

Low-background single-crystal silicon sample holders for neutron powder diffraction

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Neutron diffraction measurements on weakly scattering or highly absorbing samples may demand custom mounting solutions. Two low-background sample holders based on inexpensive single-crystal silicon are described. One uses a conventional cylindrical geometry and is optimized for weakly scattering materials, while the other has a large-area flat-plate geometry and is designed for use with highly absorbing samples. Both holders yield much lower backgrounds than more conventional null-matrix or null-scattering materials and are essentially free from interfering Bragg peaks.

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1. Introduction

Samples for neutron powder diffraction experiments must be enclosed in some form of sample holder and the choice of material used for this holder can significantly affect the quality of the data that are obtained. As any material placed in the neutron beam must lead to some scattering, the materials choice inevitably involves a compromise between broad incoherent backgrounds and sharp Bragg peaks. Vanadium metal and the null-scattering TiZr alloy provide examples at one extreme, while copper and aluminium represent the other.

Vanadium metal sample holders are the commonest choice as the material is readily available, albeit difficult to machine. There are also commercial suppliers of vanadium sample holders (MTI, 2006). Vanadium yields an almost featureless isotropic scattering pattern with some very minor Bragg peaks, and produces only short-lived activation products. The null-scattering Ti₆₈Zr₃₂ alloy ('TiZr', commonly pronounced as 'tie-zer'; Ti-47.8 wt% Zr) offers some advantages over vanadium metal and is traditionally used for high-pressure neutron diffraction. TiZr has similar machining properties to the ZrNb alloy used in nuclear-reactor tubing, with a similar additional issue: the residual filings are pyrophoric. However, once any TiZr ingot 'scale' has been removed, the material is far easier to machine than vanadium. Per rod, TiZr can be cheaper to purchase than vanadium, but TiZr normally has to be procured from a specialty titanium alloys company as a custom commercial synthesis (Titanium Metals Corporation, 2002; one of the reviewers noted that TiMet declined to quote on a synthesis request for TiZr in late 2006). Balancing the negative coherent scattering length of Ti against positive scattering from Zr means that the average scattering length of the TiZr alloy is zero and so the material is nominally free of Bragg peaks. However, incoherent scattering from the random Ti/Zr positions leads to an incoherent background comparable with

that of vanadium. Furthermore, no alloy is truly random and both chemical short-range ordering and strain due to the Ti/Zr size mismatch cause the background to exhibit significant structure (Fig. 1).

Several other null-matrix alloys have been developed for neutron scattering sample holders but have not received widespread acceptance. A vanadium–niobium null-scattering alloy has been used, but it is brittle and non-machinable (unlike pure vanadium). Suppliers or sources of vanadium–niobium null-scattering alloy are unknown to the authors, and knowledge of the synthesis and handling procedures appears to have been lost (Proffen, 2006). Smith *et al.* (1968) described the use and advantages of gamma-phase 68 at.% Mn–Cu null-scattering alloy for sample holders and neutron windows. Other exotic null-scattering materials described or mentioned in the literature include null-matrix crystals of ⁶²Ni_{0.52}Pt_{0.48} (Rodriguez *et al.*, 2006), Mn₆₀Sb₄₀ null-scattering alloy (Grosdidier *et al.*, 2002), 75 at.% Mn–Pt (Smith *et al.*, 1968), and 41 at.% Mn–Co (Smith *et al.*, 1968). Bailey (2003) also provides a review of materials found suitable for a variety of neutron sample environments.

The significant incoherent background from vanadium or null-matrix alloys like TiZr is an inevitable result of the compromise between coherent (Bragg) scattering and incoherent (background) scattering that must be made in selecting a container material. In most cases, the absence of interfering Bragg peaks is the primary concern and the background from the sample holder is treated as an additional function in the computational fit. However, where weakly scattering samples or small effects are being studied or where broad scattering features are expected, an improved peak-to-background ratio may be required and significant incoherent scattering from the holder material may not be acceptable. The favored low-background material tends to be aluminium metal, although copper metal is often used, but this latter material yields a

fairly persistent activation ($t_{1/2}$ is 7.4 days) when placed in a neutron beam. While both of these metals exhibit much lower backgrounds, the intense Bragg peaks that they contribute to the observed scattering pattern are non-trivial to model in a Rietveld refinement due to effects of uncontrolled texture and secondary scatter (Fig. 2). High-purity aluminium or copper foils are available and can be used to make holders with reduced Bragg scattering, but these holders are quite fragile, may leak powder and can contribute unexpected background effects and peaks as a result of impurities introduced during the commercial rolling process or subsequent handling. They can also be the source of secondary elastic or inelastic scattering (Fig. 3). For work at non-ambient temperatures, the sample holder should be thermally conducting to allow effi-

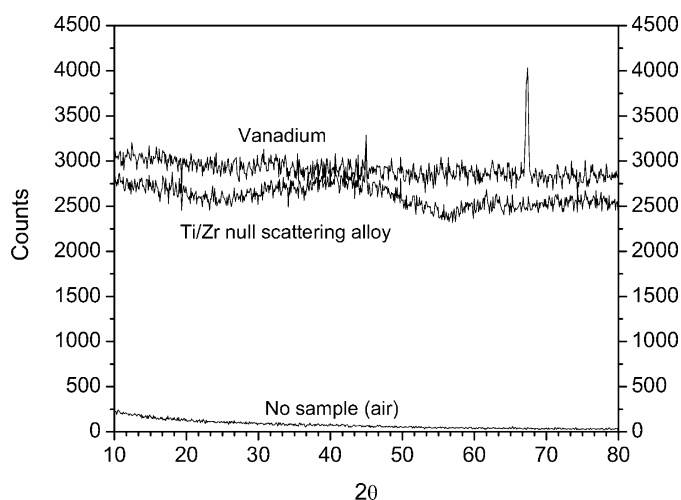


Figure 1 Neutron diffraction patterns (single detector bank) of a 0.5 inch vanadium rod (upper curve), a 0.5 inch Ti/Zr null-scattering alloy rod (middle curve) and no sample (bottom curve) at 2.37 Å, measured at room temperature in air, using identical slit settings and monitor counts. The common spike at $2\theta = 45.00^\circ$ is due to noisy detector wires. Vanadium yields a flatter background, but contributes a weak Bragg peak at $2\theta = 68^\circ$.

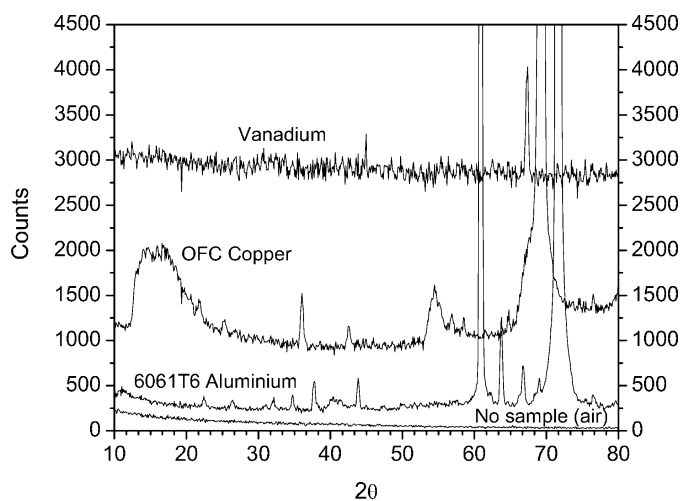


Figure 2 Room-temperature scans at 2.37 Å using 0.5 inch-diameter rods of (from top) vanadium, oxygen-free copper (OFC) and a machinable aluminium alloy (6061T6), with air shown for comparison. Data were collected using the same slit settings and monitor count as in Fig. 1.

cient cooling and heating of the sample. While in most cases, aluminium is a more convenient, lower background sample holder than copper, aluminium is superconducting below 1.175 K and therefore becomes a poor thermal conductor below this temperature. Thus copper (and silicon) may be superior to aluminium below 1 K.

Quartz glass could also be used for holding samples, and Fig. 4 compares the contributions from 8 mm-OD (outside diameter) quartz glass tubing, a vanadium sample holder, an aluminium sample holder, a 5 mm-OD quartz glass capillary tube (Charles Supper Company, 2007) and no sample (air). While standard 1 mm-walled 8 mm-OD silica glass tubes can

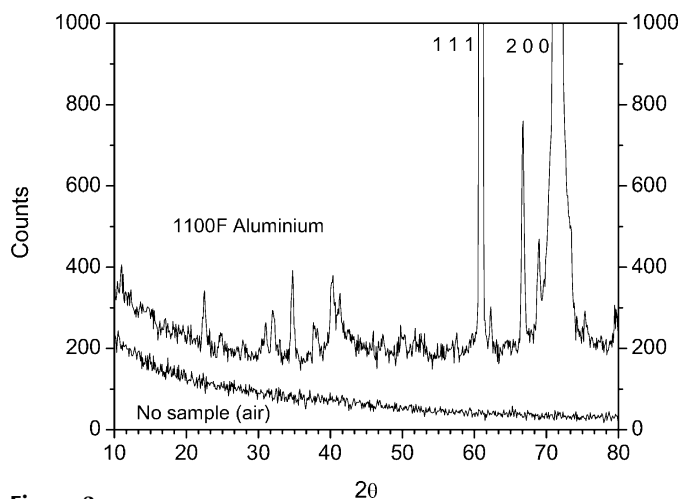


Figure 3 Neutron diffraction pattern of a 0.5 inch-diameter pure aluminium rod (1100F aluminium) (upper curve) and no sample (bottom curve) at 2.37 Å. Data were collected at room temperature with the same slit settings and monitor count as in Fig. 1. The vertical scale has been expanded to show the background and secondary scattering. Only the peaks at $2\theta = 61.3^\circ$ (111) and 72.0° (200) are due to primary Bragg scattering by the aluminium.

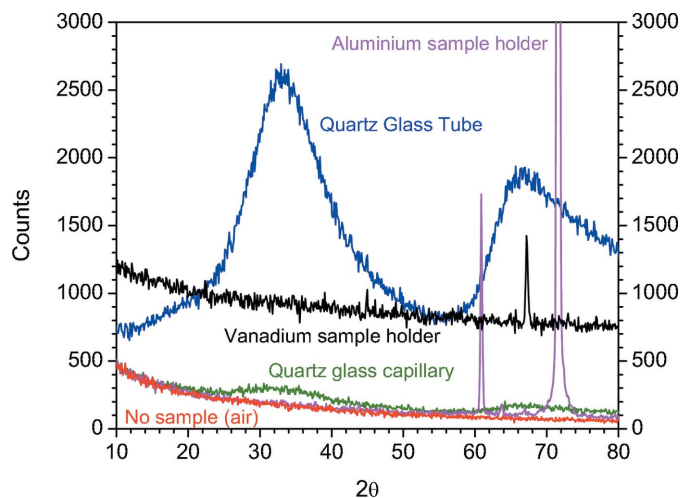


Figure 4 Neutron diffraction patterns at 2.37 Å of an 8 mm-OD quartz glass tube of 1 mm wall thickness, a 5.6 mm-OD vanadium sample holder of 0.5 mm wall thickness, a 5.6 mm-OD aluminium sample holder of 0.5 mm wall thickness and a 5 mm-OD Charles Supper quartz glass capillary tube of 0.01 mm wall thickness; air is shown for comparison. Data sets were taken at room temperature using identical slit settings and monitor count.

be ground and drilled for placement of temperature sensors, they give a substantially greater background than vanadium sample holders with significant amorphous features. Thin-walled quartz tubes are a low-background alternative for room-temperature diffraction, but they are very fragile, making both the mounting of the tubes and the attachment of sensors problematic for work at non-ambient temperature. For diffraction applications, thin-walled (0.01 mm) quartz glass capillary tubes, up to 5 mm OD, are commercially available (Charles Supper Company, 2007). A reviewer also noted that thin-walled fused silica tubes made to very high precision for EPR studies are available from Wilmad Glass (Wilmad-LabGlass, 2007). They come in a variety of sizes (to 10 mm) and have thin walls (0.38 mm for a 5 mm-diameter tube), but would be more robust than quartz glass tubes, of 0.01 mm thickness, traditionally used for diffraction. The expected contribution to the background from these EPR tubes can be interpolated from the glass data given in Fig. 4.

One material that avoids the coherent/incoherent scattering compromise entirely is single-crystal silicon: it has one of the smallest incoherent scattering cross sections of any element and, as an almost perfect single crystal, its Bragg scattering is concentrated in extremely narrow regions of q space, allowing the crystal to be oriented so that no Bragg scattering is observed. Silicon crystals are readily available as flat wafers or cylinders from a wide range of suppliers and even standard grades contain negligible levels of impurities. The material has a high thermal conductivity and does not activate when exposed to a neutron beam. Single-crystal silicon can be drilled, ground and cut using facilities available in most university science departments and neutron laboratories so that a variety of sample mount geometries are possible. Silicon also has good mechanical properties and the sample holders that we have made from it have resisted damage during routine handling.

We present here descriptions of two low-background single-crystal silicon sample holders that we have developed for two distinct situations. One employs a conventional cylindrical geometry and provides for a large sample volume while minimizing background contributions from the holder. The other was designed for work with highly absorbing materials where a large-area thin-plate geometry was needed. Examples of both applications are described. The silicon sample holders were primarily developed for neutron diffraction studies of magnetic materials, where the magnetic diffraction is often weak relative to the nuclear Bragg reflections. Magnetic crystal structures can normally only be solved and refined using neutron-based methods.

All neutron data were collected on the NRC C2 powder neutron diffractometer at Chalk River, Ontario, Canada. C2 consists of a curved 800-wire position-sensitive detector covering a range of 80° with angular wire spacing of 0.1° . Neutron beam size on the sample can vary up to a width of 20 mm and a height of 80 mm. The current angular range accessible to the detector wires is from 3 to 115° . To provide a monochromated neutron beam, a 'hot squeezed' single-crystal silicon flat plate (Barrett *et al.*, 1963; Dolling & Nieman, 1967)

is used at a take-off angle of 92.7° . Change of wavelength is under automated computer control, performed by rotating the monochromator crystal, without changing the take-off angle. Data are normally collected at two wavelengths: 1.33 \AA (the silicon 531 reflection) and 2.37 \AA (the silicon 311 reflection). For 2.37 \AA , a pre-sample graphite filter is placed in the neutron beam to eliminate the $\sim 2.3\%$ relative intensity of higher-order wavelengths diffracted in the sample direction by the silicon monochromator. Standard collection of data of 'structure refinement quality' uses $5\text{--}85^\circ 2\theta$ at $\sim 2.37 \text{ \AA}$, and $35\text{--}115^\circ 2\theta$ at 1.33 \AA (Bieringer, 2006), aiming for at least 10 000 counts on the highest peak. This covers a large range of Q in an efficient manner with minimal detector overlap. Multiple data set refinement is routine in Rietveld structure refinement packages such as *GSAS* (Larson & Von Dreele, 2004).

For detecting magnetic diffraction, the C2 detector is set around $3\text{--}83^\circ 2\theta$ with a preferred wavelength of $\sim 2.37 \text{ \AA}$. Neutrons of this wavelength are plentiful on a thermal neutron diffraction beamline, allowing access to high d spacing/low Q where magnetic peaks are often expected as a result of magnetic supercells.

Sample holders were mounted onto sample sticks for insertion into standard cryogenic ancillary stages. Cylindrical sample holders were positioned at neutron beam height on the rotation axis of the diffractometer using an automatic alignment method (Cranswick *et al.*, 2006). Flat-plate sample holders were positioned using a pre-aligned sample stick and then rotated parallel to the direct neutron beam (visualized using a home-built neutron video camera) to set $\omega = 90^\circ$ followed by rotation to $\omega = 0^\circ$ (perpendicular to the direct beam). ' ω ' would be considered the ' θ ' motor on a laboratory powder X-ray diffractometer.

2. Cylindrical single-crystal silicon sample holder for poorly scattering samples and low-intensity peaks

The most efficient approach to improving the signal-to-noise ratio for a weak Bragg peak is to reduce the background: halving the background level for a weak Bragg peak yields essentially the same improvement in signal-to-noise ratio as doubling the counting time. Our low-background holder was constructed from a single-crystal silicon rod (9 inch length, 1 inch diameter, $\{100\}$ parallel to cylinder axis) from Virginia Semiconductor (<http://www.virginiasemi.com/>). Owing to the large semiconductor industry, this material is much cheaper than rival null-scattering materials. The rod was cut to length with a diamond saw; then, using a regular bench drill press with water-cooled diamond core bit over a period of 15 min, a 6.5 mm-diameter hole of ~ 50 mm length was drilled into it to accommodate the sample (Fig. 5). An aluminium adaptor was then used to couple the silicon rod to a conventional cryostat sample stick. Teflon tape is normally wrapped around the silicon at notch level so as to avoid local stresses due to the set-screws of the adaptor.

While the holder does yield an immediate and substantial reduction in background when compared with vanadium

(Fig. 6), the use of single-crystal silicon holders is not completely free of subtleties. As a result of other scattering effects, such as phonon scattering at both the sample holder and the silicon monochromator, the background may not be flat and may vary as a function of both temperature (Fig. 7) and orientation (Fig. 8). However, it was found that by rotating the empty sample holder in the beam, an optimum angle in ω , largely free of scatter, could be found at the required wavelength and angular range for a desired detector bank (Fig. 8). The background contribution of the silicon sample holder could be improved further by cutting off excess



Figure 5 Photograph of the original and cut-down single-crystal silicon sample holders. Left: 25 mm-diameter full cylinder (mass of 80.68 g) with 6.5 mm drilled hole. Right: 11.2 × 11.8 mm silicon holder with 6.5 mm drilled hole trimmed from circular to square cross section (mass of 18.33 g). Notches near the top allow for mounting onto sample bases using set-screws. Teflon tape is normally wrapped around the silicon at notch level so as to avoid local stresses due to the set-screws.

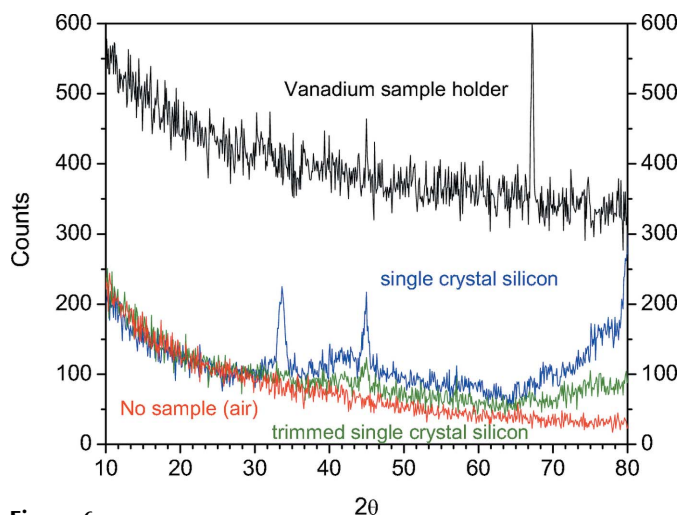


Figure 6 Comparison of a 5.6 mm-OD vanadium sample holder of 0.5 mm wall thickness, a single-crystal silicon cylinder, a trimmed single-crystal silicon cylinder, and air, using a wavelength of 2.37 Å, at room temperature in air. The peaks at $2\theta = 34^\circ$ and $2\theta = 45^\circ$ are most likely phonon scattering, the presence of which is unambiguously demonstrated in Fig. 6.

silicon from round to square cross section using a diamond saw (Fig. 5) to decrease the total silicon mass by a factor of 4.4, and thereby greatly reducing the contribution to background due to the holder (Fig. 6). The time required for each cut of silicon was approximately an hour. Further reduction of silicon holder material is feasible by cutting to hexagonal or octagonal shapes; however, the gains would be small compared with the effort required. The presence of phonon scattering from the silicon holders may make them unsuitable for total-scattering PDF analysis.

As an example of using the cylindrical single-crystal silicon sample holder, in Fig. 9 we show data on the magnetic scattering from nanocrystalline chromium particles with a size between 200 and 500 nm. The powder was made from chromium fibres dissolved from a Cu–1.56 at.% Cr eutectic alloy prepared by directional solidification (Sinclair *et al.*, 2005). As

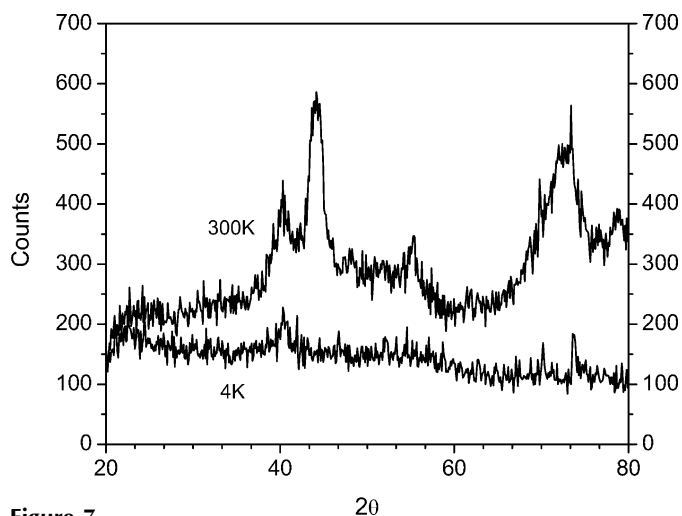


Figure 7 Neutron diffraction patterns of a single-crystal silicon cylinder at 4 and 300 K using a wavelength of 2.37 Å under identical monitor count and slit settings, showing effects of temperature on background, demonstrating the contribution of phonon scattering to the sample-holder background.

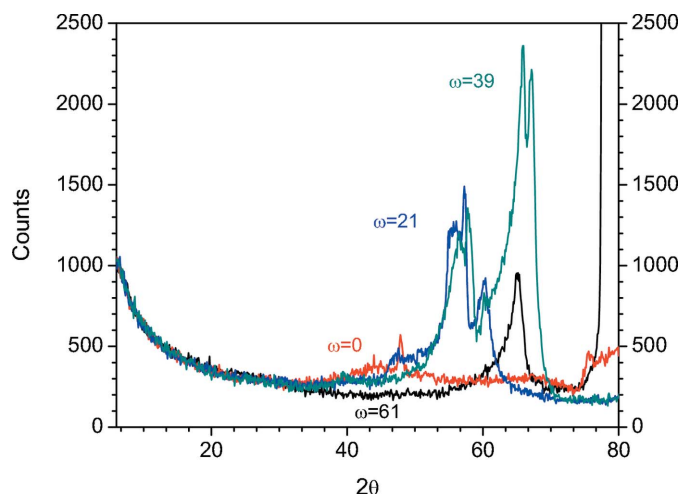


Figure 8 Neutron diffraction patterns of a single-crystal cylinder at various values of ω using a wavelength of 2.37 Å to find the optimum angle where the background is flat in the required 2θ range at a temperature of 300 K.

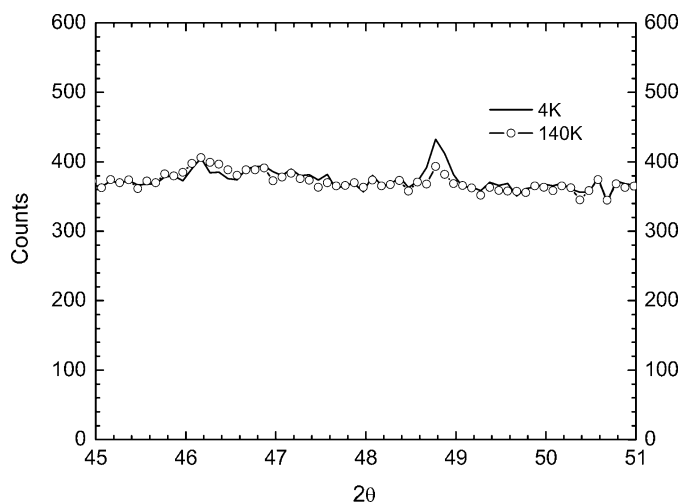


Figure 9
Powder diffraction data of nanocrystalline chromium powder at 4 K (straight line) and 140 K (dotted line with circles) using the single-crystal silicon sample cell. The peak at 48.8° 2θ is due to the antiferromagnetic structure.

can be seen in Fig. 9, the peak at $2\theta = 48.8^\circ$, which is due to magnetic scattering from the antiferromagnetic structure, is very weak. Therefore, it is crucial to reduce the background as far as possible in order to map precisely the temperature dependence of this magnetic peak. Free-standing nano-sized Cr powders are free from the strain associated with substrate-supported materials and adopt the bulk chromium lattice constant. These new materials allow unambiguous evaluation of size effects (*i.e.* the effect of the grain size on the magnetic structure) as a function of temperature without interference from changing substrate-induced strains. In contrast, all other neutron studies on the size effect in chromium have used epitaxially prepared Fe/Cr (Fullerton *et al.*, 1996; Zabel, 1999; Fritzsche *et al.*, 2002) or V/Cr multilayers (Fritzsche *et al.*, 2003) with the inherent problem of epitaxial strain, which makes it impossible to distinguish effects caused by the epitaxial strain from those caused by a reduced chromium film thickness. By placing the chromium powder in our single-crystal silicon cylinder, we were able to almost eliminate the background due to the holder (over 90% of the background remaining in Fig. 9 is due to the sample itself) and greatly improve the signal-to-noise ratio for the weak magnetic peaks of interest (Fig. 10).

3. Silicon flat-wafer sample holder for highly absorbing samples

A second class of materials that can complicate neutron powder diffraction experiments are those that contain elements with large absorption cross sections (*e.g.* Eu or Sm). Loading such materials into a conventional 6 mm-diameter sample holder leads to essentially zero transmitted signal. An example of this problem is provided by $\text{Eu}_2\text{BaNiO}_5$ (van Lierop *et al.*, 2006), where weak magnetic scattering from Ni ($\sim 1 \mu\text{B}$) and Eu ($\sim 0.2 \mu\text{B}$) was expected, but absorption by the europium in the sample led to a $1/e$ thickness of only 140 μm ,

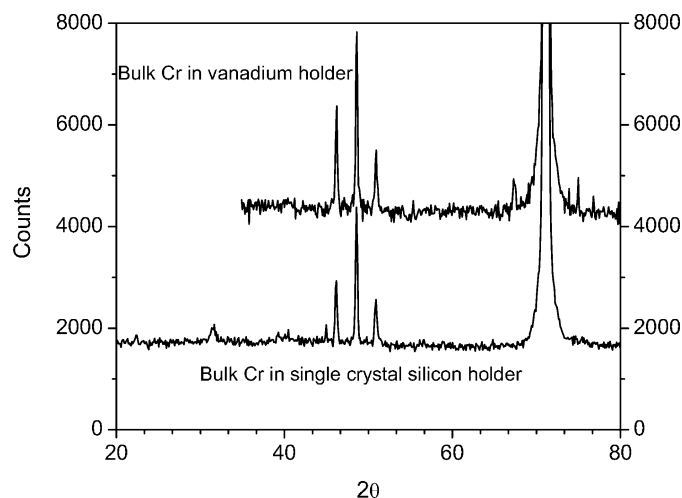


Figure 10
Neutron powder diffraction patterns at 2.37 \AA showing magnetic satellite reflections of bulk chromium metal powder at 150 K in (top) a vanadium sample holder (2.37 \AA) and (bottom) a single-crystal silicon sample holder (2.37 \AA). Most of the background contribution for the data taken using the single-crystal silicon holder is due to incoherent scattering from the sample. The vanadium holder data were normalized to an identical monitor count to the silicon sample holder to facilitate comparison with the backgrounds.

greatly limiting the sample volume that could be used in a conventional holder.

A variety of sample presentation options for transmission geometry were explored, including annular holders constructed using co-axial thin-walled aluminium cylinders, and flat-plate mounts based on thin aluminium foils. Difficulties in loading the cylindrical holder made it impractical, while lack of rigidity of the thin aluminium foils led to sagging and a severely non-uniform sample distribution when flat foil-based holders were tried. Both options also gave too much Bragg scattering, both from the aluminium itself and from impurities. Contributions to the background were also problematic.

Our solution was to retain the large-area flat-plate geometry, but replace the thin aluminium foils with more rigid silicon plates. Two 80 mm by 30 mm plates were cut from a single-crystal silicon wafer (6 inch diameter, 675 μm thickness). One plate was fitted with a vanadium gasket (75 μm thickness, 3 mm width) to act as a spacer and to set the final sample thickness. The sample area was chosen to match the characteristics of the C2 neutron powder diffractometer. The sample was floated into the gasketed plate as a slurry formed from finely ground sample mixed with ethanol. This allowed uniform filling to a known thickness. Once the slurry had dried, the second plate was positioned as a cover and held in place using a temporary clamp, while the assembly was loaded into the cryostat adaptor (Fig. 11). Teflon spacers were placed between the silicon and the aluminium clamp so as to avoid local stresses. The dimensions used here place about 1 g of sample in the beam and greatly increase the chances of seeing a signal with highly absorbing samples. A diffraction comparison between a standard vanadium holder and the silicon plate shows the silicon has significantly less intrinsic

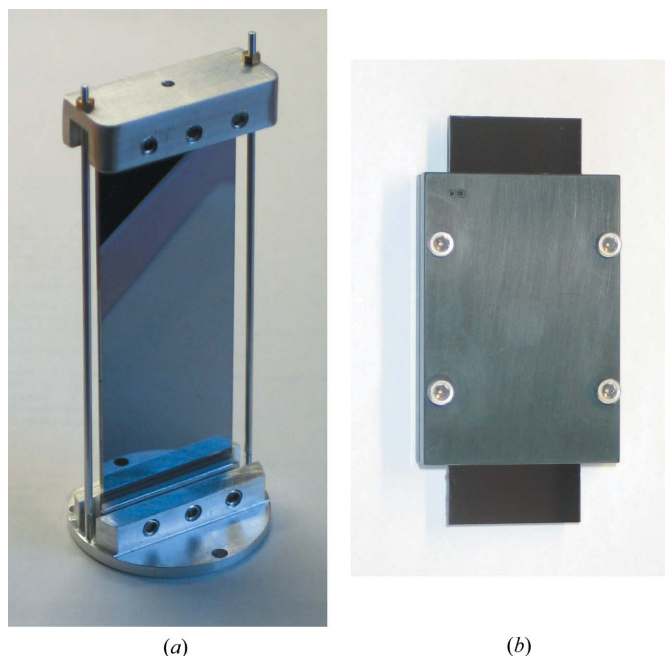


Figure 11
(a) Photograph of single-crystal silicon flat-wafer sample holder and (b) wafers with clamp system for holding the two wafers together while assembled on the Teflon/aluminium mount.

background (Fig. 12). Finally, angle-dependent absorption corrections for flat-plate samples are relatively simple, having exact analytical solutions.

Measurements of the $\text{Eu}_2\text{BaNiO}_5$ sample at 3.6 and 50 K (Fig. 13) showed excellent signal strength and put upper limits of $0.7 \mu_B$ and $0.4 \mu_B$ on the Ni and Eu moments, respectively (van Lierop *et al.*, 2006), demonstrating that this flat-plate holder can be used with highly absorbing samples.

The flat-plate sample holder is normally stored in an aluminium container for transport. For extra containment of

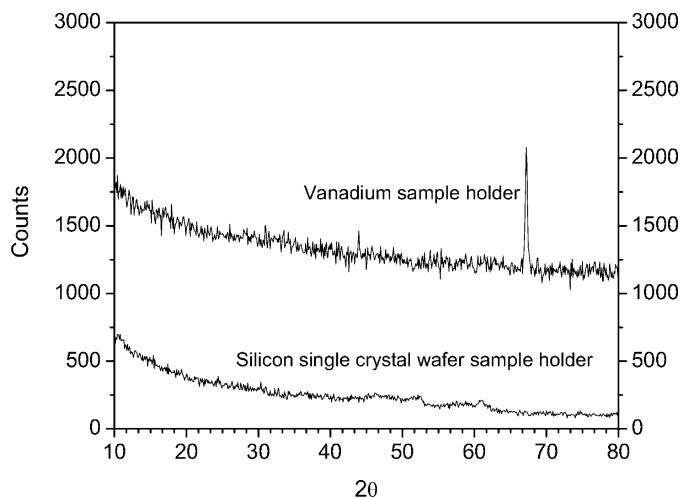


Figure 12
Neutron diffraction data of an NRC/CNBC Chalk River standard thin vanadium sample holder and a single-crystal silicon flat-wafer sample holder oriented perpendicular to the neutron beam, collected at room temperature at 2.37 \AA under identical monitor count and slit settings. The peak in the vanadium data at $45^\circ 2\theta$ is a spike from two noisy wires.

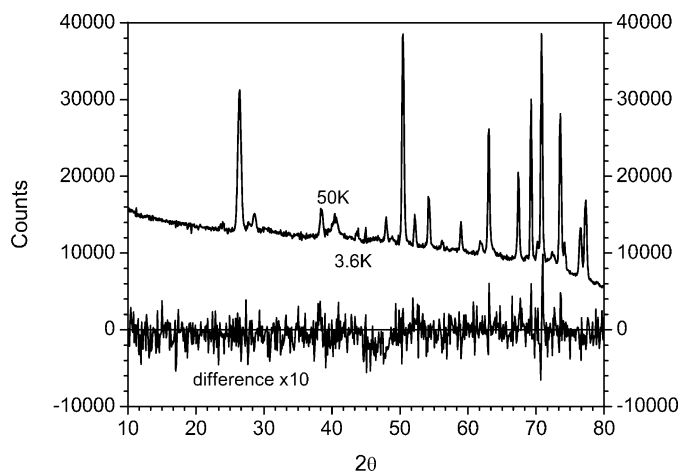


Figure 13
Neutron powder diffraction patterns of heavily absorbing $\text{Eu}_2\text{BaNiO}_5$ mounted on a single-crystal silicon wafer sample holder oriented perpendicular to the neutron beam, collected at 3 and 50 K at 2.37 \AA in transmission mode under identical monitor count and slit settings. The difference pattern ($\times 10$ with zero line) obtained by subtracting 50 K data from 3 K data shows no observable magnetic scattering (raw counting statistics per pattern were approximately 40000 counts; each was collected over seven days of neutron beam time).

neutron-absorbing air-sensitive samples intended for low-temperature diffraction, the assembly could be sealed ‘helium gas tight’ using an indium foil gasket, inside a modified aluminium container holding helium exchange gas. Some additional background might be expected as a result of the aluminium container, but as the outer environmental containment would be outside the diffraction volume of the instrument, its effects should be minimal.

4. Conclusion

The above examples show the benefits of exploring different sample containment methods using single-crystal silicon for neutron powder diffraction. While this may be of assistance in some types of neutron diffraction experiments, custom problems due to the sample, ancillary stage and diffractometer may still require experimentalists to explore other custom solutions.

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