Detection of dynamical transitions in hydrogenous materials using transmission measurements with very cold neutrons

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ABSTRACT

We have tested the transmission of very cold neutrons as a method to measure dynamical transitions in hydrogenous materials. Transmitted intensities *vs.* temperature at 30 Å neutron wavelength were measured for four materials that undergo phase transformations associated with changes in dynamics: ammonium iodide, sodium borohydride, hexamethylbenzene, and dicesium dodecahydro-*closo*-dodecaborate. In some cases, neutron vibrational spectra above and below the transformation temperatures are compared to the transmission results. The measurements show changes in transmission at or near the transition for all these compounds, reflecting dynamical changes. The results demonstrate that the transmission method is sensitive to motional changes due to a wide range of structural transitions, from first-order to much more subtle order–disorder effects and for both small molecular species and larger molecules. The technique is valuable for rapid (ca. hours) scans of new materials to guide neutron inelastic scattering experiments or to complement the results of other techniques.

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1. Introduction

For more than half a century, neutron inelastic scattering methods have been a powerful and invaluable tool to study vibrational, rotational, and diffusive motions in hydrogenous materials of all kinds. Many of these studies involve measurements to probe transitions in dynamical behavior associated with phase transformations that occur as a function of temperature, pressure, or molecular adsorption and may involve significant changes in materials properties. The extensive use of neutron spectrometers around the world in such research often relies on previous thermal scans, NMR, or diffraction experiments, which are not always sensitive to dynamical changes on a neutron time scale ($\approx 10^{-14}$ s to $\approx 10^{-9}$ s), to decide at what temperature or pressure to carry out the requisite quasielastic or inelastic scattering measurements. In the present work, we demonstrate that simple measurements of the transmission of very cold neutrons through thin samples of hydrogenous solids as a function of temperature constitute a highly sensitive *in situ* probe of such dynamical changes. Transmission scans can be a useful guide for complex neutron scattering (and other) experiments, which ultimately determine the details of the motional changes detected by transmission.

The approach described in this paper had its genesis in neutron cross section research carried out more than fifty years ago [1–7]. It was predicted and demonstrated that total cross section measurements with long-wavelength neutrons were very sensitive to the total inelastic scattering that results from neutron-energy-gain scattering processes involving large amplitude vibrational or rotational modes in hydrogenous materials. The very large bound-atom neutron scattering cross section for hydrogen, 81 barns, is at least an order of magnitude larger than for most other elements. Under scattering conditions such that the velocity of the incident neutron, v, is much less than that of the scattered neutrons, the total inelastic scattering cross section increases linearly with $1/v$ (or with incident wavelength). Thus the total scattering cross section (obtained from neutron transmission measurements) also shows a linear increase with neutron wavelength, whose slope is a measure of the total dynamics of the system. A key point is that the neutron cross section continues to increase with increasing wavelength, so that the sensitivity of the method to the overall dynamics of hydrogenous species or molecules is greatly enhanced at very long wavelengths.

2. Experimental

All measurements were undertaken using instruments at the NIST Center for Neutron Research. The transmission measurements were performed using the Disk Chopper Spectrometer

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(DCS) [8]. Thin samples of a number of hydrogenous materials known to undergo phase transitions involving a range of dynamical changes with temperature were placed in closed-cycle refrigerators capable of controlled-rate temperature ramps. The choppers were operated at 2500 rpm and phased to produce pulses of 30 Å neutrons with $\approx 0.7\%$ full width at half maximum (FWHM) resolution (neutron energy ≈ 0.09 meV). A 4 cm $\times$ 6 cm ^{3}He detector array placed 40 cm downstream from the sample position measured the intensity of the transmitted beam. No attempt was made to take into account changes in small-angle scattering that might occur if there were a major change in microstructure in the sample associated with the transformation. With no sample or sample environment in the beam, the average incident intensity was 2.3×10^4 counts/min. The background count rate with the beam closed was 2 counts/min. We did not attempt to measure absolute transmissions or cross sections; this would have required increasing the measurement time significantly. It should be noted that, at 30 Å, the contribution of Bragg reflections to the scattering cross section is minimal, or nonexistent. The transmitted intensities observed as a function of temperature directly measure changes in beam intensity due to removal by scattering, which at very long wavelengths is dominated by scattering processes with neutron energy gain. The detector bank was "black" to the 30 Å neutrons used in these experiments.

Four samples were investigated: ammonium iodide (NH_4I), hexamethylbenzene (HMB; $C_{12}H_{18}$), ^{11}B-enriched sodium borohydride ($Na^{11}BH_4$), and ^{11}B-enriched dicesium dodecahydro-*closo*-dodecaborate ($Cs_2^{11}B_{12}H_{12}$). In the latter two samples, the lack of significant ^{10}B was important to avoid complications due to its very large absorption cross section. All samples were loaded into flat-plate aluminum containers with thicknesses chosen to obtain on the order of 50% neutron transmission at 30 Å.

To demonstrate the sensitivity of the transmission method, vibrational densities of states (VDOSs) were measured at different temperatures for some of the samples. Spectra for HMB and $Na^{11}BH_4$ were collected in neutron energy loss using the Filter Analyzer Neutron Spectrometer (FANS) [9] with pre- and post-monochromator collimations of 20 min of arc. HMB was measured with the PG(002) monochromator from 9 meV to 45 meV, with instrumental resolution ranging from 1.1 meV to 2.2 meV FWHM. Sodium borohydride was measured with the Cu(220) monochromator from 32 meV to 60 meV, with instrumental resolution ranging from 1.2 meV to 1.5 meV FWHM. VDOSs for $Cs_2^{11}B_{12}H_{12}$ at various temperatures were collected in neutron energy gain at the DCS using 5 Å incident neutrons. Over the 9 meV to 27 meV region of interest, the instrumental resolution varied from 0.4 meV to 1.5 meV FWHM.

Throughout the figures in this paper, the uncertainties in the transmitted neutron measurements and VDOS spectra are commensurate with the scatter in the data.

3. Results and discussion

The measurements described in this section proceed from solid NH_4I, which undergoes a dramatic dynamical transition, to several organic and complex ionic compounds with smaller, sometimes subtle, transitions in dynamical behavior.

NH_4I, along with other ammonium halides, exhibits a first-order phase transition from a (low-temperature) body-centered cubic (bcc) structure to a (high-temperature) face-centered cubic (fcc) structure [10], involving a major change in NH_4^+ motion at 280 K, from torsional vibrations to quasi-free rotation, which leads to a major change in cross section (and thus transmission). In Fig. 1 (black dots), we show the change in transmitted intensity as the temperature is raised from 180 K to 300 K at 0.2 K/min.
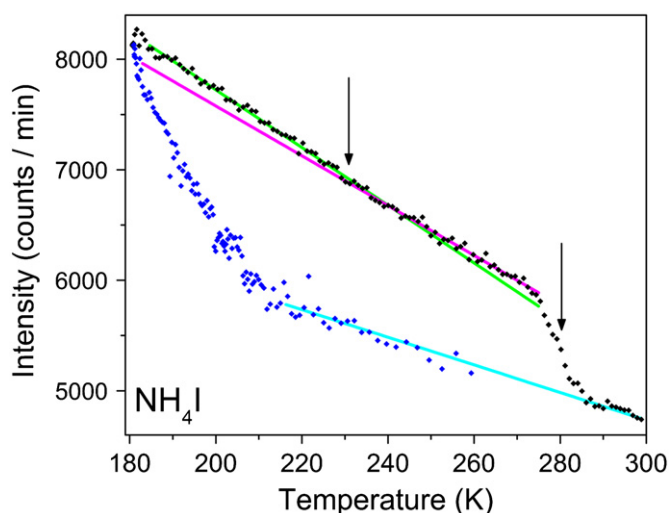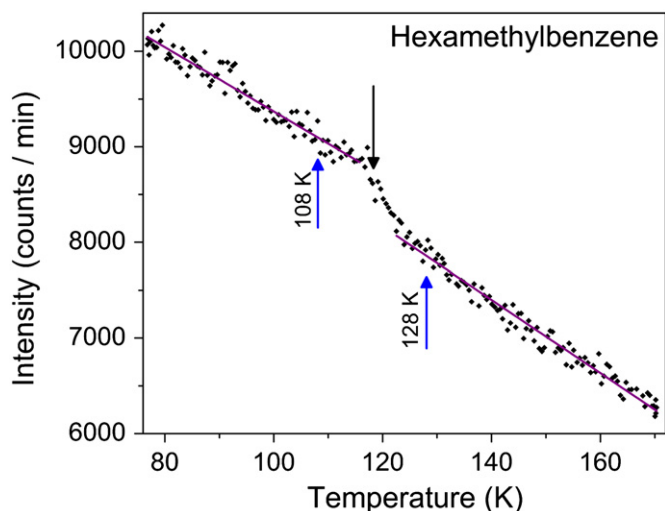

Fig. 1. Transmitted neutron intensity through NH_4I as a function of temperature, upon warming (0.2 K/min) from 180 K to 300 K (black) and cooling ($\sim$0.4 K/min) from 260 K to 180 K (blue), demonstrating significant hysteresis in the phase transition. The vertical arrows denote the phase transitions at 231 K and 280 K upon heating. The green and magenta lines are linear fits to the regions above and below the order–disorder phase transition near 231 K, to emphasize the change in slope at the phase transition. The cyan line is an interpolation across a region for which no data were collected. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A major drop in intensity is clearly observed near 280 K, reflecting the removal of 30 Å neutrons from the transmitted beam due to a sharp increase in rotational inelastic scattering at the first-order transition [4]. A slight change in slope is also observed near 231 K, where a much less pronounced order–disorder transition for the bcc structure is known to occur.

Moreover, Fig. 1 shows hysteresis effects that could affect the choice of measurement conditions for neutron spectroscopy experiments. The results obtained on cooling, from 260 K to 180 K (blue dots), show that the transition to the bcc structure shifts to ≈ 200 K, as a result of supercooling in the high-temperature phase [4,11–13]. This is consistent with the sensitivity of the neutron transmission to changes in ammonium rotations that accompany these phase transitions.

As a second example of the neutron transmission technique, we measured intensities transmitted through a sample of hexamethylbenzene, which undergoes a subtle crystallographic transition at 118 K [14] that has been shown [5,6] to involve a change in the methyl torsional mode spectrum, presumably due to a change in intermolecular interactions between methyl groups on the HMB molecules. The results (Fig. 2) clearly show a decrease in transmitted intensity as the temperature is raised through the phase transition region. In Fig. 3, we show a measurement of the VDOS just below and just above the phase transition from the low-temperature phase III to high-temperature phase II. In phase III, at 4 K, the dominant features at 16 meV and 20 meV are assigned to the lowest-level torsional modes of the "geared" methyl groups. As the temperature is raised to 108 K, the same features remain, albeit somewhat broadened. Above the transition, at 128 K, the methyl-torsion density of states is broadened and shifted to lower energies as the methyl potential is softened. This general behavior has been observed in previous measurements [6], but the main point is that this dynamical change is easily observed in the transmission measurements, primarily due to the change in neutron-energy-gain scattering processes from the increased population of CH_3-group torsional levels, which in turn increases the total hydrogen cross section.
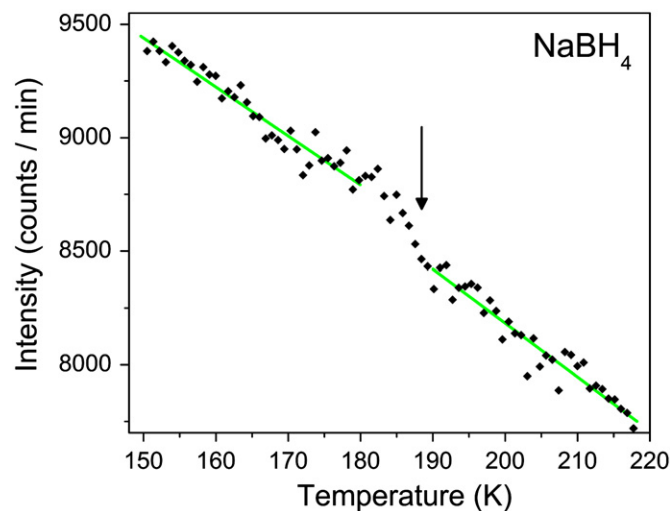
Fig. 2. Transmitted neutron intensity through HMB as a function of temperature. There is a discontinuity over the temperature range of the (III–II) phase transition at 118 K, marked with a downward arrow. The blue arrows indicate temperatures at which vibrational spectra were collected, shown in Fig. 3. The solid lines, intended as guides to the eye, are fits to temperature regions above and below the transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
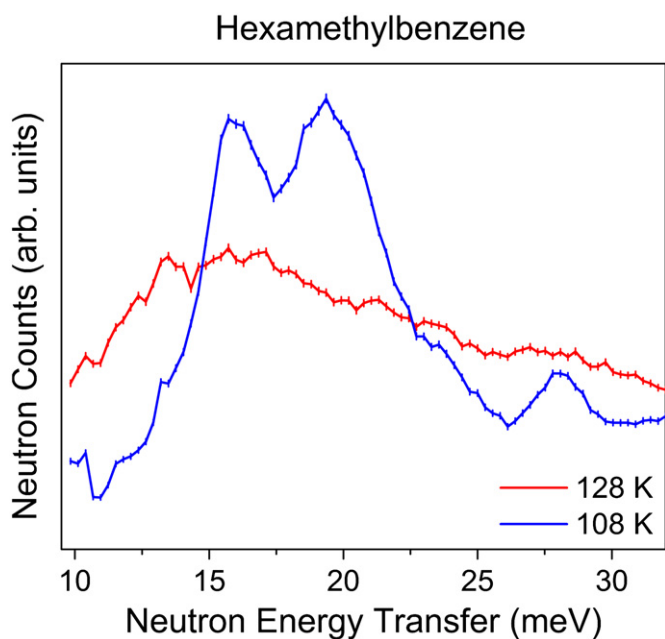
Fig. 3. Low-energy neutron vibrational densities of states of HMB at 108 K (blue), below the III–II phase transition, and at 128 K (red), above the phase transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As a third example, we show in Fig. 4 the measurement of transmitted intensities through a $Na^{11}BH_4$ sample undergoing an order–disorder transition at $\sim$188 K from a (low-temperature) tetragonal phase to a (high-temperature) cubic phase. The transmitted intensity changes are compared to observed changes in inelastic scattering due to BH_4^- ion torsional modes. We observe a small but distinct step in intensity at the $NaBH_4$ phase transition. For comparison, we show in Fig. 5 the inelastic scattering spectrum of $NaBH_4$ in the region of the BH_4^- ion torsional modes. The spectra below and above the phase transition, at 185 K and 195 K, respectively, are both broad, with a notable decrease in peak area on raising the temperature through the transition to a disordered

Fig. 4. Transmitted neutron intensity through $Na^{11}BH_4$ as a function of temperature. A phase transition is observed around 188 K, denoted by the arrow.

arrangement of borohydride groups. This result once again demonstrates the sensitivity of very long wavelength transmission measurements to relatively small changes in dynamics.

As a final demonstration, we have measured the sensitivity of the method to dynamical changes in larger molecular species in solids. Such systems generally yield smaller inelastic scattering cross sections for rotational processes due to their larger moments of inertia [15,16]; that of the $B_{12}H_{12}^{2-}$ ion is 5.3×10^{-45} kg m^2, whereas those of NH_4^+ and BH_4^- are two orders of magnitude smaller, 6.6×10^{-47} kg m^2 and 4.7×10^{-47} kg m^2, respectively. Very recent work [17] on the structure and thermal transitions in $Cs_2B_{12}H_{12}$ suggests a second-order phase transition near 529 K involving a more disordered orientational state for the $B_{12}H_{12}^{2-}$ ions.

The transmitted intensity through a sample of $Cs_2^{11}B_{12}H_{12}$ is shown in Fig. 6, and the amplitude-weighted VDOS is shown in Fig. 7 at a series of temperatures. There is a clear change in transmitted intensity, reflecting an increase in inelastic scattering, very close to the 529 K transition temperature suggested by DSC measurements [17]. On the other hand, a careful examination of the VDOS spectra in Fig. 7 does not reveal changes in the torsional (or translational) modes in the transition region, despite the order/disorder transition. This demonstrates the sensitivity of the neutron transmission method to relatively small dynamical changes in larger molecular species. The method could thus be appropriate for studies of dynamical transformations in larger organic molecules or polymers.

The sensitivity of the transmission technique that we have described in this paper could be improved by going to even longer wavelengths, as long as intensities are adequate to the task, since the energy gain cross section increases linearly with wavelength [2–5,7]. The sensitivity could be further improved using a somewhat thinner neutron detector, better matched to the very long wavelengths used in these measurements. In the present experiments, we used a normal array of ^{3}He detectors, optimized for (2–4) Å neutrons and therefore "black" to 30 Å neutrons.

Samples for neutron scattering experiments are generally prepared to have $\approx$90% transmission in order to restrict multiple scattering to an acceptable level. For hydrogenous materials, such samples will have transmissions $\approx$(30–60)% at neutron wavelengths of (30–40) Å, depending on the extent to which energy-gain processes dominate the total scattering cross section, thus providing more optimal statistics for counting transmitted neutrons. Thus a hydrogenous sample placed in a cryostat,
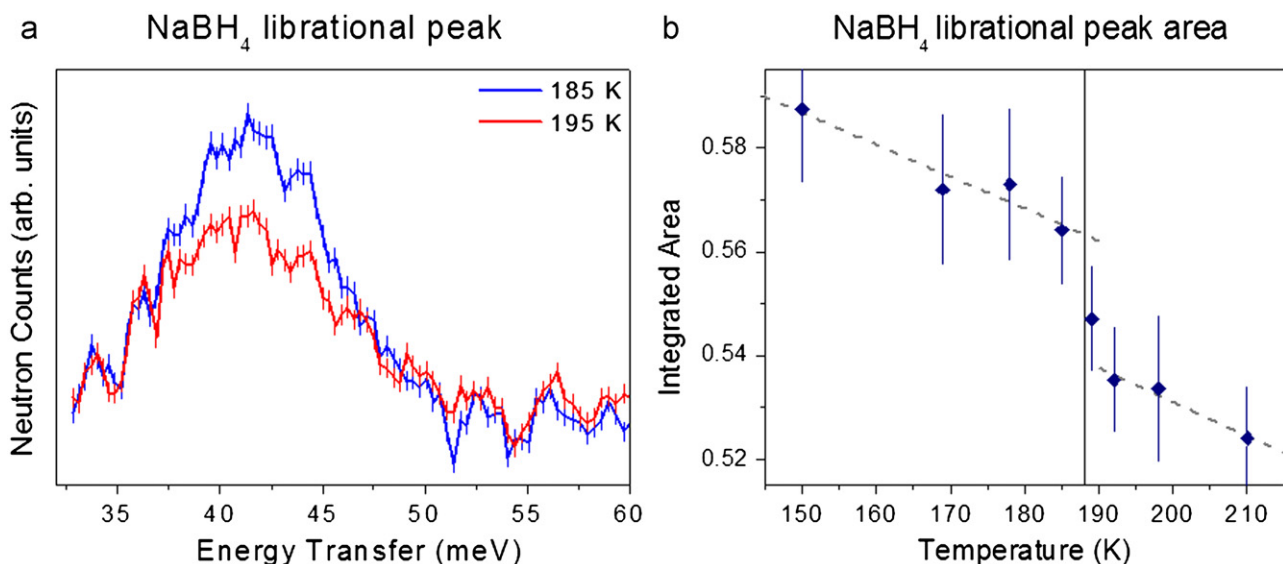
Fig. 5. (a) The 44 meV librational mode of $Na^{11}BH_4$ at 185 K (blue) and 195 K (red). (b) The peak area, integrated from 34 to 50 meV, changes dramatically across the phase transition at 188 K, denoted by the black vertical line. The error bars represent statistical error of the integrated area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
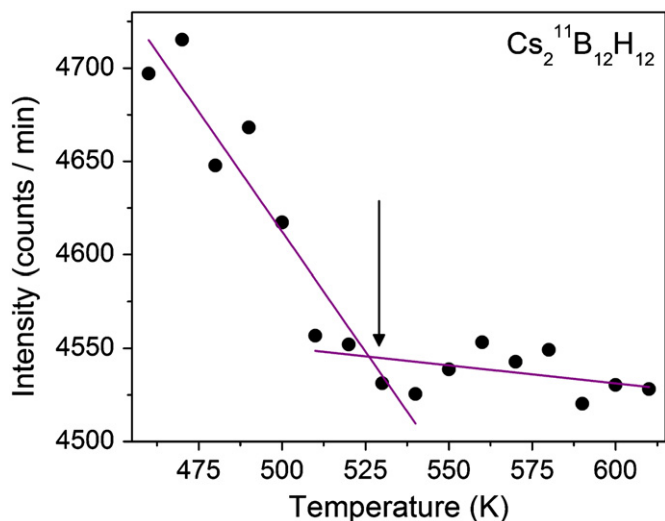

Fig. 6. Transmitted neutron intensity through $Cs_2^{11}B_{12}H_{12}$ as a function of temperature. A change in slope coincides with a recently reported phase transition at 529 K, which is indicated by an arrow.
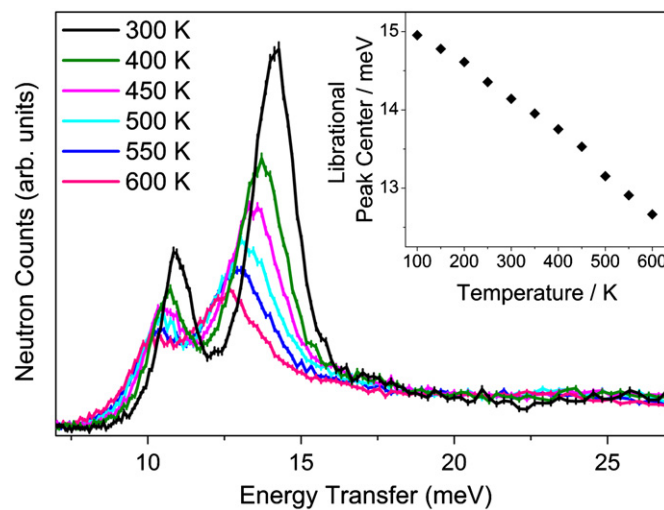

Fig. 7. The librational mode of $Cs_2B_{12}H_{12}$ broadens with temperature and shifts from 15.4 meV at 4 K (not shown) to 12.7 meV at 600 K. The inset shows the shift of the librational peak center with temperature.

furnace, or pressure device, e.g., can first be used for a quick (on the order of hours) transmission scan using very long wavelength neutrons, and then used without removal for detailed inelastic and quasielastic scattering measurements at a relatively short wavelength to probe details of the dynamics.

4. Conclusions

Neutron transmission measurements at very long wavelengths are an extremely sensitive probe of dynamical changes, which occur during phase transformations in hydrogenous solids with changes in temperature, pressure, or molecular adsorption. The results shown here demonstrate that the technique can detect motional changes due to a wide range of structural transitions, from first-order to much more subtle order–disorder effects. The method is also shown to be sensitive to the rotational dynamics of both small molecular species or ions and larger molecules or complexes, and might be used for studies of dynamical transitions in organic solids or polymers. While the method is most suitable to be used jointly with more complex inelastic neutron scattering experiments to probe the details of detected motional changes, the ability to quickly scan a hydrogenous solid for dynamical transitions would also be of value to help guide or interpret related studies by NMR, thermodynamic, spectroscopic, or diffraction methods, which are sometimes carried out sequentially or combined with neutron studies. It should be noted that a dedicated beam of very cold neutrons could be rather simply provided by placing a reflector in a guide tube and extracting very long wavelengths to allow rapid transmission measurements.

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