

THE USE OF NEUTRON SCATTERING TECHNIQUES FOR INVESTIGATION OF HYDROGEN STORAGE SYSTEMS

Ross D.K., Bull D.J., Moser D., Roach D.L., Mileeva Zh.A. and Shabalin I.L.

Institute for Materials Research, University of Salford,
Salford, Greater Manchester M5 4WT, UK

*Fax: +44 161 295 5575

E-mail: d.k.ross@salford.ac.uk

Introduction

Thermal neutron scattering is a powerful method for analyzing the properties of materials, both with regard to their structure and dynamics. The technique is particularly useful in the study of hydrogen in materials because of the very large incoherent scattering cross section of the H^1 isotope (almost two orders of magnitude greater than the average value for other isotopes of any element) and the fact that D (H^2) is easily exchanged for H^1 and has a largely coherent (but not abnormally large) cross section. It should be noted that incoherent scattering from H^1 gives information about the motions of the given nucleus itself even at low concentrations because of its large scattering cross section while coherent scattering tells us about the relative motion of two neighbouring nuclei and hence can yield the atomic position of the hydrogen. A further important advantage of the technique is that the neutron is relatively penetrating so it is easy to study the changes in a sample as hydrogen is cycled in and out of a sample capsule over a wide range of temperatures and pressures as necessary.

Results and discussion

As an example of an in situ neutron diffraction study of a potential hydrogen storage material, we would refer to our measurements on the $Li_3N/Li_2ND/LiND_2$ [1]. This system, originally proposed by Chen et al. [2], was originally envisaged as taking place in two distinct steps. In the presence of hydrogen, first the imide is formed and then the amide. In situ studies at high deuterium pressure shows that this does happen but, for lower deuterium pressures, the process is much more complex in that a cubic quasi-imide phase is formed with a variable lattice parameter. This phase appears to be a mixture of the Li_2ND and Li_4ND formula in a fluorite structure in which the Li^+ are on the $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$ sites and the $(ND)^{2-}$, N^{3-} and D^- are on the f.c.c. sites, apparently disordered. Other phases are also produced [3] and it is clear that the actual reaction pathway depends enormously on the precise D_2 pressure and temperature.

Inelastic neutron scattering from a material containing hydrogen is dominated by the vibration

frequency of the hydrogen atoms. The frequencies are uniformly sampled from throughout the first Brillouin Zone and the resulting cross section can be calculated explicitly from first principles [4]. However, in complex structures, it can be difficult to identify each feature in the spectra. We have recently developed the use of coherent inelastic neutron scattering from polycrystals to increase the information that can be extracted from the scattering. In the past, the coherent scattering from polycrystals has been too complex to analyse in any meaningful way but, with the advent of ab initio techniques, it is now possible to calculate the scattering directly from the dynamical matrix for direct comparison with experiment. Because the scattering is now coherent, the measured cross section is a function of both energy and momentum transfer (ω and Q) and contains information about the relative phase of different parts of the structure at a given frequency of vibration. One area of

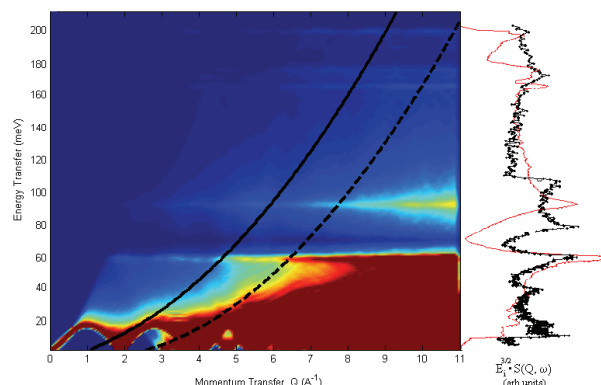


Fig. 1. Comparison of model (contour plot and red line) and data points measured on TOSCA as along the dashed curve on the contour plot (locus of scattering at 135°).

application of this approach will undoubtedly be carbons. The calculated scattering function for graphite is shown in Fig. 1, along with experimental measurements and the indicated loci in (Q, ω) space. Preliminary measurements on other forms of carbon show very different contour plots and the detailed analysis of this data is expected to yield important information on the bonding in carbons before and after adsorbing hydrogen. A further area in which this technique shows promise is in the interpretation of the

vibrations of complex Hydrides (deuterides). In Fig. 2, we show a preliminary data set for MgD_2 where significant Q-dependent intensity is apparent. Modelling of this data is in hand.

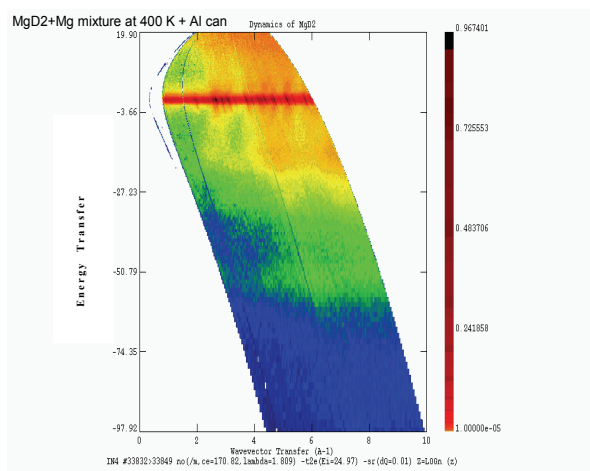


Fig. 2. The measured coherent neutron scattering function for MgD_2 measured on IN4 at Grenoble. Some acoustic phonon scattering from Mg present in the sample is visible.

A further application of neutron scattering is to the study of hydrogen diffusion in a lattice, either localized or long range, by means of quasi-elastic neutron scattering. Here again, we normally measure incoherent quasi-elastic scattering from H^1 which tells us about the mechanism by which the nucleus diffuses away from the origin (Tracer diffusion). This technique has provided very detailed information on the diffusion of hydrogen in transition metals and intermetallic phases [5]. H diffusion in light hydrides is more difficult to measure because the bonding is stronger and the corresponding H jump rates are lower. However, recently we have been able to measure localized rotational diffusion of N-H bonds in lithium imide [6]. We have also studied diffusion of H in Mg_7TiH_x . This is an interesting compound which is only formed under several GPa pressure. We believe that the diffusive jumps are between tetrahedral sites in the fluorite lattice in the vicinity of the Ti atom which is on an ordered fcc lattice with the Mg atoms. Using the elastic window technique on the IN10 spectrometer at the ILL, we have demonstrated the presence of diffusive processes but it is still difficult to be sure whether the diffusion is localized or long range.

A further technique that has proved useful in the study of hydrogen adsorption in porous carbon is Small Angle Neutron Scattering (SANS). Here we are dealing with coherent scattering from local density fluctuations rather than from individual atoms. In order to understand the nature of the porosity in a solid, we can saturate it with a suitable liquid where the local scattering density has been varied by changing the H/D ratio. When the scattering density of the liquid matches that of the matrix, the scattering from the filled pores disappears, leaving the scattering from closed pores and other inhomogeneities. We have used this technique to measure the density of an activated carbon. It is interesting to note that the contrast match point is a function of Q, indicating that there are empty pores but that the density of the carbon in the vicinity of the pore is 2.1 g/cc, very close to that of bulk graphite.

References

1. Weidner E., Bull D.J., Shabalin I.L., Keens S.G., Telling M.T.F. and Ross D.K. Observation of novel phases during the deuteration of lithium nitride from in situ diffraction. *Chem. Phys. Letts.* 2007; 265(2): 259-268.
2. Chen P., Xiong, J.T., Luo, J.Z., Lin J.Y. and Tan K.L. Interaction of hydrogen with metal nitrides and imides. *Nature.* 2002; 420: 302.
3. David W.I.F., Jones M.O., Gregory D.H., Jewell C.M., Johnson S.R., Walton A., Edwards P.P. A mechanism for non-stoichiometry in the lithium amide – lithium imide hydrogen storage reaction. *J. Am. Chem. Soc.* 2007; 129: 1594.
4. Mitchell P.C.H., Parker S.F., Ramirez-Cuesta and Tomkinson J. *Vibrational spectroscopy with neutrons with applications in Chemistry, Biology, Materials Science and Catalysis.* Singapore and London: World Scientific Publishing and Imperial College Press, 2005.
5. Ross D.K. Neutron scattering studies for analyzing solid-state hydrogen storage. In: Walker G. *Solid-state Hydrogen Storage: Materials and Chemistry.* Cambridge: Woodhead Publishing in Materials, 2008.
6. Bull D.J., Moser D., Ross D.K. et. al. to be published.