

The vibrational spectrum of magnesium hydride from inelastic neutron scattering and density functional theory

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Abstract

Light-weight magnesium metal can reversibly store up to 7 wt.% hydrogen and is therefore interesting for application as hydrogen storage material. Neutron vibrational spectroscopy has been used to study the interactions of hydrogen atoms with its surroundings. The neutron spectra are compared directly with density functional theory calculations providing detailed insight in structure and dynamics. Dispersion of the vibrational modes has to be taken into account in order to reproduce the data. This study on bulk magnesium hydride will provide a bench mark for similar studies on nanostructured magnesium alloys: these are more promising as hydrogen storage materials because of their significantly faster hydrogen sorption processes. Because of its sensitivity and the compatibility to calculations, the vibrational spectra of these nanostructured compounds can be used as a probe for the local structure and the influence of the nanostructure on the potential landscape experienced by the hydrogen. Parameters can be extracted for MD and Monte Carlo calculations of slower diffusion processes.
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1. Introduction

The use of hydrogen as an energy carrier is hindered by several technical problems. Hydrogen is a very light and volatile gas, so that high pressures (several hundred atmospheres) or very low temperatures (hydrogen condenses at 20 K and 1 bar) are needed to store an amount sufficient for mobile applications. Since several decades scientists are looking for materials which can reversibly store hydrogen. Currently, intensive research is on light-weight magnesium alloys [1]. The hydride MgH_2 stores hydrogen up to approximately 7 wt.%. However, its use at the present time is limited due to slow kinetics of the hydriding and dehydriding reaction, even at elevated temperatures.

To enhance the hydrogen sorption properties it is tried to reduce particle size, or alloy magnesium with other elements, or add catalysts [2]. Structural characterization methods such as X-ray diffraction are lacking sensitivity for

the defect-type changes in the structure of the magnesium caused by the particle size reduction treatments. Neutron vibrational spectroscopy, on the other hand, can distinguish materials having different treatment histories. By applying neutron vibrational spectroscopy and comparing the results with computer calculations a structural model can be found that reproduces the vibrational data [3]. In order to apply these methods to MgH_2 and its nanostructured varieties a first step is to understand the bulk vibrational spectra. This first step is presented here. The calculations can tell which peaks are to be assigned to which vibrational modes in the data. It may be noted that vibrational spectra obtained with neutrons are significantly more straightforward to simulate than light-scattering spectra such as obtained with Raman and infrared spectroscopy. The reason is that the neutron spectra represent the motions of the nuclei, not of the electrons, and the interaction between nucleus and neutron is known exactly. This makes that the intensities of the spectra at all relevant frequencies can be calculated much more directly. Additionally, the sensitivity is highest for the important element hydrogen. Modern calculation methods using density functional theory are able to predict the experimental

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spectra with sufficient accuracy [4]. In this paper, we present experimental work on commercial magnesium hydride powder as well as a simulated spectrum calculated using density functional theory. It is shown that it is possible to achieve a satisfying agreement between measurement and calculation if we take into account dispersion.

2. Experiment

The neutron scattering spectrometer TOSCA we used is located at the pulsed neutron spallation source ISIS in the UK¹. This spectrometer uses an ‘inverted geometry’ and is at present the fastest machine of its kind in the world. Incident on the sample is the pulsed beam of thermal neutrons which have been thermalised in water near the spallation source. Those neutrons which are scattered over an angle of 135° (backward scattering) or 45° (forward scattering) and which have a final energy of 3.5 meV are counted. By means of the time-of-flight of the neutrons their incident velocity can be calculated from which their energy transfer is derived. The sample is mounted in an air-tight aluminium sample container in a glove box. To obtain an accurate spectrum in a reasonable time, 0.30 g of magnesium hydride was loaded in the sample container. The measured spectrum from the commercially obtained bulk magnesium hydride is shown as the top curve in Figs. 1 and 2.

The broad wings in the spectrum are typical for a solid-state, dispersed phonon spectrum. An exception is the extremely narrow peak near 75 meV. The width of this peak is comparable to the width of the resolution function of TOSCA at this energy transfer. Normally such sharp peaks only arise in the case of a molecular crystal where certain internal modes of one molecule are not coupled to those of a neighbouring molecule.

In light scattering, the momentum transfer at energy transfers in the region 0–500 meV is always small compared to relevant momentum transfers in the sample. The reason is that the wavelength of light is approximately 1000 times larger than typical atomic distances. For instance, Raman spectroscopy measures at a momentum transfer close to zero, the point of the Brillouin zone which is easy to calculate. The Raman spectra do not show the dispersion therefore. The measured Raman spectrum has a huge background due to fluorescence. This background has partly been subtracted so that the spectrum fits in Fig. 1 (bottom curve).

2.1. Density functional theory and phonon calculations

With a calculation method which produces the energy of the total system for a given arrangement of the atoms and the Hellmann–Feynmann (HF) forces from the electronic wavefunction, it is possible to calculate the frequency spectrum.

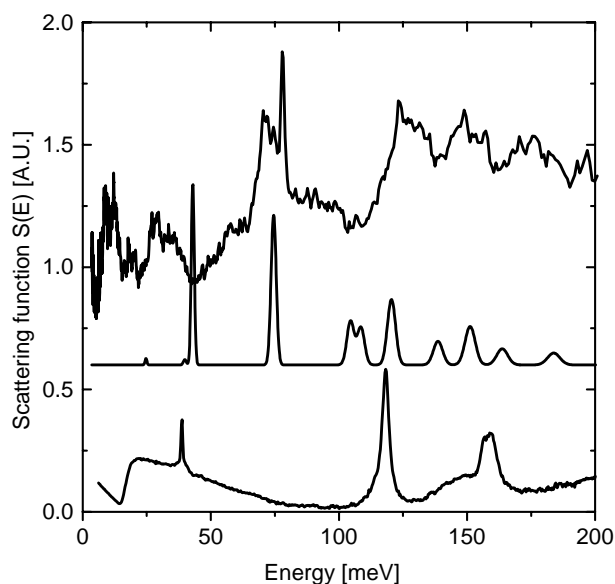


Fig. 1. Vibrational spectrum of MgH₂ obtained with neutron spectroscopy (top curve), together with a Γ -point calculation with density functional theory (middle curve) and the Raman spectrum of the same compound (bottom curve).

One starts with an optimised structure so that the atoms are in their minimum energy position for the calculation, with residual forces close to zero. Then each of the atoms in the asymmetric unit cell is displaced over a small distance along each of the Cartesian directions and the electronic structure is calculated for each displaced configuration giving the Hellmann–Feynmann forces on all atoms. Each configuration therefore gives one row of the matrix of force constants, the remaining rows being derived from the space group symmetry. Introducing the atomic masses in the force constant matrix gives the dynamical matrix, from which the normal mode frequencies and eigenvectors are obtained by diagonalization. The INS spectrum is completely determined by this information, the atomic scattering cross-sections and the scattering vector \mathbf{Q} .

The neutron scattering spectrum as calculated using DFT with Dmol³ (Γ -point only, no dispersion) is shown in Fig. 1 as the curve in the middle. This calculation used periodic boundary conditions on the unit cell. It clearly does not reproduce the neutron spectrum we measure. Note that the peaks calculated at 40 and 120 meV have analogues in the Raman spectrum. The Hirshfeld partitioning of the calculated electron density gives a charge of $-0.16e$ on the hydrogen atoms and $+0.32e$ on the magnesium atoms. This shows that the bonding is partly covalent, partly ionic.

Such a calculation with periodic boundary conditions is equivalent to a calculation at a momentum transfer of 0 \AA^{-1} (the Γ -point). The fact that this Γ -point-only calculation does not at all reproduce the neutron spectrum shows that the interactions between atoms in neighbouring unit cells are not negligible. Therefore, the energy of a wave excited in the crystal by a neutron depends on its wavevector or momentum

¹ See <http://www.isis.rl.ac.uk/molecularspectroscopy/tosca/> for a description of the instrument.

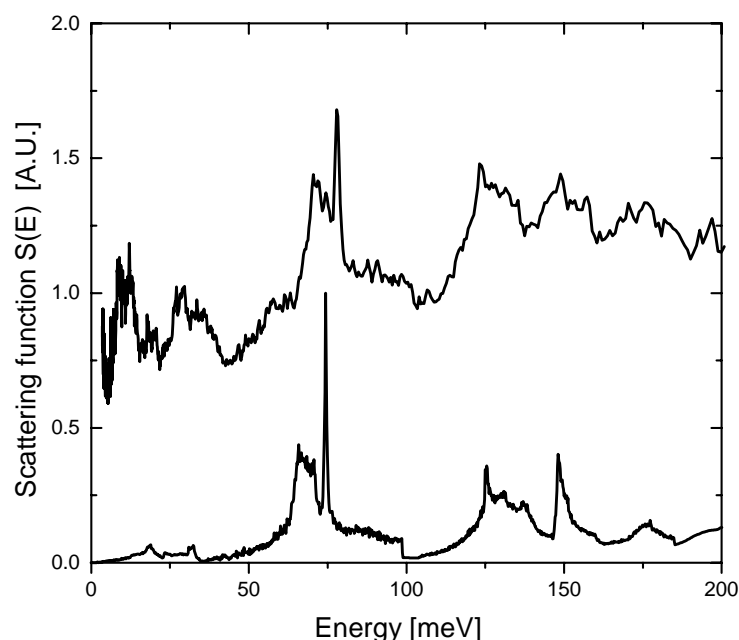


Fig. 2. Vibrational spectrum of MgH_2 obtained by neutron spectroscopy (top curve) and simulation using a phonon calculation with force constants from density functional theory (bottom curve).

k (phonon dispersion). In order to take this dispersion into account, a more detailed phonon calculation had to be done.

For the phonon calculations on magnesium hydride we chose a supercell with dimensions of $2a \times 2b \times 3c$ that is $8.5 \text{ \AA} \times 8.5 \text{ \AA} \times 9 \text{ \AA}$. This is reasonable when compared to practice: a phonon calculation is converged if the force constants between an atom at the centre of the supercell and those at the cell boundaries are effectively zero. For crystals of uncharged, organic molecules, this sphere of interaction typically has a radius of $\approx 5 \text{ \AA}$. Since DFT methods scale in computational time with the third power of the number of atoms, the supercell calculations are considerably longer than single cell calculations.

All DFT calculations were performed with VASP [5,6] using Vanderbilt-type ultrasoft pseudopotentials [7]. The recommended energy cut-off (396 eV) and a k -point spacing of 0.1 \AA^{-1} were used. Atomic co-ordinates and lattice parameters were optimised in the single unit cell before constructing the $2 \times 2 \times 3$ supercell and optimising the co-ordinates of the atoms once more. Using a reciprocal space representation for the pseudopotentials and a fine integration grid, as flagged by the ADDGRID command in VASP, very small residual forces on the atoms were obtained. The maximum residual force was 10^{-5} eV/\AA and the average force was 10^{-6} eV/\AA . A series of single point energy calculations, each of which give Hellmann–Feynman forces acting on all atoms in the supercell, were then performed on the structures obtained by displacing, one at a time, each of the three inequivalent atoms by 0.05 \AA in the inequivalent, positive and negative Cartesian directions. That gave eight HF force calculations in all.

The HF forces and optimised supercell structure were then given as input to the program PHONON [8–10], which, by

implementing the direct method, generates and diagonalises the dynamical matrix for any point in reciprocal space, using all the symmetry of the crystal structure (MgH_2 has a rutile-type structure with space group $P4_2/\text{mmm}$). Force constants were checked and found to decay by three orders of magnitude in going from the supercell centre to the closest cell boundary.

For the density of states (DOS), a large number of reciprocal space points were chosen at random. The calculated external mode spectrum was then used to generate the multiphonon contributions to the spectral profile. The calculated dynamical structure factor $S(\mathbf{Q}, \omega)$ was obtained from the DOS for an isotropic polycrystalline sample, for the scattering configuration of the instrument. Finally the spectrum was convoluted with the instrumental resolution function. The spectrum that results is shown in Fig. 2 as the bottom curve. The accordance of the measured and calculated spectrum is remarkable.

3. Discussion and conclusions

From the results obtained here we infer that an accurate description of the measured spectrum of magnesium hydride can be given if the force constants are evaluated using a supercell of at least $2 \times 2 \times 3$ unit cells. Force constants which range longer than the size of this supercell appear to be sufficiently small to be negligible. A mapping of the Brillouin zone in reciprocal space using the program PHONON then reproduces the spectrum in an accurate way. Surprisingly the sharp feature present in the spectrum of magnesium hydride has its origin not in a local mode. It is due to the existence

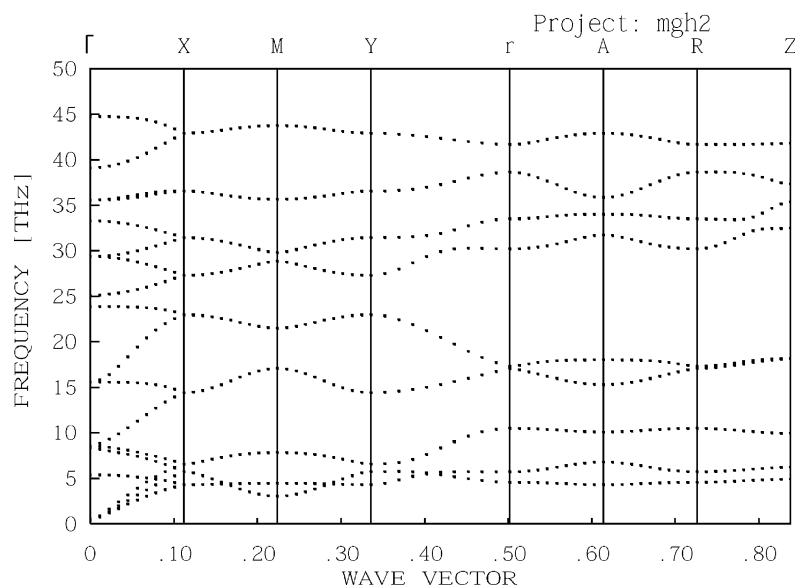


Fig. 3. The phonon dispersion curve as calculated by PHONON from force constants obtained from a density functional theory calculation using VASP.

of a relatively flat part of the phonon branch as can be seen from Fig. 3. Around the point A in the Brillouin zone, the phonon dispersion curve shows a flat part. The energy of this mode is the same as the energy of the sharp feature in the spectra. The point A in the Brillouin zone is shown in Fig. 4. The wavevector associated with this point is one which has a wavelength of twice the unit cell in all directions. This means that the vibrations in all neighbouring unit cells are anti-parallel. Phonons with wavevectors close to this point have energies very close to 75 meV so that a peak at this energy arises.

Now the spectrum is understood the vibrational spectroscopy may be applied to other than bulk MgH_2 samples. For instance, if one substitutes some atoms or induces some stress in the material, phonon frequencies are expected to change by certain amounts. It may be anticipated that a small distribution in substituent concentration or induced stress will smear out the sharp peak, and such features may thus

provide a sensitive probe for changes in the local environment of a hydrogen atom up to the length scale of a nanometre, which is not accessible by diffraction. Because of this small length scale it is also sensitive for defects, provided that the defect concentration is high enough. Defect concentrations may be very important for the hydriding and dehydriding properties of metals like magnesium. At present, results on nanostructured MgH_2 are being analysed and they do indeed show a large change of the narrow peak at 75 meV, in addition to more subtle changes.

We conclude that it is possible to reproduce the spectrum of a metal hydride system in a reliable way if one takes into account dispersion. We discussed certain features in the experimental spectrum using the calculation. This technique is potentially very useful as a probe of the environment of the hydrogen atom in magnesium hydride which is modified on nanometre length scales.

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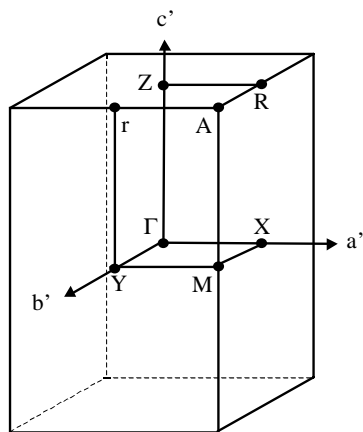


Fig. 4. The Brillouin zone of the tetragonal MgH_2 structure. Symmetry points used by the calculation are indicated.