

## NEUTRON METROLOGY FOR THE HYDROGEN ECONOMY

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### Abstract

Neutron scattering, transmission, and analysis techniques are particularly well-suited for studying materials of relevance to fuel-cell and hydrogen-storage technologies. The unusually large neutron scattering cross section for hydrogen (and deuterium) as well as the neutron's great penetrating power are routinely exploited in order to probe the amount, location, bonding states, and dynamics of hydrogen (and water) in a variety of technologically interesting materials. Developments over the past decade at the NIST Center for Neutron Research and elsewhere have greatly increased the sensitivity and dynamic range of neutron methods. In this paper, we provide a flavor of the capabilities of such modern neutron instrumentation for the study of energy systems and materials important for the hydrogen economy, from micron-scale imaging of working fuel-cell stacks and hydrogen-storage beds to atomic-scale characterization of hydrogen location, bonding, and transport mechanisms in fuel-cell membranes and hydrogen-storage materials.

### Introduction

Neutrons are an incisive probe of complex structures because of their great penetration capability in most known materials and their unique ability to distinguish different materials with very similar physical properties. Due to their unusually large scattering cross section for hydrogen (and deuterium), neutrons are particularly effective in probing and detecting hydrogen in materials [1,2]. Advancements over the past decade at the NIST Center for Neutron Research and elsewhere have greatly increased the sensitivity and dynamic range of neutron methods. These advancements can be exploited to more thoroughly characterize the physicochemical properties of both fuel-cell and hydrogen-storage materials, key components of the hydrogen economy.

Fuel cells are electrochemical devices that directly convert the chemical energy of hydrogen into electricity without combustion or moving parts. Polymer Electrolyte Membrane (PEM) fuel cells are the most common type and are of special interest for use in an extensive range of devices from cell phones to automobiles. In a PEM fuel cell (Figure 1), hydrogen enters the anode side where a catalyst (usually platinum) facilitates the separation of the hydrogen gas into electrons and protons. The protons pass through the membrane electrode assembly (MEA) and, again with the help of a catalyst, combine with oxygen and electrons on the cathode side,

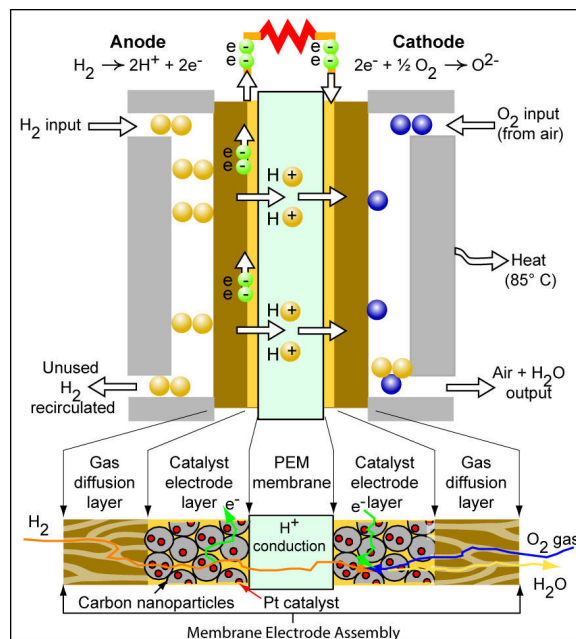


Figure 1. Schematic of a PEM fuel cell

producing water. The electrons, which cannot pass through the membrane, flow from the anode to the cathode through an external circuit thereby providing power to an external device.

The success of fuel cells in any future hydrogen economy depends, in no small part, on the ability to develop inexpensive, high-capacity hydrogen-storage materials to supply the hydrogen fuel. The Department of Energy Freedom CAR initiative sets targets for a hydrogen-storage system that is capable of reversibly storing ~6 wt. % hydrogen with an energy density of at least 1.1 kWh/liter, and is operational for at least 500 cycles at a cost of no more than \$5/kWh. Such targets require the search for new and improved materials. Similarly, the need for more efficient fuel-cell membranes requires the development of improved materials with large energy and power densities. The utility of a particular material for these applications depends critically on hydrogen transport. Thus the fundamental questions that must be answered in order to understand and tailor the performance of these systems are, "Where does the hydrogen go?" and "How does it get there?" Many types of materials have been tried or suggested for use as hydrogen-storage media or proton-conducting membranes. Proper characterization of these materials requires atomic scale information on the structure, hydrogen diffusion, and interatomic interactions as well as the nanoscale and macroscopic morphologies that govern their useful properties. Below we describe advanced neutron metrologies that promise to help overcome crucial obstacles to the development of both fuel cells and hydrogen-storage materials.

### Micro-Scale Neutron Imaging

The control of incoming humidity and the product water within the MEA is generally acknowledged as the most difficult yet most crucial aspect of operating a PEM fuel cell. Too much water within the PEM or gas diffusion layer (GDL) will result in flooding conditions that impede gas diffusion and membrane life. Too little water will reduce the membrane conductivity and thereby decrease the cell performance. Furthermore, the electrode composition may be hydrophobic or hydrophilic, adding yet another complication to water management. Many attempts have been made to improve PEM fuel-cell water management using data obtained *ex situ* or via trial-and-error. However, no satisfactory experimental method has previously been found to accurately measure or map the distribution and transport of water

within the MEA. Adequate water management is the key to a stable and long-life PEM fuel cell, and must be achieved by properly designing the flow fields, GDL, PEM, and their interfaces. This requires a fundamental understanding of the *in situ* water distribution in an operating fuel cell. Such information can be obtained via neutron transmission methods. In particular, 2-D (radiography) and 3-D (tomography) neutron-imaging techniques can enable non-destructive, *in situ* visualization and quantification of hydrogen transport and MEA structural anomalies in the most common forms of PEM fuel cells that are in development today.

The contrast that can be obtained in radiographic images depends critically on the relative cross sections of the different materials in a device. For thermal neutrons, hydrogenous compounds (such as water) are easily observed in the presence of aluminum, copper, or carbon, all of which are commonly used in fuel-cell construction. Clearly the potential impact of harnessing this capability to the study of fuel cells is quite large. In the most common form of 2-D imaging, neutrons pass through a sample and the transmitted beam intensity is spatially modulated by the scattering and absorption encountered inside the sample (Figure 2). This modulated neutron

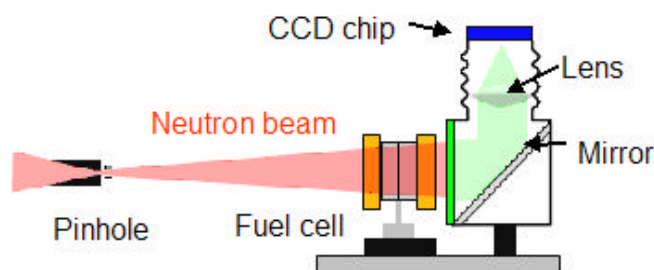


Figure 2. Schematic of a typical neutron imaging setup.

intensity is converted to light using appropriate scintillators and then recorded by a digital image detector, such as a charge coupled device (CCD). The image detector provides direct visualization of the interaction, and from known interaction cross sections, sample properties such as density, thickness, mobility, *etc.* can be directly quantified. Neutron tomography allows one to reconstruct a 3-D image of an object from the 2-D neutron radiographs taken for several orientations of the object. It is then possible to reconstruct the original point-to-point mass density of the sample. Neutron tomography can map and quantify the water distribution in different segments of an operating fuel cell. We have successfully developed a first-generation, neutron-imaging facility that is capable of employing absorption imaging. 2-D test images of water inside an MEA [3] and flow channels [4] in operating fuel cells are shown in Figure 3.

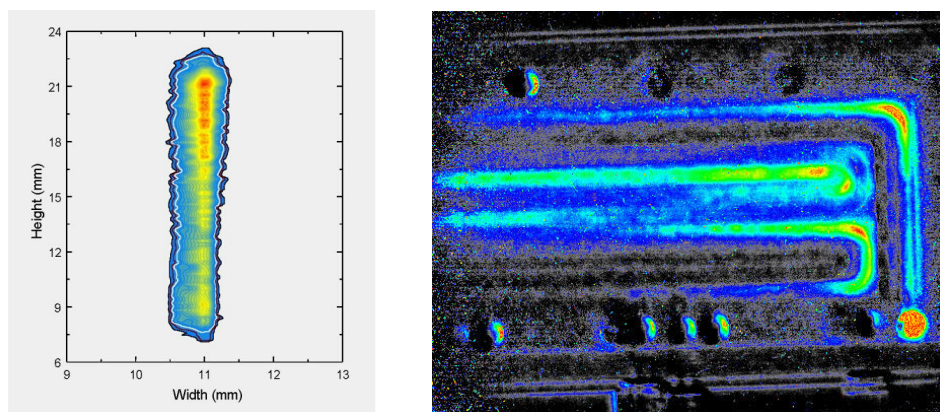


Figure 3. Test images of water in an MEA (left) [3] and a fuel-cell channel flow field (right) [4].

Neutron tomography will eventually be complemented by new advances in both refraction imaging and phase-contrast imaging [5,6,7]. This is particularly important for identifying sharp boundaries and edges, where image contrast due to absorption and scattering is poor. This type of imaging, which is based on neutron refraction by constituent elements in the sample, uses a mono-energetic neutron beam. The refracted beams from different elements are spatially separated from each other by a very small amount. A single-crystal analyzer redirects this spatially separated beam away from the original direction and a high-resolution, position-sensitive detector records the redirected beam. Since the refracted beam is now separated from the direct transmitted beam, the inherent background present in more conventional radiographs is eliminated, and an image with very sharp contrast is formed.

In phase-contrast imaging, an image of the locally varying phase shift of a neutron beam caused by the sample is formed. The observed phase variation may occur because of dimensional and constituent variations, the presence of a domain structure, rapidly varying density gradients, the presence of precipitates, or a spatial distribution of stress. Not only are the bulk properties of the sample measured, but the elemental distributions of local inhomogeneities and sharp interface boundaries are also observable. This technique is typically a few hundred times more sensitive than normal radiography. Our successful, first-generation, neutron-imaging facility is already capable of phase contrast imaging and the capability of the

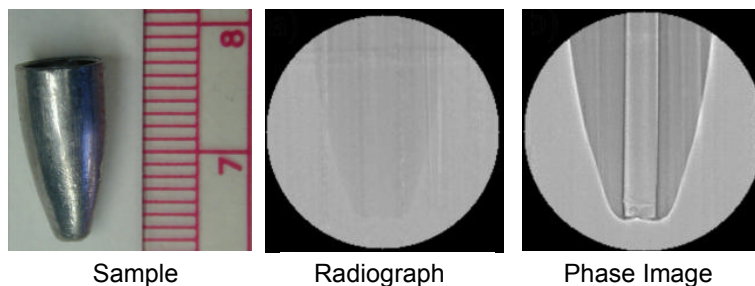


Figure 4. Enhanced edge contrast in the phase image of a lead sinker (from Allman *et al.* [6]).

technique is shown by the images of a hollow-shafted lead sinker in Figure 4. Note that the edges of the sample are much sharper in the phase image than in the radiographic image.

To date, neutron-imaging methods are the only techniques available to directly observe the water transport characteristics in an operating fuel cell. For example, neutron tomography can be used to image water transport through the GDL. This information is critical for optimizing the design of a GDL with respect to variables such as hydrophobicity, porosity, tortuosity, thickness, *etc.* In addition, micro/macro-scale neutron imaging will dramatically enhance the capability to study two-phase flow characteristics in the fuel-cell flow field. In general, wet gases are used in fuel cells, and water is generated in the cathode. There needs to be a fine balance between the vapor and condensate. However, it is most likely that some liquid water is generated in areas other than the cathode. It is critical to know where this occurs and its impact on fuel cell vapor transport characteristics such as the drop in vapor pressure. Neutron phase imaging is ideally suited for studying hydrogen and water conduction kinetics across MEA interfaces and minute thickness variations in the polymer electrolyte layers. Ultra-sensitive neutron phase-contrast imaging can be applied to image PEM's at different moisture levels to quantify dimensional variations of the polymer layers. Phase imaging will be critical in the investigation of fuel-cell membrane water gradients under different humidification conditions. It is extremely important for fuel-cell designers and manufacturers to understand how humidification influences membrane performance and lifetime.

Besides imaging fuel cells, it is clear that these neutron methods can also be used to perform real-time 2-D/3-D imaging of the hydrogen concentration gradients during the absorption/desorption cycling of hydrogen-storage beds. Such *in situ* information would be invaluable for aiding in the engineering design of commercial beds. Previous neutron-imaging measurements of Mg-Ni-based hydrogen-storage alloys [8] and current neutron imaging experiments of LaNi<sub>5</sub>-based hydrogen-storage beds during cycling at NIST [9] confirm the feasibility of such measurements.

The challenges for the successful development of neutron imaging techniques with adequate spatial and temporal resolution for fuel-cell research are substantial. At present, we can attain a spatial resolution of about 100  $\mu\text{m}$  and a time resolution of tens of seconds. We are in the process of overcoming complex instrumental and scientific barriers in order to lower the spatial resolution limit to 5  $\mu\text{m}$  while improving the temporal response to a few tens of milliseconds. These envisioned gains represent a quantum leap in neutron imaging technology and could significantly contribute not only to the understanding of current and next-generation fuel cells, but also to a myriad of issues in interface physics and chemical kinetics.

### Nanoscale Neutron Imaging by Reflectivity and Small-Angle Scattering

The water transport, which can be probed through micron-scale neutron imaging described above, actually results from nanoscale diffusion of water and/or hydrogen. In order to image the membrane water distribution on the nanoscale, one can adapt highly sensitive neutron reflectometry (NR) methods. The reflection of neutrons from films or layered media deposited on flat surfaces directly probes the composition and distribution of the constituent materials, including water and/or hydrogen, on a sub-nanometer length scale both perpendicular and parallel to the film surface. From the specular component of reflection as a function of scattering angle, the scattering length density (SLD) depth profile of the hydrogen or water along the surface normal can be obtained. Since the SLD is the product of the atomic density and neutron coherent scattering length, the SLD profile is directly related to the actual material compositional profile. Thus one can reconstruct an image of a particular component based on the extracted SLD profiles. Figure 5 shows such an image extracted from NR data for a biotech membrane system, *i.e.*, a polyelectrolyte / terpolymer / phospholipid layer sandwich [10] under 92% D<sub>2</sub>O humidity. This example illustrates the unique power of NR for determining the water fraction depth profile in a membrane with nanoscale spatial resolution.

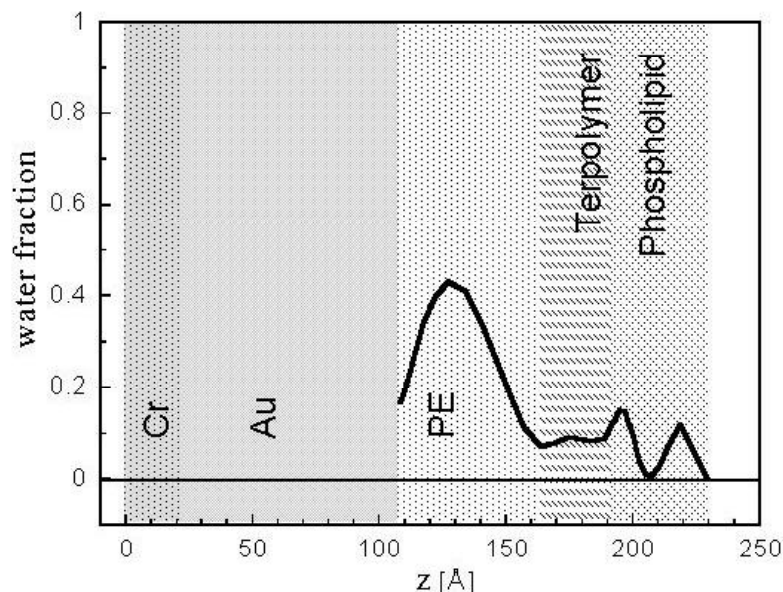


Figure 5. Water profile in a biomembrane (from Perez-Salas *et al.* [10]).

As inferred above, NR metrology cannot be performed directly on materials of macroscopic shapes and sizes contained in commercial fuel cells. However, it is straightforward with the present deposition technology to fabricate NR thin-film samples that incorporate all of the essential structural and behavioral properties of commercial materials. Furthermore, measurements can be performed *in situ* within an active electrochemical cell. This is possible since the membrane can be deposited on a flat substrate of a single-crystal material that is nearly transparent to neutrons such as Si, sapphire, or quartz. Thus, *e.g.*, the diffusion of hydrogen through such a membrane can be studied in real time under conditions relevant to those in operating fuel cells. However, to apply powerful NR metrology techniques to probe fuel-cell materials within an operating sample cell, such membranes and cells will have to be developed.

An important issue for the long-term reliability of fuel cells is the problem of catalyst layers delaminating from the polymer membranes resulting in catastrophic failure of the fuel cell. With subnanometer spatial resolution, NR can reveal, at the earliest stage, any detachment of one material from another at a particular boundary surface or buried interface. NR can be performed *in situ* on a device that replicates the actual conditions of the membrane being cycled repetitively through the drying and rehydration processes which ultimately lead to the delamination.

Although NR nonspecular scattering can be used to obtain nanoscale descriptions of the morphological character of membranes parallel to the surface, such information is best obtained via small-angle neutron scattering (SANS) [11], particularly in regard to the hydrophilic domains through which the water molecules diffuse. To help guide the synthesis of membrane materials possessing designed structural features conducive to optimal fuel-cell performance, researchers require a firm understanding of the correlation between the observed water behavior at the micron scale and the nanoscopic structure of the membrane. In this regard, SANS is an ideally suited technique since contrast variation between H<sub>2</sub>O and D<sub>2</sub>O allows one to directly probe the specific structure correlations of individual components of a multicomponent system. Therefore, one can construct an overall nanoscopic picture of the structural features of the membrane and the geometry and size of the water domains on a nanoscale.

Of particular importance to the understanding of water management is the evolution of water domains and polymer morphology as a function of swelling. As the membrane swells, it is believed that discrete water clusters eventually grow large enough such that there is a continuous water pathway spanning the entire membrane between the anode and cathode. Using SANS measurements as a function of relative humidity level, it is possible to measure the water domain geometry and size within a membrane [12], a process directly analogous to the conditions present during the startup of a fuel-cell power source. In order to perform these experiments with both NR and SANS, one must develop a humidity-controlled cell that enables the precise control of membrane swelling. Additionally, such a cell allows for the repeated cycling between swelled and dehydrated states, simulating the fuel-cell working conditions, which permits controlled monitoring of the time-evolved structural properties of the membrane.

### **Molecular-Scale Neutron Scattering Techniques**

To determine the location and motion of water and hydrogen on still shorter length and time scales than are accessible with neutron-imaging techniques, one can employ a different set of neutron scattering probes for *in situ* molecular-scale measurements [1]. Such atomistic measurements can help determine the locations, interactions, and dynamics of hydrogen (and water) in all types of fuel-cell membranes and hydrogen-storage materials.

Tailoring any of these materials for use in fuel cells and hydrogen-storage beds requires a molecular-scale understanding of the fundamental properties responsible for stable high protonic conductivity and hydrogen absorption/desorption as well as improved measurement methods to probe these properties. This requires knowledge of the materials structure, the locations of hydrogen (and water) within the material, and the strength of the interactions between the hydrogen (and water) and the material constituents. Having detailed knowledge of these molecular-scale properties is tantamount to understanding the mechanism and speed of hydrogen movement through the host matrix and provides the basis for the intelligent design of better fuel-cell membranes and hydrogen-storage materials. Neutron methods are capable of providing such molecular-scale information concerning hydrogen (and water) that is difficult if not impossible to obtain by other means. For example, neutron diffraction [13] is sensitive to the lightest elements and is thus invaluable for probing the crystallographic location of hydrogen (and water) in materials. Figure 6 shows a neutron diffraction pattern for Ti-doped NaAlD<sub>4</sub> [14]. The refinement allows one to quantify several impurity phases.

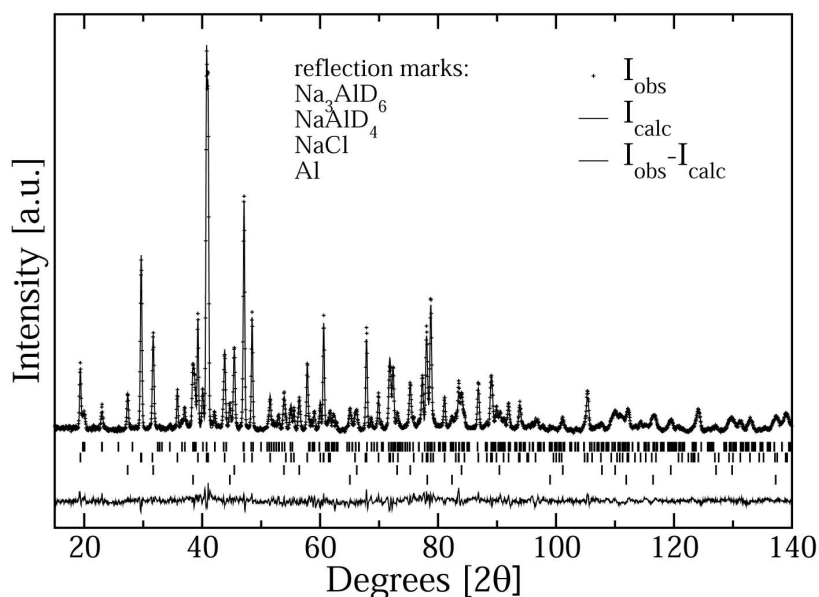


Figure 6. Neutron diffraction results for Ti-doped NaAlD<sub>4</sub> (from Majzoub, *et al.* [14]).

Due to hydrogen's extraordinarily large neutron scattering cross section, neutron vibrational spectroscopy (NVS) [15] directly reflects the interatomic interactions felt by hydrogen (and water) within hydrogen-storage materials and fuel-cell membranes. With an appropriate description of the bonding potentials, one can take advantage of the simple neutron scattering law to predict both the frequencies and intensities of the various vibrational modes. With such information, NVS can yield information on the occupancy of different hydrogen (and water) sites. Such information is particularly crucial in cases where the material is crystallographically disordered. Figure 7 illustrates a neutron vibrational spectrum of NaAlH<sub>4</sub> compared with *ab initio* calculations [16]. It is clear that good agreement between calculations and experiment requires the inclusion of both one- and two-phonon processes. First-principles calculations such as these as well as classical and quantum molecular dynamics simulations are critical to facilitate the fundamental understanding of the bonding and diffusion of hydrogen required to produce high-performance materials.

Finally, quasielastic neutron scattering [17] can provide atomic-scale temporal ( $10^{-8}$ - $10^{-14}$  s) and spatial information simultaneously on diffusive motions of hydrogen (and water) within fuel-cell materials, and as such, provides valuable insights about the molecular-scale geometry of the diffusion mechanism. This can in turn provide unique insights to the interpretation of NR



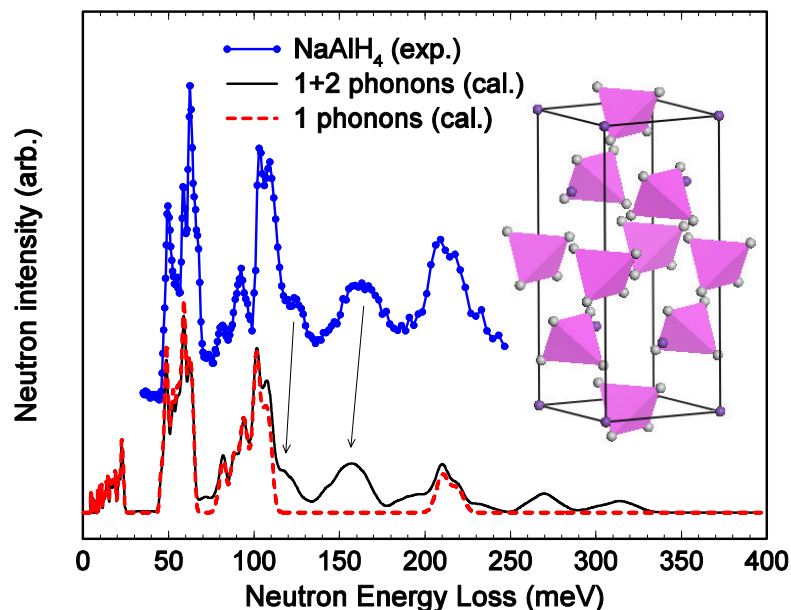


Figure 7. Neutron vibrational spectrum of NaAlH<sub>4</sub> (inset) compared with *ab initio* calculations that include one- and two-phonon processes (from Íñiguez *et al.* [16]).

and SANS imaging on the nanoscale. Figure 8 illustrates a typical quasielastic neutron scattering spectrum for the Laves-phase compound YMn<sub>2</sub>H<sub>0.65</sub> [18]. The different momentum-transfer dependence found for the two Lorentzian quasielastic components is in agreement with two different jump processes for the translations of hydrogen, a fast localized H motion between pairs of Y<sub>2</sub>Mn<sub>2</sub> interstitial sites and a much slower long-range diffusive motion.

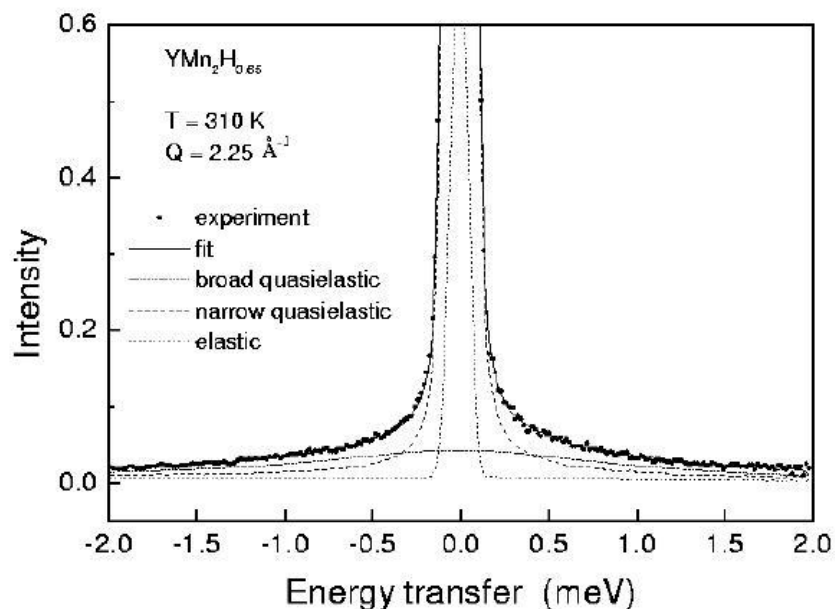


Figure 8. QENS spectrum for YMn<sub>2</sub>H<sub>0.65</sub> at 310 K and  $Q=2.25 \text{ \AA}^{-1}$  showing two quasielastic components (from Skripov *et al.* [18]).

A discussion of useful neutron techniques would not be complete without mentioning neutron prompt-gamma activation analysis (PGAA) [19]. PGAA is a novel, *in-situ*, highly-sensitive, nondestructive tool for quantitative analysis of hydrogen (down to the microgram level) as well as other elements in all types of materials, including those associated with fuel cells and hydrogen storage [20,21]. Quantitative analyses are accomplished by measuring the intensities



of element-specific, prompt gamma rays that are emitted upon nuclear capture of a neutron. Such information is difficult or impossible to obtain with other competing techniques.

### Conclusion

Neutron imaging, scattering, and analysis techniques can contribute immensely to fuel-cell and hydrogen-storage research. For the most part, this is due to the novel properties of the neutron and its interactions with matter, especially the different isotopes of hydrogen. The unusually large neutron scattering cross section for hydrogen can be exploited by a range of modern neutron methods in order to probe the amount, location, bonding states, dynamics, and concentration profile of hydrogen (and water) in any promising hydrogen-storage or fuel-cell material, over a wide range of length and time scales. Hence, neutron metrology techniques can enable us to address key issues for understanding and enhancing the performance of fuel cells and hydrogen-storage beds.

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