Technique for determination of accurate heat capacities of volatile, powdered, or air-sensitive samples using relaxation calorimetry

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We introduce a four-step technique for the accurate determination of the heat capacity of volatile or air-sensitive samples using relaxation calorimetry. The samples are encapsulated in a hermetically sealed differential scanning calorimetry pan, in which there is an internal layer of Apiezon N grease to assist thermal relaxation. Using the Quantum Design physical property measurement system to investigate benzoic acid and copper standards, we find that this method can lead to heat capacity determinations accurate to ±2% over the temperature range of 1–300 K, even for very small samples (e.g., <10 mg and contributing ca. 20% to the total heat capacity). © *2006 American Institute of Physics.* [DOI: 10.1063/1.2349606]

Accurate determinations of heat capacities over a large temperature range are required to understand many aspects of solids, including chemical thermodynamic stability and lattice dynamics. In 1983, Stewart reviewed the available techniques for low-temperature calorimetry and also indicated the trends at that time, especially to measurements on smaller samples.[1] Since then, one of the most significant developments in this field has been the availability of a commercial instrument, the physical property measurement system (PPMS) from Quantum Design.[2] This instrument allows determination of heat capacities of small samples, in the temperature range of 0.4–400 K, based on determination of the relaxation of the temperature following a heat pulse.[3] The PPMS accuracy and precision have been examined in detail for solid samples that are placed in intimate contact with the platform of this relaxation calorimeter, and it has been found that accuracy can be better than ±1% for $100\ \mathrm{K} < T < 300\ \mathrm{K}$,[4] but it is less accurate at lower temperatures.[4,5]

Many solids are not suitable for relaxation calorimetry on an open platform. One reason could be volatility of the sample, which would be problematic in the high vacuum. Another problem could be sample morphology, e.g., a powder which would not be in good thermal contact with the platform. The latter has been addressed by sealing the powder in an (ordinary) aluminum differential scanning calorimetry (DSC) pan and using a PPMS, but the results gave heat capacities that were systematically too low.[6]

We have developed a technique suitable for the determination of the heat capacity of powders or volatile crystals, using the relaxation calorimeter of the PPMS. We used hermetically sealed DSC pans (Perkin-Elmer, Kit No. 0219-0062, mass of ca. 25 mg) with Apiezon N high-vacuum grease (ca. 6 mg) inside the pan to improve thermal contact between the pan and the powdered sample. The latter was embedded in the grease, as shown schematically in Fig. 1. A thin film of Apiezon N also was used between the pan and the platform. The complete determination of the heat capacity of a sample required four sets of measurements in the following order: (a) the platform with a thin layer of grease, (b) the pan with grease inside and the lid resting in place (but not sealed), (c) the platform with grease, and (d) the sealed pan with the sample imbedded in the grease (the pan was vigorously shaken after introduction of the sample followed by sealing). Measurements (a) and (b) provide the heat capacity of the pan and grease; (c) and (d) give the heat capacity of the pan+grease+sample. Step (c) was required because it was not possible to carry out steps (b) and (d) with precisely the same mass of grease on the platform. Special care must be taken in loading (b) in the PPMS because of the loose lid, but grease placed on the lip of the pan can be used to reduce lid slippage.

We have refined this technique to the fewest steps to give the most accurate heat capacity determination. Although, in principle, it could be abbreviated by assuming that the specific heat of the pan and the grease is the same in all cases, this could lead to inaccuracies. We found[7] that the specific heats of pans from the same batch were well within 0.5% for $T > 25$ K and 4% for $2\ \mathrm{K} < T < 25$ K, but the specific heats were systematically 1%–2% lower than that reported for pure Al.[8,9] Because the pan can contribute more than 50% to the total heat capacity, particularly at high temperatures, it is prudent to accurately know the heat capacity for each pan. Similarly, the technique could be shortened by assuming that the specific heat of Apiezon N is known, but our technique shows its specific heat to be 5%–8% lower than published results,[10] although we found it to be reproducible within 10% for $T < 10$ K, 4% for $10\ \mathrm{K} < T < 40$ K, 1% for $40\ \mathrm{K} < T < 160$ K, and 3% for $160\ \mathrm{K} < T < 300$ K.[7] It has been shown that the heat capacity of Apiezon N can depend on the morphology (lump or thin film)[11] so again the most accurate results require all the steps outlined above.

Our technique has some similarities to the method developed by Schnelle *et al.* to determine the heat capacities of powders in glass ampoules.[10] The advantages here are that the DSC pans can be hermetically sealed without heat, and aluminum is a better conductor of heat than glass. The latter

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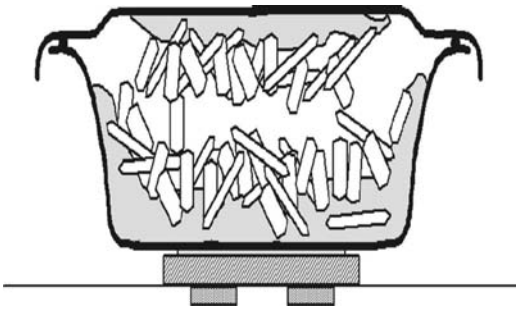

FIG. 1. Schematic illustration of crystals of the sample imbedded in Apiezon N in a hermetically sealed DSC pan.

is especially important for relaxation calorimetry: we have shown that poor intrinsic thermal conductivity of the sample can lead to precise but inaccurate heat capacity determinations using the PPMS.[5,12] Heat capacity determinations of powders carried out in DSC pans without a thermal contact aid can show systematic inaccuracy;[6] here we used Apiezon N grease to improve thermal relaxation. Javorský *et al.*[13] have encapsulated transuranium samples in either epoxy or sapphire for accurate heat capacity determinations with a PPMS. Our technique has the advantage of ready availability and low cost of the DSC pans. Additionally, our technique has the potential for application with corrosive samples, using gold DSC pans.

We tested our technique by measuring the heat capacity of standard benzoic acid (Calorimetry Conference), and comparing our results with its known heat capacity.[14–16] Before commencing, we tested benzoic acid for nonreactivity with Apiezon N, a necessary condition for this method. The results (Fig. 2), determined using the ^{4}He cryogenic system of the PPMS, generally are accurate within ±1% for 70 K$<T<$300 K and ±3%–5% at lower temperatures. This is remarkable considering that the benzoic acid sample mass was $<$10 mg and only contributed about 20% to the total heat capacity from 50 to 300 K ($\sim$50% at $T\sim$25 K and $<$20% for $T<$5 K).

To test the lowest temperatures where the heat capacity of benzoic acid is not known (it has only been reported for $T>$6 K), we performed the same types of experiments for 0.4 K$<T<$10 K with high-purity copper (which contributes

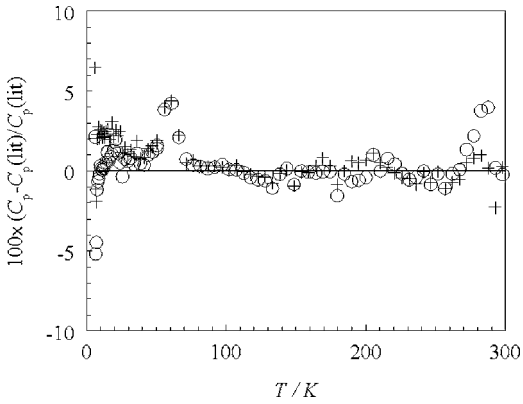

FIG. 2. Heat capacity differences for benzoic acid [(○), 9.525 mg and (+) 8.758 mg] embedded in Apiezon N and encapsulated in a hermetically sealed DSC pan, determined using the ^{4}He system of the PPMS, relative to the literature results (Refs. 14–16).

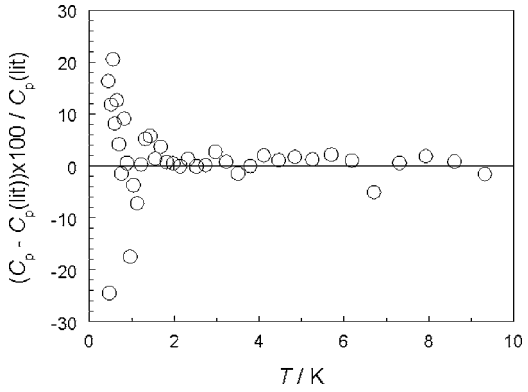

FIG. 3. Heat capacity differences for copper (m=26.515 mg) embedded in Apiezon N and encapsulated in a hermetically sealed DSC pan, using the PPMS ^{3}He system, relative to the literature reports (Refs. 17 and 18).

60%–80% to the total heat capacity) using the ^{3}He system of the PPMS. The results, shown in Fig. 3, show agreement with the literature[17,18] to within ±2% for 1.5 K$<T<$10 K, but larger deviations at lower temperatures. The latter is not an artifact of the encapsulation technique, as we have observed similar results for copper directly on the platform.[5]

The precision of heat capacity measurements using this encapsulation technique can be judged from triplicate measurements, using standard propagation of errors as the greater of the error calculated by twice χ^2 directly from the PPMS data, or the result of standard propagation of error based on the uncertainty in the sample mass, the addendum heat capacity, and the total heat capacity. On this basis, the precision of the measurements using the encapsulation technique for $T>$20 K is about 1%,[7] which is in the same range as for samples measured directly on the platform.[5]

In conclusion, we have shown that heat capacity determinations can be made using hermetically sealed DSC pans for samples requiring consolidation, such as fine powders or containment, e.g., for protection from the vacuum system. With due consideration of the addendum contributions, the accuracy for a PPMS can be accurate within ±2% over the temperature range of 1–300 K, even with very small samples. In principle, this technique can be applied to any type of relaxation calorimeter.

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