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High pressure diffraction at ISIS

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ABSTRACT
The development of the high pressure diffraction programme at ISIS is reviewed. Along with general accounts of the technique and the pressure cells used, examples of science carried out in this field are given.

I. INTRODUCTION

High pressure diffraction is ideally carried out at a pulsed spallation neutron source such as ISIS. The ability, on such a source, to collect the entire diffraction pattern from a polycrystalline sample at a single, fixed, scattering angle enables the convenient design of sample environment apparatus to minimise scattering from the pressure cell and pressure transmitting components. The elimination of the contaminating diffraction lines from these extraneous components is vital in obtaining reliable structural refinements from samples under high pressure.

The medium resolution powder diffractometer POLARIS at ISIS (Hull and Mayers, 1989), is well configured to perform such science. POLARIS (Figure 1) is relatively close to the moderator (sample to moderator distance $L_1 = 12$ m), giving high flux on the relatively small samples typical in a pressure experiment. It also has a detector bank situated at a scattering angle of 90°, the most convenient for the examination of samples under high pressure. The POLARIS 90° bank consists of 20 ^{3}He gas detectors at fixed scattering angles in the 2θ range 88–92°, covering an angle of some 25° above and below the horizontal plane of the instrument, and gives a resolution of $\Delta d/d \sim 6 \times 10^{-3}$ that is essentially independent of d spacing.

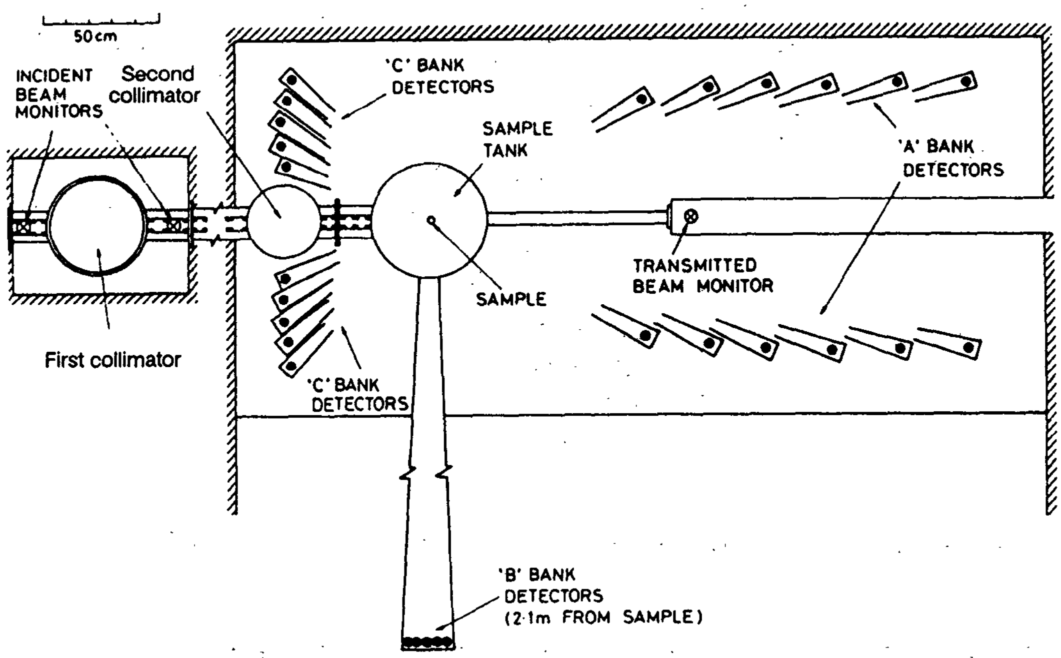


Figure 1 – Layout of the POLARIS medium resolution powder diffractometer at ISIS.

The advantage of the time-of-flight technique is illustrated in Figure 2. The ability to measure the entire diffraction pattern at fixed 2θ allows neutron collimation to be constructed inside the pressure cell, thus precluding the diffraction of neutrons from the cell casing or the Al_2O_3 insert from reching the detectors. In the McWhan cell discussed below, these B_4C collimators have apertures of some 3 mm wide by 8 mm high for the incident and scattered beams. This enables diffraction patterns to be obtained which are unaffected by scattering from the pressure cell itself. From the figure it is clear that 90° scattering maximises sample volume while minimising contamination from sample environment equipment.

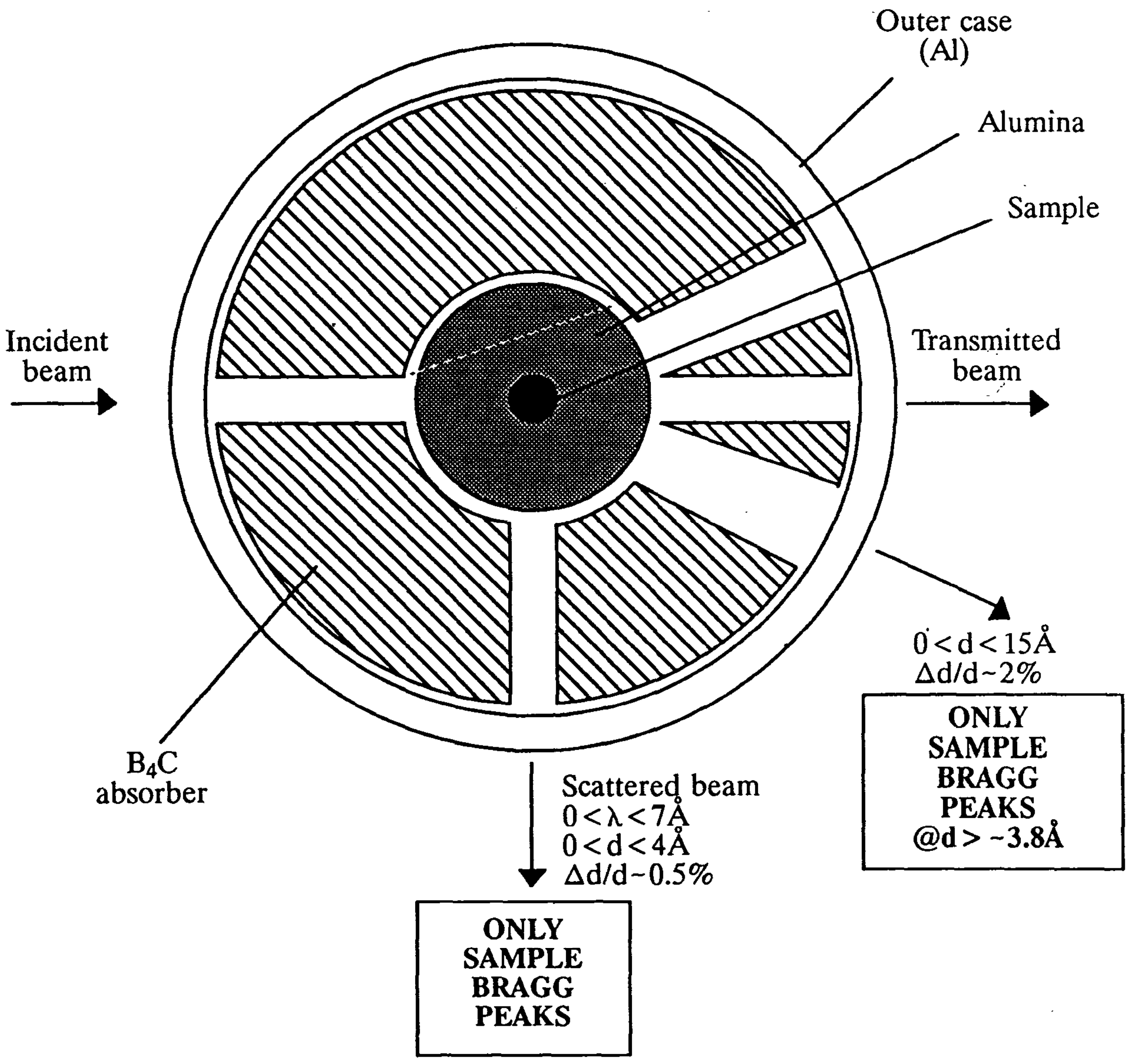


Figure 2 – Schematic view of the pressure cell collimation on POLARIS.

II. MODERATELY HIGH PRESSURES - THE McWHAN CELL ON POLARIS

For pressures up to around 25 kbar, the McWhan pressure cell design (McWhan, Block and Parisot, 1974) is widely used in neutron scattering. In this design (Figure 3; Adams, Hull and

Paranjpe, 1990) the aluminium sample can is sealed with a beryllium–copper plug and is enclosed in a pre-stressed Al_2O_3 insert. Pressure is applied via tungsten carbide pistons above and below the sample can. Approximately hydrostatic conditions are maintained by including a pressure transmitting fluid inside the sample can. Normally, calibration of the pressure value is obtained using an internal calibrant, usually NaCl, mixed with the sample. Refinement of the lattice parameter of the NaCl standard then gives the value of the applied pressure. However, in order to maximise the amount of sample present in the necessarily limited sample volume available, it is sometimes preferable to perform such calibration separately. In this case, the pressures are estimated by comparison with the applied load versus measured pressure calibration determined using separate diffraction measurements on the calibrant material alone. The pressures obtained using this method are expected to be accurate to within 10%, which is quite sufficient for a large proportion of high pressure work.

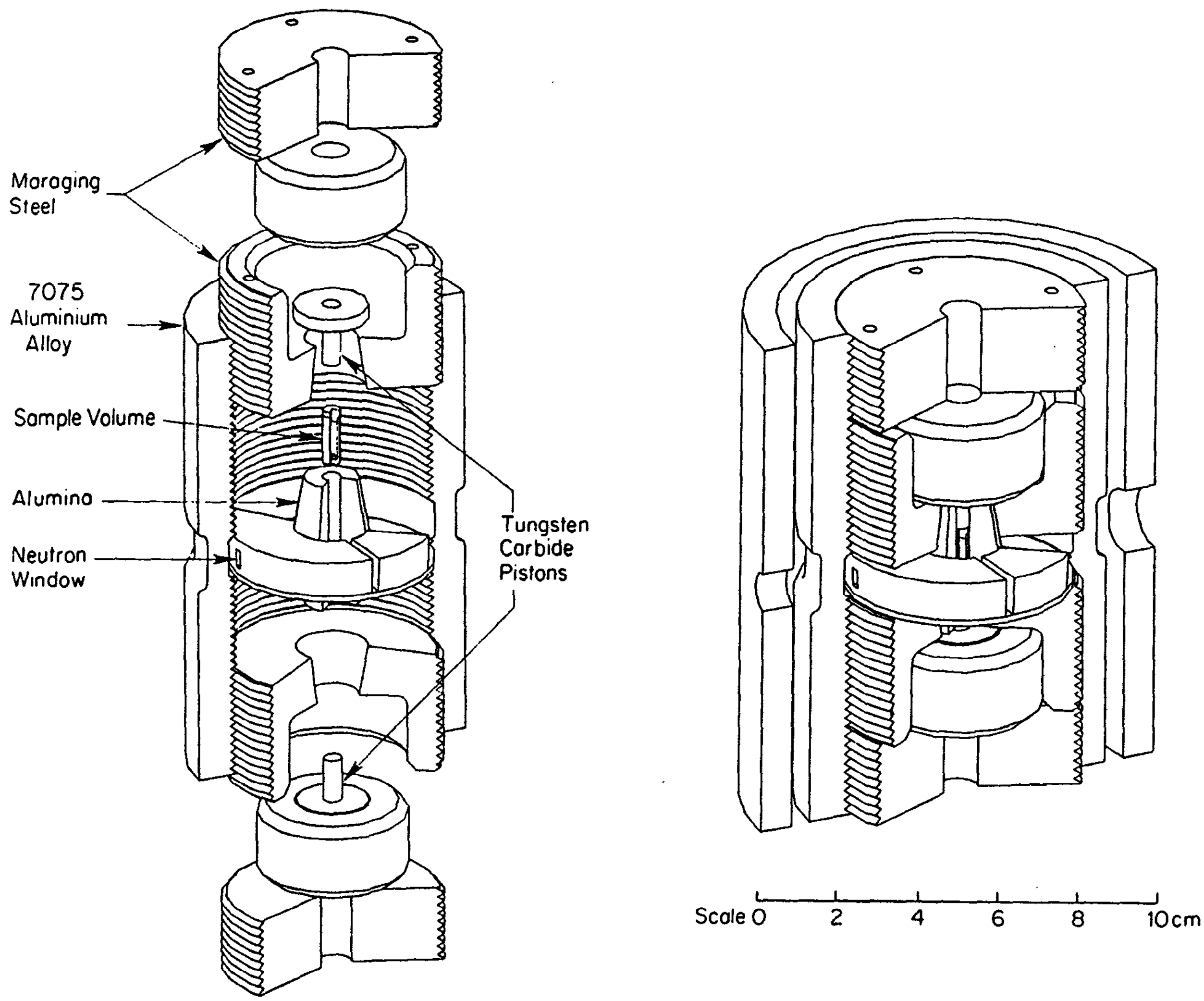


Figure 3 – An exploded and assembled view of the McWhan clamped pressure cell.

With the POLARIS set-up, and an effective sample volume in the McWhan cell of some 100 mm^3, it is necessary to count, at present ISIS current of some 100 μA, for some 10–20 hours for a typical sample, to obtain data for which a reasonable structural refinement can be carried out. This is not a prohibitively long time, and allows a great deal of high pressure structural science to be performed within the constraints of a diverse scientific programme on a user instrument such as POLARIS.

II.1 Science Using the McWhan Cell - High Pressure Studies of Ferroelastic $LaNbO_4$

$LaNbO_4$ undergoes a phase transition at high temperature from the monoclinic fergusonite structure to a ferroelastic phase with the tetragonal scheelite structure. Unlike the closely related material $BiVO_4$, the driving mechanism for this phase transition is not a soft optic mode, but instead is associated with the oxygen coordination around the Nb^{5+} anion. In niobate compounds the Nb^{5+} ion is generally octahedrally co-ordinated by oxygen but its rather small ionic radius (0.64 Å) means that the octahedral co-ordination is often rather distorted, as in the low temperature monoclinic phase of $LaNbO_4$. In the high temperature tetragonal phase of $LaNbO_4$ the Nb^{5+} ion exhibits tetrahedral co-ordination and it is the stereochemical competition between low-temperature distorted octahedral and high temperature tetrahedral co-ordination that is the driving mechanism for the ferroelastic phase transition. The application of hydrostatic pressure has the tendency to increase the number of anions surrounding a given cation. In the case of $LaNbO_4$, therefore, application of pressure will force the Nb^{5+} ion away from tetrahedral and towards octahedral co-ordination. Since the tetrahedral and distorted octahedral co-ordinations are associated with the tetragonal and monoclinic structures respectively, the application of hydrostatic pressure is predicted to increase the ferroelastic transition temperature. At constant temperature it is expected, therefore, that the spontaneous strain, that is, the monoclinic nature of the structure, should increase with increasing pressure.

To confirm this hypothesis, powder diffraction data from $LaNbO_4$ were collected on POLARIS at ambient pressure and at hydrostatic pressures of 10 and 20 kbar (David, Hull and Ibberson, 1990). The diffraction data collected in the POLARIS 90° bank are shown in Figure 4. Rietveld profile refinement was performed on each data set using the program TF14LS based on the Cambridge Crystallographic Subroutine Library (Brown and Matthewman, 1987). A typical fit is shown in Figure 5, with the resulting structural parameters in Tables 1 and 2.

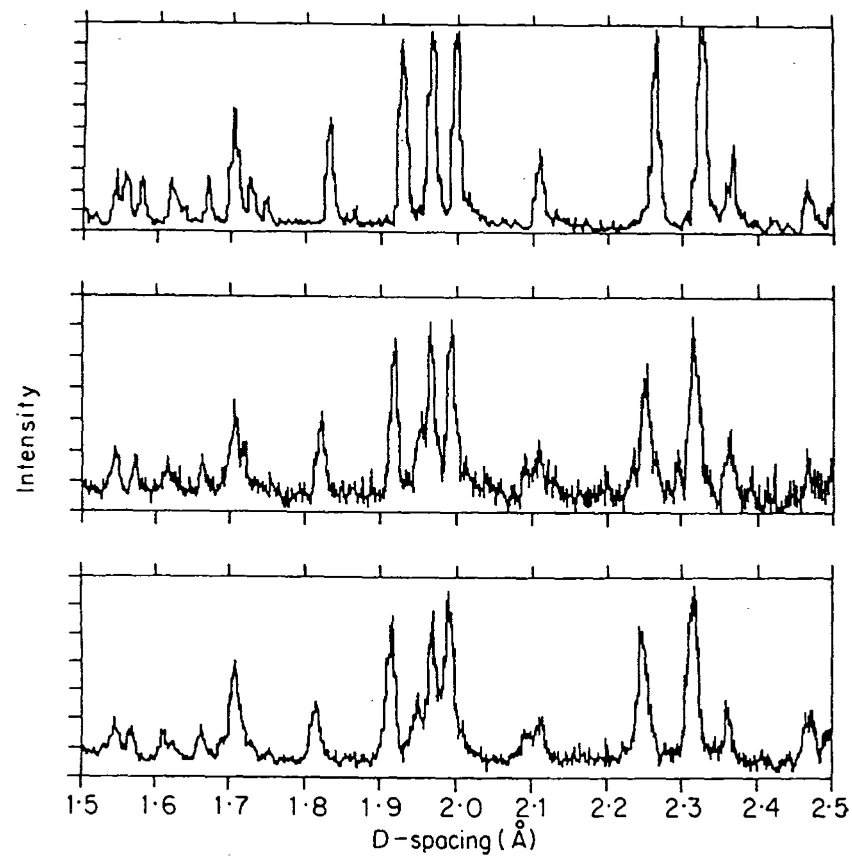


Figure 4 – Diffraction patterns from $LaNbO_4$ collected on POLARIS at ambient pressure (top), 10 kbar (middle) and 20 kbar (bottom).

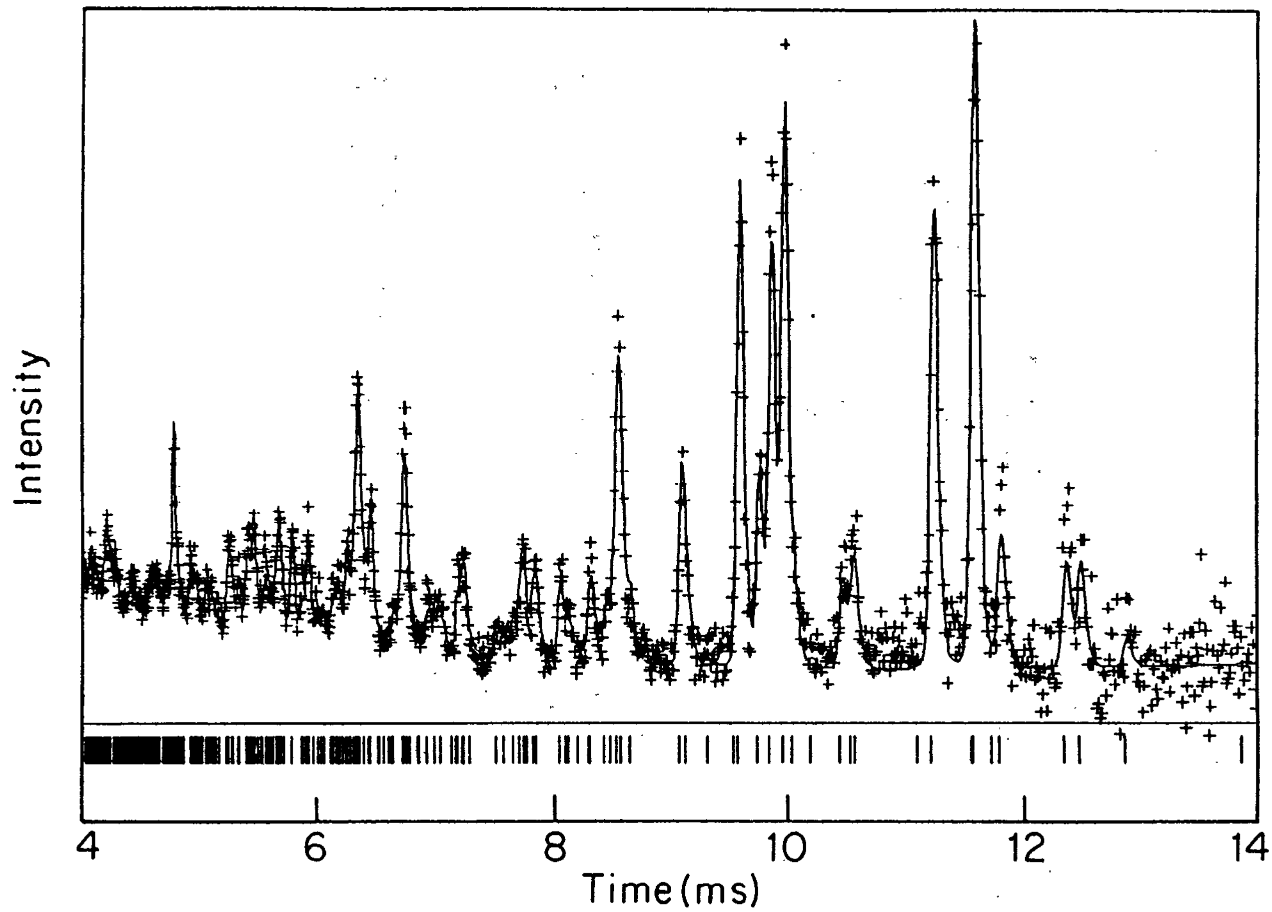


Figure 5 – Rietveld profile refinement of the data collected from $LaNbO_4$ at 20 kbar. The fitted line confirms that no additional peaks are observed from the alumina and other components of the pressure cell.

TABLE 1 – Lattice constants and spontaneous strains of $LaNbO_4$

	0 kbar	10 kbar	20 kbar
a(Å)	5.5600(4)	5.5602(12)	5.5615(8)
b(Å)	5.1963(4)	5.1703(15)	5.1616(10)
c(Å)	11.5067(8)	11.4445(25)	11.4187(20)
γ(°)	85.886(5)	85.505(12)	85.331(9)
V(Å)^3	331.59(5)	327.99(15)	326.70(10)
ϵ_{11}	3.381×10^{-2}	3.634×10^{-2}	3.729×10^{-2}
ϵ_{12}	3.592×10^{-2}	3.925×10^{-2}	4.077×10^{-2}
$\epsilon_{11}/\epsilon_{12}$	0.9413	0.9259	0.9146
ϵ_S	6.976×10^{-2}	7.565×10^{-2}	7.814×10^{-2}

$\epsilon_{11} = (a-b)/(a+b)$, $\epsilon_{12} = \tan(\tfrac{1}{2}(90-\gamma))$, $\epsilon_S = (2\epsilon^2_{11} + 2\epsilon^2_{12})^{1/2}$

TABLE 2 - Bond lengths (Å) in $LaNbO_4$

	0 kbar	10 kbar	20 kbar
Nb - 01	1.917	1.926	1.931
Nb - 02	1.824	1.795	1.781
Nb -01'	2.540	2.508	2.480
Nb - 02'	3.259	3.255	3.257
La - 01	2.484	2.489	2.472
La - 02'	2.464	2.459	2.457
La - 01'	2.553	2.539	2.561
La - 02'	2.513	2.513	2.522

The lattice parameters clearly indicate a volume reduction as a function of pressure. More importantly, however, it is clear that the expected increase in spontaneous monoclinic distortion with increasing pressure is observed. Of especial note is the fact that the length of the a axis actually **increases** with increasing applied pressure. Although the precision of the structural parameter data is modest, because of the low counting statistics in the high pressure data, significant changes in the derived bond lengths (Table 2) are observed. The most marked reduction in bond length with increasing pressure is the Nb–O(1)′ distance, which corresponds to the longest bonds in the distorted NbO_6 octahedron. This has the effect of polarising the four nearest neighbour O^{2-} ions, leading to the observed **increase** in Nb–O(1) distance with pressure. These trends in the observed distortions support the model of the phase transition in $LaNbO_4$ being driven by stereochemical factors related to the oxygen coordination around the Nb anion.

III. VERY HIGH PRESSURES - THE PARIS CELL

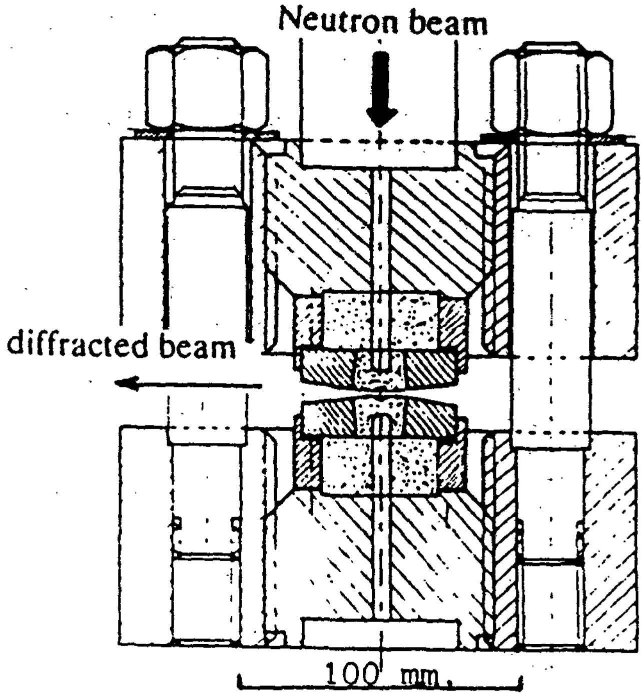
In order to extend the range of pressures accessible beyond the 25 kbar available from the McWhan cell, a collaborative project has been set up between RAL and the Universities of Edinburgh and Pierre et Marie Curie in Paris to develop a cell for very high pressure neutron powder diffraction experiments. The aim of the cell (Figure 6), designed and constructed in Paris, is to reach pressures well in excess of 100 kbar. Performing neutron powder diffraction at such extreme pressures promises to open new, unexplored areas in structural science.

After a considerable amount of development both of the cell itself and regarding its neutronic properties, the first very high pressure experiments have recently been performed on POLARIS.

III.1 Equation of State of ^{7}LiD to 60 kbar

In this experiment, diffraction patterns were measured on POLARIS from 100 mm^3 of a lithium deuteride sample enriched (to 99%) in ^{7}Li, at pressures up to 60 kbar (Besson et al, 1990). NaCl was used as an internal calibrant. From data collected in some 3–6 hours per pressure, cell dimensions were obtained to an accuracy of some 0.001 Å. This enables the volume compression versus pressure curve to be obtained to good accuracy (Figure 7). As can be seen from this plot, the POLARIS data, from both the McWhan (below 25 kbar) and Paris (above 25 kbar) cells, are well explained by the most recent theoretical calculations. These data not only extend the pressure range over previous measurements, but also are significantly more precise.

Figure 6 – Schematic view of the Paris pressure cell



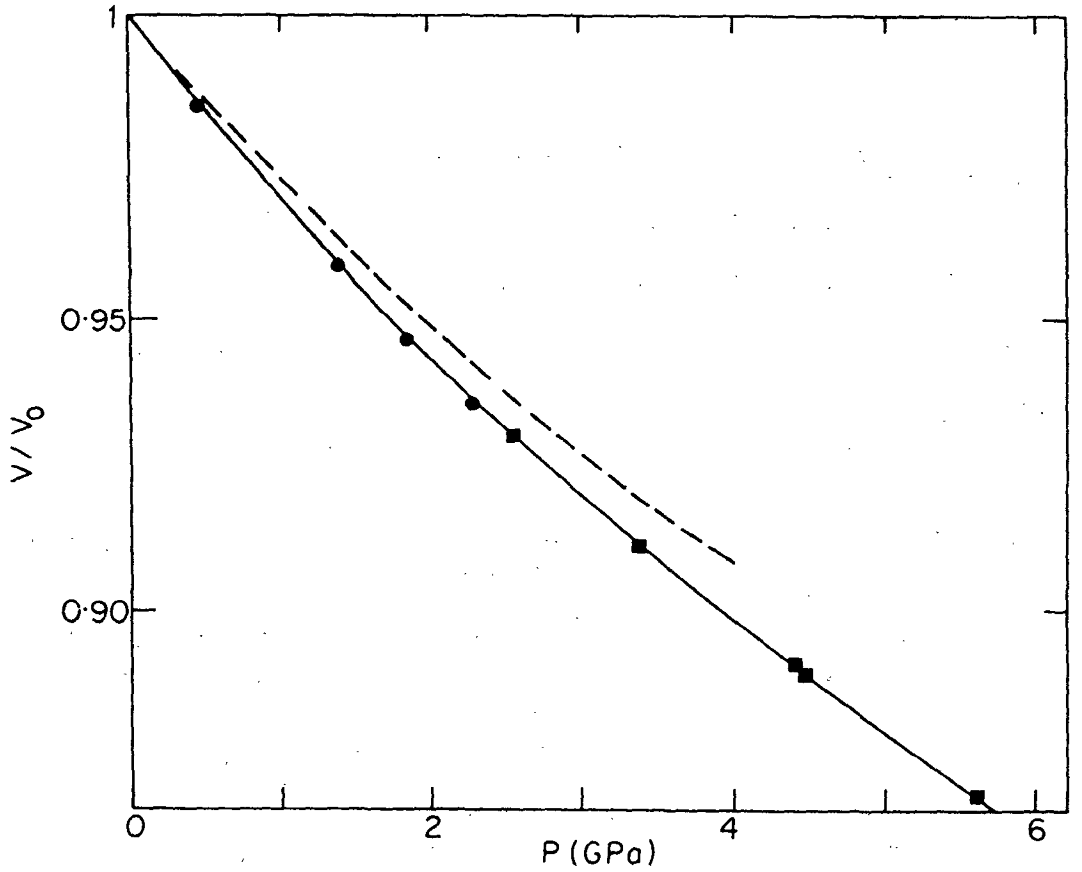


Figure 7 – Equation of state of LiD up to 60 kbar. The circles represent points measured using the McWhan cell on POLARIS, the squares from the Paris cell. The solid line is the best theoretical calculation available to date. The previous available data, represented by the dashed line, are seen not to agree with these recent calculations, whereas the POLARIS data show excellent agreement.

This demonstration of the determination of the equation of state in this fundamental quantum solid illustrates the basic physics one can probe when extremes of sample environment are attained. Pressures of over 100 kbar have already been achieved, and developments on both the Paris pressure cell and on the POLARIS instrument are continuing in an effort to further extend and exploit this new field of study.

IV. CONCLUSIONS AND FUTURE PROSPECTS

Work is expected to continue on both branches of the high pressure powder diffraction work at ISIS, with improvements planned to both the instrument and to the pressure cells. It is hoped to improve the count rate of POLARIS by installing a second 90° detector bank on the opposite side of the sample to that currently used. In addition, the prospect of performing high pressure studies at high resolution should be realised with the installation of a full 90° detector array on HRPD. On the pressure cell side, developments are planned on the McWhan cell to allow pressures up to 35 kbar to be reached, and it is hoped that 150 kbar will be obtained shortly in the Paris cell, with the replacement of the present tungsten carbide anvils by sintered diamond. In conclusion, the first year of high pressure diffraction experiments at ISIS has been rather successful, and has opened up the prospect of increased exploitation of these techniques.

V. ACKNOWLEDGEMENTS

The high pressure programme at ISIS has benefitted substantially from the input of M A Adams and I F Bailey (RAL), S K Paranjpe (BARC), and the groups of R J Nelmes (Edinburgh) and J M Besson (Paris).

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Q(Y.Endoh): The McWhan cell has been readily used for the steady source neutron scattering by opening the window wide. Then what is advantage by using McWhan cell with pulsed sources?

A(C.C.Wilson): Certainly at moderate pressure (~25kbar), the McWhan cell is well-established at steady-state sources. The ability at a pulsed source to use very tight collimation for both incident and scattered beams in a pressure cell experiment should allow the attainment of ultra-high pressures (200kbar), with designs other than the McWhan cell. The Besser/Paris clamped cell is just such a device.

Q(Y.Endoh): If anyone has an experience to use the sapphire anvil technique, I would like to know the pressure value reached.

A(C.C.Wilson): John Finney has used a sapphire anvil cell to about 7kbar.

Q(A.D.Taylor): Do these Besser cells operate at low temperatures other than ambient?

A(C.C.Wilson): Yes, the McWhan cell has operated at low temperature inside an orange cryostat. Also, a cell is in design stage to perform high pressure work at high temperatures at ISIS.