ELSEVIER

Thermochimica Acta 304/305 (1997) 165–170

thermochimica
acta

Low-temperature AC microcalorimetry: Possibilities and limitations

Alexander A. Minakov*

General Physics Institute, Vavilov st. 38, 117942 Moscow, Russia

Received 6 June 1996; accepted 24 February 1997

Abstract

The possibilities and limitations of the low-temperature modulated calorimetry are investigated experimentally and theoretically. The effects of the sample holder and of the heat leakage into the thermocouple wires on the measured temperature oscillations are discussed. It is shown that the effects can lead to incorrect measurements and impose limitations on the calorimeter sensitivity and on the width of the appropriate frequency range of the sample temperature modulation. A proper choice of materials and external parameters enables the construction of the calorimeter with sensitivity of ca. 10^{-8} J/K at 5 K. The presented calorimeter provides the possibility of the heat-capacity measurements up to 10^3 Hz at low temperatures. High sensitivity and wide frequency range are of principal importance for investigations of complex heat capacity. © 1997 Elsevier Science B.V.

Keywords: Complex heat capacity; Low temperatures; Modulated calorimetry

---

1. Introduction

Modulated calorimetry [1–4] is based on the measurement of the temperature oscillations of a sample, which is heated by an oscillating heat flux. The AC technique is very sensitive and it is useful for a fast characterization of microsamples and thin films. The AC calorimetry enables heat-capacity measurements in the steady-state mode at continuously varying temperatures. This is very important for phase transition investigations, when a narrow peak of heat capacity should be studied. On the other hand, the AC technique gives a nontrivial opportunity for measurements of a complex heat capacity $\hat{c}_{(\omega)} = c' + c''$, which is a function of the frequency $\omega/2\pi$ of the sample temperature modulation. It is interesting to investigate the physical meaning of the imaginary part of heat capacity. A nonzero imaginary part $ic''_{(\omega)}$ of heat capacity reveals that a slow-relaxation process occurs in the substance. For example, consider a magnetic system with a short time τ_{ph} of relaxation to thermal equilibrium of the phonon subsystem and a long relaxation time τ_{m} of the magnon subsystem. In the low-frequency limit, it can be shown that $c'' \sim \omega\tau_m$. The imaginary part of specific heat capacity becomes negligible, when ω tends to zero. Consequently, the ability of high-frequency measurements is of principal importance for $c''_{(\omega)}$ investigations. The lower the temperature, the higher the upper limit of frequency, which can be achieved in the AC technique. Magnetic systems may be convenient for experimental study of the physical meaning of imaginary part of $\hat{c}$, since the magnetic phase transitions and the spin-glass transitions [5] may occur at low temperatures. Another way to increase the upper limit of frequency is to study very

---

*Corresponding author. Fax: (095)-135-82-81, (095)-135-02-70; e-mail: minakov@dsdep.gpi.ru.

PII S0040-6031(97)00125-1

thin samples (of the order of 10 μm). This requires highly sensitive apparatus with low heat-capacity detection limit. The present work is devoted to optimization of the conditions of measurements and formulate recommendations for optimization of the low-temperature AC calorimeter construction. The reasons which restrict the AC calorimetry possibilities are examined.

2. Propagation of the temperature waves

Consider a cylinder face, which is heated by a uniform oscillating heat flux $Q = Q_0\cos(\omega t)$. The flux density is $q = \mathrm{Re}\,[q_0\exp(i\omega t)]$, where $q_0 = Q_0/S$, and S denotes the face area. Provided the heat leakage through the cylinder curved surface is negligible, plane temperature waves $T = \mathrm{Re}\,[\hat{T}_0\exp(i\omega t \pm \hat{k}z)]$ propagate along the cylinder axis (denoted as z axis), where $\hat{k}$ is a complex wave number and $\hat{T}_0$ complex amplitude in the $z = 0$ plane. These waves satisfy the equation for heat transfer without heat sources. This results in the dispersion law:

$$\hat{k}^2 = i\omega c/\kappa, \tag{1}$$

where c and κ are the specific heat capacity and the thermal conductivity of the cylinder. A common feature of the plane temperature waves is the equality of the damping coefficient $\mathrm{Re}\,(\hat{k})$ and the wave number $\mathrm{Im}\,(\hat{k})$, i.e. $\hat{k} = k + ik$, where $k = \sqrt{\omega c/2\kappa}$. A plane temperature wave $\hat{T}_\omega\exp(i\omega t)$ with $\hat{T}_\omega = \hat{T}_0\exp(-\hat{k}z)$ is accompanied by the oscillating heat flux of a density $q_\omega = \mathrm{Re}\,[\kappa\hat{k}\hat{T}_\omega\exp(i\omega t)]$.

3. Temperature oscillations in the sample

Now consider a disk-shaped sample of volume V, thickness d and radius $R \gg d$. The corresponding parameters of the sample and of the ambient gas are c_s, κ_s, k_s and c_g, κ_g, k_g, respectively. A uniform heat flux $Q = \mathrm{Re}\,Q_0[1 + \exp(i\omega t)]$ is supplied to one of the disk faces. Such a flux can be created by an AC current flowing through a film-heater. The oscillating part $\hat{T}_\omega\exp(i\omega t)$ of the sample temperature depends on the heat flux and on the sample parameters. The temperature waves with a wave number k_g propagate from the sample faces into the ambient gas. For $Rk_g \gg 1$, these waves decay close to the sample surface. They can be considered as plane waves. In this case, the density of the oscillating heat flux flowing from the sample into the ambient gas is

$$q_\omega = \mathrm{Re}\,[2\kappa_g\hat{k}_g\hat{T}_\omega\exp(i\omega t)].$$

The requirement $\omega \gg \kappa_g c_g/(c_s d)^2$ of the quasi-adiabatic temperature modulation defines a low limit of the frequency ω. This limit can be reduced by lowering the gas pressure p. The plane-wave approximation breaks down at $Rk_g < 1$. The heat-flux density from the sample into the gas can be expressed as:

$$q_\omega = \mathrm{Re}\,[2\kappa_g\hat{T}_\omega(\hat{k}_g + \alpha/R)\exp(i\omega t)], \tag{2}$$

where α is of the order of one. At low pressures, the second term in Eq. (2) becomes dominant. Then, the condition of the quasi-adiabaticity

$$\omega \gg 1/\tau_R \tag{3}$$

depends on the relaxation time $\tau_R = c_s dR/\kappa_g$ at pressures lower than $p_1 \approx c_s Td/R$. The condition $k_s d \ll 1$ for the quasi-static sample temperature modulation can be written in the form:

$$1/\tau_s \gg \omega, \tag{4}$$

where $\tau_s = c_s d^2/\kappa_s$. Therefore, AC calorimetry can be applied in the frequency range from $1/\tau_R$ to $1/\tau_s$. The range depends on the ratio $(\tau_R/\tau_s) = \kappa_s R/(\kappa_g d)$ which is usually large enough as $(\tau_R/\tau_s) \sim 10^3$–$10^6$ at $R/d = 10$ and $p \sim 10$ Pa. An oscillating heat flux supplied to the sample face at $z = 0$ yields a standing wave $\exp(i\omega t)[A\cosh(\hat{k}z) + B\sinh(\hat{k}z)]$, which arises as a superposition of the incident temperature wave and the wave reflected from the opposite face at $z = d$. The amplitude of the oscillating part of the sample temperature in the plane $z = d$ equals

$$\hat{T}_\omega(d) = q_0/[\hat{F}\kappa_s\hat{k}_s\sinh(\hat{k}_s d)], \tag{5}$$

where
$\hat{F} = 1 + 2\beta(1 + \alpha/\hat{k}_g R)\mathit{cotanh}(\hat{k}_s d) + (\beta\alpha/\hat{k}_g R)^2$, and $\beta^2 = \kappa_g c_g/(\kappa_s c_s) \ll 1$. Let us consider $\hat{T}_\omega(d)$ at $1/\tau_s \gg \omega \gg 1/\tau_R$ and $p < p_1$. To a first approximation on the small parameters $\omega\tau_s$ and $1/\omega\tau_R$ we can obtain the relation:

$$\hat{T}_\omega(d) \approx \hat{T}_0/(1 + i\omega\tau_s/6 + 2\alpha/i\omega\tau_R), \tag{6}$$

where $\hat{T}_0 = Q_0/(i\omega c_s V)$. The product $\omega\hat{T}_\omega$ is practically independent on the frequency in the case of the quasi-static and quasi-adiabatic temperature modulation. The value of the product equals $Q_0/(c_s V)$. The conditions (3) and (4) can be checked by controlling the phase shift φ between the flux and the temperature oscillations. The shift should be $-\pi/2$. Such a control can be carried out using a lock-in amplifier.

Note, that the AC method can be used to measure thermal diffusivity as well. In this case, one increases the sample thickness or the frequency of the temperature oscillations so that the quasi-static condition breaks. At large enough $\omega\tau_s$ values, the amplitude of the temperature oscillations at $z = d$ decreases exponentially with increasing $\sqrt{\omega\tau_s} \sim d\sqrt{c_s/\kappa_s}$, and the value of the negative phase shift grows in proportion to this parameter. On the contrary, in the case of common MDSC [6], when the temperature oscillations are measured on the same face where the heat flux is applied, the measurement of the phase shift between the flux and the temperature oscillations cannot be used for this purpose. For example, in the quasi-adiabatic limit, when $\beta = 0$, the measured amplitude equals $\hat{T}_\omega(0) = q_0/[\kappa_s \hat{k}_s \tanh(\hat{k}_s d)]$ in MDSC scheme. In this case, when d tends to infinity, the amplitude tends to the value $\hat{T}_\omega(0) = q_0/\sqrt{i\omega\kappa_s c_s}$ which is independent of the sample thickness. Hence, when we measure the complex heat capacity in the common MDSC scheme, we have to control the quasi-static condition, $k_s d \ll 1$, by means of another independent technique.

4. Temperature oscillations at the thermocouple junction

Consider a disk-shaped sample with a wire of radius $a \ll R$ attached to the center of the disk face at $z = d$. Another disk face at $z = 0$ is heated by a uniform, oscillating heat flux. The corresponding disk and wire parameters are c, κ, k and c_w, κ_w, k_w respectively. The amplitude of the temperature oscillations is disturbed in the disk close to the region where the wire is attached. Then, the amplitude $\hat{T}_\omega$ of the temperature oscillations in the sample depends on the distance r from the disk axis. It follows from [7] that the amplitude can be represented as a sum of two terms: $\hat{T}_\omega = \hat{Z}(z) + \Delta\hat{T}_\omega(z,r)$, where the plane standing wave with the amplitude $\hat{Z}(z) = A\cosh(\hat{k}z) + B\sinh(\hat{k}z)$ is accompanied by a uniform oscillating heat flux. This term equals $\hat{T}_0$, provided the oscillations are quasi-static and quasi-adiabatic. The second term yields the heat leakage into the wire on the face at $z = d$. In the case of sufficiently thick disk with $d \gg a$ the term $\Delta\hat{T}_\omega$ can be approximated by a superposition of the spherical waves: $\Delta\hat{T}_\omega \sim \exp(i\omega - \hat{k}r)/r - \exp(i\omega + \hat{k}r^*)/r^*$ at $r > a$, where r is the distance from the wave source which is placed at the center of the wire attachment and r^* from the source which is the mirror image of the former source relative to the plane $z = 0$. For $kr \ll 1$, it yields the amplitude of the temperature oscillations at $z = d$:

$$\hat{T}_\omega(d,r) = \hat{T}_0[1 - \varepsilon(a/r)/(2+\varepsilon)], \tag{7}$$

where $\varepsilon = k_w a \kappa_w/\kappa$ is a small parameter for the thin wire when $ak_w \ll 1$. The influence of the heat-leakage into the wire on the measured temperature oscillations is essential at high frequencies as well as in case of the low heat-conductive samples. The influence is more essential in the case of a thin disk with $d < a$. Then the main contribution in $\Delta\hat{T}_\omega$ is proportional to $\exp(\pm\hat{k}z)\ln(r/R)$. The general solution at any relation between a and d is obtained in [7]. In any case, the reduced disturbance $\Delta T_\omega/T_0$ of the temperature oscillations is about $\varepsilon/2$, provided $\varepsilon \ll 1$.

The amplitude of the temperature oscillations can be made practically uniform, if a high-thermoconductive sapphire substrate is placed between the sample and the thermocouple. The value $\Delta T_\omega/T_0$ can be made sufficiently small, if $1/\tau_w \gg \omega$, where $\tau_w = \kappa_w c_w a^2/(\kappa_0)^2$ is the relaxation time of the calorimeter sensor, and c_0, κ_0, k_0 are the corresponding substrate parameters. Let us suppose that the wire of 0.05 mm diameter is made of technical copper and the frequency ω is in the (0.1–1) kHz range at low temperatures, and (1–10) Hz at room temperature. Then, only if $\kappa_0 \gg 1$ W/K m, the oscillations disturbance is small: $\Delta T_\omega/T_\omega \sim k_w a \kappa_w/(2\kappa_0)$. This is the case for the sapphire substrate with $\kappa_0 \approx 10^2$ W/K m in the (1–300) K range. In this case, $\varepsilon = 10^{-3} - 10^{-2}$ at (1–300) K. Suppose the limit relative error $\Delta T_\omega/T_\omega$ equals δ. Then the condition $\delta > \varepsilon/2$ results in the following limitation:

$$1/\tau_\delta \gg \omega, \tag{8}$$

where $\tau_\delta = (2\delta)^{-2}[\kappa_w c_w a^2/(\kappa_0)^2]$ depends on the sensor relaxation time and the limiting relative error.

The condition $\omega \gg (a/R)^4[\kappa_w c_w/(c_s d)^2]$ for the quasi-adiabatic oscillations arises from the heat-leakage in the wire. If the new condition is less strict than Eq. (3), the influence of the wire can be neglected. This yields a limit for the maximal wire radius: $(\kappa_g c_s/\kappa_w c_w)R^3 d > a^4$. Let us suppose that $c_s \sim c_w$. In the case considered in this paper, we have $a^4 \approx 10^{-6}R^3 d$. Then, for $\kappa_g > 10^{-6}\kappa_w$, the wire influence can be neglected. This condition breaks down for helium gas pressures lower than $p_2 \sim 10^{-1} - 1$ Pa at (5–300) K. Therefore, the optimal gas pressure is limited by p_2 and p_1. As a rule, it is sufficient to pump the gas down to the pressure (1–10) Pa.

5. Sample-holder contribution

The heat flux from the sample to the holder depends on the area of sample-to-holder contact and on the product $\kappa_h c_h$, where κ_h and c_h denote the appropriate holder parameters. Consider the case when the only contact between the sample and the holder is around the sample perimeter. The quasi-adiabaticity condition, which relates the heat leakage into the holder, brings up the following relation: $\omega \gg 1/\tau_h$, where $\tau_h = (c_s R)^2/(\kappa_h c_h)$. If the requirement is less strict than (3), the influence of the holder can be neglected. This is true if the sample specific heat capacity is not lower than $\kappa_h c_h d/(\kappa_g R)$. The least values of the product κc are offered by polymer compounds as shown in Table 1. Thus, for the polymer holder the limitation is $c_s > 300\,\mathrm{J/(m^3\ K)}$ at 5 K and $d/R = 0.1$. This means, when measuring the heat capacity of a sapphire sample at 5 K with $c_s = 36\,\mathrm{J/(m^3\ K)}$, the quasi-adiabaticity condition should be limited by the heat leakage into the holder rather than into the ambient gas. The effect of the holder is reduced by fixing the sample on a thin nylon net, as shown in Fig. 1.

6. The calorimeter cell

The calorimeter cell is a system for creation and registration of temperature oscillations in a sample. The calorimeter cell with a disk-shaped sample is shown in Fig. 1. A plate-like polished sample is kept in heat contact with a heater and a temperature sensor. Heater and sensor are machined disks of diameter $2R = 3$ mm. The sample is fixed in the middle of the sensor–sample–heater sandwich by means of thin layers of vacuum grease (apiezon). To form the sensor a copper field is sputtered on the polished sapphire substrate. The thermocouple (Cu–Cu:Fe) microwires of 0.05 mm diameter are welded to the copper field.

Table 1

Thermophysical parameters of the materials used in the calorimeter design

Temperature/K	Sapphire	Technical copper	Polymer compounds
	specific heat capacity/ (J/m^3 K)		
5	3.6×10^1	1.4×10^3	4×10^3
20	3×10^3	6.3×10^4	8×10^4
100	5×10^5	2.3×10^6	6×10^5
300	3.1×10^6	3.4×10^6	1.4×10^6
	thermal conductivity/ (W/m K)		
5	2×10^2	10^2	2×10^{-2}
20	4×10^3	3×10^2	10^{-1}
100	3.6×10^2	5×10^2	2×10^{-1}
300	2.5×10^1	4×10^2	2×10^{-1}
	product of specific heat capacity and thermal conductivity / (J W/m^4 K^2)		
5	7×10^3	10^5	8×10^1
20	10^7	2×10^7	8×10^3
100	2×10^8	10^9	10^5
300	8×10^7	10^9	3×10^5

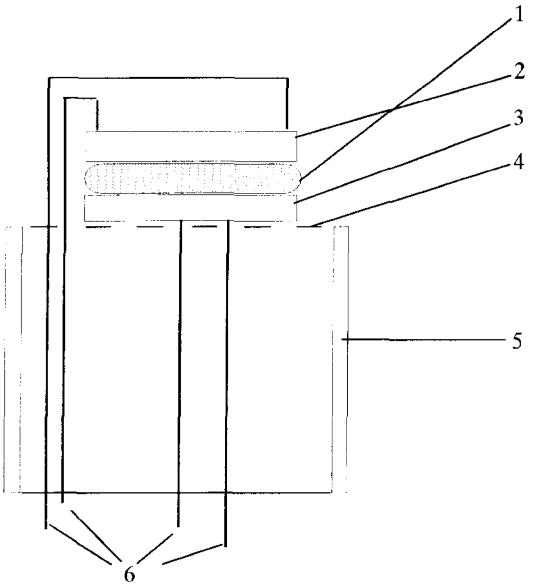

Fig. 1. The diagram of the calorimeter cell. The sample (1) is kept in heat contact with the heater (2) and the temperature sensor (3). The sensor is fixed on the thin nylon net (4). The net is stretched on the cylinder holder (5). The microwire leads (6) are welded to the heater and the sensor.

The thermocouple sensitivity is ca. 0.01 mV/K in the (1–300) K range. A thin chromium film is sputtered on a polished surface of the sapphire substrate, which serves as a heater. The copper contact pads are sputtered on the film, and copper microwires of 0.05 mm diameter are welded to the pads. The sapphire substrate thickness is $d_0 = 0.1$ mm. Note, that the frequency of the temperature oscillations should not exceed the upper frequency limit $1/\tau_0 = (\kappa_0/c_0) \times (2d_0)^{-2}$ for two sapphire substrates and the limit $1/\tau_1 = (\kappa_1/c_1) \times (2d_1)^{-2}$ for two grease layers, where c_1, κ_1, and d_1 are the corresponding parameters of the grease layer. The upper limit $\omega_{\max}$ of the frequency of the sample temperature modulation is determined by the minimal of $1/\tau_0$, $1/\tau_1$, $1/\tau_\delta$, and $1/\tau_s$. Provided the limit relative error $\Delta T_\omega/T_0$ equals $\delta = 0.03$, $2d_1 = 10\,\mu$m, and a sample is sufficiently thin, the value of $\omega_{\max}$ is determined by $1/\tau_1$ at (5–20) K and by $1/\tau_\delta$ at (100–300) K, as shown in Table 2. The relative error $\Delta T_\omega/T_0$ increases in proportion to $\sqrt{\omega}$. For example, the error is ca. 20% at 300 K and $\omega = 100\ \mathrm{s}^{-1}$.

Table 2
The upper frequency limit $\omega_{\max}$ of the AC technique, which is determined by the longest of the times: τ_0 – the time of the temperature relaxation in the sapphire substrates; τ_1 – in the grease layers; and $\tau_\delta = (2\delta)^{-2}\tau_w$, where the limit relative error $\Delta T_\omega/T_0$ equals $\delta = 0.03$; and τ_w the relaxation time of the calorimeter sensor

Temperature/K	Frequency/s^{-1}				
	$1/\tau_0$	$1/\tau_1$	$1/\tau_w$	$1/\tau_\delta$	$\omega_{\max}$
5	10^8	5×10^4	5×10^8	2×10^6	5×10^4
20	3×10^7	10^4	10^9	5×10^6	10^4
100	2×10^4	3×10^3	2×10^5	6×10^2	6×10^2
300	3×10^2	10^3	7×10^2	3	3

7. The sensitivity

The device sensitivity, i.e. the heat capacity detection limit, is limited by the magnitude of the effective heat capacity C^* of the cell. The magnitude of C^* is given by the heat capacities of two sapphire substrates, two grease layers, as well as some contribution of heat capacities of four wire connections and sample holder contribution C_h. The value of C^* is measured in advance and subtracted. It can be written as follows:

$$C^* = \pi R^2 [2d_0c_0 + 4k_w^{-1}c_w(a/R)^2 + 2d_1c_1] + C_h, \tag{9}$$

where k_w is calculated at appropriate frequencies $\omega = 10^3$, 500, 50, and 2 s^{-1} for temperatures 5, 20, 100, and 300 K, respectively. Table 3 shows that the main contribution to C^* at room temperature is determined by the sapphire substrates. At low temperatures, even relatively small amounts of an organic material, such as grease, nylon and glue, provides considerable

Table 3
The background heat capacity C^* of the calorimeter cell at different temperatures calculated as the sum of the heat capacity C_0 of sapphire substrates, the effective heat capacity C_w of copper microwires, and the heat capacity C_{gr} of grease layers

Temperature in K	Heat capacity in mJ/K			
	C_0	C_{gr}	C_w	C^*
5	5×10^{-5}	2×10^{-4}	10^{-4}	3.5×10^{-4}
20	4×10^{-3}	4×10^{-3}	2×10^{-3}	10^{-2}
100	7×10^{-1}	3×10^{-2}	6×10^{-2}	0.8
300	4	7×10^{-2}	3×10^{-1}	4.4

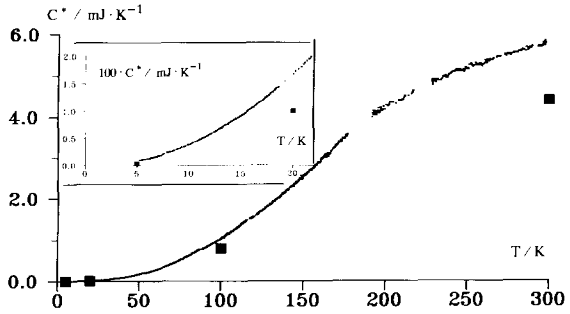

Fig. 2. Temperature dependence of the background heat capacity C^* of the calorimeter cell. Shown in the inset is the low-temperature part of the 100 × C^* vs. T dependence. The set of four squares indicate calculated C^* at four different temperatures.

contribution. The threshold sensitivity is not worse than $C^*/30$. It means that a copper sample of thickness ca. 10 μm can be investigated by the calorimeter. The dependence of C^* vs. temperature is shown in Fig. 2. The insignificant difference between calculated and actual C^* may be due to the sample holder contribution. The sensitivity to temperature oscillations equals 10^{-4} K.

8. Conclusion

In conclusion, let us consider the AC-technique possibilities for complex heat capacity measurements. It is shown that the applicability of AC calorimetry is well-founded in spite of the quasi-adiabaticity and the quasi-static limitations. It takes place because of the ratio τ_R/τ_s is large enough: $\tau_R/\tau_s \sim (10^3 - 10^6)$. The influences of sample holder and wire connections can be made insignificant. The high-vacuum technique is not required. On the contrary, the helium gas pressure should not be made lower than 1 Pa. Due to high sensitivity, the calorimeter enables heat capacity measurements of very thin (ca. 10 μm) samples and at high frequencies (ca. 1 kHz) at least at low temperatures. The main reasons which restrict potentialities of the ac technique are determined. At room temperature the disturbance of the temperature oscillations at the thermocouple junction restricts the upper frequency limit and the sapphire substrates contribution to the background heat capacity restricts the heat-capacity detection limit. At low temperatures, even relatively small amounts of organic material, such as grease, nylon and glue restrict the sensitivity an the upper frequency limit of the AC technique.

References

[1] P.F. Sullivan and G. Seidel, Phys. Rev., 173 (1968) 679.
[2] M.B. Salamon, Phys. Rev. B, 2 (1970) 214.
[3] I. Hatta and A. Ikushima, J. Phys. Chem. Solids, 34 (1973) 57.
[4] Y.A. Kraftmakher, Compendium of Thermophysical Property Measurement Methods, vol. 1, Plenum press, New York and London, 1984, p. 591.
[5] K. Binder and A.P. Young, Reviews of Modern Phys., 58 (1986) 801.
[6] M. Reading, Trend Polym. Sci., 8 (1993) 248.
[7] A.A. Minakov, O.V. Ershov, Cryogenics, Vol. 34, ICEC Supplement, 1994, p. 461.