CONTROLLING NICKEL NANOPARTICLE SIZE IN AN ORGANIC/METAL-ORGANIC MATRIX THROUGH THE USE OF DIFFERENT SOLVENTS

ADAM BERLIE, IAN TERRY AND MAREK SZABLEWSKI

Abstract. A sample holder is reported which has allowed the magnetic characterisation of air sensitive compounds to be made in a Quantum Design Magnetic Properties Measurement System as a function of applied field (0 - 5 T), and at temperatures ranging from 2 - 290 K. The sample holder is in the form of a specially designed tube, which is made from high purity quartz, utilises PTFE (polytetrafluoroethylene) plugs and is reuseable. This construction also offers the benefit that no heat treatment of the holder is required during sample loading, making the sample holder suitable for thermally sensitive compounds. The application of this sample holder is demonstrated for the case of $Ni(cod)_2$ (cod= 1,5-cyclooctadiene), a compound that decomposes when exposed to air and/or heat. This material's instability has, so far, prevented the magnetic characterisation of the compound, with nickel nanoparticles, a product of the decomposition, usually being measured instead.

Magnetometers based upon the Superconducting QUantum Inference Device (SQUID) are now quite a common feature in research laboratories. They offer high sensitivity in magnetic moment measurements ($\approx 10^{-11}$ A m^2) as well as variable applied fields ($\leq$ 7 T) and temperatures (typically 2 K to 400 K). The magnetic moment detection system usually consists of second-order gradiometrically wound coils inductively coupled to an RF SQUID. The magnetic moment being measured is located within the detection coils and it is moved along the axis of the coils while the response of the SQUID to the changing magnetic flux is recorded. In the Quantum Design Magnetic Properties Measurement System (MPMS) these data are fitted to the response of an ideal magnetic moment, the instrument usually being calibrated with a high purity palladium sample.

When making measurements on such magnetometers it is essential to minimise the magnetic contribution of the sample holder and, to this end, several approaches to the mounting of samples have been suggested [1]. For example, plastic drinking straws are frequently used as sample holders, with gelatin capsules being adopted to contain powders. However, such a method is unsuitable when making measurements at high temperatures or when working with air sensitive materials or liquids. Sample holders for high-temperature measurements have been created; one example rolled the sample in aluminum foil which gave a very low background signal and was easily compatible with the oven addition for the Quantum Design MPMS [2]. Another used a fused quartz tube that connected straight to the metal sample holder rod where the sample sat in a slit that was 104 mm from the top of the tube [3]. Air sensitive or liquid samples are usually contained within EPR (or NMR) tubes because of such tubes' low magnetic susceptibility [1]. The tubes are typically flame tipped using a manifold to pump down the tube and a gas/oxgen flame to seal it. However if the sample is heat sensitive, such a method cannot be used. Being able to measure air sensitive or liquid samples and not expose them to any external energy, such as heat, is a substantial advantage as there are many materials that decompose to give magnetic contaminants. Molecular magnetism is an important field of research involving the synthesis and characterization of metal-organic or even purely organic magnets. In a purely organic system the presence of free radicals (such as an S=$\frac{1}{2}$ system) can be one origin of paramagnetic behavior, however generally free radical systems are very unstable and air sensitive. Many organic or molecular systems will be air sensitive, which makes measurements of magnetic properties hard to accomplish as the compounds are extremely difficult to handle. One example of a metal-organic system that is extremely heat and air sensitive is $Ni(cod)_2$, which is a well known source

of Ni(0) that was discovered in 1966 by Wilke and collaborators and has important applications in synthetic chemistry, notably for catalysis and carbon-carbon bond forming reactions [4, 5, 6]. $Ni(cod)_2$ is known to decompose slowly even when stored within a freezer and when left in a solution of THF produces a Ni mirror and has, as a result, been used as starting material to produce colloidal Ni nanoparticles [7]. $Ni(cod)_2$ was suggested to be diamagnetic by Wilke [5] though, to date, no report of the magnetic properties of undecomposed $Ni(cod)_2$ have appeared in the literature. In this paper we describe a new method of mounting air sensitive/thermally sensitive samples in a SQUID magnetometer, using $Ni(cod)_2$ as an example of the application of this method.

A Quantum Design MPMS XL system, with a DC Transport, was used where -5 T $\leqslant \mu_0 H \leqslant$ 5 T and 1.9 K $\leqslant$ T $\leqslant$ 400 K. The sample was located within the second order gradiometer coils, the central coil being positioned at the center of the core of the superconducting solenoid. The other two gradiometer coils are positioned 1.5 cm above and below the central coil. The sample was usually manually located at the center of the gradiometer coils and then the magnetic moment was measured as outlined in the introduction; a sample scan length of 4 cm was adopted for all measurements of magnetic moment. $Ni(cod)_2$ was purchased from STREM (purity 98+%) and handled inside a glovebox under an inert atmosphere (<1 ppm O_2).

The sample holder is shown schematically in Figure 1. The high purity quartz tube had a diameter 0.5 cm (source: Heraeus Quartzglas). It was constructed by dividing a 12 cm tube in two, with one of the 6 cm sections having an end heat-sealed using an gas/oxygen flame. The sealed end was joined to the other 6 cm tube section, creating a bulb of quartz (typically 3-4 mm) which would be used to support the sample in the middle of the tube. The sample can then be placed inside the tube within a glovebox an under argon atmosphere and a PTFE cap was placed in the end of the tube. Powdered samples were placed in the tube with a specially made long funnel that reached to the quartz bulb so the sample could be inserted and not leave any powder on the walls of the quartz tube [10]. Once the tube had been capped and removed from the glovebox it was further sealed with a small amount of GE varnish (C5-101, purchased from Oxford Instruments), which has a very low magnetic moment and can survive at low temperatures. The sample remained yellow, with no visible decomposition during the initial handling or after subsequent magnetic measurements (see Figure 2 (top)). As shown in Figure 1, the quartz tube was contained within a clear plastic drinking straw with a folded plastic straw [11] used as packing on either end to hold the tube in place. This addition to the quartz tube was to provide a degree of mechanical flexibility to the sample holder while allowing it to be easily attached to an MPMS DC Transport brass/steel sample rod via the standard drinking straw attachment. The tube was inside the MPMS for a long period of time whilst the measurements were being conducted and it was cycled through a wide range of temperatures and applied magnetic fields. The mechanical stability of the tube remained constant during the whole experiment with no degradation of the tube and little, if any, changes of the raw data with time.

As a comparison, a similar sample was also prepared following the conventional method of flame-sealing the quartz tube. A tube of length 20 cm and diameter 0.5 cm was cut into 8 cm and 12 cm sections. The 12 cm section was sealed using a flame at one end to create a quartz bulb for the sample to sit in, the two tubes were joined with the quartz bulb now in the middle of the tube. An NMR manifold was used so that the sample tube could be pumped down and re-filled with argon inside the glove box and then closed to temporarily seal the tube before it was exposed to an oxygen/propane flame. The quartz tube, measuring 14 cm in length, is shown at the bottom of Figure 2. When we prepared the $Ni(cod)_2$ to be measured in a Quantum Design MPMS system the sample was loaded into the quartz tube, which was evactuated and filled with nitrogen. Subsequent flame-sealing of the tube, which took less than 20 seconds, inevitably caused the $Ni(cod)_2$ sample to begin to decompose, despite the sample sitting in the middle of the tube; the yellow crystals transformed into a black solid over a period of 15 minutes. This process could not be stopped even by quickly placing the sample inside the MPMS and cooling the temperature to 250 K. The sample tube was connected to the DC transport rod in a similar

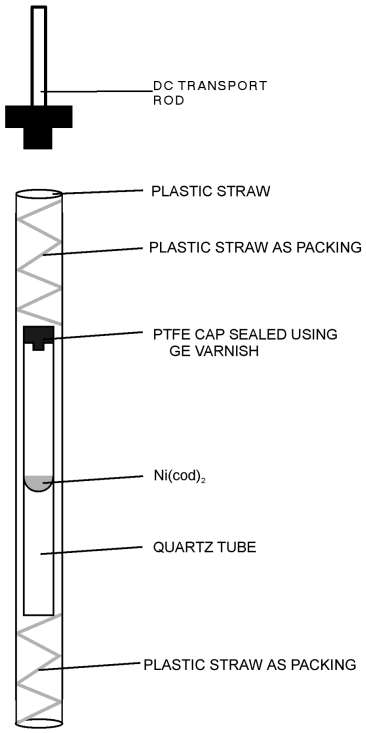

FIGURE 1. Schematic diagram of the sample holder to be attached to an MPMS brass/steel sample rod using the standard straw holder

fashion to the PTFE-sealed tube. Note that it is recommended to store $Ni(cod)_2$ in a freezer [8] at a temperature of -18 °C, thus magnetic measurements were made below this temperature to prevent decomposition.

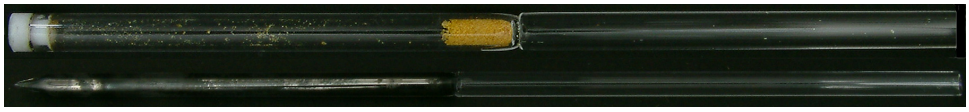

FIGURE 2. Top: Photograph of the specially designed tube taken after sample tube containing the $Ni(cod)_2$ had been left in an ambient atmosphere for 7 days. Bottom: Tube that was flame tipped where the $Ni(cod)_2$ decomposed and formed a Ni film. Pictures are not to scale; the bottom tube is 19.5 cm in length (after flame sealing) and the top is 12 cm in length. Both tubes have an equal diameter of 0.5 cm.

A longitudinal magnetic moment vs. applied field scan was conducted on the empty, PTFE-capped, quartz sample holder to observe the contribution from the background. Initially, the sample holder was centered using a small piece of Ni foil sandwiched between Kapton tape and attached to the outside of the plastic straw so as to avoid contamination of the inside of the quartz tube. The Ni foil could then easily be removed and the background signal measured, the results of which are shown in Figure 3. The results from the background scan appear to show a small paramagnetic moment ($\approx 10^{-7}$ Am^2 at 5 T) for both 250 and 10 K. At fields lower than 3 T the scatter of the data points is larger than the standard error. This is a result of the failure of the MPMS fitting algorithm to fit the raw data successfully, even after detrending (see Figure 3B). The complicated data set is a result of the magnetic responses of all the components making up the sample. In fact, even at 4 T, the fitted data are still poor. Nevertheless, the generally small standard errors associated with the data suggest the scans are reproducible and

may be subtracted from sample-related data using the background subtraction facility of the MPMS software [9].

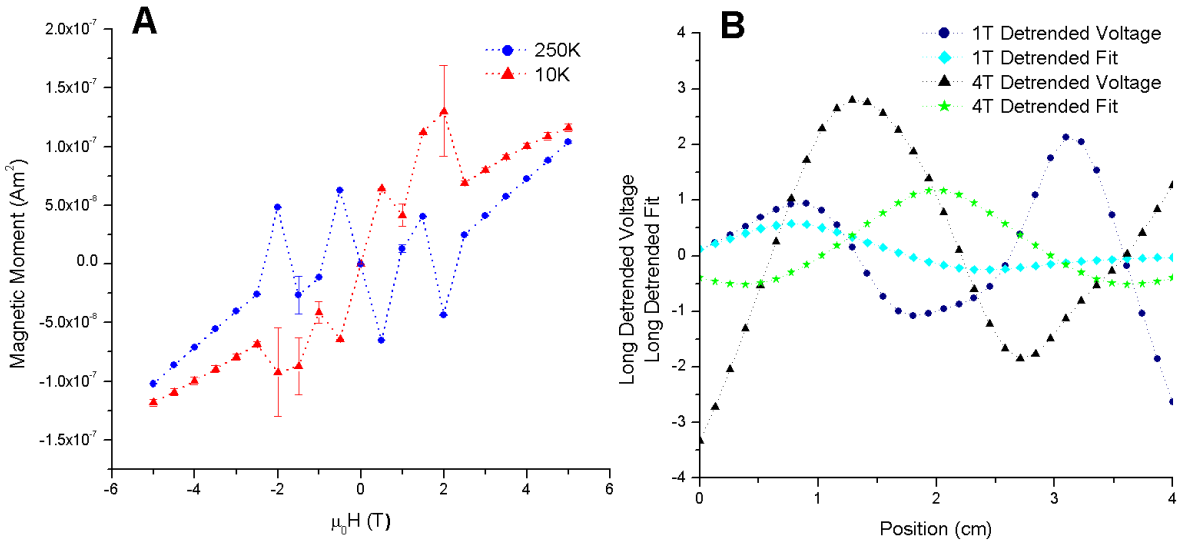

FIGURE 3. **A:** Magnetic moment vs applied field illustrating the background response of the tube at 250 K (blue circles) and 10 K (red triangles). **B:** Shows the detrended voltage and the detrended fit against position at 250 K. This illustrates that the fit to the raw data at low fields (1 T) and at high fields (4 T) are extremely poor.

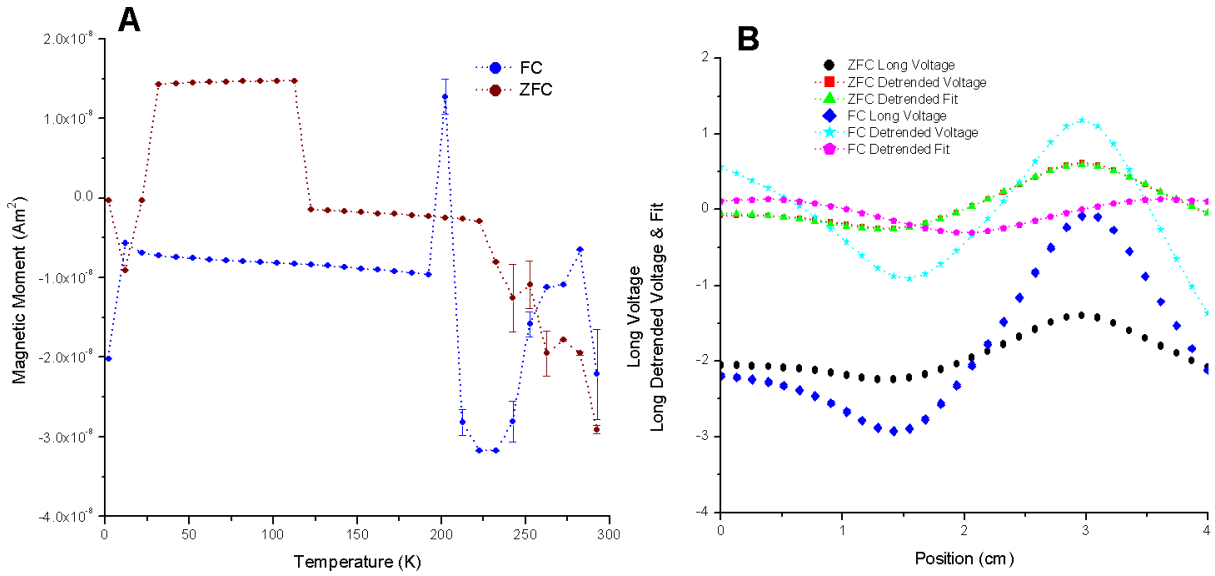

FIGURE 4. **A:** Magnetic Moment vs Temperature showing the Zero Field Cooled (ZFC) and Field Cooled (FC) response where $\mu_0 H = 0.015$ T. **B:** Shows the raw data at 50K to illustrate the poor fits to the FC data and that although the response of the ZFC and FC data is similar, the fits to each data set is different.

The temperature dependent data can be seen in Figure 4A where the applied field is at 0.015 T. There appears to be no general trend however although the moment is relatively small one encounters the same problem as illustrated for Figure 3. The raw data, Figure 4B, shows

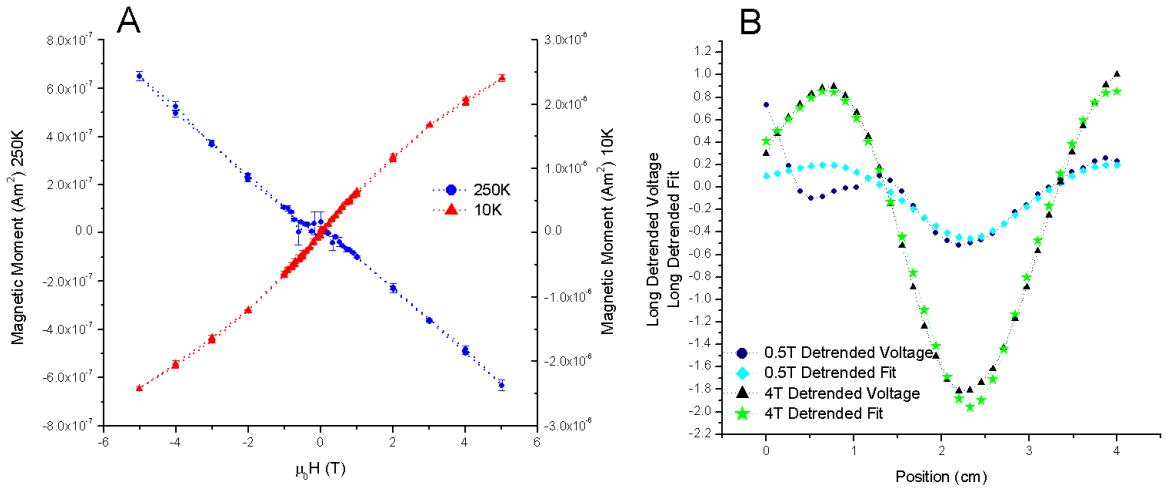

FIGURE 5. **A:**Magnetic moment vs applied field of the $Ni(cod)_2$ sample at 250 K (blue circles) and 10 K (red triangles)**B:**The raw data at 250 K showing that the fit to the detrended voltage at low fields (0.5 T) is suitable however it improves significantly at high fields (4 T). Long regression fit values for the 250 K data; 1 T: 0.84 and 4 T: 0.90. For the 10 K data: 1 T: 0.88 and 4 T: 0.96.

the long voltage for the ZFC and FC measurements at 50 K where the detrended voltage is a combination of three separate scans shown by black circles (ZFC) and blue diamonds (FC). Each individual scan over 4 cm appears to be reproducible with small standard deviation. The detrended voltage and fit for the ZFC data agree however for a similar curve, the detrended voltage and fit for the FC data do not. This illustrates that the moments that the Quantum Design software calculates are not correct and it is the SQUID voltage versus position curves that are needed for background substraction. From knowing the response of the background one can determine whether the sample that is being measured is what is truly being seen.

Figure 5A shows the result of hysteresis loops obtained from the $Ni(cod)_2$ sample, which is clearly different from the background shown in Figure 3A. The $Ni(cod)_2$ shows a diamagnetic response at 250 K and the moment is larger than that of the sample holder ($\approx 7 \times 10^{-7}$ Am^2 at 5 T for a sample of mass $\approx$ 30.4 mg). The diamagnetic result agrees with Miller and Pokhodnya's work on $Ni(C_4(CN)_8)$ where they see a diamagnetic component for $Ni(cod)_2$ that is attributed to the cyclooctadiene ligands [12]. For fields of less than 1 T the data may suggest a small ferromagnetic component, but the standard errors are relatively large and the influence of the sample holder on the results is significant as indicated in the detrended raw data shown in Figure 5B. However, at higher fields the fit to the raw data is good, as demonstrated with the 4 T dataset in Figure 5B. At 10 K, there is a strong paramagnetic signal at all fields ($\approx 3 \times 10^{-6}$ Am^2 at 5 T). The transition from a diamagnetic to a paramagnetic signal, with decreasing temperature, suggests the presence of unpaired spins within defects or impurites in the $Ni(cod)_2$; this issue will be discussed in more detail in a subsequent paper [13].

The magnetic response of $Ni(cod)_2$, which had decomposed in the flame-sealed sample holder at 250 K saturated at a field of less than 2 T. At 5 T $m = 1 \times 10^{-5}$ Am^2 (for an initial $Ni(cod)_2$ mass of 46 mg) [14]. At 10 K the sample showed a similar response, with $m = 1.4 \times 10^{-5}$ Am^2 at 5 T. Hysteresis loops measured at 250 and 10 K were clearly different those of the $Ni(cod)_2$ measured using the sample holder shown in Figure 1. The presence of spontaneous magnetic moments at both temperatures suggested ferromagnetic ordering within the material that would be expected from the presence of bulk Ni within the sample.

In summary, a quartz sample holder has been prepared to carry out magnetic measurements on air and heat sensitive samples in a Quantum Design MPMS. A PTFE plug seals the sample holder in an inert atmosphere to stop decomposition of the sample, avoiding the use of heat

associated with the conventional flame-sealing method. The tube is reusable and works well, especially if the moment of the sample is large ($\gtrsim 10^{-7}$ Am^2). Magnetic measurements can be made over a large temperature range and we have tested the sample holder from 2 K to 290 K. The sample holder has been used to investigate Ni(cod)$_2$, which has been shown to be diamagnetic at 250 K, crossing over to a paramagnetic response at 10 K. The data were obtain with a DC transport but the sample holder could also be used with the Reciprocating Sample Option (RSO) transport as long as the sample is confined with, say, quartz wool, to prevent movement within the tube. It may also be possible, with a slight modification, for the sample tube to also be adapted for a Quantum Design PPMS. The high purity quartz allows the sample tube to be used in an Electron Spin Resonance spectrometer and UV/visible optical absorption experiments may also be made on materials within the sample holder.

We would like to thank Malcolm Richardson of the Chemistry Department for help making the tube. AB thanks the EPSRC for financial support.

References

[1] Quantum Design, www.qdusa.com. *MPMS Application Note 1014-201*. Jan 2001. (Note that Quantum Design also make a Delrin sample holder that can be used for measuring air sensitive materials)

[2] J. Sese, J. Bartolome and C. Rillo. Disposable sample holder for high temperature measurements in MPMS superconducting quantum interference device magnetometers *Rev. Sci. Instrum.*, **78**(4) 046101, Apr 2007.

[3] S Bedanta, O Petracic, M Aderholz and W Kleemann. A sample holder design for high temperature measurements in superconducting quantum interference device magnetometers *Rev. Sci. Instrum.*, **76**(8) 083910, Aug 2005.

[4] B Bogdanov, M Kroner and G Wilke. Ubergangsmetallkomplexe .1. Olefin-Komplexe Des Nickels(0) *Liebigs Ann. Chem. Bd*, 699, Nov 1966.

[5] G Wilke. Contributions to Organo-Nickel Chemistry *Angew. Chem. Int. Ed*, **27**(1),185–206, Jan 1988.

[6] W Keim. Nickel: An Element with Wide Application in Industrial Homogeneous Catalysis *Angew. Chem. Int. Ed*, **29**(3), 235–244, Mar 1990.

[7] Y Koltypin, A Fernandez, TC Rojas, J Campora, P Palma, R Prozorov and A Gedanken. Encapsulation of nickel nanoparticles in carbon obtained by the sonochemical decomposition of $Ni(C_8H_12)_2$ *Chem. Mater.*, **11**(5), 1331–1335, May 1999.

[8] Sigma-Aldrich. *Bis(1,5-cyclooctadiene)Nickel MDMS*. www.sigmaaldrich.com, 25 Jan 2010.

[9] Quantum Design, www.qdusa.com. *MPMS Application Note 1014-213*. Feb 2002.

[10] We recommend weighing the empty sample tube and again after the sample has been added (whether using the funnel or not) to determine an accurate mass of the sample particularly if the sample is quite adhesive to the funnel wall.

[11] The clear plastic drinking straws are recommended by Quantum Design to be used in magnetic measurements as they have a very low moment and can endure cycling through temperature ranges within the region of 2-300 K.

[12] JS Miller and KI Pokhodnya. Formation of Ni[C-4(CN)(8)] from the reaction of Ni(COD)(2) (COD=1,5cyclooctadiene) with TCNE in THF *J. Mater. Chem*, **17**, 3585, Jul 2007.

[13] A Berlie, I Terry, and M Szablewski. To be published 2010.

[14] See supplementary material for the two hysteresis loops of the decomposed $Ni(cod)_2$ at 250 K and 10 K.