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A simple system for neutron diffraction at 4 K and elevated pressures

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We describe a unique cryogen-free closed-cycle refrigerator system using a beryllium-copper VX1 variant of the Paris-Edinburgh press which enables approximately 3 GPa to be generated on a sample volume of 66 mm^3, over the temperature range 4-300 K. The main advantage of this system is its versatility; it has been designed to be fully compatible with the PEARL neutron powder-diffraction instrument at the ISIS facility, but is also compatible with several other instruments at the facility with minor modifications. We provide a full description of the system, along with representative data collected on PEARL from MnF_2 at 13 K and 2.4 GPa.

Neutron diffraction complements and has a number of distinct advantages over X-ray diffraction, which have been discussed extensively in the literature [1]. Most pertinent to this paper is that the high penetration of neutrons, and their intrinsic spin, makes them sensitive to probing bulk magnetic structure. High-pressure conditions can be used to strongly alter interatomic separations, atomic co-ordination, and ultimately the crystallographic symmetry of materials, controlling the vast majority of physical properties. As such, high-pressure is an influential tool in understanding structure-property relationships. Diffraction at extreme pressures (both X-ray and neutron) is therefore essential, with many studies requiring simultaneous pressure and temperature control. The Paris-Edinburgh (PE) press is a prominent device for performing high-pressure neutron diffraction measurements beyond 3 GPa, and is found at the majority of neutron and X-ray synchrotron sources worldwide. The largest variants of the press (the V7 or V8, 90 kg), are capable of applying up to 450 t, whilst the smallest variants (the VX1 or VX2, 10 kg) can apply 50 t [2]. Other high-pressure devices, such as diamond anvil cells [3], or large volume pressure vessels such as gas cells [4] have their own advantages and disadvantages relating to achievable pressure range and sample volume, but they do not compete in terms of the ease of use of the PE press, essential for a large-scale user program.

The original method to access low temperatures using the PE press, uses liquid nitrogen to cool the entire press assembly, and can achieve temperatures as low as 77 K in 2 h. Advantages of this technique are that the temperature is very stable due to the large thermal mass, and that the lack of vacuum allows direct access to the sample for recovery to true ambient pressure and/or removal from the press whilst at low temperature. The disadvantages are that it requires a significant volume of liquid nitrogen both for the initial cool-down, and to maintain base temperature, which may also cause issues with blocking certain regions of detector coverage, and hydraulic oil can no longer be used due to its high freezing temperature. Suitable alternatives are either a 5:1 mixture (by volume) of iso-n-pentanes, or helium gas (see details in [2]). Pentanes freeze below 120 K, whereas He gas requires an indium Bridgman seal, which is more complex to install, and is therefore potentially more prone to failure. Band heaters, attached to the body of the cell, are used to control at temperatures above base. The time required to change temperature using this method is in excess of 5 h to return the cell to 290 K from base.

Alternatively, the anvils and gasket are cooled while the rest of the press is thermally insulated and kept at room temperature. This is achieved by circulating liquid nitrogen through Cu rings surrounding the anvil and fret assembly. Variations on this principle can cool the sample to: $\sim$100 K in 45 min using the variable temperature insert (V3 press) at the PEARL instrument (ISIS facility, UK); 85 K in 30 min (VX5 press) at the SNAP instrument (SNS facility, US); 80 K in $\sim$12 min according to [5], though in practice closer to $\sim$30 min (MTP press, Mitsubishi Corporation) at the PLANET instrument (J-PARC facility, Japan). All of these systems require the press to be within a vacuum. The main advantages of this technique are fast temperature control, and that the press is kept at 300 K so hydraulic oil can be used, enabling full automation of the system.

A comparatively complex system at the ILL (France) and PSI (Switzerland) uses a He driven VX5 press (35 kg) to achieve 3.5 K up to pressures of 10 GPa [6]. The press is rapidly pre-cooled through immersion in liquid nitrogen, before a closed-cycle refrigerator (CCR) cools the cell to 3 K in a He exchange gas. Liquid He can then be used to cool the press down to below 1.8 K reaching base temperature in a total $\sim$12 h. At the ISIS facility a VX3 press can be cooled to 35 K in 60 h or a VX1 press to 12 K in 12 h using a CCR, but this system is bespoke to the SXD instrument [7], and cannot easily adapted for other scattering geometries. In the remainder of this manuscript we present a simple, cryogen-free approach to cooling samples below 77 K in a VX1 PE press, suitable for multiple detector geometries. The main advantage of a cryogen-free system is the temperature stability, which is crucial for long duration neutron diffraction experiments. We present details of its operation, and a representative study on MnF_2 from the PEARL instrument (ISIS facility, UK) [8].

A schematic for the setup is shown in Figure 1. It consists of a dual-stage Sumitomo cryocooler (RDK-415D) attached to a 400 mm diameter vacuum-flange, with a beryllium-copper (BeCu) VX1 PE press attached to the second-stage of the cryocooler. BeCu has significant thermal advantages over steel, with a much larger thermal diffusivity [4]. The seats are tungsten carbide, and the anvils are zirconia-toughened alumina (ZTA), with both components pressed into BeCu frets. The anvils are the same profile as for the V4 press (66 mm^3 sample volume) with a reduced outer diameter (25 mm to 17.3 mm). The cell is fitted with a stainless steel capillary which is thermally anchored to the first stage of the cryocooler using a copper link. The piston of the VX1 press is fitted

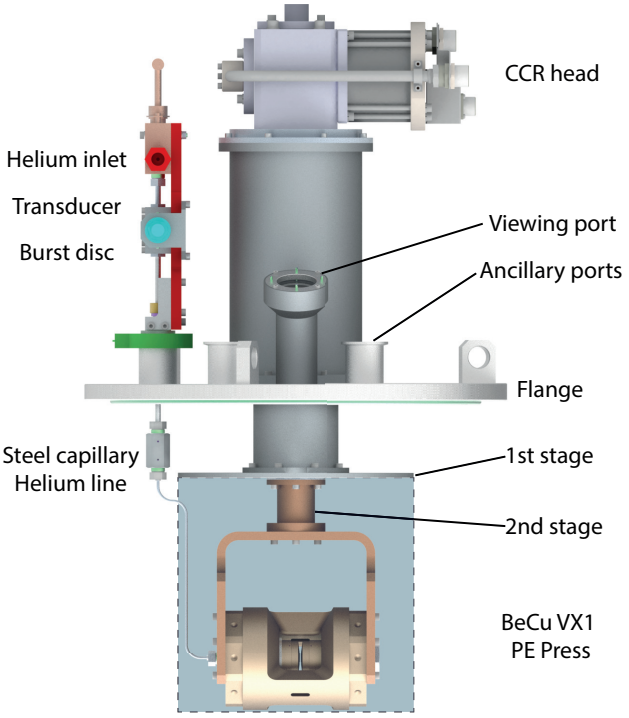

FIG. 1. Overview of BeCu VX1 PE press mounted onto CCR, in the $2\theta = 90^\circ$ scattering geometry for the PEARL instrument. The cell is linked to the second stage via an oxygen-free high-conductivity Cu bracket. An aluminium radiative heat shield (depicted as shaded/dashed region) is linked to the first stage, and surrounds the second stage and cell. The capillary line is weakly linked to the first stage via a braided Cu wire to reduce the heat load on the cell. BN collimation and Cd masking are not shown for clarity.

with a pre-stressed layered PTFE-Pb-In-Pb-PTFE seal, as detailed elsewhere [9]. This assembly allows the load on the cell to be controlled using helium gas, remaining sealed up to the maximum working pressure of 2.5 kbar down to liquid helium temperatures. An aluminium heat shield is anchored to the first-stage, which surrounds the cell assembly, reducing radiative heating from the warm surrounding vacuum vessel (described in [8]). The shield includes a small hole to remove aluminium from the direct incident neutron-beam, and vanadium windows matching the opening angle of the cell windows, advantageous where a fixed scattering angle is used. The temperature of the cell is monitored using several RhFe sensors, coupled with resistive heaters. An optical window is included on the flange to maintain gasket alignment to the centre of the instrument (the gasket is displaced with the movement of the piston, changing the length of the primary neutron flight path), as for other presses on the PEARL instrument [8].

The system is compatible with a number of scattering geometries; primarily for use of the PEARL instrument, it is set up to pass the incident neutron-beam through the back of the anvils, allowing scattered neutrons to be measured on the $2\theta = 90^\circ$ detector banks. This geometry provides the most tightly collimated neutron beam, and hence fewer parasitic contributions to the diffraction pattern. However, where higher resolution, or access to a d-spacing range beyond 8 Å is required, the entire system may also be rotated 90° around the axis of the cryocooler, to pass the incident neutron beam between the two anvils, providing access the high- and low-angle detector banks of the PEARL instrument. This can be changed during the experiment, in-situ. Additionally, there is an alternative Cu bracket, which holds the cell with its axis parallel to the axis of the cryocooler. This makes it compatible with different detector geometries, such as found on other instruments. All possible orientations of the cell correctly position the sample at the correct beam-height for the majority of ISIS-facility instruments.

MnF_2 powder ($\geq$ 99.95% trace purity, Sigma Aldrich) was finely ground and loaded with 4:1 perdeuterated methanol:ethanol into a null-scattering TiZr encapsulated gasket, with a BeCu outer gasket. A small piece of lead was included with the sample, to enable the sample pressure to be determined using the well documented equation of state. Prior to cooling the press, 250 bar of helium gas (equivalent to $\sim$5 t) was applied to ensure that the piston seal holds on cooling, and to seal the sample and medium in gasket assembly. The tank and press assembly was then evacuated to $\sim 10^{-6}$ mbar. The cell cools to a base temperature of 4 K or 10 K in approximately 12 h with or without the heat shield respectively. The cooling rate is constant (0.35 K min^{-1}) to 70 K, taking a further 1 h to reach base temperature. On warming, the cell heats at $\sim$ 5 K min^{-1}, though 10 min is allowed for equilibration at each temperature. To facilitate efficient use of the diffractometer, the cell is cooled offline from the instrument. The vacuum is then sealed, the compressor detached, and the tank loaded into the instrument when ready/required. The temperature of the system was found to drift by approximately 20 K during this operation, though base temperature is reachieved within approximately 20 min once the compressors are reattached. The maximum pressure achieved was 2.8 GPa at 300 K, requiring 2 kbar He gas pressure in the VX1. On cooling, the He gas pressure is maintained using a buffer volume, though the pressure on the sample was observed to drop by approximately 0.4 GPa, due to thermal effects in the sample and gasket assembly. The load was varied at room temperature to maintain the hydrostaticity of the methanol:ethanol. The PEARL instrument was used in the $2\theta = 90^\circ$ geometry, and the data were fitted using Rietveld analysis.

MnF_2 is a well characterised material at ambient pressure, used for many as an introduction to magnetic neutron scattering. It has tetragonal symmetry ($P4_2/mnm$, $a = 4.8734(2)$ Å, $c = 3.3099(5)$ Å at ambient pressure, 300 K), with a rutile structure, Mn on Wyckoff $2a$ $(0,0,0)$, and F on Wyckoff $4f$ $(x,x,0)$ $(x \approx 0.3)$. The mixture of positive (F) and negative (Mn) scattering lengths means that the nuclear structure doesn't scatter particularly strongly. Magnetically, the material orders as a G_z-type antiferromagnet ($T_N = 67.3$ K) in the Shubnikov group $P4_2'/mnm'$ with $\mu_z = 5.83(6)\mu_B$. Figure 2(a) shows the diffraction data collected from PEARL at 0.5 GPa and 2.4 GPa, each at ambient temperature and 13 K. The strong reflection that appears in the 'long-frame' is entirely magnetic in origin, corresponding to the (010) reflection. The near-ambient pressure collection at 13 K yielded a refined fluorine coordinate $x_F = 0.3019(5)$, and a moment

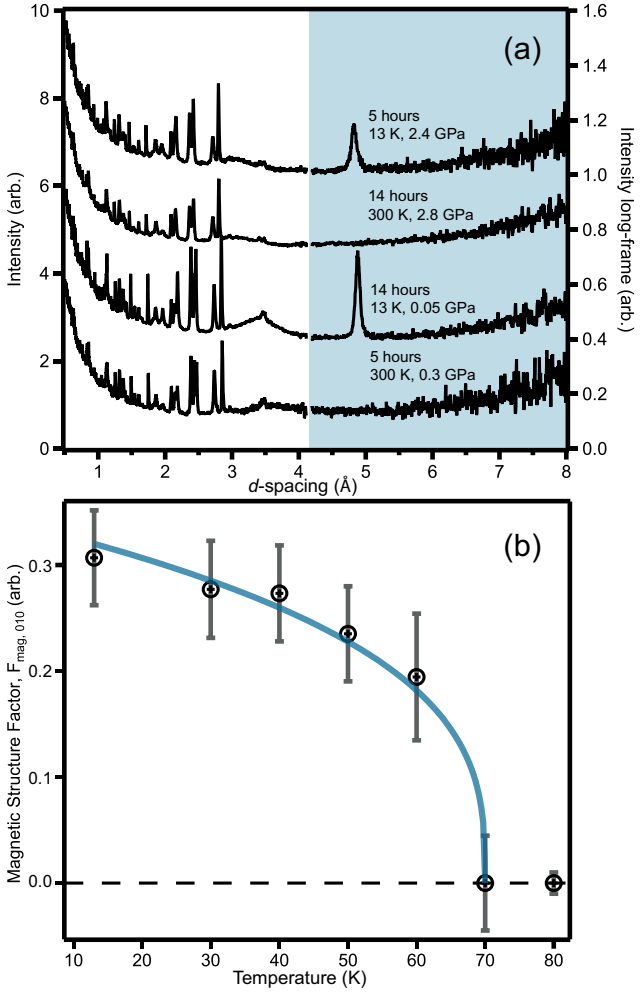

FIG. 2. (a) Stack-plot of neutron powder-diffraction data collected from MnF_2 within the VX1 at the indicated loads and temperatures, data collection times are also shown. The shaded region indicates data collected from the 'long-frame' on the PEARL instrument (see main text). A strong magnetic contribution is seen from the antiferromagnetic sample just below 5 Å, corresponding to the (010) reflection. (b) The integrated intensity of this (010) reflection as a function of temperature collected on heating at constant 2.4 GPa. The blue line is the fit, discussed in the text.

on the manganese $\mu_{Mn} = 5.83(6)\mu_B$ with $a = 4.8786(2)$, $c = 3.2940(2)$ Å, whereas at 2.4 GPa these become $x_F = 0.2977(8)$ and $\mu_{Mn} = 5.84(11)\mu_B$ with $a = 4.8266(5)$, $c = 3.2741(5)$ Å. This shows that the Mn-F polyhedra become slightly (2.5%) more distorted at 2.4 GPa, though since the exchange mechanism between Mn atoms is direct, the moment is essentially unchanged within the error of the measurement. Shorter 1 h collections on heating at 2.4 GPa were insufficient for a full refinement of the magnetic structure, but a simple integration of the magnetic (110) reflection yields a measure of the moment. The square-root of the integrated intensities are plotted in Figure 2(b), and are fitted $\sim (T_N - T)^\beta$, yielding a critical exponent $\beta = 0.25(16)$, which within error agrees with that expected from a 3d Ising model, similar to FeF_2 [10]. The coarse temperature steps preclude a precise determination of the shift in T_N, though where the exponent is fixed ($\beta = 0.33$), the fitted value $T_N = 70(1)$ K, shows an increase of ~ 2.7 K at 2.4 GPa.

To conclude, we have developed a cryogen-free system for cooling the PE press to 4 K, which can generate up to 2.8 GPa with 66 mm^3 of sample. The simplicity of the system affords it a number of advantages over other PE press cryo-systems, such as ease of use and long term temperature stability. Future developments include the use of smaller anvil variants [9] (sample volume 30 mm^3), which will allow pressures up to 6 GPa to be accessible with the 50 t load available from the VX1. However, where still smaller sample volumes are acceptable, such as at synchrotrons or next generation neutron facilities, significantly higher pressures may be achieved with the available load. MnF_2 may warrant further investigation, to determine the change in magnetic structure through the transition to orthorhombic symmetry under pressure (~3 GPa) [11], observed with neutrons in thin films [12].

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