Magnesium transition-metal based lightweight hydrogen storage materials: a NMR study

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Magnesium Transition-Metal based lightweight hydrogen-storage materials. A NMR study

PROEFSCHRIFT

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Chapter 1

1.1 Introduction

Since the industrial revolution, the energy demand has increased dramatically together with the world population from \( \sim 5 \times 10^{12} \) kWh in the year 1800 to \( \sim 120 \times 10^{12} \) kWh in 2000.\(^1\) Fossil fuels have been used for transportation, power generation and industrial processes. The finite availability of these is a major concern. Moreover, oil reserves are concentrated in particular places in the world whereas the demand for oil is all over the world. The disadvantage of using fossil fuels is the environmental pollution, especially emission of greenhouse gases. These gases trap heat and are the cause of global warming. This has large negative effects such as thinning of glaciers in polar regions and sea level increase.

1.2 Hydrogen Economy

In a future hydrogen-based economy\(^2,3,4,5\) conventional fossil fuels will be replaced by hydrogen. Direct hydrogen combustion like in fuel cells, only produces water and also the output from battery-powered cars do not pollute the environment unlike combustion of fossil fuels. This fact makes the shift towards hydrogen-based economy more favorable. Already, cars based on liquid hydrogen as fuels (BMW) and battery-powered hybrid cars (Toyota) are available in the market. Hydrogen is not a fuel but an energy carrier. Although the amount of pure hydrogen gas in atmosphere is negligible, it is abundantly available in other chemical forms, such as water.
1.3 Hydrogen Storage

The main factors for a material to be considered a potential candidate for hydrogen storage are

- High gravimetric and volumetric storage capacity
- High recyclability
- Fast (de)sorption kinetics
- Low desorption temperature

Hydrogen can be stored in the form of gas at high pressures in metal cylinders. Another way is to store it in a cryogenic liquid form at, e.g., 20 K, which is the boiling point of liquid hydrogen at 1 bar. The advantage of storing as a liquid is that of hydrogen can be stored at high volumetric density compared to compressed gas. However, the energy required for liquefaction and the boil-off hydrogen loss have also to be considered. These storage methods do not (yet) meet the targets for hydrogen storage set by the US Department of Energy (DOE). Hydrogen can also be stored by physisorption in carbon nanotubes and metal organic frameworks (MOF).

An alternative for physical storage as high-pressurized gas or cryogenic liquid is to store hydrogen chemically in metal hydrides or other chemical hydrides. Since hydrogen is stored as atoms rather than molecules, chemical storage can yield higher volumetric capacity. The thermodynamic properties of a metal hydrogen system are obtained from the calorimetric or pressure-composition isotherm (PCI). In a PCI measurement, the Van’t Hoff plot is constructed to obtain thermodynamic parameters. At equilibrium, the hydrogen pressure and temperature are related by the Van’t Hoff equation, according to

\[
\ln \left( \frac{P_{eq}(T)}{P_{eq0}} \right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}
\]

where \( \Delta H \), \( \Delta S \), \( R \) are the formation enthalpy, the entropy change and the universal gas constant, respectively. Ideally, to have an equilibrium pressure of 1 bar at room temperature, the optimum formation enthalpy can be calculated to be \( \sim -40 \text{ kJ/mol H}_2 \). Fig. 1.1 schematically shows the Pressure-composition isotherms of a typical metal hydride, such as LaNi\(_5\). When hydrogen absorbs into a metal, it first forms a hydrogen-poor solid-solution phase, the so-called \( \alpha \) phase. The equilibrium pressure increases as more hydrogen is absorbed in this phase until a critical
concentration \(x_\alpha\) is reached, after which an additional hydrogen-rich phase, called the \(\beta\) phase is formed. The gas-equilibrium pressure in the two-phase coexistence region remains constant until a second critical concentration \(x_\beta\) is reached, where further hydrogen absorption results in the formation of only \(\beta\) phase and pressure also increases. The coexistence of \(\alpha\) and \(\beta\) phases is characterized by plateau. The equilibrium plateau pressure depends on the temperature according to the Van 't Hoff equation. (Eq. 1.3.1)

Interstitial hydrides are studied for decades for their reversible hydrogen storage properties. One of the first commercial materials were LaNi\(_5\) and FeTi alloys.\(^{14,15,16}\) These compounds are formed by combining an element which has a high affinity towards hydrogen with another element that has low affinity towards hydrogen. LaNi\(_5\) has an equilibrium pressure of 1.7 bar at room temperature and it forms LaNi\(_5\)H\(_6\) after complete hydrogenation. In general, these materials are AB\(_5\) type materials, where A is lanthanide element (atomic number 57 – 71) and B element is Ni, Co, Al, Fe, Sn, Cu, Ti, etc. These materials have superior (de)sorption kinetics but suffer from low gravimetric capacity. They are not suitable for on-board hydrogen storage systems.

![Figure 1.1](image)

**Figure 1.1** Pressure-composition isotherms of metal hydrides. (reproduced from Ref 21) The solid solution (\(\alpha\)-phase), the hydride phase (\(\beta\)-phase) and the coexistence of the two phases are shown. The coexistence region is reflected by the plateau and exists only below the critical temperature \(T_c\). The construction of the Van't Hoff plot is shown on the right-hand side. The slope of the line reflects the hydride-formation enthalpy and the intercept the formation entropy. (see Eq. (1.3.1))
Another class of materials is that of the complex hydrides. In these hydrides, hydrogen atoms are covalently bonded to a central atom in an anion complex (e.g. $\text{AlH}_4^-$, $\text{BH}_4^-$, $\text{NH}_2^-$) and are stabilized by a cation, typically an alkaline or alkali earth metal. Depending on the cation and anion complex, the gravimetric storage capacity varies between ~ 6 to 18 wt.% of hydrogen. Fig. 1.2 summarizes the volumetric and gravimetric capacities of hydrogen storage materials. The various classes of hydrogen storage materials along with their desorption temperature are depicted with distinct colors. Each color represents a particular type of hydrogen storage material. High-pressure storage of hydrogen gas has lower volumetric and gravimetric capacities than other methods of hydrogen storage. Moreover, the gravimetric hydrogen density decreases with increasing pressure due to the increasing thickness of the walls of the pressure cylinder. Hydrogen chemisorbed on carbon, such as in alkanes, in general have a higher gravimetric capacity. However, they produce carbon-dioxide on complete combustion which is a greenhouse gas. Moreover, on incomplete combustion, they also produce carbon-monoxide which is toxic. The gravimetric storage capacity of complex hydrides is greater than in metal hydrides. However, full dehydrogenation takes place in two steps in most of the materials and in some materials reversible storage of hydrogen is an issue. The decomposition temperature is also high. Metal hydrides can reversibly store hydrogen. The most common is the $\text{LaNi}_5$ which has good thermodynamic and kinetic properties. The equilibrium pressure is 2 bars at 300 K. However, it suffers from low gravimetric capacity. In general, metal hydrides with higher gravimetric capacities suffer from thermodynamic and/or kinetic properties.

1.4 Recent progress in hydrogen storage in $\text{MgH}_2$

In search for an ideal hydrogen-storage metal hydride, many studies have been done on $\text{MgH}_2$. Mg is available in abundance. Its hydride, $\text{MgH}_2$, has a high gravimetric capacity and can store 7.6 wt.% of hydrogen. This property makes $\text{MgH}_2$ a potential candidate for hydrogen storage. However, major challenges have to be overcome in order to put $\text{MgH}_2$ into practical use. $\text{MgH}_2$ is thermodynamically highly stable. Its enthalpy of formation is $-74$ kJ/ mol $\text{H}_2$. This corresponds to an equilibrium pressure of 1 bar at 555
Figure 1.2 Volumetric and gravimetric capacities of different hydrogen storage materials (reproduced from Ref 21). Different colors indicate types of storage materials. Red and pink colors represent hydrogen storage in metal hydrides and complex hydrides. The gravimetric hydrogen storage capacity of complex hydrides is higher than that of the metal hydrides.

The goal is to destabilize MgH$_2$ in order to achieve the same equilibrium pressure of 1 bar at or near room temperature conditions. Apart from high stability, MgH$_2$ also suffers from poor sorption kinetics. Hydrogen diffusion within MgH$_2$ lattice is slow. Moreover, once the outer layer of MgH$_2$ is formed, it blocks further hydrogenation of inside layers. Many studies are in progress to improve kinetic and thermodynamic limitations with different strategies. MgH$_2$ has a rutile crystal structure with lattice constants $a = 4.50 \, \text{Å}$ and $c = 3.01 \, \text{Å}$.\textsuperscript{22} The Wyckoff position of Mg and H are 2a (0, 0, 0) and 4f (0.306, 0.306, 0), respectively.

Notten and his group have improved the kinetics of MgH$_2$ by doping Mg with a Transition Metal (TM) element.\textsuperscript{23,24,25,26,27} The addition of minimally 20 at.% of a TM causes a change from the rutile structure of MgH$_2$ to a fluorite structure after hydrogenation. In the fluorite structure, the hydrogen mobility is higher. Fig. 1.4.2 shows the structure and lattice parameters of rutile and fluorite MgH$_2$ and Mg-TM-H$_2$, respectively. The lattice parameter in the
fluorite structure of Mg$_x$-TM$_{(1-x)}$H$_2$ depends on the doping percentage of the TM and follows Vegards law.\textsuperscript{28}

![MgH$_2$](image1.png)

![Mg$_{1-x}$TM$_x$H$_{2x}$](image2.png)

**Figure 1.4.2.** Crystal structures of (a) MgH$_2$ (b) Mg$_{1-x}$TM$_x$H$_{2x}$. MgH$_2$ crystallizes into the rutile structure. Green and yellow spheres denote Mg and hydrogen atoms. Upon addition of minimally 20 at.% of a transition element, the crystal structure turns into a fluorite structure after hydrogenation. In the fluorite structure hydrogen atoms located in tetrahedral and octahedral sites represented by yellow and grey spheres, respectively. The red spheres denote either Mg or a TM element.

Starting from MgH$_2$ and TM-H$_2$, high pressure up to 8 GPa and high temperature (600 °C) conditions were used to obtain Mg$_{6-7}$TM$_{14-16}$ (TM = Ti, Zr, Hf, V, Nb and Ta).\textsuperscript{29,30,31,32} The resulting material crystal structures are fluorite with lattice constants $\sim$ 4.8 Å. The TM atoms are arranged in an ordered way and can best be described by a superlattice of type Ca$_7$Ge structure.\textsuperscript{33} Powder X-ray diffraction using synchrotron radiation revealed two types of tetrahedral sites for hydrogen atoms. At one of the sites, hydrogen is coordinated by three Mg atoms and one TM atom, and in the other site, it coordinates four Mg atoms. These ternary hydrides were initially thought to be metastable as they tend to phase separate into constituent binary hydrides upon complete dehydrogenation.\textsuperscript{29} Later, these materials were observed to be thermodynamically stable and reversible if not fully dehydrogenated.\textsuperscript{29}
In another approach, nano-structuring is employed to improve the hydrogenation properties. The crystallite size of bulk MgH\textsubscript{2} is reduced from micrometer (\(\mu\)m) to nanometer size (nm) by ball-milling. The kinetics is faster for nano-crystalline MgH\textsubscript{2} than for \(\mu\)m-sized crystallites\textsuperscript{34,35}. The ball-milling process reduces the crystallite size and as a result the surface area is enhanced. The diffusion path lengths are also decreased as a result of ball-milling. This allows hydrogen atoms to penetrate more easily to form a hydride. The defects and distortions introduced by ball-milling were also considered to be a cause for improved kinetics\textsuperscript{35}. However, later it was shown that they do not play a decisive role in contributing towards the increased kinetics\textsuperscript{36,37}. MgH\textsubscript{2} ball-milled with TM elements also increased the kinetics but thermodynamic properties of MgH\textsubscript{2} were not affected\textsuperscript{38}. It was found that the kinetics of ball-milled MgH\textsubscript{2} with Ti or V was higher when compared to ball-milled MgH\textsubscript{2} with any other TM elements. MgH\textsubscript{2} ball-milled with TM oxides were also found to be very effective in increasing the kinetics of hydrogen (ab) desorption\textsuperscript{39,40}.

Even though crystallite-size reduction enhances the sorption kinetics of MgH\textsubscript{2}, agglomeration of particles occurs on subsequent cycles of hydrogen absorption and desorption. This again led to slower (de)sorption kinetics which is comparable to bulk MgH\textsubscript{2}. A recent quantum chemical study\textsuperscript{41} showed that the thermodynamic stability can be altered by reduction of crystallite-size down to \(~\)1.3 nm which consisted of at the most 20 metal atoms. De Jongh et.al\textsuperscript{42} showed that Mg can be held in nm-sized form in a carbon support. The process is to melt and infiltrate Mg into porous carbon.

In an alternative approach to stabilize the particle size, addition of compounds such as TiF\textsubscript{3} was proposed\textsuperscript{43,44}. The added compound forms a new compound/alloy with MgH\textsubscript{2}. On hydrogenation, these alloys act as nucleation centers for the metal hydride phase to be formed. The phase/compound that acts as nucleation centers is known as grain refiner.

Apart from hydrogen storage, Mg-RE-based materials are also studied for technological applications such as hydrogen sensors\textsuperscript{45}, switchable mirrors or solar collectors\textsuperscript{46}. Magnetron sputtered Mg-TM films are investigated for the same type of applications\textsuperscript{47,48,49,50}. Using recently developed Hydrogenography method, the authors proposed a model for Mg\textsubscript{y}Ti\textsubscript{(1-y)} films, wherein, Mg and Ti are not phase separated, instead a coherent crystal consisting of MgH\textsubscript{2} and TiH\textsubscript{2} domains were formed upon hydrogenation.
1.5 NMR methodology

In most studies of materials for hydrogen storage, diffraction-based techniques are used to determine the structure, (macroscopic) hydrogen-absorption measurements to determine the thermodynamics properties. These methods give information about the energy carriers in an indirect way. NMR probes the location, as well as the mobility of energy carriers directly. Every characterization technique has its limitations. For nanometer-structured materials with short structure-coherence lengths, XRD yields patterns consisting of broad and overlapping peaks. In contrast, $^1$H NMR can yield detailed information about hydrogen in XRD-amorphous materials. However, it does not give direct information about the non-hydride parts of hydrogen storage materials.

Metal hydrides have been studied with NMR for decades. Especially, diffusion-studies on hydrogen atoms in metal hydrides received much interest. Hydrogen mobility at a nanosecond or millisecond timescale was studied with wideline NMR relaxometry techniques. Activation barriers for hydrogen motion were also obtained from temperature variation measurements. Apart from static relaxometry based techniques, Pulsed Field Gradient (PFG) NMR experiments gave information on diffusion coefficients of hydrogen mobility.

Although the above-mentioned NMR methods were useful to obtain insight into hydrogen mobility, a major problem associated with static $^1$H NMR of metal hydrides is its broad lines in the spectra. In metal hydrides, there are very short $^1$H-$^1$H distances. Dipole-dipole interactions among the $^1$H spins cause strong linebroadening their resonance. Magic-angle spinning (MAS) narrows the resonance. The availability of ultra-fast MAS up to 70 kHz, advanced pulse sequences to obtain resolved lines in the NMR spectra and better spectrometers offer opportunities to view metal hydrides in a different perspective. However, other challenges have to be addressed that concerns NMR on metal hydrides. Eddy currents can be a problem with MAS at high spinning rates. This will force to work at lower MAS rates and hence resolution of spectral lines will be an issue. Moreover, for conducting materials, radio-frequency (rf) skin depth is a problem. For materials with large dimensions compared to skin-depth, the rf field does not penetrate completely and hence the signal will not be observed or attenuated strongly. The skin-depth issue is addressed in more detail in Chapter 6.
1.6 Goal and Scope of this thesis

This thesis describes the NMR investigation of siting and mobility of hydrogen in Mg-based hydrogen storage materials. Most studies on Mg-based hydrides utilize diffraction-based techniques and/or Sievert methods to obtain structural, kinetic and thermodynamic parameters. NMR has the advantage that the chemical location of hydrogen as well its mobility can be monitored directly. This will give an atomistic view of the energy carriers, i.e. the hydrogen atoms and also their mobility within in the energy storage material. In our MAS NMR study of Mg-TM-hydrides, the primary goal is to distinguish between hydrogen atoms with different metal coordination, $Q^n = H_{\text{Mg}}n\text{TM}_{4-n}$, where $n$ is the number of Mg atoms in the first coordination sphere. Do hydrogen atoms from one metal-coordination environment move to all other coordination environments? How are the different metal coordinations arranged within the lattice? What is a typical length scale separation between different metal coordinations?

Chapter 1 gives a general introduction to the thesis. The importance of the hydrogen economy is discussed. The criteria for a material to be considered for hydrogen storage are elucidated. General overviews of different types of materials that are currently studied for hydrogen storage are mentioned. We narrow down to MgH$_2$ and other Mg-based hydrogen storage materials, which this thesis about. A short overview is given about NMR methodology and its advantages to study metal hydrides. The aim of the thesis and important results are described in each chapter.

Chapter 2 gives an overview of the theory behind the characterization techniques. NMR is used extensively in this thesis and therefore more emphasis is given for various pulse sequences that are used to study the Mg-TM based hydrogen storage materials.

Chapter 3 describes the nano-structure of Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ synthesized by ball-milling Mg and Ti and subsequent gas phase deuterium loading at high pressure and temperature. MAS NMR spectroscopy, powder X-ray diffraction (XRD) and neutron diffraction (ND) were used to study the complex structure of the material. Deuterium dynamics were studied by use of 2D Exchange NMR spectroscopy (2D Exsy) at room temperature and by use of 1D Exchange NMR spectroscopy (1D Exsy) at various temperatures. XRD and ND indicate macro-phase separation of MgTi alloy into MgD$_2$ and TiD$_2$ after deuteration. However, NMR shows the presence of an
additional TiD₃ nanophase which is XRD-invisible. Further, 2D Exsy NMR reveals deuterium exchange between this XRD invisible TiD₃ nanophase and MgD₂. Comparing the intrinsic cell parameters of rutile MgH₂ and fluorite TiH₂, we propose that stabilization of the mixed nanocomposite may arise from a coherent coupling between the crystal structures of the rutile MgD₂ nanodomains and the thin layers of fcc TiD₃.

Chapter 4 deals with Mg₀.₆₅Ti₀.₃₅D₁.₁, where first the MgTi alloy is synthesized as a film by magnetron sputtering and, subsequently, deuterated by means of gas absorption at room temperature. For this co-sputtered material NMR shows no macro-phase separation into MgD₂ and TiD₂, unlike for the ball-milled Mg₀.₆₅Ti₀.₃₅D₀.₆₅ material discussed in the preceding chapter. It does reveal the presence of deuterium in Mg-rich and Ti-rich coordination states. Interestingly, 2D Exsy shows that most of the of deuterium atoms within Ti-rich clusters and Mg-rich clusters exchange with one another. A minor fraction, which does not participate in the exchange process appears stably bound to titanium. The observed deuterium exchange and the reduced Knight shift compared to bulk TiD₂ are explained using a model with TiD₃ nanoslabs.

In general NMR is considered to be quantitative. This is very much important in the present study as we quantify the energy carriers.

Chapter 5 deals with the NMR visibility of deuterium atoms in the melt-cast Mg₀.₆₅Sc₀.₃₅D₂.₂. By use of ²H-{⁴⁵Sc} Double Quantum spectroscopy, we were able to distinguish between deuterium in Mg-rich and Sc-rich sites. 1D Exsy reveals that total peak area is not conserved during deuterium exchange between the Mg-rich and Sc-rich sites which indicates the presence of an NMR-invisible or “dark” deuterium fraction. As possible origins of the reduced deuterium visibility deuterium mobility at the sample-rotation timescale and second-order quadrupolar line broadening are discussed.

Chapter 6 discusses hydrogen storage in Mg melt-infiltrated nanoporous carbon at different MgH₂: carbon ratio. The complex nanostructure of the material is characterized by a combined NMR, XRD and Temperature Programmed Desorption(TPD) approach. The conductive nature of nano-porous carbon reduces the NMR visibility of the hydrogen atoms. The variation of NMR signal intensity with the packing density of the material is probed to estimate the NMR visibility in these materials. MgH₂ within the pores of carbon is not detected by XRD. However, static ¹H NMR can distinguish between an hydrogen-containing MgH₂ or Mg(OH)₂
nanophase inside the pores of the carbon support and bulk MgH$_2$ outside the carbon on the basis of spin-lattice relaxation, motional lineshape narrowing in static NMR and chemical-shift differences in MAS NMR.

Chapter 7 gives the summary of the present research work.

1.6 References

Chapter 1

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Chapter 2

Characterization Techniques

2.1 Introduction

A single characterization technique alone will not give a complete picture of heterogeneous materials. Every technique has its own advantages and disadvantages. Diffraction-based techniques such as powder X-ray diffraction, neutron diffraction are commonly employed to study the crystalline phase composition of metal hydrides. However, these methods require long-range ordering of the atoms in materials. The long-range ordering is not necessary for Nuclear Magnetic Resonance (NMR) spectroscopy. The disadvantage is that unhydrogenated portions of a metal hydride cannot be detected with $^1$H NMR. Therefore, a combination of characterization techniques to exploit the advantages of every technique is a must to get a full picture of materials. This chapter describes the theory behind the techniques that are used to characterize the metal hydrides. A major part of the work described in this thesis involves solid state Nuclear Magnetic Resonance (NMR). This will be dealt with in a more detailed way. In the last section, basic aspects of powder X-ray diffraction are given.

2.2 Nuclear Magnetic Resonance (NMR)

NMR is a tool, which is widely used in many disciplines of fundamental and applied sciences. Most often NMR is used as a structural characterization tool, mobility can also be probed. NMR involves resonance absorption of electro-magnetic energy by nuclear moments. This phenomenon is observed for atomic nuclei which have non-zero spin I. These nuclei have magnetic dipole moments given by
\[ \mu = \gamma \hbar I \]  \hspace{1cm} (2.2.1)  

where \( \gamma \) is the gyro-magnetic ratio of the nucleus, and \( I = (I_x, I_y, I_z) \) the spin-operator vector composed of the three spin operators \( I_x, I_y \) and \( I_z \). As a result if their magnetic moment atomic nuclei interact with a magnetic field \( B_0 \). The corresponding Zeeman interaction is given by the Hamiltonian:

\[ H_z = -\mu \cdot B_0 = -\gamma \hbar I \cdot B_0 \]  \hspace{1cm} (2.2.2)  

The eigen values of this Hamiltonian represent the so-called Zeeman energy levels. A nucleus with spin \( I \) has \( |2I + 1| \) energy levels associated with equally many spin angular momentum projections on the magnetic-field axis. A spin \( \frac{1}{2} \) nucleus has two energy levels, separated by \( \Delta E = \gamma B_0 = \hbar \gamma \omega_0 \), \( \omega_0 \) is the larmor frequency. This directly indicates that sensitivity of NMR signal is enhanced with increasing magnetic field.

The basic nuclear spin interactions in solid-state NMR,\(^1,2\) are:

(i) Chemical shift interaction
(ii) Dipole-dipole interaction
(iii) J- coupling interaction
(iv) Quadrupole interaction

(i) Chemical shift interaction. The magnetic field experienced by the nucleus is shielded by the surrounding bonding electrons. The chemical shielding Hamiltonian acting on a spin \( I \) is

\[ H_{cs} = -\hbar \gamma I \sigma B_0 \]  \hspace{1cm} (2.2.3)  

where \( \sigma \) is the second rank tensor describing the chemical shielding. The chemical shielding can be separated into isotropic and anisotropic components. The isotropic component is

\[ H_{cs}^{iso} = -\hbar \gamma B_0 \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})I_z \]  \hspace{1cm} (2.2.4)  

and the anisotropic component is

\[ H_{cs}^{aniso} = -\frac{1}{3} \sigma_0[\sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22})](3\cos^2 \beta - 1)I_z - \frac{1}{2} \sigma_0[(\sigma_{11} - \sigma_{22}) \sin^2 \beta \cos 2\gamma]I_z \]  \hspace{1cm} (2.2.5)  

where \( \sigma_{11} \), \( \sigma_{22} \) and \( \sigma_{33} \) are the principal axis values of the chemical shielding tensor, and the angles \( \beta \) and \( \gamma \) relate the Principal Axes System (PAS) of the chemical shielding tensor to the lab frame in which the magnetic field is oriented along the \( z \) axis.
If the chemical shift anisotropy, $\Delta \sigma$, is defined as $\sigma_{33} - \sigma_{\text{iso}}$ and the chemical shift asymmetry, $\eta$ as $(\sigma_{22} - \sigma_{11})$, $\Delta \sigma$, the chemical shielding Hamiltonian can be rewritten as:

$$\hat{H}_{\text{cs}} = -\hbar \omega_0 \sigma_{\text{iso}} \hat{I}_z - \frac{1}{2} \hbar \omega_0 \Delta \sigma [(3 \cos^2 \beta - 1) + \eta \sin^2 \beta \cos 2\alpha] \hat{I}_z$$  \hspace{1cm} (2.2.6)

(ii) Dipolar interaction. In the strong field approximation, the truncated form of homonuclear dipolar Hamiltonian representing the magnetic dipole coupling between two spins is given by

$$\hat{H}_d = -\omega_0 P_2(\cos \theta)(3I_{z}^{(1)}I_{z}^{(2)} - I^{(1)}I^{(2)})$$  \hspace{1cm} (2.2.7)

where $\omega_0$ is the dipolar coupling constant given by

$$\omega_0 = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{\gamma_1 \gamma_2 \hbar}{r^3} \right)$$  \hspace{1cm} (2.2.8)

with distance $r$. $P_2(\cos \theta)$ is the second order Legendre polynomial given by

$$P_2(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1)$$  \hspace{1cm} (2.2.9)

with $\theta$ the angle between the internuclear vector connecting the two spins and the external magnetic field $B_0$.

(iii) $J$-coupling interaction. Indirect spin-spin interaction which is also called $J$-coupling interaction is the interaction between nuclei mediated through the bonding electrons in the molecule. The Hamiltonian is given by

$$\hat{H}_J = \hat{I}^{(1)} \hat{J} \hat{I}^{(2)}$$  \hspace{1cm} (2.2.10)

where $\hat{J}$ is a second-rank tensor.

(iv) Quadrupolar interaction: Nuclei with spin $I > \frac{1}{2}$ have electric quadrupole moment which interacts with the electric filed gradients from surrounding charges. In a strong magnetic field the quadrupolar interaction can be treated as a perturbation to the Zeeman interaction and can be expressed as a sum of first- and second-order terms.

$$\hat{H}_Q = \hat{H}_{Q1} + \hat{H}_{Q2}$$  \hspace{1cm} (2.2.11)

The first-order quadrupolar Hamiltonian is given by

$$\hat{H}_{Q1} = \frac{1}{6} \hbar \omega_q (\beta, \gamma) \left[ 3I_{z}^2 - I(I+1) + \eta(I_x^2 - I_y^2) \right]$$  \hspace{1cm} (2.2.12)

where $\omega_q (\beta, \gamma)$ is the orientation dependent quadrupolar frequency given by

$$\omega_q (\beta, \gamma) = \frac{\omega_Q}{2}(3\cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\gamma)$$  \hspace{1cm} (2.2.13)
where $\beta$ and $\gamma$ denote the polar angles defining the orientation of the quadrupolar tensor $\mathbf{V}$ in the laboratory frame. The quadrupolar constant $\omega_Q$ and asymmetry parameters $\eta$ are given by

$$\omega_Q = \frac{3e^2 qQ}{2I(2I-1)h} V_{zz}$$  \hspace{1cm} (2.2.14)

and

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$  \hspace{1cm} (2.2.15)

whereby $V_{zz}$, $V_{yy}$, and $V_{xx}$ are the principal axis values of the quadrupolar tensor $\mathbf{V}$.

The first-order quadrupola shift of the unperturbed Zeeman levels is proportional to $(3m^2 - 1)$, where $m$ is the magnetic quantum number associated with a particular Zeeman level. Therefore, the frequency of the central transition $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ of half integer quadrupolar nuclei, like $^{27}$Al or $^{45}$Sc, or, in general, “symmetric” transition $-m \leftrightarrow m$ is not affected by the first-order interaction. For large quadrupolar coupling interactions, the second-order energy correction has to be considered. The second-order quadrupolar Hamiltonian is of the form:

$$H_Q^{(2)} = -\frac{\omega_Q^2}{\omega_0} \left[ A(\beta, \gamma) I_z^1 + B(\beta, \gamma) I_z^3 \right]$$  \hspace{1cm} (2.2.15)

where $A(\beta, \gamma)$ and $B(\beta, \gamma)$ are orientation dependent geometrical factors. The second-order term is inversely proportional to the Larmor frequency. Thus the significance of this term becomes less at increasing magnetic field.

### 2.2.1 Spectral editing

A challenge for most of solid-state NMR spectroscopist is to obtain a liquid like spectrum for solid samples. In solids, broad NMR lines are caused by Chemical Shift Anisotropy (CSA), dipole or quadrupolar interactions. The nuclear spin Hamiltonian consists of a spatial and spin part. The spatial part can be averaged by the mechanical rotation of the samples. This gives a narrow signal with spinning sidebands. The spin part can be dealt by applying radio-frequency (RF) pulses sequences, which allow us to obtain specific information, for example, forbidden transitions corresponding to multiple quantum transition can be observed in an indirect two-dimensional method. For spin 5/2 nuclei, triple quantum spectrum gives narrower linewidth than the single quantum spectrum. In this section, various pulse sequences which are mentioned in this thesis to study the siting and dynamics of hydrogen atoms are described.
2. 2.1.1 Magic Angle Spinning

Magic Angle Spinning (MAS)\textsuperscript{4,5} is often employed to get higher chemical resolution. This involves rotating the sample at a angular velocity $\omega_r$ around an axis, inclined at a particular angle $\beta$ with respect to the magnetic field. Fig. 2.1 shows the description of the same. $r_{ij}$ is the internuclear vector connecting the two spins $i$ and $j$. $\theta_{ij}(t)$ is the angle that $r_{ij}$ makes with the applied magnetic field, $H_0$. The angle $\theta_{ij}$ representing the angle between $r_{ij}$ and magnetic field, becomes time dependent given by

\[
\cos\theta_{ij}(t) = \cos\beta\cos\beta_{ij} + \sin\beta\sin\beta_{ij}\cos(\varphi_{ij} + \omega_{rt}) \tag{2.2.1.1.1}
\]

The $\beta_{ij}$ is the angle the rotor makes with the internuclear vector $r_{ij}$. After substituting Eq 2.2.17, the $\cos^2\theta$ term in Eq. 2.2.9, we get,

\[
\frac{1}{2}(3\cos^2\beta - 1)(3\cos^2\beta_{ij} - 1) + 3/2\sin2\beta\sin2\beta_{ij}(\varphi_{jk} + \omega_{rt}) + 3/2\sin^2\beta\sin^2\beta_{ij}\cos2(\varphi_{jk} + \omega_{rt}) \tag{2.2.1.1.2}
\]

\[
\text{Figure 2.1 Diagram showing the rotation of internuclear vector } r_{ij} \text{ when the sample is rotated at an angle } \beta \text{ with respect to the direction of applied magnetic field.}
\]

The first term vanishes for $\beta = \acos(\sqrt{1/3}) = 54.74^\circ$ (magic angle) and hence gives a narrow resonance. The second and third term is periodic with $\omega_{r}$ and gives rotation sidebands at multiples of $\omega_{r}$.
2.2.1.2 Deuteration Effect

Most of the experiments described in this thesis are performed on deuterated compounds. The dipolar coupling constant for protons separated by a distance 1 Å can be calculated with Eq 2.2.8. This corresponds to ~120 kHz. As mentioned before, MAS is often employed to get narrower lines. However, even the state-of-art ultrafast MAS upto 70 kHz will not be able to average dipolar coupling completely. Another way to get narrow lines is with deuterium NMR. The gyro-magnetic ratio of deuterium (²H) is ~ 1/6.5 less than that of hydrogen (¹H). Hence, the dipolar coupling constant for two deuterium atoms separated by 1 Å, is ~ 2.8 kHz. This can be easily averaged with relatively moderate spinning rates.

2.2.1.3 TRAPDOR (TRAnsfer of Population in DOuble Resonance)¹⁰

The heteronuclear dipolar coupling between two spins, I and S, is probed by use of this pulse sequence. In the strong-field approximation the heteronuclear dipolar Hamiltonian is given by

\[ H_d = -\omega_p P_z (\cos \theta) (I_z S_z) \]  

(2.2.1.3.1)

This corresponds to ~120 kHz. As mentioned before, MAS is often employed to get narrower lines. However, even the state-of-art ultrafast MAS upto 70 kHz will not be able to average dipolar coupling completely. Another way to get narrow lines is with deuterium NMR. The gyro-magnetic ratio of deuterium (²H) is ~ 1/6.5 less than that of hydrogen (¹H). Hence, the dipolar coupling constant for two deuterium atoms separated by 1 Å, is ~ 2.8 kHz. This can be easily averaged with relatively moderate spinning rates.

\[ H_d = -\omega_p P_z (\cos \theta) (I_z S_z) \]  

(2.2.1.3.1)

Fig. 2.2 shows the TRAPDOR pulse sequence. The nucleus I is observed with and without irradiation at the resonance frequency of S spins as a function of irradiation time.

\[ H_d = -\omega_p P_z (\cos \theta) (I_z S_z) \]  

(2.2.1.3.1)

During MAS, the orientation of the dipole and quadrupolar tensors becomes time dependent. The combined action of MAS as well as rf irradiation on S spins results in exchange of population of the Zeeman states of the S spins. This has a clear effect on dipolar coupling.
between the spins I and S. The Hahn-echo signal with S spin recoupling decays faster as a function of the echo time $2\tau$ than the signal without irradiation on the S spins.

### 2.2.1.4 Deuterium Double Quantum (DQ) NMR

Deuterium nuclei have spin 1 and therefore there are three energy levels in a strong magnetic field. The double-quantum (DQ) transition $-1 \leftrightarrow 1$ is independent of quadrupolar coupling to first order. This is illustrated in Fig. 2.3. Therefore, narrow lines are expected in a double quantum spectrum.\textsuperscript{1112} As a novel approach, we have irradiated on $^{45}$Sc nuclei during the DQ evolution time $t_1$. Fig. 2.2.1.4.2 shows the pulse sequence and the coherence pathway diagram\textsuperscript{13} used to record the two-dimensional DQ spectrum.

\textbf{Figure 2.3} The energy levels of spin 1 nucleus. The observable single-quantum transitions are affected by the first-order quadrupolar interaction, whereas, the double-quantum coherences are not affected.

\textbf{Figure 2.4} (a) Pulse sequence used to record Two-Dimensional (2D) Double Quantum MAS NMR spectra. The pulse length of all pulses are $\pi/2$. $^{45}$Sc is irradiated during the evolution period.
The DQ coherences are excited by first pair of pulses and reconverted to longitudinal magnetization by the second pair of pulses. The time interval, $\tau_Z$, has negligible duration and it is present to allow a clean phase shift of the pulses. In our DQ MAS NMR experiments we have used rotor synchronization in the indirect dimension by increasing the evolution time $t_1$ in steps of the sample rotation time $T_1$. The States-Haberkorn-Ruben method is used for sign discrimination in F1 dimension and pure-absorption 2D spectrum is obtained by hypercomplex Fourier transform.

### 2.2.2 Mobility from NMR/ Dynamics

NMR is a powerful technique to probe the motions in solids. The motion of hydrogen atoms in metal hydrides can be monitored. By studying the rate of the motions as a function of temperature, we can experimentally probe the activation barriers. This is crucial if we are to fundamentally understand the structure and properties of hydrogen-storage materials. This gives scope for further improvement of materials that are used in the battery electrode.

Different NMR experiments are employed to probe the dynamics at various time scales. Motions with correlation time ($\tau_c$) in the order of $10^{-2}$ s or longer are best studied with Two-Dimensional exchange spectroscopy (2D Exsy).\(^{14,15}\) Motions with rates $\tau_c^{-1}$ of the order of the nuclear spin interaction anisotropy can be accessed via lineshape analysis.\(^{16,17}\) Motions in the order of $10^{-6}$ to $10^{-9}$ s are out of the dynamic range of lineshape analysis. Spin-lattice relaxation is investigated in such circumstances. Thus, in cases where relaxation is dominated by one particular nuclear spin interaction, the spin-lattice relaxation times can be calculated for different motions and compared with experimental values to reveal motional details.\(^{18,19}\) Molecular mobility regimes and the corresponding NMR experiments to observe the same are summarized in Table 2.2.2.1.
Table 2.2.2.1. Motional regimes which can be probed by various NMR techniques are given below.

<table>
<thead>
<tr>
<th>NMR technique</th>
<th>Correlation time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D Exsy/1D Exsy</td>
<td>$10^{-2}$ - $10^1$</td>
</tr>
<tr>
<td>Lineshape analysis/T₂</td>
<td>$10^{-2}$ – $10^{-4}$</td>
</tr>
<tr>
<td>T₁ρ</td>
<td>$10^{-4}$ – $10^{-3}$</td>
</tr>
<tr>
<td>T₁</td>
<td>$10^{-6}$ - $10^{-9}$</td>
</tr>
</tbody>
</table>

2.2.2.1 Two-Dimensional Exchange NMR spectroscopy (2D Exsy)

The hydrogen motion between NMR distinct sites is probed by this experiment. Hydrogen or deuterium exchange processes between two NMR distinct states a and b can be classified into three categories: slow, intermediate and fast exchange depending on the exchange rate k and the frequency separation $|νₐ - νₖ|$ between NMR frequencies $νₐ$ and $νₖ$ of sites a and b. In the slow-exchange regime, $k << |νₐ - νₖ|$, the NMR lineshapes are not broadened significantly. For fast exchange, $k >> |νₐ - νₖ|$, a single signal is observed at a weighed-average frequency, $ν = Pₐ \cdot νₐ + Pₖ \cdot νₖ$ where $Pₐ$ and $Pₖ$ are the population of each site with $Pₐ + Pₖ = 1$. In the intermediate exchange regime, $k \sim |νₐ - νₖ|$ and the two NMR lines coalesce into a broad line. 2D Exsy is a powerful technique to observe slow exchange processes.

In general, all 2D experiments consist of a preparation, evolution, mixing and detection period. Fig. 2.5 shows the typical pulse sequence of a 2D Exsy experiment. In the preparation period, the first pulse creates the transverse magnetization. During the evolution time, $t_1$, the magnetization vectors of the individual resonances precess at their characteristic resonant frequencies. Hence, initial resonances are frequency-labeled during $t_1$. At the end of $t_1$, the second pulse flips the x or y magnetization component onto the longitudinal axis and the mixing period starts. It is in this period that spins have an opportunity to move to a chemical distinct site. The final pulse generates the observable signal during the detection period, $t_2$. The 2D spectrum is obtained by Fourier transform with respect to $t_1$ and $t_2$. The exchange between spins from chemical distinct sites is reflected as cross-peaks. Only diagonal peaks are observed for the spins...
that do not exchange. Complete exchange of spins from chemical distinct sites is indicated by the similarity of the horizontal or vertical trace and the horizontal or vertical projection onto the direct or indirect frequency axis, respectively. The mixing period, \( t_m \), plays a crucial part in a 2D experiment as this is the time during which the exchanges are monitored. Very low values of \( t_m \) compared to exchange time will result in diagonal peaks only and very high values compared to spin-lattice relaxation time (\( T_1 \)) will result in a weak signal.

\[
t_1 \quad t_m \quad t_2
\]

**Figure 2.5:** Pulse sequence used in a typical 2D Exsy experiment. The pulse widths of all pulses are \( \pi/2 \).

The 2D spectrum can be amplitude modulated or phase modulated. The amplitude-modulated spectrum gives pure absorption lineshapes whereas phase-modulated spectrum results in phase-twisted lineshapes. A typical 2D Exsy spectrum is illustrated in Fig. 2.6. It concerns a \(^2\)H MAS NMR spectrum recorded for ball-milled \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65} \) which is the topic of Chapter 3. Three signals A, B and C can be recognized in the 1D spectrum and projection above the 2D spectrum, as well as along the spectral diagonal. The cross peaks between A and B denote deuterium exchange of spins between the corresponding environments. The interpretation of the resulting 2D spectra is essentially model free. However, it tends to be time consuming. E.g., for the materials investigated in our study, it takes approximately 18 hrs for a single experiment. The exchange rate can also be estimated in a faster way from one-dimensional exchange spectroscopy (1D Exsy), which is explained in the next section.
Figure 2.6 (a) 1D $^2$H NMR spectrum of ball-milled $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.7}$. The three signals labeled A, B and C are assigned to deuterium atoms at three inequivalent sites. (b) 2D Exsy spectrum: The crosspeaks between A and B indicate that there is exchange of deuterium atoms between A and B sites.

2.2.2.2 One Dimensional Exchange Spectroscopy (1D Exsy)

As mentioned in sec 2.2.2.1, 1D Exsy is used for obtaining the exchange rate constant. In this technique, the polarization of hydrogen atoms from one of the sites is selectively perturbed followed by a non-selective pulse. As a result of hydrogen exchange during the following mixing time, hydrogen atoms with perturbed polarization will replace hydrogen atoms at the “unperturbed” sites and vice versa. As a consequence, the signal intensity of the originally non-perturbed sites will decrease, and that of the initially perturbed sites will increase as function of the mixing time. The longest exchange timescales that can be probed by this method is determined by spin-lattice relaxation. Even without deuterium exchange, any perturbed spin polarization of the deuterium nuclei will relax to the thermal equilibrium value.

The polarization of deuterium atoms from site A (Fig. 2.6 a) is selectively perturbed and monitored as a function of time. Fig. 2.7 shows the polarization of deuterium atoms from A, B and C sites. The polarization of the B site decreases initially and then
Figure 2.7. Polarization of deuterium atoms as a function of time from distinct sites A, B, C after perturbation of only the A site.

Spin-lattice relaxation dominates. Magnetization recovery of site A shows bi-component behavior in time. The fast component is related to the exchange and the slow component to spin-lattice relaxation time ($T_1$). The polarization of deuterium atoms from the site C remains constant, which indicates that deuterium atoms from this site do not take part in the exchange with A or B site. This is also seen in the 2D Exsy spectrum in Fig.2.6b, where there are no crosspeaks between site C and other sites.

The 1D Exsy is performed at different temperatures and the exchange rate is monitored as a function of the same. This gives the activation barrier for the deuterium atom exchange between A and B sites.

There are different ways to achieve selective perturbation of polarization of the nucleus. One way is to apply a long soft pulse at a desired resonance frequency. In another approach, shaped pulses are applied. A Gaussian shaped pulse is considered as an example. This has a disadvantage that amplitude is not constant throughout the width of the resonance. This will lead to phase distortion of the signal.

In another method to selectively perturb a resonance line, DANTE\textsuperscript{20} pulse sequence is employed. DANTE is an abbreviation for Delays Alternating with Nutations for Tailored
Excitation. This consists of series of mRF pulses separated by time, $\tau$. The overall duration of the pulse sequence is $\Delta t$. Upon Fourier transformation, the excitation pulse in the frequency domain consists of series of pulses of width $1/\Delta t$ Hz, separated by $1/\tau$ Hz. The RF carrier should be positioned at the desired frequency of perturbation. The number of pulses ($m$) and power of the pulse can be varied to achieve a certain flip angle for a particular resonating signal. For MAS experiments, the value of $\tau = \tau_{\text{MAS}}$ is chosen in such way so as to perturb the centerband and the sidebands (if present) of the signal in a similar way. The time as well as frequency domain spectrum of excitation pulses are shown in the Fig. 2.8.

![Figure 2.8](image)

**Figure 2.8.** Selective Excitation using DANTE pulse sequence. (a) Time domain pulse sequence. (b) Fourier transformation of the excitation pulse.

Both 2D and 1D Exsy techniques are powerful tools to monitor the motion in millisecond to a second timescale. However, each technique has its advantages and limitations.

### 2.2.2.3 Relaxometry

#### 2.2.2.3.1 Spin-lattice relaxation

This process probes the mobility in nanosecond time scale. There are different techniques to extract the spin-lattice relaxation time ($T_1$) namely inversion recovery, saturation recovery, progressive saturation. The saturation recovery technique (SR) will be discussed since this
technique has been used it in this work. The pulse sequence for SR is shown in the Fig. 2.9 (a)
The intensity of the signal is given by
\[ S(\tau) = M_0(1 - \exp(-\tau/T_1)) \]  
(2.2.3.1.1)
Fig 2.9 (b) shows the signal intensity as a function of time.

![Figure 2.9](image)

**Figure 2.9** (a) Pulse sequence for saturation recovery. (b) Plot of signal intensity as a function of time using the SR technique.

### 2.2.2.3.2 Spin-lattice relaxation in rotating frame

The atomic motions in the order of kHz are monitored via this technique. Fig. 2.10 shows the pulse sequence to measure the spin-lattice relaxation in rotating frame (\(T_{1p}\)). The first pulse rotates the magnetization from equilibrium to x-y plane. The spinlock pulse is applied along x or y direction. A typical strength of spinlock field (\(\omega_1\)) is \(\sim 50-100\) kHz. The intensity of the signal as a function of spinlock time is given
\[ S(\tau) = M_0 \exp(-\tau/T_{1p}) \]  
(2.2.3.2.1)

Typically, \(T_1\) and \(T_{1p}\) are measured as a function of temperature and their values goes through a minimum. The minimum happens when the product of the Larmor frequency (\(\omega_0\)) or the spinlock field (\(\omega_1\)) and the motion correlation time (\(\tau_c\)) is roughly equal to 1.
Figure 2.10 Pulse sequence for measuring spin lattice relaxation time in rotating frame. The signal intensity is monitored as a function of spinlock time $\tau$.

2.3 X-ray diffraction (XRD)

XRD\textsuperscript{33} technique is commonly employed to determine the crystallographic phases present in a material. A lattice consists of periodic arrangement of atoms with lattice parameters $a$, $b$, and $c$ representing the lengths in three different orthogonal axis. In three dimensions, the lattice points form into set of planes separated by a distance called as interplanar distance, $d$. There can be different sets of planes with distinct $d$ values. The rays are scattered by the electrons from the atoms. The scattered rays from different planes undergo constructive interference to give a peak. The condition for interference is given by Bragg equation,

$$n\lambda = 2d \sin \theta$$

where $n$ is an integer known as order of diffraction, $\lambda$ is the wavelength of x-rays and $\theta$ is the angle of incidence.

Fig 2.11. Illustration of X-ray diffraction. $\theta$ is angle of incidence of the X-rays. The distance between atomic planes is given by $d$.

Miller indices are used to describe the planes in the crystal. They are represented by $(hkl)$. The distance between two planes ($d_{hkl}$) and the miller indices is related to the crystal dimension. For simple cubic lattice,
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\[ d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \quad (2.3.2) \]

The width of the diffraction peak gives an estimate about the crystallite size. The crystallite size is given by

\[ D = \frac{K\lambda}{\beta \cos \theta} \quad (2.3.3) \]

Where D is the diameter of the crystal, K is the (typical value is 0.9) shape factor, \( \lambda \) is the wavelength of the incident X-ray beam, \( \beta \) is the full-width at half-maximum (FWHM) measured in radians and \( \theta \) is the Bragg angle.

2.4 References

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Chapter 3

Nanostructures of $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_x$ studied with X-ray diffraction, neutron diffraction, and magic-angle-spinning $^2\text{H}$ NMR spectroscopy *

Abstract

Magnesium transition-metal alloys have a high hydrogen-storage capacity and show improved hydrogen uptake and -release kinetics compared to pure magnesium. In the present study we have investigated the structure of bulk magnesium-titanium deuteride $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_x$ prepared via mechanical alloying and gas-phase deuterium absorption by combined use of x-ray diffraction (XRD), neutron diffraction, and magic-angle-spinning $^2\text{H}$ nuclear magnetic resonance (NMR). The initial ball-milled alloy has two XRD-distinct Mg and Ti fcc phases. Even after prolonged exposure to deuterium gas at 75 bar and 175 °C the materials with and without palladium catalyst are only partly deuterated. Deuterium loading causes the formation of, on the one hand, bct (rutile) MgD$_2$ nanodomains with interdispersed TiD$_y$ layers and, on the other hand, a separate fcc (fluorite) TiD$_z$ phase. The TiD$_y$ phase is XRD invisible, but shows clearly up at a $^2\text{H}$ NMR shift of $-43$ ppm between the shift of MgD$_2$ (3 ppm) and the Knight shift of the TiD$_z$ phase ($-143$ ppm). Exchange NMR indicates complete deuterium exchange at 25 °C between the MgD$_2$ and TiD$_y$ phase within 1 s, as consistent with intimate contacts between these phases. Combined analysis of the XRD and NMR peak areas suggests that the deuterium concentrations $y$ and $z$ in the TiD$_y$ and TiD$_z$ domains are about 1.5 and 2.0, respectively. Comparing the intrinsic cell parameters of rutile MgH$_2$ and fluorite TiH$_2$, we propose that stabilization of the mixed nanocomposite may arise from a coherent coupling between the crystal structures of the rutile MgD$_2$ nanodomains and the thin layers of fcc TiD$_y$.

3.1 Introduction

The increasing demand for energy puts the conventional fossil fuel sources under stress as these are already running out. An attractive alternative energy carrier would be hydrogen, if it can be efficiently stored. This can be achieved by means of pressurized gas or liquefied hydrogen. However, high pressure (typically 70 Mpa) or low temperature (21 K) are necessary to reach practical capacities. Alternative options at lower pressure and higher temperature are physical hydrogen storage in porous materials\(^1,2\) or chemical hydrogen storage in the form of hydride compounds, such as reversible metal hydrides.\(^3\) Metal-based hydrogen storage materials have the advantage of being operable under closer to ambient conditions when compared to other types of storage. The typical usage would be for stationary hydrogen storage or for electrode materials in rechargeable batteries for portable devices such as cell phones and cameras. Since hydrogen is absorbed in metal hydrides as atoms, rather than molecules, these hydrides typically have a volumetric hydrogen density similar to or higher than liquid hydrogen (71 kg m\(^{-3}\) at 20 K).\(^4\) Magnesium hydride, for instance, can theoretically store 110 kg m\(^{-3}\), and because magnesium is a light metal, it also has a high gravimetric storage capacity of 7.6 wt. % hydrogen. However, MgH\(_2\) suffers from slow sorption kinetics.

Notten and co-workers\(^5\)–\(^7\) have recently found that the kinetics can be improved by alloying magnesium with scandium. A Sc fraction > 20 at. % transition metal causes a change from the rutile structure of MgH\(_2\) to a fluorite structure of transition-metal hydrides and thereby enhances the mobility of the hydrogen.\(^8\) As revealed by NMR relaxometry,\(^9\) hydrogen mobility is significantly faster in Mg\(_{0.65}\)Sc\(_{0.35}\)H\(_{2.2}\) than in MgH\(_2\) and ScH\(_2\). Since scandium is a precious metal, an economically more feasible option is to use its less expensive neighbor in the periodic table of elements, titanium, which has similar electrochemical properties in Mg-based thin films as scandium.\(^10\) Magnesium and titanium are thermodynamically immiscible,\(^11\) but alloys can be produced, e.g., in the form of thin films by e-beam deposition,\(^10\) physical vapor deposition\(^12\) and magnetron cosputtering,\(^13\) or as bulk powders by mechanical mixing.\(^14\)–\(^19\) The boiling point of Mg is less than the melting point of Ti which rules out melt mixing techniques. The crystal structure of pure Mg and Ti is hexagonal, but ball milling of mixed Mg and Ti powders with micron-sized particles yields a material with two face-centered cubic (fcc) crystal phases.\(^18\) This is promising for its properties as a hydrogen storage material, because an fcc Mg-Ti lattice with hydrogen at the tetrahedral (T) interstitial sites would form the favorable fluorite ternary
compound. Indeed, thin films of magnesium-titanium hydride have a coherent fcc crystalline structure with a composition-dependent lattice constant, and show strongly enhanced kinetics of hydrogen uptake and release compared to thin magnesium hydride films without titanium. In addition, compressing the hydrides MgH$_2$ and TiH$_{1.9}$ at high temperature (600 °C) and pressure (8 Gpa) yields single-phase Mg$_7$TiH with an fcc unit cell (4.77 Å) as the basic structure building block of a superstructure with non-random ordering of Mg and Ti atoms over the metal positions.

X-ray diffraction (XRD) is commonly employed to characterize the crystal structure of metal hydrides and gives information about the lattice positions of the metal atoms. Due to the high scattering of the metal atoms hydrogen and deuterium are not observable with XRD. This is especially the case in conducting materials, in which the electron of hydrogen or deuterium atoms is delocalized. These light atoms are visible with neutron diffraction (ND), because neutrons interact with the atomic nuclei, rather than the electrons. Both XRD and ND require structural coherence in sufficiently large crystalline domains or particles. These techniques cannot detect amorphous domains or ordered domains with too short coherence lengths. In contrast, nuclear magnetic resonance (NMR) spectroscopy does not require crystallinity. Magic-angle-spinning (MAS) $^1$H NMR spectroscopy gives direct information about the local chemical environment of hydrogen or deuterium in metal hydrides or deuterides. Although the NMR frequency of $^1$H nuclei is higher than that of $^2$H nuclei at a given magnetic field, the chemical resolution in $^2$H NMR spectra of metal deuterides tends to be actually higher than in $^1$H NMR spectra of the corresponding metal hydrides. This is because the dipolar coupling between $^1$H nuclei is also stronger than between $^2$H nuclei at the same internuclear distance. As a consequence, MAS $^1$H NMR lines tend to be broadened by higher-order multispin effects not completely averaged by the sample rotation. For magnesium-scandium deuteride we were recently able to distinguish quantitatively between deuterium atoms with pure magnesium coordination and those with at least one scandium neighbor, and establish the rate at which deuterium exchanges between these two environments. This yielded insight into the non-random ordering of Sc and Mg over the metal positions in the lattice at a length scale below the coherence length required for XRD and ND. In the present study we combine x-ray powder diffraction, neutron powder diffraction, and MAS $^2$H NMR spectroscopy to characterize bulk
magnesium-titanium deuteride prepared via mechanical alloying of Mg and Ti and subsequent deuterium absorption at 175 °C.

4.2 Experimental

Two ball-milled Mg-Ti alloys (with and without Pd catalyst) were synthesized by mechanical mixing of Mg and Ti powders (particle size < 50 µm) in a Spex 8000 ball mill at 1750 rpm. The powders were loaded in a 55 ml vial with tungsten-carbide lining together with 12 stainless steel balls of 10 mm diameter. Ball-to-powder weight ratio was 16 to 1. 1.5 wt. % of stearic acid was added as a process-control agent at the start of the milling process to reduce cold welding of the powder. After 5 h of milling, the alloy (without Pd catalyst) was loaded into a Parr high pressure vessel and exposed to 75 bar deuterium gas and heated to 175 °C for ~ 24 h. The other MgTi alloy was activated by milling for 90 min. with 2 at. % of Pd as hydrogen-absorption catalyst prior to the ND experiment. A total amount of 4.85 g of the obtained \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{Pd}_{0.02} \) was introduced in a stainless steel cylindrical container connected to a manometric device allowing in situ loading and unloading of the sample with deuterium gas (Sievert’s method) inside the ND measuring device. The sample holder was first evacuated under secondary vacuum \((10^{-4} \text{ mbar})\) and then introduced in a furnace at the center of the diffractometer. Two reference samples were prepared by ball milling. The TiD\(_2\) was obtained by ball milling the Ti powder for 1 h. and subsequent deuterium loading under high pressure and temperature (450 °C). MgD\(_2\) was prepared in a similar way with ball-milling steps followed by deuterium loading at 75 bar and 300 °C. Ex situ x-ray powder diffraction of the material before and after deuterium loading was measured on a PANalytical X’Pert-Pro MPD diffractometer by use of an X’Celerator detector or on a Rigaku D/MAX-B. Data were collected over a 20 angular range of \(10^\circ - 100^\circ\) using Cu \(K_\alpha\) radiation at 40 kV and 40 mA. The materials were measured at room temperature with normal exposure to air. In situ neutron powder diffraction patterns have been recorded for different temperature and hydrogen-pressure ranges with the position sensitive detector (PSD) of the D1B instrument at the Institut Laue Langevin in Grenoble. The wavelength was set to 1.287 Å and the patterns were recorded every 5 min for absorption and every 10 min for desorption in the range \(18^\circ - 98^\circ\) by the 400 cells of the PSD (step = 0.2° in 2θ). The diffraction patterns were sequentially refined using the program FULLPROF. Ex situ \(^2\text{H}\) NMR spectra of the material after deuterium loading were recorded on a Bruker DMX500 spectrometer operating at a \(^2\text{H}\) NMR frequency of 76.7 MHz. MAS was applied to eliminate the first-order
Nanostructures of Mg$_{0.65}$Ti$_{0.35}$D$_x$ studied with….

Line broadening effect of the quadrupolar interaction. The typical sample-rotation rates were between 8 and 24 kHz. The NMR sample holder was packed at room temperature in normal air, closed with a tight cap and rotated in a flow of dry nitrogen inside the spectrometer. Two-dimensional exchange spectroscopy (2D Exsy) was carried out by use of the standard pulse sequence consisting of three 90° pulses of 5 s each.$^{29}$ The time interval between the first two pulses (evolution time $t_1$) was systematically incremented in the course of the experiment, while the time interval between the second and third pulses (mixing time $t_{mix}$) was fixed to either 0.01, 1, or 5 s. For 2D Exsy, the microcrystalline Mg$_{0.65}$Ti$_{0.35}$D$_x$ powder was packed into 4 mm MAS sample holders and rotated at a rate of 14 kHz. One-dimensional Exsy (1D Exsy) was measured by selectively perturbing the polarization of the deuterium nuclei in the MgD$_2$ phase resonating at 3 ppm using a rotor synchronized DANTE pulse train$^{30}$ of six soft pulses of 1 s at a reduced rf power level corresponding to a $^2$H nutation frequency of 12.5 kHz, and monitoring the polarization a variable time interval (mixing $t_{mix}$) later by means of a nonselective 90° read pulse of 5 s. The one-dimensional exchange spectra were recorded at varied mixing times between 0.01 and 1 s and varied temperatures between −75 and 25 °C to monitor the possible deuterium exchange from the MgD$_2$ phase to the other two phases. For 1D Exsy the sample was packed into a 2.5 mm MAS rotor and spun at a rate of 20 kHz. The exchange curves were always compared with the $T_1$ relaxation observed after nonselective perturbation resulting from replacing the DANTE pulse train by a single nonselective 90° pulse. Because of its high specific weight, TiD$_2$ was mixed with alumina to obtain stable sample rotation. The ternary system Mg$_{0.65}$Ti$_{0.35}$D$_x$ was not diluted with alumina because it was spinning without any problem at high MAS speeds.

MAS $^2$H NMR sideband patterns were analyzed in combination with static $^2$H NMR line shapes using the spectrum fit program DMFIT (2008 version).$^{31}$

3.3 Results

3.3.1 XRD Characterization

Figure 3.1 shows the XRD patterns of the ball-milled magnesium-titanium alloys with and without Pd catalyst (b and c2), and the deuterium-loaded ball-milled alloy without Pd (c1). For comparison, the patterns of (a) MgD$_2$ and (d) TiD$_2$ are shown as well. All patterns were deconvoluted in terms of Gaussian-Lorentzian line shapes and the extracted peak positions and widths are given as Appendix I.$^{32}$ The Pd-containing alloy was the sample investigated with
neutron diffraction (vide infra) and the deuterium-loaded material without Pd was investigated with $^2$H NMR (see below). The MgD$_2$ has a rutile structure with lattice constants $a = 4.516(8)$ Å and $c = 3.011(5)$ Å. There are also reflections from a small amount of hcp Mg. The x-ray pattern of TiD$_2$ shows the main fcc hydride phase with cell parameter 4.444(2) Å (consistent with Ref. 33), as well as a minor hcp Ti phase. The XRD reflections of the magnesium-titanium alloys with and without Pd are broad, which is indicative for small crystalline-domain sizes. Both materials have two fcc phases, the smaller one of which (cell parameters 4.28(2) Å in Mg$_{0.65}$Ti$_{0.35}$ and 4.33 Å in Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$) is assigned to a Ti-rich phase on the basis of published lattice constants of fcc Ti metal (4.34 Å) (Ref. 34) and Ti$_{0.94}$Mg$_{0.06}$ alloy (4.26 Å).$^{35}$ It has been reported before that ball milling causes the pure titanium metal to undergo a structure transition from hcp to fcc, as well.$^{34}$ The fcc phase with the larger constant, 4.42 Å, both for alloys with and without Pd, is assigned to a Mg rich phase. The (111) reflection (around $2\theta = 35^\circ$) of this phase is narrow compared to the other reflections for both alloys, indicating longer coherence length (25 nm) in this direction than in other directions (3–9 nm).$^{32}$ The molar volume of this phase, 13.0 cm$^3$ mol$^{-1}$, lies between the molar volumes 14.0 and 10.6 cm$^3$ mol$^{-1}$ of pure Mg and Ti in the hcp phase, respectively. Such a molar volume can be interpreted according to Vegard’s law$^{36}$ in terms of a phase composition Mg$_{0.71}$Ti$_{0.29}$, which is close to the overall composition Mg$_{0.65}$Ti$_{0.35}$. However, given the fact that a significant Ti fraction resides in the Ti-rich phase, the relative Mg content in the Mg-rich phase is probably higher. The alloy with Pd coating (added at the end of the ball milling) also shows the reflections from a separate fcc Pd phase with lattice constant 3.89 Å. Upon prolonged exposure to deuterium at 175 °C and 75 bar, the XRD reflections of Mg$_{0.65}$Ti$_{0.35}$ alloy have become weaker, but stay at approximately the same angles. At close inspection, it turns out that the XRD peaks of the originally 4.42 Å fcc phase show slight broadening toward smaller reflection angles. At first thought, we have considered a small lattice expansion of the Mg-rich fcc phase upon deuterium uptake. Because of the above-mentioned different molar volumes of Mg and Ti, however, one would expect such Mg-rich deuteride fcc phase to have a substantially larger cell parameter than fcc TiD$_2$ (4.44 Å), probably similar to the computed value for fcc MgH$_2$ (4.79 Å),$^{37}$ and the experimentally found value of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ (4.81 Å).$^8$ However, such fcc phase is not observed (Fig. 3.1). Therefore, as an alternative explanation, the asymmetric broadening toward lower reflection
angles could also indicate the formation of fcc TiD$_{2-2}$ upon deuterium absorption. In addition to this

![XRD pattern of MgD$_2$, Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$, Mg$_{0.65}$Ti$_{0.35}$D$_x$, and TiD$_2$.](image)

**Figure 3.1**: (Color online) XRD pattern of (a) MgD$_2$, (b) Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$, (c1) Mg$_{0.65}$Ti$_{0.35}$D$_x$, (c2) Mg$_{0.65}$Ti$_{0.35}$, and (d) TiD$_2$. • fcc Mg-rich (4.42 Å), fcc Ti-rich (4.26 Å), ◊ fcc TiD$_{2-2}$, * hcp Ti, ▲ hcp Mg, and ▼ fcc Pd (3.89 Å).

asymmetric broadening, wide reflections at the positions of rutile MgD$_2$ become also visible after deuterium loading. Indeed, the XRD pattern of Mg$_{0.65}$Ti$_{0.35}$D$_x$ is quite well described as a linear combination of the patterns of the initial alloy Mg$_{0.65}$Ti$_{0.35}$, on the one hand, and the pure deuterides MgD$_2$ and TiD$_2$, on the other (Fig. 3.2(a)). Deuterium loading of the magnesium-titanium alloy thus appears to cause the material to segregate into bct MgD$_2$ and fcc TiD$_{2-2}$. Magnesium hydride always occurs as the stoichiometric MgH$_2$. At lower overall hydrogen concentration, the hydride separates into a MgH$_2$ phase and almost MgH$_{0.001}$.
hydride exists in varying non-stoichiometric states. These TiH\textsubscript{x} compounds have an fcc crystal structure with a lattice constant slightly depending on the hydrogen concentration \( z \) (Table 3.1). Even after prolonged exposure of the alloy Mg\textsubscript{0.65}Ti\textsubscript{0.35} to deuterium, part of the original Mg-rich and Ti-rich phases has not become deuterated. As shown later in this chapter, ND and NMR analyses qualitatively support this interpretation. The implicit suggestion from the XRD analysis that the Mg-rich and Ti-rich phases are equally converted, however, is probably an artifact of the linear regression model, which treats the XRD pattern of the alloy as one of the invariant components. Furthermore, the rutile reflections of the MgD\textsubscript{2} phase formed during deuterium

Figure 3.2: (Color online) Analysis of the XRD pattern of Mg\textsubscript{0.65}Ti\textsubscript{0.35}D\textsubscript{0.65}. (a) Linear regression in terms of the observed patterns of Mg\textsubscript{0.65}Ti\textsubscript{0.35}, TiD\textsubscript{2}, and MgD\textsubscript{2} (Fig. 3.1); [(b) and (c)] Coupled deconvolution of the inhomogeneous (111) and (200) reflections of (b) Mg\textsubscript{0.65}Ti\textsubscript{0.35}D\textsubscript{x} and (c) Mg\textsubscript{0.65}Ti\textsubscript{0.35} with the overall peak-area ratio \( A_{111}/A_{200}=1.4 \) as a fit restriction for the individual components, as well. (d) observed pattern of TiD\textsubscript{2} for comparison.
uptake are obviously much broader than those of MgD$_2$, and the (111) reflection of the TiD$_{2-2}$ phase in the ternary system is also broader than that of the TiD$_2$ reference compound. Broad reflections are typical of crystalline nanostructures with a small coherence length.

**Table 3.1** Cell parameters for fluorite and rutile MgH$_2$, and fluorite ScH$_2$ and TiH$_2$ at varying hydrogen content $\varepsilon$. The value for fluorite MgH$_2$ is a theoretical prediction based on two consistent DFT studies (Refs. 37 and 55). Other values have been experimentally determined.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fluorite (Å)</th>
<th>Rutile (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH$_2$</td>
<td>4.79</td>
<td>a = 4.52; c = 3.01</td>
</tr>
<tr>
<td>ScH$_2$</td>
<td>4.78</td>
<td></td>
</tr>
<tr>
<td>TiH$_2$</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>TiH$_{1.8}$</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>TiH$_{1.23}$</td>
<td>4.39</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3.2 Neutron Diffraction

Before starting the *in situ* deuterium-loading ND experiment, the Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$ sample was measured in the beam (at time $t=0$). Figure 3.3(a) shows the refinement of this first pattern. The five sharp lines marked with stars in the figure belong to the stainless steel sample holder. Beside these lines, tiny lines belonging to the sample were observed. They have been identified as an averaged main phase (Mg$_{0.65}$Ti$_{0.35}$) adopting an fcc structure with cell parameter $a=4.40(2)$ and pure hcp magnesium ($a = 3.22(1)$ and $c = 5.21(4)$ Å. As a consequence of the limited resolution of the instrument, it was not possible to distinguish in the refinement between the 4.28 and 4.42 Å fcc phases recognized in the XRD patterns. Although Mg lines look stronger than those of the fcc phase, the relative amount of Mg is low (∼3 wt. %). This results from the fact that hcp Mg has a positive Fermi length ($b_{\text{Mg}} = 0.5375$), whereas the fcc phase is made by alloying Mg and Ti with positive and negative Fermi length ($b_{\text{Mg}}=0.5375$ and $b_{\text{Ti}}=−0.3438$) leading to weaker intensities for this latter phase. Deuterium gas was introduced into the sample holder and both diffraction pattern and pressure evolutions were followed. For the first step, 24.8 bar of D$_2$ was introduced into the device, but only little absorption, 0.014 deuterium atom per metal atom (D/M), was observed. After 20 min, a second amount of gas ($P=24$ bar) was added to the system. After 629 min, the total absorbed amount was estimated to be 0.163 D/M but the pressure drop remained very slow. To speed up the absorption process, the temperature of the
sample holder was gradually increased from 14 to 175 °C in steps of ~50 °C. A significant improvement in the kinetics was then observed. The pressure decreased rapidly and the deuterium uptake reached 0.94 D/M after 853 min. A third amount of deuterium was again added to the system (P=24.56 bar) and a small extra uptake was obtained (1.01 D/M). The sample was then cooled down to room temperature and the final deuterium content at room temperature reached 1.03 D/M.

Figure 3.3: (Color online) Refined neutron-diffraction pattern [measured (open circles) and calculated (solid line)] for the alloy Mg<sub>0.65</sub>Ti<sub>0.35</sub>Pd<sub>0.02</sub> (a) before and (b) after deuterium absorption. Vertical bars correspond to diffraction line positions for each phase. Stars indicate the sharp lines arising from the stainless steel container.
During the reported absorption process, a series of neutron diffractograms were recorded as a function of time. After 480 min, new lines attributed to bct (rutile) MgD₂ and fcc TiDₓ are appearing. These lines become stronger as a function of deuterium loading and are observed till the end of the absorption process. A typical refined pattern taken after 880 min of absorption is shown in Fig. 3.3(b). This pattern shows the coexistence of at least three phases: the averaged fcc Mg₀.₆₅Ti₀.₃₅ phase with lattice constant $a = 4.34(4)$ Å and two deuteride phases, bct MgD₂ ($a = 4.56(3)$ Å and $c = 2.96(3)$ Å, and fcc TiDₓ ($a = 4.478(5)$ Å) in the weight ratio 73(27)%, 8(2)%, 8(2)%.

Figure 3.4: (Color online) Phase fractions during (a) absorption at 25 °C with a temperature jump to 175 °C after 630 min and (b) temperature-programmed desorption from 40 °C at $t=0$ to 460 °C at $t=420$ min (1 K min⁻¹). In the absorption experiment the Mg-Ti fraction stays constant until the temperature is raised to 175 °C. Most of the hydrogen desorption takes places between 180 and 300 °C.
and 19(8)% respectively. The large error (+/-27%) for the main phase is related to its poor scattering factor and strong overlap with neighboring diffraction lines from other phases. The TiDz lattice constant determined with ND is 1% larger than the value 4.44 Å for the TiDz phase estimated from XRD. However, the XRD value could only be accurately determined for pure TiD2. Estimation of the cell parameter for this phase in Mg0.65Ti0.35Dx from the XRD pattern is complicated by the overlap with the reflections of the non-deuterated Mg-rich phase (Figs. 3.1 and 3.2). The advantage of the poor ND visibility of the non-deuterated main phase is a better resolution of the ND signals of the TiDz phase. The diffraction patterns have been refined sequentially. From this data analysis, the amount and volume of each phase can be extracted and are given in Fig. 3.4(a), respectively, as a function of loading time. Finally, the two possible available sites (octahedron and tetrahedron) for deuterium in the TiDz phase were also tentatively refined. This shows that only the T site is significantly occupied with about 1.24+0.25 D/M, whereas the octahedral (O) site is nearly empty. From the absorption study, it can be concluded that upon deuteration the averaged fcc phase partially transforms into MgD2 and TiDz with z~1.2. The latter deuterium concentration, z, is best regarded as an underestimate, because the large cell parameter 4.478 Å indicates a higher deuterium content (Table 3.1). The transformation of the alloy into MgD2 and TiDz is enhanced by raising the temperature to 175 °C. However, despite this thermal improvement, the reaction was not complete after 16 h. After absorption, the sample was thermally discharged using temperature programmed desorption. The heating rate was set to 1 K/min from room temperature up to 730 K (457 °C). To improve the counting statistics, each pattern was measured for 10 min. A sharp pressure increase is observed above 180 °C up to 300 °C (Fig. 3.4(b)), which is attributed to deuterium desorption from the sample. Above 275 °C the MgD2 reflections disappear and new lines attributed to pure Mg become visible. The diffraction patterns have been refined sequentially for the whole thermal desorption experiment. From this analysis the fractions of the different phases have been extracted as a function of time. The amount of the averaged main fcc phase remains nearly constant during temperature programmed desorption (TPD) and does not seem affected by the thermal treatment. The MgD2 phase desorbs at 280 °C giving rise to the increase in the pressure signal and to the formation of pure Mg. This desorption temperature is in good agreement with the value expected for pure MgD2. Surprisingly the TiD2 phase seems to increase. However, this may well be caused by the fact that an increasing fraction of the material becomes amorphous, so that the neutron diffractogram does
not reflect the complete quantitative picture. At the end of the TPD process, only three phases are coexisting.

3.3.3 NMR characterization

Figure 3.5 shows the MAS $^2$H NMR spectra of TiD$_2$, Mg$_{0.65}$Ti$_{0.35}$D$_x$, and MgD$_2$, as well as Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$, for comparison. At first sight, the spectrum of Mg$_{0.65}$Ti$_{0.35}$D$_x$ seems a simple superposition of the MgD$_2$ and TiD$_2$ spectra, which confirms a phase separation into MgD$_2$ and TiD$_x$ as indicated by XRD and ND. Both MgD$_2$ and the corresponding phase in Mg$_{0.65}$Ti$_{0.35}$D$_x$ show a similarly narrow MAS center band at 3 ppm, and similarly intense spinning sidebands caused by the sample rotation (Figs. 3.5 (a) and 3.5(c)). The envelope of the sideband pattern reflects the size of the quadrupolar coupling of the deuterium nuclei to local electric field...
gradients. In combination with the static $^2$H NMR line shape the extended sideband pattern for MgD$_2$ (Fig. 3.5(a)) i.e. well described by a quadrupolar anisotropy $\nu_Q$ of 8 kHz and $\eta$ asymmetry parameter = 0.65. The deuterium atoms at the 4f positions in the rutile MgD$_2$ structure have a planar threefold Mg coordination, resulting in a relatively strong local electric field gradient. In contrast, deuterium atoms in fluorite TiD$_2$ are located at the tetrahedral interstitial sites, at which the electric field gradient vanishes.\textsuperscript{39,40} This is consistent with the relatively weak sidebands observed in Fig. 3.5(d). The size of the quadrupolar coupling for deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ (Fig. 3.5(b)) is between that of deuterium in MgD$_2$ and TiD$_2$. The sideband pattern is reasonably fitted by various combinations of quadrupolar anisotropy and asymmetry parameters ($\nu_Q$, $\eta$) ranging from $\nu_Q$=15 kHz for $\eta$=1 to $\nu_Q$=17 kHz for $\eta$=0, but none of these combinations yields a consistent fit to the static $^2$H NMR spectrum.\textsuperscript{32} The impossibility to consistently describe the sideband pattern and the static NMR line shape by a single component may well reflect a distribution of electric field gradients at the tetrahedral interstitial sites in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$. This is perhaps associated with the heterogeneous distribution of partial charges in this ternary compound. In addition, motional averaging of the quadrupolar interaction by deuterium mobility could also affect the static line shape and sideband pattern. All in all, the fact that the sideband pattern of the MgD$_2$ phase in Mg$_{0.65}$Ti$_{0.35}$D$_x$ is practically the same as that of pure MgD$_2$ is consistent with the similar rutile crystal structure also observed with XRD and ND.

The spectrum of TiD$_2$ and the corresponding phase in Mg$_{0.65}$Ti$_{0.35}$D$_x$ contains a signal at −151 and −143 ppm, respectively. Such strongly negative shift values result from the Knight shift typical of conducting materials. The Knight shift depends on the local density of states (LDOS),\textsuperscript{41,42} which may vary with position in the crystal structure of a complex metal hydride. For instance, the LDOS in theoretical model structures for Mg-Ti hydrides with random Mg and Ti distribution over the metal positions in the fcc lattice is higher at deuterium sites close to Ti, than Mg atoms.\textsuperscript{43} In general, the Knight shift is an anisotropic interaction, i.e., it depends on the orientation of the shift tensor and thus the crystallite with respect to the magnetic field. However, the relatively weak sidebands in the MAS $^2$H NMR spectrum of TiD$_2$ (Fig. 3.5(d)) indicate that the Knight-shift anisotropy for this material is relatively small, as consistent with the cubic crystal structure of TiD$_2$. Since TiD$_2$ has a fluorite structure, we assign the signal at −151 for TiD$_2$ and −143 ppm for Mg$_{0.65}$Ti$_{0.35}$D$_x$ to deuterium atoms at the T interstitial sites. As $^2$H NMR of bulk titanium deuteride at varied deuterium content has revealed a stepwise jump from
Nanostructures of $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_x$ studied with... approximately $-50 \text{ ppm}$ at $\text{D}/\text{M} < 1.5$ to $-150 \text{ at } \text{D}/\text{M} > 1.7$. The signal at $-143 \text{ ppm}$ in the $^2\text{H}$ NMR spectrum of $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_x$ thus indicates the presence of a $\text{TiD}_2$ phase with a rather high deuterium concentration $z \sim 1.7$.

**Figure 3.6:** (a) 2D exchange $^2\text{H}$ NMR spectra of $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_x$ at a mixing time of 1 s. Off-diagonal intensity in the 2D spectrum at mixing time $t_{\text{mix}}=1 \text{ s}$ indicates deuterium exchange between MgD$_2$ and TiD$_z$ nanodomains. (b) Projections on the horizontal axis $P(t_{\text{mix}})$ and horizontal sections $S(t_{\text{max}})$ crossing the vertical axis at 4 ppm. Comparison of $P(1 \text{ s})$ and $S(1 \text{ s})$ indicates that complete deuteron exchange takes place between MgD$_2$ and TiD$_z$ nanodomains within 1 s. $S(5 \text{ s})$ shows that hardly any exchange occurs between the TiD$_z$ _macro_phase and MgD$_2$ or the TiD$_z$ clusters in contact with MgD$_2$. (c) 1D exchange at 25 °C: transient response of the 3 ppm ($\bigcirc$) and $-45 \text{ ppm}$ ($\blacktriangle$) intensities after selective polarization perturbation of the deuterium spins in the MgD$_2$ phase resonating at 3 ppm ($\bigstar$) recovery of the 3 ppm intensity after nonselective perturbation. (d) Temperature dependence of exchange rate extracted from 1D Exsy.

For the ternary system there is an additional signal at $-43 \text{ ppm}$ with peak area roughly equal to that of the $-143$-ppm signal. This may be compared with a much smaller signal at $-48 \text{ ppm}$ in the TiD$_2$ spectrum. The shift values $-43$ and $-48 \text{ ppm}$ suggest deuterium sites in a Ti
environment with a lower LDOS. Given its small peak area of a few percent for pure TiD$_2$, we have considered a possible assignment to a small fraction of deuterium atoms at O sites.$^{33,45-47}$

MAS $^2$H NMR of the second-row transition metal hydride YD$_{x-2}$, which also has a fcc structure, shows a minor O signal $\sim$27 ppm downfield to the major T signal.$^{48}$ For Mg$_{0.65}$Ti$_{0.35}$D$_x$, however, no exchange between deuterium sites resonating at $-43$ and $-143$ ppm is observed with two-dimensional exchange NMR spectroscopy up to the second time scale (4.3.3.2). In short, this technique correlates the chemical shift before and after a selectable time window $t_{\text{mix}}$, during which the deuterium atoms have the opportunity to move to another environment.$^{49-51}$ The lack of such correlation between the signals at $-43$ and $-143$ ppm in 2D Exsy is inconsistent with the small distance between T and O sites inside the fcc unit cell. 2D Exsy does reveal exchange between deuterium atoms in the MgD$_2$ phase and the unknown type of sites resonating at $-43$ ppm (Fig. 3.6). This suggests an alternative assignment of the $-43$ ppm signal to small clusters or thin layers of TiD$_y$ dispersed between rutile MgD$_2$ nanodomains (Fig. 3.7(b)). Comparison of the horizontal cross-section at 3 ppm with the overall spectral projection on the horizontal frequency axis shows that at room temperature the exchange between the MgD$_2$ phase resonating at 3 ppm and the supposed TiD$_y$ clusters resonating at $-43$ ppm is complete at the second time scale (Fig. 3.6 (b)). Unlike the isolated TiD$_z$ phase, there is no substantial MgD$_2$ fraction, which is not close to TiD$_y$ clusters. The smaller Knight shift, $-43$ ppm, of deuterium in the TiD$_y$ clusters than in the separate TiD$_z$ phase can be caused by their small size or their lower deuterium content. On the one hand, there have been several reports that the size of the Knight shift decreases upon particle-size reduction.$^{52,53}$ In particular, the LDOS appears to be lower at the particle surface, and nanoparticles have a relatively large surface area. However, there is no reason why ball milling would produce a bimodal size distribution, like, in this context, suggested by the two resolved titanium deuteride signals at $-43$ and $-143$ ppm. On the other hand, if the earlier mentioned stepwise loading dependence of the $^2$H NMR shift observed for bulk TiD$_z$ (Ref. 44) also applies for the titanium deuteride phases in Mg$_{0.65}$Ti$_{0.35}$D$_x$, a broad distribution of locally varying deuterium content would effectively produce two $^2$H NMR resonances. In fact, since smaller metal hydride clusters tend to be thermodynamically less stable, and therefore bind deuterium less strongly,$^{16}$ size and deuterium loading are correlated and therefore difficult to disentangle. 2D Exsy yields two-dimensional $^2$H NMR spectra which can be interpreted in terms
of exchange without a prior model. A disadvantage is its generally time consuming character: recording a single 2D spectrum of Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ takes about 16 h.

![Figure 3.7: Mesoscopic picture of for the mixed deuterated phases in (a) Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ with fcc MgD$_2$ and ScD$_2$ nanodomains and (b) Mg$_{0.65}$Ti$_{0.35}$D$_x$ with bct MgD$_2$ nanodomains and fcc layers TiD$_y$, as well as separate domains TiD$_z$. [(c) and (d)] Enlarged crystal structure at the phase boundary in the respective materials emphasizing the possible stabilization by coherent coupling of the crystal lattices. (Lattice constants in Table 3.1.)](image)

We have therefore used 2D Exsy only to confirm our exchange model qualitatively. To study the deuterium exchange quantitatively as a function of, e.g., time and temperature, we have employed the related 1D Exsy technique.$^{48,51}$ Systematic 1D Exsy measurement of the transient response of the deuterium spins in the TiD$_y$ phase at varying mixing times after a selective polarization inversion of the deuterium spins in the MgD$_2$ phase indicates an exchange time scale of 0.9 s at room temperature (Fig. 3.6(c)) with only a weak temperature dependence represented by an effective activation energy of 12 kJ mol$^{-1}$ (Fig. 3.6(d)).

Roughly comparing deuterium hopping across the boundary between MgD$_2$ domains and TiD$_y$ clusters with a chemical reaction, like

\[
\text{MgD}_2 + \text{Ti} \leftrightarrow \text{Mg} + \text{TiD}_2
\]

(3.3.3.1)
we find the low barrier of 12 kJ mol\(^{-1}\) hard to interpret as a true microscopic parameter. The barrier for such reaction should be bigger than the difference between the formation enthalpies of MgH\(_2\) (−38 kJ/mol H) and TiH\(_2\) (−72 kJ/mol H). Instead, the weak temperature dependence of the deuterium exchange between the MgD\(_2\) nanodomains and the TiD\(_y\) clusters could be the signature of a broad range of activation barriers. For a Gaussian distribution \(\exp[-(E_a-\langle E_a \rangle)^2/W^2]\) of microscopic barriers \(E_a\) with average barrier \(\langle E_a \rangle\), distribution width \(2W\) and negligible density at \(E_a=0\) (\(3W < \langle E_a \rangle\)), the behavior in a narrow range around a central temperature \(T_c\) would be\(^{54}\)

\[
\exp\left(\frac{-E_a}{RT}\right) = \exp\left(-\frac{\langle E_a \rangle}{RT} + \frac{W^2}{(2RT)^2}\right) \approx \exp\left(-\frac{E_{\text{eff}}}{RT}\right) \tag{3.3.3.2}
\]

with apparent activation energy \(E_{\text{eff}} = \langle E_a \rangle - \frac{W^2}{4RT_c}\). Here we have used the property \(\langle \exp(X) \rangle = \exp\left[ \langle X \rangle + \frac{1}{2} \left( \langle X^2 \rangle - \langle X \rangle^2 \right) \right]\) of a variable \(X\) with Gaussian statistics. At sufficiently low temperature, \(2RT_c < W\), \(E_{\text{eff}}\) can be significantly smaller than the average value \(\langle E_a \rangle\) of the true microscopic barriers.

### 3.4 Discussion

According to the combined XRD, ND, and NMR results, the studied material with overall composition Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_x\) has at least five main phases, a Mg-rich and a Ti-rich fcc phase without deuterium, as well as a rutile Mg-rich deuteride and two fcc Ti-rich deuteride phases, respectively, with and without direct contacts to the rutile Mg-rich deuteride phase. It is interesting to estimate the relative abundances of these phases and see whether a consistent picture can be obtained. Quantitative estimation is not trivial, because the material may have a more complex structure with composition gradients, rather than clearcut phase boundaries. Moreover, all of the three applied characterization techniques have their own blind spots. Both XRD and ND require crystallinity over sufficient coherence-length scales. Amorphous domains are undetectable with these techniques. Even for the crystalline domains, deuterium atoms were not detected by XRD in the present study and ND showed low sensitivity resulting from the opposed scattering properties of Mg and Ti in the main phase alloy (but not for MgD\(_2\) and TiD\(_y\)). In contrast, deuterium nuclei are directly observed with \(^2\)H NMR and no crystallinity is required.
However, NMR cannot readily detect the phases without deuterium. In principle, NMR visible isotopes $^{25}\text{Mg}$ and $^{47,49}\text{Ti}$ exist, but their properties are far from NMR friendly. Therefore, a quantitative picture of the material as a whole can only be obtained by combining the various techniques. Let us start with a rough estimate of the composition and relative abundances of the Mg-rich and Ti-rich phases in the alloy before hydrogen loading. Deconvolution of the XRD pattern of this material is complicated by the strong overlap between the broad reflections of the Mg- and Ti-rich phases. This tends to yield big correlation errors in the fit parameters. As a kind of regularization we have analyzed the (111) and (200) reflections at \( \sim 35^\circ \) and \( \sim 41^\circ \) in a coupled manner under the restriction that the area ratio between the (111) and (200) peaks in each of the Mg-rich and Ti-rich pattern is equal to the overall peak-area ratio 1.4, which unambiguously follows from integration. This gives a good fit to the observed XRD pattern (Fig. 3.2(b)). From this coupled bicomponent analysis of the (111) and (200) reflections (Fig. 3.2(a)) a peak area ratio \( R=0.6 \) between the Mg-rich and Ti-rich phases can be estimated. To interpret this ratio in terms of the underlying metal-atom fractions in the Mg-rich \((u)\) and Ti-rich phase \((1-u)\) with respective compositions $\text{Mg}_u\text{Ti}_{(1-u)}$ and $\text{Mg}_w\text{Ti}_{(1-w)}$, the different x-ray scattering factors of Mg \((f_{\text{Mg}})\) and Ti \((f_{\text{Ti}})\) need to be taken into account. The respective peak areas of the Mg-rich and Ti-rich fcc phases in the XRD pattern are proportional to the square of their effective scattering factors. If the Mg-rich phase $\text{Mg}_u\text{Ti}_{(1-u)}$ has scattering \( uf_{\text{Mg}} + (1-u)f_{\text{Ti}} \) and the Ti-rich phase $\text{Mg}_w\text{Ti}_{(1-w)}$ has scattering factor \( wf_{\text{Mg}} + (1-w)f_{\text{Ti}} \), the relation between the molar and peak-area ratio is implicitly given by

$$ R = \frac{vu + (1-v)w}{v(1-u) + (1-v)(1-w)} = 0.65 $$

If all phases are indeed XRD visible (a nontrivial requirement for ball-milled alloys and their hydrides), a second condition follows from the overall Mg fraction 0.65 of the alloy

$$ \frac{vu + (1-v)w}{v(1-u) + (1-v)(1-w)} = \frac{0.65}{0.35} $$

With \( R=0.6 \) estimated from the coupled line shape fit, and \( f_{\text{Ti}}/f_{\text{Mg}}=22/12 \) from the number of electrons of Ti and Mg atoms, Eqs. (3) and (4) represent two equations with three unknowns. Fortunately, the alloy has also been studied by energy-dispersive x-ray analysis (EDX), which revealed the presence of pure Ti domains with diameters in the order of 0.5 µm, and smaller domains with a Ti content of at least 80 at. %. On this basis, we estimate that the composition \( w \)}
of the Ti-rich phase in the alloy typically ranges between 0 and 0.2. Substitution of these lower and upper bound values for \(w\) permits solving Eqs. (3) and (4). For \(w=0\), we find \(v=0.66\) and \(u=0.99\), while for \(w=0.2\), \(v=0.60\) and \(u=0.95\). Thus, the Mg-rich fcc phase with lattice constant 4.42 Å is rather pure, as well. This is quite consistent with the outcome of DFT calculations predicting an fcc Mg structure with lattice constant \(a=4.52\) Å, which is only 1.18 kJ mol\(^{-1}\) less stable than the usual hcp Mg structure.\(^{55}\) Let us return with this information to the deuterated system, and try to find the molar fractions of \(v_{\text{Ti}}, v_{\text{Mg}}, v_{\text{MgD}_2}, v_{\text{TiD}_y}, \text{and } v_{\text{TiD}_z}\) of, respectively, the non-deuterated Ti and Mg phases, the MgD\(_2\) phase and the two deuterated Ti phases TiD\(_y\) and TiD\(_z\). Our goal is to determine these fractions and the composition of the TiD\(_y\) and TiD\(_z\) phases as consistently as possible with the quantitative information from XRD, ND, and NMR. The basic restriction for this discrete five-phase model is

\[
v_{\text{Ti}} + v_{\text{Mg}} + v_{\text{MgD}_2} + v_{\text{TiD}_y} + v_{\text{TiD}_z} = 1 \tag{3.4.3}
\]

By assumption, the overall Mg:Ti ratio is conserved during deuterium loading:

\[
\frac{v_{\text{Ti}} + v_{\text{TiD}_y} + v_{\text{TiD}_z}}{v_{\text{Mg}} + v_{\text{MgD}_2}} = \frac{0.35}{0.65} \tag{3.4.4}
\]

Comparing the overall peak area in the \(^2\)H NMR spectrum of Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_x\) with known amounts of D\(_2\)O and CD\(_3\)OD as external reference, we have determined the overall deuterium content \(x=0.65\). This value is consistent with the 3.7% weight loss in the thermogravimetric analysis of the NMR sample,\(^{32}\) but \(~1.6\) times smaller than the deuterium content of the Pd-free sample studied with ND (D/M\(~1.03\)). The higher loading of the ND sample is probably caused by the Pd catalyst. However, it may also be a consequence of the \textit{in situ} character of the concentration measurement. The deuterium content of the NMR sample was determined \textit{ex situ} by quantitative \(^2\)H NMR, and the material may have already lost a particularly unstably bound deuterium fraction before the D/M ratio was determined. The overall deuterium content \(x=0.65\) yields the boundary condition:

\[
2v_{\text{MgD}_2} + yv_{\text{TiD}_y} + zv_{\text{TiD}_z} = 0.65 \tag{3.4.5}
\]

Deconvolution of the MAS \(^2\)H NMR spectrum indicates that roughly half of the deuterium atoms are located in the MgD\(_2\) phase resonating at 3 ppm, and the remaining deuterium atoms are
Nanostructures of Mg_{0.65}Ti_{0.35}D_x studied with….

approximately equally divided over the TiD_y clusters at −43 ppm and in the isolated TiD_z phase at −143 ppm. This yields two additional equations

\[ 2v_{MgD_2} = yv_{TiD_y} + zv_{TiD_z} \]  
\[ yv_{TiD_y} = zv_{TiD_z} \]  

Finally, from coupled-decoupled deconvolution of the XRD pattern with the same overall restriction \( A_{111}:A_{200} = 1.4 \) (similarly to in the analysis of the pattern of the alloy before deuterium loading), we obtain a peak-area ratio equal to 0.97. Assuming that the left set of reflections consists of the overlapping signals from the isolated TiD_y and the residual Mg phase, and taking the different x-ray scattering factors \( f_{Ti} \) and \( f_{Mg} \) of Ti and Mg into account, this yields the condition

\[ \frac{f^2_{Mg} v_{Mg} + f^2_{Ti} v_{TiD_y}}{f^2_{Ti} v_{Ti}} = 0.97 \]  

Here we have assumed that the XRD scattering of the TiD_2 phase is purely controlled by the Ti atoms. Equations (3.4.3)–(3.4.8) represent six equations for seven unknowns. An upper bound value for the deuterium concentration in the TiD_y clusters \( y \) is given by the Knight shift, −43 ppm, which indicates a concentration \( y \leq 1.5 \). Entering \( y = 1.5 \) we obtain the solution

\[ v_{Ti} = 0.16 \]  
\[ v_{Mg} = 0.49 \]  
\[ v_{MgD_2} = 0.16 \]  
\[ v_{TiD_y} = 0.08 \]  
\[ v_{TiD_z} = 0.11 \]  
\[ z = 2 \]

Substitution of lower \( y \) values yields nonrealistic solutions with D concentrations in the TiD_z phase above 2. The combined quantitative analysis thus suggests a picture of this complex material, in which a quarter of the Mg atoms in the original alloy Mg_{0.65}Ti_{0.35} have been converted into rutile MgH_2 nanodomains, and half of the Ti atoms into either segregated TiD_2, or TiD_{1.5} nanoclusters dispersed between the MgH_2 domains. The formation enthalpy of bulk TiD_2, 144 kJ mol\(^{-1}\), is higher than that of bulk MgH_2, 76 kJ mol\(^{-1}\). The coexistence of MgD_2 and TiD_{1.5} therefore suggests that the latter somehow deviates from the bulk state, perhaps as a result of the
small cluster size, or local crystal lattice distortions induced by the surrounding MgD₂. Scandium and titanium are neighboring elements in the transition-metal series, differing by one 3d electron only. From a “chemical” point of view, it is thus remarkable that scandium stabilizes the fluorite structure of magnesium-scandium hydrides, whereas titanium has no such stabilizing effect on hydrides of magnesium-titanium alloys. The different effect is even more amazing, if one considers the fact that before hydrogen loading the Mg₀.₆₅Sc₀.₃₅ alloy has a bcc structure, and Mg₀.₆₅Ti₀.₃₅ a (nano) phase separated fcc Mg-rich and fcc Ti-rich structures. With the metal atoms already at the proper fcc positions, one would expect the Mg-rich phase in the Mg₀.₆₅Ti₀.₃₅ alloy to readily transform into the fluorite structure. Instead, however, it is the bcc Mg₁₋ₓScₓ alloy, which transforms into the fluorite structure, whereas the fcc Mg-rich phase in Mg₀.₆₅Ti₀.₃₅ transforms into the rutile structure. A possible explanation for this apparent inconsistency may be an expitaxial rather than chemical mechanism. Comparison of the cell parameters of fcc ScH₂ and fcc TiH₂ with those of rutile and fcc MgH₂ indicates that the cell constants of fcc MgH₂ and ScH₂ match almost perfectly, whereas the cell constant of fcc TiH₂ matches the lattice constant a of rutile MgH₂. By analogy to the coherent coupling in Mg-Ti hydride films,²³ we propose a model for the mixed MgD₂ and TiDₓ phases with coupling between the rutile MgD₂ nano-domains and thin layers of fcc TiDₓ (Fig.3.7).

### 3.5 Conclusions

After our previous investigation of magnesium-scandium hydride,²⁷ which has good hydrogen-storage capacity and improved sorption kinetics compared to pure MgH₂, magnesium-titanium deuteride has now been investigated by use of XRD, ND, and MAS ²H NMR. The material was prepared by exposing ball-milled alloys with overall composition Mg₀.₆₅Ti₀.₃₅ and Mg₀.₆₅Ti₀.₃₅Pd₀.₀₂ to deuterium gas at elevated temperature. Before deuterium loading, the alloy consists of a separate fcc Mg and Ti phases with cell parameters 4.42 and 4.28 Å. Even after prolonged deuterium loading at 175 °C the material is only partly deuterated. Deuterium loading induces the formation of a separate fluorite TiD₂ phase, as well as a composite of rutile MgD₂ nano-domains and small clusters or thin layers of TiD₁.₅. Comparison of the cell parameters of fluorite TiD₂ and rutile MgD₂ suggests that the interactions between the rutile MgD₂ and, presumably, fcc TiD₄ nano-domains could well be controlled by coherent coupling of the crystal structures. We propose that the different stabilization effect of Sc and Ti on the crystal structure
of the corresponding magnesium transition-metal hydrides is directly related to the different lattice constants of the respective fluorite structures of ScH₂ and TiH₂.

3.6 References

Chapter 3


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Chapter 4

Siting and mobility of deuterium absorbed in co-sputtered Mg\(_{0.65}\)Ti\(_{0.35}\). A MAS \(^2\)H NMR study*

Abstract

Nano-structured magnesium titanium alloys are interesting light-weight materials for chemical hydrogen storage. We have therefore investigated the siting and dynamics of deuterium absorbed in a Mg\(_{0.65}\)Ti\(_{0.35}\) alloy generated by magnetron co-sputtering, and made a comparison to the corresponding features in bulk samples of deuterium-loaded Mg\(_{0.65}\)Ti\(_{0.35}\) and Mg\(_{0.65}\)Sc\(_{0.35}\) prepared by ball-milling and melt-casting, respectively. Magic-angle spinning \(^2\)H NMR of co-sputtered Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_{1.1}\) shows partly resolved signals of deuterium located in non-conductive domains at tetrahedral Mg\(_4\) and mixed Mg\(_n\)Ti\(_{4-n}\) sites (4 ppm), and deuterium at Ti\(_4\) sites in conducting TiD\(_2\) nano-domains (-29 and -68 ppm). No bulk-TiD\(_2\) signal at -150 ppm is observed, in contrast to what we find in ball-milled Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_{0.65}\), which is largely phase separated. The deuterium species with shift values of 4 and -29 ppm undergo complete exchange at a sub-second timescale in one- and two-dimensional exchange NMR, and must therefore be close together in the lattice. In contrast, deuterium resonating at -68 ppm does not show deuterium exchange, and thus appears to be located at more stable sites. The observed deuterium exchange and the reduced Knight shift compared to bulk TiD\(_2\) are explained using a model with TiD\(_2\) nanoslabs.

4.1 Introduction

Hydrogen is an important candidate for replacing fossil fuels as energy carrier. A major challenge is its storage in compact and safe ways suited for specific applications, such as in cars and portable devices. Physical storage is possible as high-pressure (< 70 MPa) compressed gas,\(^1\) cryogenic liquid (20 K),\(^2\) or at milder pressures and temperatures in cryogenic pressure tanks\(^3\) or in porous solids.\(^4,5\) Hydrogen can also be chemically stored at high gravimetric and volumetric density in metal, organic or other hydrides.\(^6,7\) Several of such hydrides can be operated as hydrogen-storage materials under conditions much closer to ambient than the physical types of storage. A key issue for many of these hydrides is to develop optimal combinations of storage capacity and uptake and release rates.

Magnesium-based hydrides are important hydrogen-storage materials. The light-weight magnesium metal itself has a high storage capacity in the form of MgH\(_2\) (7.6 wt %), but suffers from slow absorption and desorption kinetics. Hydrogen uptake and release can be accelerated by confining nano-MgH\(_2\) in nanoporous carbon.\(^8\) Another way to enhance the hydrogen mobility is to partly substitute Mg by a transition metal, like scandium, which causes the rutile structure of MgH\(_2\) to transform into a fluorite structure.\(^9,10,11,12,13\) For the ternary compound, Mg\(_{0.65}\)Sc\(_{0.35}\)D\(_{2.2}\), the deuterium atoms were found to be located at the tetrahedral interstitial sites between the metal positions in a coherent fcc lattice with no evidence for any Mg or Sc clustering from X-ray, nor Neutron-Diffraction.\(^12\) However, \(^2\)H-{\(^{45}\)Sc} NMR, which is sensitive to the local chemical structure around the deuterium atoms, revealed that roughly half of the deuterium atoms have fourfold Mg coordination, which is more than expected for a random Mg\(_{0.65}\)Sc\(_{0.35}\) lattice.\(^14\)

Since scandium is a rare and expensive element, its neighbor titanium in the transition-metal series is often investigated as a component in Mg-based alloys for hydrogen storage. Mg and Ti are thermodynamically immiscible. Ball-milled Mg\(_{y}\)Ti\(_{1-y}\) alloys tend to separate into MgD\(_2\) and TiD\(_2\) upon deuterium gas absorption at elevated temperature.\(^15\) The material, however, is not totally segregated. In addition to the separate rutile MgD\(_2\) and fluorite TiD\(_2\) phases, there are also XRD-invisible TiD\(_x\) nano-domains in close contact to the MgD\(_2\) phase.\(^15\) Starting from the hydrides MgH\(_2\) and TiH\(_2\) rather than the metals Mg and Ti it is possible to make the ternary compound Mg\(_7\)TiH\(_x\) at high pressure (8 GPa) and temperature (873 K). Its crystal structure is...
Siting and mobility of deuterium absorbed in co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$. A MAS NMR study

Conserved upon partial hydrogen release and absorption, but it does decompose into Mg and TiH$_{1.9}$ upon full hydrogen release.\textsuperscript{16} It basically has an fcc structure with Ga$_7$Ge superorder, in which Ti occupies specific positions. As a result, deuterium at the tetrahedral interstitial sites in this material has two possible types of metal coordination, Mg$_4$ and Mg$_3$Ti, at a ratio 1:1. This is remarkably consistent with the 50\% fraction Mg coordinated deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$. For the latter material, however no indications for such a superstructure have been found so far.

Instead of bulk alloys in the form of powders, Mg$_x$Ti$_{1-x}$ alloy films can be prepared by means of electron beam deposition,\textsuperscript{17} physical vapor deposition,\textsuperscript{18} and magnetron co-sputtering.\textsuperscript{19} Unlike the bulk alloys, these films are stable upon several cycles of gas phase (un)loading and electrochemical (dis)charging\textsuperscript{20} of hydrogen which makes them promising materials for hydrogen storage. They are also studied for technological applications such as hydrogen sensors,\textsuperscript{21} switchable solar collectors.\textsuperscript{22} According to X-ray diffraction (XRD) the as-deposited film has a hexagonal close-packed (hcp) structure and upon hydrogenation, it changes into a face centered cubic (fcc) structure.\textsuperscript{23} Analyses of Optical transmission,\textsuperscript{23} EXAFS\textsuperscript{24} and positron Doppler-broadening\textsuperscript{25} suggest that Mg and Ti are not randomly distributed within the lattice. Instead, they are partially segregated into Mg-rich and Ti-rich domains without affecting the long-range order determined by XRD. The coherence of this structure is also evident from electron microscopy, which reveals a single hcp and fcc lattice in the metallic and the hydrogenated state, respectively.\textsuperscript{23} The persistence of the structure coherence on hydrogenation cycling is attributed to the fact that the lattice volume of TiH$_2$ matches that of Mg. Indeed, in Mg-V thin films this coherence is lost after several hydrogenation cycles.\textsuperscript{26} Note, that this class of Mg-based hydrides is to be distinguished from the complex metal hydrides which are formed with the more heavy transition metals, such as Fe, Co and Ni.\textsuperscript{27}

Solid-state NMR spectroscopy is increasingly employed to investigate solid hydrides, like borohydrides,\textsuperscript{28} alanates\textsuperscript{29} and metal hydrides and deuterides.\textsuperscript{13} Using $^1$H or $^2$H NMR one can directly detect hydrogen or deuterium in metal hydrides or deuterides. The technique yields information about the local chemical and electronic structure at the hydrogen sites, as well as hydrogen mobility, which is particularly interesting for the potential application of metal hydrides as hydrogen-storage materials. Since crystallinity is not required for NMR, the technique can also “see” hydrogen inside XRD-amorphous parts of metal hydrides. Although the
isotope $^1$H has higher NMR frequency and sensitivity, $^2$H nuclei tend to have relatively narrower resonances in MAS NMR spectra of metal deuterides compared to the corresponding metal hydrides. This results from the weaker dipole coupling between $^2$H than between $^1$H nuclei. Using the high chemical resolution of magic-angle spinning (MAS) $^2$H NMR, we have investigated deuterium absorbed in a co-sputtered Mg$_{0.65}$Ti$_{0.35}$ film of the same type investigated by Dam et al.$^{19,22,23,24}$ In particular, we aim at resolving the $^2$H NMR signals from deuterium atoms at Mg-rich and Ti-rich interstitial sites. In addition, we want to study the timescale and completeness of deuterium exchange between these NMR distinct sites to determine the binding stability and segregation length scale.

4.2 Experimental

4.2.1 Material preparation

A 1-µm thick Mg$_{0.65}$Ti$_{0.35}$ film was prepared by magnetron co-sputtering on a quartz substrate as described previously.$^{30}$ The top and bottom of the film were covered with 30-nm thick Pd layers to promote H$_2$ dissociation, and prevent oxidation of the underlying film. As a result of the Pd layer between the film and the support, the film came readily off the support upon hydrogenation. Deuterium was loaded at 25 ºC by gradually increasing the D$_2$ gas pressure up to 10$^5$ Pa.

4.2.2 NMR characterization

NMR experiments were performed on a Bruker DMX500 spectrometer, operating at 76.77 MHz for deuterium. Ca. 3 mg of Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$, prepared as described above, was packed in the glove box under argon into a 2.5-mm NMR sample holder, which was closed with a tight cap and rotated in a flow of dry nitrogen inside the NMR probe head. The sample spinning rates were 8 kHz and 12 kHz and typical number of scans 1024. The deuterium : metal (D/M) atom ratio in ballmilled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ and co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ was estimated by comparison with peak areas in $^2$H NMR spectra of known amounts of D$_2$O and CD$_3$OD. The deuterium content of MgD$_2$ and TiD$_2$ was assumed to be stoichiometric. If the overall deuterium content would be D/M < 2, MgD$_2$ splits into MgD$_{x<0.001}$ and MgD$_2$. The $^2$H NMR spectrum thus (predominantly) reflects deuterium in MgD$_2$ anyway. It is well known that the -150 ppm $^2$H NMR shift observed for TiD$_2$ corresponds to at least D/M > 1.7.$^{32}$ Two-dimensional exchange spectroscopy (2D
Siting and mobility of deuterium absorbed in co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$. A MAS NMR study

1D Exsy) was carried out by use of a pulse sequence with three 90° pulses of 5 µs each. The time interval between the first two pulses (evolution time $t_1$) was systematically incremented in the course of the experiment, while the time interval between the second and third pulse (mixing time $t_{\text{mix}}$) was fixed to 0.01, 0.1, or 1 s. One-dimensional exchange spectroscopy (1D Exsy) was measured by selectively perturbing the polarization of the deuterium nuclei at the Mg-rich sites resonating at 4 ppm using a rotor-synchronized DANTE pulse train of six soft pulses of 1 µs at a reduced rf-power level corresponding to a $^2$H nutation frequency of 12.5 kHz, and monitoring the polarization after a variable time interval $t_{\text{mix}}$ by means of a nonselective 90° pulse of 5 µs. The 1D exchange spectra (64 scans) were recorded for 21 $t_{\text{mix}}$ values between 0.01 and 12 s and four temperatures 230, 247, 265 and 283 K (temperature calibrated from the peak separation in the $^1$H NMR spectrum of methanol.

4.2.3 Data analysis

All 1D exchange spectra were analyzed by use of the program DM2008 in terms of four Gaussian-Lorentzian lineshape components with fixed positions 14, 4, –29 and –68 ppm, fixed linewidths and fixed quadrupolar lineshape parameters as given in Table 4.1. The height of the –68 ppm component, tentatively assigned to a irreversibly bound deuterium fraction, was estimated from the longest mixing time, $t_{\text{mix}} = 12$ s, and kept constant as a function of $t_{\text{mix}}$. This only leaves the heights of the other three signal components as free fit parameters. These fit restrictions were necessary to reduce correlation errors resulting from the peak overlap. The thus obtained peak area $I_A(t_{\text{mix}})$ of the –29 component components as a function of mixing time $t_{\text{mix}}$, as well as the combined peak area $I_B(t_{\text{mix}})$ of the 14 and 4-ppm components, were further analyzed using the coupled bi-exponential fit model:

\[
I_A(t_{\text{mix}}) = I_A^\infty + C_A \exp\left(-t_{\text{mix}} / T_1\right) + D_{AB} \exp\left(-t_{\text{mix}} / \tau_{\text{ex}} - t_{\text{mix}} / T_1\right) \quad 4.2.3.1
\]

\[
I_B(t_{\text{mix}}) = I_B^\infty + C_B \exp\left(-t_{\text{mix}} / T_1\right) - D_{AB} \exp\left(-t_{\text{mix}} / \tau_{\text{ex}} - t_{\text{mix}} / T_1\right) \quad 4.2.3.2
\]

where $I_A^\infty$ and $I_B^\infty$ denote the final peak areas, $D_{AB}$ and $\tau_{\text{ex}}$ the extent and the characteristic time of the exchange, and $C_A$ and $C_B$ ensure the initial peak areas $I_A(0) = I_A^\infty + C_A + D_{AB}$ and $I_B(0) = I_B^\infty + C_B - D_{AB}$. The spin-lattice relaxation time $T_1$ was separately determined from a mono-exponential fit to the sum intensity $I_A(t_{\text{mix}}) + I_B(t_{\text{mix}})$, and then used as a fixed parameter in above mentioned bi-exponential analysis of the separate curves $I_A(t_{\text{mix}})$ and $I_B(t_{\text{mix}})$. The combined sum
of square deviations was then minimized by varying the fit parameters $I_A^\infty$, $I_B^\infty$, $C_A$, $C_B$, $D_{AB}$ and $\tau_{ex}$. Once such optimal set of fit-parameter values was obtained, the accuracy of $\tau_{ex}$ was estimated by repeating the least-square fit procedure with $\tau_{ex}$ fixed to different values, followed by re-adjustment of the other parameters using the Solver routine in the Microsoft program Excel. As an arbitrary criterion for acceptable $\tau_{ex}$ values we took that the sum of squares (after optimizing the other parameters) should not be larger than 1.5 times the minimum value.

**Table 4.1** fixed parameters of the five lineshape components

<table>
<thead>
<tr>
<th>lineshape component</th>
<th>position $\delta$ (ppm)</th>
<th>width $\Delta\delta$ (ppm)</th>
<th>shape (G / L)*</th>
<th>QCC $\nu_Q$ (kHz)</th>
<th>asymmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>15</td>
<td>G</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>8</td>
<td>L</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>-29</td>
<td>83</td>
<td>G</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
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<td>31</td>
<td>L</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>5 †</td>
<td>-10</td>
<td>29</td>
<td>G</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

*: G: Gaussian; L: Lorentzian

†: this component only $\geq 296$ K

### 4.3 Results and Discussion

This section is divided into three parts. The first part describes a comparison of the MAS $^2$H NMR spectrum of deuterium-loaded co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}$ with those of related metal hydrides to interpret the spectra and assign the observed signals. In the second part we focus on the mobility of deuterium in co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1}$ by analyzing $^2$H NMR exchange spectra recorded at varied timescales and temperatures. This does not only give insight into deuterium mobility and apparent activation energies, but also into the spatial separation of NMR-distinct deuterium sites. Finally, in the third part we propose a possible nano-structure model that is consistent with both the current $^2$H NMR results and previous studies of co-sputtered $\text{Mg}_y\text{Ti}_1-y\text{D}_x$ films based on other characterization techniques.
4.3.1 MAS $^2\text{H}$ NMR comparison of different metal deuterides

Fig. 4.1 shows $^2\text{H}$ NMR spectra of (a) TiD$_2$, (b) ball-milled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$, (c, black curve) co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$, and, for comparison, (c, grey curve) melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$, and (d) MgD$_2$. With “ball-milled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$” we mean the ball-milled alloy with overall composition Mg$_{0.65}$Ti$_{0.35}$ which after deuterium loading contains 0.65 deuterium atoms per metal atoms (D/M). Likewise, “co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$” and “melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$” refer to the deuterated materials prepared from the corresponding co-sputtered and melt-cast alloys. Deuterium nuclei have spin 1 and interact with the local Electric Field Gradient (EFG) caused by asymmetric charge distribution over the surrounding metal atoms. The EFG together with deuterium mobility determines the static $^2\text{H}$ NMR lineshape. Broad lines are caused by a strong EFG, whereas mobility tends to narrow the line. Magic-angle-spinning (MAS), i.e. sample rotation under the angle arccos(1/$\sqrt{3}$) ~ 54° with respect to the magnetic field, is used to remove the first-order quadrupolar linebroadening and increase the chemical resolution in solid-state NMR spectra. At low sample-rotation rates compared to the static linewidth the MAS NMR spectrum consists of a centerband and manifold of spinning sidebands, which extend over a frequency range similar to the static lineshape, and thus reflect the underlying EFG. Therefore, the sideband patterns observed for the various compounds (Fig. 4.1) are indicative of the coordination state of deuterium atoms in the respective crystal lattices.
Figure 4.1 MAS $^2$H NMR spectra of (a) bulk TiD$_2$ (b) ball-milled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ (c) melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ (grey) and co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ (black) and (d) bulk MgD$_2$. Spinning sidebands are marked with stars, *. The spectra of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ and Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ film are overlaid to show the sideband pattern similarity reflecting a similar underlying distribution of electric-field gradients at the tetrahedral sites in these ternary compounds with XRD homogeneous fcc structure. All spectra were recorded at a sample rotation rate of 8 kHz, except TiD$_2$ (10 kHz) at room temperature.
This is illustrated by the $^2$H NMR sideband pattern observed for MgD$_2$ (Fig. 4.1d). The broad sideband envelope reflects the strong EFG at the positions of the deuterium atoms in the rutile crystal structure. The static NMR lineshape and the 8-kHz MAS sideband pattern are consistently described by quadrupolar linewidth $\nu_Q = 28$ kHz and asymmetry $\eta = 0.65$ (Fig. S1, Appendix II). Deuterium atoms in MgD$_2$ have a planar threefold Mg coordination ($d_{\text{Mg-D}} = 1.95$ Å) with Mg at the corners of a triangle with one side of 3.01 Å and two sides of 3.52 Å. Theoretically, such coordination should result in an asymmetry parameter $\eta = 0.61$ (Appendix II) which is indeed close to the experimentally found value. Deuterium atoms in TiD$_2$ are tetrahedrally coordinated by Ti atoms and as a result of the coordination symmetry, the EFG vanishes. This is consistent with the relatively weak $^2$H NMR sidebands surrounding the centerband at $-150$ ppm observed for TiD$_2$ (Fig. 4.1a). The spectrum of ball-milled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ approximately looks like the superposition of the extensive sideband pattern of MgD$_2$ centered at 4 ppm and the almost sideband-free signal at $-150$ ppm, the typical Knight shift for bulk TiD$_2$ (Fig. 4.1b). This is consistent with the phase separation into MgD$_2$ and TiD$_2$ also observed with XRD and ND. The $^2$H NMR spectrum of the ballmilled material also contains a signal at $-43$ ppm, which we have previously assigned to small TiD$_2$ nanodomains in close contact to the MgD$_2$ phase. For co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ the $^2$H NMR sideband envelope (Fig. 4.1c) is significantly narrower than that of bulk MgD$_2$ (Fig. 4.1d) or the corresponding phase in the ball-milled material (Fig. 4.1b). In fact, the sideband envelope is practically the same as that of melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ (Fig. 4.1c, grey curve), which has a single-phase fluorite structure with deuterium atoms at the tetrahedral sites, like in TiD$_2$ and Mg-Ti-H thin films. Indeed, the sideband pattern is less extensive than that of MgD$_2$ (Fig 4.1d), but the average EFG does not vanish like for TiD$_2$. This is caused by the asymmetric partial-charge distribution in the lattice consisting of Mg and transition-metal atoms and the resulting lattice distortions. The sideband pattern centered at 4 ppm observed for Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ and co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ is reasonably reproduced by different combinations of quadrupolar lineshape parameters ($\nu_Q$, $\eta$), such as (15 kHz, 1) and (17 kHz, 0). However, no single parameter combination, and thus no single EFG tensor, properly explains the static $^2$H NMR lineshape of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ (Appendix II). This is indicative of EFG heterogeneity consistent with the varying Mg$_6$Sc$_{4-n}$ coordination of deuterium in this material. Due to partial charge differences
between Mg and Sc atoms in the fcc lattice deuterium atoms at tetrahedral sites with different \( \text{Mg}_n\text{Sc}_{4-n} \) coordination experience a different EFG.

![Figure 4.2](image)

**Figure 4.2** (a) \(^2\text{H} \) NMR spectrum of co-sputtered \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1} \) at 230 K decomposed into four lineshape components at 14, 4, -29 and -68 ppm (Table 4.1). The lineshape of the 4 ppm component in the spectral simulation is also defined by the observed spinning sidebands. The other lineshape components have no sidebands. (b) Difference spectrum (2× magnified) after subtraction of the combined 14 and 4 ppm components. This difference spectrum reflects the Knight-shifted signals of deuterium in conducting regions, and is decomposed into two components at -29 and -68 ppm. (c) \(^2\text{H} \) NMR spectrum of the sample after deuterium release during 1 hour at 100 °C. The \(^2\text{H} \) NMR lineshape of the remaining, strongly bound deuterium defines the -68 ppm component in the spectral simulation. The sample rotation rate was 12 kHz.

The MAS \(^2\text{H} \) NMR spectrum of co-sputtered \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1} \) at 8 kHz (296 K; Fig. 4.1b) and 12 kHz (230 K; Fig. 4.2a) shows overlapping centerband signals between 20 and -120 ppm. The centerband region at 230 K can be decomposed into four lineshape components at 14, 4, -29 and -68 ppm (Fig.4.2; Table 4.1). Only the 4-ppm component has spinning sidebands, which actually help to define its linewidth in the spectrum simulation. The lineshape of the component at -68
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A 67 ppm is taken from the spectrum of the co-sputtered material after deuterium release during 1 h at 100 °C (Fig. 4.2c). This component is tentatively assigned to a (collection of) resonance(s) of relatively stable bound deuterium. The lineshape components at 14 and -29 ppm components, respectively, represent the downfield foot of the centerband and the intermediate signal intensity between 4 and -68 ppm. The 4-ppm component has a chemical shift close to that of MgD$_2$ and melt-cast $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$. Our previous $^2\text{H}-\{^{45}\text{Sc}\}$ NMR study of $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$ revealed that its centerband contains overlapping signals from two types of deuterium, respectively, with and without Sc in the first coordination sphere. By analogy, the combined 4 and 14-ppm components of co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1}$ probably comprise signals from deuterium at tetrahedral sites with pure Mg, and mixed Mg$_{4-n}$Ti$_{n}$ coordination, as well.

The NMR shifts of the centerband signals at -29 and -68 ppm may be compared to the more negative Knight shift, -150 ppm, of bulk TiD$_2$ (Fig. 4.1a) and the comparable shift, -43 ppm, of TiD$_x$ nanodomains in ballmilled $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.6}$ (Fig. 4.1b). Obviously, there is no separate TiD$_2$ macrophase in co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1}$, in contrast to the ball-milled material (Fig 4.1b), but a significant deuterium fraction (ca. 45%, as estimated from the relative peak area) may be located in TiD$_x$ nanodomains. Given their shift values between that of MgD$_2$ (4 ppm; Fig. 4.1d) and TiD$_2$ (-150 ppm; Fig. 4.1a), we have also considered an alternative assignment of the -29 and -68 ppm components to deuterium at mixed Mg$_2$Ti$_2$ and MgTi$_3$ sites. According to DFT the local density of states in a fcc Mg$_5$Ti$_{1-x}$ hydride with random Mg/Ti substitution is higher at hydrogen sites close to Ti than Mg atoms. In principle, this could explain a varying Knight shift depending on the number of closest Ti atoms at the interstitial sites. However, the absence of strong spinning sidebands associated with these lineshape components indicates against such interpretation, because deuterium nuclei should experience strong quadrupolar coupling to the local electric field gradient at mixed coordination states Mg$_{4-n}$Ti$_n$. Instead, the sideband-free components at -29 and -68 ppm are more typical of deuterium at undistorted tetrahedral Ti$_4$ sites in TiD$_x$ nano-domains without Mg, as we have also proposed for the ballmilled compound. The Knight shift $\delta$ of conducting nano-particles is known to decrease at decreasing size as a result of surface effects. We will come back to this, when proposing a possible Mg-Ti segregation model in the third part of the Results and Discussion section.
4.3.2 Deuterium dynamics at different timescales and varied temperatures

To investigate deuterium exchange between the NMR-distinct Mg-rich and Ti rich sites in co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ we have employed two-dimensional exchange spectroscopy (2D Exsy). This NMR technique is a powerful tool to study complex slow-exchange processes in a model-free manner. In short, the technique correlates the chemical shift before and after a selectable time window, the so-called mixing time $t_{\text{mix}}$, during which the deuterium atoms have the opportunity to move to another environment. The exchange is reflected by off-diagonal crosspeaks between the signals of the exchanging sites. Deuterium that does not participate in the exchange process (either because it is stably bound, or separated from the other sites) shows only autocorrelation peaks on the diagonal of the 2D spectrum.

Fig. 4.3 illustrates room-temperature 2D exchange spectra of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ recorded at mixing times $t_{\text{mix}}$ of 0.01, 0.1 and 1 s. For $t_{\text{mix}} = 0.01$ s there is mainly peak intensity along the spectrum diagonal indicating that there is practically no deuterium exchange between sites with different chemical shifts at this timescale. The slight broadening perpendicular to the diagonal between −20 and −120 ppm is probably due to homogeneous linebroadening. However, the horizontal (and vertical) cross-section at 4 ppm shows a asymmetric lineshape with an elevated upfield foot. This is atypical for homogeneous linebroadening, but indicative of some deuterium exchange already taking place at this timescale between sites resonating at 4 and −10 ppm, respectively. At $t_{\text{mix}} = 0.1$ s, the upfield foot in the cross-section becomes higher and extends to lower NMR shifts, indicating that at this longer timescale deuterium initially resonating at 4 ppm probes more and more sites with different NMR shifts. Finally, at $t_{\text{mix}} = 1$ s the spectrum contains clear crosspeaks reflecting extensive deuterium exchange between Mg-rich and Ti-rich sites. Still, the deuterium exchange is not “complete” in the sense that deuterium becomes randomly redistributed over all sites, irrespective of its initial site. Complete exchange would be recognized in 2D Exsy from the similarity between traces in the 2D spectrum and projections onto the frequency axes. If the traces and projections are similar, deuterium is homogeneously redistributed at the timescale probed, irrespectively of the initial site at the start of the mixing time. Comparison of the horizontal trace through the 4 ppm position and the horizontal projection of the 2D Exsy spectrum of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ at a mixing time...
of 1 s (Fig. 4.3), shows that there is complete exchange among deuterium sites with chemical shifts between 20 and ~ -60 ppm, but not between these sites and sites with shifts < -60 ppm. Recording 2D Exsy spectra at $t_{\text{mix}} > 1$ s to see whether the latter sites are accessible at a longer timescale is impractical because of the signal loss resulting from spin-lattice relaxation ($T_1 = 4$ s).

**Figure 4.3** 2D exchange spectra at 296 K with a mixing time of 0.01, 0.1 and 1 s. The off-diagonal intensity in the latter spectrum indicates deuterium exchange at the timescale of a second between Mg-rich and part of the Ti-rich sites. The horizontal traces at 4 ppm (lower traces above the 2D spectra) indicates how deuterium at Mg-rich sites (and thus initial NMR shift 4 ppm) has moved to Ti-rich sites during the mixing time. Comparison between these traces and the corresponding horizontal projections (upper traces above the 2D spectra) confirms that there is no complete exchange within 1 s. In particular, sites with deuterium resonating below -80 ppm are not accessed at the probed timescale.

2D Exsy thus confirms the above assignment of the –68 ppm component in the 1D spectrum (Fig. 4.2) to deuterium at some type of stable binding sites, and suggests that deuterium freely exchanges between the other types of sites. To study this deuterium exchange systematically as a function of mixing time, one-dimensional (1D) Exsy was performed in combination with lineshape deconvolution. Our 1D Exsy experiments start with selective perturbation of the deuterium spins resonating in a narrow range around 4 ppm. As a result of deuterium exchange during the following mixing time, deuterium atoms with perturbed polarization will replace deuterium atoms at the “unperturbed” sites and *vice versa*. As a
consequence, the signal intensity of the originally non-perturbed sites will decrease, and that of
the initially perturbed sites will increase as function of the mixing time. The longest exchange
timescales that can be probed in this way is determined by spin-lattice relaxation, because even
without deuterium exchange, any perturbed spin polarization of the deuterium nuclei will relax to
the thermal equilibrium value.

The left side in Fig. 4.4 illustrates typical 1D exchange spectra with mixing times of 0.01,
0.1, 1, and 12 s, which are part of a series of 21 exchange spectra recorded at 283 K. The
exchange spectrum with $t_{\text{mix}} = 0.01$ s shows the effect of the initial selective perturbation of the
polarization of the deuterium nuclei resonating around 4 ppm. As can be been seen by comparing
the perturbed lineshape with the fully restored lineshape at $t_{\text{mix}} = 12$ s, the pulse train mainly
affects the signal in a narrow range around 4 ppm. In the spectrum recorded with 0.1 s the
initially inverted signals around 4 ppm have already partly recovered as a result of deuterium
exchange with sites represented by the initially less perturbed parts of the centerband. Likewise,
the flux of deuterium with perturbed polarization to sites with originally unperturbed deuterium
polarization causes a transient decrease of the polarization at the latter sites. The final restoratio
of the spin polarization to thermal equilibrium occurs under the influence of spin-lattice
relaxation. Like in 2D Exsy, the upfield lineshape components $<-60$ ppm appear less active in
the exchange.

To quantify deuterium exchange as a function of mixing time, all 1D exchange spectra
were decomposed into the same four Gaussian-Lorentzian lineshape components with fixed
positions 14, 4, –29 and –68 ppm and fixed linewidths, as mentioned above (Table 4.1). The –68
ppm component, which is directly derived from the spectrum of the deuterium-released material
(Fig. 4.2 c), was kept constant in the series because of its assignment to a strongly bound
deuterium fraction not taking part in deuterium exchange (Fig. 4.3). This leaves only the three
amplitudes of the components at 14, 4 and –29 ppm as free fit parameters. We chose such
restricted lineshape fitting to suppress fluctuations in the fit parameter values resulting from
covariance effects between the overlapping signals. Moreover, the 14 and 4 ppm components are
combined in the analysis because of their overlap and close covariance. Fig. 4.4 c shows how the
peak heights of the –29 ppm component, the combined 14 / 4 ppm components and the overall
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Intensity vary with mixing time at 283 K. After selective perturbation of the 14 and 4 ppm components, their combined peak area builds up, while the -29 ppm component initially decays as a function of mixing time. Beyond 1 s all components increase at the same rate as the overall peak area reflecting spin-lattice relaxation. Coupled bi-exponential analysis of these two curves yields an effective deuterium-exchange time $\tau_{ex} = 0.13$ s (Fig. 4.4 c). Thus, at 283 K this is the effective timescale at which deuterium atoms are moving reversibly between Mg$_n$Ti$_{4-n}$ sites in non-conducting domains and Ti$_4$ sites in conducting nandomains. Note, that 1D and 2D Exsy cannot detect intra-domain deuterium mobility between sites with identical chemical shifts. The exchange probed thus reflects the overall result of multi-step and multi-trajectory deuterium self-diffusion across the boundaries between conducting and non-conducting nandomains. To estimate the effective energy barrier for deuterium motion in co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ 1D Exsy was carried out at varied temperature. At $T \leq 283$ K the deuterium exchange depends only weakly on the temperature. 1D exchange spectra recorded at the same mixing time at 283 K and 230 K are closely comparable (Figs. 4.4 a and 4.4 b). There is a slightly faster recovery of the combined 14 and 4 ppm peak area especially visible in the 0.1 s spectrum at 283 K than at 230 K. Coupled bi-exponential analysis of the peak area curves extracted from the 1D Exsy series at 230, 247, 265 and 283 K yields and effective deuterium-exchange time $\tau_{ex}$ with weak temperature behavior from $\tau_{ex} = 0.55$s at 230 K to $\tau_{ex} = 0.13$ s at 283 K (Fig. 4.5). This corresponds to an apparent activation energy $E_A = 13$ kJ mol$^{-1}$, comparable to the value, 12 kJ mol$^{-1}$ for deuterium exchange in ballmilled Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$.\textsuperscript{15}
Figure 4.4: (a,b) 1D Exsy spectra of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ at varied mixing times of 0.01, 0.1, 1 and 12 s after selective perturbation of the deuterium spins resonating at 4 ppm. These spectra are part of series recorded at (a) 283 K and (b) 213 K. For comparison the fully relaxed spectrum at 12 s mixing time is illustrated in the background of all traces (grey curve). All spectra are decomposed into four lineshape components with fixed shift values 14, 4, -29 and -68 ppm and linewidths (4.3.1.1). The component at -68 ppm has been directly determined from the room-temperature spectrum of Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ after major deuterium release during 1 hour at 373 K (bottom trace). Because of its assignment to a strongly bound deuterium fraction its peak area has been kept constant in the lineshape deconvolution. (c,d) Peak areas of the -20 ppm lineshape component and the combined 4 and 14 ppm component (including their MAS sidebands) as well as the total peak area at (c) 283 K and (d) 213 K. The fit curves are based on a bi-exponential model with an exchange time $\tau_{ex}$ and the spin-lattice relaxation time $T_1$ as characteristic decay times. $T_1$ was separately extracted from a exponential fit to the total peak area versus $t_{mix}$ (see Experimental).
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Such barrier is similar to the effective activation energies found for macroscopic non-equilibrium diffusion of hydrogen in Nb$_y$V$_{1-y}$ and V$_y$Ti$_{1-y}$ alloys.$^{41,42}$ It is low compared to, the formation-enthalpy difference between MgH$_2$ and TiH$_2$ ($\Delta H = 34$ kJ mol$^{-1}$ H), but the thermodynamic stability of individual DMg$_4$ and DTi$_4$ clusters in the ternary compound Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ is probably different from that in the respective binary compounds. In addition, since neighboring tetrahedral sites in a coherent fcc crystal structure share three metal atoms, deuterium atoms never hop directly from Mg$_4$ to Ti$_4$ sites, but always via a sequence of sites with mixed Mg$_3$Ti, Mg$_2$Ti$_2$ or MgTi$_3$ coordination. The calculated differences in formation energy between subsequent Mg$_n$Ti$_{4-n}$ sites are indeed in the order of 20 kJ mol$^{-1}$. The relatively weak temperature dependence can also be an artificial result from the multitude of diffusion pathways in the complex nanostructure of this material. As pointed out before,$^{15,43}$ barrier heterogeneity may lead to a weaker temperature dependence of the observed overall dynamics. Attempts to probe this dynamic heterogeneity further with double-quantum $^2$H NMR$^{44}$ were unsuccessful because of signal-to-noise problems resulting from the small amount (3 mg) of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$, which is obtained as a micron-thick film. When comparing these results with hydrogen dynamics and energy barriers in metal hydrides, one should bear in mind that deuterium tends to be more stably bound and show slower dynamics in metal deuterides, than hydrogen in the corresponding hydride. This is, because, as a heavier isotope, deuterium has a factor $\sqrt{2}$ lower zero point vibration energy than hydrogen in analogous compounds.
Figure 4.5 Arrhenius plot of the effective deuterium exchange rate $\tau_{\text{ex}}$ estimated from the approximately bi-exponential dependence of the signals component at -29 ppm and the combined components at 4 and 14 ppm on the mixing time $t_{\text{mix}}$, as illustrated in Fig. 4.4. Error bars indicate ranges of $\tau_{\text{ex}}$ values which yield still acceptable curve fits after re-adjustment of the other fit parameters (except $T_1$).

1D and 2D Exsy probe slow deuterium exchange between deuterium sites with different NMR shifts. Here, “slow” means that the exchange rate $k = t_{\text{ex}}^{-1}$ is less than the NMR-frequency difference between the sites, i.e. $k < \omega_0 \Delta \delta \sim 10^4$ s$^{-1}$. Faster deuterium dynamics, if present, should be reflected by lineshape effects in the $^2$H NMR spectrum. To investigate such faster deuterium mobility MAS $^2$H NMR spectra of co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1}$ were recorded between 213 and 349 K (Fig. 4.6). The spectra are normalized with respect to the overall peak area to correct for the temperature-dependent Boltzmann polarization. Between 213 and 283 K the $^2$H NMR spectrum hardly changes. At 296 K and above the centerband signal at 4 ppm with its sideband pattern decreases at increasing temperature, while a new signal at –10 ppm without spinning sidebands appears. To quantify these temperature trends in the spectra we used the same lineshape deconvolution as for the 1D Exsy lineshape analysis, but now without height restriction for the –68 ppm component. For spectra at temperatures $\geq$ 296 K a fifth component at –10 ppm was incorporated into the lineshape fit (Fig. 4.6).

Fig. 4.7 summarizes the relative peak areas of the lineshape components as a function of temperature. Over the whole temperature range (210 - 350 K) a fairly constant area fraction of 14 ± 3 % is found for the –68 ppm component. This is as expected for a rigidly bound deuterium fraction.
Figure 4.6 12-kHz MAS $^2$H NMR spectra of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ at varied temperature, as well as their coupled deconvolution into four ($T \leq 283$ K) or five ($T \geq 296$ K) lineshape components at 14, 4, -10, -29 and -68 ppm with fixed linewidths (Table 4.1). For comparison the 213 K spectrum is illustrated in the background of all traces (grey curve). The upfield part ($\delta < -20$ ppm) of the lineshape hardly changes as a function of temperature. Above room temperature, the 14 ppm component and the 4 ppm component with its sidebands decay in favor of a new component without sidebands coming up at -10 ppm.

The relative peak area of the -29 ppm component changes only slightly from 42 % at 213 K to 48 % at 347 K. At 230 K and below the combined peak area of the 4 and 14 ppm components is
approximately equal to that of the –29 ppm component. Above 230 K it becomes significantly lower and above 295 K the combined at 4 and 14 ppm drops, in favor of a new component at –10 ppm coming up above room temperature.

![Graph](image)

**Figure 4.7** Relative peak areas of the five signal components at 14, 4, -10, -29 and -68 ppm, as extracted from the varied-temperature spectra shown in Fig. 4.5. The -68 ppm component is fairly constant over the temperature range (14 %). At and below 247 K the combined peak areas of the 4 and 14 ppm component approximately equals the intensity fraction of the -29 ppm (43 %). Above 247 K it starts to decay, and above 296 K it decreases steeply, while a new signal component at -10 ppm is coming up.

The origin of the signal at –10 ppm is not immediately evident. Its appearance at increasing temperature is correlated with the disappearance of the combined 14/4 ppm signal. Therefore it probably represents a high-temperature state of deuterium derived from deuterium located at Mg-rich sites at lower temperatures. As mentioned above, 2D Exsy also shows that at 296 K the two deuterium types with respective chemical shifts of 4 and –10 ppm exchange with each other at the timescale of $10^2$ s (Fig. 4.3). The new -10 ppm signal cannot directly result from fast exchange between Mg-rich sites (4 ppm) and Ti-rich sites (–29 ppm), because the exchange is too slow ($\tau_{ex} \sim 10^{-2}$ s, estimated from extrapolation in Fig. 4.5) compared to the frequency separation $\omega_0 \Delta \delta \sim 10^4$ s$^{-1}$. Furthermore, such fast-exchange interpretation is contradicted by the fact that the relative peak area of the signal component at –29 ppm does not decrease in the same way as the 4 ppm resonance at increasing temperature. The absence of sidebands associated with this signal, and the fact that it shows up at higher temperature are indicative for deuterium with increased mobility. If faster than the static quadrupolar linewidth $\Delta \omega_0$ estimated to be $\sim 10^4$ Hz from the MAS sideband pattern, such mobility can cause motional
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Averaging of the quadrupolar interaction between the deuterium nuclei and the local electric field gradients. Motional averaging alone cannot explain the observed temperature-induced shift change from 4 to –10 ppm. In principle, it could reduce the second-order quadrupolar induced shift, but given the size of the quadrupolar coupling estimated from the sideband pattern, this should typically account for a few ppm only. Perhaps the Mg – Ti interface contains sites with higher enthalpy and entropy, which thus become thermodynamically favorable at higher temperature. As the temperature rises, an increasing number of deuterium atoms move from Mg-rich sites to the sites at the Mg – Ti interface. There they become exposed to conduction electrons, resulting in the observed negative Knight shift.

4.3.3 Mg-Ti nano-segregation model consistent with the $^2$H NMR results

In the following we set up a nanostructure model for co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ consistent with the observed $^2$H NMR shifts, peak areas and exchange. The coupled line shape deconvolution of the 1D Exsy spectra recorded at varied mixing time and the varied-temperature spectra ≤ 283 K yield a peak area of 14 % for the exchange-inactive signal component at –68 ppm, and approximately equal peak areas, 43%, for the broad component at –29 ppm, and the asymmetric component at 4 ppm. The scaling of these Knight shifts, –29 and –68 ppm, compared to the bulk value –150 ppm is an indication for the small size of the conducting TiD$_2$ nanodomains embedded in the insulating MgD$_2$ matrix. The combined lineshape of the two components after subtraction of the simulated sideband patterns associated with the 4 and 14 ppm components (Fig. 4.2 b) may be compared to static $^{195}$Pt or $^{103}$Rh NMR lineshapes of conducting Pt or Rh nanoparticles on a non-conducting support or surrounded by air.$^{38,39,40}$ At room temperature the Knight shift of conducting nano-particles is affected by surface effects. A “NMR layer model” has been proposed, in which the Knight shift in such nanoparticle varies with the layer depth z relative to the particle surface according to:$^{38,39}$

$$\delta(z) = \delta_{\text{bulk}} - (\delta_{\text{surf}} - \delta_{\text{bulk}}) \exp(-z/L)$$  \hspace{1cm} (4.3.3.1)

where the “healing length” L represents a characteristic length scale over which the Knight shift changes from the surface value $\delta_{\text{surf}}$ into the bulk value $\delta_{\text{bulk}}$. E.g., for fcc Pt nano-particles L has been found to be 3.1 Å, i.e. 78% of the lattice constant $a = 3.92$ Å. By analogy we assume, that
the Knight shift of deuterium in conducting TiD$_2$ nanodomains has a similar depth dependence with $\delta_{\text{bulk}} = -150$ ppm ($^2$H NMR shift of bulk TiD$_2$) and $\delta_{\text{surf}} \sim 0$ for deuterium at mixed Mg$_n$Ti$_{(4-n)}$ sites in the non-conducting interface with the surrounding MgD$_2$ matrix. The Knight shifts $\delta_A = -29$ and $\delta_B = -68$ ppm then represent relative depths $z_a/L = 0.2$ and $z_b/L = 0.6$, respectively. The observed non-exchangeability of deuterium resonating at -68 ppm can then be explained by the larger distance from the nano-cluster interface. Deeper buried Ti$_4$ sites may also bind deuterium intrinsically more stably.

With the outcome that there are two types of Ti$_4$ sites at different depths from the Mg-Ti interface, we have considered various shapes for fcc TiD$_2$ nano-domains within a fcc MgD$_2$ matrix. The reduced Knight shift suggests a domain size of a few Ti layers, but a suitable model should combine this with a relatively large fraction of Ti$_4$ sites, corresponding to the 57% joint peak area of the $-29$ and $-68$ ppm signals in the $^2$H NMR spectrum. As an Ansatz we have tested a model with flat nano-slabs of four Ti layers coherently embedded in a fcc Mg/MgD$_2$ matrix (Fig. 4.8). At the overall composition Mg : Ti $\sim 2$ in co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$, every four-layered Ti nano-slab would - on the average - be sandwiched between three fcc Mg layers on both sides. This is well within the range for stable structures with fcc TiD$_2$ and MgD$_2$ layers according to DFT.$^{45}$ Only beyond 12 Mg layers (Mg:Ti $> 3$ for 4-layered Ti nanoslabs) the MgD$_2$ matrix tends to adopt the rutile structure typical of bulk MgD$_2$. Four-layered fcc Ti nanoslabs have two types of Ti$_4$ sites, A and B, at respective depths $z_A = 0.25a$ and $z_B = 0.75a$ from the interface, where $a$ denotes the lattice constant. The factor 3 difference in depth is consistent with the conditions $z_a = 0.2$ L and $z_b = 0.6$ L (Eq. 4.3.3.1 and below), and the corresponding healing length $L = 1.25a$ is reasonable compared to the 2.6 atom layers found for Pt nanoparticles covered with hydrogen.$^{39}$
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Figure 4.8 Distribution of (100) TiD$_2$ nanoslabs with different layer thickness $n \leq 5$ coherently embedded in a fcc Mg/MgD$_2$ matrix. Mg$_2$Ti$_2$ sites at the Mg-Ti interface are labelled as “2”. Subsurface tetrahedral Ti$_4$ sites indicated as “A” and deeper Ti$_4$ sites as “B”. Deuterium at A sites contribute to the broad signal at -29 ppm, and those at B sites to the -68 ppm signal.

The fraction of the subsurface Ti$_4$ sites A in the model is twice as high as that of the deep Ti$_4$ sites B. This is slightly different the observed peak area ratio 3 : 1 between the signals at –29 and –68 ppm, assigned to A and B, respectively. The model can be improved in this respect by assuming a 2 : 1 distribution of 4-layer and 3-layer Ti nano-slabs (Fig. 4.8). The latter have only
Ti\textsubscript{4} sites of type A, and thus contribute to the -29 ppm signal only. Likewise, 2- and 5-layered slabs with different contributions of Ti\textsubscript{4} sites A and B can be added to the distribution. It is realistic that nano-slab structures of varied thickness exist in co-sputtered Mg\textsubscript{0.65}Ti\textsubscript{0.35}D\textsubscript{1.1}. Type A Ti\textsubscript{4} sites in 2-, 3-, 4- and 5-layered nano-slabs probably have minor Knight-shift differences, which explains the large linewidth of the –29 ppm component.

The relative occurrence of Ti\textsubscript{4} sites for nano-slabs with n Ti layers coherently embedded in a fcc Mg/MgD\textsubscript{2} matrix, \(g_n\), equals \(f_{\text{Ti}}(n-1)/n\), where \(f_{\text{Ti}}\) denotes the atom fraction of Ti atoms. For the nominal composition Mg : Ti = 0.65 : 0.35, the Ti\textsubscript{4} occurrence \(g_4\) for 4-layered nanoslabs equals 0.26. This means that maximally 0.52 deuterium atoms per metal atom (D/M) can be accommodated at Ti\textsubscript{4} sites. This is low compared to the 0.63 D/M Ti\textsubscript{4} occupation reflected by the 57\% combined peak area of the -29 and -68 ppm signals at the overall deuterium loading of 1.1 D/M. An explanation for the apparent inconsistency may be a minor over-estimation of the deuterium content \(x\), or the Mg : Ti ratio. If either of the two, or both, would actually be lower than we think, the fraction of deuterium bound to Ti\textsubscript{4} sites could be higher, and thus closer to peak-area fraction observed with \(^2\)H NMR. The corrections needed to explain the NMR data, \(f_{\text{Ti}} = 0.35 \rightarrow 0.38\) and \(x = 1.1 \rightarrow 1.0\), are well within the experimental error. The formation enthalpy of deuterium at tetrahedral Mg\textsubscript{4}Ti\textsubscript{4-n} sites increases with the number of Ti atoms 4-n\textsuperscript{0,46}. At intermediate deuterium loading Ti\textsubscript{4} sites will thus be preferentially occupied. The deuterium loading (D:M) as estimated from NMR is 1.1. As will be shown in Chapter 5, we do not observe the NMR signal from all the deuterium atoms from Mg\textsubscript{0.65}Sc\textsubscript{0.35}D\textsubscript{x}. Since, Mg\textsubscript{0.65}Ti\textsubscript{0.35}D\textsubscript{x} is similar to Mg\textsubscript{0.65}Sc\textsubscript{0.35}D\textsubscript{x} structurally, this could indicate that even in Mg\textsubscript{0.65}Ti\textsubscript{0.35}D\textsubscript{x} there is a possibility that we do not observe NMR signal from mixed coordination. Electrochemical loading\textsuperscript{23} of Mg\textsubscript{0.7}Ti\textsubscript{0.3}H\textsubscript{x} indicated that \(x \sim 1.55\) and some amorphous or partly oxidized material could be present. In our samples, the thickness of film is 1 micron. Therefore, there is a possibility that even in the present sample, there might be oxidized material without hydrogenation. Another possibility is desorption of part of deuterium during transportation.

In our model structure consisting of 4- and 3-layered Ti nanoslabs the only Ti atoms with Mg atoms in their 12-fold metal coordination sphere are Ti atoms with 4 Mg neighbors at the Mg-Ti interface. As a consequence, the average number of Mg neighbors around Ti atoms is rather low,
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$N_{\text{Mg}}(\text{Ti}) = 2.2$. This may be compared to the higher value $N_{\text{Mg}}(\text{Ti}) = 5.5$ determined with EXAFS for co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}$ films before and after one cycle of hydrogen uptake and release.$^{22}$ This indicates that a small Ti fraction occurs outside the TiD$_2$ nano-domains as highly dispersed Ti atoms in the Mg/MgD$_2$ matrix. Note, that in this NMR study we have investigated material prepared by deuteration of 1-µm thick $\text{Mg}_{0.65}\text{Ti}_{0.35}$ films. In these thick films a more pronounced Mg – Ti segregation may have taken place than in the 0.2-µm thick films studied in the previous EXAFS investigation.$^{22}$

4.4 Conclusion

In contrast to ball-milled $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65}$, co-sputtered $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.1}$ shows no $^2\text{H}$ NMR sign of TiD$_2$ macrophase separation, which is consistent with homogeneous crystal structure determined by XRD and electron microscopy. It does contain conducting TiD$_2$ nano-domains consisting of a few Ti atom layers, embedded in a non-conducting fcc $\text{Mg}_{1-y}\text{Ti}_y\text{D}_x$ matrix. $^2\text{H}$ NMR shows that deuterium atoms in the Mg-rich matrix exchange with deuterium at subsurface Ti$_4$ sites in TiD$_2$ nano-domains, but not with deuterium at deeper Ti$_4$ sites in these nano-domains, at least at the second timescale. This deuterium exchange shows only weak temperature dependence, indicative of a heterogeneous distribution of activation barriers. At increasing temperature $\geq 296$ K the NMR signal of deuterium in the Mg-rich matrix reduces and a new signal at $-10$ ppm appears. This implies a temperature induced reversible deuterium transfer from sites in the non-conducting Mg-rich matrix to sites at the Mg-Ti interface.

4.5 References

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Chapter 5

Dark deuterium in the lightweight hydrogen-storage material Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ studied with MAS $^2$H NMR

Abstract

Part of the deuterium atoms in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$, a candidate lightweight material for hydrogen storage, is $^2$H MAS NMR invisible. The presence of such “dark deuteron” states follows from the observed drop in overall intensity in $^2$H NMR exchange spectroscopy (Exsy) at the $10^{-3}$ – $10^{-2}$ s timescale, much faster than spin-lattice relaxation. A theoretical model is presented which explains the decrease in overall intensity in terms of deuterium exchange between two states with different NMR visibility and initial polarization. Two possible causes for the MAS NMR invisibility are considered: (1) second-order quadrupolar linebroadening and (2) rotational motion at the sample-rotation timescale. On the basis of the observed magnetic-field dependence of the overall polarization drop in Exsy we conclude that the first mechanism dominates the NMR invisibility of deuterium. Our Exsy experiments start with an initial $^2$H Hahn-echo or $^2$H-$^{45}$Sc TRAPDOR filter. Despite the NMR invisibility of the dark deuteron states it is still possible to get information about their Hahn-echo and TRAPDOR decay features indirectly via the visible deuterium states with which they exchange. Dark deuterons appear to have only slightly shorter T$_2$ times than their visible counterparts, and are probably located at tetrahedral interstitial sites with a mixed Mg and Sc coordination. Deuterium has spin 1 and couples to the strong electric field gradients at such sites. The NMR invisibility of a significant deuterium fraction in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ has consequences for the quantitative interpretation of $^2$H MAS NMR spectra in terms of site occupation in magnesium transition-metal deuterides, and other metal deuterides.
5.1 Introduction

$^1$H and $^2$H MAS NMR spectroscopy are powerful characterization tools for hydrogen storage materials because these can directly detect hydrogen or deuterium in metal hydrides or deuterides, respectively. NMR provides information about the local structure at the hydrogen sites, as well as about hydrogen mobility.$^{1,2,3,4,5,6}$ This is relevant for the potential application of metal hydrides as hydrogen-storage materials. Since crystallinity is not required for NMR, the technique can also “see” hydrogen inside XRD-amorphous parts of metal hydrides. Although the isotope $^1$H has higher NMR frequency and sensitivity, $^2$H nuclei tend to have relatively narrower resonances in MAS NMR spectra of metal deuterides compared to the corresponding metal hydrides. This results from the weaker dipole coupling between $^2$H than between $^1$H nuclei.

Magnesium is a lightweight metal capable of safely storing large amounts of hydrogen, but its ab- and desorption kinetics has to be improved. Our group is currently investigating the sorption boost caused by alloying magnesium with transition metals, such as scandium and titanium.$^{7,8,9}$ We have previously investigated deuterium absorbed in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ by means of MAS $^2$H NMR.$^5$ Using double-quantum $^2$H NMR and $^2$H-{$^{45}$Sc} TRAPDOR we were able to distinguish between deuterium at tetrahedral sites with or without scandium atoms in the first coordination sphere. Quantitative analysis of the data suggested that about half of the deuterium atoms were located at Mg$_4$ sites and the others at Mg$_n$Sc$_{4-n}$ (n≠4) sites. On the basis of the 50% fraction of Mg$_4$ sites in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ we proposed that the material was segregated into Mg-rich and Sc-rich nano-domains. The size of these nano-domains should be in the order of a few crystal unit cells, because we observed complete deuterium exchange at a sub-second timescale between the Mg-rich and Ti-rich sites in two-dimensional exchange $^2$H NMR spectra even at 213 K. Such small nano-domain size is also consistent with the fact that the material looks homogeneous in the earlier X-ray and neutron diffraction studies.

Following up on our earlier study$^5$ we have further investigated deuterium exchange in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ by using one-dimensional exchange spectroscopy (1D Exsy). Compared to two-dimensional exchange spectroscopy (2D Exsy), 1D Exsy is less model-free, but also less time consuming. Thus, once a suitable model has been chosen on the basis of a few 2D exchange
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One of the surprising findings was, however, that the total spin polarization was not conserved during the deuterium exchange. Deuterium polarization was lost at a timescale much faster than expected from spin lattice relaxation. This made us speculate about NMR invisible deuterium states, or “dark deuterium”. The possibility that a significant part of deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ may not show up in $^2$H MAS NMR can have important consequences for our earlier quantitative interpretation of the $^2$H-{Sc} TRAPDOR decays. If, e.g., part of the deuterium atoms at mixed Mg$_{4-n}$Sc$_n$ sites would be less visible than deuterium at Mg$_4$ sites, the 50% fraction of Mg$_4$ sites estimated from $^2$H MAS NMR spectra could have been too high. The material would then be less (nano-)segregated than originally estimated.

The issue of MAS NMR invisibility is well-known for $^{27}$Al spins in alumina and aluminosilicates, such as zeolites. $^{27}$Al has spin 5/2 and a quadrupolar moment, so that it interacts with local electric field gradients arising from a (distorted) asymmetric oxygen coordination of the aluminium atoms. To first-order the central transition – $\frac{1}{2}$ $\leftrightarrow$ $\frac{1}{2}$, which is usually monitored in $^{27}$Al NMR of multi-crystalline alumina or zeolite powders, is insensitive to the quadrupolar interaction. However, the central-transition frequency is still broadened by the second-order quadrupolar effect. This second order effect is not completely averaged by magic-angle spinning, and may be strong enough to obscure part of the $^{27}$Al resonances in $^{27}$Al MAS NMR. High-field $^{27}$Al MAS NMR with fast sample rotation (> 25 kHz) helps to keep the amount of invisible $^{27}$Al NMR as small as possible. The second-order quadrupolar linewidth is inversely proportional to the magnetic field, and the MAS rate must exceed this linewidth. Deuterium has spin 1, and as a consequence, its two single-quantum resonances – 1 $\leftrightarrow$ 0 and 0 $\leftrightarrow$ 1 in static $^2$H NMR are already broadened by the first-order quadrupolar interaction. In fact, static $^2$H NMR lineshapes are informative about motion of molecules or moieties in deuterium-labeled systems, such as lipid membranes. Magic-angle spinning averages out the first-order quadrupolar linebroadening, but not completely the weaker second-order effect. To the best of our knowledge there have been no NMR publications with a detailed analysis of this second-order broadening in $^2$H NMR of deuteride materials. Like for $^{27}$Al NMR, the second-order quadrupolar linewidth in $^2$H NMR is inversely proportional to the magnetic field, and one can
expect deuterium spins with second-order quadrupolar exceeding the sample-rotation rate to be invisible in \(^2\)H MAS NMR.

Another important source of linebroadening in \(^2\)H MAS NMR spectra of metal deuterides could be deuterium mobility. Especially, deuterium mobility at the sample-rotation timescale strongly interferes with the coherent averaging of the quadrupolar interaction caused by MAS. Spectral simulations of rotational mobility effects on MAS sideband patterns can be carried out using Floquet theory.\(^\footnote{11}\) The detailed effect depends on the type of motion, its timescale and its amplitude. To first-order approximation, however, any rotational motion slower than the sample-rotation rate tends to increase the linewidth of the centerband and the sidebands. At constant overall peak area, this motional line broadening goes together with a inversely proportional decrease of the peak heights. Thus, in case of a mobility distribution with various mobility rates below and around the MAS speed, the readily visible features of the sideband pattern are dominated by the narrow bands of the static and very slow components. In contrast, the broader features of the intermediate components may become hidden under the noise level, or even be accidentally removed in the baseline-correction process. The remedy against NMR-invisible deuterium resulting from deuterium mobility would be to check the temperature effect. At sufficiently low temperature all deuterium motions should be slow enough to give rise to well-resolved sideband patterns in \(^2\)H MAS NMR.

5.2 Theory

5.2.1 Dynamic-equilibrium deuteron exchange between two states with different NMR visibility

In this section we develop a model for the time-dependence of the \(^2\)H NMR polarization of deuterons exchanging between two states or phases A and B with different NMR visibilities. From a kinetic point of view the ensemble is in dynamic equilibrium, but we are interested in the transient polarization effects after an unequal polarization perturbation of the two deuterium species at \(t = 0\). The relative deuterium amounts in state A and B are \(f_A\) and \(f_B\), respectively. In dynamic equilibrium deuterons are continuously exchanging between the two states. According to their states at time \(0\) and \(t\) we define subfractions \(f_{AA}(t)\) and \(f_{BB}(t)\) as the time-dependent
relative amounts of deuterons which have stayed in, respectively, state A and B during the time interval t. Likewise, \( f_{AB}(t) \) and \( f_{BA}(t) \) denote the amount of deuterons, which have changed from A to B, or vice versa. In thermal equilibrium the following relations hold:

\[
\begin{align*}
\dot{f}_{AA}(t) + f_{BA}(t) &= f_A \\
\dot{f}_{AB}(t) + f_{BB}(t) &= f_B \\
\dot{f}_{AB}(t) &= f_{BA}(t)
\end{align*}
\]

whereby \( f_{AB}(0) = f_{BA}(0) = 0 \), and thus \( f_{AA}(0) = f_A \) and \( f_{BB}(0) = f_B \). All subfractions can be conveniently rewritten in terms of conditional steady-state probability \( g_{AA}(t) \) that a deuteron in A will stay in A during the next interval t, as:

\[
\begin{align*}
\dot{f}_{AA}(t) &= f_A g_{AA}(t) \\
\dot{f}_{BB}(t) &= 1 - f_A g_{AA}(t) \\
\dot{f}_{AB}(t) &= f_{BA}(t) = f_A \{ 1 - g_{AA}(t) \}
\end{align*}
\]

whereby \( g_{AA}(0) = 1 \). Since deuterons initially in A will be homogeneously distributed over A and B after sufficiently long time, \( g_{AA}(t) \) generally decays from 1 to \( f_A \). Assuming the usual mono-exponential decay (typical of a two-site exchange) we obtain:

\[
g_{AA}(t) = f_B \exp\left[-t/\tau_c\right] + f_A
\]

The differently perturbed, initial polarization of A and B deuterons serves a marker of their state at \( t = 0 \). The NMR shifts of A and B deuterons are generally different, so that their state at time \( t \) can also be determined. Careful analysis of the NMR spectra as a function of exchange time then offers the opportunity to disentangle the underlying information about the various subfractions \( f_{ij}(t) \). For deuterons exchanging between states A and B with different NMR visibility \( v_A \) and \( v_B \) and initial polarization \( p_A \) and \( p_B \) (relative to the equilibrium spin polarization at the specific temperature), the exchange-time dependent intensities \( I_A(t) \) and \( I_B(t) \) in the \(^2\text{H} \) NMR spectrum can be derived from Eq. 5.2.2 as:

\[
\begin{align*}
I_A(t) &= v_A p_A f_A g_{AA}(t) + v_A p_B f_A \{ 1 - g_{AA}(t) \} \\
I_B(t) &= v_B p_A f_A \{ 1 - g_{AA}(t) \} + v_B p_B \{ 1 - f_A g_{AA}(t) \}
\end{align*}
\]

Parallel to the polarization effects caused by deuteron exchange, the perturbed polarization is also affected by spin-lattice relaxation. To correct for this in our exchange NMR experiments, Eq. 5.2.4 needs to be multiplied by a factor \( \exp(-t/T_1) \), whereby \( T_1 \) is the spin-lattice relaxation
time. Using such overall correction for $T_1$ relaxation we assume that the exchange is fast enough to average out possible intrinsic $T_1$ differences between A and B, but this can be experimentally verified by independent measurements. Substitution of $g_{AA}(t)$ by $f_B \exp(-t/\tau_c) + f_A$ (Eq. 5.2.3) yields a similar behavior of the intensities $I_A(t)$ of states A normalized against the total intensity $I_{all}(0) = I_A(0) + I_B(0) \propto f_A v_A p_A + f_B v_B p_B$ at $t = 0$:

$$I_A(t) = \left\{ I_A(0) + C_A \exp[-t/\tau_c] - C_A \right\} \exp(-t/T_1) \quad (5.2.5a)$$

with constant $C_A$ for state A given by:

$$C_A = \frac{f_A f_B v_A (p_A - p_B)}{f_A p_A v_A + f_B p_B v_B} \quad (5.2.5b)$$

The intensity $I_B(t)$ and constant $C_B$ for state B are given by the same equations but with the subscripts A and B interchanged. As Eq. 5.2.5 shows, without an initial polarization difference, $|p_A - p_B| = 0$, the peak intensities are not affected by deuteron exchange, but by $T_1$ relaxation only. With $g(t)$ decaying from 1 to 0, $C_A$ and $C_B$ represent the size of the partial intensity drop or rise caused by deuteron exchange. If the $^2$H NMR signals of A and B deuterons overlap, their respective contributions to the heterogeneous resonance may be estimated from detailed lineshape deconvolution. A less resolved, but robust approach is to inspect the overall intensity $I_{all}(t) = I_A(t) + I_B(t)$ by integrating the resonance as whole. The time-dependence of $I_{all}(t)$ is similar to the behavior described by Eq. 5.2.5a:

$$I_{all}(t) = \left\{ 1 + C_{all} \cdot g(t) - C_{all} \right\} \exp(-t/T_1) \quad (5.2.6a)$$

where $C_{all}$ denotes:

$$C_{all} = \frac{f_A f_B (p_A - p_B)(v_A - v_B)}{f_A p_A v_A + f_B p_B v_B} \quad (5.2.6b)$$

As a result of the difference in visibility, $|v_A - v_B| \neq 0$, and initial polarization, $|p_A - p_B| \neq 0$ the overall intensity is not conserved under deuteron exchange. If the state with lowest visibility, say, by definition B, is also initially prepared with the lowest polarization, Eq. 5.2.7 describes an exchange-induced overall-intensity drop. This makes sense, because under such conditions deuterons with relatively high polarization and visibility move to states where their polarization becomes partly hidden, and this not fully compensated by the influx of lowly polarized deuterons from the states with low visibility. In case that state B is totally NMR invisible, $v_B = 0$, Eq. 5.2.6b simplifies to:
\[ C_{\text{all}} = f_B \left[ 1 - \left( p_B / p_A \right) \right] \]  

Thus, if, in addition, the initial polarization of the NMR invisible state is much smaller than that of the NMR visible state, \( p_B \ll p_A \), the initial overall intensity drop \( C_{\text{all}} \) equals the fraction \( f_B \) of NMR invisible or “dark deuterium”. The ratio \( p_B/p_A \) depends on the initial NMR filter, for which in this study we have used a Hahn-echo or TRAPDOR echo with selectable echo time \( 2\tau \). If after the initial echo filter the initial polarization \( p_B \) of the invisible deuterium fraction is not negligible with respect to that of the visible deuterium fraction, \( p_A \), values for \( f_B \) and \( p_B/p_A \) can be separately estimated by comparing \( C_{\text{all}} \) values for at least two different filter times \( 2\tau_1 \) and \( 2\tau_2 \). By assumption, the initial polarization ratio \( p_B/p_A \) decays mono-exponentially versus the filter time \( 2\tau \), \( \exp(-\Delta R \ 2\tau) \), whereby \( \Delta R \) denotes the difference between the echo decay rates \( R_A \) and \( R_B \) of visible and invisible deuterium, respectively. Then, the rate difference \( \Delta R \) can be solved from the ratio:

\[ \frac{C_{\text{all}}(2\tau_2)}{C_{\text{all}}(2\tau_1)} = \frac{1 - \exp(-\Delta R \ 2\tau_2)}{1 - \exp(-\Delta R \ 2\tau_1)} \]  

As the Hahn-echo or TRAPDOR decay rate \( R_A \) of the visible deuterium fraction can be measured independently, we can thus also estimate the decay rate \( R_B \) of the invisible deuterium fraction. Interestingly, it is thus possible to obtain information about the invisible deuterium fraction via the NMR detectable state with which they exchange.

### 5.3 Experimental

#### 5.3.1 Material

Mg and Sc metal pieces were sealed in an airtight Molybdenum crucible and heated at \( \sim 1150 \) °C and annealed for four days at \( 450 \) °C. The ingot was hammered down to pieces smaller than 5 mm and subsequently milled with Pd in a Spex 8000 ball-mill for 2 hrs. The ball-to-powder ratio was 10:1. The as-milled material was deuterated at 70 bars at 175 °C.

#### 5.3.2 MAS \(^2\)H NMR

MAS \(^2\)H NMR spectra of \( \text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2} \) were recorded at a NMR frequency of 77 MHz and a sample-rotation rate of 8 kHz unless explicitly specified differently. To suppress baseline artifacts caused by probe ringing Bloch spectra were recorded by use of an alternate-inverse-recovery (AIR) pulse sequence \( 90_x-90_x-\tau-90_y-\tau_{\text{eq}} \) with \( 90^\circ \) pulse \( p1=5 \) µs and filter time \( \tau=1\)ms
and alternating phase of the second pulse to suppress probe-ringling artifacts. The natural-abundance $^2$H NMR signal of TMS was used as an external reference for the chemical shift.

### 5.3.3 Double-quantum MAS $^2$H NMR with $^{45}$Sc recoupling

Double-quantum 8-kHz MAS $^2$H NMR spectra without $^{45}$Sc recoupling were recorded according to ref. 11 as two-dimensional spectra with the pulse sequence $p_1$-τ-$p_1$-t$_1$-$p_1$-τ-$p_1$-t$_2$-$p_1$-t$_2$ with 90° pulse $p_1 = 4$ µs, double-quantum excitation and reconversion time $\tau = 4.5$ µs, z-filter time $t_z = 3$ µs and rotor-synchronized sampling of the evolution time $t_1$ and acquisition time $t_2$. As a result, MAS sidebands fold back onto the centerband. MAS suppresses the dipole coupling between deuterons and scandium nuclei, yielding a narrow $^{45}$Sc-decoupled MAS $^2$H NMR lineshape. By on-resonance irradiation at 121.5 MHz of the $^{45}$Sc nuclei during the evolution time, the deuterons with nearby scandium atoms are temporarily “recoupled”, resulting in a selective broadening of the DQ-lineshape component from deuterons with scandium neighbors. This offers the opportunity to discriminate between signal contributions from deuterons at interstitial sites with different metal coordination. The magnitude of the rf-field corresponds to a 50-kHz nutation on spin-1/2 $^{13}$C nuclei resonating at 125 MHz (see TRAPDOR conditions below).

### 5.3.4 $^2$H-{$^{45}$Sc} TRAPDOR

TRAPDOR $^2$H NMR spectra were recorded with a Hahn-echo $p_1$-τ-$p_2$-τ pulse sequence (90° pulse $p_1 = 5$ µs, 180° pulse $p_2 = 10$ µs) with rotor-synchronized time intervals $\tau = T_r n - (p_1+p_2)/2$ ($T_r = 125$ µs) and with on-resonance $^{45}$Sc NMR irradiation (121.5 MHz) during-alternatingly - the first or the second interval. In this way we suppress echo-phase artifacts $\pm \Delta \phi$ caused by the Bloch-Siegert shift during the irradiation. This is important to interpret the lineshape difference between spectra with and without $^{45}$Sc NMR irradiation. As a test, Bloch-Siegert-shift suppressed TRAPDOR spectra with and without irradiation at a 4-MHz shifted frequency, 125 MHz, did not show spectral differences. So, the difference we observe with and without irradiation at 121.5 MHz really involves the $^{45}$Sc spins. The interscan delay was 20 s, which is about three times longer than the spin-lattice time $T_1 \sim 6$ s independently measured at 213 K, and ensures that the spectra are quantitative. To further ensure the quantitativeness of the
spectra, full sideband patterns were recorded with sufficient spectral width (100 kHz). In this way we can also detect possible broad lineshape components associated with intermediate-exchange deuterons or deuterons with mobility at the sample-rotation timescale. Such broad components can be overlooked in 1D and 2D-spectra recorded with rotor-synchronous time sampling. (Indeed visible in room-temperature spectra, but not at 213 K). The $^{45}$Sc NMR rf-field was calibrated via 125-MHz $^{13}$C NMR on adamantane. The resulting nutation frequency, 50 kHz for the spin-1/2 $^{13}$C nucleus, is about twice the full width at half height of the $^{45}$Sc NMR central transition observed in 8-kHz MAS $^{45}$Sc NMR spectra. Direct $^{45}$Sc NMR nutation experiments show faster modulation, indicating that the rf field is weak relative to the quadrupolar coupling.

5.3.5 $^2$H MAS NMR Exchange Spectroscopy

Two dimensional exchange $^2$H NMR spectra were recorded with the $p_1$-$t_1$-$p_1$-$t_{\text{mix}}$-$p_1$-$t_2$ pulse sequence with a 90° pulse $p_1 = 5$ µs and time-proportional phase incrementation (TPPI). In general, this type of recording (echo/anti-echo combination; asynchronous mixing time) yields cross-peaks between the MAS centerband and the sidebands, even in the absence of chemical exchange$^{12}$. Only interested in chemical exchange between $Q^4$ and $Q^{<4}$ deuteron states, we used rotor-synchronous sampling in both time dimensions. (Dwell time equal to rotation time $T_r = 125$ µs.) As a result, the sidebands fold back onto the centerband in both frequency domains and the relative loss of diagonal intensity and increase of off-diagonal intensity in the resulting spectrum is only correlated with chemical exchange.

One-dimensional exchange spectroscopy (1D Exsy) was carried out by inhomogeneously perturbing the polarization of the deuterium nuclei by use of a Hahn-echo or $^2$H-$\{^{45}$Sc$\}$ TRAPDOR filter with an echo time $2\tau$ of 2 or 4 ms. The 1D exchange spectra were recorded at varied mixing times between 0.01 and 1 s and varied temperatures between 213 and 296 K to monitor the possible deuterium exchange from the MgD$_2$ phase to the other two phases. The exchange curves were always compared with the $T_1$ relaxation observed after non-selective perturbation resulting from replacing the DANTE pulse train by a single nonselective 90° pulse.
5.3.6 Lineshape analysis

Coupled lineshape analyses of the Hahn-echo and TRAPDOR spectra series of typically 15 spectra each at 213 and 296 K were carried out using the program DM2008. The fit model contains four Lorentzian-Gaussian lineshape components \#1, \#2, \#2’ and \#3 with fixed positions, linewidths and quadrupolar-coupling anisotropy (see table 5.1 below) and the four peak heights as variable fit parameters.

Table 5.1: parameters of the four lineshape components used for deconvolution of the Bloch, Hahn-echo and TRAPDOR spectra at 296 and 213 K. Positions \(\sigma\), widths \(\Delta\sigma\), Gauss or Lorentzian centerband shape \(G : L\), quadrupolar coupling constant \(v_Q\) and asymmetry parameter \(\eta_Q\) were fixed in the coupled lineshape analysis. Chemical shifts are referenced to the natural-abundance \(^2\text{H}\) NMR signal of tetramethylsilane (TMS).

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5.4 Results

5.4.1 Distinct deuterium species in magic-angle spinning \(^2\text{H}\) NMR spectra

Without sample rotation the \(^2\text{H}\) NMR lineshape of Mg\(_{0.65}\)Sc\(_{0.35}\)D\(_{2.2}\) at room temperature is broadened by the quadrupolar coupling of the deuterium spins with the local electric field
gradient (EFG) in the overall rutile crystal structure (Fig. 5.1a). Magic-angle-spinning (MAS) at intermediate sample rotation rates < 15 kHz breaks up the broad static lineshape into a resolved sideband pattern (Fig. 5.1b). The sideband pattern can be reasonably simulated for quadrupolar coupling constants ν₀ between 15 and 17 kHz depending on the chosen quadrupolar asymmetry η parameter between 0 and 1. However, no single parameter combination (ν₀, η) properly explains the static ²H NMR lineshape (Fig. 5.1a). This is indicative for EFG heterogeneity. The top of the centerband lies at 3 ppm (Fig. 5.1c), which is close to that of MgD₂ (4 ppm),²⁶ and the same as the ¹H NMR shift of the corresponding hydride Mg₀.₆₅Sc₀.₃₅H₂.₂ (Fig. 5.1d). The chemical resolution in ²H MAS NMR tends to be higher than the ¹H MAS NMR.³⁴ ¹H has a higher gyromagnetic ratio and thus higher NMR frequency than ²H in the same magnetic field. Nevertheless, the 30 kHz-MAS centerband of the hydride is broader in terms of ppm than the 8 kHz-MAS centerband of the deuteride. ¹H nuclei have a gyromagnetic ratio γ which is ~6.5 times higher than that of deuterium, so that the homonuclear coupling in a given configuration, proportional to γ² I (I+1), is ~16 times stronger in kHz, and 2.4 times stronger in ppm. MAS averages the first-order dipolar Hamiltonian, but not completely higher-order terms associated with relayed dipolar coupling in multi-proton systems.¹⁴ In the fluorite structure every ¹H spin is octahedrally surrounded by six other ¹H spins at a distance of 2.23 Å (half the lattice constant) with a corresponding dipolar coupling constant ~11 kHz. In contrast, the deuterium coupling constant in the deuteride is only ~0.26 kHz.
Figure 5.1: (a) Static and (b) 8-kHz MAS $^2$H NMR spectra of $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$, (c) centerband region of $^2$H MAS NMR spectrum. (d) centerband region from the previously recorded 30-kHz MAS $^1$H NMR spectrum for comparison. The $^2$H MAS NMR sideband pattern in (b) is well described by several combinations of quadrupolar coupling constants and asymmetry parameters ($\nu_Q$, $\eta$) varying from (15 kHz, 0) to (17 kHz, 1), but none of these combinations correctly predicts the static lineshape, as shown by the grey simulated lineshapes in (a).
Although narrower than in the $^1$H NMR spectrum, the $^2$H NMR centerband is still broader than that of MgD$_2$. The bigger linewidth reflects unresolved, overlapping signals associated with different Mg$_n$Sc$_{4-n}$ coordination of deuterium at the tetrahedral interstitial sites. This becomes apparent in double-quantum (DQ) $^2$H NMR and $^2$H-{$^{45}$Sc} TRAPDOR NMR. Fig. 5.2 shows 2D DQ NMR spectra with and without $^{45}$Sc NMR irradiation during the evolution time. The DQ NMR lineshape in the projections of the 2D spectra on the DQ axis (Fig. 5.2d, f) are narrower than in the conventional MAS NMR spectrum (Fig. 5.2c). This is because the DQ frequency is twice higher than the single-quantum (SQ) frequency, so that any constant linewidth in Hz is relatively narrower in ppm. In addition, to first-order approximation the frequency of the DQ transition $-1 \leftrightarrow 1$ is independent of the quadrupolar interaction. The DQ frequency is therefore less broadened by slow deuterium motions than the single-quantum frequency. In the DQ projection of the 2D spectrum without $^{45}$Sc NMR irradiation (Fig. 5.2d) two partly overlapping signals at $\sim$4 and $\sim$2 ppm are recognized (Fig. 5.2e). The 2-ppm signal disappears when $^{45}$Sc NMR irradiation is applied (Fig. 5.2f). This indicates that this signal belongs to deuterium at tetrahedral interstitial sites with at least one scandium atom.
Indeed, we observe a similar sensitivity to $^{45}\text{Sc}$ NMR irradiation in $^2\text{H}-\{^{45}\text{Sc}\}$ TRAPDOR and Hahn-echo spectra (Fig. 5.3). For a more detailed analysis the series of TRAPDOR and Hahn-echo spectra as a function of echo time at 300 K were decomposed in a coupled manner into Gaussian-Lorentzian lineshape components with fixed shift values $\delta$, linewidths $\Delta\delta$ and quadrupolar sideband pattern parameters $\nu_Q$ and $\eta$ (see Table 5.1). The 15 rotor-synchronized Hahn-echo and 15 TRAPDOR spectra recorded with systematically varied echo times can be consistently decomposed in two major components 1 and 2 at 4.3 and 2.5 ppm, respectively, and a minor third component 4 at -10.1 ppm (Fig. 5.3). Component 4 belongs to deuterium in the Pd catalyst layer and is not further included in the following spectral analysis. Component 1 is insensitive to $^{45}\text{Sc}$ irradiation and is therefore assigned to deuterons without $^{45}\text{Sc}$ in their direct vicinity (D Mg$_4$). In contrast, the TRAPDOR decay of 2 is significantly accelerated by $^{45}\text{Sc}$ NMR irradiation (Fig. 5.3e). This component is therefore assigned to deuterium atoms with at least one scandium neighbor at the tetrahedral site Mg$_n$Sc$_{4-n}$ ($n \neq 0$) In contrast, the component 1 is independent of $^{45}\text{Sc}$ NMR irradiation (Fig. 3e), and therefore assigned to deuterium at Mg$_4$ sites. The characteristic Hahn-echo decay times of the components 1 and 2 obtained from the fit are 1.3 -1.4 ms, respectively (Table 5.1). At the $^2\text{H}$ NMR frequency of 77 MHz this corresponds to a homogeneous linewidth of ~ 3 ppm, which is practically the same as the total linewidth of the component 1 and about halve the linewidth of component 2. Apparently component 1 reflects a homogeneous type of deuterium, whereas component 2 may comprise contributions from different types of deuterium.

The Bloch spectrum at room temperature (Fig. 5.3) shows a broad lineshape component 3 without MAS sidebands and with a relative peak area of ~25%, which is not observed in rotor-synchronized TRAPDOR and Hahn-echo spectra. Thus, TRAPDOR cannot yield information about the specific Mg$_n$Sc$_{4-n}$ coordination of the deuterium atoms contributing to the broad component. Apparently, the transverse relaxation time $T_2$ associated with this broad component at 300 K is too short to survive even the shortest possible echo time $2\tau = 0.25$ ms. Short $T_2$ times in MAS NMR may be a sign of mobility at the sample-rotation timescale, which may be suppressed by decreasing the temperature. Indeed, at 213 K the broad component is absent in the Bloch spectrum (Fig. 5.3a, right). The Bloch spectrum and the rotor-synchronized Hahn-echo spectrum for the shortest echo time $2\tau = 0.25$ ms are closely similar at 213 K. The centerband is slightly asymmetric, which can be accommodated in the lineshape fit by adding a small
component at –2 ppm. This fifth component is also sensitive to $^{45}$Sc NMR irradiation. It is labeled $2'$, because it overlaps and co-varies with component $2$ (2 ppm) in the spectral simulation.

**Figure 5.3:** Centerband region in (a) Bloch spectra, (b) 4-ms Hahn-echo (c) 4-ms $^2$H-$\{^{45}$Sc$\}$ TRAPDOR and (d) difference spectra recorded at (left) 296 and (right) 213 K. (e) decay of the fitted lineshape components (left) 1 and 2 at 296 K and 1 and combined $2 + 2'$ at 213 K. Chemical shifts and linewidths of the lineshape-fit components are given in Table 5.1. Open and closed symbols indicate Hahn-echo and TRAPDOR fitted intensities, respectively.

TRAPDOR and Hahn-echo spectra: For the same reason, the peak areas of components 2 and $2'$ are combined in the TRAPDOR analysis. By extrapolating the TRAPDOR and Hahn-echo decays at 213 K back to echo time $2\tau = 0$, we have previously found roughly equal fractions of deuterium sensitive and insensitive to $^{45}$Sc NMR irradiation. On this basis we assign the signal component at 4 ppm to deuterium without direct Sc neighbours at Mg$_4$ sites, and the combined
Chapter 5

signal components at 2 and −2 ppm to deuterium at tetrahedral sites with at least one Sc neighbor.

Deuterium at the center of a perfect Mg$_4$ or Sc$_4$ tetrahedron should experience no electric field gradient, because the EFG contributions of the four Mg or four Sc atoms cancel one another as a result of the symmetry. In contrast, a significant EFG should arise at the center of mixed Mg$_n$Sc$_{4-n}$ tetrahedrons ($n = 1, 2, 3$) with unequally charged Mg and Sc atoms at the corners. In this respect it is surprising that the quadrupolar constants underlying the sideband patterns associated with signal components 1, 2 and 2’ at room temperature are the same. If, indeed, component 1 would arise from D at Mg$_4$ sites only, and components 2 and 2’ from mixed coordination states, the spinning sidebands at 296 K should be strongly dominated by the latter two components. This is not the case. In fact, apart from the broad component, the overall lineshapes of the centerband and spinning sidebands are closely similar. A possible explanation could be that component 2 (or the combined components 2 and 2’ at 213K) actually reflect only deuterium at Sc$_4$ sites. Then, the observed quadrupolar sideband patterns observed for component 2 and combined components 2 (and 2’) have nothing to do with any mixed coordination state, but have another cause, such as lattice distortions, which may be effectively similar for Mg$_4$ and Sc$_4$ sites.

The lack of chemical resolution between Mg-rich and Sc-rich deuterium sites differs from the $^2$H NMR spectra of the related compound Mg$_{0.65}$Ti$_{0.35}$D$_x$ which also contains Knight-shifted $^2$H NMR signals from conducting TiD$_2$ macro- and nanodomains. A possible explanation for the poorer chemical resolution in the $^2$H NMR spectrum of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ is the relatively small $^1$H NMR Knight shift of bulk ScH$_2$, -7 ppm, compared to TiH$_2$ and TiD$_2$, -150 ppm.

5.4.2 Deuterium exchange at room temperature from 1D and 2D Exsy

2D exchange spectra explicitly reveal exchange between components 1 and 2 at a timescale $> 10^{-2}$ s (Fig. 5.4). At mixing times $< 10^{-3}$, the spectrum shows an oval shape along the spectral diagonal typical of an inhomogeneous resonance. At mixing time $> 10^{-2}$ ms the off-diagonal intensity arising from deuteron exchange between 1 and 2 gives the lineshape a butterfly shape. Comparison of vertical slices with the vertical and horizontal spectral projections shows that the system is completely exchanged after $10^{-1}$ s. 2D exchange NMR spectroscopy is a valuable and
model-free technique to obtain a picture of deuteron exchange in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$. However, it is too time-consuming to be used for extensive measurement of the exchange versus the mixing time. For *quantitative* information we have therefore employed faster 1D exchange NMR spectroscopy with the Hahn-echo and TRAPDOR pulse sequences as initial spin polarization filters. Using a Hahn-echo filter we selectively suppress the polarization of deuterons with short coherence lifetimes, such as 3. With the TRAPDOR filter we can further discriminate between 1 and 2, i.e. deuterons without and with scandium in the first coordination sphere. This initial preparation stage in the exchange experiment is followed by a mixing time, during which the deuterons can move away from their initial environment into another. After the mixing time, the new state of the deuterons, which still carry the polarization reflecting the initial state, is monitored during the final signal detection stage. In this way, one can establish correlations between different deuterium states or environments through time. The 1D version is less model-free, since we do not observe direct correlations between signals at different chemical shifts, but the intensity changes of the spectral components as a function of the mixing time can be interpreted within the qualitative model established from a few 2D spectra.

![2D Exchange $^2$H NMR spectra at 296 K with mixing times of 0.003 and 100 ms.](image)

*Figure 5.4:* 2D Exchange $^2$H NMR spectra at 296 K with mixing times of 0.003 and 100 ms. Horizontal spectral projections are shown above the spectra, vertical projections on the left, as well as the vertical slices taken at 4 and 0 ppm. At mixing times > 10 ms, the deuterons are fully exchanged, as indicated by the similar lineshapes in the projections and slices.

Series of 1D exchange spectra were analyzed with the same lineshape components as above. Fig. 5.5 shows, how the respective intensities vary as a function of the mixing time after an initial 4-
ms TRAPDOR perturbation at 296 K and 213 K. The PdD₂ impurity 4 is prominently present in the 4-ms filtered spectra at 296 K as a result of its relatively long T₂ time at that temperature. Apart from this, the spectra converge within 0.1 s into the respective AIR spectra (Fig.5) independent of the initial perturbation. This suggests that there is open, unrestricted exchange between components 1, 2 and 3 (but not 4) at the 0.1 s timescale. The exchange is mainly driven by component 1, the supposed deuterons with pure Mg coordination, DMg₄. This is in line with the lower initial polarization of the other components resulting from the TRAPDOR filtering. In line with our earlier published TRAPDOR analysis, at 213 K the peak area fraction of component 1 is roughly equal to that of the combined components 2 and 2’ in Bloch spectra and in exchange spectra with tₘᵢｘ ≥ 0.1 s. At 296 K the relative peak area of 2 in the corresponding spectra is approximately equal to that of components 1 and 3 together. Thus, at increasing temperature part of the deuterium atoms represented by component 1 at 213 K are converted into - probably- mobile - deuterium giving rise to the broad component 3. Interestingly, we have observed a similar temperature transition of Mg₄-coordinated deuterium around room temperature in co-sputtered Mg₀.₆₅Ti₀.₃₅D₁.₁. The peak-area variation of the lineshape components as a function of mixing time were fitted in coupled manner with bi-exponential decays as in Eq. 5.2.5a with the long decay time fixed to spin-lattice relaxation time T₁ which was measured independently. The apparent deuterium exchange time τₑₓ estimated in this varies weakly from 6.3 × 10⁻³ s at 296 K to 1.1 × 10⁻² s at 213 K. The remarkably weak temperature dependence is consistent with our previous 2D Exsy results obtained for Mg₀.₆₅Sc₀.₃₅D₂.₂ and 1D Exsy results for ballmilled and co-sputtered Mg₀.₆₅Ti₀.₃₅Dₓ and is probably a sign of a broad mobility distribution.
5.4.3 Overall peak-area analysis

Independently of any detailed lineshape analysis, straightforward spectral integration shows, that the overall intensity is not conserved in the exchange. There is a fast initial decay at a timescale $10^{-3} - 10^{-2}$ s followed by a slower decay at the same timescale as spin lattice relaxation (Fig. 5.6). Such initial loss of overall intensity as described by the constant $C_{\text{all}}$ in Eq. 5.2.7 is indicative for deuterium exchange between states with different NMR visibility. Fig. 5.6 shows how this initial drop $C_{\text{all}}$ depends on different factors. $C_{\text{all}}$ becomes bigger with increasing Hahn-echo filter time, and decreasing sample rotation rate below 16 kHz, although above 16 kHz it is fairly constant. The intensity loss is slightly bigger in TRAPDOR- than in Hahn-echo filtered exchange experiments. In 4-ms Hahn-echo filtered exchange experiments $C_{\text{all}}$ decreases from 0.26 at 296 K
to 0.08 at 213 K (relative to the total peak area in the exchange spectrum recorded with \( t_{\text{mix}} = 0.001 \text{s} \)). The overall intensity drop is also bigger at 4.7 than at 11.7 T.

**Figure 5.6**: Decay of the overall intensity, i.e. the total spectral integral including MAS sidebands, as a function of exchange time up to 0.15 s after an initial (a) 4-ms Hahn-echo and TRAPDOR filter, (b) 4-ms Hahn-echo filter at MAS rates of 4, 8, 16 and 24 kHz, (c) 2-ms and 4-ms Hahn-echo filter, (d) 4-ms Hahn-echo filter at 296, 253 and 213 K and (e) at 4.7 and 11.7 T. (f) temperature dependence of the overall peak intensity in Bloch spectra relative to the intensity at 296 K. Unless specified differently, the temperature was 296 K and the MAS rate 8 kHz. Background decays caused by spin-lattice relaxation are also shown. Curves generally reflect restricted bi-exponential fits of a fast and slow component with the characteristic rate of the slow component fixed to the spin-lattice relaxation rate measured independently.

As mentioned in the introduction, MAS NMR invisibility of quadrupolar nuclei can have two types of origins: (1) the second-order quadrupolar linebroadening > MAS rate, or (2) rotational mobility at the sample-rotation timescale. In both cases MAS does not yield a resolved sideband
pattern, and the corresponding blurred MAS pattern could be invisibly hidden within the noise under the sharper signals of slower or faster components. The clear dependence of $C_{\text{all}}$ on the temperature (Fig. 5.6d) suggests that the reduced MAS NMR visibility of part of the deuterium atoms is caused by deuterium motions at the sample rotation scale. Cooling down the sample may reduce the fraction of deuterium mobile at the MAS timescale and in this way increase the overall visibility. The magnetic-field dependence (Fig. 5.6e) cannot be explained by mobility, however, because deuterium mobility is not affected by the magnetic field. Instead, second-order quadrupolar linebroadening beyond the sample rotation rate could give an explanation, because this broadening is inversely proportional to the $^2$H NMR frequency. Thus at 4.7 T a larger deuterium fraction may have quadrupolar linewidths exceeding the 8-kHz MAS rate, than at 11.7 T. However, quadrupolar broadening is essentially temperature independent. Thus, this cannot explain the observed temperature dependence of $C_{\text{all}}$ (Fig. 5.6f).

As an independent check we have estimated the $^2$H MAS NMR visibility of deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ by comparing the peak area of the MAS sideband pattern in Bloch spectra with the peak area in a separately recorded MAS NMR spectrum of D$_2$O. Careful and repeated peak-area comparison suggests that the peak area in the spectrum of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ at 296 K corresponds to an overall NMR visibility of ~60 %. Then, taking the peak area at 296 K as reference, we have probed the relative change of the peak area as a function of temperature between 253 and 333 K. As illustrated in Fig. 5.6f, the overall peak area in Bloch spectra exactly follows the inverse-temperature dependence of the Boltzmann polarization in this range. Note that the line plotted in the Fig. 5.6f is not a fitted trendline, but the exact representation the Boltzmann polarization: $P(T) = (T_0/T) P(T_0)$, where we took the peak area $P(T_0)$ at the reference temperature $T_0 = 296$ K as 1. Thus, whichever deuterium fraction is NMR invisible at 296 K stays also invisible at higher and lower temperature. Together with the observed magnetic-field dependence, this is evidence for second-order quadrupolar linebroadening as the main cause of the reduced NMR visibility of some of the deuterium spins. These “dark deuterium” atoms are probably located at tetrahedral sites with mixed coordination Mg$_n$Sc$_{4-n}$ ($n=1,2,3$) and thus with strong electric field gradients. In principle, not only raising the magnetic field, but also increasing the MAS rate can raise the MAS NMR visibility of quadrupolar nuclei. The condition for NMR visibility is that the sample rotation exceeds the second-order line broadening. For
deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ faster spinning does not yield a strong effect on the overall peak area in Bloch spectra (Fig. 5.7). At most, the peak area at a MAS rate of 24 kHz is increased by 12% compared to that at 8 or 4 kHz. This indicates that the second-order quadrupolar linewidth of most NMR invisible deuterium is probably larger than 24 kHz at 11.7 T.

![Figure 5.7: Comparison of total peak area at different sample rotation rates. (a) 4 and 8 kHz (4-mm MAS probehead) and (b) 24 and 8 kHz (2.5-mm MAS probehead)](image)

If dark deuterium arises from the second-order quadrupolar linebroadening, what then causes the temperature dependence of the initial overall intensity drop in 1D exchange experiments? It should be noted that $C_{\text{all}}$ does not only depend on the difference in visibility ($v_A - v_B$), but also on the initial polarization difference ($p_A - p_B$) after the Hahn-echo or TRAPDOR filter. The second-order quadrupolar coupling is actually refocused by the $\pi$ pulse in the Hahn-echo. This follows from the inversion of the corresponding spin-operators in the Hamiltonian under rotation over $\pi$ about the x or y axis. For deuterium with its spin $I = 1$ the second-order quadrupolar Hamiltonian without sample rotation is of the form:

$$H_Q^{(2)} = -\frac{\omega_Q^2}{\omega_0} \left[ A(\beta, \gamma) I_z + B(\beta, \gamma) I_z^3 \right]$$  \hspace{1cm} (5.4.3.1)
Dark deuteriums in lightweight hydrogen storage….

with quadrupolar frequency $\omega_Q$ proportional to the local electric field gradient, Larmor frequency $\omega_Q$ proportional to the magnetic field. $A(\beta,\gamma)$ and $B(\beta,\gamma)$ are geometrical factors which in the static NMR case depend on the orientation of the quadrupolar tensors in the multi-crystalline powder with respect to the magnetic field. Explicit expressions for $A(\beta,\gamma)$ and $B(\beta,\gamma)$ can be found in ref. 16. The main thing is that they do not transform as rank-2 tensors and are therefore not completely averaged out by magic angle spinning. At sample rotation rates sufficiently fast to separate the spinning sidebands from the centerband, the residual average Hamiltonian term is essentially of the same form as Eq. 5.4.3.1, but with new geometrical factors $A_{\text{MAS}}(\beta',\gamma')$ and $B_{\text{MAS}}(\beta',\gamma')$ which now depend on the tensor orientation in the rotor axis system. Magic angle spinning reduces the second-order quadrupolar linewidth of the central transition by a factor 3.1 compared to without sample rotation. As follows from the spin-rotation symmetry of Eq. 5.4.3.1, there is no direct effect of the second-order quadrupolar interaction on Hahn-echo and TRAPDOR decays $I(2\tau) = \exp(-R \cdot 2\tau)$ (Fig. 5.2) or the initial polarizations $p_A$ and $p_B$ after the Hahn-echo and TRAPDOR filters.

Let us, for simplicity, assume that the deuterium spins in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$ can be divided into NMR visible deuterium spins, on the one hand, and totally invisible, “dark” deuterium spins, on the other. Then, according to Eq. (5.2.7), $C_{\text{all}}$ equals the product of the invisible deuterium fraction $f_B$ and the relative initial polarization difference $(1-p_B/p_A)$. Interestingly, this means that we may get insight into the Hahn-echo and TRAPDOR decay behavior of the invisible deuterium spins despite their NMR invisibility. Table 5.2 shows $C_{\text{all}}$ values for 1D Exsy with initial 2-ms and 4-ms Hahn-echo and TRAPDOR filters at 296 K. The factor 2 difference between the selected filter times $2\tau_2 = 4\tau_1 = 4$ ms allows us to divide the numerator and denominator in Eq. 5.2.8 by $1+\exp(-R \cdot 2\tau_1)$ and simplify this equation to:

$$r = 1 + \exp(-\Delta R \cdot 2\tau_1)$$  \hspace{1cm} (5.4.3.2)

where $r = C_{\text{all}}(4\tau_1)/C_{\text{all}}(2\tau_1)$ denotes the ratio between the initial intensity drops in 4-ms and 2-ms filtered Exsy. Once determined, $\Delta R$ can be substituted into Eq. 5.2.7 to calculate the invisible deuterium fraction $f_B$. If the Hahn-echo or TRAPDOR decay rate $R_A$ of the visible deuterium fraction is known from independent measurements, the corresponding decay rate $R_B$ of the invisible fraction:

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\[ R_B = R_A - \frac{\ln(r - 1)}{2\tau_1} \]  
(5.4.3.3)

Table 5.2 shows the resulting \( f_B \) and \( R_B \) values for Hahn-echo and TRAPDOR filtered Exsy with initial polarization filter times of 2 and 4 ms at 213, 253 and 296 K. Earlier in this chapter, we concluded from the Boltzmann temperature dependence of the overall NMR intensity (Fig. 5.6), that the overall \(^2\text{H}\) MAS NMR visibility does not change as a function of temperature. In contrast, analysis of \( C_{\text{all}} \) values from Exsy at different temperatures by use of Eqs. 10 and 7 suggests that the NMR invisible fraction does change with temperature. This apparent contradiction is probably a sign that the real deuteride material is more complex than the “black-and-white” exchange model with only visible and completely invisible deuterium states.

Table 5.2: Fit parameters to the overall intensity decays in 2-ms and 4-ms Hahn-echo Exsy at 296, 253 and 213 K. The spin lattice relaxation time \( T_1 \), Hahn-echo decay rates were obtained from separate experiments. \( \Delta R \) is the difference in the decay rate \( (R_B - R_A) \). The MAS rate was 8 kHz.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>echo time (ms)</th>
<th>( \tau_B ) (ms)</th>
<th>( T_1 ) (s)</th>
<th>( C_{\text{all}} )</th>
<th>( \Delta R ) (ms(^{-1}))</th>
<th>( f_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>2</td>
<td>10</td>
<td>2</td>
<td>0.20</td>
<td>0.55</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7</td>
<td></td>
<td></td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>253</td>
<td>2</td>
<td>13</td>
<td>3</td>
<td>0.11</td>
<td>0.38</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td></td>
<td></td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>213</td>
<td>2</td>
<td>9</td>
<td>6</td>
<td>0.07</td>
<td>0.90</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>
5.5 Conclusion

The initial decrease of the overall intensity, which we observe after a Hahn-echo or TRAPDOR filter in $^2$H MAS NMR Exsy, can be explained by deuterium exchange between NMR visible “bright” states and less visible, or even invisible “dark” states in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$. The dependence of this phenomenon on the magnetic field and MAS rate suggests that the $^2$H MAS NMR invisibility is controlled by the second-order quadrupolar linebroadening, like also known for $^{27}$Al MAS NMR of alumina and zeolites. In such picture, part of the deuterium atoms, most probably those at mixed tetrahedral sites Mg$_n$Sc$_{4-n}$ (n=1,2,3) with strong local electric field gradients in the material, have a second-order linebroadening well beyond the MAS rates 8-24 kHz applied in this study. As judged from the observed Boltzmann temperature dependence of overall NMR intensity, the effective $^2$H MAS NMR visibility of deuterium atoms in in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ appears temperature independent, as expected for NMR visibility controlled by quadrupolar linebroadening. Nevertheless, the initial drop of overall intensity in Exsy does depend on the temperature. This indicates that this phenomenon is not only controlled by differences in NMR visibility, but also by transverse relaxation caused by deuterium mobility.

With part of the deuterium atoms being NMR invisible, the observed sideband pattern in $^2$H MAS NMR probably consists of signals at tetrahedral Mg$_4$ and Sc$_4$ sites. As a result of the tetrahedral symmetry, the local electric field gradients at these sites should theoretically vanish, and in practice result in relatively small first- and second-order quadrupolar linebroadening. This also explains better, why the $^2$H-$^{45}$Sc TRAPDOR insensitive part of the $^2$H MAS NMR signal assigned to deuterium at Mg$_4$ sites, has similar relative sideband intensities as the TRAPDOR sensitive part attributed to deuterium at sites with at least one Sc atom. If the $^2$H MAS NMR signal of deuterium at mixed sites is broadened beyond detection, the first-order linebroadening reflected by the sideband-pattern envelope in $^2$H MAS NMR of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ is probably caused by lattice distortion. Analysis of the Exsy data in terms of a two-state model for deuterium exchange between NMR visible and invisible states suggests that at room temperature as much as ~30 % of the deuterium fraction seems NMR invisible. The existence of a significant fraction of invisible deuterium atoms has consequences for our previous conclusions from $^2$H-$^{45}$Sc TRAPDOR. In that study we concluded that ~50% of deuterium in Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ is
located at Mg$_4$ sites, and that therefore the Mg and Sc atoms in this material show a fair degree of segregation. With part of the deuterium atoms being NMR invisible, the fraction of deuterium atoms at Mg$_4$ sites is actually less. E.g., taking the 30% invisible fraction estimated from Exsy at room temperature, or the – earlier mentioned- 50% overall visibility estimated from comparison with the $^2$H NMR signal of D$_2$O, the actual Mg$_4$ coordinated deuterium fraction would be between 0.25 and 0.33, which is closer to the statistical value of $0.65^4 = 0.18$ expected for random distribution of Mg and Sc over the metal positions in the fluorite structure of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$. A lower degree of (nano)segregation is also naturally consistent with the relatively fast and complete deuterium exchange between Mg rich and Sc rich sites, which we have observed in our previous study.

5.6 References


16 Iuga, D., Nuclear magnetic resonance studies of half-integer quadrupolar nuclei, Thesis (Radboud University 2003)
Chapter 6

$^1$H NMR quantification of different hydrogen-containing phases in nano-composites of MgH$_2$ and carbon

Abstract

We have investigated MgH$_2$ encapsulated in nanoporous carbon prepared by melt-infiltration both qualitatively and quantitatively. Solid-state $^1$H NMR, powder XRD and TPD were used in a combined approach to study these nanocomposites. Magic-angle spinning $^1$H NMR shows two components with different spin-lattice relaxation times. XRD shows the presence of bulk Mg and bulk MgH$_2$. The component with long $T_1$ time is assigned to a bulk MgH$_2$ phase which is also observed with XRD. The other component with shorter spin-lattice relaxation time is assigned to hydrogen inside the pores of carbon, MgH$_2$ or Mg(OH)$_2$. Static $^1$H NMR spectra show a narrower linewidth for nano-MgH$_2$ or Mg(OH)$_2$ than for bulk-MgH$_2$. This implies higher mobility of hydrogen atoms within the pores of carbon. Two-Dimensional Exchange Spectroscopy reveals interaction of hydrogen from the carbon support with the hydrogen from MgH$_2$ or Mg(OH)$_2$ within the pores of carbon. Quantification of the hydrogen-containing phases is difficult. We have utilized a combined approach to identify and quantify different phases within MgH$_2$ carbon nano-composites.
6.1 Introduction

Fossil fuels provide approximately 80% of the total world energy supply.\(^1\) They are of great concern because of their finite availability and also harmful effects on the environment such as global warming and pollution. An attractive option is the use of hydrogen as an energy carrier. Hydrogen storage in the form of pressurized gas or cryogenic liquid is possible. The challenge is to store the hydrogen with higher volumetric and gravimetric densities than in the gaseous or liquefied state. Metal hydrides are promising materials to store hydrogen chemically in a more compact and effective way. Some of these, such as LaNi\(_5\) and Mg\(_2\)Ni, are already in use as anode materials in rechargeable batteries. However, the gravimetric capacity of the current materials is too low to meet the storage specifications set by US Department of Energy.\(^2\) Therefore, materials with higher gravimetric capacity are investigated such as alanates,\(^3\) borohydrides.\(^4\)

In search of an ideal metal hydride, Mg is studied for its cost effectiveness and high abundance. Its hydride has a high gravimetric capacity of 7.7 wt.-% of hydrogen. However, it suffers from slower absorption/desorption kinetics and a high thermodynamic stability. Its formation enthalpy is \(-74\) kJ/mol and hence \(\sim 300\) °C is needed to obtain an equilibrium pressure of 1 bar. There are different approaches to overcome these problems. Notten and co-workers demonstrated that the kinetics can be improved by structural modification of MgH\(_2\) from rutile to fluorite.\(^5,6,7,8,9\) Upon addition of a minimum of 20 at.-% of a transition metal to Mg, the crystal structure after hydrogenation transforms into a fluorite type. Nano-structuring\(^10,11\) by use of ball-milling with and without Transition metal (TM) additives improves the kinetics. Nano-structuring of MgH\(_2\) initially increases the hydrogen-sorption kinetics, but the agglomeration of the nano-particles (from \(\sim 20\) nm to \(\sim 80\) nm) after cycles of hydrogen absorption/desorption deteriorates the kinetics. To stabilize the particle size, addition of grain refiners were proposed.\(^12,13\)

In a third approach, the thermodynamics of thin Mg films with thickness \(<\) 10 nm were shown to be affected by the elastic constraints.\(^14\) A DFT study\(^15\) showed that desorption energy of MgH\(_2\) decreases when the crystallite size is smaller than 1.3 nm. Several studies are reported on the confinement of MgH\(_2\) within the pores of carbon-based materials.\(^16,17,14\) One way to obtain the nano-meter sized Mg particles is by melt-infiltration\(^18\) of Mg into a nano-porous carbon...
substrate. In this way, agglomeration of MgH₂ nano crystallites into bigger crystallites can be avoided while absorption/desorption cycles are performed.

For analyzing complex metal-hydride materials, a single characterization technique may not give sufficient information to define the material structural properties completely. X-ray diffraction and Neutron Diffraction are useful for materials that possess long-range structural ordering. Nuclear Magnetic Resonance (NMR) spectroscopy does not require crystallinity. Moreover, with NMR, we can locate and also study the dynamics of energy carriers, i.e. hydrogen atoms, directly instead of indirectly studying the properties of hydrogen-storage materials by observing the surrounding matrix of metals atoms. NMR study on hydrogen-storage Mg₀.₆₅Sc₀.₃₅D₂.₂ revealed the presence of deuterium in Mg-rich and Sc-rich clusters within the XRD determined homogenous lattice.¹⁹ In a previous study, preparation of Mg:C nanocomposites via Mg melt-infiltration and characterization with XRD, SEM and N₂ physisorption techniques were reported.¹³ Mg goes into pores of carbon up to ~ 10-15 wt.-% of MgH₂ loading. The reflections from Mg and MgH₂ within the pores are not observed with XRD and hence lack long-range crystallinity.

In this chapter, we combine NMR along with X-ray Diffraction (XRD) and Temperature Programmed Desorption (TPD) to identify and quantify different hydrogen-containing phases present in the Mg-nano-composites. Quantification of different phases present in these nano-composites poses a challenge in two ways. First, nano-particles within the pores of carbon are too small to be detected by XRD. Second, the conductivity of the nano porous carbon results in the so-called skin-depth and as a consequence, NMR visibility is affected.²⁰

6.2 Experimental

MgH₂ was obtained as a powder from Goldschmidt GmbH (35µm Tego Magnan). Carbon/High surface area graphite with pores of size 2-3 nm was obtained from Timcal Ltd., Bodio, Switzerland. In a typical experiment, 1 g of carbon was dried and mixed with MgH₂ in a mortar. This mixture was placed in a flash-dried alumina cup (20 × 20 × 50 mm) and transported under a nitrogen atmosphere to a tube furnace. The quartz tubes (50 × 1000 mm) in the tube furnace (Thermolyne 79300) were pre-dried at 100 °C under an Argon flow (300 ml/min). To limit the evaporation of magnesium, we placed the sample cup in a narrow alumina tube (30 × 60 mm) inside the quartz tube. A cup with sacrificial MgH₂ was placed in the gas stream just before
the sample as an oxygen and water scavenger. The sample was heated to 625 °C at 2.5 °C/min and kept there for 10 min before heating further to 666 °C at 1 °C/min with an Ar flow of 30 ml/min. After 10 min just above the melting point of magnesium, the samples were slowly cooled to room temperature and at around 350 °C, H\textsubscript{2} was introduced to replace Ar in the gas stream. The melt infiltration is always followed by hydrogenation at 50 bar and 325 °C for 6 hrs. After preparation, all samples were stored and handled under argon atmosphere. The nano-composites prepared by melt infiltration method with 5, 10, 15 and 20 wt.-% loading of MgH\textsubscript{2} will be denoted by 5 wt.-% MgH\textsubscript{2}:C, 10 wt.-% MgH\textsubscript{2}:C, 15 wt.-% MgH\textsubscript{2}:C and 20 wt.-% MgH\textsubscript{2}:C respectively.

NMR experiments were performed on a Bruker DMX 500 and 200 spectrometer operating at 500 and 200 MHz for protons, respectively. A 2.5-mm probehead was used for Magic-Angle Spinning (MAS) experiments and 7-mm probehead was used for static measurements. The typical sample spinning rate was 20 kHz. A three pulse sequence 90\textsubscript{ax}−90\textsubscript{ax}−\tau-90\textsubscript{y} with short T\textsubscript{1} filter time \(\tau = 5\) ms was used to eliminate the background signal from the probe materials. The time interval between every scan was kept at 6000 s to allow magnetization to reach equilibrium value. Tetramethylsilane was used as a reference. Two-Dimensional Exchange spectroscopy (2D Exsy) was performed with the three-pulse NOESY sequence\textsuperscript{21} with a 90° pulse length of 1.25 μs. The mixing times were 0.001, 0.01 and 0.1 s, respectively. Powder X-ray diffraction patterns were recorded with a Bruker AXS D8 diffractometer equipped with Co-K\textsubscript{α12} radiation of wavelength 1.7889 Å, covering 2θ range from 20° to 90° with a step size of 0.0085°. Samples were kept in an air-tight dome holder during measurement to prevent oxidation. Rietveld analysis was performed with Rietica 1.7.7 software. CeO\textsubscript{2} was used as internal standard for quantitative analysis. TPD was performed with Micromeritics AutoChem II RS232 equipped with a TCD detector. The sample was heated from room temperature to 400° C at the rate of 5° C/min.

6.3 Results and Discussion

We have utilized X-ray diffraction, (XRD), Temperature Programmed Desorption (TPD) and solid-state Nuclear Magnetic Resonance (NMR) to identify and quantify the different hydrogen-containing phases in MgH\textsubscript{2} nano-composites. Since each method identifies one or more components, here we summarize the phases that are identified with every method and give a correlation map between every method to obtain the information the hydrogen-containing
phases. To start, the hydrogen-containing phases within the pores of carbon and outside the carbon are termed nano and bulk, respectively. Both in nano and bulk phases, there are Mg, MgH$_2$ and Mg(OH)$_2$. Table gives the method and also the phases that can be identified with that method.

Table 6.1: TPD, XRD and NMR detectability of the different species in the nano- and bulk phase in MgH$_2$-carbon nano-composites.

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Nano phase</th>
<th>Bulk phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
<td>Mg(OH)$_2$</td>
</tr>
<tr>
<td>TPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>![Red Block]</td>
<td>![Red Block]</td>
</tr>
<tr>
<td>NMR</td>
<td>![Red Block]</td>
<td>![Red Block]</td>
</tr>
</tbody>
</table>

The red blocks indicate the species in the nano and bulk phases that can be identified. If a red blocks crosses a column border, both species cannot be identified separately. They can be quantified as a single phase. E.g. with NMR we cannot separate the signals from MgH$_2$ and Mg(OH)$_2$ within the overall nano-phase, as a result of the strong susceptibility broadening caused by the carbon support. However, we can distinguish between nano and bulk phase. Likewise, the TPD used in this study detects the overall amount of released H$_2$. Other possibly released compounds, such as water from Mg(OH)$_2$ are not detected. Finally XRD can only detect crystalline structures in the bulk phase. Species in the nano-phase are XRD-invisible due to the short coherence length. By combining XRD, TPD and NMR we hope to get a detailed picture of MgH$_2$ carbon nano-composite. E.g., to get the hydrogen content in nano MgH$_2$ phase, the difference between the overall hydrogen content from TPD and the hydrogen content from the bulk MgH$_2$ as estimated from XRD can be utilized.
6.3.1.1 XRD characterization

In a previous study,\textsuperscript{18} de Jongh et al. reported that up to \(~ 10\text{-}15\) wt.-% of MgH\textsubscript{2} loading at the start of the melt impregnation, no bulk Mg was formed, which implies that most of the Mg is within the nano-pores of the carbon support. Fig. 6.1 shows XRD patterns of nano-composite materials loaded with different amounts of MgH\textsubscript{2}. The diffraction lines of carbon occur at \(2\theta\) values of 30.4° and 50-55°. The reflections corresponding to bulk hcp-Mg are seen at angles \(2\theta\) equal to 37.5, 40.1, 42.8, 56.2, 67.6 and 74.8° \(2\theta\) for 15 and 20 wt.-% MgH\textsubscript{2}:C. The reflection at 42.8° \(2\theta\) is the most intense line in the XRD pattern of Mg. This peak is seen along with another peak at 37.5° \(2\theta\) for 10 wt.-% MgH\textsubscript{2}:C. This indicates that bulk Mg is present, but in negligible amounts. The reflections at 32.6, 41.7, 46.6, 64.4, 68.2, 77.2 and 80.1° \(2\theta\) correspond to rutile MgH\textsubscript{2} and they are seen for all the nano-composites. The presence of bulk Mg indicates that not all bulk Mg was converted to bulk MgH\textsubscript{2} after hydrogenation. CeO\textsubscript{2} was used as internal reference for quantitative analysis. The reflections at 33.4, 38.7, 56.0, 66.8, 70.1 and 83.0° \(2\theta\) arise from cubic CeO\textsubscript{2}. The crystal coherence length can be calculated using Debye Scherrer formula given by

\[
L = \frac{0.9\lambda}{\beta \cos \theta} \tag{6.3.1.1}
\]

where \(L\) is crystallite size, \(\lambda\) is X-ray wavelength, \(\beta\) is the Full Width at Half Maximum (FWHM) of diffraction peak in radians and \(\theta\) is Bragg angle. The FWHM of peaks in the XRD pattern of carbon varies and as a consequence value of \(L\) also varies between 4-10 nm. The coherence lengths of bulk-Mg and bulk-MgH\textsubscript{2} are in the order of 50 - 60 nm.
6.3.1.2 XRD quantification

Carbon is highly amorphous and this gives broad peaks in the XRD patterns. Therefore, probably, this fact makes Rietveld refinement for carbon a difficult task. Hence, another calibration procedure was followed. Peak areas from individual reflections from a pattern were used instead of Rietveld refinement. First, physical mixtures of known weight proportions of carbon and CeO$_2$ were used. Once the amount of carbon is calibrated from this procedure, physical mixtures of known amounts of Mg and MgH$_2$ with carbon were analyzed. The peak areas of Mg and MgH$_2$ in the physical mixtures were independently calibrated with respect to the peak area of carbon. After this calibration procedure, the MgH$_2$ nanocomposites were analyzed.
MgH₂ or Mg(OH)₂ within the pores of carbon are not observed with XRD and hence, we quantify the bulk MgH₂. Even though the amount of bulk-MgH₂ phase is obtained from the scattering of X-rays by the electrons of Mg atoms in bulk-MgH₂ phase, it is easier to compare the amount of hydrogen from bulk-MgH₂ phase with the amounts obtained from TPD and NMR methods as the latter techniques observe only the hydrogen atoms. The absolute amount of hydrogen from bulk-MgH₂ is given in Table 6.2. As the amount of MgH₂ in the starting material increases, the amount of bulk-MgH₂ phase also increases.

Table 6.2 Absolute amount of hydrogen in bulk MgH₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absolute amount of hydrogen in bulk-MgH₂ (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt.-% MgH₂:C</td>
<td>0.07</td>
</tr>
<tr>
<td>15 wt.-% MgH₂:C</td>
<td>0.44</td>
</tr>
<tr>
<td>20 wt.-% MgH₂:C</td>
<td>0.76</td>
</tr>
</tbody>
</table>

### 6.3.2 Temperature Programmed Desorption

While XRD gives the amount of bulk MgH₂ and Mg phases present in these nanocomposites, Temperature Programmed Desorption (TPD) gives the overall hydrogen content from nano-MgH₂ phase as well from bulk-MgH₂ phase. Fig 6.2 shows TPD curves of 10, 15 and 20 wt.-% MgH₂:C. For the 10 wt.-% MgH₂:C material the hydrogen desorption starts above ~ 200 °C which is well below the value of 400 °C for the bulk MgH₂. TPD curves of 15 and 20 wt.-% MgH₂:C are shifted to higher temperature than curve of the 10 wt.-% MgH₂:C, although a small percentage of hydrogen starts to desorb at ~ 300 °C onward. The increased temperature for desorption could indicate two possibilities. The first possibility is that the hydrogen from nano-MgH₂ has already desorbed before the TPD measurement and only hydrogen desorption from bulk MgH₂ is observed. The second possibility is formation of Mg(OH)₂ layer on top nano-MgH₂ and as a result hydrogen release starts only after the Mg(OH)₂ layer decomposes into magnesium oxide and water vapor. To check the quality of the samples for the stored amount of hydrogen and also for possible oxidation during transportation, handling, or during the NMR measurement, one part of the sample was used for NMR measurements and the other part of the
sample was stored in the glove box. TPD was performed for samples that were measured with NMR and, also that were only stored in the glove box.

![Temperature Programmed Desorption curves of 10 (green), 15 (red) and 20 (blue) wt.-% MgH₂:C immediately after preparation.](image)

**Figure 6.2: Temperature Programmed Desorption curves of 10 (green), 15 (red) and 20 (blue) wt.-% MgH₂:C immediately after preparation.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>As prepared (wt.-%)</th>
<th>After NMR characterization (wt.-%)</th>
<th>Stored in the glove box (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt.-% MgH₂</td>
<td>0.43</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>15 wt.-% MgH₂</td>
<td>0.63</td>
<td>0.46</td>
<td>0.45</td>
</tr>
<tr>
<td>20 wt.-% MgH₂</td>
<td>1.04</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Table 6.3: TPD quantification of hydrogen content at different stages of measurement**

Table 6.3 summarizes the results. The desorbed amount of hydrogen after preparation of the samples increases with the initial composition of MgH₂ in the nano-composites. However, the amount of hydrogen desorbed from every sample decreases compared to the amount after preparation for the samples after NMR characterization. This is very important since the NMR measurement takes approximately 20 hrs for each measurement because of long \(^1\)H spin-lattice relaxation time. During this time, the samples are more vulnerable to oxidation. The similarity of
the amount of desorbed hydrogen for samples after NMR characterization with the samples stored in the glove box implies that quality of the samples is not affected significantly between these measurements. The effect of oxidation will be discussed in a separate section along with the NMR results.

6.3.3 NMR characterization

6.3.3.1 Susceptibility and rf penetration

Fig. 6.3 shows the Magic Angle Spinning (MAS) $^1$H NMR spectrum of carbon nanocomposite with 5 wt.-% MgH$_2$:C recorded at 11.7 and 4.7 T, respectively. Both spectra show a gaussian centerband with no obviously resolved signals from MgH$_2$ or Mg(OH)$_2$. (The narrow signal at ~ 1 ppm corresponds to background signal from probe material). The Full Width at Half Maximum (FWHM) of the centerband is ~50 ppm at both magnetic fields (25 and 10 kHz at 11.7 and 4.7 T, respectively). This broadening is probably caused by bulk magnetic susceptibility of carbon support. The strong susceptibility broadening at 11.7 T explains the unresolved sideband pattern at that field strength. Dipolar line broadening mechanism cannot be a major source of line broadening of the center and sidebands, since the associated linewidth would be field independent in Hz. Regarding susceptibility broadening, the Magnetic flux density, $B$, is given by

$$B = \mu_0 H_0 (1 + \chi) \quad (6.3.3.1.1)$$

where, $H_0$ is the magnetic field and $\mu_0$ is permeability of vacuum, $\chi$ is the susceptibility tensor. This implies that local field experienced by a nucleus is modified by the bulk magnetic susceptibility (BMS) and is proportional to the magnetic field. The ratio between the centerband linewidth (in units of Hz) and MAS rotation frequency is $> 1$ at 11.7 T compared to ratio at 4.7 T and hence we observe a spectrum without resolved sidebands at 11.7 T.

If the susceptibility is isotropic the induced magnetic moment of a volume element in the sample is independent of the orientation with respect to the external field. The magnetic dipole coupling between a nuclear spin and such volume element would simply follow the standard orientation dependence of the dipole coupling between nuclear spins, and thus be averaged by MAS. However, if the susceptibility is anisotropic (Anisotropic Bulk Magnetic Susceptibility (ABMS), the induced magnetic moment of a volume element in the sample depends on the
orientation. Then, the dipole interaction between a nuclear spin and the volume element does not transform as a rank-2 tensor and, as a consequence, the susceptibility broadening is not averaged out completely by MAS. According to Samoson et. al. the dominant effect of anisotropic bulk magnetic susceptibility under MAS conditions is an isotropic term of the form:

$$\omega_K = -\frac{\omega_0}{9\pi} \int \frac{\chi_D}{r^3} dV$$

(6.3.3.1.2)

where $\omega_0$ is the Larmor frequency of the nuclear spin and $\chi_D$ is the susceptibility tensor component along the vector $r$ connecting the spin $I$ and the volume element with induced magnetization. The above equation shows that chemical shift varies inversely with the cube of the distance from the induced magnetization. For a heterogeneous, nano-porous material with a high susceptibility, such as carbon, this leads to a range of isotropic shifts and therefore strong inhomogeneous broadening of the centerband in MAS NMR spectra.

![Figure 6.3: 20-kHz MAS $^1$H NMR spectra of 5 wt.-% MgH$_2$C. The red and black colored spectra are recorded at 11.7 and 4.7 T respectively. The narrow signal at ~ 1.5 ppm is from probe materials. Spinning sidebands are marked with stars, *.

On a closer look at both spectra, the relative peak area of the $^1$H NMR signal scaled with respect to a diamagnetic material such as adamantane, is smaller at 11.7 T than at 4.7 T. The carbon support present in these materials is highly conductive in nature. One problem associated with NMR experiments on conducting samples is the so-called skin-depth, d. An electromagnetic
(EM) wave entering a conducting sample is damped and reduces in amplitude by a factor $1/e$ over the distance $d$ given by

$$d = \sqrt[\sqrt{\mu_r \nu_{rf}}]{\frac{\rho}{\mu_0 \nu_{rf}}}$$  

(6.3.3.1.3)

Where $\rho$ is resistivity, $\nu_{rf}$ is applied frequency of EM wave and $\mu_r$ is relative permeability of medium. Therefore, those nuclei that are present at a distance greater than $d$ will not feel the RF field and hence will not be excited. As a result, NMR signal will not be observed from these nuclei. This will lead to non-quantitative spectra compared to a signal from diamagnetic material. As can be seen from Eq. 6.3.3.1.3, $d$, is inversely proportional to the applied frequency. Hence, RF penetration depth is higher at a lower field. To assess the quantitativity of the NMR measurement, we systematically varied the amount of the sample and measured the NMR signal intensity at two different fields. Fig. 6.4 shows the relative peak areas calibrated with respect to the peak area of 1 g of adamantane at 11.7 and 4.7 T. The intensity at 0 mg refers to the background signal from the empty sample holder and probe-head material. At 11.7 T, the NMR signal intensity increases linearly with the amount of the sample up to 5-6 mg. However, beyond 6 mg, the observed intensity decreases. In contrast, at 4.7 T, the NMR signal intensity increases linearly even up to ~ 7-8 mg. This implies that lower field is better for a quantitative approach. The data at 11.7 T up to ~ 5-6 mg of the sample can be fitted with a linear fit. The absolute amount of hydrogen was obtained and then the linear fits at two magnetic fields can be fitted with the same slopes.
Figure 6.4: Relative peak area compared with respect to 1 g of adamantane at 11.7 and 4.7 T with varied amounts of nano-composite material. Finite amount of hydrogen at 0 mg represents NMR signal from probehead materials or from the sample holder. The lines connecting the points are just guide to eye.

Fig. 6.5 shows the absolute amount of hydrogen calibrated with respect to 1 g of adamantane and also the background is subtracted. The slope of the line at 11.7 T and 4.7 T are similar which indicates that NMR signal intensity is proportional with the amount of sample at both fields.
Chapter 6

Figure 6.5: Absolute amount of hydrogen after background subtraction and calibrated with respect to 1 g of adamantane at 11.7 and 4.7 T with varied amounts of nano-composite material.

The loss of signal intensity at 11.7 T for samples with amounts > 6 mg indicates that skin-depth plays a role. We were not able to get exact values of the resistivity of the carbon. However, using the values of graphite, we get skin-depth values in the order of 60 and 95 microns at 500 and 200 MHz, respectively. The particle size is in the order of nanometers and hence skin-depth theoretically, should not be an issue for the loss of signal at higher magnetic field. However, smaller particles can have conductive contacts and form an effective bigger particle of size greater than the skin-depth. In a report on NMR of Cu particles, signal intensity turned weak when the Cu particles were tightly packed into NMR sample holder. This was attributed to the skin-depth of conducting Cu particles. We can conclude that skin-depth is the cause of loss of signal intensity for densely packed samples at higher magnetic field and quantitative NMR can be performed at 4.7 T.

6.3.3.2 MAS NMR spectra

Fig. 6.6 shows the $T_1$-filtered MAS $^1$H NMR spectra of bulk MgH$_2$, the physical mixture of carbon with 20 wt.% of MgH$_2$ and MgH$_2$:C with varied MgH$_2$ composition. The black and purple colored spectra denote $T_1$-filtered spectra at a filter time of 0.005 and 5 s, respectively.
Figure 6.6: $T_1$-filtered $^1$H MAS NMR spectra of (a) bulk MgH$_2$ (b) a physical mixture of carbon with 20 wt. % bulk MgH$_2$ (c) 10 wt.-% MgH$_2$:C (d) 15 wt.-% MgH$_2$:C (e) 20 wt.-% MgH$_2$. The spectra with black and red color are recorded with a $T_1$-filter time of 0.005 and 5 s respectively. The inset at the top of the figure shows the centerband of bulk-MgH$_2$ and physical mixture of carbon with MgH$_2$ (black and red respectively). The broader centerband of physical mixture carbon with MgH$_2$ compared to bulk-MgH$_2$ illustrates the effects of susceptibility of carbon support. The centerband of all MgH$_2$ nanocomposites contains an upfield shifted component and this component vanishes with a $T_1$-filter time of 5 s. The spectrum in brown color in Fig. 6.6 e shows the difference spectrum between $T_1$-filtered spectrum at a filter time of 0.005 and 5 s. This yields a peak at $\sim$ –8 ppm. Spinning sidebands are marked with stars, *.

Bulk-MgH$_2$ shows a peak centered at 3.5 ppm with spinning sideband pattern. The spectrum of physical mixture of MgH$_2$ with carbon is shifted upfield and shows a peak at 1.5 ppm. The inset at the top of the Fig 6.6 shows the centerbands for comparison. The red and black
lines correspond to bulk MgH$_2$ and physical mixture of bulk MgH$_2$ with carbon respectively. The centerband of the physical mixture of MgH$_2$ with carbon is broader by ~ 2 ppm than that of bulk MgH$_2$ and shifted upfield by ~ 2ppm. This is probably caused by the susceptibility of carbon. The centerband of 10, 15 and 20 wt.-% MgH$_2$:C is asymmetric with an upfield shoulder. This suggests different chemical sites or phases within this peak. With a T$_1$-filter time of 5 s, the peak position of this main line is not affected, but the upfield shoulder disappears. The spectrum in red in Fig. 6.6 e shows the difference spectrum between the spectrum at T$_1$-filter time of 0.005 and 5 s of 20 wt.-% MgH$_2$:C. This shows a peak at -8 ppm, which is even more shifted upfield compared to the signal from the physical mixture of bulk MgH$_2$ with nano-porous carbon. Hence, the hydrogen, which resonates at -8 ppm, is closer to nano-porous carbon than the hydrogen from physical mixture of MgH$_2$ with carbon.

### 6.3.3.3 Static NMR spectra

In static $^1$H NMR experiments of metal hydrides, the dipole interactions between the hydrogen spins are not averaged like in MAS NMR. This gives rise to a broad line in static $^1$H NMR spectra. Hydrogen mobility causes averaging of the dipole couplings yielding motionally averaged resonance lineshapes. Fig.6.7 shows the static T$_1$-filtered $^1$H NMR spectra of bulk MgH$_2$, a physical mixture of carbon with 20 wt.-% of MgH$_2$ and MgH$_2$ nano-composites with varied MgH$_2$ loading. The spectra with black and purple color indicate T$_1$-filtered spectrum at a filter time of 0.005 and 5 s, respectively. The Quasi Pake-like$^{26}$ feature in the spectrum of bulk MgH$_2$ has been observed before$^{27}$ and is an artifact arising from the fast signal decay compared to the receiver dead time of the spectrometer. As a result, the initial points in Free Induction Decay (FID) are not properly recorded.

The lineshape of 10, 15 and 20 wt.-% MgH$_2$:C consists of superposition of narrow and a broad component. The narrow component vanishes at a short T$_1$ time. The lineshape of the remaining broad component is similar to that of bulk MgH$_2$. 

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Figure 6.7: Static $^1$H NMR $T_1$-filtered spectra of (a) bulk-MgH$_2$ (b) a physical mixture of carbon with 20 wt.-% MgH$_2$ (c) 10 wt.-% MgH$_2$:C (d) 15 wt.-% MgH$_2$:C (e) 20 wt.-% MgH$_2$. The spectra with black and red color are recorded with a $T_1$-filter time of 0.005 and 5 s respectively. The brown colored spectrum in (d) is recorded with a filter time of 500 s. The spectra of all MgH$_2$:C (represented by black color) at a $T_1$-filter time of 0.005 contain narrow as well as broad peak. The narrow peak vanishes at a $T_1$-filter time of 5 s. The narrow peak indicates higher mobility of hydrogen atoms.

Static as well as MAS NMR spectra show two components with different spin-lattice relaxation time $T_1$. The fact that two lineshape components with such different $T_1$ times are observed indicates that these are well separated. Otherwise, spin-diffusion or hydrogen exchange would be able to average the $T_1$ time. Therefore, based on above arguments, we can assign the narrow component from static NMR spectra to the component which is shifted upfield and
resonates at \sim -8 \text{ ppm} in the MAS NMR spectrum. XRD (Fig. 6.1) reveals the presence of bulk-MgH$_2$ for 10, 15 and 20 wt.-% MgH$_2$:C. Hence, on the basis of XRD and also long-$T_1$ behavior of the broad component in the MgH$_2$ nanocomposites, we assign the signal at 1.5 ppm to the bulk-MgH$_2$ phase. This line position is similar to that of physical mixture of bulk-MgH$_2$ with carbon. The signal at -8 ppm belongs to protons with a shorter $T_1$ time is assigned to MgH$_2$ or Mg(OH)$_2$ encapsulated within the nanoporous carbon and henceforth called the MgH$_2$/Mg(OH)$_2$ nano-phase. The nano-porous carbon also contains hydrogen. (see section 6.3.3.6 for more details). Therefore, the signal at – 8 ppm also contains the signal from carbon support.

We have distinguished the bulk-MgH$_2$ phase and MgH$_2$/Mg(OH)$_2$ nano-phase in MgH$_2$ nano-composites on the basis of their $T_1$ relaxation. Pure bulk MgH$_2$ relaxes very slowly ($T_1 \sim 900 \text{ s}$), which makes it impractical to measure the $T_1$ of the bulk MgH$_2$ phase in the nanocomposite. Instead we have measured the $T_1$ time of the fast relaxing component alone with a repetition time of 20 s. In this way we estimate a $T_1$ time in the order of $10^{-1} \text{ s}$ for the short-$T_1$ component, which appears to relax with a single exponential decay. In a previous study$^{30}$ on ball-milled bulk MgH$_2$, the $T_1$ time was also found to be in the order of $10^{-1} \text{ s}$. The typical crystallite size of few nm to few tens of nm is formed as a consequence of ball-milling. In the present study, nano-MgH$_2$, if present, outside the carbon, will also have shorter $T_1$ time. The relative peak areas from static as well from MAS NMR experiments are summarized in Table 6.4. There is a good correspondence between relative peak area in the bulk MgH$_2$ and nano-MgH$_2$/Mg(OH)$_2$ phase from static as well as from MAS $T_1$-filtered experiments for all the nanocomposites. This indicates that hydrogen atoms with a short-$T_1$ time can be completely associated with the MgH$_2$/Mg(OH)$_2$ nano-phase. The overall amount of hydrogen increases with the initial MgH$_2$ composition in the melt infiltrated nanocomposites. The relative peak area calibrated with respect to weight of 10 wt.-% MgH$_2$:C in the nano-particles is roughly the same for all the nano-composites. The peak area from the background and the protons of carbon constitute approximately half of the peak area of 10 wt.-% MgH$_2$:C.
Table 6.4: Relative peak areas present in the form of nano-\((\text{MgH}_2/\text{Mg(OH)}_2)\) and bulk \(\text{MgH}_2\) in MgH\(_2\):C nanocomposites estimated from \(^1\)H NMR peak area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Static NMR</th>
<th></th>
<th>MAS NMR</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative peak area</td>
<td>Nano(^{\ast}) - MgH(_2) (Peak area fraction)</td>
<td>Overall peak area calibrated with respect to weight of 10 wt.-% MgH(_2):C</td>
<td>Nano(^{\ast}) - MgH(_2) (Peak area fraction)</td>
</tr>
<tr>
<td></td>
<td>Over all peak area calibrated with respect to weight of 10 wt.-% MgH(_2):C</td>
<td>Nano(^{\ast}) - MgH(_2) w.r.t. 10 wt.-% MgH(_2):C</td>
<td></td>
<td>Nano(^{\ast}) - MgH(_2) w.r.t. 10 wt.-% MgH(_2):C</td>
</tr>
<tr>
<td>10 wt.-% MgH(_2):C</td>
<td>1</td>
<td>0.85</td>
<td>0.85</td>
<td>1</td>
</tr>
<tr>
<td>15 wt.-% MgH(_2):C</td>
<td>1.4</td>
<td>0.54</td>
<td>0.76</td>
<td>1.3</td>
</tr>
<tr>
<td>20 wt.-% MgH(_2):C</td>
<td>1.9</td>
<td>0.40</td>
<td>0.76</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\(^{\ast}\) Nano\(^{\ast}\) MgH\(_2\) refers to Nano-MgH\(_2\) or Mg(OH)\(_2\)

6.3.3.4 NMR quantification

To quantify the amount of hydrogen in these materials from NMR, two factors have to be taken into account. First, as mentioned, skin-depth may be a problem even at 200 MHz. The second factor is that for broad NMR signals, the initial few points in the time domain are not recorded because of the dead time of spectrometer. This could lead to reduced peak area in frequency domain. Therefore, we compared the peak area of hydrogen signal from a known amount of adamantane with bulk-MgH\(_2\). This showed that the peak area of bulk-MgH\(_2\) is underestimated by 30\%. From \(^1\)H NMR, the ratio between the amount of hydrogen in nano and bulk-MgH\(_2\) can be determined. The peak area of the spectrum with a \(T_1\)-filter time of 0.005 s and 5 s gives the overall amount of hydrogen in both MgH\(_2\)/Mg(OH)\(_2\) nano-phase and bulk-MgH\(_2\) phase and bulk-MgH\(_2\) respectively. The peak area of difference spectrum with the two \(T_1\)-filtered spectra gives the amount of hydrogen in the nano-MgH\(_2\) phase. The absolute amount of
hydrogen content was determined by comparing the total peak area of the signal to a signal from known quantity of water and adamantane. Table 6.5 shows the absolute of hydrogen calibrated with respect to peak 100 mg of sample. The carbon-support also contains hydrogen. Therefore, the amounts in the Table 6.5 are corrected for the background, the carbon support and also the underestimation from the faster signal decay.

**Table 6.5**: Absolute amount of hydrogen in the MgH₂ nano-composites after correcting for the background and carbon support.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Overall amt. of hydrogen from NMR (wt.-%)</th>
<th>Absolute amt. of hydrogen in bulk-MgH₂ from NMR (wt.-%)</th>
<th>Absolute amt. of hydrogen in nano-MgH₂/Mg(OH)₂ from NMR (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt.-% MgH₂:C</td>
<td>0.10</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>15 wt.-% MgH₂:C</td>
<td>0.21</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>20 wt.-% MgH₂:C</td>
<td>0.30</td>
<td>0.24</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**6.3.3.5 Combined Analysis**

Let us combine the results of XRD, TPD and NMR quantification. XRD quantifies the bulk-MgH₂ and hence the amount of hydrogen in the *bulk* form can be obtained. TPD gives the overall hydrogen content. Therefore, the difference between TPD and XRD should give the amount of hydrogen in the nano-MgH₂ phase. In the setup that we have used, TPD detects only H₂ and not, e.g., water vapor released from Mg(OH)₂. From NMR, the amount of hydrogen in the bulk-MgH₂ and MgH₂/Mg(OH)₂ nano-phase can be determined.

First let us focus on NMR. We have found that bulk MgH₂, when exposed to air, slowly transforms into Mg(OH)₂ over a period of 3-4 months. Since the present measurements were done over a period of two weeks and the materials were preserved in an inert atmosphere, we expect bulk-MgH₂ to be stable in our nano-composites. Hence, instead of focusing on nano-MgH₂/Mg(OH)₂, it is preferable to look into bulk MgH₂ for quantification with different methods. In Table 6.6, the absolute amount of hydrogen in bulk-MgH₂ determined from XRD and NMR are shown. The NMR data is corrected for the background, the hydrogen that is chemically bound to carbon and also the under-estimation from the faster signal decay. Both XRD and NMR show that the amount of H₂ in bulk-MgH₂ increases with the loading of MgH₂ in the nano-composite. The last column shows the ratio between the amount of hydrogen in bulk-
MgH$_2$ determined XRD analysis and NMR analysis. The hydrogen content from the NMR is under-estimated by approximately a factor of 2.87 (average of 2.33, 3.14 and 3.16) and let us call this average value as NMR invisibility factor.

**Table 6.6:** Combined quantitative analysis: Absolute amount of hydrogen estimated from different characterization techniques is shown in this table. The last column shows the ratio between the XRD determined and NMR determined amount of hydrogen from bulk MgH$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TPD yield-Absolute amount of hydrogen (wt.-%)</th>
<th>Absolute amount of hydrogen in bulk-MgH$_2$ from XRD (wt.-%)</th>
<th>Absolute amt. of hydrogen from NMR (wt.-%)</th>
<th>Absolute amt. of hydrogen in bulk-MgH$_2$ from NMR (wt.-%)</th>
<th>Ratio between the absolute amount of hydrogen in bulk MgH$_2$ (XRD/NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt%–MgH$_2$:C</td>
<td>0.43</td>
<td>0.07</td>
<td>0.10</td>
<td>0.03</td>
<td>2.33</td>
</tr>
<tr>
<td>15 wt%–MgH$_2$:C</td>
<td>0.74</td>
<td>0.44</td>
<td>0.21</td>
<td>0.14</td>
<td>3.14</td>
</tr>
<tr>
<td>20 wt%–MgH$_2$:C</td>
<td>1.08</td>
<td>0.76</td>
<td>0.30</td>
<td>0.24</td>
<td>3.16</td>
</tr>
</tbody>
</table>

### 6.3.3.6 Effect and extent of oxidation

MgH$_2$ nano-particles are extremely sensitive to oxidation. Therefore, to observe the effect of oxidation, TPD was performed before and after the NMR measurements. TPD shows reduced amount of hydrogen desorption after NMR measurement and desorption occurs at a higher temperature compared to the TPD desorption profile of 10 wt.-% MgH$_2$:C before the NMR measurement (see Table 6.3). This could indicate oxidation of MgH$_2$ nano-particles to Mg(OH)$_2$. Mg(OH)$_2$ decomposes into MgO and water vapor upon heating. However, water vapor is not detected by TPD and hence hydrogen observed from the TPD of the samples after NMR measurement corresponds to H$_2$ desorption from MgH$_2$ nano-particles. The signals of solid MgH$_2$ and Mg(OH)$_2$ in a physical mixture of the two are separated by ca. 2 ppm, which can be easily resolved with $^1$H MAS NMR. However, the strong susceptibility broadening makes it difficult, if not impossible, to distinguish between MgH$_2$ and Mg(OH)$_2$ on the carbon support unambiguously. Fig. 6.8 shows MAS NMR spectra of carbon support, 5 wt.-% MgH$_2$:C and 5
wt.-% MgH₂:C after prolonged exposing to air in order to provoke oxidation. Table 6.7 shows the relative peak area of the hydrogen signal calibrated with respect to the weight and number of scans of the carbon support after hydrogenation.

Figure 6.8: $^1$H MAS NMR spectra of (a) carbon support heated at 500 °C (b) carbon support after hydrogenation (c) carbon support exposed to air. (d) 5 wt.-% MgH₂:C (e) 5 wt.-% MgH₂:C exposed to air (f) 10 wt.-% MgH₂:C. The relative peak area calibrated with respect to the mass of carbon support after hydrogenation and number of scans. Spinning sidebands are indicated by asterisk.

The NMR signal intensity of 5 wt.-% MgH₂:C after hydrogenation is approximately twice higher than that of the carbon support. The carbon support, as such, does not absorb hydrogen significantly even after exposure to air and after heating the carbon support upto 500 °C also ~
80% of hydrogen is still present in it. We do find increased amount of hydrogen after exposure to air in 5 wt.-% MgH₂:C. Fig. 6.8 (d) could also represent the hydrogen signal of Mg(OH)₂ and it is not clear whether the major portion of the NMR signal corresponds to Mg(OH)₂. When the sample was exposed to air the NMR signal intensity approximately doubles compared to the hydrogenated sample and the peak position shifts further upfield to -14 ppm. The oxidation of MgH₂ with oxygen to Mg(OH)₂ does not change the hydrogen content and carbon support does not absorb significant amounts of hydrogen after exposure to air. Therefore the increased NMR signal intensity after exposure to air indicates that there is Mg that is either present as metallic Mg or MgO which forms Mg(OH)₂ upon oxidation.

Let us compare the TPD results after NMR characterization with the NMR results. The amount of hydrogen from NMR in and nano-MgH₂/Mg(OH)₂ is multiplied by 2.8 for the NMR invisibility factor on the assumption that invisibility factor is the same for both bulk MgH₂ and nano MgH₂/Mg(OH)₂. The invisibility factor is already corrected for the under-estimation of the ¹H NMR signal, which is a consequence of faster signal decay. However, the narrower lineshapes observed in ¹H NMR spectra (see Fig. 6.7) for nano-MgH₂/Mg(OH)₂ may indicate that the NMR signal is most likely to be within quantitative limits. Therefore, the amount of hydrogen obtained for the nano-MgH₂/Mg(OH)₂ after the multiplication of NMR invisible factor is over estimated by 30%. We will subtract the contribution from bulk MgH₂ as determined from XRD in the TPD results after NMR characterization. Table 6.7 shows the comparison of amount of hydrogen in nano-MgH₂ from TPD and nano-MgH₂/Mg(OH)₂ from NMR.
Table 6.7: Comparison of amount of hydrogen from TPD after NMR characterization and NMR results in nano-composites. The contribution from bulk MgH₂ is subtracted from the TPD results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absolute amount of hydrogen in nano-MgH₂ (wt-%) (from TPD)</th>
<th>Absolute amount of hydrogen in nano-MgH₂/Mg(OH)₂ (wt-%) from NMR</th>
<th>Absolute amount of hydrogen in nano-MgH₂/Mg(OH)₂ (wt-%) from NMR after correction for the 30% over estimation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt.% MgH₂:C</td>
<td>0.10</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>15 wt.% MgH₂:C</td>
<td>0.02</td>
<td>0.18</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The estimated amount of hydrogen from NMR in nano-MgH₂/Mg(OH)₂ is higher than the combined analysis from TPD and XRD (see Table 6.7). This indicates Mg(OH)₂ formation. However, for the 10 wt.-% MgH₂:C we do find ~ 77% of hydrogen in nano-MgH₂ whereas for the 15 wt.-% MgH₂:C there is only 15% in the nano-MgH₂.

NMR reveals the presence of bulk MgH₂ and hydrogen in the form of MgH₂ or Mg(OH)₂ within the pores of carbon and XRD reveals bulk-Mg and bulk-MgH₂ phase. To know the presence of Mg or MgO within the pores of carbon, let us first consider the case that all Mg atoms within the pores of carbon are fully hydrogenated.

\[ \text{MgH}_2 + \text{O}_2 \rightarrow \text{Mg(OH)}_2 \]  

Eq. 6.3.3.6.1 suggests that first oxygen has to penetrate completely inside the pores of carbon. However, we do observe (from combined quantitative analysis) nano-MgH₂ in 10 wt.-% MgH₂. This suggests that oxygen has not penetrated completely. Even if Mg atoms are not fully hydrogenated, only the surface atoms are oxidized initially. Therefore, the increased \(^1\text{H}\) NMR intensity found in 5 wt.-% MgH₂:C after exposure to air suggests that there are Mg atoms within pores of carbon without oxidation before exposure. A cartoon of nano-composite materials is shown in Fig 6.9.
**6.3.3.7 Two-Dimensional Exchange Spectroscopy (2D Exsy)**

It is clear from the Fig. 6.8 that carbon support also contains hydrogen in it and from a simple One-dimensional NMR spectra alone we cannot unambiguously distinguish hydrogen from carbon support, Mg(OH)$_2$ and MgH$_2$ in these nano-composite materials. As already discussed in section 6.3.3.1, the susceptibility of the carbon support creates dispersion in chemical shifts. In Two-dimensional Exchange Spectroscopy (2D Exsy) NMR spectrum, we expect a resolved signal if the *susceptibility length scale* is larger than the average distance between MgH$_2$ and Mg(OH)$_2$ species. If MgH$_2$ and Mg(OH)$_2$ in the nano-phase would be separated by ~1 nm and their hydrogen atoms would experience the same local field, then their resonances would always be separated by ~2 ppm (as in a homogeneous field). $^1$H spin diffusion between these two should show up as 2-ppm off-diagonal ridges in the 2D Exchange spectrum. At least, from 2D Exsy, we can observe the hydrogen exchange, if present, among different species within the nano-composite materials. This will give information about any possible interaction of MgH$_2$/Mg(OH)$_2$ nano-phase with the carbon support. 2D Exsy correlates the chemical shift before and after a selectable time window $t_{\text{mix}}$, during which the hydrogen atoms have the opportunity to move to another environment. The exchange is visible by the

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**Figure 6.9:** A cartoon illustrating the nano-structure of MgH$_2$:C after hydrogen absorption. The dimensions of the cartoon and the objects within it are not to be scaled. Rectangular black objects represent carbon support. The red, brown and rose colored objects represent Mg, MgH$_2$ and Mg(OH)$_2$ respectively confined within the pores of carbon. Bulk-MgH$_2$ and bulk-Mg outside the pores of carbon are represented by circles shaded with green and blue colors respectively.
presence of cross peaks between the exchanging sites. Complete exchange is recognized from the similarity of the lineshapes of either horizontal projection with the horizontal trace at a chemical shift position or vertical projection with the vertical trace at a chemical shift respectively. Fig 6.10 shows 2D exchange spectra at mixing times of (a) 0.001, (b) 0.01 and (c) 0.1 s. The 2D exchange spectrum at mixing time of 0.001 s contains only diagonal peak and the shape of contour is along the diagonal. The rows at positions along the diagonal are shown in Fig. 6.10 (f). We do not observe the same difference between the line positions in both spectra. This implies that susceptibility length scales are shorter than the frequency separation between the line positions of MgH$_2$ and Mg(OH)$_2$ without the carbon support.

When the mixing time is increased to 0.01 s, magnetization exchange process begins between hydrogen atoms at different chemical sites. On further increasing the mixing time to 0.1 s, the horizontal projection and horizontal trace at –8 ppm are similar. This indicates a complete exchange of proton magnetization between all chemical sites. When 2D Exsy is performed on carbon support, even at a mixing time of 0.3 s, we do not observe full exchange of polarization from hydrogen atoms within the carbon. Probably, hydrogen atoms from the C-H bonds of the carbon support are separated by a large distance that it takes sufficiently longer time for polarization transfer to take place or there is no polarization transfer at all. Comparing the hydrogen exchange time scales of 10 wt.-% MgH$_2$:C and the carbon support it is clear that there is interaction of hydrogen from nano-MgH$_2$/Mg(OH)$_2$ with the hydrogen from the carbon support.

Let us investigate the exchange process more carefully. The anisotropic bulk medium susceptibility (ABMS) causes the dispersion in chemical shifts dominating the width of the centerband in $^1$H MAS NMR of this material. Let us consider hydrogen atoms resonating at chemical shifts ~ 10, -8 and -40 ppm. These are shown in Fig 6.10 (a). As the mixing time is increased from 0.001 to 0.01 s we do observe cross peaks between hydrogen atoms resonating at 10 and -8 ppm and as well as from -8 and -30 ppm respectively. However, we do not observe crosspeaks between hydrogen atoms resonating at 10 and -30 ppm. This suggest that magnetization exchange process happens only between neighboring sites and at a timescale of 0.1 s there is a complete exchange of magnetization between all sites. Before describing the
exchange process completely, there is one more important point to be addressed, i.e. does the
exchange process take place between the pores or within a pore itself? The distribution in the
orientation of the carbon support with the applied magnetic field and hence also the susceptibility
tensor results in dispersion of chemical shifts. Therefore, in the 2D Exsy spectrum at a mixing
time of 0.01 s, we should also expect hydrogen exchange between 10 and – 40 ppm as well,
which we do not observe. This suggests exchange process happening within a pore and not
between the pores of carbon support.

N\textsubscript{2} Physisorption experiments show that pores of diameter 2-3 nm are filled by nano-
composites. Therefore, combination of the timescale given by NMR and spatial dimension given
by N\textsubscript{2} physisorption experiment would give us an estimate of diffusion coefficient of hydrogen
atoms in nano-Mg(O\textsubscript{2})H\textsubscript{2} phase. Using Einsteins’ relation given by \( \langle x^2 \rangle = 6Dt \), where \( \langle x^2 \rangle \) is
mean–square displacement, D is diffusion coefficient and t is the time, the D is calculated to be
1.5*10\(^{-17}\) m\(^2\)/s. The diffusion coefficient of bulk-MgH\textsubscript{2} is reported\textsuperscript{31} to be 4*10\(^{-19}\) m\(^2\)/s at 100 °C.
This clearly shows that hydrogen diffusion in nano-MgH\textsubscript{2}/Mg(OH)\textsubscript{2} is higher by minimally two
orders of magnitude. However, with presence of Mg(OH)\textsubscript{2}, the value of diffusion coefficient thus
represents hydrogen mobility more qualitative rather than quantitative.
Figure 6.10: 2D Exchange spectra of 10 wt.-% MgH₂:C with a mixing time of (a) 0.001, (b) 0.01 and (c) 0.1 s. Horizontal projection and horizontal trace at –8 ppm are shown on top of the spectra. At a mixing time of 0.1 s, the horizontal projection and horizontal trace are similar which indicates a complete exchange of magnetization within all sites. (d) Carbon support with a mixing time of 0.3 s. (f) The traces along the diagonal at the same intensity in the contour plot of (a). The development of the shape of the contour with the mixing time for 10 wt.-% MgH₂ indicates that the exchange of magnetization takes place between neighboring sites. The green arrows in (a) represent hydrogen atoms resonating at 10, -8, -40 ppm respectively.
6.4 Conclusions

Mg nanocomposites synthesized via Mg melt-infiltration were studied with NMR, XRD and TPD. The NMR experiments were performed at 11.7 and 4.7 T magnets. Susceptibility and conductivity of carbon support caused a broad MAS NMR signal and lower signal to noise ratio spectrum, respectively. These effects are reduced at lower magnetic field. NMR visibility is severely affected by the packing density of the materials at 11.7 T. However, our results suggest quantitative NMR can still be performed at 4.7 T.

MAS $^1$H NMR shows two lineshape components that are distinguished on the basis of their spin-lattice relaxation time ($T_1$). On the basis of XRD and also comparison with the long $^1$H NMR $T_1$ time of pure MgH$_2$, the component with long-$T_1$ time is assigned to bulk-MgH$_2$. The protons with short $T_1$ time is assigned to hydrogen that are present within nano-pores of carbon either in the form of MgH$_2$, Mg(OH)$_2$ or hydrogen from the carbon support. Quantification of nano-MgH$_2$ is a challenge since this phase is not observed with XRD. The combination of techniques for quantification shows that part of the hydrogen atoms within the pores of carbon are still in the form of MgH$_2$ without oxidation. Two dimensional exchange spectroscopy reveals interaction of hydrogen atoms from the carbon support with the hydrogen atoms from MgH$_2$/Mg(OH)$_2$ nano-phase.

6.5 References


7.1 Summary

MgH$_2$ has a high gravimetric capacity of 7.7 wt.-% of hydrogen storage. However, it suffers from slow absorption/desorption kinetics and a high thermodynamic stability, which prevents it to be used in mobile applications. Several studies$^{1-7}$ have been done so far to improve these kinetic and thermodynamics limitations.

The primary goal of this research was to get an atomistic view of hydrogen location and also its mobility within Mg-TM based hydrides. We have studied gas-phase deuterated Mg$_{0.65}$Sc$_{0.35}$ and Mg$_{0.65}$Ti$_{0.35}$ materials. In Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$, with a novel $^2$H double-quantum NMR with $^{45}$Sc irradiation and TRAPDOR NMR techniques, we were able to observe that Mg and Sc are not randomly distributed within the XRD determined coherent lattice, instead we found Mg-rich and Sc-rich clusters.$^8$ With Two-Dimensional Exchange Spectroscopy (2D Exsy), the length separation between these clusters was found to be within few unit cells. Sc is a expensive element and hence, its neighbor in the periodic table, Ti, was investigated.

Mg and Ti are immiscible under equilibrium conditions. Therefore, we have investigated MgTi alloy prepared by ball-milling and subsequently deuterated at 175 °C and 70 bars. Both NMR and XRD showed that the alloy, after deuteration, phase-separates into MgD$_2$ and TiD$_3$. Additionally, NMR indicates the presence of another TiD$_y$ phase that is not visible with XRD. Two-Dimensional Exchange Spectroscopy (2D Exsy) reveals deuterium exchange between the XRD invisible TiD$_y$ phase and MgD$_2$. With One-Dimensional Exsy, a weak temperature dependence is found corresponding to an effective activation barrier for deuterium exchange of approximately 12 kJ/mol. This low effective activation energy is probably the result of a broad
deuterium-mobility distribution. Comparing $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$ and $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65}$, we propose that the stabilization of the nano-structure of the later maybe a possible outcome from the coherent coupling of individual crystal lattices of $\text{MgD}_2$ and $\text{TiD}_2$. Fig. 7.1 shows the same.

![Diagram of crystal structures](image)

**Figure 7.1**: Comparison of the crystal structures of (a) $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$ and (b) ball-milled $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65}$. White spheres represent Mg and black spheres denote Sc and Ti in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_{2.2}$ and $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65}$ respectively. The interaction between fcc $\text{TiD}_2$ and bct $\text{MgH}_2$ may be a controlled by coherent coupling of crystal lattice parameters.

XRD homogenous $\text{Mg}_{0.65}\text{Ti}_{0.35}$ film has been prepared by rf magnetron sputtering. After gas-phase deuterium loading at room temperature, we did not observe a macro-phase separated $\text{TiD}_2$ phase unlike in the ball-milled material. We do observe, partly resolved signals of deuterium located in non-conductive domains at tetrahedral $\text{Mg}_4$-sites and, possibly, mixed $\text{Mg}_n\text{Ti}_{4-n}$ sites (4 ppm), and deuterium at $\text{Ti}_4$-sites in conducting $\text{TiD}_2$ nano-domains (-29 and -68 ppm). No bulk-$\text{TiD}_2$ signal at -150 ppm is observed, in contrast to what we find in ball-milled $\text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{0.65}$, which is largely phase separated. 2D Exsy indicates deuterium exchange between deuterium states resonating at position +4 and -29 ppm, but not with those giving rise to the resonance at -68 ppm. The signal at -68 ppm probably represents deuterium atoms which are stably bound to Ti. The observed deuterium exchange and the reduced Knight shift compared to bulk $\text{TiD}_2$ are explained using a model with $\text{TiD}_2$ nano-slabs or nano-clusters. (Fig. 7.2). At temperatures $T \geq 300$ K, the intensity of the signal from the Mg-rich sites decreases and a new
signal appears at –10 ppm. This is a reversible phase transition and the upfield shift indicates that deuterium is in contact with Ti, probably at Mg-Ti interface.

![Graphical representation of (100) surface in nano slab model of Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$.](image)

**Figure 7.2:** Graphical representation of (100) surface in nano slab model of Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$. Deuterium atom at positions A and B has pure Ti$_4$ coordination. The Knight shift is affected by the surface effects and hence deuterium at A sites contribute to the broad signal at -29 ppm, and those at B sites to the -68 ppm signal. a is the unit cell length. Mg$_2$Ti$_3$ sites at the Mg-Ti interface are labelled as “2”.

Since we study the energy carriers, i.e. hydrogen or deuterium atoms directly with NMR, it is of most importance to know the visibility of all the energy carriers. The loss of the overall signal intensity in 1D Exsy of melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ indicate the presence of NMR-invisible or “dark” deuterium states. We explain the invisibility on the basis of second-order quadrupolar line broadening arising from the unequal charge distribution in the mixed co-ordination states, $Q^n = H\text{-Mg}_n\text{Sc}_{4-n}$, (1 ≤ n ≤ 3) where n is the number of Mg atoms in the first coordination sphere. Approximately 30% of deuterium atoms are invisible. With this correction for deuterium visibility, the distribution of Mg and Sc over the metal within the lattice tends to be closer to statistical distribution rather than clustering of Mg and Sc rich domains.

Nano-sizing and confinement is another approach employed to overcome the disadvantages of MgH$_2$. Carbon supported MgH$_2$ nano-composites were prepared by Mg-melt infiltration. Temperature Programmed Desorption (TPD), X-ray Diffraction (XRD) and NMR were used to identify and quantify different hydrogen-containing phases in MgH$_2$ nano-composites. The susceptibility of the nano-porous carbon support results in broad resonances in $^1$H MAS NMR spectra. For highly packed samples at 11.7 T (500 MHz) the NMR visibility is
severely affected by the conductivity of carbon. We show that the problems associated with conductivity and susceptibility of nano porous carbon can be overcome by working at a lower magnetic field, 4.7 T (200 MHz). The NMR visibility at a lower field is not affected by the packing density of the materials, which implies quantitative NMR is still feasible. MgH₂ within the nano-pores of carbon are not detected with XRD. Static and MAS ¹H NMR of a series of MgH₂ carbon nano-composites with different MgH₂ content, indicate the presence of two hydride phases with different spin-lattice relaxation time and chemical shift. The component with the broad static ¹H NMR lineshape and long relaxation time (~10² s) is assigned to bulk MgH₂. The second component has a narrower static ¹H NMR lineshape and a shorter relaxation time (~10⁻¹ s) and is tentatively assigned to a nano-phase consisting of MgH₂ and Mg(OH)₂. The ¹H NMR lineshape of MgH₂/Mg(OH)₂ nano-phase is narrower than that of bulk-MgH₂, which indicates a higher mobility of the hydrogen atoms in the MgH₂/Mg(OH)₂ nano-phase. We have tried to separately identify ¹H NMR signals from MgH₂ and Mg(OH)₂ in the nanophase by using 20-kHz MAS. However, the susceptibility broadening by the nanoporous carbon is too strong. Assuming that the length scale of the susceptibility variation might be longer than the typical distance between MgH₂ and Mg(OH)₂ we have further tried to enhance the chemical resolution in the inhomogeneous local field caused by susceptibility by use of 2D ¹H MAS NMR Exsy. However, 2D Exsy shows only non-specific broadening as a function of mixing time. At the timescale of 10⁻¹ s, there is a complete non-specific spin exchange or hydrogen exchange over the susceptibility broadened resonance. This indicates that the length scale of susceptibility variation is smaller or equal to that of the average distance between MgH₂ and Mg(OH)₂ spin- or the susceptibility-determined NMR chemical shifts. Fig. 3 shows a cartoon illustrating various phases identified with a combination of XRD and NMR methods.
Figure 3: Cartoon illustrating the nano-structure of MgH$_2$:C after hydrogen absorption. The relative sizes of the objects within the cartoon are not drawn to scale. Rectangular black objects represent carbon support. The red, brown and rose colored objects represent Mg, MgH$_2$ and Mg(OH)$_2$, respectively, confined within the pores of carbon. Bulk-MgH$_2$ and bulk-Mg outside the pores of carbon are represented by circles shaded with green and blue colors, respectively.

7.2 References


Summary

Magnesium Transition-Metal based lightweight hydrogen storage materials. A NMR study

As the world is running out of fossil fuels, sustainable energy sources and efficient forms of energy storage are studied nowadays. Hydrogen is an energy carrier and has advantages that it is abundant and does not pollute the environment. Metal hydrides are studied for their reversible hydrogen storage properties. MgH$_2$ is a promising candidate for light-weight hydrogen storage material. It can store up to 7.7 wt-% of hydrogen. However, it suffers from high thermodynamic stability and poor sorption kinetics. To improve its performance, Mg is doped with transition metals (TM). The resulting complex alloys are not fully understood on an atomistic level. This doctoral dissertation therefore examines the following central research questions:

Is it possible to distinguish between hydrogen atoms with different metal coordination, $Q^n = H$-Mg$_n$TM$_{4-n}$, where $n$ is the number of Mg atoms in the first coordination sphere.

Do hydrogen atoms from one metal-coordination environment move to all other coordination environments? How are the different metal coordinations arranged within the lattice? What is a typical length scale separation between different metal coordinations?

A single technique alone is not adequate to characterize these complex materials completely. Therefore, we have used a combination of techniques such as fast Magic Angle Spinning (MAS) solid state Nuclear Magnetic Resonance (ssNMR) spectroscopy, powder X-ray diffraction (XRD) and Neutron diffraction (ND) to elucidate the nanostructure of Mg-based hydrogen-storage materials. Diffraction-based techniques are applicable to materials which possess long-range structural ordering. Long-range ordering is not required for NMR. Information about the local environment of the energy carrier i.e hydrogen (deuterium) is necessary to optimize the hydrogen-storage materials. ssNMR is unique and powerful method in this respect. Advanced pulse sequences can be employed to obtain information about the local environment of the energy carrier itself, directly. Moreover, motion of the energy carrier can be monitored which is essential for hydrogen-storage materials. Chapter 2 gives the theoretical understanding of the methodologies that are used in this study to investigate Mg-TM based hydrides.

We have studied gas-phase deuterated Mg$_{0.65}$Sc$_{0.35}$ and Mg$_{0.65}$Ti$_{0.35}$ materials. In Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$, with a novel $^2$H double-quantum NMR with $^{45}$Sc irradiation and TRAPDOR NMR techniques, we were able to observe that Mg and Sc are not randomly distributed within the XRD determined coherent lattice, instead we found Mg-rich and Sc-rich clusters. With Two-Dimensional Exchange Spectroscopy (2D Exsy), the length separation between these clusters was found to be within few unit cells. Sc is a valuable element and hence, its neighbor in the periodic table, Ti, was investigated.

Mg and Ti are immiscible under equilibrium conditions. Therefore, we have investigated Mg$_{0.65}$Ti$_{0.35}$ alloy prepared with non-equilibrium methods, namely ball-milling and magnetron sputtering. Chapter 3 describes MgTi alloy prepared by ball-milling and subsequently deuterated at 175 °C and 70
bars. Both NMR and XRD showed that the alloy, after deuteration, phase separates into MgD\(_2\) and TiD\(_2\). Additionally, NMR indicates the presence of another TiD\(_y\) phase that is not visible with XRD. Two-Dimensional Exchange Spectroscopy (2D Exsy) reveals deuterium exchange between the XRD invisible TiD\(_y\) phase and the MgD\(_2\). With One-Dimensional Exsy, a weak temperature dependence is found corresponding to an effective activation barrier for deuterium exchange of approximately 12 kJ/mol. This low effective activation energy is probably the result of a broad deuterium-mobility distribution. Comparing Mg\(_{0.65}\)Sc\(_{0.35}\)D\(_{2.2}\) and Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_{0.65}\), we propose that the stabilization of the nano-structure of the later maybe a possible outcome from the coherent coupling of individual crystal lattices of MgD\(_2\) and TiD\(_2\).

XRD homogenous MgTi films can be prepared by rf magnetron sputtering. Chapter 4 elucidates the hydrogen siting and dynamics in Mg\(_{0.65}\)Ti\(_{0.35}\) prepared by this method. After gas-phase deuterium loading at room temperature, we did not observe a macro-phase separated TiD\(_2\) phase unlike in ball-milled material. We do observe, partly resolved signals of deuterium located in non-conductive domains at tetrahedral Mg\(_4\) and, possibly, mixed Mg\(_n\)Ti\(_{4-n}\) sites (4 ppm), and deuterium at Ti\(_4\) sites in conducting TiD\(_2\) nanodomains (-29 and -68 ppm). No bulk-TiD\(_2\) signal at -150 ppm is observed, in contrast to what we find in ball-milled Mg\(_{0.65}\)Ti\(_{0.35}\)D\(_{0.65}\), which is largely phase separated. 2D Exsy indicates deuterium exchange between deuterium states resonating at position 4 and -29 ppm, but not with those giving rise to the resonance at -68 ppm. The signal at -68 ppm probably represents deuterium atoms which are stably bound to Ti. The observed deuterium exchange and the reduced Knight shift compared to bulk TiD\(_2\) are explained using a model with TiD\(_2\) nano-slabs. At temperatures T \(\geq\) 300 K, the intensity of the signal from the Mg-rich sites decreases and a new signal appears at -10 ppm. This is a reversible phase transition and the upfield shift indicates that deuterium is in contact with Ti, probably at Mg-Ti interface.

Since we study the energy carriers, i.e. hydrogen or deuterium atoms directly with NMR, it is of most importance to know the visibility of all the energy carriers.

Chapter 5 investigates the visibility of deuterium atoms in the melt-cast Mg\(_{0.65}\)Sc\(_{0.35}\)D\(_{2.2}\). The loss of overall signal intensity in 1D Exsy indicate the presence of NMR-invisible or “dark” deuterium states. We explain the invisibility on the basis of second-order quadrupolar line broadening arising from the unequal charge distribution in the mixed co-ordination states, Q\(^n\) = H-Mg\(_n\)Sc\(_{4-n}\), \(1 \leq n \leq 3\) where n is the number of Mg atoms in the first coordination sphere. Approximately 30% of deuterium atoms are invisible. With this correction for deuterium visibility, the distribution of Mg and Sc over the metal within the lattice tends to be closer to statistical distribution rather than clustering of Mg and Sc rich domains.

Nano-sizing and confinement is another approach employed to overcome the disadvantages of MgH\(_2\). Carbon supported MgH\(_2\) nano-composites prepared by Mg-melt infiltration is studied in Chapter 6. The susceptibility of the nano-porous carbon support results in broad resonances in \(^1\)H MAS NMR spectra. For highly packed samples at 11.7 T (500 MHz) the NMR visibility is severely affected by the
conductivity of the carbon. We show that the problems associated with conductivity and susceptibility of nano porous carbon can be overcome by working at a lower magnetic field, 4.7 T (200 MHz). The NMR visibility at a lower field is not affected by the packing density of the materials, which implies quantitative NMR is still feasible. MgH$_2$ within the nano-pores of carbon are not detected with XRD. Static and MAS $^1$H NMR of a series of MgH$_2$ carbon nanocomposites with different MgH$_2$ content, indicate the presence of two hydride phases with different spin-lattice relaxation time and chemical shift. The component with the broad static $^1$H NMR lineshape and long relaxation time (~10$^2$ s) is assigned to bulk MgH$_2$. The second component has a narrower static $^1$H NMR lineshape and a shorter relaxation time (~10$^{-1}$ s) and is tentatively assigned to a nanophase consisting of MgH$_2$ and Mg(OH)$_2$. The $^1$H NMR lineshape of MgH$_2$/Mg(OH)$_2$ nano-phase is narrower than that of bulk-MgH$_2$, which indicates a higher mobility of the hydrogen atoms in the MgH$_2$/Mg(OH)$_2$ nano-phase. We have tried to separately identify $^1$H NMR signals from MgH$_2$ and Mg(OH)$_2$ in the nanophase by using 20-kHz MAS. However, the susceptibility broadening by the nanoporous carbon is too strong. Assuming that the length scale of the susceptibility variation might be longer than the typical distance between MgH$_2$ and Mg(OH)$_2$ we have further tried to enhance the chemical resolution in the inhomogeneous local field caused by susceptibility by use of 2D $^1$H MAS NMR Exsy. However, 2D Exsy shows only non specific broadening as a function of mixing time. At the timescale of 10$^{-1}$ s, there is a complete non-specific spin exchange or hydrogen exchange over the susceptibility broadened resonance. This indicates that the length scale of susceptibility variation is smaller or equal to that of the average distance between MgH$_2$ and Mg(OH)$_2$ spin- or the susceptibility-determined NMR chemical shifts.

Finally, chapter 7 summarizes the main findings of the study described in previous chapters.


# Appendix I

## (A) XRD data

Table S1: XRD signals for bulk MgD$_2$, Mg-rich and Ti-rich phase in Mg$_{0.65}$Ti$_{0.35}$ alloy, Pd reflections in Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$ alloy and TiD$_2$. The reflections of the Mg-rich and Ti-rich phases in the Mg$_{0.65}$Ti$_{0.35}$Pd$_{0.02}$ alloy are well described by the corresponding reflections in the alloy without palladium.

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s = $\sqrt{h^2 + k^2 + (c/a)l^2}$, a/c = 1.5

Mg$_{0.65}$Ti$_{0.35}$, / Mg$_{0.65}$Ti$_{0.35}$Pd$_2$ Mg-rich phase, fcc, a/c =1

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4.417(2)

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Figure S1: (a) 2D view of the ND pattern evolution as function of time during absorption. The temperature evolution is also shown on the right hand side of the figure. The arrow on the left hand side indicates the pattern shown in Fig. 3b of the main text. (b) 2D view of the ND pattern evolution as function of temperature during temperature programmed desorption (1 K/min).
(C) Thermogravimetric analysis

![Graph showing weight-loss vs. temperature](image)

**Figure S2:** relative weight-loss of the magnesium-titanium deuteride at increasing temperature. The limiting value ~ 3.7 wt-% corresponds within experimental error to the overall D/M ratio (0.65 ~ 3.8 wt-%) estimated from $^2$H NMR.
**Figure S1:** Static and 8-kHz MAS $^2$H NMR lineshapes of (a) MgD$_2$ and (b) Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ compared to simulated quadrupolar lineshapes

$$
\Delta \nu = \frac{\nu_Q}{2} \left[ 3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi \right]
$$
for selected values of the quadrupolar coupling constant $\nu_Q = \text{asymmetry parameter } \eta$. (a) Main component $\nu_Q = 28 \text{ kHz}$ and $\eta = 0.65$ combined with 1 % isotropic component due to unknown impurity. (b) lineshapes generated for (green) $\nu_Q = 15 \text{ kHz}$ and $\eta = 1$ and (purple) $\nu_Q = 17 \text{ kHz}$ and $\eta = 0$. Both combinations ($\nu_Q, \eta$) describe the MAS sideband pattern of Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ equally well, but not the static $^2$H NMR lineshape of this ternary compound.

The inset above the MgD$_2$ spectrum in Fig. S1a illustrates the rutile structure of MgD$_2$, in which each deuterium atom has a planar threefold Mg coordination ($d_{\text{Mg-D}} = 1.95 \text{ Å}$) with Mg at the corners of a triangle with one side of 3.01 Å and two sides of 3.52 Å. The inset also shows the principal axes system of the quadrupolar tensor $\mathbf{V}$ associated with deuterium at $(1-\xi, \xi, \frac{1}{2})$ with $\xi = 0.303$. The principal tensor values $\{V_{11}, V_{22}, V_{33}\}$ are proportional to the 2$^{\text{nd}}$ order derivatives of the electric potential energy mainly caused by the closest three Mg atoms at (1,0,0), (1,01) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The asymmetry parameter $\eta = |V_{11} - V_{22}| / V_{33}$ computed from the three 2$^{\text{nd}}$-order derivatives equals 0.61.
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Subramanian Srinivasan
Curriculum Vitae

Subramanian Srinivasan was born on December 12th 1979 in Chennai, India. After his graduation from high school in 1997, he continued studying physics at the Sri Satya Sai Institute of Higher Learning in Puttaparthi, India. He obtained his Masters’ degree in 2004 after completion of the thesis “Optical Solitons – A simulation study of Non Linear Switching using Long Period Fibre Gratings”. From 2003-2006, he was working as junior research fellow in Dept. of Physics, Indian Institute of Science, Bangalore. In March 2007, he started his PhD-study in the Inorganic Chemistry and Catalysis group of Eindhoven University of Technology, under the supervision of Prof. Rutger A. van Santen. The aim of the project is to study Mg-based based hydrogen storage materials by solid state NMR. The most important results of the research project are described in the thesis.
List of Publications


(3) S. Srinivasan and P. C. M. M. Magusin, Dark deuterium in the lightweight hydrogen-storage material Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ studied with MAS $^2\text{H}$ NMR, (submitted to J. Magn. Reson.).

(4) S. Srinivasan, P. C.M. M. Magusin, S. Tatiparti, Y. S. Au, P. de Jongh, $^1\text{H}$ NMR quantification of different hydrogen-containing phases in nanocomposites of MgH$_2$ and carbon, (in preparation).