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ILL-ISIS High Resolution Powder Diffractometer Comparison

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The high resolution powder diffractometers D1A and D2B at the ILL, and HRPD at the SNS are complementary in the science they cover. D1A is still one of the best machines anywhere, and is more readily available for longer term users, including industrialists, and urgent experiments such as superconductors. D2B is unique for very high resolution work on complex structures such as zeolite catalysts, magnetic materials and experiments where complete diffraction patterns must be collected in times as short as 15 minutes at many different temperatures. HRPD is unique for the collection of very high resolution data at short d-spacings (for simple structures), for resolving small line splittings at longer d-spacings, and for studies of sample texture. Where they do overlap, mild competition is perfectly healthy in stimulating a better service to users. In fact user demand has strongly increased with the availability of the new diffractometers. This preliminary report compares the advantages of the different machines, and provides some statistics on user demand: for example about 1/3 of all college 5 proposals, which themselves represent 1/3 of all ILL proposals, are in this area.

Introduction

Bragg's law applies to both types of powder diffractometer

$$2d \sin\theta = \lambda$$

For atomic planes of various d-spacing, Bragg peaks are obtained by varying θ with constant wavelength (CW) on D1A[1] and D2B[2], or varing λ with fixed θ (TOF) on HRPD[3]. Resolution is determined by differentiating Bragg's law:

$$\Delta d/d = \Delta\theta \cot\theta$$

High resolution (small $\Delta d/d$) is obtained in both cases with $\theta \sim 90^o$ (backscattering).

Resolution

Resolution is ultimately determined by the powder particle size, and both D2B and HRPD have been designed to achieve $\Delta d/d = 5x10^{-4}$ with perfect samples. Fixed backscattering geometry is en principe an advantage for the variable λ TOF machine, but very long wavelengths $\lambda = 2d$ (20Å or more) are then needed, especially for magnetic structures (equation 1). There are few neutrons at such wavelengths on a pulsed source. Of course, low angle detectors may also be used on the TOF machine, but the detector solid angle is then greatly reduced for high resolution (next section).
The resolution of the reactor machine is well matched to the density of peaks at all scattering angles.

Intensity

Jorgensen et al.[4] have made order-of-magnitude intensity comparisons, from which it results that the counting efficiency is in both cases

$$E = \varphi_S V_S \Omega$$

where φ_S is the time averaged flux at the sample
V_S is the sample volume
Ω is the detector solid angle

Since $\Delta\theta$ may be quite large, the backscattering TOF machine can use a position sensitive detector with an order of magnitude larger solid angle Ω than the collimated multidetector D1A /D2B. Sample volumes are similar. However, this advantage is cancelled by the fact that the time-averaged flux on the sample may be an order of magnitude larger on the best reactor (10^7 n.cm^{-2}.sec^{-1}) compared to the best pulsed source (10^6 n.cm^{-2}.sec^{-1}). Even on a pulsed source, φ_S is (almost) constant with time, the slowest neutrons arriving just before the fastest from the next pulse: the high instantaneous pulsed source flux is then averaged over the cycle time. On a reactor, φ_S is increased using large focussing monochromators, and $\Delta\lambda/\lambda$, determined by the monochromator mosaic, may be much larger than $\Delta d/d$, limited by the detector collimation. Optimum φ_S has not yet been obtained on either HRPD or D2B.

Consequences

The preceding paragraphs should serve merely as a warning that simplistic theoretical arguments about the relative advantages of the TOF and CW methods may not apply in practice. There is no order-of-magnitude advantage for one machine or the other.

Standard Al_2O_3 sample

Al_2O_3 has a very simple structure, and an 'ideal' standard sample has been run on all diffractometers. Figure 1a shows the comparison between the new ILL machine D2B, and the old machine D1A (insert). Clearly D2B has much better resolution. It is also faster - the complete diffraction pattern was collected in only 100 minutes, or 15 minutes with resolution similar to D1A. Figure 1b shows the same sample on the new ISIS machine HRPD, compared to the old Argonne machine GPPD (insert). HRPD represents a big improvement.
For such a simple structure, the data can be usefully extended to shorter d-spacings on HRPD than on D2B, but the actual refinement of the structure is still probably best done on D1A ! It is more difficult to fit higher resolution patterns.

Figure 1a.

Al_2O_3 standard on D2B (D1A inset) -ILL

(*) Note that the 3 D1A lines are resolved as 4 on D2B

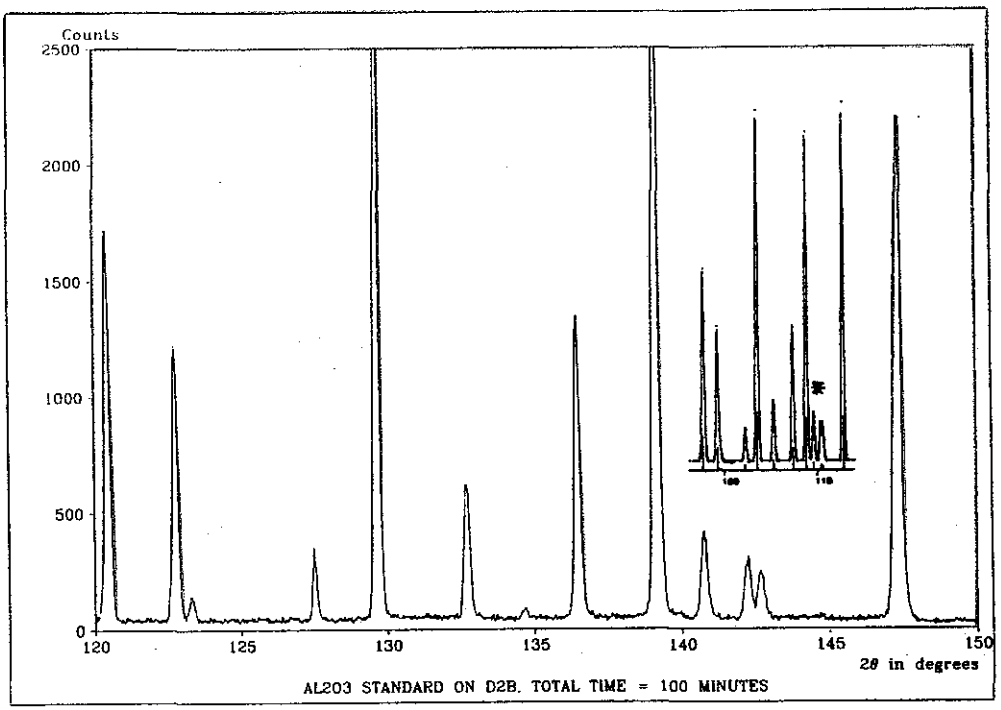
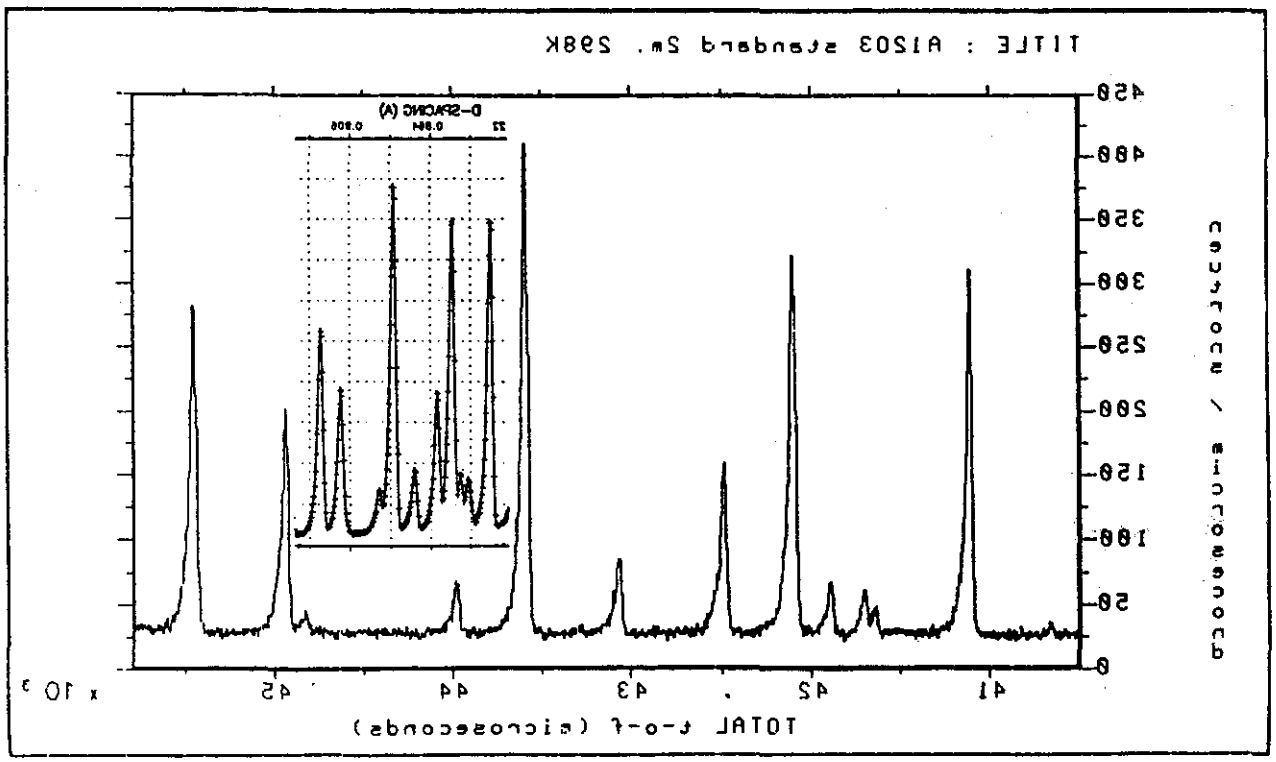


Figure 1b.

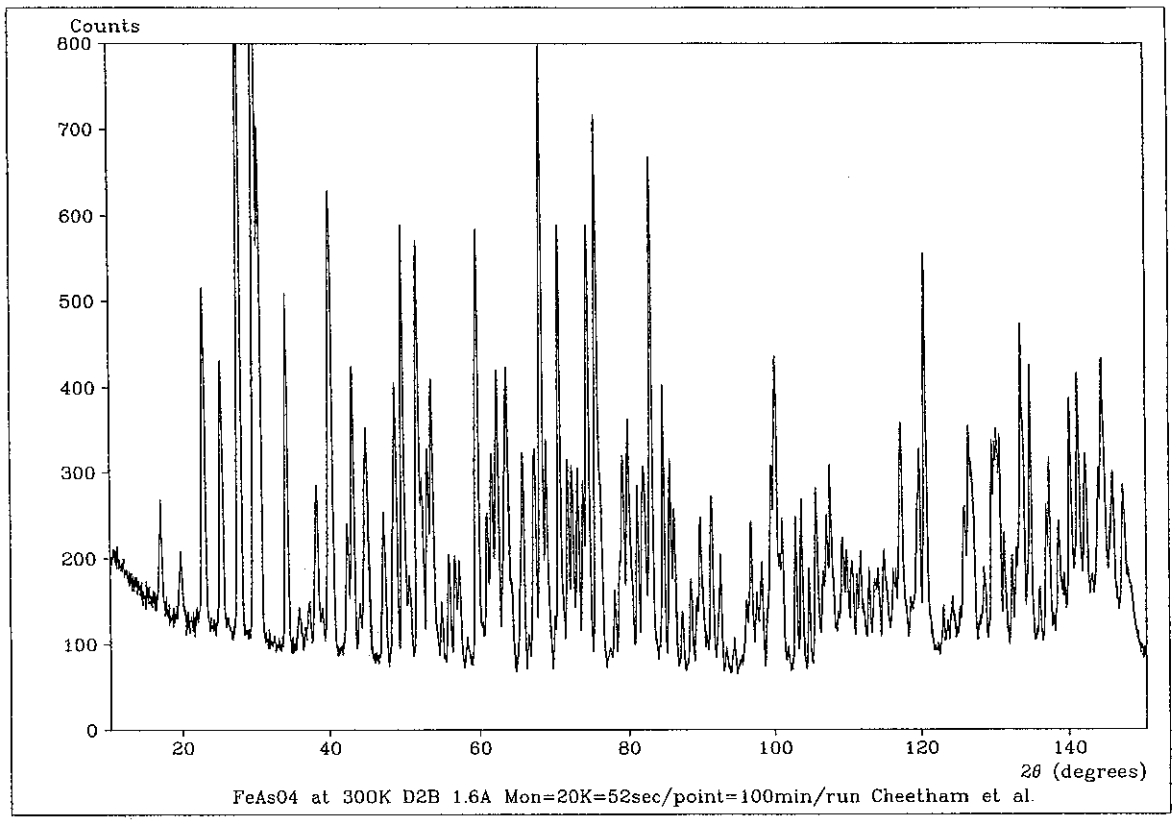
Al_2O_3 on HRPD (GPPD inset) -RAL

The plot has been inverted for comparison with reactor machines

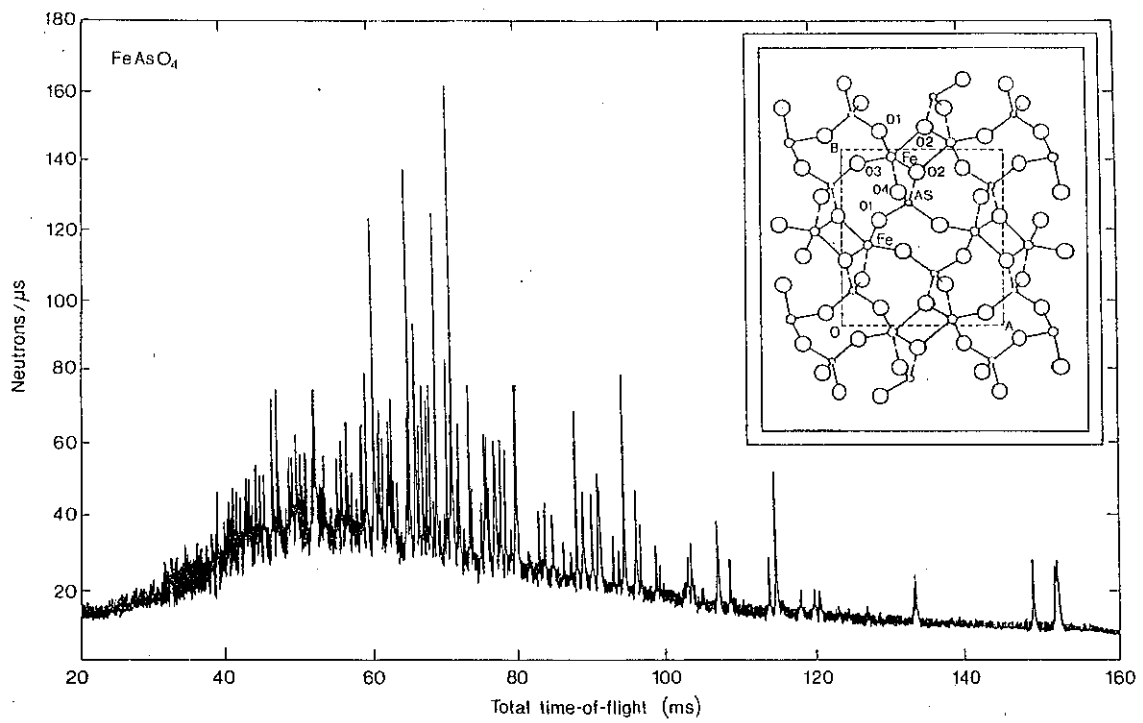


Crystal Structure determination by Powder Diffraction of $FeAsO_4$.

Cheetham et al.[5] have recently published a very interesting example of the potential for direct solution of crystal structures from high resolution powder data. The interest of this paper lies in the techniques used rather than the example itself, and the method is probably more applicable to synchrotron radiation than to the HRPD neutron data used. However, the same $FeAsO_4$ sample has been run on D2B (fig.2a) for comparison with the published HRPD results (fig.2b). In both cases, the raw data without any corrections or 'normalisation' is presented, and in both cases the number of resolved Bragg peaks is impressive.

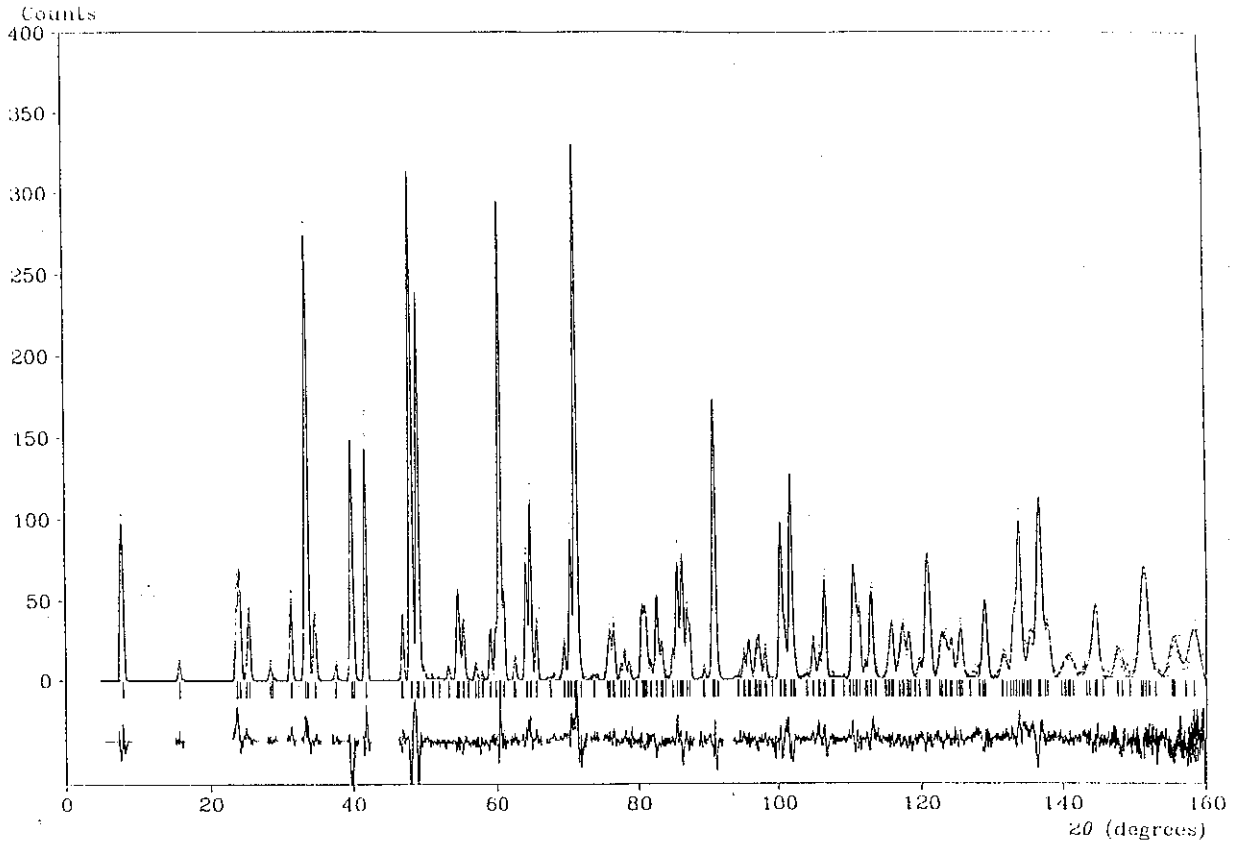


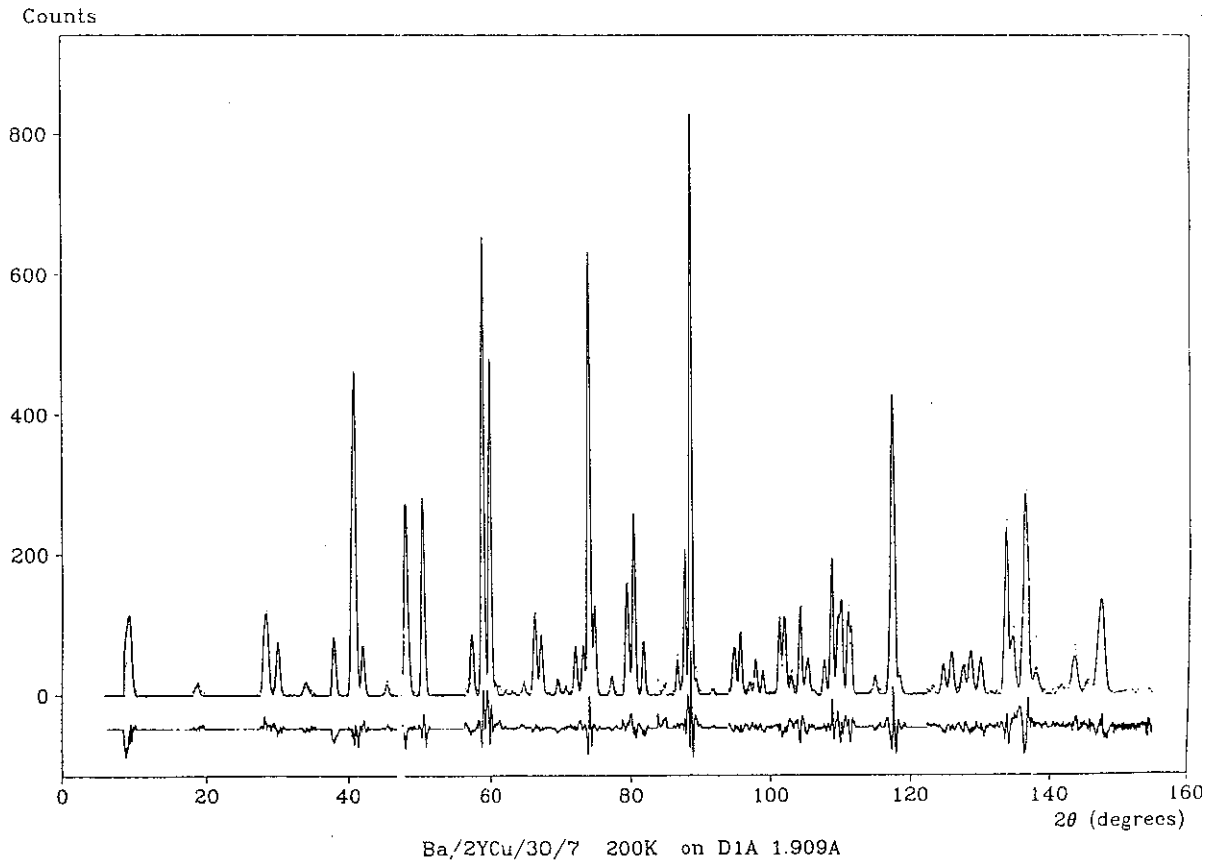
A K Cheetham, W I F David, M M Eddy, R J B Jakeman, M W Johnson, and C C Torardi, Nature **320** 46 (1986)



High Tc Superconductors $YBa_2Cu_3O_7$ on D1A/D2B

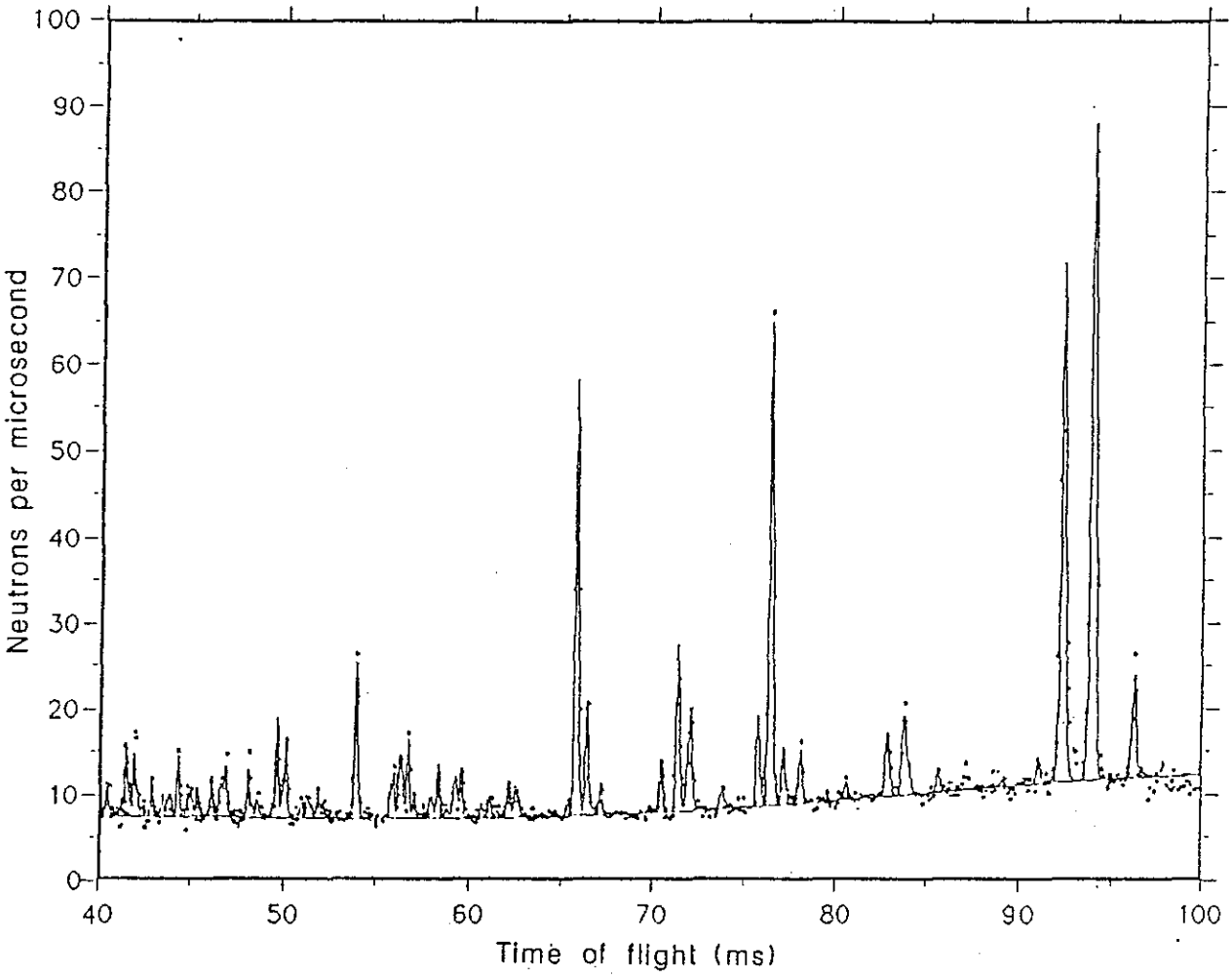
These materials are more typical of real samples, and again they have been run on all diffractometers. Figure 3a shows published D2B data[7] obtained in the 'low' resolution mode to permit rapid data collection at many different temperatures compared to the first published D1A pattern[6] in figure 3b.





High Tc Superconductors $YBa_2Cu_3O_7$ on HRPD

Figure 3c shows comparable results published on HRPD[8]. It is disappointing that no real improvement on D1A was obtained with the higher resolution machines. In fact the best structure *refinements* were probably obtained on D1A, and on a 'D1A clone' on the NBS Washington reactor.



User Demand for High Resolution Powder Diffraction

The table opposite shows the number of ILL proposals for use of D1A/D2B at the last four Science Council meetings. These instruments alone represent 10% of all ILL proposals, although there is only one ILL scientist responsible for this area. The availability of HRPD at ISIS has had no obvious impact on the demand for ILL beam time.

Proposals	1986 Mar	1986 Oct	1987 Mar	1987 Oct
D1A/D2B	56	52	41	55
ILL Total	605	532	520	579

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