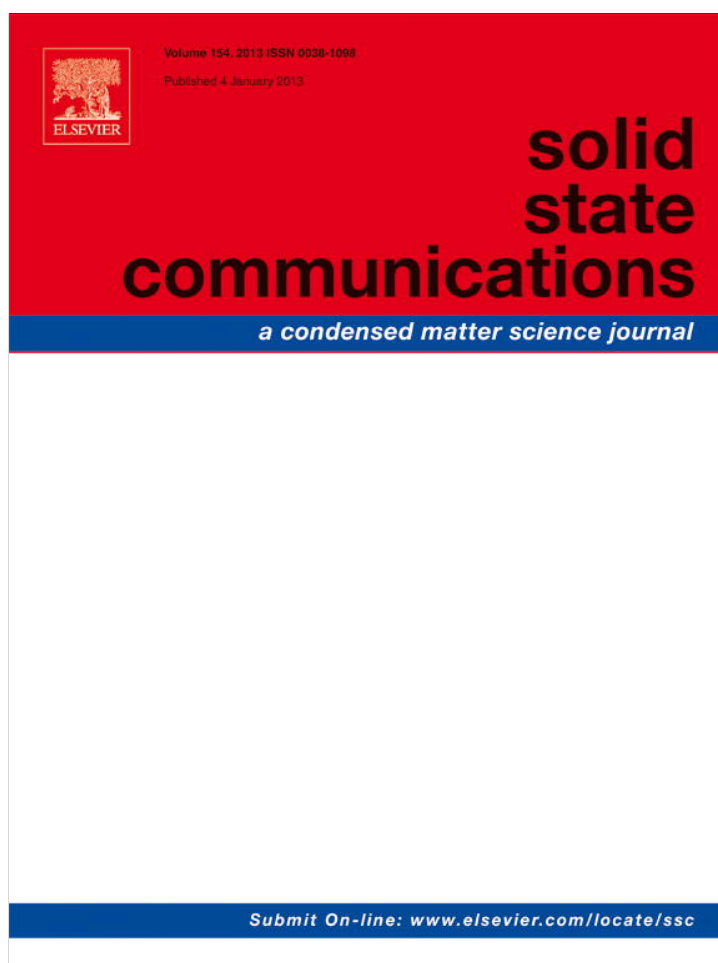




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Raman scattering study of α -MgH₂ and γ -MgH₂

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ABSTRACT

Two modifications of MgH₂ have been studied by Raman spectroscopy: α -MgH₂ with the $P4_2/mnm$ space group and γ -MgH₂ with the $Pbcn$ space group. The latter was prepared from α -MgH₂ by exposing it to a pressure of 5.6 GPa at 470 °C for 1.5 h. A comparison of the experimental spectra with ab-initio calculations allowed identification of a few phonon modes. A broad feature in the Raman spectrum of α -MgH₂ in the range 1470–1790 cm^{−1} was identified as the B_{2g} phonon mode. A Raman spectrum of γ -MgH₂ consists of five discernible peaks at 186 cm^{−1}, 313 cm^{−1}, 509 cm^{−1}, 660 cm^{−1}, 706 cm^{−1} and of three broad features in the regions 890–980 cm^{−1}, 1010–1220 cm^{−1} and 1240–1430 cm^{−1}. The peaks are identified as the 1A_g (186 cm^{−1}), 3B_{3g} (509 cm^{−1}), 2A_g (660 cm^{−1}) and 3B_{1g} (706 cm^{−1}) phonon modes.

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1. Introduction

MgH₂ is a promising material for hydrogen storage. It has several polymorphs, the tetragonal α -MgH₂ with the $P4_2/mnm$ space group being the most common. Despite the high hydrogen capacity of 7.7 wt% of this compound, its industrial application as a hydrogen storage material is still rather limited due to the high decomposition temperature, slow kinetics of re-hydrogenation and irreversible oxidation in contact with oxygen or water vapor. The first two limiting factors stem from the relatively strong interaction between magnesium and hydrogen in the compound.

Application of high pressure transforms α -MgH₂ to more dense polymorphs: orthorhombic γ , space group $Pbcn$ [1]; cubic β , space group $Pa-3$ [2]; orthorhombic HP1, space group $Pbc2_1$ [3] (previously identified as δ' with the $Pbca$ space group [2]) and orthorhombic HP2, space group $Pnma$ [3]. The tetragonal α -MgH₂ phase has a rutile-type structure with 2 formula units per unit cell, and γ -MgH₂ has a α -PbO₂ type structure with 4 formula units per unit cell. The atoms in the α and γ phases have similar nearest environments: each magnesium atom is surrounded by an octahedron of hydrogen atoms, and each hydrogen atom belongs to three such octahedra (see Fig. 1). The γ phase has a density that is 1.6% higher than α [1]. Other phases are considerably more dense and their synthesis requires the pressure higher than 10 GPa. Our

experiments suggest that the γ phase becomes more stable than the α phase at pressures above 1.5 GPa at $T=700$ °C.

Another way to transform the α phase into γ is by ball milling [4].

For better understanding of hydrogen–magnesium interatomic forces a study of the lattice dynamics of different phases of MgH₂ is needed. The best experimental methods to do this are inelastic neutron scattering, IR and Raman light scattering.

Raman spectra of α -MgH₂ were measured in Refs. [5] and [6] up to 1600 cm^{−1}. In these studies, three peaks at 300, 950 and 1280 cm^{−1} were observed and identified as the B_{1g}, E_g and A_{1g} phonon modes, correspondingly. A Raman study of the γ phase was carried out only in-situ in a diamond anvil cell in Ref. [3], and two features were observed at 200 and 650 cm^{−1}. Theoretical calculations of the lattice dynamics and Raman frequencies of α -MgH₂ were performed in Refs. [7] and [8]. The present paper reports on an experimental Raman scattering study of the α and γ phases of MgH₂. The experiment is supplemented with ab-initio calculations aimed at identifying the observed atomic vibration modes.

2. Experimental details

2.1. X-ray powder diffraction

A flat sample holder was made of a silicon single crystal and had a hole 7 mm in diameter and 0.5 mm in height encircled with an O-ring of vacuum grease. The powder samples were placed in

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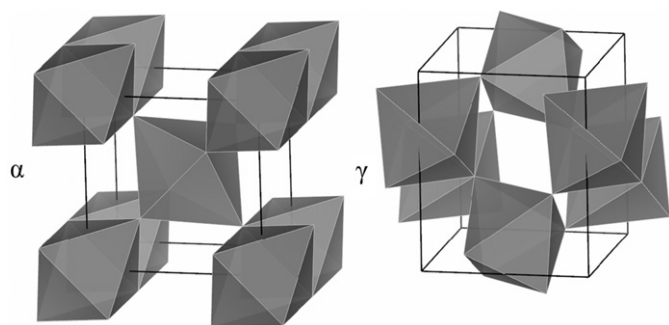


Fig. 1. Crystal structures of α - and γ -MgH₂. The octahedra of H atoms surrounding Mg atoms are shown.

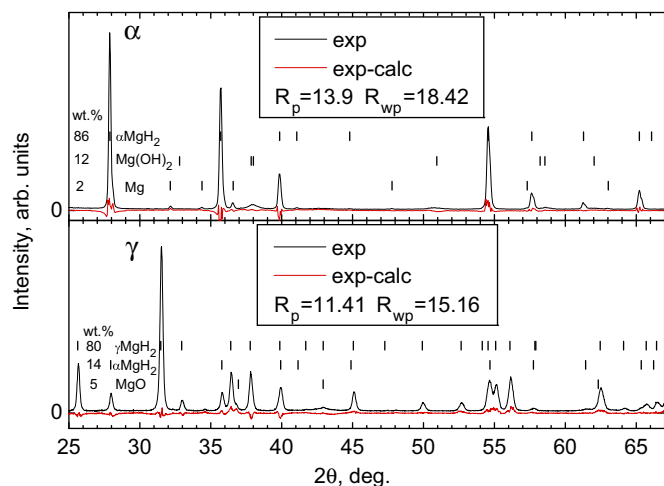


Fig. 2. (Colour Online) X-ray powder diffraction patterns of α -MgH₂ (top) and γ -MgH₂ (bottom) samples. Room temperature, Cu K _{α} radiation. Black curves represent the experimental patterns, and the differences between experimental and calculated patterns are shown by red curves. Residual functions are $R_p(\%) = \sum |I_{obs} - I_{calc}| / \sum I_{obs}$ and $R_{wp}(\%) = \sqrt{\sum (I_{obs} - I_{calc})^2 / \sum I_{obs}}$.

this hole and hermetically sealed with a mylar film in a glove box under an Ar atmosphere. The samples were examined with a Siemens D500 powder X-ray diffractometer using CuK _{α} radiation. The obtained X-ray patterns were analyzed using the POWDER-CELL2.4 software [9]. The VESTA software [10] was used for rendering the crystal structures.

2.2. High pressure–High temperature synthesis

MgH₂ powder was purchased from Aldrich. An X-ray diffraction pattern of the initial MgH₂ powder is shown at the top of Fig. 2. The powder contained 91 wt% α -MgH₂, 7 wt% Mg(OH)₂ and 2 wt% Mg. A copper capsule 9 mm in diameter and 9 mm in height was filled with 0.2 g MgH₂ powder under an Ar atmosphere, covered with a copper disc and hermetically sealed with a lead plug pressed inside the capsule. The capsule was then placed in the working zone of a toroid-type high pressure chamber. The pressure in the chamber was calibrated against the oil pressure in a hydraulic press using well-defined phase transitions in bismuth and thallium determined with a four-point electroresistance method. The accuracy of the pressure measurement was ± 0.2 GPa. The heater was made of 14 nichrome wires encompassing copper capsule. The temperature during the high pressure experiment was controlled by a chromel–alumel thermocouple with an accuracy of ± 10 °C. The heater, thermocouple and

copper capsule were electrically isolated from each other using mica sheets. The synthesis of γ -MgH₂ was performed at 5.6 GPa and 470 °C for 90 min. The high pressure chamber was further cooled to room temperature and disassembled. The sample was extracted out of the copper capsule under liquid nitrogen. The extracted sample was loaded to a hermetical vial, removed from the liquid nitrogen and transported to the Ar glove box, where it was placed onto the X-ray sample holder. The diffraction pattern of the sample is shown at the bottom of Fig. 2. The sample was found to contain 82 wt% γ -MgH₂, 14 wt% α -MgH₂ and 3 wt% MgO.

2.3. Raman scattering study

The MgH₂ powder samples were placed into hermetically sealed glass cells to avoid any contact with air.

The samples were irradiated with a 488-nm Ar⁺ laser line (laser power ~ 10 mW) at room temperature using a back-scattering geometry. The laser beam was focused to a spot of approximately 2 μ m in size, while the samples consisted of particles with the characteristic sizes of about 10 μ m. That allowed to select various particles of the sample.

The spectra were recorded by a Dilor XY-500 spectrometer equipped with a micro-Raman setup and a Peltier cooled charge-coupled device (CCD) detector. Several spectral ranges were covered, and the corresponding spectra were glued using standard procedures.

The recorded spectra consisted of a Raman signal and luminescence background, which intensity increased with the frequency. Luminescence background was subtracted from the spectrum of γ -MgH₂ shown at the bottom of Fig. 3. In the case of α -MgH₂, the baseline was not subtracted from the spectrum shown at the top of Fig. 3.

3. Calculations

A factor group analysis shows that α -MgH₂ has the following phonon modes at the center of the Brillouin zone:

$$(A_{2u} + E_u)_{\text{acoustic}} + (A_{2u} + 3E_u)_{\text{IR}} + (A_{1g} + B_{1g} + B_{2g} + E_g)_{\text{Raman}} + (A_{2g} + 2B_{1u})_{\text{silent}}$$

The E_u and E_g phonon modes are doubly degenerate.

The analysis for γ -MgH₂ gives the following phonon modes:

$$(B_{1u} + B_{2u} + B_{3u})_{\text{acoustic}} + (4B_{1u} + 3B_{2u} + 4B_{3u})_{\text{IR}} + (4A_g + 5B_{1g} + 4B_{2g} + 5B_{3g})_{\text{Raman}} + (4A_u)_{\text{silent}}$$

All optic modes are non-degenerate in the case of the γ phase. Due to the presence of inversion center in both α and γ phases, the Raman and infrared activities are incompatible with each other for any phonon mode.

The vibrational properties of MgH₂ in both polymorphic phases were calculated by density-functional theory and the plane-wave pseudopotential method as implemented in the CASTEP code [11,12]. Pseudopotentials were of the optimized norm-conserving variety with a plane-wave cutoff of 990 eV. Calculations were performed under the PBE approximation to exchange and correlation. Brillouin-zone integration was performed according to the Monkhorst–Pack scheme with a $4 \times 4 \times 3$ for α -MgH₂ and $4 \times 4 \times 3$ for γ -MgH₂, which gave convergence of all modes to a precision of better than 3 cm^{−1}. Density functional perturbation theory was used to calculate the dynamical matrices [11]. Raman intensities were calculated using the method as described in [13].

The results of the calculation are shown in Fig. 3. To distinguish between different phonon modes with the same character

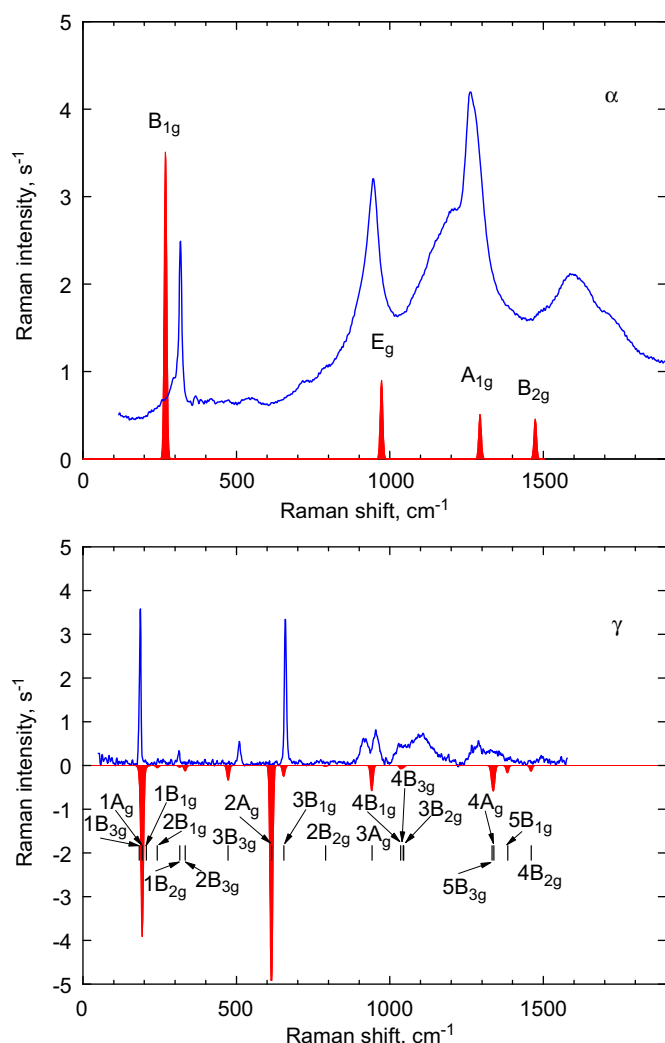


Fig. 3. (Colour Online) Raman spectra of α -MgH₂ (top) and γ -MgH₂ (bottom). The experimental spectra are plotted by the blue curves and the calculated spectra by the red ones. The strong luminescence background rising with the frequency was subtracted from the experimental spectrum of γ -MgH₂; the experimental spectrum of α -MgH₂ is shown without modifications. The calculated spectrum of γ -MgH₂ is plotted downwards.

in the case of γ -MgH₂, we label them with a number prefix in the order of the increase in the calculated Raman shift.

4. Results and discussion

Animations demonstrating the atomic movements in the phonon modes considered in this Section are presented as [Supplementary material](#).

The basic features of the Raman spectrum of α -MgH₂ (the top of Fig. 3) are the same as in Ref. [6]: the peak at 310 cm⁻¹ is narrow and the peaks at 945 and 1270 cm⁻¹ are broad and the 1270 cm⁻¹ peak has a long shoulder towards lower Raman shifts. The origin of such a broadening is unclear. In addition to these previously known features, a broad band in the 1470–1790 cm⁻¹ range is seen in the spectrum. Its intensity is of the same order of magnitude as the intensities of other features. Our first-principle calculation predicts a B_{2g} phonon mode in this range with the Raman scattering intensity similar to that of other modes. On these grounds, we assign this feature to the B_{2g} phonon mode.

The Raman spectrum of γ -MgH₂ (the bottom of Fig. 3) consists of intense narrow peaks at 186 and 660 cm⁻¹, which were earlier seen in Ref. [3]; weak peaks at 509 cm⁻¹, 313 cm⁻¹ and 706 cm⁻¹ (listed in the order of decreasing intensity), and three broad bands in the 890–980 cm⁻¹, 1010–1220 cm⁻¹ and 1240–1430 cm⁻¹ ranges. Several phonon modes are predicted by our calculations to be near 186 cm⁻¹ peak, the most intense being 1A_g. In the neighborhood of the 660 and 706 cm⁻¹ peaks, there are two modes in the calculation, 2A_g and 3B_{1g}, the first one being much more intense. This enables us to do the assignment for these peaks. The 509 cm⁻¹ peak can be assigned to the 3B_{3g} mode, because this is the only mode in its vicinity. There are two modes, 1B_{2g} and more intense 2B_{3g}, near the 313 cm⁻¹ peak. However, we cannot assign this peak to 2B_{3g} mode with certainty, because the B_{1g} mode of α -MgH₂ contributes to the same energy range (the top of Fig. 3) and the sample was contaminated with α -MgH₂. An inspection of the broad bands in the spectrum shows that their positions are the same as in the Raman spectrum of α -MgH₂, which could be evidence of contamination. The profile of the 890–980 cm⁻¹ band, however, cannot be explained in this way. It has a two-peak shape, the position of the higher peak being the same as that of the E_g mode in α -MgH₂. Taking into account that there is a 3A_g mode with a comparable intensity in the vicinity, one can speculate whether or not the lower peak at 915 cm⁻¹ represents this phonon mode.

5. Conclusion

Raman spectra of α -MgH₂ and γ -MgH₂ have experimentally been studied and compared with ab-initio calculations that allowed us to assign the phonon modes to some experimental peaks. Despite the similar nearest-neighbor environment of the Mg and H atoms in α -MgH₂ and γ -MgH₂, the Raman spectra of these phases are very different because of the different crystal symmetries. A work is in progress to study the interatomic interactions and phonon properties in these modifications of MgH₂ with inelastic neutron scattering, which is a symmetry insensitive method in contrast to Raman scattering.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ssc.2012.09.022>.

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