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Low-temperature heat capacity measurements on encapsulated transuranium samples

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Abstract

To enable safe specific-heat experiments on transuranium materials, we have tested the reliability of such measurements on encapsulated samples. We describe several encapsulation techniques and present the heat capacity of Stycast® 2850 FT used for one encapsulation technique. A number of test measurements (on $PuGa_3$, PuSb, $PuCoGa_5$, $NpCoGa_5$, NpTe) are in good agreement with previous data or results of other experimental techniques and show that the experimental errors remain acceptable in most cases, depending of course also on the intrinsic specific heat of the studied material.

PACS: 65.40.+g; 75.40.Cx

1. Introduction

Materials containing transuranium elements are of high interest not only in nuclear physics and chemistry but also in solid state physics. They exhibit various kinds of magnetic order and often surprising properties (e.g. superconductivity with a transition temperature above 18 K was recently discovered in $PuCoGa_5$ [1]).

The specific heat gives essential information about the physical properties of materials. It reflects phase transitions of different kind (e.g. structural, magnetic, superconducting), lattice vibrations, energy excitations and gives important information on electronic properties; its knowledge is indispensable for determination of other thermodynamic quantities. It is relatively simple to measure the heat capacity of a common solid. Low-temperature specific heat measurements of actinide compounds, and especially materials containing transuranium elements, are more complex due to (i) the safety aspects when handling such radioactive materials and (ii) the self-heating generated by the decay of these isotopes, and therefore very few data are available in the literature. Indeed, in actinide research, experimental access

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is complicated by the intrinsic nuclear instability of the elements requiring the experimentalist to protect himself and the environment from radiation and contamination, to handle limited amount of material (safety and availability), and to take into account in the determination of properties the influence of radiation damage or decay heat.

The self-heating of some isotopes means that the lowest achievable temperatures can be then up to several Kelvin higher than the instrumental limits, depending on the isotope and the sample mass. This self-heating also causes the different parts (sample, thermometer, wires) of the sample platform to be at slightly different temperatures. The measured data can be corrected for these errors [2], but the corrections were found not to be significant for the measurements described in this paper.

To fulfil the safety criteria, one can consider experiments on 'encapsulated' samples. We have tested the possibility to measure the specific heat of transuranium materials placed inside different capsules. In this paper, we describe the encapsulation technique used at ITU Karlsruhe, summarize the results of our test measurements and discuss the experimental errors. We present also the specific heat data of several compounds obtained on encapsulated samples compared with previous literature data and other experimental methods.

2. Experimental

The specific heat experiments were performed using the PPMS-9 (Physical Property Measurement System, Quantum Design) instrument installed at ITU Karlsruhe. The specific heat is determined by a relaxation method that allows to measure relatively small samples with a mass of a few mg. All the experiments were performed in the temperature range 1.8–300 K and in magnetic fields up to 9 T.

Two different encapsulation procedures have been tested. In the first, more simple one, the sample is enclosed by Stycast® 2850 FT. The addenda heat capacity (i.e. sample platform, wires, grease) is obtained as for any other non-active sample and then, in addition the heat capacity of the measured amount of Stycast is subtracted. The use of Stycast® 2850 KT was also tested but its consistency is more grainy, less suitable for our purposes.

For the other procedure, the sample is placed in a capsule of a cylindrical shape with a diameter 2–3 mm and height 2–4 mm covered by a flat disc as a cap (see also [3] for details). The capsule and the cap can be thermally connected by a grease (apiezon N) and measured as an addenda. Then the sample is put on the bottom of the capsule (small amount of grease there ensures the thermal contact to the capsule) and the top cap is sealed by the Stycast® 2850 FT. The heat capacity of the given amount of the Stycast epoxy and the addenda capacity are subtracted from the total measured value to get the sample heat capacity. We have tested capsules made from boron carbide and sapphire. The former were found to be not suitable for our measurements (bad mechanical properties, large heat capacity at low temperatures, not well reproducible results), so we concentrate here on the sapphire encapsulation. These have been provided by the Impex company and have a mass of 30–40 mg depending on the precise dimensions.

Taking into consideration the very small amount of material necessary for our measurements, and the main type of isotopes investigated, protection against radiation is ensured by the shielding effect of the capsule itself and of the PPMS (shielded cryostat). To avoid spreading of the contamination, the samples are mounted in clean glove-box and decontaminated. Before and after mounting of the sample in the PPMS chamber, wipe test are made to ensure that the sample surface and the sample's puck are contamination free.

We present results of specific-heat measurements on PuSb (19 mg, containing ^{242}Pu), $PuGa_3$ (5 mg, with ^{239}Pu), NpTe (51 mg, with ^{237}Np), $PuCoGa_5$ (19 mg, with ^{239}Pu), $NpCoGa_5$ (6 mg, with ^{237}Np), Au (7 mg, NBS/NIST purity) and URhAl (5 mg, U_{nat}) polycrystalline materials.

3. Results and discussion

3.1. Heat capacity of Stycast® 2850 FT

The heat capacity of the Stycast® 2850 FT is represented in Fig. 1. It exhibits a rather smooth dependence without any significant anomalies. These data were obtained on a relatively large piece (piece 'A') of Stycast (≈27 mg) one month after preparation. We have performed several other measurements on pieces of different sizes (ranging between 1 and 30 mg), measured at different periods after preparation (between almost immediate up to three months). The difference between these data and those of piece 'A' are represented in Fig. 2 for several such measurements. It stays below 8% in the whole temperature range, but exceeds somewhat the usual experimental errors due to the instrument [4]. This can be due to the fact that it is a two-component epoxy, and there is always some uncertainty in the mixing ratio when preparing it. We also cannot rule out small amount of (inhomogeneously distributed) impurities present in the as-supplied material.

The heat capacity of Stycast® 2850 FT measured in our present study (as shown in Fig. 1) follows qualitatively the same temperature dependence as reported in [5] (studied up to 100 K) but the absolute values are somewhat smaller (15% at 40 K) than reported in [4]. Possible explanation can be the sample preparation.

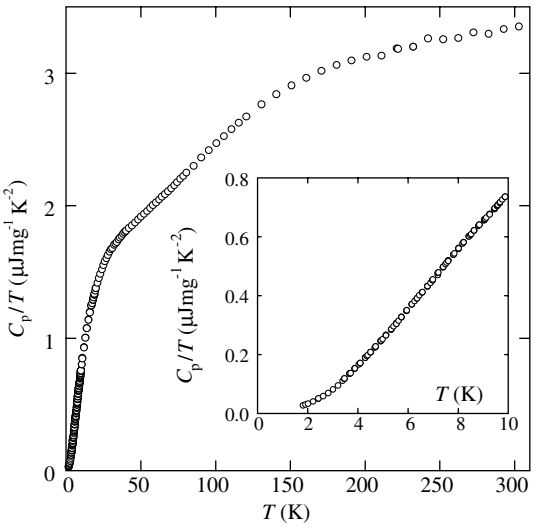

Fig. 1. Heat capacity of Stycast® 2850 FT.

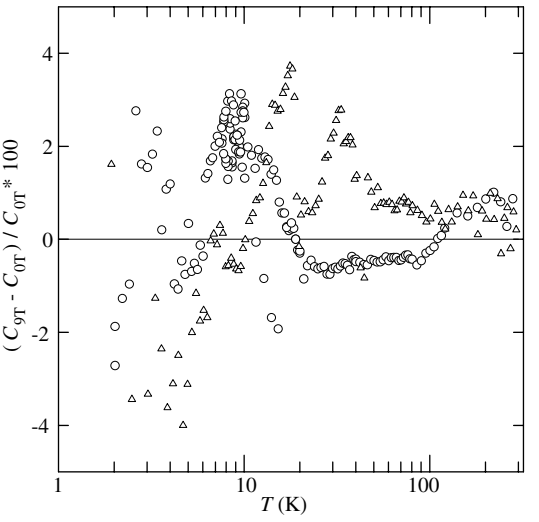

Fig. 3. Field influence on the heat capacity of Stycast® 2850 FT; circles correspond to piece A (28 mg), triangles to a small sample of 1.4 mg.

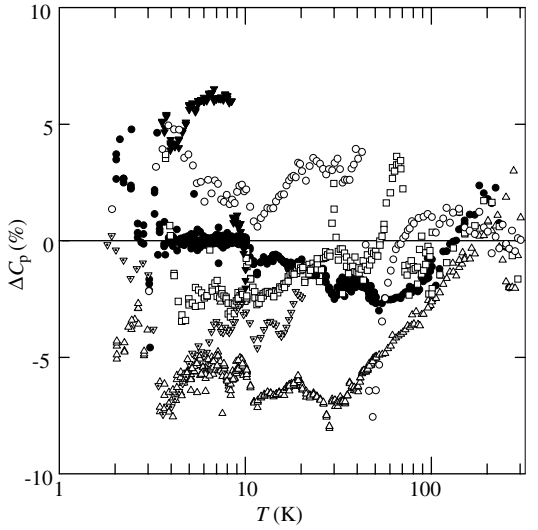

Fig. 2. Difference between the heat capacity measured on several different pieces of Stycast® 2850 FT (each symbol corresponds to one Stycast® sample) and that presented in Fig. 1.

As described in [5], heat capacity measurements were performed only on sample cured at 95 °C for 20 h, while our samples were cured at room temperature. Such explanation is corroborated by difference in linear thermal expansivity between samples cured at room temperature and at 95 °C [5].

The effect of an applied external magnetic field is demonstrated in Fig. 3 for piece 'A' and one smaller sample. No significant field influence was observed. The scatter of points remains at an acceptable level, especially for the large piece A.

As far as encapsulation is concerned, we have tested first several non-transuranium materials. The specific heat of samples encapsulated by the Stycast does not differ, within usual instrumental accuracy of 2–3%, from that measured on non-encapsulated samples. The amount of Stycast used to cover the sample is typically 10–20% of the sample mass, depending on the sample size and shape. The heat capacity due to the Stycast represents then in most cases only a minor contribution to the total measured value, and the uncertainties introduced by having Stycast as an additional addendum are below other experimental errors including mainly instrumental accuracy [4].

3.2. Measurements on selected transuranium materials using Stycast® 2850 FT

Next let us mention some of our results achieved on transuranium materials encapsulated by Stycast® 2850 FT. We concentrate on comparison with previous literature data, and do not give all the details for individual compounds because most of these specific-heat data will be published in separate papers. Presented results also illustrate several different types of specific-heat behavior in transuranium materials.

The specific heat of ^{242}PuSb (see Fig. 4) can be well compared to data obtained by a quasi-adiabatic method [6] in a wide temperature range between 10 and 300 K. The two phase transitions described in the literature are observed also in our experiment. The major

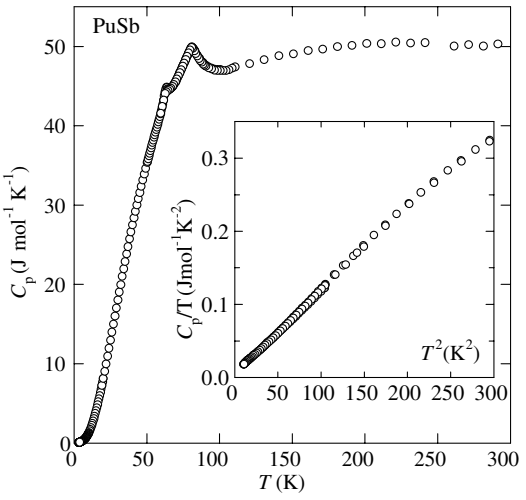

Fig. 4. Specific heat of ^{242}PuSb.

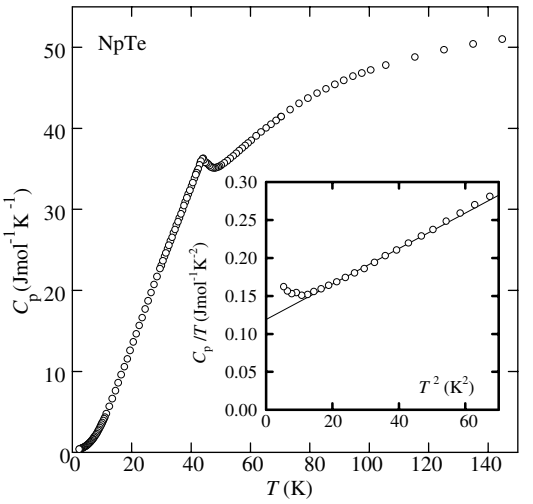

Fig. 5. Specific heat of ^{237}NpTe in zero magnetic field; no change is observed in a field of 9 T.

contribution to the specific heat represent the lattice vibrations. It reaches the classical Dulong–Petit limit ($C_{\text{lat}} = 6R \cong 50\ \text{J mol}^{-1}\text{K}^{-1}$ for the two atoms in formula unit) above 200 K in PuSb. Another contribution in this temperature range is due to the conduction electrons. The total entropy at 298 K, $S_{298\,\text{K}} = 106.2\ \text{J mol}^{-1}\text{K}^{-1}$, determined from our data agrees very well with $S_{298\,\text{K}} = 107.23\ \text{J mol}^{-1}\text{K}^{-1}$ reported in [6] (the entropy below 10 K not accounted in [6] is very small and can be well neglected), although we get somewhat smaller specific heat at room temperature: $C_{298\,\text{K}} = 51.5\ \text{J mol}^{-1}\text{K}^{-1}$ compared to $C_{298\,\text{K}} = 53.68\ \text{J mol}^{-1}\text{K}^{-1}$. Concerning the low-temperature part, the specific heat due to the lattice vibrations is proportional to T^3, so the specific heat can be described as:

$$C_{\text{p}} = \gamma T + \beta T^3, \tag{1}$$

where γ is the coefficient characterizing the electronic specific heat and β can be related to the Debye temperature θ_{D} describing lattice vibrations. The fit to our data between 10 and 17 K, i.e. the same as used in [6], gives the values of $\gamma = (22 \pm 3)\ \text{mJ mol}^{-1}\text{K}^{-2}$ and $\theta_{\text{D}} = (154 \pm 2)$ K, in good agreement with the literature values of $\gamma = (20 \pm 10)\ \text{mJ mol}^{-1}\text{K}^{-2}$ and $\theta_{\text{D}} = (151 \pm 10)$ K [6]. We should note that the slope of C_{p}/T vs T, as inferred from our experiment, slightly changes when going to lower temperatures, and the analysis of data between 3 and 10 K, not achievable in the former study, gives $\gamma = (6 \pm 2)\ \text{mJ mol}^{-1}\text{K}^{-2}$ and $\theta_{\text{D}} = (151 \pm 1)$ K. This latter fit to low-temperature data provides more reliable results because Eq. (1) describes well the heat capacity of lattice vibrations only at temperatures well below their characteristic energies (i.e. at $T \ll \theta_{\text{D}}$).

Previous measurements on $PuGa_3$ (DO19 crystal structure) [7] and NpTe [8] concentrated on the low-temperature part only. The γ-values are in general obtained again by a fit of low-temperature data to Eq. (1). The values of $\gamma = (205 \pm 10)\ \text{mJ mol}^{-1}\text{K}^{-2}$ ($PuGa_3$) and $\gamma = (120 \pm 5)\ \text{mJ mol}^{-1}\text{K}^{-2}$ (NpTe) derived from our data agree with those from literature: $\gamma = (225 \pm 25)\ \text{mJ mol}^{-1}\text{K}^{-2}$ and $\gamma = (130 \pm 10)\ \text{mJ mol}^{-1}\text{K}^{-2}$ for $PuGa_3$ [7] and NpTe [8], respectively. In the case of NpTe (see Fig. 5), we reproduce also an increase of C_{p}/T below 3 K in agreement with the former study. Such effect in Np-based materials can arise from a Schottky term due to a hyperfine splitting of the nuclear ground state as recently shown for the case of $NpCoGa_5$ [9].

Our measurements were performed up to 300 K. In addition to low-temperature data already published in literature, we observe magnetic phase transitions at 44 K (NpTe), 25 K ($PuGa_3$, DO19 structure) and 21 K ($PuGa_3$, R-3m structure). The detailed description of the type and origin of the magnetic order in $PuGa_3$ will be given in [10]. Here we just point out the different specific-heat behavior in magnetic field for a ferromagnet ($PuGa_3$, R-3m structure) and an antiferromagnet ($PuGa_3$, DO19 structure; NpTe) as can be seen in Fig. 6. In the former case, the ferromagnetic phase transition is gradually smeared out and the magnetic entropy shifts to higher temperatures when applying magnetic field (field acts in accord with internal ferromagnetic interactions). On the other hand, the antiferromagnetic phase transitions remain relatively sharp and the critical temperature as well as the magnetic entropy somewhat shift to lower temperatures (field acts against internal antiferromagnetic interactions). The phase transitions remain almost unchanged in 9 T in the presented cases of NpTe and DO19-$PuGa_3$, indicating relatively strong antiferromagnetic interactions.

The specific heat of $NpCoGa_5$ was shown and discussed in detail in [9]. Here we just point out that the

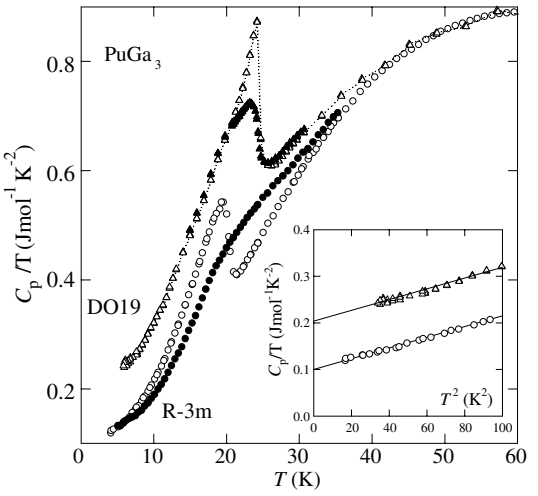

Fig. 6. Specific heat of the two structural modifications of $^{239}PuGa_3$: DO19 (triangles) and R-3m (circles) crystal structures measured in zero magnetic field (empty symbols) and in 9 T (filled symbols).

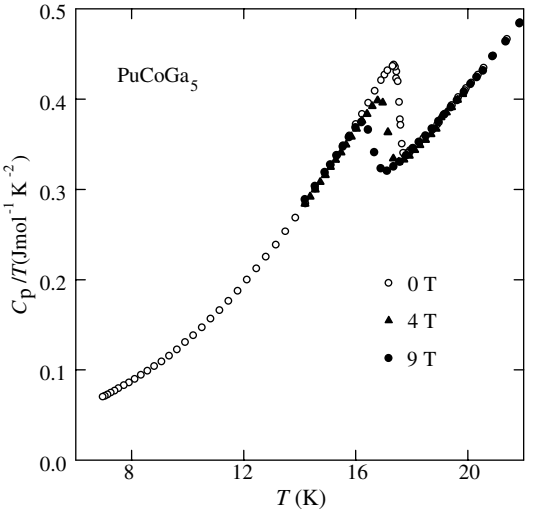

Fig. 7. Specific heat of $^{239}PuCoGa_5$, well comparable to that shown in Fig. 1 of Ref. [1].

phase-transition temperatures (in the range between 30 and 50 K) including their development in magnetic fields up to 9 T agree very well with the magnetization and Mössbauer spectroscopy data.

Finally, let us mention the case of $PuCoGa_5$. This compound was recently discovered to be superconducting below 18 K [1]. The specific heat in this recent study was measured on a single crystal using the same type of equipment (PPMS, Quantum Design) as in the present work. Comparing our data plotted in Fig. 7 with those shown in Fig. 1 of [1], almost identical results are found. The transition to the superconducting state is accompanied by a well pronounced anomaly in the specific heat, that is gradually suppressed by application of external magnetic field. The height of the jump in C_p/T at the critical temperature in zero field as derived from our measurement reaches $(116 \pm 8)\,mJ\,mol^{-1}\,K^{-2}$, well in agreement with the previously reported value of $(110 \pm 4)\,mJ\,mol^{-1}\,K^{-2}$. Also the Debye temperature (i.e. parameter reflecting the slope of $C_p(T)$ in a given temperature region) estimated from specific heat above the critical temperature agree well: our value of 246 K, estimated from our data between 18 and 23 K, compares with 240 K [1]. Note that this value of θ_D is just a parameter describing data in the given temperature range in a very simplified model that we use only to compare both experimental data sets. It can differ from real phonon energies in this material [11].

3.3. Encapsulation using sapphire capsules

The method of encapsulation using Stycast described here excludes further use of the sample because it can be hardly removed from the Stycast. To enable safe measurements on valuable samples that need to be used for further experiments, we have tested another possibility of encapsulation with use of sapphire capsules. The procedure has been described in the experimental part. In distinction to the first method, the heat capacity of the capsule is relatively large due to its comparatively large mass. Comparison of the heat capacity of the various individual contributions is represented in Fig. 8.

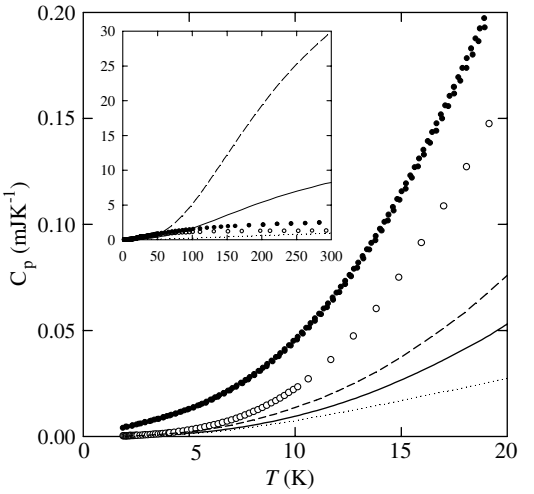

Fig. 8. Heat capacity of the 30 mg sapphire capsule (dashed line) compared to that of sample platform (full line), 1 mg of Stycast® 2850 FT (dotted line), 10 mg URhAl sample (full circles) and 10 mg Au (empty circles); $\gamma = 67\,mJ\,mol^{-1}\,K^{-2}$ and $0.7\,mJ\,mol^{-1}\,K^{-2}$ for URhAl [12] and Au [13], respectively.

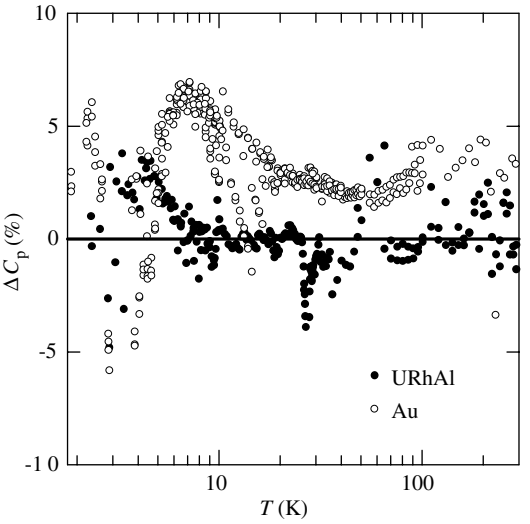

Fig. 9. Difference between the heat capacity obtained on encapsulated and non-encapsulated sample of Au (7 mg) and URhAl (5 mg).

Despite the additional heat capacity of sapphire, the measurements obtained on samples placed inside such a capsule give rather reliable data as shown in Fig. 9. The experimental error increases in comparison to the usual measurement, but remains acceptable in most cases. Of course, it depends strongly on the intrinsic specific heat of the given compound. The observed deviation for Au sample is then obviously larger because of its lower heat capacity. Nevertheless, characteristics derived when fitting the low-temperature part (1.8–10 K) to Eq. (1), $\gamma = (0.80 \pm 0.20)\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $\theta_D = (163 \pm 2)$ K do not differ substantially from the literature data $\gamma = 0.689\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $\theta_D = 161.8$ K [13].

4. Conclusions

The heat capacity of Stycast® 2850 FT was determined between 1.8 and 300 K. We have shown that the heat capacity measurements on samples encapsulated by this Stycast give reliable results. The possibility of specific-heat measurements inside sapphire capsules was also examined with a positive result.

Acknowledgements

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