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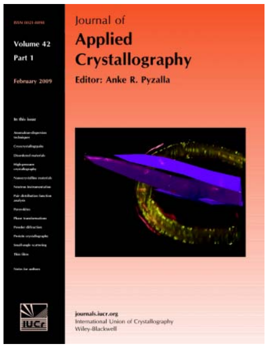

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Mounting powder samples for sub-Kelvin neutron diffraction

D. H. Ryan[a]* and I. P. Swainson[b]

[a]McGill University, Centre for the Physics of Materials, Department of Physics, Rutherford Physics Building, 3600 University Street, Montreal, Quebec, Canada H3A 2T8, and [b]Canadian Neutron Beam Centre, National Research Council, Chalk River Laboratories, Ontario, Canada K0J 1J0. Correspondence e-mail: dhryan@physics.mcgill.ca

The increasing availability of ^{3}He-based cryostats is making it possible to add sub-Kelvin capabilities to powder diffraction instruments. However, there are many problems associated with cooling powders below 1 K, and if great care is not taken, the sample temperature may be far higher than that reported by a thermometer attached to the sample holder. This contribution describes two practical and effective strategies for mounting powder samples that yield equilibration times of at most a few tens of minutes.

1. Introduction

The increasing availability of commercial ^{3}He cooling systems is making sub-Kelvin temperatures accessible to a much broader community. Unfortunately, the move from pumped ^{4}He-based cryostats ($T_{\rm min} \simeq 1.5$ K) to ^{3}He-based systems ($T_{\rm min} < 0.3$ K) brings with it severe sample equilibration problems that may not be widely appreciated. Cooling the thermometers that are bolted to the ^{3}He pot and to the end of an oxygen-free high-conductivity (OFHC) copper sample holder is relatively straightforward, so that time lags of only a few minutes between the two sensors are common. However, a powdered sample contained within the holder may exhibit cooling times of days unless proper procedures are followed, and with typical hold times for most sorb-pumped ^{3}He systems being 2–3 d, after which the system must be re-cycled to ~5 K to regenerate the sorb, it is possible that the sample will not cool below ~1 K at any point during the experiment.

Our direct experience with equilibration problems while working on $Er_3Cu_4X_4$ (X = Si, Ge and Sn; Ryan *et al.*, 2004) and an iron-based molecular magnet (Vecchini *et al.*, 2008) led us to investigate the two mounting strategies for powder samples that are reported here.

2. The problems

Conventional ^{4}He exchange-gas coupling between the sample and the cryostat cold stage, common at higher temperatures, cannot be used in ^{3}He cryogenic systems because the saturated vapour pressure of ^{4}He drops very rapidly at low temperatures (Preston-Thomas, 1990*a*,*b*), making it ineffective as an exchange gas. In addition, limitations on both the cooling power and the total cooling capacity available with sorb-pumped ^{3}He cryogenic systems make it critically important to thermally isolate the ^{3}He stage and its associated sample mount from the surroundings. This requirement leads to cryostat designs in which the sample holder is bolted either directly onto the ^{3}He pot or onto an OFHC copper extension rod that is in turn bolted to the ^{3}He pot. The sample holder and ^{3}He pot are then surrounded by radiation shields and enclosed in a hard vacuum for thermal isolation. Cooling of the sample relies entirely on thermal conduction through the OFHC copper to the walls of the holder and then to the sample itself.

Where intimate electrical contact between the OFHC copper and a solid, electrically conducting sample can be assured (*e.g.* for large single-crystal metallic specimens), the bulk of the heat is transported by the electrons and cooling can be relatively effective. However, for insulators or powder samples with large numbers of poor electrical contacts, phonons must provide the thermal transport, and these suffer from two problems at very low temperatures: (i) the number density of phonons falls as T^3, so progressively fewer carriers are available for conduction; (ii) acoustic mismatch at the copper–sample interface and at the sample–sample boundaries in powders reduces the efficiency of phonon transport and leads to a Kapitza resistance, $R_{\rm K}$, that grows as $\sim T^{-3}$ (Challisi, 1974; Swartz & Pohl, 1989). As a result, cooling an insulating or poorly connected powder sample becomes increasingly difficult as the temperature drops and it is very easy to have the sample fall out of equilibrium.

One final problem arises from the choice of materials used for sample holders in neutron scattering experiments. While copper has a high thermal and electrical conductivity, it has a tendency to activate in a neutron beam, has a modest absorption cross section [$\sigma_{\rm abs}$ = 3.78 (2) b] and has a moderate coherent scattering length which leads to strong Bragg scattering peaks. Vanadium is a more popular choice as it yields almost no coherent scattering but has a similar absorption cross section [$\sigma_{\rm abs}$ = 5.08 (4) b]. Finally, both the absorption cross section [$\sigma_{\rm abs}$ = 0.321 (3) b] and the coherent scattering length for aluminium are much lower than those in copper, so

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the former yields better transmission and weaker Bragg peaks. Both vanadium and aluminium are more popular than copper, but they suffer from one potential drawback at low temperatures: both are superconductors (T_c^V = 5.38 K, T_c^{Al} = 1.14 K). The paired electons in superconductors do not transport heat, making V and Al poor thermal conductors at the temperatures of interest here.

3. Solutions

3.1. Hydraulically pressed in copper

Our simplest and most direct solution to the thermal conduction problem was to mix the powdered sample with an approximately equal volume of copper powder and hydraulically press the mixture into an OFHC copper sample holder to form a solid plug. The holder was supported by enclosing it in a steel case to prevent bursting, and the pressing was carried out in stages (we added 1–2 mm-thick layers of powder at each pressing). The block and a loaded holder are shown in Fig. 1. Complete packing was verified by sectioning a finished holder. Pressing the contents of the entire 50 mm-high sample holder in one shot does not work as it leads to the formation of a shallow solid plug at the base of the piston. This plug then supports the external pressure and prevents compaction of the majority of the powder.

Neutron powder diffraction experiments were carried out at the Canadian Neutron Beam Centre (CNBC) using the DUALSPEC C2 800-wire powder diffractometer at the NRU reactor, Chalk River Laboratories. The neutron diffraction data were collected between 3 and 83° in one bank at a wavelength of ~2.37 Å, with a pyrolytic graphite filter to remove λ/2 contamination. The diffraction pattern of $Er_3Cu_4Si_4$ taken at 0.33 K (Fig. 2) shows the expected strong reflections from the copper in both the holder walls and the powder used to ensure thermal contact; however, these reflections obscure only limited ranges of 2θ and do not preclude analysis of the pattern. The temperature dependence of several magnetic reflections shown in Fig. 3 reveals the complexity of the magnetic ordering in this system. We emphasize that the intensities shown in Fig. 3 were derived from measurements made in an essentially random temperature sequence, both on heating and on cooling, with many points interleaved between others. There were also several breaks where the system was re-cycled above 5 K to regenerate the sorption pump and counting was resumed immediately after restabilization at the set temperature. No time-delay or hysteretic effects were detected, indicating that the sample equilibrated in at most a few tens of minutes.

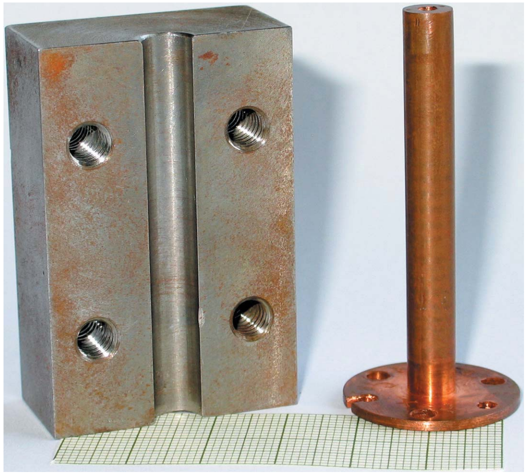

Figure 1
(Left) One-half of the steel block used to support the OFHC copper holder while the sample, mixed with copper powder, was being hydraulically pressed. (Right) Sample holder with material pressed into it. There is a tapped hole in the end of the holder to permit mounting of a thermometer. Scale is provided by mm/cm graph paper.

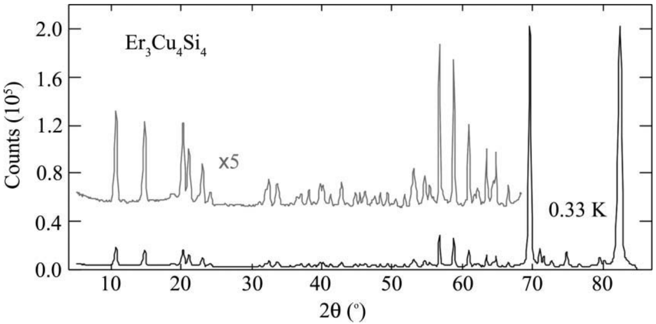

Figure 2
Neutron scattering pattern for $Er_3Cu_4Si_4$, mixed and pressed with copper powder, taken at 0.33 K using a wavelength of ~2.37 Å. The lower curve shows the entire data set with the strong reflections from the copper (at $2\theta \simeq 69$ and 82°) used to mount and equilibrate the sample. The upper curve covers a narrower angle range and is scaled by a factor of five to make the reflections from the sample more evident. The two magnetic peaks just above $2\theta = 20°$ were used to follow the cooling of the samples in this study.

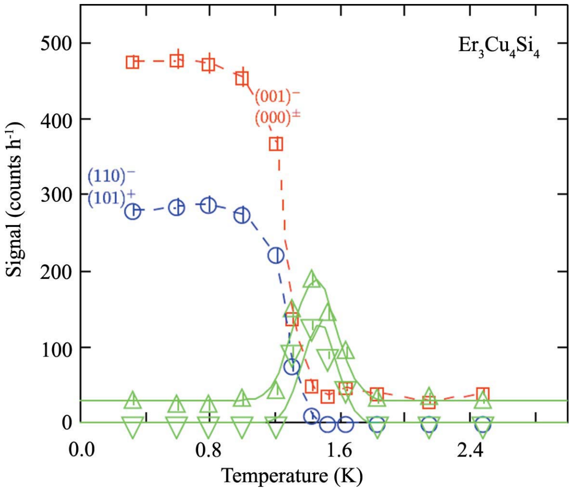

Figure 3
Temperature dependence of several magnetic reflections from $Er_3Cu_4Si_4$, mixed and pressed with copper powder, showing the complex evolution of magnetic order at low temperatures. The two strongest peaks associated with the ordering at ~1.2 K are $(001)^-/(000)^\pm$ at $2\theta = 20.2°$ (squares) and $(110)^-/(101)^+$ at $2\theta = 21.1°$ (circles) (Cadogan, 2008). The two weaker satellites at $2\theta = 19.2°$ ('up' triangles) and $2\theta = 21.7°$ ('down' triangles) occur only between 1.6 and 1.2 K, and were used to follow the early stages of cooling.

A subsequent susceptibility study of several superconducting standards mounted in an identical sample holder showed that the equilibration time at 0.61 K (T_c^{Zr}) was about 10 s. Given the rapid equilibration, and the complexity of the magnetic order in $Er_3Cu_4Si_4$, we adopted this material as a standard for evaluating other mounting methods and regarded the intensity data shown in Fig. 3 as providing an empirical temperature scale.

3.2. Sealed under helium

While the hydraulically packed samples exhibit effectively instant equilibration (for neutron scattering purposes) and so leave no doubt as to the actual measurement temperature, the process is somewhat destructive, and the sample is not readily available for other studies once it has been mounted. We therefore evaluated the effectiveness of small amounts of helium gas sealed in with the sample as an alternative strategy.

Our first holders were fabricated from OFHC copper as we already knew that the first Bragg reflections from copper, while strong, lay well outside our regions of interest. We initially avoided the more popular Al and V in favour of Cu, as we expected that the superconducting transitions in the first two materials would render the walls of the sample holder thermally insulating and greatly reduce their ability to thermalize a sample effectively (this expectation is tested below).

Working with ^{4}He at these temperatures presents special problems. In addition to the extremely low vapour pressure noted above, ^{4}He undergoes a transition to a superfluid state at T_λ = 2.17 K, and extreme care is needed to seal any vessel holding superfluid ^{4}He as it has effectively zero viscosity and can escape through ‘superleaks’. We built the indium-sealed OFHC copper sample holder shown in Fig. 4. Initial test cycling in liquid nitrogen confirmed that the seal was reliable, and loaded sample holders were checked after neutron scattering runs down to 0.3 K to confirm that they still contained ^{4}He. As the holder is sealed at ambient temperature and pressure and then cooled at fixed volume, the internal pressure will fall, and we do not expect liquid formation until the saturated vapour pressure is less than the internal pressure. This should occur at about 1.5 K with the helium gas condensing directly into the superfluid state.

Samples were loaded into the holders as loose powders, with no binder or added copper powder. All loading and sealing was carried out at ambient pressure within a helium-filled glove-box. Both mating surfaces were cleaned and polished before the vacuum-greased indium o-ring seal was installed. The sample holder was fully sealed before it was removed from the glove-box. For comparison, the same sample was also loaded in air after all helium had been flushed from the holder. At 0.3 K all of the components of air are very low vapour pressure solids, and so this arrangement is effectively equivalent to mounting the sample in vacuum. The sample was established at ~3 K for several hours while the ^{3}He system was brought online, then the system was taken directly down to its base operating temperature of ~0.34 K. Neutron diffraction patterns were collected in 6 min intervals for about 10 h.

Fig. 5 shows the time dependence of the two magnetic peaks associated with the ordering at 1.2 K in $Er_3Cu_4Si_4$ (see Fig. 3). The differences in cooling behaviour are striking. The two diffraction peaks from the sample loaded under helium reach their saturation intensities by the second measurement (about 12 min after the thermometers reached their base temperature), while those from the sample loaded in air are still changing at the end of the run. The sample loaded in air is still cooling 10 h after the thermometers on the ^{3}He pot and at the end of the sample holder have both reached their final temperatures. It is also clear that the sample loaded in air remains far from ~0.34 K after 10 h of cooling.

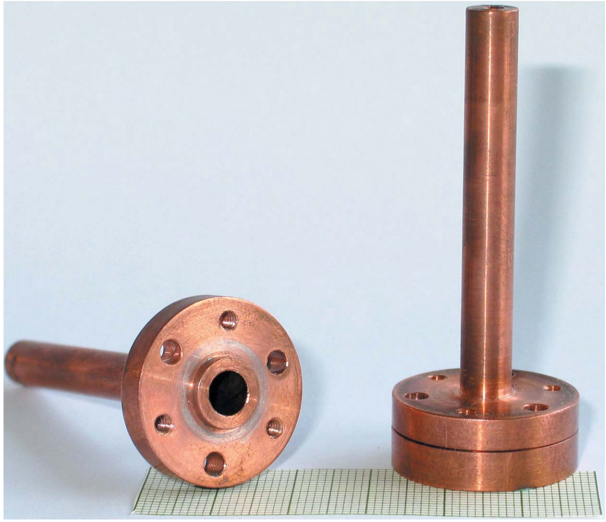

Figure 4
(Left) Top of OFHC copper sample holder showing bolt circle and raised ring used to centre the indium o-ring. (Right) Fully assembled sample holder. Scale is provided by mm/cm graph paper.

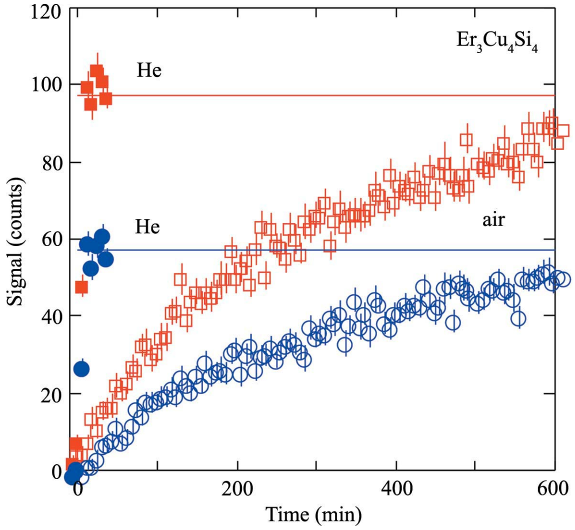

Figure 5
Time dependence of two magnetic reflections for samples of $Er_3Cu_4Si_4$ sealed under helium (solid symbols) and air (open symbols) showing the very different cooling rates. Symbol shapes correspond to those used in Fig. 3. The solid lines show the expected saturation values for the two peaks at 0.34 K.

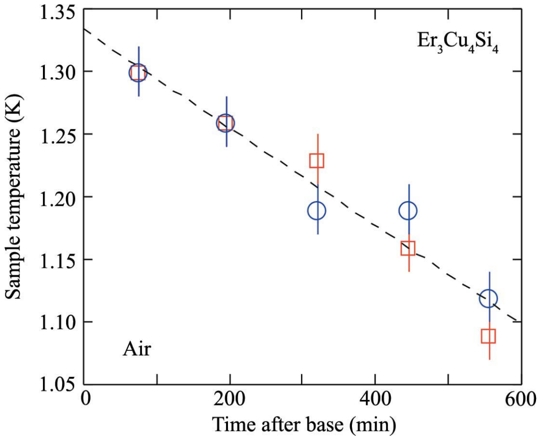

Figure 6
Sample temperature deduced from the intensities of the two reflections shown in Fig. 5 for the sample loaded in air (symbols correspond to those used in Figs. 3 and 5). Time zero was taken as being the point at which both thermometers cooled below 0.4 K. The average cooling rate, shown by the dashed line, is 0.39 (3) mK min^{-1}.

A more detailed examination of the diffraction patterns taken with the air-filled sample holder reveals that the two satellite peaks (denoted by 'up' and 'down' triangles in Fig. 3) are weaker than the main peaks almost as soon as the thermometers reach their base values. This means that the sample cools through ~1.4 K fairly promptly; however, this efficient cooling does not continue. After one hour, the sample is at ~1.3 K, and the average cooling rate observed through to the end of the experiment was ~0.4 mK min^{-1} (Fig. 6). The estimated sample temperature after 10 h was only 1.06 (3) K: far hotter than either thermometer and nowhere near the system's base temperature of 0.34 K. A similar failure to cool below 1 K was observed during initial work on a molecular magnet compound (Vecchini *et al.*, 2008) before pressing in copper was adopted.

The substantial difference in cooling rates between in-helium and in-air apparent in Fig. 5 serves to emphasize the critical role played by the superfluid ^{4}He film that coats the sample and the interior of the copper sample holder. While the thermal conductivity of superfluid ^{4}He is formally infinite, finite size effects reduce it to values closer to that of copper (Greywall, 1981); however, the film is in intimate contact with both the walls and the sample and clearly serves to effectively connect the two thermally. In order to distinguish the effects of this film from the cooling provided by contact with thermally conducting walls, we also built a sealed sample holder using vanadium. As vanadium is a superconductor below T_c^V = 5.38 K, the thermal conductivity of the walls should be two to three orders of magnitude smaller than that for the OFHC copper sample holder at 1 K (Tsai *et al.*, 1981). The Er$_3$Cu$_4$Si$_4$ was again loaded into the holder under helium and sealed as before; however, we used an OFHC copper lid for the vanadium sample holder so as to provide direct contact between the enclosed helium and the ^{3}He cold stage. The results of this test were indistinguishable from those of the helium-filled OFHC copper sample holder, demonstrating that essentially all of the heat transport at these temperatures is by the superfluid ^{4}He film and that, contrary to our initial expectations, the material making up the walls is not relevant to the final cooling behaviour. The incoherent scattering from the vanadium led to a factor of three increase in the observed background, so the trade-off in the choice between copper and vanadium is one of strong Bragg peaks at specific locations from copper, *versus* fairly uniform background scattering from vanadium that may obscure weak magnetic peaks. We have since built and tested holders made from 7075 aluminium alloy, which yields weaker Bragg peaks, and are developing a holder based on single-crystal silicon that should yield essentially no background and no Bragg peaks and be optimized for very weakly scattering samples (Potter *et al.*, 2007). Specific applications would determine the optimum choice.

Since the presence of superfluid ^{4}He is critical to obtaining proper cooling of the sample, and the sample holder is mounted in an evacuated space during the measurements, it is essential that the indium seal be installed correctly so as to avoid superleaks. We noticed that the thermometer at the end of the sample holder exhibited a much larger lag when the sample was loaded in air than when it was loaded under helium. While no systematic studies were made, it is possible that such a lag with a sample loaded under helium might serve as an indication that the seal has failed and that the superfluid ^{4}He has been lost. Finally, confirming that the sample holder contains helium after the run provides additional confidence that the sample did indeed cool properly during the measurements.

4. Conclusions

Improper mounting of powder samples can lead to extremely poor cooling below 1 K. We show that hydraulic pressing of the sample mixed with copper powder, and sealing the loose powder sample under an atmosphere of ^{4}He, both yield adequate cooling performance for neutron powder diffraction measurements. In the latter case, the material used for the walls of the sample holder is shown to be irrelevant as the primary heat transport is by the film of superfluid ^{4}He that coats the sample. It is important to note that the holders are not flooded with liquid ^{4}He and that the 1–2 cm^3 of ^{4}He gas loaded in with the sample at ambient pressure and temperature is sufficient to permit complete thermalization of the sample.

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(University of Manitoba) on the $R_3T_4X_4$ compound family drove the development of the sub-Kelvin sample holders. The $Er_3Cu_4Si_4$ sample used here was prepared by Robert Gagnon (McGill University).

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