] E.S.R. Gopal, Specific Heat at Low Temperatures, Heywood, London, 1966.
[65] T.W. Kenny and P.L. Richards, Rev. Sci. Instrum., 61 (1990) 822.
[66] R. Geer, T. Stoebe, T. Pitchford and C.C. Huang, Rev. Sci. Instrum., 62 (1991) 415.
[67] C.W. Garland, Thermochim. Acta, 88 (1985) 127.
[68] G.M. Schmiedshoff, N.A. Fortune, J.S. Brooks and G.R. Stewart, Rev. Sci. Instrum., 58 (1987) 1783.
[69] J.M. Viner, D. Lamey, C.C. Huang, R. Pindak and J.W. Goodby, Phys. Rev., A28 (1983) 2433.
[70] M. Castro and J.A. Puértolas, J. Therm. Anal., 41 (1994) 1245.
[71] T. Suzuki, T. Tsuboi and H. Takaki, Jpn. J. of Appl. Phys., 21 (1982) 368.
[72] G. Kämpf, H. Selisky and W. Buckel, Physica, 108B (1981) 1263.
[73] H. Yao and I. Hatta, Jpn. J. Appl. Phys., 27 (1988) L121.
[74] I. Hatta, Y. Sasuya, R. Kato and A. Maesono, Rev. Sci. Instrum., 56 (1985) 1643.
[75] M. Meichle and C.W. Garland, Phys. Rev., A27 (1983) 2624.
[76] A.A. Kurichenko, A.D. Ivliev and V.E. Zinovev, Teplofiz. Vys. Temp., 24 (1986) 493.
[77] K. Nahm, C.K. Kim, M. Mittag and Y.H. Jeong, J. Appl. Phys., 78 (1995) 3980.
[78] D.G. Cahill, H.E. Fischer, T. Klitsner, E.T. Swartz and R.O. Pohl, J. Vac. Sci. Technol., A7 (1989) 1259; D.G. Cahill, Rev. Sci. Instrum., 61 (1990) 802.
[79] I.K. Moon, Y.H. Jeong and S.I. Kwun, Rev. Sci. Instrum., 67 (1996) 29.
[80] A. Kishi, R. Kato, T. Azumi, H. Okamoto, A. Maesono, M. Ishikawa, I. Hatta and A. Ikushima, Thermochim. Acta, 133 (1988) 39.
[81] F.L.A. Machado and W.G. Clark, Rev. Sci. Instrum, 59 (1988) 1176.
[82] Ya.A. Kraftmakher and V.Ya. Cherepanov, Teplofiz. Vys. Temp., 16 (1978) 647.
[83] R.C. Smith, J. Appl. Phys., 37 (1966) 4860; R.C. Smith and R.L. Holland, J. Appl. Phys., 37 (1966) 4866.
[84] H.S. Carslaw and J.C. Jäger, Conduction of Heat in Solids, Clarendon Press, Oxford, 1959.
[85] S. Imaizumi, K. Suzuki and I. Hatta, Rev. Sci. Instrum., 54 (1983) 1180.
[86] D.H. Howling, E. Mendoza and J.E. Zimmermann, Proc. R. Soc. London Ser. A, 229 (1955) 86.

[87] M.B. Salamon, R.P. Garnier, B. Golding and E. Buechler, J. Phys. Chem. Solids, 35 (1974) 851.
[88] K. Ema, G. Nounesis, C.W. Garland and R. Shashidher, Phys. Rev., A 39 (1989) 2599.
[89] K.K. Smith and P.W. Bigler, Phys. Rev., 19 (1922) 268.
[90] G.C. Loewenthal, Austral. J. Phys., 16 (1963) 47.
[91] L.P. Filippov and R.P. Yurchak, Teplofiz. Vys. Temp., 3 (1965) 901.
[92] S. Ikeda and Y. Ishikawa, Jpn. J. Appl. Phys., 18 (1979) 1367.
[93] Ya.A. Kraftmakher, High Temp. High Pressure, 24 (1992) 145.
[94] I. Hatta, R. Kato and A. Maesono, Jpn. J. Appl. Phys., 25 (1986) L493.
[95] Y. Gu and I. Hatta, Jpn. J. of Appl. Phys., 30 (1991) 1137.
[96] Y. Gu and I. Hatta, Jpn. J. of Appl. Phys., 30 (1991) 1295.
[97] W. Brill and E. Gmelin, J. Therm. Anal., 33 (1988) 365.
[98] I. Hatta, K. Sakakibara, J. Suzuki and H. Yao, Jpn. J. of Appl. Phys., 27 (1988) 2156.
[99] I. Hatta, Pure and Appl. Chem., 64 (1992) 79.
[100] P.R. Garnier and M.B. Salamon, Phys. Rev. Lett., 27 (1971) 1523.
[101] I. Hatta, Jpn. J. Appl. Phys., 33 (1994) L686.
[102] K. Ema, Ferroelectrics, 168 (1995) 147.
[103] I. Hatta, H. Ichikawa and M. Todokai, Thermochim. Acta, 267 (1995) 83.
[104] I. Hatta and S. Muramatsu, Jpn. J. Appl. Phys., preprint.
[105] I. Hatta, J. Therm. Anal., 272 (1996) 49.
[106] K. Ema, T. Uematsu, A. Sugata and H. Yao, Jpn. J. Appl. Phys., 32 (1993) 1846.
[107] S.-M. Lee and S.-I. Kwun, Rev. Sci. Instrum., 65 (1994) 966.
[108] Y. Saruyama, K. Takamizawa and Y. Urabe, Netsu Sokutei, 21 (1994) 61.
[109] I. Hatta, Pure and Appl. Chem., 64 (1992) 79.
[110] I. Hatta, H. Yao, R. Kato and A. Maesono, Jpn. J. Appl. Phys., 29 (1990) 2851.
[111] H. Yao and I. Hatta, Jpn. J. Appl. Phys., 27 (1988) L121; Solid State Physics, 24 (1989) 769.
[112] R.E. Schwall, R.E. Howard and G.R. Stewart, Rev. Sci. Instrum., 46 (1975) 1043.
[113] C.Y. Ho, Specific Heat of Solids, Hemisphere, New York, 1988, pp. 299.
[114] E. Gmelin, Thermochim. Acta, 29 (1979) 1.
[115] A. Junod, Specific heat of high temperature superconductors, in: D.M. Ginsberg (Ed.), Physical Properties of High Temperature Superconductors, World Scientific Publ., Sinagapore, 1990.
[116] E.F. Westrum, G.T. Furukawa, and J.P. McCullough, in: J.P. McCullough and D.W. Scott (Eds.), Experimental Thermodynamics, Vol.1, Butterworth, London, 1968, pp. 133.
[117] E. Gmelin, Thermochim. Acta, 110 (1987) 183.
[118] G.R. Stewart, Rev. Sci. Instrum., 54 (1983) 1.
[119] Ya.A. Kraftmakher, High Temp. High Pressure, 5 (1973) 645; Ya.A. Kraftmakher, in: E.G. Peggs (Ed.), Thermal Expansion, Vol.6, Plenum Press, New York, 1978, pp. 155.
[120] S.Yu. Glazkov and Ya.A. Kraftmakher, Teplofiz. Vys. Temp., 21 (1983) 769; S.Yu. Glazkov, Int. J. Thermophys., 6 (1985) 421.
[121] M.B. Salamon, D.S. Simons and P.R. Garnier, Sol. State Commun., 15 (1969) 1035.
[122] M. Kawai, T. Miyakawa and T. Tako, Jpn. J. Appl. Phys., 23 (1984) 1202.
[123] E. Papp, Z. Phys., B 55 (1984) 17.
[124] W. Kettler, S.N. Kaul and M. Rosenberg, Phys. Rev., B 29 (1984) 6950.
[125] G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1; H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Höhne and St.M. Sarge, Thermochim. Acta, 219 (1993) 333.
[126] St.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger and W. Eysel, Thermochim. Acta, 247 (1994) 129.
[127] M. Barrio, J. Font, J. Muntasell and J. Tamarit, J. Therm. Anal., 37 (1991) 39.
[128] C.A. Schantz and D.L. Johnson, Phys. Rev., A 17 (1978) 1504.
[129] B. Kasting, K.J. Lushington and C.W. Garland, Phys. Rev., B 22 (1980) 321.
[130] D.L. Connelly, J.L. Loomis and D.E. Mapother, Phys. Rev., B 3 (1971) 924.
[131] M. Yoshizawa, T. Fujimura, T. Goto and K.I. Kamiyoshi, J. Phys. C: Solid State Phys., 16 (1983) 131.
[132] A.A. Minakov and O.V. Ershov, Cryogenics, 34 (1994) 461.
[133] S. Sarge, S. Bauerecker and H.K. Cammenga, Thermochim. Acta, 129 (1988) 309.
[134] J.K. Gimzewski, C. Gerber, E. Meyer and R.R. Schlittler, Chem. Phys. Lett., 217 (1994) 589; *ibid*, NATO ASI Ser., Ser. E 292 (1995) 89.
[135] R.H. Bruce and D.S. Cannell, Rev. Sci. Instrum., 47 (1976) 1323.
[136] A.A. Varchenko, Ya.A. Kraftmakher and T.Yu. Pinegina, Teplofiz. Vys. Temp., 16 (1978) 844.
[137] C.C. Huang, J.M. Viner, R. Pindak and J.W. Goodby, Phys. Rev. Lett., 46 (1981) 1289.
[138] M. Inoue, Y. Muneta, H. Negishi and M. Sasaki, J. Low Temp. Phys., 63 (1986) 374.
[139] M. Mertig, G. Pompe and E. Hegenbarth, Solid State Commun., 49 (1984) 369.
[140] G.S. Iannachione and D. Finotello, Phys. Rev. Lett., 69 (1992) 2094.
[141] G. Nounesis, K.I. Blum, M.J. Young, C.W. Garland and Rj. Birgeneau, Phys. Rev., E 47 (1993) 1910.
[142] R.R. Vargas and A.J. Sanchez, Rev. Mex. Fis., 31 (1985) 663.
[143] I. Hatta and W. Rehwald, J. Phys. C: Solid State Phys., 10 (1977) 2075.
[144] K. Ema, K. Hamano, K. Kurihara and I. Hatta, J. Phys. Soc. Jap., 43 (1977) 1954.
[145] M. Maszkiewicz, Phys. Stat. Sol. (a), 47 (1978) K77.
[146] G. Sanchez, M. Meichle and C.W. Garland, Phys. Rev., A 28 (1983) 1647.
[147] P.R. Garnier, Phys. Lett., 35A (1971) 413.

[148] H.T. Shang, C.C. Huang and M.B. Salamon, J. Appl. Phys., 49 (1978) 3.

[149] N. Polandou, V.A. Chernenko and K. Novik, High Temp. High Pressures, 13 (1981) 399.

[150] G.H.J. Wantenaar, S.J. Campbell, D.H. Chaplin and G.V.H. Wilson, J. Phys. E: Sci. Instrum., 10 (1977) 825.

[151] R. Viswanathan and D.C. Johnston, J. Low Temp. Phys., 25 (1976) 1.

[152] V. Calzone, M. Putti and A.S. Siri, Thermochim. Acta, 162 (1990) 127.

[153] E.D. Yakushkin and V.N. Anisimova, Instruments and Experimental Techniques, 36 (1993) 492.

[154] G. Tannacchione, A. Strigazzi and D. Finotello, Liquid Crystals, 14 (1993) 1153.

[155] R.K. Wunderlich, H.J. Fecht and R. Willnecker, Appl. Phys. Lett., 62 (1993) 3111.

[156] P. Geraghty, M. Wixon and A.H. Francis, J. Appl. Phys., 55 (1984) 2780.

[157] G. Yang, A.D. Migone and K.W. Johnson, Rev. Sci. Instrum., 62 (1991) 1836.

[158] A.A. Varchenko and Ya. A. Kraftmakher, Phys. Stat. Sol. (a), 20 (1973) 387.

[159] N. Ohsawa, N. Tatan and S. Uchiyama, Jpn. J. Appl. Phys., 17 (1979) 1059.

[160] J.E. Smaardyk and J.M. Mochel, Rev. Sci. Instrum., 49 (1978) 988.

[161] Ya.A. Kraftmakher and V.Ya. Cherepanov, J. Chem. Phys., 21 (1978) 647.

[162] M. Ivanda and D. Djurek, J. Phys. E: Sci. Instrum., 22 (1989) 988.

[163] T. Tamane, S.-I. Katayama and M. Todoki, Rev. Sci. Instrum., 66 (1995) 5305.

[164] A. Maesono, R. Kato, I. Hatta and R.P. Tye, Therm. Conduct., 22 (1994) 473.

[165] Y. Gu, X. Tang, Y. Xu and I. Hatta, Jpn. J. Appl. Phys., 32 (1993) L1365.

[166] N.O. Birge and S.R. Nagel, Phys. Rev. Lett., 54 (1985) 2674.

[167] J.K. Wang, J.H. Campbell, D.C. Tsui and A.Y. Cho, Phys. Rev., B 38 (1988) 6174.

[168] S. Imaizumi, K. Tsuchida, T. Matsuda and I. Hatta, Suzuka Kogyo Koto Semmon Gakko Kiyo, 13 (1980) 197.

[169] J.A. Harrington, B.L. Bobbs, M. Braunstein, R.K. Kim, R. Stearns and R. Braunstein, Appl. Opt., 7 (1978) 1541.

[170] D.M. Ginsberg, S.E. Inderhees, M.B. Salamon, N. Goldfeld, J.P. Rice and B.G. Pazol, Physica, C153/555 (1988) 1082; S.E. Inderhees, Phys. Rev. Lett., 60 (1988) 1178.

[171] C.C. Huang, A.M. Goldman and L.E. Toth, Solid State Commun., 33 (1980) 581.

[172] C.C. Huang, J.M. Viner and J.C. Novack, Rev. Sci. Instrum., 56 (1985) 1390.

[173] D.W. Denlinger, E.N. Abarra, K. Allen, P.W. Rooney, M.T. Messer, S.K. Watson and F. Hellman, Rev. Sci. Instrum., 65 (1994) 946.

[174] J. Dutzi and W. Buckel, Z. Phys. B: Condensed Matter, 55 (1984) 99.

[175] B.C. Gibson, D.C. Ginsberg and C.P.L. Tai, Phys. Rev., B 19 (1979) 1409.

[176] R.L. Greene, C.L. King, R.B. Zubeck and J.J. Hauser, Phys. Rev., B 6 (1972) 3297.

[177] H.T. Shang and M.B. Salamon, Phys. Rev., B 22 (1980) 4401.

[178] J.D. LeGrange and J.M. Mochel, Phys. Rev., A., 23 (1981) 3215.

[179] D. Bittner and M. Bretz, Phys. Rev., B 31 (1985) 1060.

[180] W. Statius, J.R. Dillinger and D.L. Huber, AIP Conf. Proc., No., 10(Pt2) (1973) 1029.

[181] J. Vanderdeelen and L. Baert, Meded. Fac. Landbouwwet, Rijksuniv., Gent, 40 (1975) 1427.

[182] K. Tashiro, N. Ozawa, K. Sugihara and T. Tsuzuku, J. Phys. Soc. Jap., 59 (1990) 4022.

[183] O.S. Tanasijczuk and T. Oja, Rev. Sci. Instrum., 49 (1978) 1545.

[184] A. Hensel, J. Dobbertin, J.E.K. Schawe, A. Boller and C. Schick, J. Therm. Anal., 46 (1996) 935.

[185] O.L. Mayorga, A.N. Rascon and E. Freire, Thermochim. Acta, 238 (1994) 309. S.N. Lee and S.I. Kwun, Rev. Sci. Instrum., 65 (1994) 966.

[186] A. Schilling and O. Jeandupeux, Phys. Rev., B 52 (1995) 9714.

[187] R.W. Willekers, H.C. Meijer, F. Mathu and H. Postma, Cryogenics, 31 (1991) 168.

[188] R.P. Tye, R.L. Gardner and A. Maesono, J. Therm. Anal., 40 (1993) 1009.

[189] P. Garoche and W.L. Johnson, Solid State Commun., 39 (1981) 403.

[190] J.A. Lipa and T.C.P. Chui, Phys. Rev. Lett., 51 (1983) 2291.

[191] R. Forster and E. Gmelin, Rev. Sci. Instrum., 67 (1996) 4246.