NOTES

BRIEF contributions in any field of instrumentation or technique within the scope of the journal should be submitted for this section. Contributions should in general not exceed 500 words.

Heat capacity of silver paint

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The heat capacity $[C_P(T)]$ of a silver loaded paint has been measured between 3 and 30 K. It is shown to be ideal for mounting small calorimeter samples for measurements above 1 K or where good thermal contact to the sample is essential.
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Measurement of the specific heat capacity, $C_P(T)$, of small samples (<1 g) generally requires the material to be secured in some way to the calorimeter assembly. Any glue used for this purpose should have a low heat capacity, to minimize errors involved in the subtraction of its contribution from the total signal. Furthermore, it should be possible to deposit reproducible amounts of the glue to avoid the need for a separate measurement of the glue heat capacity each time. Convenient removal is also essential to avoid a buildup on the calorimeter and a high thermal conductivity is desirable, since poor thermal contact between the sample and the calorimeter will cause erroneous calorimetry measurements.[1] One standard glue used for low temperature calorimetry is Apiezon N grease,[2,3] however, we have found a silver paint [Flexible Silver No. 16 (Ref. 4)] to be better than Apiezon N for many applications.

The paint consists of fine silver powder (~35% by weight) dispersed in a polymer/solvent binder. We have found overnight drying at room temperature adequate to eliminate the solvent (ethylene glycol monoethyl ether acetate) and yield a reproducible heat capacity. In repeated runs of both calibration standards (~100 mg of Au and Cu) and ~50 mg metallic glass samples, no significant background variations ($<1\%$) were observed in $C_P(T)$ which could be attributed to changes in curing procedures. The glue is thin enough to be painted onto the calorimeter stage, or dispensed using a 10 μl syringe intended for gas chromatography. The latter method allows the reproducible deposition of glue and thus a fixed background contribution from the silver paint can be included with the addenda heat capacity. Once dry, a bond comparable to GE 7031 varnish is formed. We have found acetone to be a suitable solvent for removing the glue after a run, and have experienced no problems with buildup. The silver loading gives the glue a high thermal conductivity and greatly improves thermal contact to irregularly shaped samples. The improved contact coupled with the effective mechanical bond formed on curing has proved essential in the measurement of the heat capacity of metallic glass ribbons, where tens of centimeters of coiled ribbon 1 mm wide by 20 μm thick had to be mounted on the calorimeter stage.[1]

Absolute calorimetry measurements were done using a time relaxation calorimeter[5] described previously.[6] For the purposes of measuring $C_P(T)$ of the silver paint, a large amount was deposited on the addenda stage to form a ~60 mg mass once dried. Figure 1 shows a comparison of $C_P(T)/T^3$ vs T for the silver paint, pure silver[7] and one-tenth the $C_P(T)$ of Apiezon N grease.[3] The data are accurate to within 5%.

In Fig. 1, we can see that at high temperatures ($T \geqslant 20$ K) the heat capacities of both pure silver and the silver paint are roughly the same, reflecting the dominance of the metal loading in this region. The similarity between the two materials at higher temperatures is an indication that the dried silver paint is dominated by the silver contribution. At lower temperatures however, the heat capacity of the silver paint exceeds that of pure silver, being about 60% greater at 5 K. We attribute the excess heat capacity of the paint at these

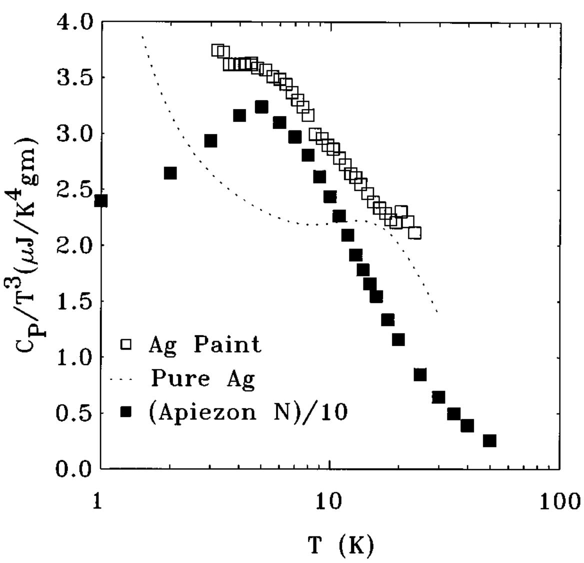

FIG. 1. Heat capacity $[C_P(T)]$ of dried silver paint (Ref. 4) (□) and pure silver (Ref. 7) (---) plotted as C_P/T^3 vs T. One-tenth of the heat capacity $[C_P(T)/10]$ of Apiezon N grease (Ref. 3) has also been shown for comparison (■).

temperatures to the phonon heat capacity of the polymer binding agent, which freezes out at a lower temperature because of its lower Debye temperature. Below 2 K, where the lattice heat capacities of both the binder and silver are negligible, $C_P(T)$ of silver and the paint again begin to converge, and the electronic heat capacity of the silver begins to dominate the low temperature behavior of the glue. Since the heat capacity of the silver paint does not accurately follow a simple $T+T^3$ Debye law with a single characteristic temperature, we found it convenient to simply subtract off the glue contribution with those of other addenda rather than use a fitted correction term. However, to facilitate evaluation of this material for other applications, the following expression for $C_P(T)$ (in μJ/g K) provides an adequate ($\pm 5\%$) approximation:

$$C_P(T) \sim 2.5\times T + 3.84\times T^3 - 0.091\times T^4.$$

It is clear from Fig. 1, that over the temperature range considered here, the heat capacity of Apiezon N grease is approximately ten times that of the silver loaded paint. As a result much larger amounts of the silver paint can be used to mount the samples, or a much smaller glue contribution has to be subtracted. A further problem with Apiezon N is its low thermal conductivity, a feature that makes measurement of its $C_P(T)$ difficult.[3] However, being an electrical insulator $C_P(T)$ of Apiezon N contains no electronic contribution. Consequently, somewhere below 1 K the signal from the silver paint will exceed that of Apiezon N. In some applications, the fact that Apiezon N does not cure can also be used to advantage. The bare calorimeter may be run with a dab of Apiezon N to determine the total addenda signal, and the sample added later. In this way, the glue contribution is included with the other addenda, and can be subtracted off in a single step. Once cured, the silver paint cannot be reused to mount a sample. It must be removed with acetone and then the same amount used to mount the sample. In our case, the silver paint was dispensed with a 10 μl syringe, to accurately control the amount used.

In summary, Apiezon N grease remains the best choice of calorimeter glue for regularly shaped samples at temperatures below 1 K. At higher temperatures, however, the background from the silver paint is much smaller, and in cases where thermal contact to the sample is a problem, or where a stronger mechanical bond is needed at room temperature, silver paint offers significant advantages.

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