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First Results from SANDALS – the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples at ISIS

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Abstract. SANDALS is a liquids and amorphous diffractometer which uses the broad epithermal flux of neutrons available at a pulsed neutron source. It exploits the fact that the Placzek or inelasticity correction in diffraction data from liquids is minimized at small scattering angles and high incident neutron energies. At the same time it measures the structure factor, S(Q), over a broad range of wave vector Q and this enables the pair correlation function to be evaluated more reliably than on conventional diffractometers. The physical constraints on the design of such an instrument are fairly severe: any vacuum windows and apertures in the neutron beam must not be seen by the small angle detectors, in order to keep backgrounds as low as possible. Only boron carbide can be used for the collimator apertures because traditional absorbers such as cadmium are transparent over the broad range of energies used by the instrument. And there is a minimum requirement to have the resolution $\Delta Q/Q$ in the range 1-4% for most liquids experiments. Three modules of 20 zinc sulphide scintillator detectors, out of a possible complement of 90 modules, have been run for a trial period. A further group of 15 modules is currently being installed. The instrument fulfilled all its design specifications, with backgrounds at the 1% level compared to scattering from a standard vanadium scatterer. A significant effort has gone recently into evaluating the absolute stability of the detector. Some of the initial results using hydrogen/deuterium substitution on molecular liquids are presented.

1. INTRODUCTION

After a long design and construction period SANDALS began operation in December 1989, albeit with only 3% of its full complement of detectors in place. This was the culmination of several years of design studies and some tests with a prototype detector. In the course of this period the basic specification for the instrument, which was extremely stringent as originally proposed [1], was modified slightly so as to ensure that the likely count rate at ISIS would be competitive with or exceed the capabilities at equivalent facilities worldwide. This would be in addition to the unique features of SANDALS as a small angle diffractometer. The result is a compromise between the ideal instrument as originally envisaged and the requirements of most users who would be unable and unwilling to spend more than a few days at a time running an experiment. The initial results indicated that this compromise is not severe and the instrument has already demonstrated its potential to map out partial pair correlation functions over a range of state conditions in a relatively short time. As further detectors are added it will become increasingly powerful in this regard and in the future there is a very real likelihood that the sample preparation and data analysis stages will become the rate limiting factors.

A key element of the design of SANDALS and of other high count rate pulsed neutron diffractometers of its type is the construction of large solid angle banks of detectors. For SANDALS the solid angle of the detectors in the scattering angle range 3° to 41° is 40% of its theoretical value of 1.5sr because the engineering constraints imposed by other factors in the design simply prevent it being made any larger, yet this already presents a major project to install and monitor the performance of the ~1800 individual detector elements involved. The use of ^{3}He proportional counters was ruled out early on partly for reasons of cost, but also because they would not make optimal use of the epithermal neutron flux. Instead a major effort has gone into developing a zinc sulphide scintillator detector which can be made twice as efficient as ^{3}He and can also be packed much more compactly into the available space. All the indications are that the performance of this detector is excellent in terms of quiet count, deadtime, efficiency, and γ-sensitivity, but as with any new design unexpected difficulties, primarily associated with the detector, stability were encountered. This was partly a result of the very stringent requirements imposed on a liquids diffractometer of this type. As a result the completion of the first bank of detectors has been delayed by about 9 months while a full analysis of the stability question has been conducted. It is now believed that the main elements of the problem are understood and construction of the next batch of 15 modules is proceeding rapidly.

A review of the background which lead to the present SANDALS instrument was given in the previous ICANS proceedings [2]. In this paper the underlying design principles are reviewed with the main part of the article concentrating on the early commissioning runs. In addition the results of some of the first user experiments are described.

2. DESIGN CONSIDERATIONS

ISIS is a 50Hz pulsed neutron source. On a methane moderator the neutron spectrum has declined to about 1/10th of its peak intensity in the maxwellian at a wavelength of about 5Å, which corresponds to a time-of-flight of 1260μs per m. Therefore in order to avoid serious frame overlap problems without the use of either a filter or a frame overlap chopper (both of which have the effect of reducing the incident flux significantly) the maximum allowable total flight path from source to detector is limited by the 20ms window to about 15m. The present SANDALS has been designed around this constraint, although there is nothing to prevent the flight path being increased in the future, with the inclusion of a chopper, in order to improve the resolution. It is unlikely the final flight paths can be increased very much without a substantially increased detector cost.

The second major constraint was the resolution. Although the structure peaks from a liquid or amorphous material are generally quite broad, the resolution is normally expressed (and obtained) as a ratio in $\Delta Q/Q$ so that the true resolution, ΔQ, gets *broader* at large Q. Therefore if the structure factor persists to large Q, as occurs very often in molecular liquids and amorphous solids the instrument resolution can become a significant factor in determining the true width and shape of peaks in the pair correlation function. Normally the ideal resolution for a liquids diffractometer is

in the region of 1-2% , but in SANDALS this has been set to 2-4% for most angles because to make it much smaller results in a factor of 20 or more reduction in count rate. However there is some provision for changing the beam defining apertures to alter the resolution to a lower value if so needed.

The requirement for resolution couples strongly with the collimator design. Since energies as high as 100eV are to be used for diffraction on SANDALS, the collimator can be made only of materials with significant absorption at epithermal energies, like boron carbide. Special emphasis was placed on ensuring that a series of beam defining rings along the collimator could not be seen directly by the small angle detectors. In this way the background from collimator scattering has been held to a minimum. Since the resolution function at small angles is dominated by the angular divergence of the incident beam, the viewed area of moderator and the sample size are important factors when calculating the resolution and these in turn control the rate of decrease in the collimator aperture with increasing collimator length.

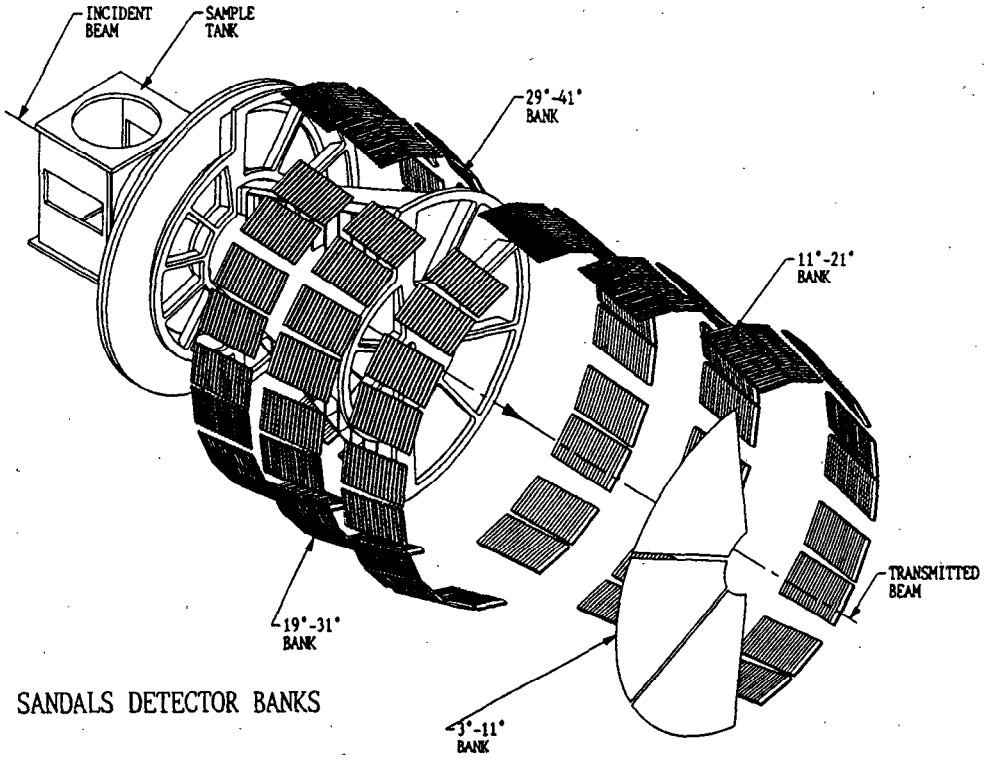

Figure 1. Drawing of the SANDALS vacuum tank and detector array. The beam enters at the top left and leaves at the bottom right. The detectors are arranged on the surface of a cylinder corresponding to a constant resolution trajectory. The odd shaped vacuum tank allows a continuous span in scattering angle from 3° to 41°

Obviously optimising the count rate has been a major item in the final design, in order to be able to exploit fully the scientific opportunities for looking at the state dependence of *partial* structure factors. In addition provision has been made to allow significant amounts of shielding between detector modules and to have a continuous coverage of detector angles from 3° to 41°. The same design also has a continuous variation in resolution over this angular range. Furthermore the resolution is nearly constant resolution for the angular range 11° to 41°: this will greatly assist in experiments

which attempt to determine the inelasticity correction by comparing diffraction data at different scattering angles, and also for experiments where anomalous dispersion near a resonance is attempted. There is provision for further detectors at larger angles should the demand arise in the future. An outline drawing of the instrument in completed state is shown in figure 1.

3. SANDALS DETECTORS

As described above the zinc sulphide scintillator detectors form the backbone to the design of SANDALS. The detectors are grouped into modules of 20 detectors each, and each detector consists of a zinc sulphide scintillator/glass sandwich which views the neutrons scattered by the sample. Each detector is viewed by two photomultiplier tubes via an air coupled light guide made from silvered milar film. The whole unit, consisting of 20 scintillator sandwiches, 20 light guides, and 21 photomultiplier tubes is housed in mold made from boron carbide powder and expoxy resin, with provision for attachment of the associated wiring at the back of the module. The modules are mounted on the circumference of a cylinder of radius 0.8m about the transmitted beam, by means of a large steel and aluminium frame, figure 2. The entire detector array and vacuum tank are housed in a blockhouse made from 300mm thick wax tanks.

The signal cables from each module are fed out through holes in the blockhouse to racks of electronics, where the signals are first amplified and discriminated and then fed to an encoder units which looks for coincidences between neighbouring phototubes and generates an appropriate computer address. The rest of data acquisition electronics and computer hardware is identical to that found on the other ISIS neutron spectrometers.

Evidence that this system of neutron detection is successful is shown in figure 3, where the diffraction pattern from sintered magnesium oxide is shown for the initial batch of 60 detectors (3 modules). The uniformity from one detector to another is generally very good, as is the signal to noise ratio in the Bragg peaks. Note that the Bragg peaks all occur at short times of flight because the scattering angle is small and in the range 11^o to 21^o. In addition it will be noted that the resolution is almost the same across this angular range, even though the value of $\cot\theta$, which dominates the resolution at small angles (2θ is the scattering angle), changes by a factor of 2 in the same region.

A difficulty which had not been anticipated was the large amount of heat produced by the crates of electronics: coupled with an unusually hot summer the temperature immediately above the crates often rose above 40°C at times with a diurnal variation of up to 15°C. As a result a significant temperature instability was observed. This was cured by installing temperature compensation in all the relevent electronic modules. A further step to be executed early in 1991 will be to install air conditioning both inside the blockhouse and around the sensitive electronics. Other sources of instability possibly associated with mains supply fluctuations have also been investigated. Obviously since most liquids or amorphous materials experiments rely on comparison of sample scattering to a standard scatterer it is imperative that good detector stability is achieved.

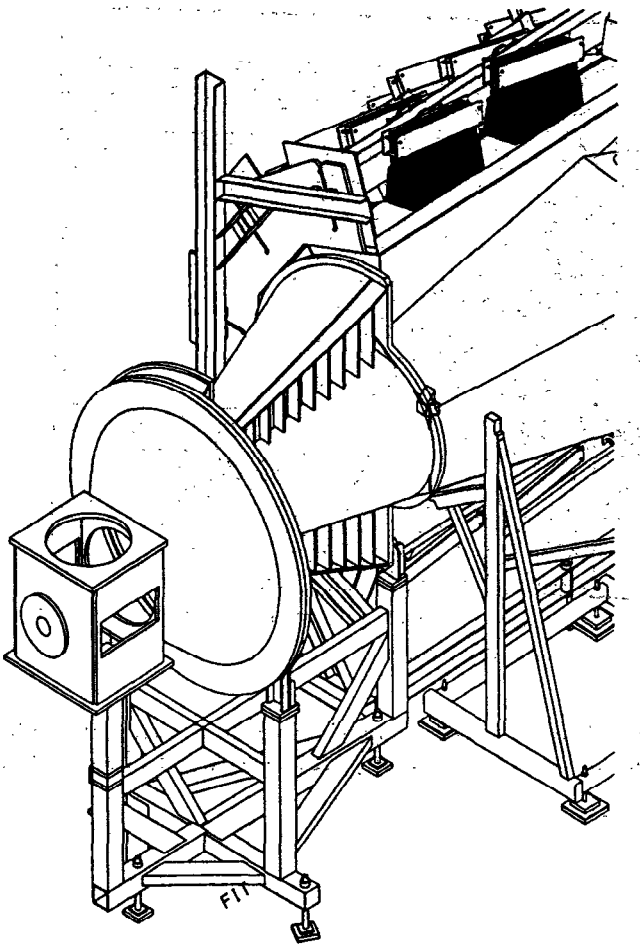

Figure 2. Drawing of part of the mounting for the SANDALS detector modules. The sample vacuum tank is shown at the bottom left mounted on a steel frame. This is where the neutron beam enters. In the middle are the conical-shaped vacuum and argon-filled flight paths and at the top are the scintillator modules (shaded black) in their support frame

4. NEUTRON BACKGROUND

For all three modules the beam on, no sample background was extremely good, and lay at the 1-3% level, compared to the scattering from a standard vanadium rod, over a very wide energy range (see figure 4). A slight turn up is seen at the lowest energies, and this arises from the intrinsic quiet count of ~15 counts per minute of these high efficiency detectors. It is expected that this quiet count can be reduced with an improved discrimination system

5. COUNT RATE

The measured C-number (see [2] or the ATLAS Manual [3] for the definition of C-number) for the first three modules is shown plotted in figure 5. The measured numbers have been scaled by a factor of 6 to correspond to the situation when installation of 1/5th of the detectors is completed early in 1991. For comparison the D4 diffractometer

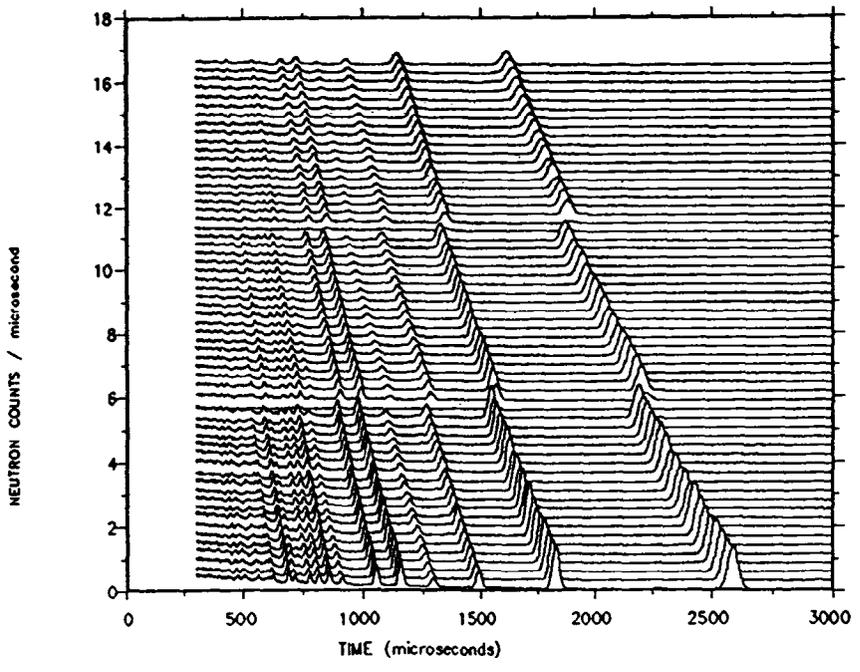

Figure 3. Diffraction pattern from sintered magnesium oxide showing 60 SANDALS detectors in operation simultaneously. The steps in the lines of peaks correspond to the different flight paths for each module

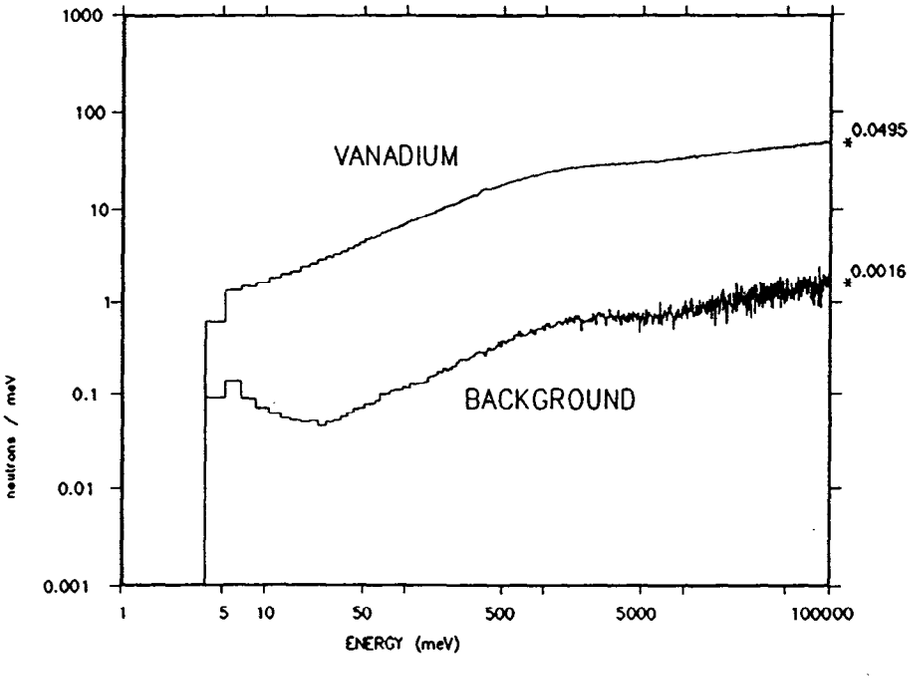

Figure 4. Background on SANDALS compared to the scattering from vanadium at a scattering angle of 12°. Note that even at 100eV the background is still 3% . This is much better than has been achieved on other ISIS diffractometers.

at ILL has a C-number of 53 n/0.05Å^{-1}/s/cm^{3}V over the wave vector range 0.4Å^{-1} to

$17Å^{-1}$. The measured numbers appear to be below the expected count rate by about a factor of 2, but this is a function of the detector set up. The method of coincidence used to determine if a neutron event has occurred is extremely good at discriminating against bad events, but it maybe that the discrimination is too severe at present.

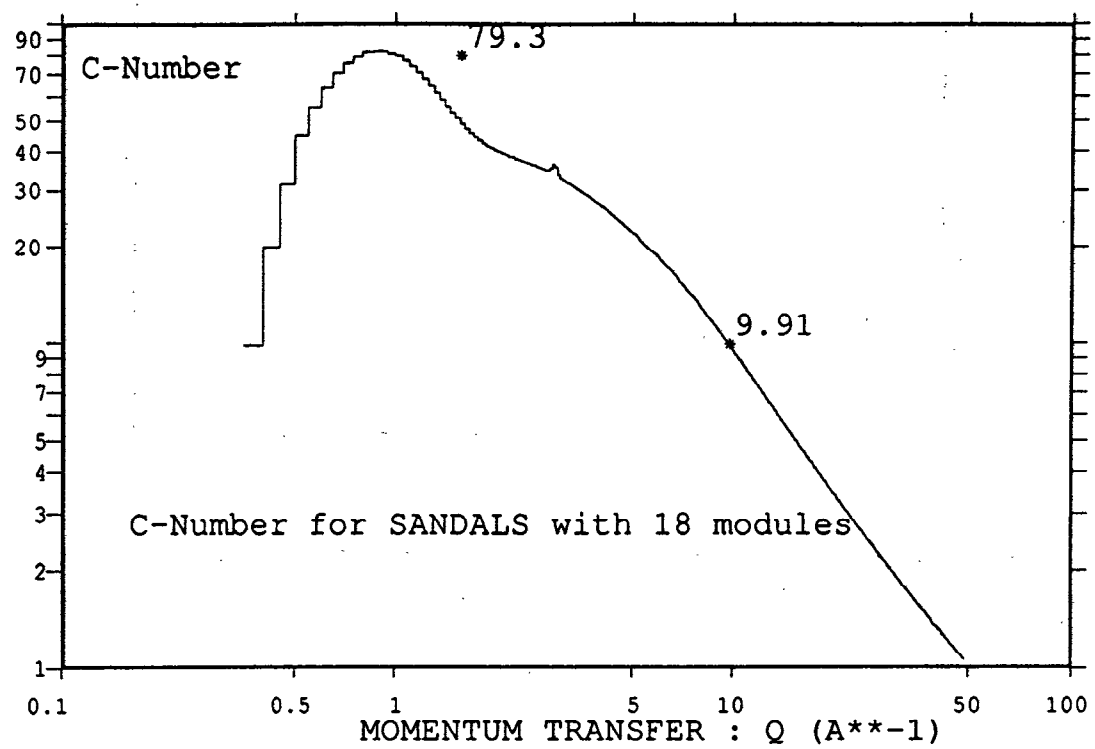

Figure 5. Measured count rate for SANDALS scaled up to the 18 modules which are to be installed shortly

6. RESULTS FOR SILICA AND WATER

Figure 6 shows the pair correlation function obtained from SANDALS data taken on two sheets of silica, each 3mm thick. The Si-O and O-O distances can be clearly identified in this curve, and the width and height of the main peaks is in good agreement with that obtained elsewhere [4]. The data were recorded in 6 hours on SANDALS and the transform procedure [5] used all the data out to $Q=50Å^{-1}$ and included the resolution function in the calculation.

For water this was a standard hydrogen/deuterium substitution experiment in which the H-H, O-H and O-O partial structure factors were extracted. The data was recorded at the rate of 1 sample per 24hrs. The oscillations in the O-O function (see figure 7) appeared to damp out quicker than had been expected from earlier work and this leads to a slightly broader main peak in g(r), but otherwise the agreement with the earlier reactor work was extremely good, with coordination numbers entirely as expected.

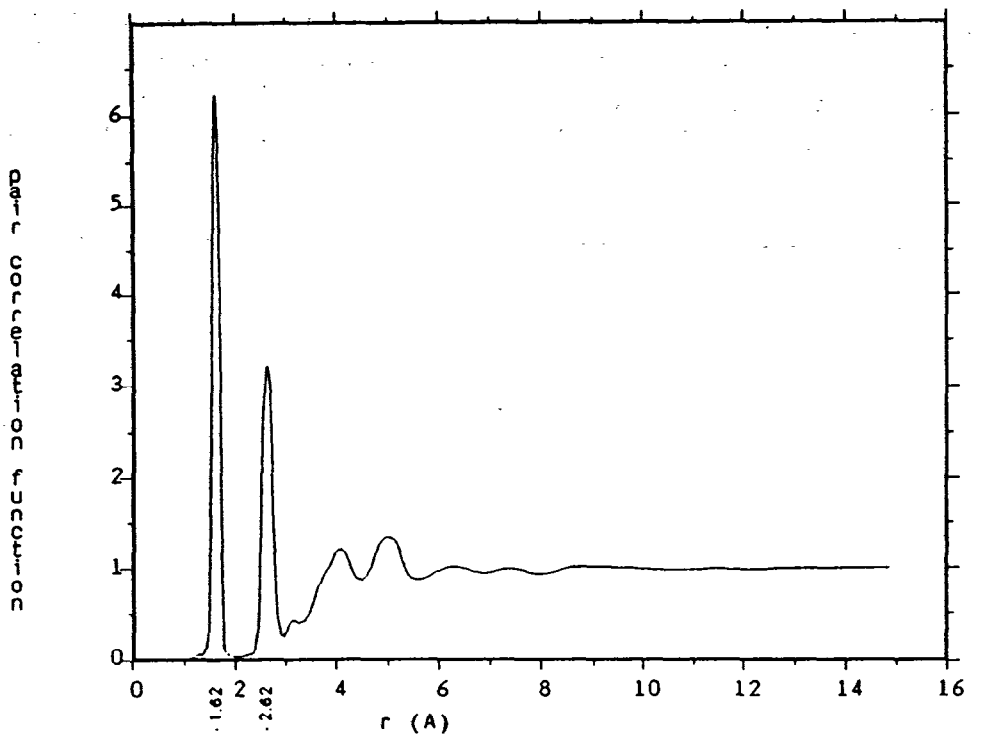

Figure 6. Pair correlation function obtained from the SANDALS data on Silica. Note the sharpness and height of the first two peaks, even though all the data has been accumulated at scattering angles below 20°.

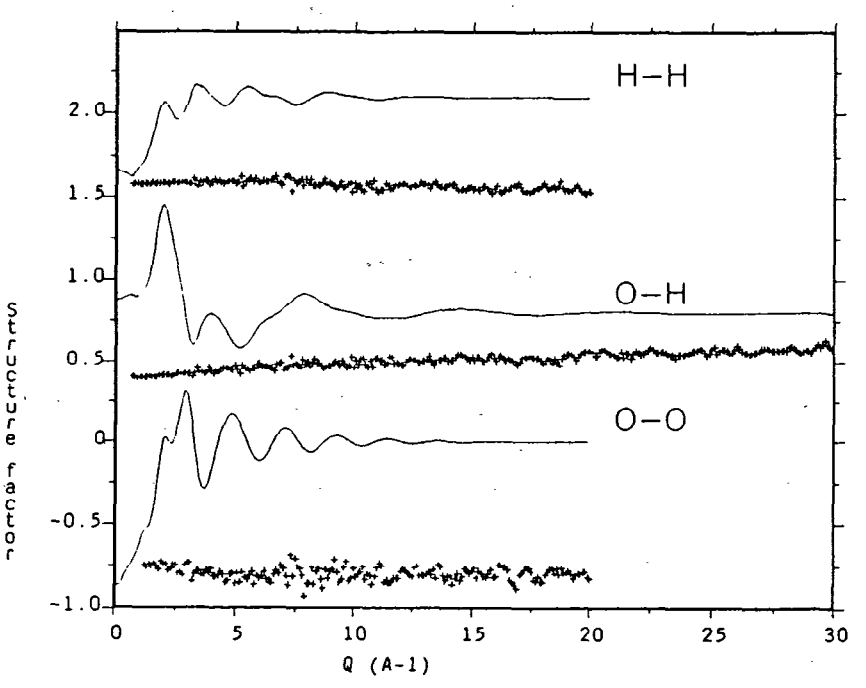

Figure 7. Minimum noise [5] fits to the measured partial structure factors for water as measured on SANDALS. The crosses show the residual between data and fit.

7. THE FIRST USER RESULTS

To date four user experiments have been completed on SANDALS. These include a study of the structure of water in dimethyl sulphoxide (DMSO) solutions, the structure of water and the distribution of cations in tetramethylammonium (TMA) chloride solutions, the structure of water in ethylene glycol solutions ("anti-freeze") as a function of lowering the temperature, and most recently the structure of superheated water up to 175°C. All involved the use of the H/D substitution method to extract partial correlation functions. Where there are more than two components present this method still extracts three correlation functions, but the partials are themselves composite correlation functions, consisting of a weighted sum of several correlations. For this reason the H-H function is the easiest to interpret.

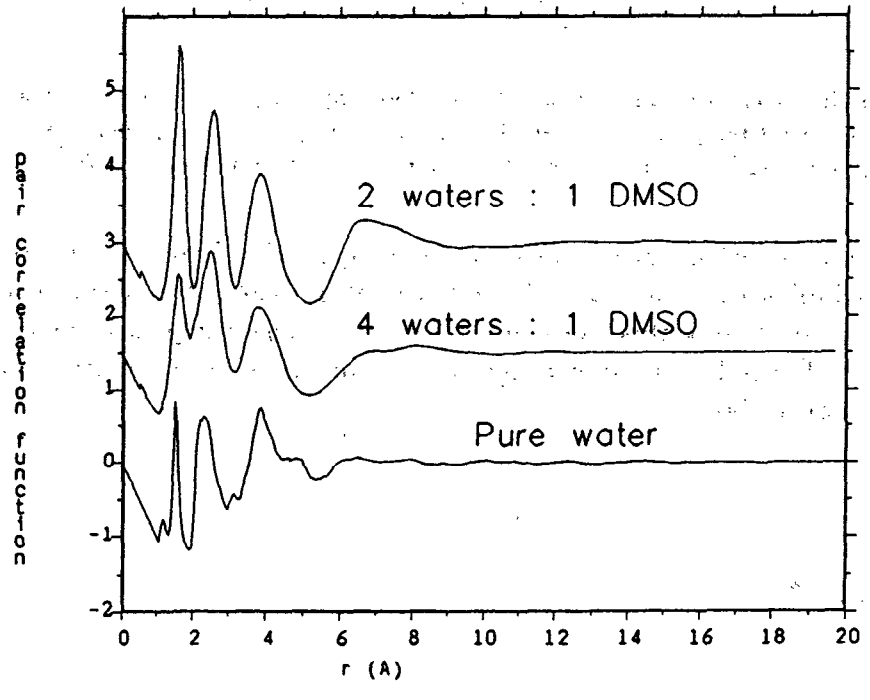

Figure 8. H-H correlation for two concentrations of DMSO in water compared to the same function for bulk water. A general broadening and shift of the peak at 2.4Åcan be seen at the highest concentration.

For the DMSO solutions the main result was that this molecule apparently forms stronger hydrogen bonds with water than water does to itself: the g(r) functions remain quite structured at high concentrations but there is a shift in the peak at 2.4Åto larger r values as the concentration increases, figure 8. This is what would be expected if the oxygen on the DMSO formed 2 or 3 hydrogen bonds with the water, leaving fewer water molecules bonded to themselves. This result is in direct contrast to what was found for TMA, methanol [6] or ethylene glycol, where the tetrahedral water structure is preserved even at high concentrations.

The ethylene glycol solutions also revealed an iteresting result. At the lowest temperature, 160K, the solution is expected to become a mixture of a glassy ethylene

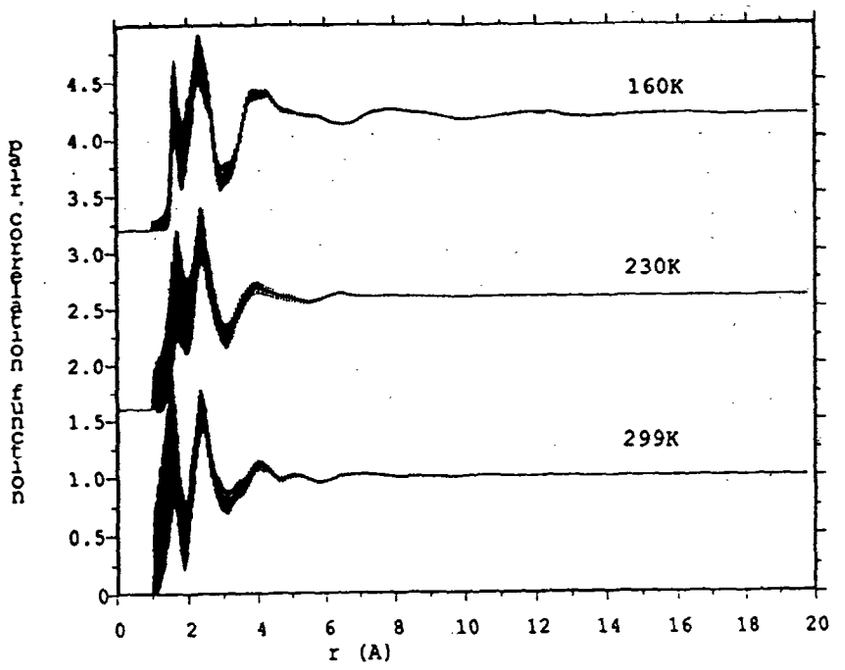

Figure 9. The H-H correlation function in concentrated ethylene glycol solutions as a function of temperature. In the lowest temperature phase (166K) the freezing does not appear to affect the short range significantly but does introduce a long range correlation out to and beyond 20Å

glycol/water mixture, with excess water appearing in the form of ice. In fact the diffraction data indicated that most of the water was frozen, by virtue of the Bragg peaks which appeared, but this does not affect the short range proton correlations very significantly, figure 9: the long range order appears as an oscillation in the pair correlation function to large r.

8. CONCLUSION

The initial results on SANDALS described here give an indication of the powerful and exciting science that will be possible as the detector banks are completed. It is already clear that the instrument is performing up to design characteristics, with a particular emphasis at present on ensuring the detector stability is adequate for the likely counting statistics. The number of user derived experiments will increase steadily as expertise at operating the instrument and performing the data analysis increases, and it is likely that the time taken to acquire datasets will become less. Hence it is hoped to realize the aim expressed long ago of mapping out the pair correlation function as a function of state conditions. This serves as an extremely stringent test of the computer simulation models. It is likely that the full power of small angle diffraction from liquids and amorphous materials will only be realised when methods like Reverse Monte Carlo [7] can be incorporated into the data analysis.

Acknowledgments

The development of SANDALS would not have been possible without the considerable assistance from a large number of people, in particular K. Brine, B. Holsman, S Spurdle and A F Gilleard of the ISIS design team, P L Davidson, N J Rhodes and E Mott of the ISIS detector group, and B C Boland and R Hall of the ISIS operations groups. Invaluable support and advice have been received from P A Egelstaff, J Penfold, J L Finney, A D Taylor, M W Johnson, W S Howells, A C Hannon and many others of the ISIS team.

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Q(P.A.Egelstaff): SANDALS will give a lot of new and exciting information on amorphous samples; can you tell us of the ideas the U.K. amorphous materials group may have for exploiting this instrument?

A(J.L.Finney): The major demand immediately is in studying partial paircorrelations in hydrogenous systems, eg, aqueous solutions of ions and molecules TMACl, DMSO, ethyleneglycol as functions of temperature and pressure. As the detector component increases, we expect a major increase in work probing structural changes as a function of state point.