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SHORT NOTE

On intensities in high pressure neutron powder diffraction using single and polycrystalline diamond anvils: Small versus large sample volumes

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Abstract

We report a quantitative comparison of measured intensities of neutron powder diffraction data collected in a single-crystal diamond anvil cell and in large-volume sintered diamond anvils. As expected from the difference in sample volumes, the latter provides 1-2 orders of magnitude higher intensities, depending on the anvil material. The remaining differences are due to effects of absorption and angular aperture.

Keywords: High pressure, neutrons, diamond anvil cell, Paris-Edinburgh cell

There is a long history of attempts to use (single-crystal) diamond anvil cells (DACs) for high pressure neutron scattering studies [1-5]. The extremely small sample volume of ~ 10^{-2}-10^{-4} mm^3 compatible with such devices seems to contradict the accepted belief that neutron scattering requires "large" samples of at least several mm^3, even at high-intensity diffractometers. A recent comparison between diffraction patterns of a 0.2 mm^3 Si sample collected in a DAC and a 17 mm^3 sample collected in a Paris-Edinburgh (PE) press using sintered diamond anvils even reports that data is collected with a vastly shorter exposure time and high signal to noise ratios in a DAC, despite the ≈ 100 times smaller sample volume [6]. The aim of this note is to provide a more accurate and meaningful comparison which allows the general neutron user to draw conclusions on this issue.

For this purpose, neutron powder diffraction data were collected at the PEARL diffractometer [7] of the ISIS neutron and muon Facility, Rutherford Appleton Laboratory, Didcot (U.K.). In the first experiment a DAC with 1.3 mm culet diameter was used with a stainless steel gasket, pre-indented to 190 μm thickness and a hole drilled measuring 800

μm in diameter. The size of the incident beam directed upon the sample within the DAC was reduced using bespoke BN collimation. In the second measurement we used double-toroidal sintered diamond anvils with encapsulating null-scattering TiZr gaskets and a Paris-Edinburgh (PE) press as a load frame [1]. Again, the incident beam size was controlled using bespoke BN collimation. The anvil dies were machined from COMPAX 5913 wire drawing dies and hence identical to those in Ref. [6]. To allow for a meaningful comparison, the scattering geometries in the DAC and PE measurements were identical, i.e. with the incident beam aligned with the thrust axes. The cells were loaded in both cases with finely ground Ge powder and immersed in a 4:1 deuterated methanol-ethanol mixture to ensure hydrostatic pressure conditions. The filling factor (ratio sample/fluid) is expected to be comparable for both loadings. The DAC sample was compressed to 5 GPa as determined by ruby fluorescence and time-of-flight diffraction data were collected for 8 hours. The PE sample was compressed to 7.8 GPa as determined from the refined lattice parameters and known equation-of-state [8] and measured for 1 hour, with data collected over 5 minute intervals. The DAC was not located at the ideal sample position which makes the measured lattice parameters smaller than expected for the measured pressure.

It is possible to estimate the difference in expected intensities between the PE and DAC setup and can be summarized as follows. The average absorption across the ≈ 11 mm sintered diamond anvil and the TiZr gasket in the PE setup is approximately 85 % [1]. In addition, the Cd-shielded anvils only allow passage of neutrons diffracted within ≈ +/− 6° from 2θ=90°, thereby using only 80% of the available detector coverage. Since the DAC setup does not suffer from these limitations, the expected signal ratio is approximately 1/(0.15x0.8)≈ 8 for a given sample volume. Figure 1 shows a comparison of the measured patterns where the intensity was normalized to proton beam current (which is effectively proportional to counting times). It is clear that the intensities in the PE press are orders of magnitude higher than in the DAC. Based on the strongest reflection - the (111) - of the Ge powder, the sample in the PE press provides 21 times higher count rate with a 170 times larger sample volume.

An important consideration is the role of background scattering in these measurements. Sources of which include scattering from the instrument (including air scatter), the pressure cell, and the sample/pressure medium (which will be dependent on absolute volume), and also from electronic noise (both intrinsic and from high energy gamma radiation). Fig. 1 shows a signal to noise ratio for the PE press and DAC of 13 and 0.6, respectively. To investigate the sources of the backgrounds, we performed empty cell measurements for each, see Fig.1 right panel. At d ≈ 3 Å, 35%/10% of the background results from the empty DAC/PE press. The empty DAC and empty PE press background levels are comparable at longer d-spacing, but are larger by approximately a factor of two for the PE press at 1 Å. Comparing these with the background measured from the evacuated instrument tank, we can conclude that the background for both the DAC and PE press may be improved to differing extents through better shielding and collimation. Nevertheless, it is clear that the fundamental difference between the two setups is dominated by sample quantity, and its coherent scattering.

In a further series of measurements, Ge powder was loaded in *single*-toroidal anvils which allow ≈ 2.6 times more sample volume (45 mm^3) than double-toroidal anvils. The first measurement made use of use Co-binder sintered diamond, the same material as in the previous experiment, the second measurement a SiC-binder material. The latter was described in [1,9] and has an absorption length of ≈ 20 mm for λ=4.6 Å neutrons, i.e. absorbs considerably less. Both types of anvils had the same geometry and approximately the same filling factor. Figure 2 demonstrates a gain in intensity by a factor ≈ 2 in the region of the (111) reflection of Ge, i.e. *double*-toroidal anvils made of this material would give ≈ 40-50 times higher count rate compared to a DAC. For further comparison, data from a loading using ZTA anvils (a high-tensile Al_2O_3 sinter) [7] with the same profile are also shown.

Generally speaking, it should be noted that the success of the various reported measurements in DACs is mostly due to the exceptional scattering power of the sample under investigation. Simulations show that the ice VII phase of D_2O scatters ≈ 2 orders of magnitude better than, for example, Bridgmanite ($MgSiO_3$, *Pbmn*, *a*=4.7780(2), *b*=4.9298(3), *c*=6.8990(3) Å [10]), a sample which we consider an 'average scatterer'. Likewise, the EuX (X=O,S,Se,Te) and GdX (X=As,Sb,Bi) compounds studied by Goncharenko *et al*. to pressures up to 42 GPa [3] involve huge magnetic moments of Eu^{2+} and Gd^{3+} of m=7 μ_B. The magnetic diffraction signal scales with the square of the magnetic moment [11]. Therefore, these compounds produce magnetic reflections which are up to almost 2 orders of magnitude more intense than those of more "conventional" magnetic 3d-elements such as Cu^{2+} (m=1 μ_B).

In addition, one should point out that all of the above cited record measurements were carried out with filling the available pressure chamber only with sample, i.e. *without* the addition of pressure transmitting fluids. In measurements *with* such fluids, which is the standard procedure with solid powders to ensure hydrostaticity, the amount of sample has to be reduced by typically 50%. As a result of this, the non-hydrostatic DAC data provide *per se* at least twice as much signal than if pressure fluids would be included.

To resume, for a given volume and scattering geometry, DACs provide 4-10 times higher count rates than conventional large-volume sintered diamond anvils. But this advantage is outweighed by a ≥ 100 times smaller sample volume currently necessary to achieve pressures beyond 30 GPa.

To conclude, the effect of strong sample scattering power arising from high symmetry, crystallinity and elemental scattering power is the key ingredient in the success of DACs for neutron powder diffraction to date. For more "conventional" samples, typically 2 orders of magnitude higher count rates are still required to obtain diffraction patterns required to perform successful crystallographic studies. This might be achievable by the use of larger CVD grown diamonds, as pointed out in Ref. [6], combined with a significant higher neutron flux available in future. However, this may be at the expense of resolution of the diffracted signal, where guide technology is increasingly being relied upon to achieve higher flux at the sample position.

Disclosure statement

The authors declare no potential conflict of interest

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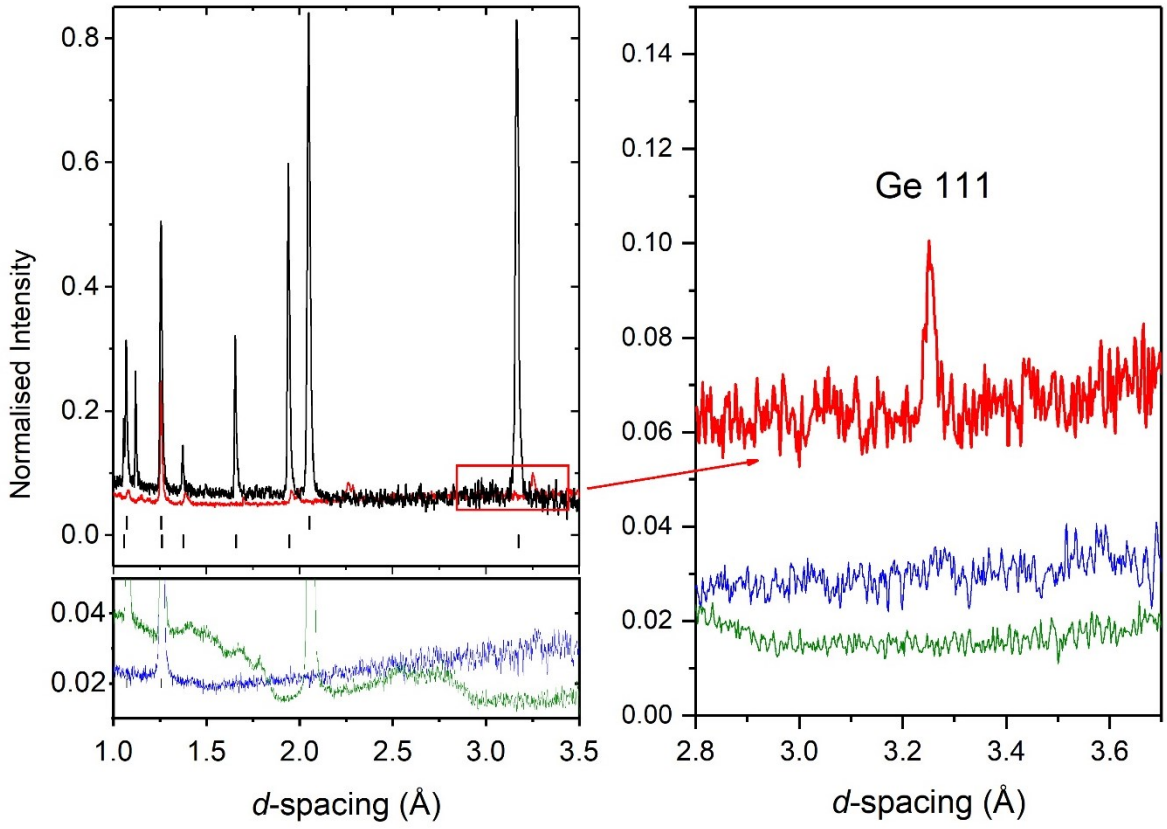

Figure 1. Left: Neutron diffraction patterns of Ge powder collected in "large-volume" double-toroidal sintered diamond anvils (black) with an applied load of 60 tonnes (sample pressure of 7.8 GPa) and in a DAC (red) at a pressure of 5 GPa. Accumulation times are 5 mins and 8 hrs, respectively. The vertical marks show the Bragg reflection positions from the sintered diamond anvils (top ticks) and Ge powder (bottom ticks) in the PE setup data. Right: Enlarged area of DAC data around the Ge (111) reflection. The lines below are measured background intensities: Empty DAC (upper, blue), empty PE (lower, green). The gasket and collimation in the empty DAC and with the sample were not exactly identical which may contribute to differences in background. The environmental background at closed shutter is estimated to be less than 0.01. Intensities is normalized to proton current (which is approximately time). For details see text.

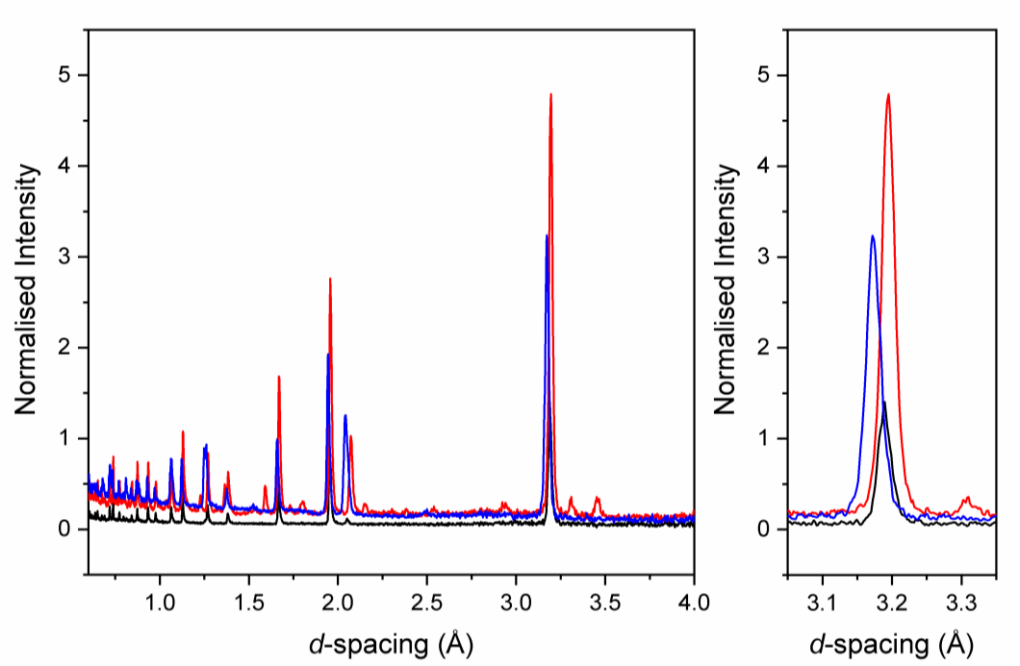

Figure 2. Neutron diffraction patterns of Ge powder collected in *single*-toroidal SiC-sintered diamond anvils (blue) compared to Co-sintered diamond anvils (black). For comparison, data collected in ZTA anvils (red) are also shown. The load on the anvils is 60 tonnes (in all three data sets), producing a pressure of 7-8-6 GPa. In the right hand panel enlarged region around the (111) reflection from germanium is shown from each anvil for comparison. The accumulation time 1 hr for each pattern, the intensity is normalized to proton current (approximately time).