Flat plate single crystal silicon sample holders for neutron powder diffraction studies of highly absorbing gadolinium compounds

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Neutron diffraction is, without doubt, the most important technique for studying magnetic order, but many of the rare earths exhibit significant absorption, making their use in diffraction experiments difficult, and the extreme absorption cross section of natural gadolinium (49700 ± 125 b, the largest of any element) makes it more suitable for neutron shielding than neutron diffraction. Despite the extreme problems gadolinium causes, the importance of understanding the magnetic behaviour of its many remarkable compounds has led us to seek ways to carry out powder diffraction measurements on gadolinium-based materials.

Three basic strategies currently exist:

(1) Exploit the energy dependence of the absorption and work at higher energies (shorter wavelengths) where the absorption is weaker. The short wavelengths (~ 0.5 Å) drive the scattering signal down to quite small angles in 2θ leading to reduced resolution and problems with line overlap. This is especially problematic for magnetic diffraction signals, which tend to be concentrated in the low angle range.

(2) The problem with natural gadolinium comes almost entirely from the 15% of ^{155}Gd and 16% of ^{157}Gd that are present. If isotopically separated ^{160}Gd is used in the preparation of the samples, then the absorption problem can be eliminated. This solution is not perfect as it involves trading the problem of almost total absorption for that of making samples from relatively small amounts of expensive starting material. Final sample sizes are of order 500 mg. As a result, such studies are confined to only the most promising of materials.

(3) Ignore the Gd-based member of the series entirely. A brief examination of the literature quickly reveals that this is the dominant strategy.

Our solution

The total scattered signal depends on the mass of the sample exposed to the beam and the total flux incident on that sample. The extreme absorption cross sections of samarium and gadolinium severely limit the sample thickness that can be used (for $Sm_3Ag_4Sn_4$ the 1/e absorption thickness is ~ 140 μm, while for $Gd_3Ag_4Sn_4$ it is only 14 μm), however the beam at C2 is much wider than the standard 5 mm cans normally employed, and the acceptance of the multi-wire detector is quite loose (forcing the furnaces and cryostats to have very large inner bores to avoid spurious scatter from environmental components). We therefore developed a large-area flat plate sample holder that spreads the sample across as much of the beam as possible to make the best use of the total available flux.

The holder consists of two 600 μm silicon wafers cut to 90 mm × 30 mm in size. 5 mm wide strips of vanadium foil are glued (GE 7031 varnish) around the edges as gaskets to define the sample volume (the foil thickness is chosen to match the intended sample thickness). The finely powdered sample is then spread as a slurry, mixed with highly diluted GE 7031 varnish (~ 1% by weight in 50:50 toluene:methanol) and allowed to dry before the second wafer is glued in place to protect the sample. The use of a small amount of glue has proved to be essential to prevent settling of the powder in the holder. We also determined that the amount of glue used added less than 1% to the background already present.

Fig 1. Photograph of the assembled holder loaded with $Sm_3Ag_4Sn_4$ with neutron (left) and x-ray (right) density images showing the settling that occurs if glue is not used. The shadow of the cadmium markers used to identify the edges of the sample are evident in the neutron picture, and the vanadium gasket shows as a light border in the x-ray image.

In order to obtain a GSAS instrument parameter file [1, 2] appropriate for our flat plate geometry, NIST silicon 640c and annealed cubic Y_2O_3 were mixed and loaded into a flat plate holder using strips of 150 μm thick vanadium foil as a gasket/spacer. The Y_2O_3 was added to provide extra reflections for modelling the zero offset at 2.37 Å, since silicon gives only three diffraction peaks in the available 80° 2θ range and thus provides insufficient information for a refinement. The plate was orientated perpendicular to the beam. The refined peak widths are shown in Figure 2 and it is clear that there is some loss of resolution associated with this large-area scattering geometry. The effect of the flat plate is to have a minimum FWHM of 0.328° at around 2θ = 67° at 2.37 Å whereas a standard vanadium sample holder yields a minimum width of 0.187° at 2θ=53°.

Our first test of the large-area flat-plate holder with a metallic sample used $Sm_3Ag_4Sn_4$. Estimates of absorption for this material yielded an expected 1/e thickness of 125 mg/cm^2 or about 140 μm so we used strips of 150 μm thick vanadium foil around the four edges of the silicon plate to form a gasket that would define the space for the sample to occupy. The sample was loaded as a slurry with ethanol which could then be spread uniformly into the gasketed volume. After drying overnight, the cover plate was installed and clamped in place. The total sample mass used was 1.57 g, giving a final area density of 80 mg/cm^2.

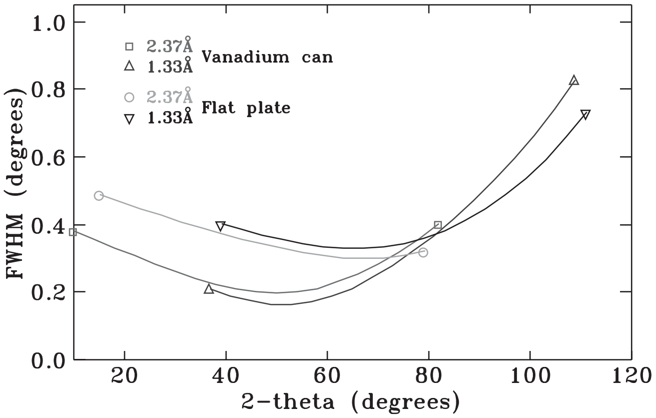

Fig 2. *Comparison of linewidths derived from Rietveld fits to a mixture of NIST silicon 640c and annealed cubic Y_2O_3 on the C2 spectrometer. Curves show the fitted linewidths for a sample in a standard 4.8 mm i.d. vanadium can and our flat-plate holder.*

No glue was used for this run and the sample clearly settled (Figure 1). All subsequent samples were mounted using diluted varnish to make the slurry rather than ethanol. Despite the settling, we were able to collect data at 50 K that were of sufficient quality to permit a Rietveld refinement using GSAS (Figure 3 and the results were consistent with x-ray data. The full analysis of the low-temperature magnetic data is given in another report in this volume, and has also been published elsewhere [3].

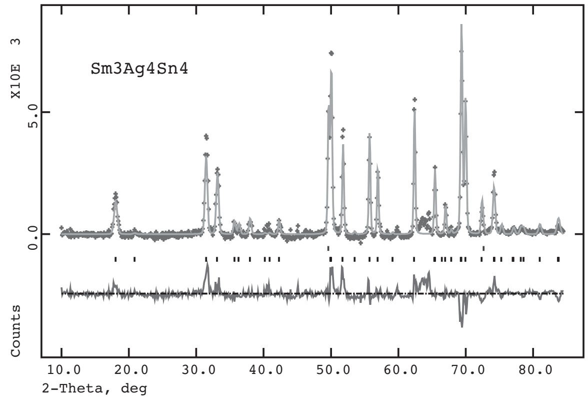

Fig 3. *Scattering data at 2.37 Å for Sm3Ag4Sn4 measured at 50 K with a Rietveld refinement showing typical data quality after about two days of counting.*

Encouraged by our success with $Sm_3Ag_4Sn_4$, we considered the possibility of repeating the experiment using the gadolinium member of the series. The absorption cross section of natural gadolinium at a wavelength of 1.80 Å is 49700 ± 125 b, however our interest is in magnetic ordering and the expectation that many of the magnetic peaks will occur at low q makes the longer wavelength of 2.37 Å more appropriate. Here the absorption cross section is estimated to be 60000 b and this value yields a 1/e thickness of about 14 μm or 12 mg/cm^2 for $Gd_3Ag_4Sn_4$ giving a total sample mass of 230 mg in our flat-plate holder. This might seem small, but examination of the literature reveals that most of the gadolinium samples that have been prepared using ^{160}Gd have masses of 500–600 mg. We would be losing a factor of two in total scattering by using the smaller sample, and a further factor of e for absorption, however we expect to compensate by using the full area of the incident beam and so making our total incident flux much higher. Furthermore, the expected 7 μ_B moment on the gadolinium should yield nearly 200 times more magnetic scattering than the 0.5 μ_B samarium moment that we were able to detect in $Sm_3Ag_4Sn_4$, so the magnetic signal should be much clearer.

An initial room temperature test run using 300 mg of $Gd_3Ag_4Sn_4$ fixed to a silicon plate with a 1% solution of GE-7031 varnish was performed to confirm feasibility. This resulted in ~ 50 counts per hour on the maximum peak to give Rietveld refinement quality data in 51 hours (Figure 4). As expected, there was no background from the GE-7031 varnish used to immobilise the sample.

More details of the results obtained from a variable temperature study of $Gd_3Ag_4Sn_4$ are given in another report in this volume, and a complete analysis of the data and resulting magnetic structures has been published elsewhere [4].

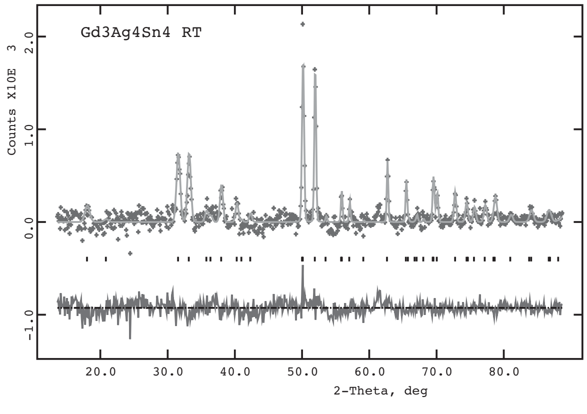

Fig 4. *Scattering data at 2.37 Å for $Gd_3Ag_4Sn_4$ measured at ambient temperature with a Rietveld refinement showing typical data quality after about one day of counting.*

References

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