# The Super-D2B project at the ILL

E. SUARD AND A. HEWAT
*Institut Laue Langevin*
*B.P. 156*
*F-38042 Grenoble Cedex 9*
*France*

Demand for neutron powder diffraction (NPD) is still increasing strongly, despite the development of techniques such as synchrotron radiation and electron microscopy. This is because NPD has unique advantages, and new, more powerful neutron diffractometers address the only real problem—intensity. In particular, the strong magnetic scattering of neutrons, and the strong scattering power of the light elements, are two major advantages compared to X-ray and electron diffraction. As well, powder diffraction itself often has advantages over single crystal diffraction for both neutrons and X-rays. High resolution powder diffraction reveals subtle phase transitions that might be missed with single crystals, and special sample conditions of pressure and temperature are often easier to apply with NPD. But, finally, the main advantage of powder diffraction comes from the fact that new materials are almost always first available only as powders.

D2B was built to fulfill all these requirements 20 years ago [1] and has been essential in many fields of research, producing some of the most cited ILL publications. The present instrument is characterized by a high take off angle of 135°, a vertical focusing Ge monochromator and 5′ Soller collimators in front of each of its 64 $^3$He detectors. One of the main advantages of D2B is that it is possible to choose the best resolution suitable for a particular experiment by inserting either a 10′ or 5′ collimator in front of the monochromator and/or a slit after it to control the divergence of the monochromatic beam (Figure 1). D2B was designed for crystallographic studies and is particularly well suited for Rietveld refinements even with relatively large structures such as zeolites with absorbed molecules. It was also designed for work on magnetism and high resolution at very large d-spacing using wavelengths of 2.4 Å or 6 Å.

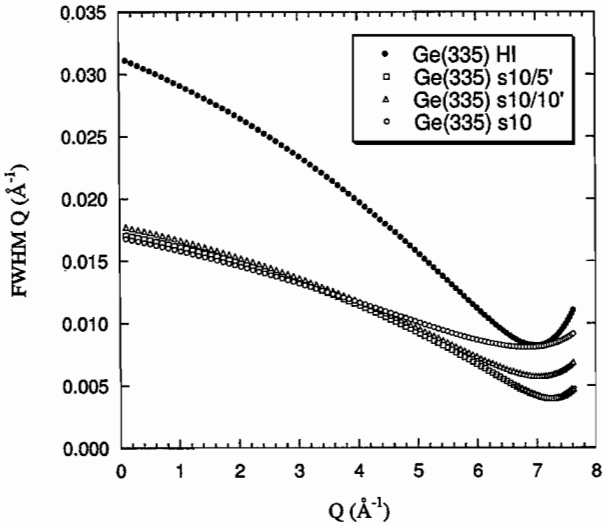


***Figure 1.*** *Instrument resolution for D2B neutron powder diffractometer for the Ge(335) monochromator reflection (corresponding to a wavelength of 1.59A). The Cagliotti function was calculated based on experimental measurements on a high quality $CeO_2$ sample. The curves correspond to various configurations of the instrument: using either a high intensity configuration (HI) without any collimation, or a 5' (10') pre-monochromator collimation with a 10mm after monochromator slit (s10/5' or s10/10'), or only a 10mm slit after monochromator slit (s10).*

The statistics of the use of D2B at the ILL show the success of the instrument. The user demand is very high and still growing, even with the competition of powerful new

diffractometers such as HRPD and GEM at ISIS. The statistics on user demand show that D2B has a large overload in the number of requested days, although the majority of proposals receive at least some time. This behavior is explained by the fact that subcommittees try to spread the time between as many groups as possible, and the only way to do this is to reduce the number of days per experiment. The good point here is that many users then have access to the instrument, but very short experiments (on average two or three days) may sometimes be at the expense of quality. Despite this fact, ILL statistics also show that D2B is one of the ILL instruments producing the greatest number of publications as well as the most cited papers. These results would be even better with an improved instrument, which would give to the users the possibility to do better measurements during their experimental time.

The lack of time during experiments is not the only limitation of the present instrument. The urgent need for an improved D2B with higher flux and higher resolution can clearly be demonstrated with some specific examples. The most obvious one is the need to measure tiny samples, which is essential for the characterization of new materials, often only available in milligram quantities. But there are other requirements. Good resolution and counting statistics are needed for high quality Rietveld refinement; high resolution is necessary for the study of complex phase diagrams (pressure, temperature, magnetic field...); a choice of wavelengths is useful for optimizing the experiment; and again high flux is needed with special sample environments (high pressure, reaction cells...) where the amount of sample in the beam is necessarily small. Some experiments, such as the work on nickelates by J.A. Alonso and M.T. Fernandez-Diaz [2], combine several of these needs. In this PRL, the metallic to insulating transition at 582K in YNiO3 is shown to be accompanied by an orthorhombic to monoclinic transition, which is due to Ni charge disproportionation. Although the monoclinic transition could also be seen with synchrotron radiation, neutrons were essential, since they provided two kinds of evidence for this charge transfer. The first was the existence of different Ni-O distances, evidence for two different octahedral sites for the Ni atoms. The second evidence is the occurrence of a magnetic superstructure due to different moments on the Ni sites. These two results prove that below the metal-insulator transition, the crystallographic structure is characterized by a monoclinic distortion due to a charge transfer in YNiO3, resulting in two distinct crystallographic sites for Ni, each having a different valence: V(Ni1)=2.62 and V(Ni2)=3.17. Neutrons provided proof of charge transfer, but high resolution

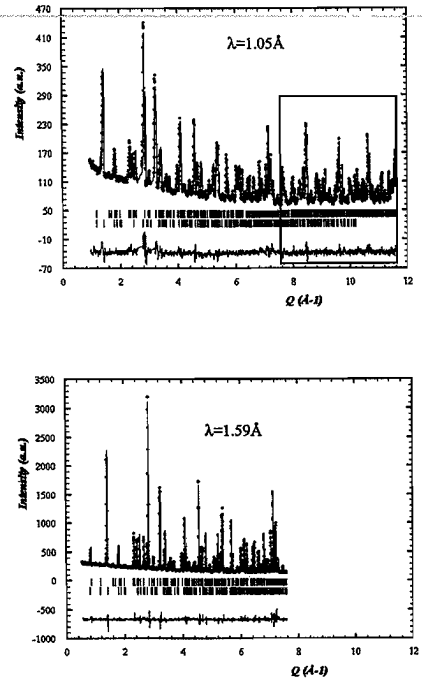


*Figure 2. Data collected on D2B at two different wavelengths on $HoBaCo_2O_5$ at 2K. The frame shows the gain in Q-range when working at a shorter wavelength.*

was also needed to resolve the symmetry, as well as high flux to see the magnetic superstructure. Moreover, for this experiment, the samples were prepared at high pressures and were only available in small amounts. Even if this experiment was possible on the present D2B with long measuring times, it was surely at the border of its possibilities and only one sample could be examined. Yet it would be extremely interesting to measure a whole series of this nickelate family to understand changes in physical properties on changing the rare earth. But since all samples are available in only small quantities, and since a whole temperature diagram must be measured at high resolution, it is essential that we improve the present machine.

A second example illustrates the increase in reliability of results when using multiple wavelengths. The oxygen deficient cobaltites LnBaCo2O5 (Ln=Tb,Dy,Ho) [3] exhibit two successive crystallographic transitions at $T_N$=340K

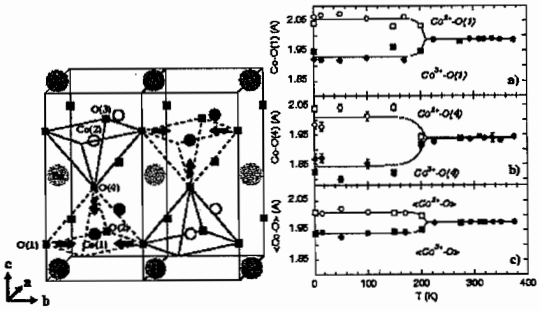

*Figure 3. Crystallographic structure and temperature dependence of selected Co-O bond lengths and of the mean (Co-O) distances in $HoBaCo_2O_5$ (taken from ref. 3).*

and at $T_{CO}$=210K. Whereas the first transition (*P4/mmm to Pmmm*) is related to the long-range anti-ferromagnetic ordering of the Co ions (spin ordering), the second transition (*Pmmm to Pmmb*) corresponds to the long-range ordering of the $Co^{2+}$ and $Co^{3+}$ ions (charge ordering), occurring in 1:1 ratio in the structure. The charge ordered (CO) state was inferred by the observation of additional superstructure peaks in neutron and electron diffraction patterns, but with both methods these superstructure peaks were so weak that it was impossible to refine the structure and so prove charge ordering between $Co^{2+}$ and $Co^{3+}$. The idea was then to characterize this CO structure by examining Co-O distances, bond valences sums (BVS) and the magnetic structure. For this purpose we needed high quality neutron powder diffraction data, with very good resolution at low Q (to obtain precise magnetic moments), and with a very large Q-range in order to get accurate crystallographic positions for the bond distances needed for the BVS calculation. The only way to get both requirements was to measure our samples as a function of temperature using two different wavelengths. This was performed on D2B using a short wavelength of 1.05 Å to get large Q-range data for the crystal structure determination, and 1.6 Å or 2.4 Å to obtain high resolution at low Q for the magnet structure (Figure 2). The new feature of the CO structure is the existence of two distinct crystallographic sites for the Co cations. Although both sites retain a pyramidal Co-$O_5$ oxygen environment, analysis of the inter-atomic Co-O distances show that the Co-O distances on the two sites differ considerably (Figure 3). As can be seen in Figure 2, both the O1-basal and the O4-apical oxygen atoms move toward the Co1 site. This leads to a smaller volume of the Co-$O_5$ pyramid as shown by the evolution of the mean Co-O distances. With reference to the tabulated ionic radii of Shannon [4], we can reasonably assume the smallest of the pyramids, that is the Co1 site, is occupied by $Co^{3+}$ ions exclusively. This picture is further confirmed by bond valence calculations yielding approximate valences of +2.7 for the Co1 site and +2.1 for the Co2 site for T < TCO. Hence, each of the Co1 and Co2 site can be considered to be exclusively occupied by the $Co^{3+}$ and $Co^{2+}$ species occurring in $LnBaCo_2O_5$ (Ln=Tb,Dy,Ho). This feature is further confirmed by the almost 1 μB difference between the refined magnetic moment of these two sites. This 1 μB difference reflects perfectly the one electron difference between the two Co sites. The resulting charge ordered structure can thus be described by an alternate stacking of $Co^{2+}O_5$ and $Co^{3+}O_5$ pyramids along the *b* and *c* directions, and $Co^{2+}O_5$ or $Co^{3+}O_5$ pyramids files along the *a* direction. Two pictures, with $Co^{3+}$ ions either in intermediate spin state ($t^5_{2g}e^1_g$) or in high spin state ($t^4_{2g}e^2_g$), describe equally well our experimental data. In both cases, the observed magnetic structure can be explained using the qualitative Goodenough-Kanamori rules for super-exchange [5]. These results were obtained on these specific samples using combined wavelength refinements. It is certain that, in other cases, this technique of measuring at different wavelengths would improve considerably the accuracy of results. Since such methods require longer acquisition times, they are usually not feasible at present. The proposed upgrade of D2B will mean that such techniques can be used more often.

Much exiting new science would be possible with an improved machine. Another example concerns new forms of meta-stable ice, which have recently been discovered on D2B by Kuhs, Lobban and Finney [6]. The ice phase diagram is extremely rich and is still not fully understood. Several meta-stable phase of ice were obtained *in-situ* and their structures were characterized. The main feature of these experiments was the discovery of a totally new ice structure, ice XII, which was found within the stability region of ice V and prepared *in-situ* by crystallization from the liquid phase. The topology of ice XII is unlike any of the known ice phases, and contains a mixture of 5- and 7-membered rings. This work has also demonstrated that NPD is the best method to explore the phase diagram of ice, since it is possible to detect very subtle effects due to changes in H-

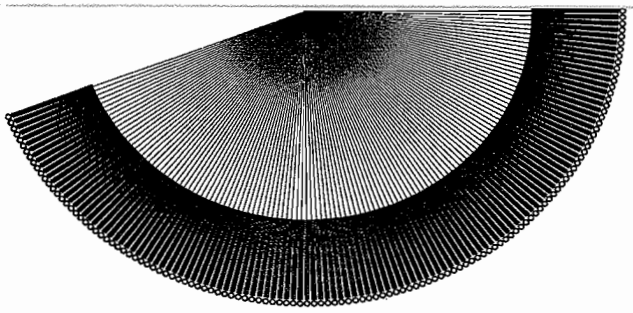

*Figure 4. Schematic view of the future D2B detector bank with 128 $^3$He linear wire detectors, 300mm high and 128 300mm high five minutes collimators.*

ordering. But again working at high pressure means very small samples, and high resolution is needed to sort out the different ice phases.

We therefore propose to build a unique new type of pseudo-2D high-resolution position sensitive detector. In the horizontal plane, high-resolution will be obtained by scanning a large bank of very fine five minute collimators (Figure 4). In the vertical plane lower resolution would be obtained using a stack of linear wire position sensitive detectors. This vertical resolution is needed to correct for the curvature of the diffraction cones. We already have prototypes of 300 mm high collimators built by Euro-Collimators in Cheltenham, and the detectors too are commercially available. Such a detector would collect six times as many neutrons for the same resolution. Following this proposal, a similar detector has been planned for the new Munich reactor, but with lower resolution and flux.

In a second stage, we propose to upgrade the monochromator and neutron optics to give even more intensity and a larger choice of wavelengths. The total gain would be an order of magnitude in intensity, which would allow the highest possible resolution to be used for most experiments. This project is complementary to the new GEM machine at ISIS, which has higher intensity, but lower resolution, and therefore better compared to ILL's D20 with the new high take-off geometry.

Neutrons are scattered from a powder in cones of a fixed angle, depending on the wavelength and "d-spacing" of crystal planes. At present we only collect those neutrons scattered within a narrow band in the equatorial plane. The essence of our proposal is very simple—to increase the height of the detector to collect a x3 larger band, and to double the number of detectors for a total gain of x6. Of course in practice it is not quite so easy. Because our linear detectors intersect cones of radiation, the peaks are broadened if we average over a longer detector, and the centers of intensity of the peaks shift; this is unacceptable on a high-resolution machine. We can only increase the height if we use some kind of position sensitive detector to correct for the curvature of the cones. Fortunately we only require low-resolution in the vertical direction, since we still only intersect a relatively small segment of the cones, except at very low and very high scattering angles. A simple linear wire detector, with a resolution of 2-3 cm is sufficient. The collimators are already being constructed, and it is expected that this new detector will be completed by the end of 2002.

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