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Neutron spectroscopy of magnesium dihydride

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ABSTRACT

Inelastic neutron scattering spectra of α-MgH_2 powder have been measured at $T = 7$ K with an energy resolution better than 1.5% using the time-of-flight direct geometry spectrometer SEQUOIA. Based on these spectra, the density $g(E)$ of phonon states in α-MgH_2 has been experimentally constructed for the first time. Comparing the available experimental data on the heat capacity of α-MgH_2 with those calculated using the obtained $g(E)$ confirmed the good accuracy of its determination.

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1. Introduction

Due to the very large neutron scattering cross-section of H atoms, inelastic neutron scattering (INS) is one of the most direct and powerful means of studying the lattice dynamics of metal hydrides. Under rather realistic simplifying assumptions, the one-phonon scattering contribution can be derived from the INS spectrum of a powder sample and further converted to the phonon density of states, $g(E)$, where E is the phonon energy. The "experimental" $g(E)$ spectra thus obtained can directly be compared with results of computer calculations and are traditionally used to establish the main features of vibrational spectra of the studied hydrides, such as the peaks positions, cut-offs of the vibrational bands, etc.

The $g(E)$ spectrum can also be used to calculate the contribution from lattice vibrations to the heat capacity $C_V(T)$ at constant volume. For dielectric hydrides like those of Mg and Al and many other metals, this spectrum therefore fully determines the heat capacity and, consequently, every standard thermodynamical potential. The $g(E)$ spectrum derived from INS measurements at low temperatures allows, in principle, calculating the $C_V(T)$ dependence up to very high temperatures, much exceeding the temperature of thermal decomposition of the hydride at ambient pressure. This is a definite advantage of applying the INS technique to hydrides because the high-energy modes of H vibrations in hydrides make the standard Debye model inapplicable for the quantitative description and any extrapolations of their $C_V(T)$ dependences. Meanwhile, the thermodynamical properties of hydrides above the decomposition temperature are usually most interesting for applications, e.g., for the hydrogen storage.

Constructing the $C_V(T)$ dependence based on $g(E)$ requires accurate and detailed INS data, and such a dependence was only recently obtained for α-AlH_3 in our work [1] using the INS results of Ref. [2]. The heat capacity of α-AlH_3 was calculated at temperatures 30–1000 K with an accuracy of no worse than few per cent [1] and further used to construct the line of the $Al + (3/2)H_2 = AlH_3$ equilibrium at temperatures up to 900 K and hydrogen pressures up to 9 GPa [3] (a brief description of these results can also be found in the review paper [4] in this issue).

It should be noted, however, that the good accuracy of the $C_V(T)$ determination for α-AlH_3 was partly achieved thanks to the specific shape of its $g(E)$ spectrum divided into three well-separated vibrational bands. To estimate the accuracy of the $C_V(T)$ determination that neutron spectroscopy can provide in the general case of a dielectric hydride with broad bands of lattice and optical vibrations, we have chosen α-MgH_2 for the present investigation. A unique feature of α-MgH_2, which decomposes to Mg and H_2 at ~550 K under ambient pressure, is that its heat capacity has earlier been determined up to a temperature as high as 2000 K [5] using the analogy with a more thermally stable and thoroughly studied MgF_2 compound. A comparison with results of Ref. [5] gave a rare opportunity to check the accuracy of calculation of the heat capacity of α-MgH_2 using the INS data.

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α-MgH_2 with a tetragonal rutile-type structure, space group $P4_2/mnm$, is the most stable modification of magnesium dihydride under ambient conditions [6]. Lattice dynamics of powder samples of α-MgH_2 were earlier studied by INS with the beryllium filter spectrometer IN1-BeF at ILL, France [7] and inverse-geometry spectrometer TOSCA at ISIS, UK [8,9]. These studies revealed the basic features of the α-MgH_2 phonon spectrum, and the origin of these features was well established by *ab initio* calculations supplemented the experiment in Ref. [8]. However, the experimental results of works [7–9] were insufficient to construct $g(E)$ suitable for calculating the heat capacity. The main obstacle was that at energy transfers exceeding 100 meV, the one-phonon scattering intensity could not be reliably isolated from the intense multi-phonon contribution caused by the large neutron momentum transfers Q. Large neutron momentum transfers at high energy transfers are intrinsic to spectrometers with small energy of the registered neutrons, like IN1-BeF and TOSCA.

In the present work, we studied α-MgH_2 powder using a direct-geometry neutron spectrometer SEQUOIA at ORNL, USA. The obtained INS spectra had much smaller contributions from the multiphonon neutron scattering due to the ability of the spectrometer to provide small momentum transfers at large energy transfers. This allowed us to get a more accurate one-phonon INS spectrum than previously and to construct the experimental phonon density of states for α-MgH_2 for the first time. With this $g(E)$, we calculated the dependence $C_V(T)$ of heat capacity of α-MgH_2 at constant volume and further estimated the corrections converting the $C_V(T)$ to $C_P(T)$ at constant pressure at temperatures up to 2000 K by using the literature data on the compressibility of α-MgH_2 [6,10] and the coefficient of thermal expansion determined from our own X-ray diffraction measurements at 11–300 K.

2. Experimental details

Powder of magnesium dihydride was purchased from Sigma–Aldrich. An X-ray examination showed the powder to consist of 98% α-MgH_2 and 2% Mg metal. A one gram sample of this powder was measured at 7 K using the newly constructed fine energy resolution spectrometer SEQUOIA at the Spallation Neutron Source (Oak Ridge National Laboratory) [11]. SEQUOIA is a direct geometry time-of-flight spectrometer with variable energies of incident neutrons, from 10 to 2000 meV. To get the best energy resolution of $\Delta E/E_i = 1$–1.5% at every studied energy transfer, we measured the INS spectra with 5 different incident energies of $E_i = 45$, 115, 220, 350 and 750 meV selected by the Fermi chopper that was rotating at 420 Hz for $E_i = 45$ meV and 600 Hz for other energies. The data were recorded over a wide range of scattering angles, from −30° to +60° in horizontal plane and ±18° in vertical directions. Prior to further treatment, the collected neutron scattering data were transformed from the time-of-flight and instrument coordinates to the dynamical structure factor $S(Q,E)$. The background spectra for the empty container were measured under the same conditions and subtracted from the original data.

To determine the coefficient of thermal expansion of α-MgH_2, X-ray diffraction patterns of the α-MgH_2 powder were collected at temperatures from 11 to 300 K using monochromated synchrotron radiation with a wavelength of λ = 0.10798 Å at beam line 11-ID-C at the Advanced Photon Source, ANL. The patterns were recorded on a Perkin-Elmer 2D detector. Rietveld refinements were performed with the GSAS and EXPGUI [12].

3. Results and discussion

3.1. Inelastic neutron scattering

Fig. 1 shows the $S(Q,E)$ spectrum of α-MgH_2 merged from the spectra measured with the five different energies of the incoming neutrons. The spectrum mostly agrees with results of Refs. [8,9]. According to the *ab initio* calculations in Ref. [8], the phonon density of states of α-MgH_2 is composed of the ranges of lattice modes at $E < 40$ meV and optical vibrations at $40 < E < 190$ meV. The contributions from the Mg atoms to the INS spectrum are small for all vibrations, because the neutron scattering cross-section of H is about 20 times larger than that of Mg [13]. Furthermore, in the case of optical vibrations, the scattering intensity is inversely proportional to the mass of the atom, which is 24 times smaller for H than for Mg. The INS spectrum in Fig. 1 thus well represents vibrations of the H atoms in α-MgH_2.

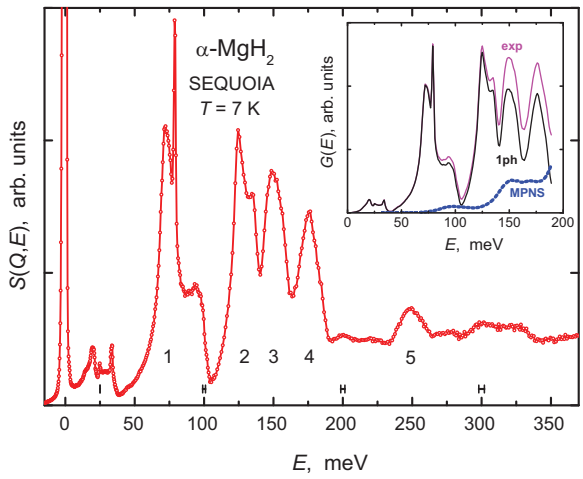

Fig. 1. The dynamical structure factor $S(Q,E)$ of the α-MgH_2 powder sample (open circles) as a function of the energy loss ($E > 0$) or gain ($E < 0$) of the inelastically scattered neutrons measured at 7 K with the SEQUOIA spectrometer at ORNL, USA. The strong peak at $E = 0$ is due to the elastic neutron scattering. The horizontal bars at the bottom of the figure indicate the energy resolution. In the inset, the thick solid line labelled "exp" shows the generalized phonon density of states, $G(E)$, derived from $S(Q,E)$ with subtracted elastic peak; the dashed line "MPNS" represents the multiphonon contribution to $G(E)$ calculated in an isotropic harmonic approximation, and the thin solid line "1ph" is the one-phonon $G(E)^{1ph}$ spectrum of α-MgH_2 obtained from $G(E)$ by subtracting the MPNS contribution.

As seen from Fig. 1, the spectrum of optical H vibrations consists of a band between 40 and 105 meV (two pronounced peaks at 72 and 79 meV, and a shoulder at ≈94 meV) and another band between 105 and 190 meV (a peak at 125 meV with a shoulder at 134 meV, and two peaks at 150 meV and 176 meV). According to the calculations in Ref. [8], the scattering intensity at higher energy transfers, including the peak at 250 meV, could only have resulted from multiphonon neutron scattering. To prove this, we analyzed the momentum transfer dependences of the integral intensities of peaks numbered 1–5 in Fig. 1. These dependences are shown in Fig. 2 and fitted with curves

$$I(Q) = (a \cdot Q^2 + b \cdot Q^4)\exp(-u_H^2 Q^2) \quad (1)$$

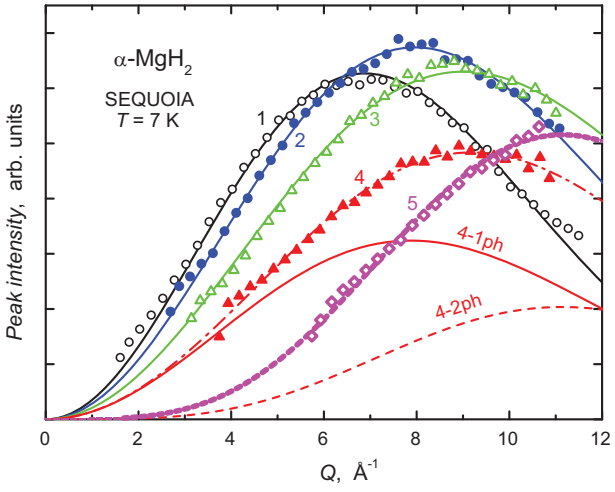

Fig. 2. The integral intensities of peaks 1–5 in Fig. 1 plotted as a function of neutron momentum transfer. The experimental data (symbols) are fitted using Eq. (1). The solid and dashed lines represent, respectively, the one-phonon and two-phonon scattering contributions to the fits (see text).