Cold Neutrons on Pulsed Sources for High Resolution Spectroscopy and Long d-spacing Diffraction

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Abstract

Using the IRIS spectrometer on the ISIS pulsed neutron source as an example it is demonstrated that, in the area of cold neutron production, the present generation of pulsed sources and their instruments can produce fluxes and count rates which are at least equal to those of the most powerful reactors. This is contrary to the generally accepted view and therefore is important when sources such as the European Spallation Source and AUSTRON are being considered by funding bodies. The instrumentation on pulsed sources can be quite novel, leading to new scientific applications, and there is still an immense amount of potential for instrument development which has not yet even been glimpsed.

Introduction

Cold neutrons have traditionally been defined as those which will pass relatively unattenuated through a polycrystalline beryllium block beyond its Bragg edge. Beryllium was often used in order to filter out of a reactor beam the long wavelength or cold neutrons. Conveniently this means that those neutrons whose wavelengths are longer than 4Å, whose energies are greater than 5meV and whose reciprocal velocities exceed 1000μsec/metre (i.e. velocities less than Mach 3) are defined as *cold*. In an ambient temperature research reactor the flux of such neutrons is relatively low and not until low temperature "cold moderators" were installed in reactors could the use of cold neutrons for scattering experiments be properly developed. These cold moderators (hence the name cold neutrons) were normally composed of liquid hydrogen or deuterium and served to shift the peak of the Maxwell-Boltzmann spectrum to lower energies.

Their early development was a strictly European venture, taking place in the late 1950's and early 1960's at laboratories such as Mol, Saclay, Jülich and Harwell. The availability of intense cold neutron beams led directly to significant progress in instrumentation in Europe which resulted, for example, in the development of neutron guides, and the exploitation of small angle scattering and high resolution time of flight and backscattering spectrometers by the physics and, significantly, the chemistry community. These instrumentational advances can now be seen as milestones on the road to the building of the Institut Laue-Langevin with its strong emphasis on the imaginative use of cold neutrons and its resulting *flagship* status in neutron scattering world-wide during the 1970's and 1980's.

During this period the perceived saturation of technological advances in the development of reactors led to a revival in interest in accelerator-driven pulsed neutron sources, which promised higher effective fluxes than reactors, in the U.S.A., Japan and the U.K. This led to the building of IPNS at Argonne, LANSCE at Los Alamos, KENS at Tsukuba and ISIS at Rutherford. ISIS has been operating now for seven years and has reached its design goal: 200uamps of 800MeV protons at 50 Hz which yield a fast neutron source flux of 3×10^{16} n/sec ISIS is recognised as the premier pulsed source in the world, standing side by side with ILL as two of the world's leading neutron scattering laboratories.

Experience on pulsed sources in the late 1970's when ISIS was being designed, was very limited and it was inconceivable then that it, or indeed any pulsed source, could challenge the supremacy of ILL in the cold neutron field. Accordingly pulsed sources, with their harder fast

neutron source fluxes and undermoderated slow neutron fluxes, were seen primarily as sources of epithermal neutrons and therefore as being naturally complementary to reactor sources.

Comparisons on paper of pulsed sources and reactors are fraught with difficulty as is any simplistic comparison of basically dissimilar objects. Although more complex algorithms have been developed, the enduring *performance indicator* for a reactor is its time-averaged flux and for a pulsed source its peak flux, and a comparison of these two quantities provides a broad-brush indication of relative instrument performance. These single numbers cannot represent the full story, and there are examples which run counter to it, but they are generally realistic.

The liquid hydrogen moderator on ISIS was designed at a time and in a climate when little could be reliably predicted about the performance of pulsed source instruments and cold neutrons instruments on pulsed sources were foreseen at best as providing local facilities for testing out and selecting those experiments which could be better done on high flux reactors. Accordingly the liquid hydrogen moderator was situated downstream on the ISIS target in the lower fast neutron flux position with a flux penalty, in comparison to the prime moderators, approaching a factor of two.

Therefore, if we take the published average and peak fluxes of ILL (1) and ISIS (2) respectively, we can produce a performance ratio which does indeed show, in figure 1, an increasing advantage of pulsed sources as neutron energy increases, approaching a factor of 100 at 1eV. What is surprising however is that the crossover between reactors and pulsed sources occurs well into the cold neutron regime, at a neutron energy of 3meV (or 5Å wavelength). If the ISIS hydrogen moderator were to have been situated in an upstream position this crossover would have occurred at 1meV (or 9Å wavelength).

Clearly the only proper method to compare instruments and sources is by scientific output and enough experience has now been gained to do this, even though it is still early days for the blossoming techniques of pulsed neutrons. We will illustrate the power of cold neutrons on pulsed sources by reference to the high resolution spectrometer and long d-spacing diffractometer IRIS (3) currently operational at ISIS.

The IRIS Instrument

High resolution incoherent neutron spectroscopy is used for the study of diffusional processes in a wide variety of materials ranging from hydrogen in metals and superionic conductors to liquid crystals and

biological materials such as tRNA. The technique is also widely used for the study of quantum tunnelling processes in molecular crystals, crystal field splitting in magnetic materials, including high T_c superconductors, and dispersion curves in quantum fluids such as helium. The demand for such instruments is high, partly because their capabilities appeal to a broad distribution of specialities, and such measurements continue to expand into new areas of science. High absolute resolutions in the μeV range are achieved by using slow (i.e. cold) neutrons when small changes in the neutron's energy can be detected with high accuracy.

Energy analysis of a neutron beam by Bragg reflection from a single crystal is a common procedure used, for example, in triple axis spectroscopy. When the Bragg angle is increased towards 90° the energy resolution becomes extremely good, limited only by the uncertainty in d-spacing of the crystal itself. Therefore backscattering analysers have been used to achieve the highest direct resolutions yet reached in neutron spectroscopy - 0.3 μeV. The neutron energy of the incident beam can be scanned by a number of different methods. In the earliest instruments Döppler shifting of the monochromatic beam reflected from a silicon crystal, again in backscattering geometry, was used. This method was developed at Munich and Jülich before being incorporated into the IN10 backscattering machine at ILL. A later development of this method was to scan the temperature of the backscattering monochromator thereby using the expansion of the lattice parameter to select a continuous range of energies. On pulsed sources the incident beam is naturally energy-sorted when observed some distance from the moderator. The further from the moderator, the higher the resolution achievable and this is the method used on the IRIS spectrometer to obtain high resolutions.

The energy transfer range ΔE accessible by Döppler shifting is quite limited because of the ultimate strengths of materials to withstand the high accelerations. Typically $\Delta E \sim 0.015 E_a$. For temperature scanning the energy transfer range is higher, but limited to $\Delta E \sim 0.06 E_a$ by the coefficients of expansion and melting points of most materials. Scanning the incident energy by time-of-flight however, as is done on pulsed source instruments, gives a higher accessible energy transfer range because of the ability to dispense with a crystal monochromator. In this case the energy transfer range is typically $\Delta E \sim 0.6 E_a$.

The IRIS instrument is fully described in reference (3). IRIS views the liquid hydrogen moderator on the ISIS pulsed neutron source. The incident beam is transported by a curved neutron guide to the sample position about 36 metres from the moderator. Overlap of neutrons from pulse to pulse is avoided by the use of two disc choppers situated

close to the target station. The second disc chopper serves to eliminate ISIS pulses thus allowing very long wavelengths to be used. The neutron guide terminates in the analyser tank with a 2.5 metre long supermirror converging guide, which increases the flux on the sample by a factor close to 3. The guide is well shielded along its full length and earlier anxieties about the contamination of the beam with very energetic spallation neutrons have been shown to be unfounded. The beam at the sample position can be stopped by a sheet of cadmium. The sample sits in the white beam delivered by the guide. Scattered neutrons are analysed by two arrays of analyser crystals - pyrolytic graphite and mica - on either side of the 2 m diameter analyser vacuum tank. The analyser crystals are close to backscattering geometry to benefit from the optimum resolution of this geometry but sufficiently offset (θ_B=87.5°) to install a large number of detectors (51 on each side) and to avoid the need for a beam modulation chopper in the incident beam (as on IN10 and IN13 at ILL) to discriminate against neutrons scattered directly into the detectors. This latter measure improves the usable flux on the sample by a factor of 2.5. Resolutions of 15 and 50 μeV are available with the pyrolytic graphite analysers and 11, 4 and 1 μeV with the mica analysers. The 1 μeV resolution uses neutrons of 20 Å wavelength. The 2.25 metre-long graphite analyser has been cooled to 25K resulting in a ten-fold reduction in background from Thermal Diffuse Scattering (TDS).

At scattering angles around 170° a small 10-tube diffraction detector is installed. This facility was included to allow the crystallographic phase of the sample under spectroscopic study to be monitored during measurements. It has proved to have important consequences when studying unique samples prepared in-beam or samples in unusual sample environment conditions (such as high pressures) where unexpected crystallographic changes can occur. *Simultaneous* dynamic and structural measurements of equal quality can therefore be carried out. Equally well the diffraction capability can be used in its own right for long d-spacing diffraction with very good resolution. The resolution is constant at 2.5 10^{-3} in $\Delta d/d$ over a d-spacing range from 2 to 12 Å using neutrons with wavelengths out to 24Å. A diagram of the IRIS analyser tank is shown in Figure 2. In order to emphasis the intense cold fluxes coming from the ISIS hydrogen moderator a plot of the flux at the sample position for both IRIS and the high resolution powder diffractometer is shown in figure 3. The λ^4-dependence of the structure factor for Bragg scattering means that, even though the flux is falling considerably beyond 10 Å on IRIS, the detected data rate is still acceptably high.

Scientific Examples

The scientific programme of the instrument is very broad but this can be illustrated with the aid of a few examples.

More than half the work done on the instrument is carried out using the graphite analysers at 6.7Å where the flux delivered by the guide is highest. Nevertheless the very long wavelength neutron flux is remarkably intense. Since this is the precise wavelength range in which pulsed sources are thought *not* to perform well (or even at all), all examples will be taken from this range. It is particularly important when considering instrument designs for AUSTRON that they are assessed taking advantage of the latest developments on pulsed sources rather than relying on outdated notions.

Nitromethane CH_3NO_2 represents one of the most well-studied materials by tunnelling spectroscopy. It contains only one type of CH_3 group in the orthorhombic unit cell having space group $P2_12_12_1$ and 4 molecules per unit cell. Thus the tunnel spectrum contains one single line. The profile is resolution limited, which is interpreted as meaning that direct methyl-methyl interactions are negligible. This sample was re-examined using the mica (002) reflection on IRIS to investigate the feasibility of this instrument option for tunnelling spectroscopy. The resolution of 1.2 μeV is attained using very slow neutrons (19.8Å or 208 μeV) which consequently provides low momentum transfers Q from 0.1 $Å^{-1}$ to 0.6 $Å^{-1}$ where form factors can be low. The spectrum is shown in figure 4 where a sharp single line spectrum is clearly seen at 35.4 μeV, broadened by about 1.5 μeV.

Quasielastic scattering spectroscopy is ideal for the study of random translational and rotational diffusive motions in solids and liquids on a time scale between 10^{-9} and 10^{-12} s. Because of the high incoherent cross-section of hydrogen, hydrogenous organic materials and hydrogen-containing samples, in general, have benefited from this technique. Some studies of the diffusion of other atoms such as silver and sodium are feasible but only very few have successfully been carried out. A recent experiment (4) on IRIS has observed what may be the lowest diffusion constant observed with neutron quasielastic neutron scattering, 3.1 10^{-8} cm^2/s. A sample of sodium silicate glass was studied as a function of temperature, again using the mica (002) analysers, and line broadenings of 0.1 to 0.5 μeV were observed at low Q in exact agreement with macroscopic tracer measurements of the sodium self-diffusion. The data is now being analysed to determine the precise details of the diffusional jumps. This experiment was served by a fair degree of serendipity since the sample has a high coherent scattering

cross-section which ought to have drowned the relatively weak incoherent cross-section of sodium. Because of the long wavelength used however, the Q-range of the measurement was well below the first peak of the coherent structure factor so that no contamination was present in the data.

Small molecules such as hydrogen, methane and ammonia will absorb, in an apparently continuous and non-stoichiometric manner, into the large two-dimensional galleries in graphite intercalation compounds. In the second stage caesium compound (two layers of graphite and one layer of caesium) ammonia chemically binds to the caesium atom, in what is thought to be a tetrammine molecule. Thermodynamic limits on gas uptake also point to a $Cs(NH_3)_4$ molecule and this is consistent with the evolution of the tunnelling spectra with ammonia concentration, and the simultaneous high resolution neutron diffraction studies. The inelastic spectra out to an energy transfer of 2meV and the diffraction pattern in the region of the *(003)* interplanar reflections were studied simultaneously using IRIS (5). The data are shown in figure 6 as a function of NH_3 concentration up to 1.9 molecules of ammonia per caesium atom. The diffraction patterns show that the absorption process is not continuous as might be inferred from the thermodynamic data. Instead there exist at least two well-defined intermediate phases with distinct c-axis swellings and probably more, and these phases coexist over wide concentration ranges.

The inelastic spectra show a similar variation of distinct features with ammonia concentration and these features can be directly linked to the changes in the structure indicated by the diffraction data. The conclusion that there is a direct causal link between the structural evolution of the absorption process and the dynamical behaviour of the NH_3 groups is clearly valid when simultaneous measurements are carried out.

There are a wide range of experiments which can benefit from the extended d-spacing coverage which can be accessed using long wavelength time of flight diffraction with good resolution. These include the investigation of superstructures in ordered magnetic materials, the study of large unit cell organic samples such as clathrated compounds and biomolecular materials, and the study of certain materials in massive sample environment equipment such as pressure cells, where it is possible to measure beyond the Bragg edge of the materials surrounding the sample. An example is the study of magnetic ordering in ferric vanadate $FeVO_4$ (7) which exhibits two ordering transitions at low temperatures (9.5K and 14.5K). A temperature scan

of the diffraction pattern from 4K to 20K in Fig 7 shows the onset of ordering in both phases and the disappearance of all magnetic Bragg lines above the second transition temperature. In similar measurements split lines at 11.9Å, using almost 24Å neutrons, have been clearly observed, underlining the need for such resolutions at long d-spacings.

Conclusions

Cold neutron intensities on pulsed sources, in contrast to the accepted view only 2 or 3 years ago, have been demonstrated to be very high and data rates on high resolution spectrometers are at least as high as those available on the best reactor-based instruments. Unique instrumentation providing simultaneous diffraction capabilities or long d-spacing diffraction, and white beam reflectometry can and has taken advantage of these fluxes. More significantly this demonstration shows that pulsed neutron sources have the potential to be complete neutron sources and not just speciality generators of thermal and epithermal neutrons. This has important consequences as decisions are taken on the next generation of neutron sources in Europe such as the European Spallation Source, ESS, and AUSTRON.

References

(1) "A Guide to Facilities at the ILL" The ILL yellow book. B Maier and H Blank ILL Scientific Secretariat.

(2) A D Taylor Rutherford Appleton Laboratory report RAL-120-1984

(3) C J Carlile and M A Adams Physica B 182 (1992) 431

(4) D Beyer, Ch Kaps, C J Carlile and R Hempelmann Z für Physik 1993 (submitted)

(5) C J Carlile, I McL Jamie, G Lockhart and J W White, Mol. Phys. 76 (1992) 173

(6) J B Forsyth, C Wilkinson and C J Carlile to be published.

Figure Captions

Fig 1. A comparison of the peak fluxes at ISIS with the average fluxes at ILL

Fig 2. The IRIS analyser tank showing the two sets of analyser/detectors and the diffraction detector at high scattering angles.

Fig 3. The flux at the sample position as a function of neutron wavelength on the IRIS spectrometer and the HRPD diffractometer on the ISIS pulsed source. IRIS views the 20K hydrogen moderator and HRPD views the 120K methane moderator.

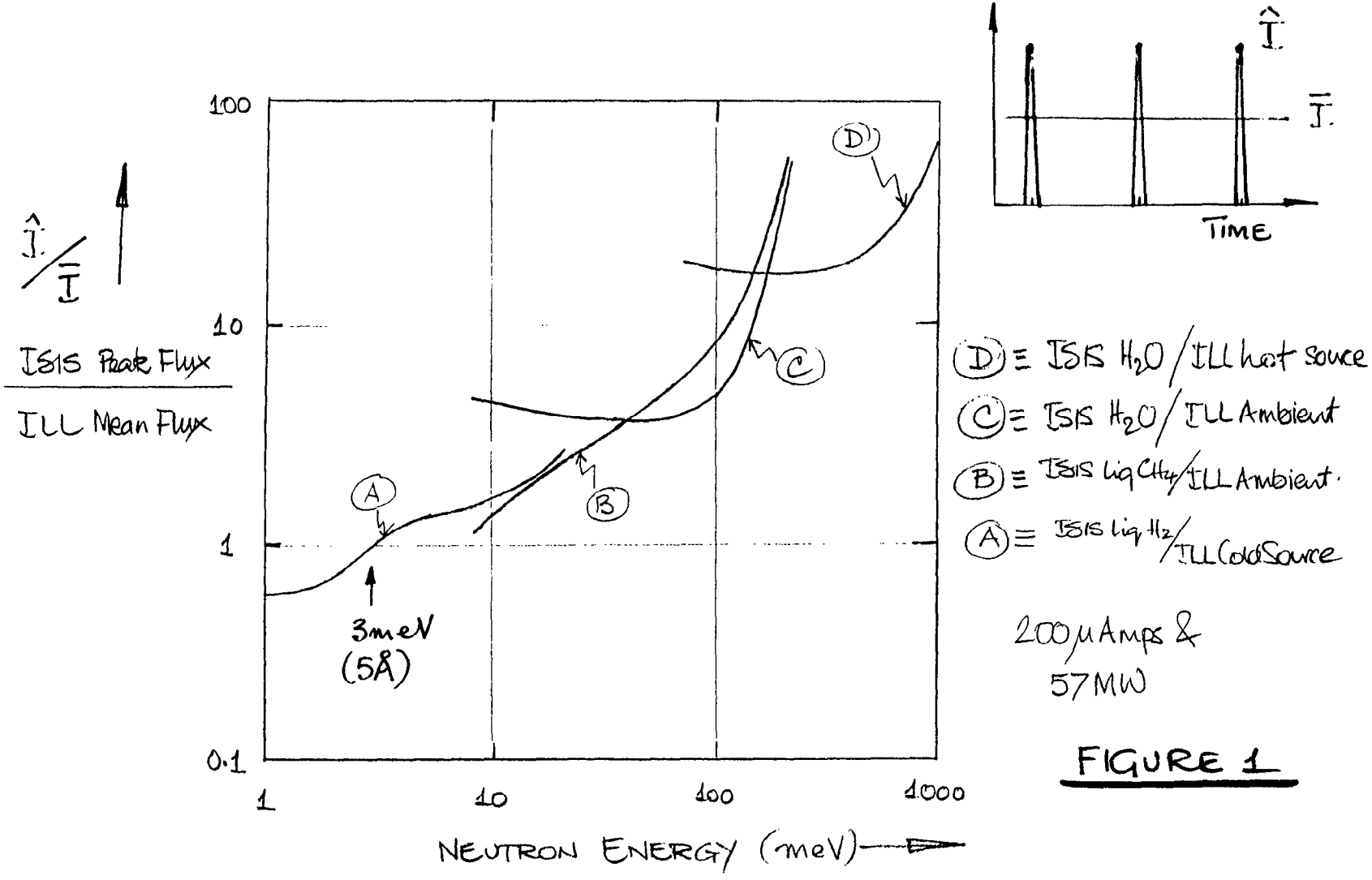
Fig 4. Tunnelling in nitromethane measured using the mica (002) analyser with a resolution of 1.2 μeV at a final analysed wavelength of 19.8 Å.

Fig 5. The diffusional broadening in sodium silicate glass caused by the self-diffusion of sodium.

Fig 6. Simultaneous diffraction patterns around the *(003)* reflection, and tunnelling spectra from $C_{28}Cs(NH_3)_x$ as a function of NH_3 concentration x showing the parallel evolution of structural and dynamic features.

Fig 7. The onset of magnetic ordering in Ferric Vanadate using cold neutron diffraction showing the two phase transitions at 9.5K and 14.5K.

ISIS Peak Flux / ILL Mean Flux as Function of Energy



(D) ≡ ISIS H_2O / ILL hot source

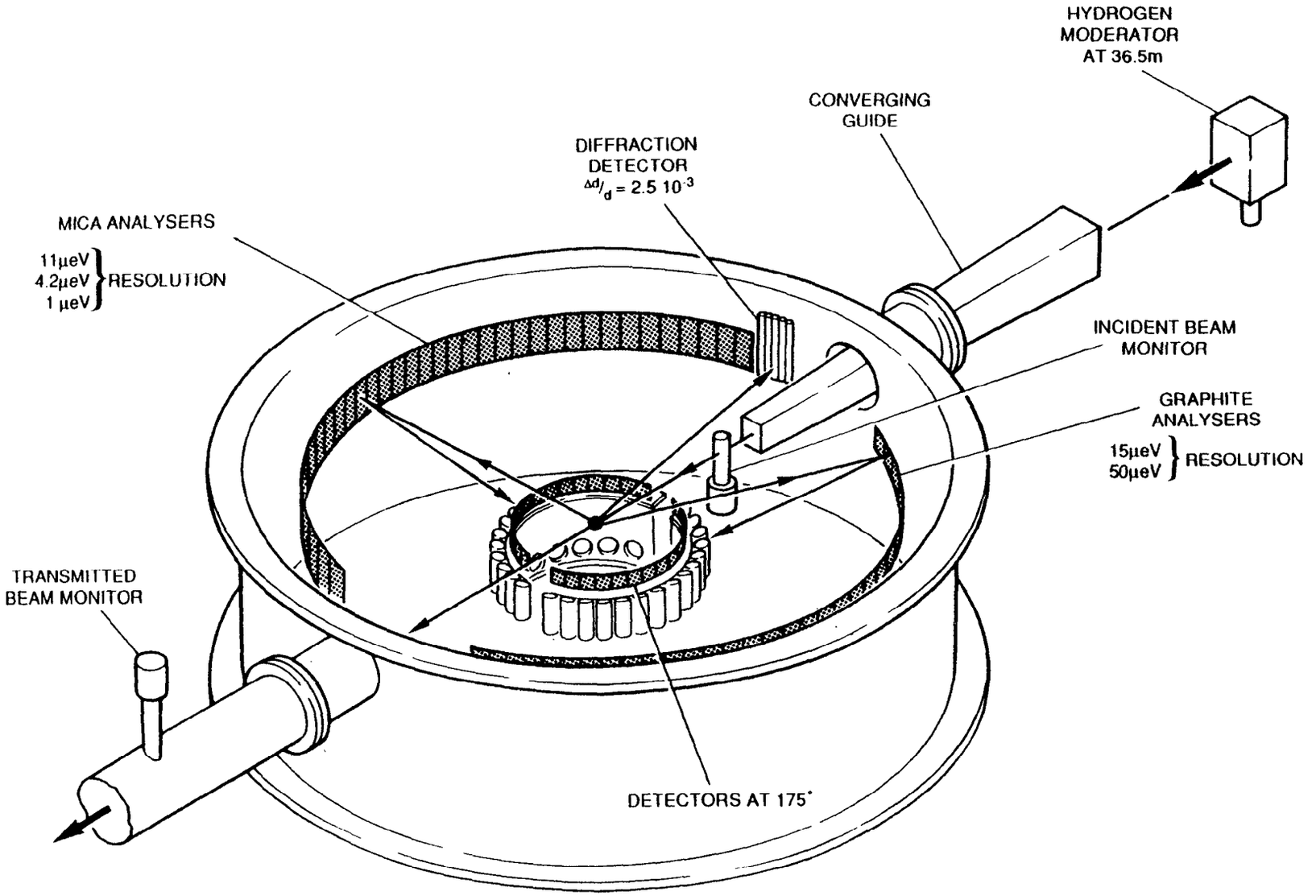
(C) ≡ ISIS H_2O / ILL Ambient

(B) ≡ ISIS Liq CH_4 / ILL Ambient.

(A) ≡ ISIS Liq H_2 / ILL Cold Source

200 μAmps & 57MW

FIGURE 1



THE IRIS SPECTROMETER

FIGURE 2

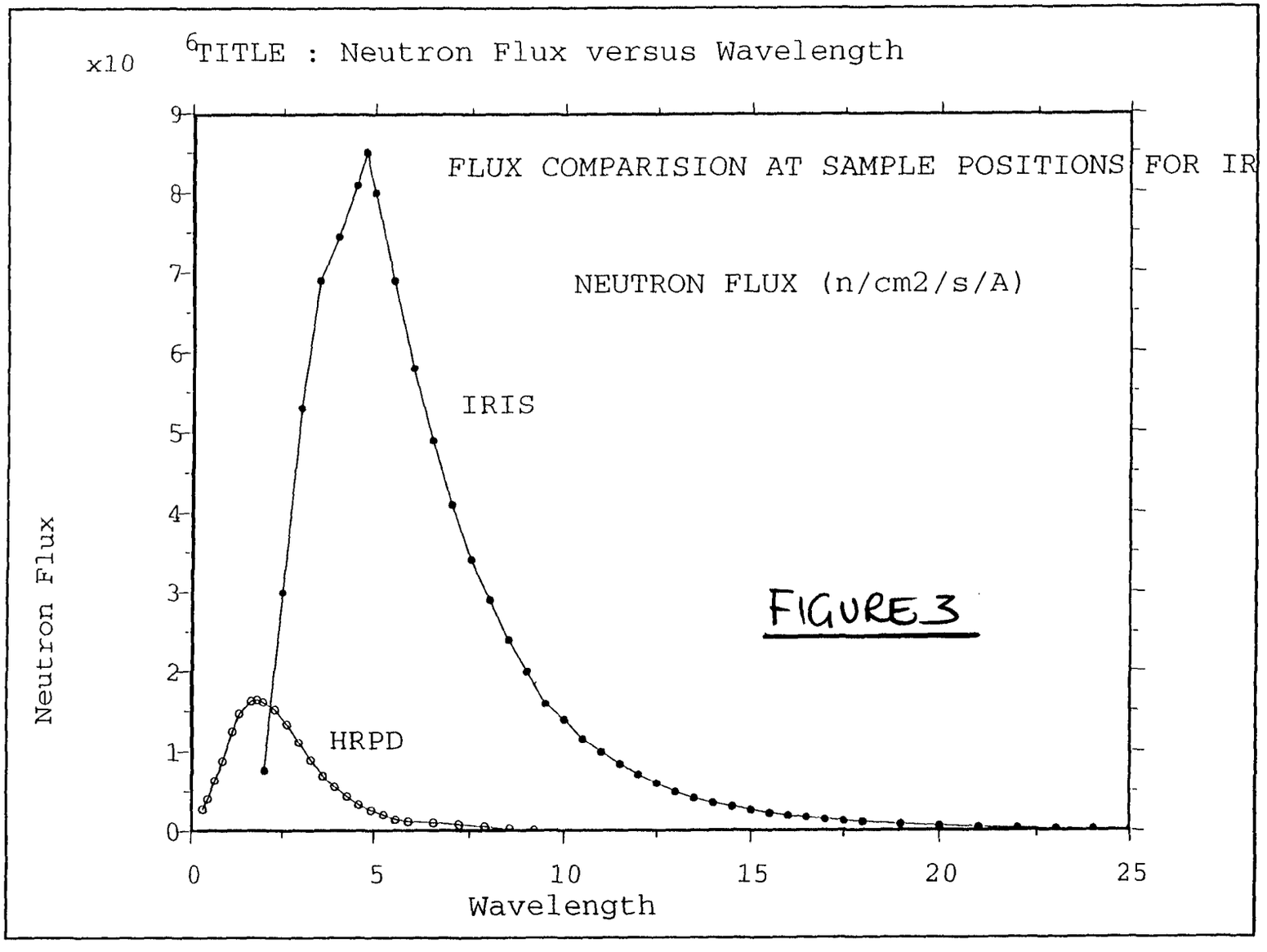
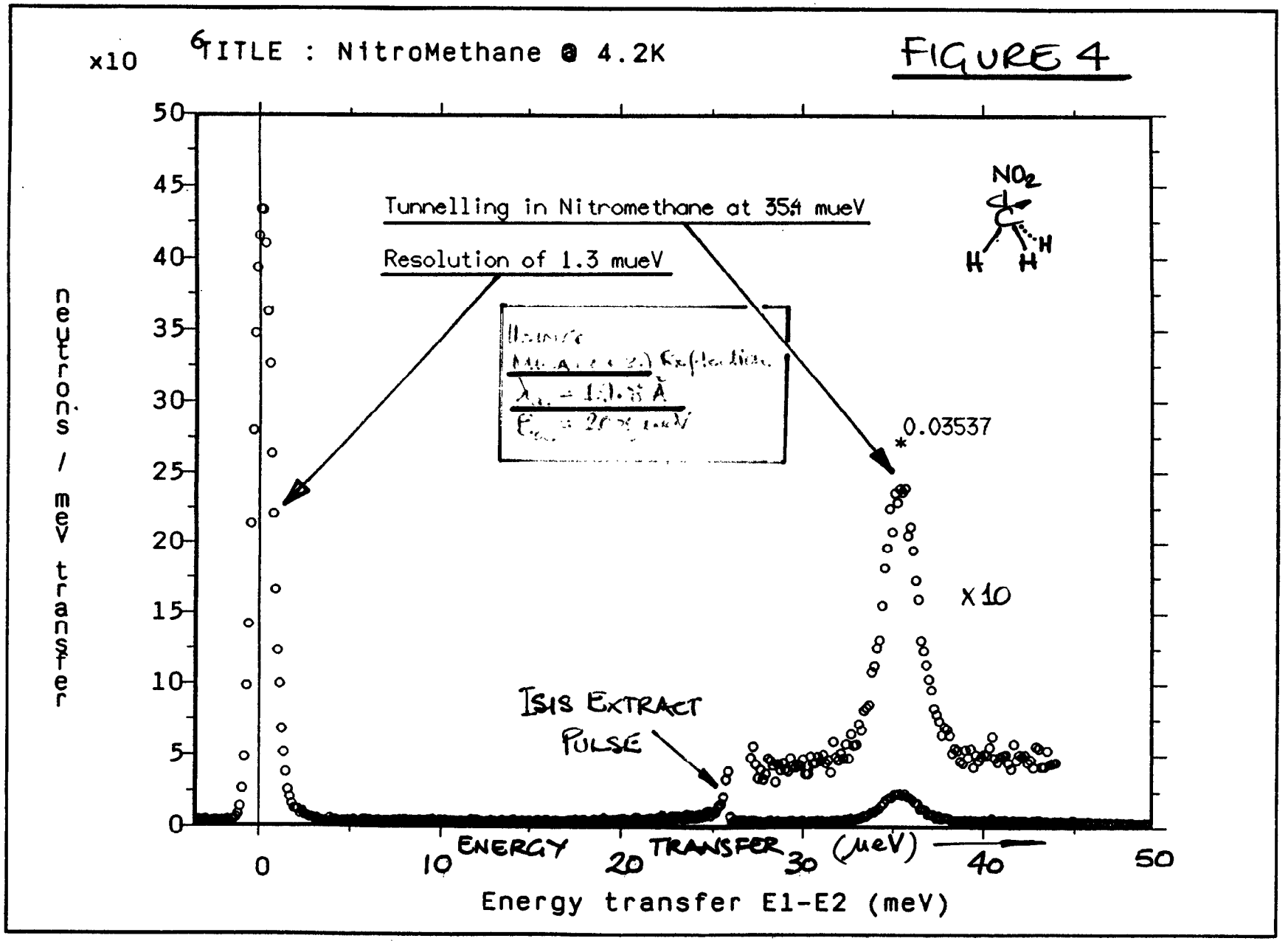
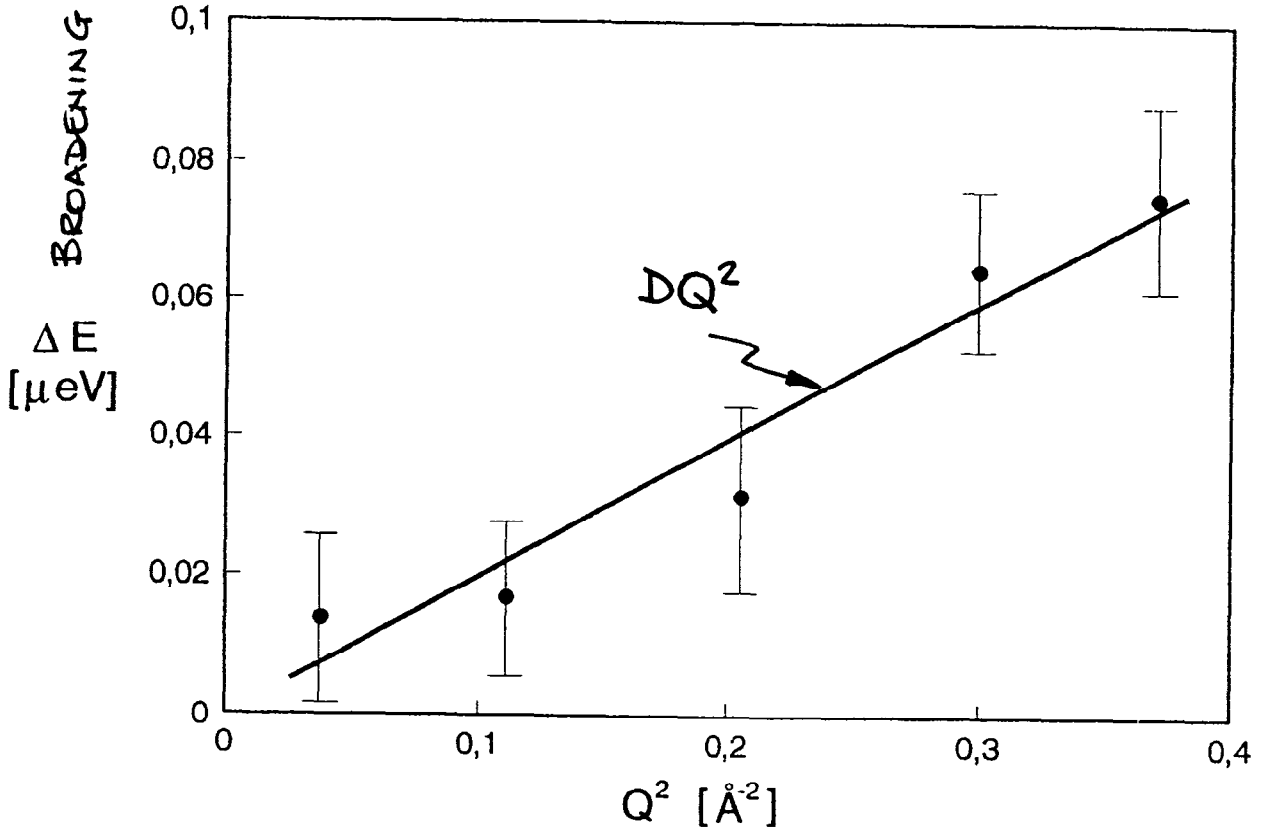

x10 6
TITLE : Neutron Flux versus Wavelength
FLUX COMPARISION AT SAMPLE POSITIONS FOR IR
NEUTRON FLUX (n/cm2/s/A)
IRIS
HRPD
Neutron Flux
Wavelength
0
1
2
3
4
5
6
7
8
9
0
5
10
15
20
25

FIGURE 3


x10
TITLE : NitroMethane @ 4.2K
FIGURE 4
Tunnelling in Nitromethane at 354 mueV
Resolution of 1.3 mueV
NO2
H
H
H
0.03537
x10
ISIS EXTRACT PULSE
neutrons / mev transfer
ENERGY TRANSFER (meV)
Energy transfer E1-E2 (meV)
0
10
20
30
40
50
5
15
25
35
45


BROADENING
ΔE
[μeV]
0,1
0,08
0,06
0,04
0,02
0
DQ²
0
0,1
0,2
0,3
0,4
Q² [Å⁻²]

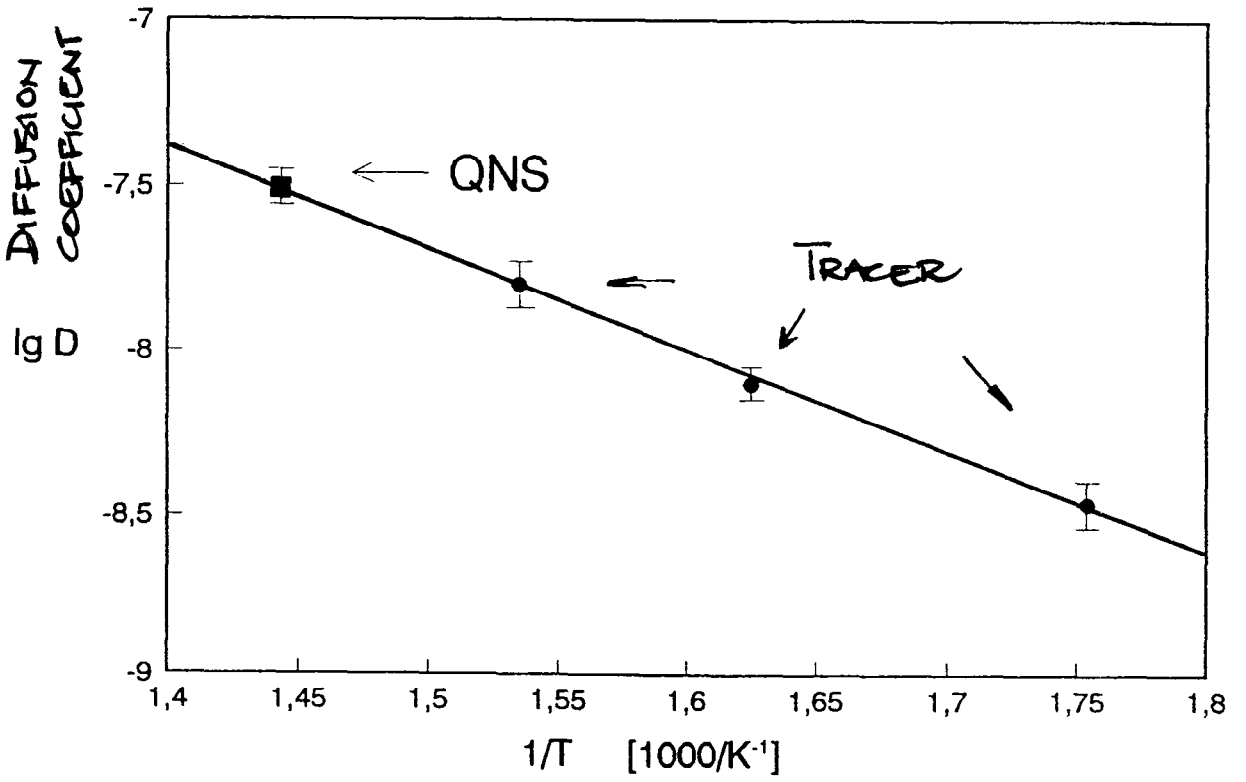

DIFFUSION
COEFFICIENT
lg D
-7
-7,5
-8
-8,5
-9
QNS
TRACER
1,4
1,45
1,5
1,55
1,6
1,65
1,7
1,75
1,8
1/T [1000/K⁻¹]

FIGURE 5

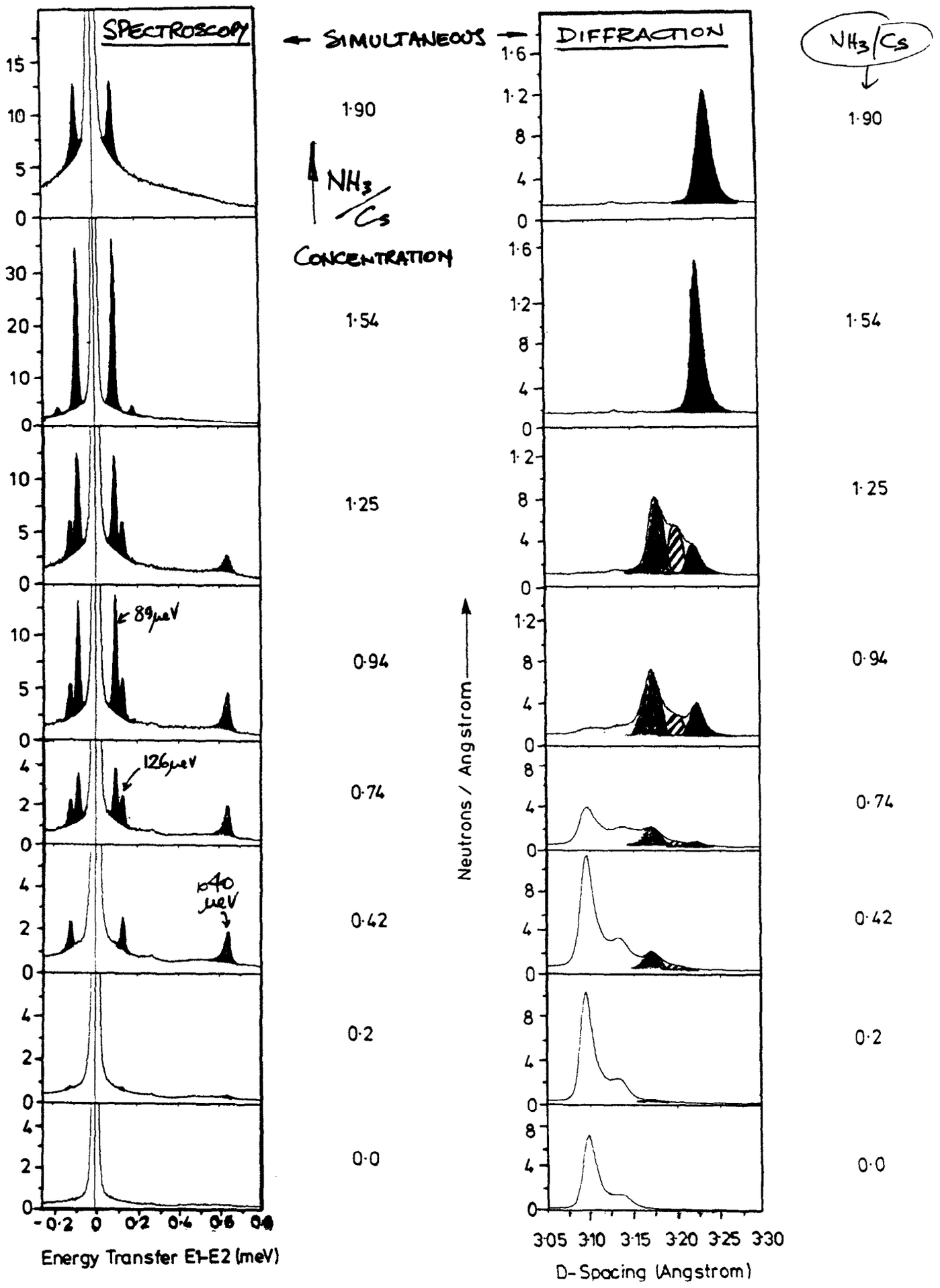

SPECTROSCOPY
← SIMULTANEOUS →
DIFFRACTION
NH3/Cs
1·90
NH3/Cs
CONCENTRATION
1·54
1·25
0·94
0·74
0·42
0·2
0·0
89 μeV
126 μeV
40 μeV
Neutrons / Angstrom
Energy Transfer E1-E2 (meV)
D-Spacing (Angstrom)

FIGURE 7 *Repeat pattern of FeVO4 at 5 K taken with new detector.*