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Research and Technical Note

Specific heat capacity of Apiezon N high vacuum grease and of Duran borosilicate glass

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Abstract

The specific heat capacity of Apiezon N high vacuum grease and of Duran borosilicate glass have been measured in the temperature range 16.2–319K and 1.75–323K, respectively. Apiezon N has a large heat capacity at low temperatures and displays a step-like anomaly at ≈ 215K and a peak-shaped transition at ≈ 289K. The heat capacity of Duran glass is similar to that of Pyrex glass and is smooth in the temperature range investigated. The equations and coefficients of fits to the data, including earlier literature values are given. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For calorimetric experiments at low temperatures the mounting of the sample is of great importance. In basic materials research of today the available amount of sample is often very small. This has led to the development of new calorimetric methods and miniature calorimeters. Many calorimeters are now suitable for measurements on samples weighing milligrams or even micrograms. The sample holders for these calorimeters are usually build very lightly, i.e. they have small heat capacities (addenda).

Instead of using a closed sample container filled with the sample and with helium exchange gas, as in traditional adiabatic calorimetry, open platform-type sample holders are often in use. One example is the sample holder type used in our laboratory for about 20 yr now (and on which the current measurements were performed). It consists in a thin sapphire platelet which is suspended by three thin threads from the isothermal shield. On the lower side of the platelet a thin metal film meander is evaporated which serves as the sample heater. Also the thermometer is permanently glued to the lower side of the holder. On top of the holder the sample can be mounted and unmounted easily. The arrangement offers both small addenda and good handling.

A serious problem is the thermal contact from the sample holder platform (i.e. the heater and thermometer) to the sample. For a good contact it is inevitable to use a contact agent (interposer) [1]. Many materials have been used for this purpose: low-melting metal solders, silver paint [2], varnishes [3,4], high vacuum grease [5] and other glues or epoxies. In order to remove the sample from the sample holder without damage to the fragile sapphire platelet one needs a suitable solvent for the interposer. The most commonly used contact agents are Apiezon high vacuum grease products [6] and IMI–7031 varnish (previously GE–7031). Especially Apiezon N [7] has been used widely because it is inert and convenient to apply. It can be easily washed off by petroleum ether (boiling range 40–60°C).

The design of the sample holder and this kind of mounting is, however, not suitable for powder samples or air or/and moisture sensitive materials. For these materials we developed small sized glass ampoules with a flat bottom side in which the samples can be sealed. For thermal contact these ampoules are filled with an exchange gas (natural helium or helium-3 isotope of about 10^4–10^5 Pa pressure) prior to sealing the ampoule by a flame. In our laboratory Duran glass for glassblower works [8] is used for making these ampoules. Duran is

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a borosilicate glass with the approximate composition (by weight) 81% SiO_2, 13% B_2O_3, 4% Na_2O/K_2O and 2% Al_2O_3 [9]. Over the past 20 yr data on the specific heat capacity of Duran glass were measured several times in different calorimeters in our laboratory. They agree quite well with each other. Numerous scientific results where these glass ampoules were used have been published, e.g. [10–14].

Here we present the results of our most recent re-determinations of the specific heat of these two materials. Accurate data for the specific heat capacity of a bulk sample of Duran glass (1.75–323K) and of Apiezon N high vacuum grease (16.2–319K) are given. In combination with earlier literature data for Apiezon N grease for lower temperatures we present for the first time equations for the calculation and interpolation of the specific heats of the two materials for the temperature ranges 0.10–320K (Apiezon N) and 2.14K–320K (Duran), respectively.

2. Experimental details

The calorimeters used for the measurements were either equipped with a calibrated Pt100 ($T > 20$K) or Cernox ($T < 20$K) sensor on the sample holder platform. The quasi-adiabatic (isoperibol) heat pulse method (Nernst's method) with isothermal shield control was utilized for the measurements (see e.g. [15]). The Apiezon N grease sample was smeared out flatly on the sapphire sample holder platform at room temperature. By this method the mass of the sample was limited to 22.1(1) mg, but the mass, the thermal diffusivity and the experimental overall conditions were close to those with a sample in place (typically 2–8 mg). The calorimeter was then sealed, pumped to a vacuum of 10^{-4} Pa and subsequently cooled. For the Duran glass measurement a cylindrical block of weight 1.3488 g was glued to the sample holder with 3.9 mg of Apiezon N grease. The sample holder contribution was measured in a separate run and subtracted from the raw data as was the contribution of the Apiezon N.

Heat pulses of 3% of the absolute temperature or of 1.0K (1.5K for Duran) maximum 'height' were used. The pre-heating sample temperature drift rate (in the Apiezon N and in the empty sample holder measurement) was kept within $\pm$ $3\cdot10^{-6}$K/s. This low value of the allowed drift rate leads to a good reproducibility of the heat pulses and is essential for low inaccuracy of the resulting data. The post-heating sample temperature relaxation was fitted exponentially (see e.g. [16]). The external relaxation time τ_{ext} varied from 150–840 s for the heat pulses on the grease sample and from 480 to 6000 s for the measurements on the glass sample. The evaluation of the heat pulse height included a correction for the heat loss during the heating time [16]. The inaccuracy of the data for Duran glass above 50K is estimated to be $\pm$ 0.5% growing to $\pm$ 2% at 5K. Due to the low mass of the sample the estimated inaccuracy for the Apiezon N data is $\pm$ 2% between 50 and 200K, increasing to higher and lower temperatures.

3. Results and discussion

The specific heat capacity of Apiezon N grease is presented in Fig. 1. The curve is smooth without anomalies in the range below 200K. Above this temperature the heat capacity increases by $\approx$ 25% in a stepwise manner at $\approx$ 215K. At $\approx$ 289K the heat capacity shows a pronounced peak (first order transition). For temperatures above the peak $c_p(T)$ decreases slightly. However, the viscosity of the grease decreases significantly at temperatures above the transition and the lowering in $c_p(T)$ might be an artifact.

In Fig. 1 (lower panel) the current data are presented along with data from the literature. The data of Schink and von Löhneysen [17] are given as a fit in the original publication and span the range from 0.1–2.5K. The data by Wun and Phillips [18] are for the range 0.4–20.0K.

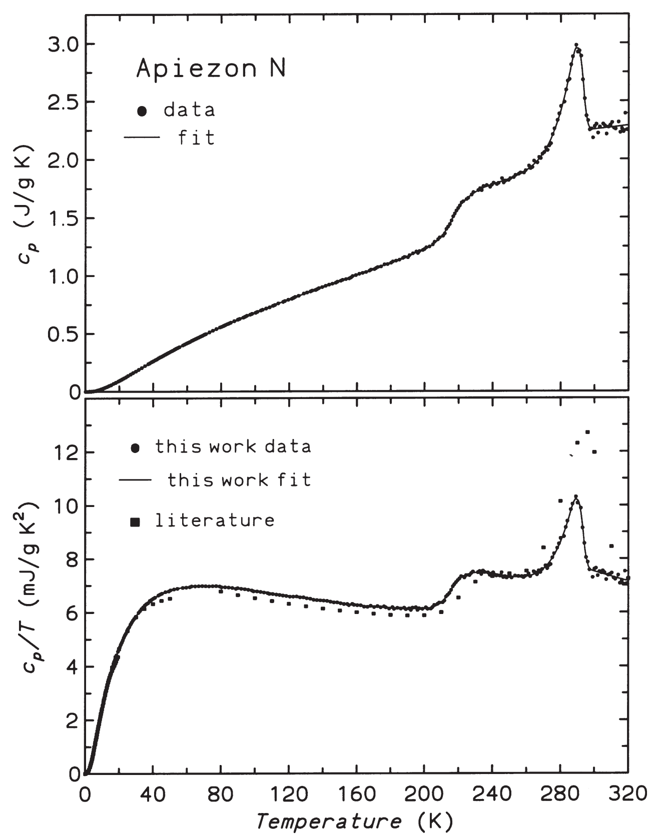

Fig. 1. Specific heat capacity $c_p(T)$ of Apiezon N high vacuum grease. Upper panel: the data (●) and the fit (see Tables 1 and 2). Lower panel: comparison of the data of this study with previous literature results [17–20] in a $c_p(T)$ vs T representation.

Further data are by Bevolo [19] for temperatures from 1–50K and by Bunting et al. [20] (range 80–324K).

In principle all data sets were measured on the same material and should be comparable. The composition and manufacturing technique have not changed for Apiezon N since the 1960s [21]. Apiezon N is produced by the molecular distillation of specific petrolatums (petroleum jelly). The latter are natural products and there most probably have been changes in the petrolatum stock used for production over the decades [21]. Apiezon N also contains a small percentage of a high molecular weight polymer but it does not contain aluminium stearate [21], as pointed out in a previous publication [17].

At temperatures below 40K there is excellent agreement of our data with the data sets of Wun and Phillips [18] and Bevolo [19]. The data of Bevolo above 40K and Bunting et al. [20] show overall slightly smaller values for $c_p(T)$. The step-like phase transition, however, is about 10K higher in temperature in the data of Bunting et al. which were published about 30 yr ago. Also the peak is about twice as high and twice broader in the old data. Bunting et al. noted that the heat capacity of Apiezon N is only reproducible to within 5% for temperatures above 260K. This group used a continuous heating method with a sweep rate of 10K/h for the determination of the heat capacity of about 27 g of Apiezon N grease. Assuming the existence of an internal time-relaxation behaviour of the large grease sample the experimental conditions in [20] are strongly different from our experimental conditions. Our step-by-step measurements were made on a much smaller sample and the collection of the data for 1K took about 2 h at temperatures near the transition. On the other hand subtle variations in the properties of Apiezon N over the years cannot be excluded fully.

The available data for Apiezon N in the range 0.1–320K were fitted by a least-squares method to polynomial equations $c_p(T) = \exp(\Sigma a_i(\ln T)^i)$ in three intervals. The coefficients are given in Table 1. The anomalous region for $T > 200$K, however, could not be fitted by a such a polynomial equation. Instead we used a cubic spline interpolation [22] with nine points in this range (see Table 2).

The specific heat capacity $c_p(T)$ of Duran glass is shown in the upper panel of Fig. 2. The curve is smooth

Table 1
Coefficients a_i for the fits with polynomial equations $c_p(T) = \exp(\Sigma a_i(\ln T)^i)$ [J/g·K] in three temperature intervals to the specific heat capacity of Apiezon N cryogenic high vacuum grease. The range of validity of the fits is given by T_{min} and T_{max}

	1st interval	2nd interval	3rd interval
T_{min}	0.1K	4.1K	17.5K
T_{max}	4.1K	17.5K	187K (200K)
Fit	6th degree	6th degree	8th degree
a_0	−10.52866	+12.2989721	−2.75837754173
a_1	+2.897589	−62.6817877	+0.84486512587
a_2	+0.155439	+76.8567527	−4.54429428312
a_3	+0.012134	−46.5409791	+3.13777287014
a_4	+0.032469	+15.4668540	−0.55002150873
a_5	−0.017000	−2.69704827	−0.12583882143
a_6	−0.007715	+0.19320089	+0.06299457091
a_7			−0.00902755312
a_8			+0.00045531915

Table 2
Points $c_p(T)$ and curvature changes for the cubic spline fit [22] to the specific heat capacity $c_p(T)$ [J/g·K] of Apiezon N high vacuum grease. The range of the validity of this spline is 187–320K

i	T_i	$c_p(T_i)$	$(d^2c_p/dT^2)(T_i)$
1	196.8253	1.20763	0
2	216.3449	1.49235	+0.0026443
3	216.9505	1.51164	−0.0045976
4	223.1712	1.64062	−0.0008989
5	262.2828	1.93115	+0.0007737
6	285.2162	2.73267	+0.0045473
7	293.1346	2.68081	−0.0691204
8	293.7141	2.57092	+0.0695749
9	299.0213	2.25367	0

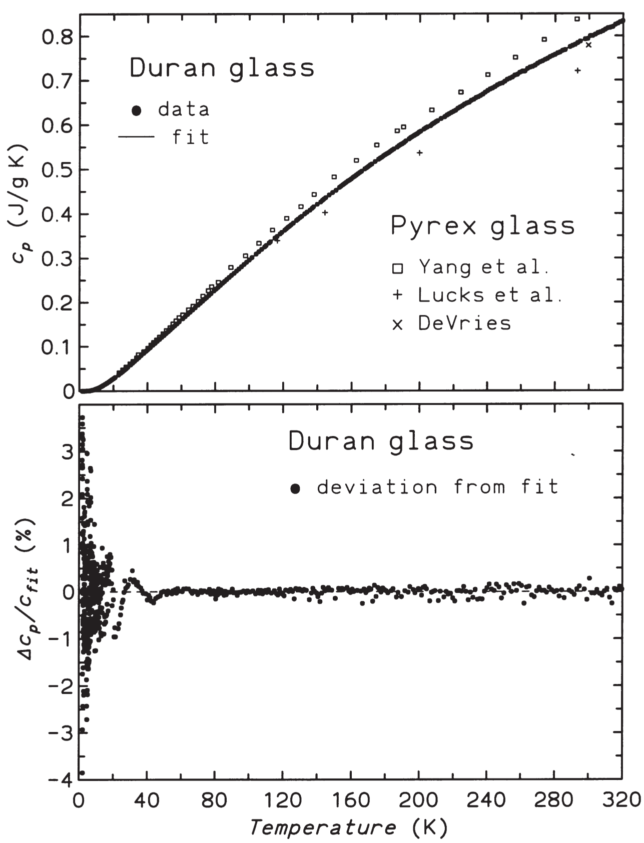

Fig. 2. Specific heat capacity $c_p(T)$ of Duran borosilicate glass. Upper panel: the data (●) and the fit (see Table 3). In addition, literature data for Pyrex glass [23,25,27] are given. Lower panel: percentage deviation of the fit from the data for Duran.

and shows no anomalies. Polynomial equations $c_p(T) = \exp(\Sigma a_i(\ln T)^i)$ have been fitted to the data in two temperature intervals. For $T < 2.14$K an extrapolation is made (see below). The coefficients are given in Table 3. The percentage deviation of the data from the fit is displayed in the lower panel of Fig. 2. The standard deviation of the data from the fit is 0.08% for $T > 50$K but increases severely with lower temperatures.

In spite of their technical importance there is little information on the heat capacity of silicate glasses at sub-ambient temperatures. Data are available for the borosilicate glass Pyrex (7740). The composition by weight is SiO_2 80.5%, B_2O_3 13.0%, Na_2O 4.0%, Al_2O_3 2.3%, and other traces 0.1%, i.e. similar to Duran glass. Data are available for various temperature ranges: [23] (300–446K), [24] (2–20K), [25] (116–700K), [26] (0.05–2K), [27] (20–310K), [28] (glass melts; 450–1700K). The Pyrex data of Yang et al. [27] are 5–7% higher than our Duran data while the few data points for Pyrex taken from [23,25] are smaller by about the same amount (see Fig. 2 upper panel). In Fig. 3 the heat capacities of Duran and Pyrex glass are compared for $T < 50$K. Between 4 and 20K the heat capacity of Duran glass is up to 10% higher than the data for Pyrex by Smith and Wolcott [24]. The Pyrex data of Yang et al. [27] are higher while no useful comparison is possible with the data of Stephens [26]. As also observed in [26] the small upturn in c_p/T^2 below 2.5K might indicate the influence of magnetic oxide impurities (e.g. iron oxides) in the glass. Magnetic impurities of $\approx$ 0.2% (of 2 μ_B-moments) were found in Duran glass by a susceptibility study [29]. Nevertheless, the inductance in a.c. susceptibility increased only significantly below 100 mK [29].

Finally, in Fig. 4, which gives the specific heat capacities of the investigated materials below 8K, it can be seen that $c_p(T)$ of Duran glass is comparatively low. The inaccuracy of our $c_p(T)$ data increases at temperatures well below 4.2K due to the very small total heat capacity. Our measurements have been made down to 1.75K. For temperatures lower than 2.14K we give an extrapolation with $c_p(T) = \gamma^* T + \beta T^3 + \delta T^5$ (for the coefficients see Table 3). It should be useful down to the lowest temperatures obtainable in ^{4}He cryostats (1.2K). The measurable linear term with $\gamma^* = 7.9\cdot10^{-6}$ J/g·K^2 is of interest. A linear term is a characteristic feature of amorphous (glassy) materials at low temperatures [26,30].

The data of Apiezon N grease and of copper metal [31] are also plotted in Fig. 4. The plot clearly demonstrates that the heat capacity of Apiezon N is huge in comparison to other dielectric materials or metals (up to 30 times the value of Cu) at low temperatures and that grease has a measurable contribution to the addenda in

Table 3
Coefficients a_i for the fits in two temperature intervals to the specific heat capacity of Duran glass with polynomial equations $c_p(T) = \exp(\Sigma a_i(\ln T)^i)$ [J/g·K]. In addition, an extrapolation to lower temperatures with a polynomial equation $\Sigma a_i T^i$ is given (see text). The range of validity of the fits is given by T_{min} and T_{max}

	Extrapolation	1st interval	2nd interval
T_{min}	1.20K	2.14K	48.7K
T_{max}	2.14K	48.7K	320K
Fit	5th degree linear	9th degree double log.	7th degree double log.
a_0	0	−14.54468855	−125.5033401
a_1	$7.9186\cdot10^{-6}$	+20.24806316	+113.8768670
a_2	0	−48.56745106	−33.07021492
a_3	$8.4202\cdot10^{-7}$	+65.74967353	−1.282090223
a_4	0	−51.19294382	+2.857340497
a_5	$1.1730\cdot10^{-7}$	+24.89165699	−0.6670997544
a_6		−7.715413410	+0.0664620062
a_7		+1.481455723	−0.0025253112
a_8		−0.1604427047	
a_9		+0.0074843343	

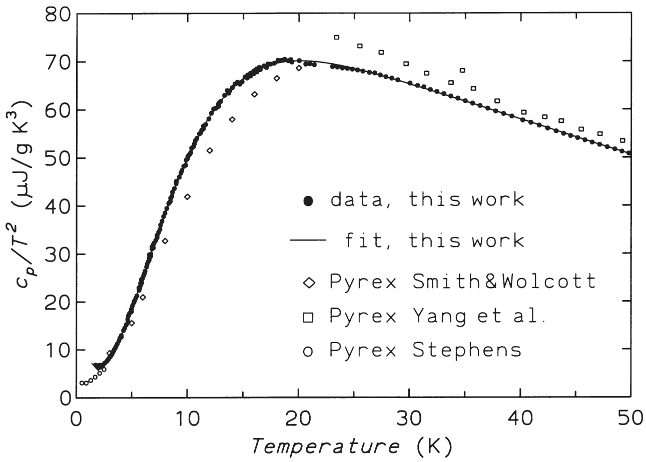

Fig. 3. Specific heat capacity $c_p(T)$ of Duran glass and of Pyrex glass according to references [24,26,27] for temperatures up to 50K.

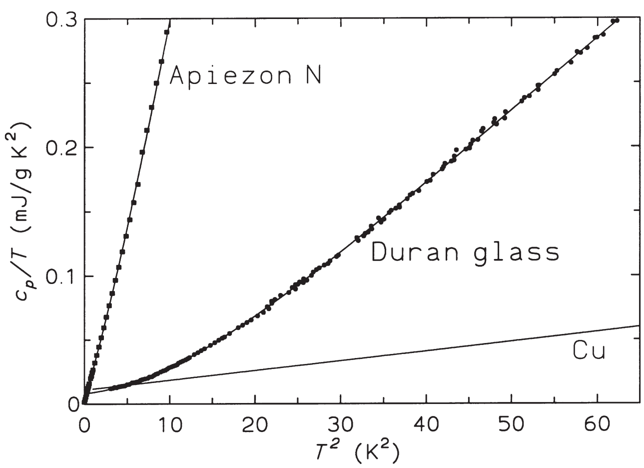

Fig. 4. Specific heat capacity $c_p(T)$ of Duran glass, of Apiezon N high vacuum grease and of copper [31] at low temperatures in a c_p/T vs T^2 representation.

calorimetric experiments, even when used in small amounts. Careful determination of the mass of the applied Apiezon N and subtraction from the raw data is thus important, even for samples weighing about 1 g.

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