Deuterium MAS NMR Studies of Mg-Ti Deuteride Formed During High Pressure Ball Milling

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Deuterium MAS NMR Studies of Mg-Ti Deuteride Formed During High Pressure Ball Milling
by
Samuel Beckham Emery

A dissertation presented to
The Graduate School
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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Magnesium hydride has long been considered a candidate onboard hydrogen storage material for hydrogen fuel cell powered vehicles due to its low cost, abundance (of magnesium metal), and high hydrogen content (7.6 wt%). However, its use has been limited by the poor kinetics and thermodynamics of the reversible hydriding/dehydriding reaction. Improvements to hydrogen uptake and release have been previously demonstrated when Mg is alloyed with Sc. The resulting MgSc-hydride adopts a cubic, fluorite crystal structure (as opposed to the rutile, tetragonal structure for bulk MgH2) that exhibits a significantly lower activation energy for thermally driven hydrogen motion. However, Sc is too expensive for widespread implementation. Here we investigate the formation of metastable Mg-Ti-D compounds. Mg and Ti are not mutually soluble at equilibrium, so a molybdenum-lined high pressure vessel (to avoid ferrous and other contamination) has been developed to allow for the ball milling of Mg-Ti powders under high deuterium gas pressures. The local atomic structural properties of the resulting Mg-Ti-D composites have been studied by deuterium Magic Angle Spinning (MAS) nuclear magnetic resonance (NMR), which is sensitive to the deuterium atom siting within the Mg-Ti lattice. The change from rutile to cubic structure is known to play an important role in
promoting hydrogen motion within the lattice and thus improving the hydrogen storage properties of the compound. Thus the formation of a fluorite-structured Mg-Ti-D is desired.
Chapter 1: Introduction

Magnesium hydride (MgH\textsubscript{2}) has long been considered a candidate for onboard hydrogen storage due to its high gravimetric hydrogen content (7.6 wt% H), high volumetric hydrogen density (~110 g H per liter), its low cost, abundance, and, perhaps most importantly, its ability to reversibly store hydrogen. This reversible hydriding / dehydriding reaction is detailed below:

\begin{equation}
Mg(s) + H_2(g) \rightleftharpoons MgH_2(s) + \Delta H_f
\end{equation}

where \(\Delta H_f\) is the enthalpy of formation. For MgH\textsubscript{2}, \(\Delta H_f = -74.4\) kJ/mol indicating a release of energy upon the formation of the hydride phase (reaction proceeds to the right). Adding energy (heat) to the hydride will drive the reaction in the opposite direction (to the left) resulting in the release of H\textsubscript{2} gas and the formation of magnesium metal. In principle, this reaction can be cycled indefinitely.

Although MgH\textsubscript{2} possesses many positive attributes for a solid state hydrogen storage system, it is hampered by two fundamental limitations. Thermodynamically, MgH\textsubscript{2} is too stable: |\(\Delta H_f\)| is too large. The temperature for 1 bar of H\textsubscript{2} equilibrium pressure for the reaction depicted in equation 1-1 is ~300 °C, thus it costs too much energy to drive H off of MgH\textsubscript{2}. In addition, the kinetics of the hydriding/dehydriding reaction, the time it takes the reaction shown in equation 1-1 to reach equilibrium, are notoriously slow. For bulk MgH\textsubscript{2}, these slow kinetics are exhibited by figure 1-1 below which details the evolution of hydrogen gas upon heating of bulk MgH\textsubscript{2}. Notably, meaningful hydrogen desorption does not occur until roughly three hours after the start of heating. Even more notable, the bulk sample spends over an hour at 400 °C (with P\textsubscript{eq} ~ 27 bar) before the rate of hydrogen desorption increases substantially.
Several studies have determined that the rate limiting step in the hydriding/dehydriding reaction (equation 1-1) is diffusion of H through the bulk hydride phase, the so called “hydrogen blockade” problem.\textsuperscript{c–j} Additional work has identified the important role that crystal structure plays on hydrogen diffusion through the lattice.\textsuperscript{z,aa,ab} Indeed, Notten and co-workers first demonstrated the impact of structure on hydrogen lattice diffusion in Mg-based systems while studying Mg-Sc alloys for metal-hydride battery electrodes.\textsuperscript{k,1,m} For Mg alloyed with Sc, it was demonstrated that the alloy exhibited much improved electrochemical kinetics when the alloy assumed a cubic (fcc fluorite structural motif) crystal structure.

Our own group has studied the hydrogen atomic hopping rate, $\omega_H$, in both a Mg-Sc-H alloy, with the kinetic promoting fluorite structure, as well as standard, bulk MgH$_2$ with tetragonal (rutile structural motif) crystal structure.\textsuperscript{n} The fundamental result of that study is depicted in figure 1-2 below.
Importantly, Conradi and coworkers' demonstrated that hydrogen diffusion through the lattice in bulk magnesium hydride, often the rate limiting step for the hydrogen uptake and release reaction (equation 1-1), was significantly improved when magnesium adopted a fluorite (cubic) crystal structure. Provided the scandium content was greater than 20 at% (so \( y > 20 \) for \( \text{Mg}_{1-y}\text{Sc}_y\text{H}_x \)), Mg-Sc formed a fluorite structured hydride with dramatically improved hydrogen diffusion through the bulk. However, scandium is too expensive for widespread use, so attention

---

**Figure 1-2:** The hydrogen atomic hopping rate, \( \omega_{H} \), for various metal hydrides. The slope of the lines are proportional to the activation energy for the thermally driven hydrogen lattice site hopping motion. Thus a smaller slope indicates a lower activation energy, \( E_a \), and faster diffusion through the lattice. Figure reproduced from reference (n). A lower activation energy is found in fluorite structured metal hydrides (\( \text{ScH}_2 \)) and (\( \text{Mg}_{65}\text{Sc}_{35}\text{Pd}_{2.4}\text{H}_{220} \)) compared to rutile structured \( \text{MgH}_2 \). In addition, the fluorite structured hydrides shown are metallic compared to insulating \( \text{MgH}_2 \) (ionic).
has turned to other transition metals, especially titanium.

Unfortunately, Mg and Ti are not mutually soluble at equilibrium. Thus, several groups have pursued non-equilibrium synthesis techniques like ball milling (also called mechanical alloying, mechanical milling, and mechano-chemistry, among other names). These methods have resulted in the formation of MgH$_2$ – Ti and MgH$_2$ – TiH$_2$ composites that exhibit remarkably improved hydrogen kinetics as compared to bulk MgH$_2$. However, the observation of a fluorite structured Mg-Ti-H phase in the bulk has remained unrealized. Yet, it is a bulk, cubic structure magnesium hydride that is desired for onboard hydrogen storage applications.

A recent collaboration between our group and Z. Zak Fang’s metallurgy group at the University of Utah studied MgH$_2$ – TiH$_2$ ball milled under high hydrogen pressure. Deuterium magic-angle spinning (MAS) nuclear magnetic resonance was utilized to study the structural properties of the milled powders and revealed a cubic structured magnesium deuteride in the bulk, ball-milled powder. The body of work for this thesis has been the extension of those initial findings, which were published in 2015. Those findings are briefly discussed in the next chapter.

In summary, the work of this thesis was to study the structural properties of magnesium-titanium deuterides prepared by high pressure ball milling (generally under D$_2$ gas) using deuterium MAS NMR. The goal was to form a cubic structured MgD$_2$ due to the beneficial impacts of the fluorite structure on H/D diffusion in the bulk hydride/deuteride phase, an important improvement for hydrogen storage purposes.

Recent review articles by Crivello et al and Wang and Wang on magnesium hydride-based
hydrogen storage materials provide good overview of the current state of research. General overview texts on hydrogen storage in metal hydrides are provided by Walker and Hirscher.
1.1 References


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Chapter 2: High Pressure Ball Milling  

Apparatus

2.1 Introduction

A major component of this research project was the development of a high pressure milling vessel for ball milling Mg, Ti, MgH\textsubscript{2}, and TiH\textsubscript{2} powders under high pressure hydrogen and deuterium gas. This effort is a continuation and extension of previous work in collaboration with Z. Zak Fang’s metallurgy group at the University of Utah. The results of that work were published in 2015\textsuperscript{a}.

The major finding of that work was the direct observation of cubic (calcium fluoride, CaF\textsubscript{2}, structural motif) MgD\textsubscript{2} in bulk powders of MgH\textsubscript{2} that had been ball milled under high hydrogen pressure (~750 PSI) with TiH\textsubscript{2}. The powders later underwent an H → D exchange so that deuterium MAS NMR could be used to study their local atomic structure. As discussed in the introduction chapter, the cubic crystal structure has been shown to promote improved hydrogen diffusion through the MgH\textsubscript{2} lattice, enhancing the kinetics of the hydriding/dehydriding reaction and therefore important to the implementation of MgH\textsubscript{2} as a hydrogen storage material. Thus, the results from that work, which showed the conversion of standard bulk MgH\textsubscript{2} from the tetragonal crystal structure with poor kinetics to a cubic MgH\textsubscript{2}, have promising implications for hydrogen storage efforts, especially since the fluorite structured MgD\textsubscript{2} was observed in bulk powder form (not thin film), beneficial for large scale implementations.

However, these exciting results were clouded by the high level of impurities in the ball milled powders. The aggressive, high-energy nature of the ball milling technique often results in the
presence of impurities from the milling vessel walls and milling balls in the milled powders. For that work, high pressure ball milling of MgH$_2$ – TiH$_2$ powders was performed at the University of Utah using a custom stainless steel high pressure milling vessel and a custom planetary ball mill. Initial MgH$_2$ – TiH$_2$ powders suffered from iron contamination (from the stainless steel), which spoiled the magnetic field homogeneity and made NMR investigations of the samples impossible. To prevent iron impurities, the stainless steel ball milling vessel was fitted with a brass (roughly CuZn) liner and yttria-stabilized zirconia (YSZ) milling balls were utilized, eliminating all contact of the sample powders with the stainless steel.

Again, the aggressive nature of the ball milling technique resulted in significant brass contamination in the milled powders; sometimes as much as 50 percent by weight. Literature review revealed that MgH$_2$ can react with Cu at high temperatures if a sufficient H$_2$ overpressure is not applied to block MgH$_2$-Cu reaction, which forms Mg$_2$Cu and releases H$_2$. The milled MgH$_2$ – TiH$_2$ powders were heated to high temperature (250 °C, 450 °C) as part of the H → D exchange and later heat treatment process. After the higher (450 °C) temperature heat treatment, a reduction in the relative $^2$H MAS NMR peak area for MgD$_2$ as compared to TiD$_2$ was observed. This reduction suggests a decrease in the presence of MgD$_2$ in our samples after the high temperature heat treatment. Further review of the literature data for the MgH$_2$ + Cu reaction informed that the supplied D$_2$ overpressure used during the heat treatment, while sufficient to block the MgD$_2$ → Mg + D$_2$ dehydriding reaction, was insufficient to block the MgD$_2$ + Cu → Mg$_2$Cu + D$_2$ reaction. We therefore concluded that some MgD$_2$ had been consumed by Cu to form the non-hydrogen/deuterium bearing Mg$_2$Cu. Fortunately, Mg – Cu does not form a
hydrogen (or deuterium) bearing compound\textsuperscript{bc}, thus the \textsuperscript{2}H MAS NMR results, which indicate a cubic structured deuterium bearing species, are still valid. That is, we do observe fluorite structured MgD\textsubscript{2}. However, the role of the brass impurity, if any, in the formation of the bulk, cubic MgD\textsubscript{2} is not clear. Therefore, the motivation for the continuation and extension of this previous work is to ball mill MgH\textsubscript{2} – TiH\textsubscript{2} powders under high H\textsubscript{2} or D\textsubscript{2} pressure in the absence of such impurities. To that end, a molybdenum-lined stainless steel high pressure milling vessel was developed for ball milling MgH\textsubscript{2}, TiH\textsubscript{2}, Mg, and Ti powders under high H\textsubscript{2} and D\textsubscript{2} pressures.

2.2 Design criteria
To guide the development process, several design and performance criteria were identified. First, the high pressure milling vessel should fit the commercially available SPEX 8000 Mixer/Mill\textsuperscript{d}. The SPEX is a high powered shaker-type ball mill considered to be one of the highest energy mills available for small-batch, bench-top powder processing due to the high number of collisions induced per unit of time and due to the high velocity imparted to the milling balls as part of the ball milling process. A detailed description of the SPEX Mixer/Mill can be found in section 4.2 of C. Suryanarayana's in-depth review article, “Mechanical Alloying and Milling”\textsuperscript{e}.

The SPEX 8000 Mixer/Mill was targeted due to equipment access. Prof. Eric Majzoub, a long time collaborator of the group, owns a SPEX and graciously agreed to give us uninterrupted access to it. Without such access, this work would not have been possible.

The 2\textsuperscript{nd} criteria was that the vessel interior should be composed of a strong, hard material to maximize the efficiency and effectiveness of ball milling the powders. Suryanarayana provides
an informative discussion on milling container materials in section 4.3.2. Tungsten-carbide (WC) and hardened steel are commonly used milling container media.

Third, the vial must be pressure worthy for milling the powders under up to 2 kPSI H₂ or D₂ gas. Thus, the vessel dimensions (e.g., wall thickness) must be structurally strong enough to withstand the applied pressure. In addition, the vessel material must not suffer from exposure to H₂ or D₂ gas. For example, titanium, a high strength yet light weight material commonly used in applications where strength and support are required, is not suitable for use with H₂ gas. This incompatibility is due to the well known hydrogen embrittlement phenomenon in which the ductility of Ti is reduced significantly when the hydrogen content of the metal is increased, leading to fracture.

Fourth, the vessel and milling ball materials should be chosen such that any impurities introduced, and there will likely be some contamination due to the aggressive nature of ball milling, will not form hydrogen or deuterium bearing compounds under reasonable conditions. Since deuterium MAS NMR is intended to be the primary characterization technique of the ball milled Mg, Ti, MgH₂, TiH₂ powders, it is critical that the formation of hydride phases be avoided. Any deuterium bearing species will generate a signal in the ²H MAS NMR spectrum. Since the hydrogen and deuterium chemical shift range is generally small (~ 1 – 10 ppm, so 0 – 460 Hz here), and the linewidths of the solid state powders are non-negligible even under MAS (FWHM ~ 200 – 400 Hz), it is difficult to separate ²H MAS NMR signals originating from different deuterium-bearing chemical species except in special cases (e.g., TiD₂ with a large, ~ -150 ppm
{-6.9 kHz} Knight Shift). To simplify the interpretation of the $^2$H MAS NMR spectra and to avoid being fooled by spurious deuterium signal, the vessel material and milling balls must be sourced from materials that do not readily form hydrides. This criteria is perhaps surprisingly non-trivial, since hydrogen is highly reactive and readily forms thermodynamically stable compounds with many materials (see figure 2-1 below).

In a similar vein, the milling vial and milling ball materials must not readily react with Mg or Ti. Oxides, which have extremely high melting temperatures and which are also inert under most conditions, are reasonable choices. Similarly, high strength and high melting temperature metals, like refractory metals, are adequately stable to alloying under the conditions likely to be experienced as part of this work. This criteria was established to avoid the formation of Mg-
impurity or Ti-impurity alloys as we believe occurred for samples in the University of Utah work discussed previously. There, the formation of a Mg-Cu compound during the heat treatment of the ball milled MgH$_2$ – TiH$_2$ powders obscured the positive findings of a cubic-structured MgD$_2$ in the bulk.

Finally, the impurities introduced into the ball milled powders as part of the milling process must not be magnetic (that is Ni, Co, Fe, Gd; the high T$_\text{Curie}$ elements). The presence of ferromagnetic impurities in the ball milled samples, even in small amounts, will significantly distort the static magnetic field ($B_0$) used in NMR, spoiling the field's homogeneity, leading to significantly broader lines in the observed $^2$H MAS NMR spectrum, and making high-resolution solid state NMR characterization of these samples all but impossible. Thus steels, which are commonly used in situations requiring high strength and which are in many cases compatible with high pressure H$_2$, are unfortunately not applicable for a milling vial in this case. Steels are made up mostly of iron, which is introduced as in impurity during the ball milling process. Even the use of non-magnetic steels, 316 or 304 stainless steel for example, is not sufficient as the high energy ball milling process releases elemental iron from these materials, eliminating the non-magnetic property of those specific alloys. Indeed, this effect was witnessed in the first batch of ball milled samples produced by the University of Utah in our earlier work.

### 2.3 High pressure ball milling of metal hydrides – literature review

Prior to the development of a new, custom high pressure ball milling vessel, a literature review was undertaken to investigate what vessel designs had previously been implemented. Early
attempts to ball mill powders under a hydrogen atmosphere were developed independently by Chiang and coworkers as well as Dunlop and coworkers in 2000. Chiang et al. used a stainless steel milling vial and the SPEX 8000 Mixer/Mill. A 1 mm hole was drilled into the side of the cylindrical milling vessel allowing the vessel to be connected to a volumetric gas system via flexible plastic tubing. Thus, the milling vessel remained connected to the gas reservoir throughout the milling process. Their design supported pressures up to ~90 PSI and allowed the group to synthesize Ti–Fe hydrides in-situ. Dunlop et al. developed a similar technique where a hardened steel vessel was used with the SPEX mill. Again, a small hole drilled in the sidewall of the cylindrical milling vial allowed the vessel to be connected to an H$_2$ gas reservoir using tygon tubing. The vessel remained connected to the gas manifold during the milling process. Using this technique, Dunlap and coworkers successfully formed several binary transition metal hydrides (e.g., Ti, Zr, V, Nb, Hf, and Ta) in-situ. All milling was under 1 atm of H$_2$.

In 2002, Raman et al. reported ball milling Mg and Fe powders under 10 atm (~147 PSI) H$_2$ using a custom steel vessel with a Szegvari attritor-type milling system.

In 2008, Baum and colleagues implemented a similar setup as Chiang et al. and Dunlop et al. with the milling vessel connected to an H$_2$ reservoir during ball milling. They employed a steel milling vial and a Retsch 2000 oscillatory mill to ball mill Mg with the ferromagnetic elements Fe, Ni, and Co. Like Chiang et al. and Dunlop et al., this setup was only able to support mild H$_2$ overpressure, approximately 45 PSI.
A significant increase in H₂ overpressure during ball milling was achieved in 2005 by Felderhoff, Bogdonovic, and coworkers. There, a commercial hardened steel milling vessel was modified to be pressure worthy up to 200 bar (~2,900 PSI) H₂. The milling vessel was designed for the Fritsch Pulverisette 7 planetary mill and was equipped with on-board temperature and pressure monitoring, which relayed real-time temperature and pressure within the milling vessel via radio communication. Using their vessel, the group successfully synthesized Ti-doped NaAlH₄ in a single step by ball milling NaH, Al, and TiCl₃ under 83 bar (~1,200 PSI) H₂. Their design was later developed into a commercially available milling vessel compatible with most commercial planetary ball mills. The vessel is now offered by Evico-magnetics. Felderhoff et al later demonstrated the vessel's capabilities by synthesizing several metal hydrides including CaH₂ and TiH₂ by ball milling metal powders under H₂ overpressure. In 2011, Felderhoff and coworkers ball milled MgH₂ – 0.1 TiH₂ under 30 MPa (~4,350 PSI) H₂ using the same setup described above to study reported kinetic enhancements of the MgH₂ hydriding/dehydriding reaction upon ball milling with TiH₂. Their results are especially relevant to the work of this thesis.

During the same time period, Z. Zak Fang's metallurgy group at the University of Utah developed a custom ultra high energy – high pressure (UHEHP) planetary ball milling apparatus. The device is described in detail in Butler et al where it was used to create nanocrystalline tungsten carbide. The milling vessel is made of stainless steel and is capable of operating at H₂ pressures of up to 150 bar (~2,176 PSI). The apparatus has been used for the ball milling of several combinations of MgH₂, TiH₂, Mg, and Ti powders. In fact, it was Fang and coworkers' success in demonstrating significant kinetic enhancements for the
hydriding/dehydriding reaction in their UHEHP ball milled MgH₂ – TiH₂ powders (compared to bulk MgH₂) that lead to our collaboration and ultimately the results discussed above and previously published.⁹

More recently, and related to the work discussed here, Latroche and coworkers employed the Evico-magnetics⁹ milling vessel to reactively ball mill Mg with Fe, Co, and Ni powders under 7.5 MPa (~1,088 PSI) H₂ pressure.¹⁰ In 2012, Latroche et al used the same technique to ball mill Mg and Ti powders under 8 MPa H₂ (~1,160 PSI).¹¹ In 2013, the group repeated the experiments of 2012, this time ball milling Mg and Ti powders under 6 – 8 MPa (~870 – 1,160) PSI) of D₂.¹² In all cases, high pressure ball milling was carried out using a commercially available hardened steel high pressure milling vessel⁹, stainless steel milling balls, and a Fritsch Pulverisette planetary ball mill¹³. The 2012¹⁰ and 2013¹¹ publications are notably related to the work of this thesis.

In 2013, Huot, Latroche, and colleagues published an in-depth review of the mechanical synthesis of hydrogen storage materials.¹⁴ Included is detailed commentary on ball milling Mg- and Ti-based hydrides (and composites) under hydrogen pressure. Particularly relevant is the discussion of section 3, which serves as a good overview of previous work involving ball milling of Mg, Ti, MgH₂, and TiH₂ under H₂ atmosphere.

This discussion of previous instances of ball milling powdered metals and their hydrides under H₂ atmospheres is not exhaustive, but provides a general overview of the state of reactive ball
milling of metal hydrides at the outset of this project. Clearly, several groups have developed
high pressure ball milling techniques and have applied them to metal hydrides. However, what
we have offered is the development of a milling vessel capable of ball milling powders under
high pressure gaseous atmospheres using the commercially available SPEX 8000 Mixer/Mill.
Previous attempts at ball milling under controlled atmospheres in the SPEX were limited to
modest H$_2$ pressures (< 100 PSI). To our knowledge, our vessel is the first and only vessel
capable of high pressure ball milling using the SPEX 8000 Mixer/Mill. This development may
prove to be important because of the commercially available laboratory-scale ball mills, the
SPEX is considered to be the highest energy and most effective for mechanical alloying and
amorphization. While in many cases the linear velocity of the milling balls is higher for
planetary-type ball mills (and higher velocity leads to higher energy collisions), the frequency of
impacts is much greater for the SPEX (~2,000 collisions per minute per ball). Therefore, the
energy supplied to the powder per unit time is generally much higher for the SPEX, and the
SPEX has been shown in several instances to reduce the particle size of ball milled powders in a
much shorter milling time than planetary-type ball mills.

In addition, for every case of high pressure ball milling discussed, the high pressure milling
vessel has been composed of either hardened steel or stainless steel. Thus, in all cases, the milled
powders are exposed to some degree of ferrous contamination. While this iron contamination
may be of no importance to the final chemical make-up of the milled powders (i.e., the iron
impurity behaves as an inert bystander), its presence is extremely consequential to NMR
colorization of such powders. As will be discussed in chapter 4, NMR can provide useful
local structural information that often cannot be obtained using standard structural analysis
techniques (e.g., powder XRD) due to the nanometer-scale crystallite sizes that result in heavily
ball milled powders. Therefore, our second contribution was to develop a high pressure ball
milling vessel lined with molybdenum. The choice of molybdenum is specific to our application:
molybdenum is non-magnetic, and chemically inert to hydrogen, magnesium, and titanium under
the conditions (ball milling, high temperature, high H₂/D₂ pressure) imposed in this work. Our
vessel is, therefore, the first customized for generating Mg(H/D)₂ – Ti(H/D)₂ powders by high
pressure ball milling for subsequent NMR study.

Finally, this work demonstrates the feasibility of the direct synthesis of metal deuterides by high
pressure ball milling of metal powders under high pressure deuterium gas. In nearly all of the
high pressure ball milling studies described above, H₂ served as the milling atmosphere. Latroche
and coworkers were the first to ball mill their metal powders under a deuterium atmosphere, a
process which we have continued here. Metal deuterides, which behave chemically in a similar
fashion to their hydride counterparts, are receptive to alternative characterization techniques such
as neutron powder diffraction and deuterium MAS NMR (used here). Thus, direct synthesis of
metal deuterides, as opposed to the indirect methods like the H → D exchange used in the
University of Utah work described above, removes questions concerning the impact of the
deuteration technique on sample behavior while providing access to information that is unique to
deuterides (e.g., the quadrupole interaction in NMR). Even though the first (to our knowledge)
direct synthesis of metal deuterides by high D₂ pressure ball milling was reported in 2013, it has
not since been extensively mentioned in literature.
2.4 Choice of material – mechanical considerations

Molybdenum was chosen to satisfy the design criteria of a strong, hard material for effective ball milling that was non-magnetic and chemically inert to hydrogen/deuterium, magnesium, and titanium. Molybdenum, a member of the refractory metals (Nb, Ta, W, Re) is known for its high melting temperature (~2,600 °C). The high melting point is indicative of the strong chemical bonds present in metallic molybdenum that result in high strength (tensile strength ~120 kPSI)\(^{ah, ai, aj}\). This high strength is paired to a reasonable hardness (resistance to localized plastic deformation induced by mechanical indention) of HV = 230 (Vickers hardness number)\(^{ah, ai, aj}\). For reference, stainless steel has HV = 152\(^{ai, aj}\), but tungsten carbide has HV = 2,600\(^{ai, aj}\), and tungsten carbide is considered to be one of the best materials for ball milling vessels and milling balls due to its extreme hardness.\(^{e}\) A simple approximation of the force (and therefore energy) applied to a powder sample when it is “crushed” between the vial wall and an oncoming milling ball is:

\[
\vec{F} = \frac{\Delta \vec{p}}{\Delta t}
\]

(2-1)

For a given velocity of a milling ball (determined by the mill and, to some extent, the geometry of the milling vessel)\(^{e}\), with a given mass (determined by the size and material of the ball), the impact force is determined by the duration of the collision (impulse length). The collision duration is the length of time the ball, powder, and vessel wall are in contact. A shorter impulse length (\(\Delta t\)) yields a greater force. Harder, more rigid materials, which are more resistant to deformation under impact, have significantly shorter impulse lengths as compared to softer, more flexible materials.\(^{ak}\) Thus harder materials for the vessel and milling balls will result in higher
energy collisions and more effective ball milling.

For molybdenum, the relatively high hardness is balanced by its high ductility. High tensile strength combined with high ductility results in materials with high toughness, the ability to absorb energy without fracturing. In general, metals have better fracture toughness than harder materials like oxides and carbides since the high strength (metals, oxides, and carbides) is balanced by high ductility. For ball milling, toughness is desired because it reduces the contamination from the vessel and ball materials.

2.5 Choice of materials – magnetism

Elemental molybdenum is paramagnetic with a magnetic susceptibility of $\chi_M = 72 \times 10^{-6}$ cm$^3$/mol (cgs units). Compared to the ferromagnetic elements (Fe, Ni, Co, Gd), this level of magnetism, which must be induced by an external field, is orders of magnitude smaller, satisfying the critical design criteria of not introducing strongly magnetic impurities into the ball milled powders. For reference, the magnetic susceptibility of Gd at 350 k (where it has just transitioned from ferromagnetic to paramagnetic, $T_{\text{curie}} = 292$ K) is $\chi_M = 185,000 \times 10^{-6}$ cm$^3$/mol (cgs units). While, that susceptibility is describing paramagnetic behavior, it can be thought of as setting a lower bound on the strength of ferromagnetism.

2.6 Mo-Ti

The molybdenum-titanium system has been well studied due to molybdenum's use as an additive for steels and titanium alloys that exhibit high strength and corrosion resistance at elevated temperatures. The Mo-Ti phase diagram was studied by J.L. Murray in 1981. Reported
equilibrium phases include the liquid phase (above titanium's melting temperature of 1,668 °C) and a solid solution of the two metals known as the β phase, which forms when titanium undergoes a solid-solid phase transition from its room temperature stable hexagonal close packed (hcp) α phase to a body-centered cubic (bcc) β phase at 882 °C. After the hcp → bcc transformation, molybdenum, which has a bcc structure, and titanium are completely miscible, forming a substitutional alloy. If the mixture is properly cooled (quenched), a metastable β phase Mo-Ti alloy can be retained even at room temperature. Of importance here, the formation of a Mg-Ti alloy only occurs upon the transition of α-Ti to β-Ti at 882 °C or above. The conditions present during ball milling will not lead to temperatures high enough to cause the α → β transition. In addition, during the ball milling process, Ti rapidly absorbs H₂/D₂ to form Ti(H/D)₂ (see chapter 4 for details). As a hydride, titanium transforms from an hcp metal to an fcc (CaF₂ structural motif) hydride structure that has high thermodynamic stability (ΔH ~ -145 kJ/mol). The ball milled titanium quickly transitions to an fcc hydride making it unlikely that β-Ti is ever present, a necessity for alloying titanium with molybdenum. The Mo-Ti phase diagram is reproduced below for reference.
Recently, Barzilai et al reported a Mo-Ti phase diagram based on ab initio density functional theory calculations that predicted several stable stoichiometric Mo-Ti phases that form below 200 °C and some even present at room temperature. However, to date, no experimental evidence has confirmed the results of their calculations.

Finally, the Mo-Ti-H system has less available information and it is possible that more complicated chemistry could result in stable Mo-Ti-H compounds under conditions where no Mo-Ti phases exist. Nevertheless, our results (discussed in chapter 4) have shown molybdenum
to be phase segregated from the hydride phases formed during high pressure ball milling, even in samples with extensive molybdenum impurity present.

2.7 Mo-Mg
The molybdenum-magnesium system is less well studied. However, from the limited information available, no known stable Mg-Mo alloys exist. Thus chemical reaction between magnesium (from the sample powder) and molybdenum impurities (introduced by ball milling) should be non-existent; a significant improvement over the Mg-Cu reaction that resulted from brass contamination in the University of Utah work. Similar to the Mo-Ti system discussed above, no data exists for the Mo-Mg-H system. The Mo-Mg phase diagram is provided below for reference.
2.8 Mo-H

The molybdenum-hydrogen phase diagram is reported in the “Phase Diagrams of Binary Hydrogen Alloys” based on solubility measurements of H in Mo for temperatures up to 2,300 °C and H₂ pressure up to 100 atm (~1,470 PSI H₂). No Mo-H phases are reported within that temperature-pressure range. The solubility of hydrogen in molybdenum is briefly discussed in Mueller, Blackledge, and Libowitz ("Metal Hydrides"; known in the group as the "Metal Hyride Bible") who report a maximum solubility of 0.52 x 10⁻⁴ H atoms per Mo atoms at temperatures up to 1,100 °C. Effectively, molybdenum does not absorb hydrogen or form a hydrogen bearing phase and can be considered to be chemically inert to H.
In summary, molybdenum possesses several properties that make it an ideal candidate vessel material for high pressure ball milling Mg, Ti, MgH$_2$, TiH$_2$ under H$_2$/D$_2$ gas.

2.9 Vessel design – all-molybdenum approach
Initially, an all-molybdenum milling vessel was designed and produced. However, this approach met with several setbacks. First, a 1/4” female pipe thread (FPT) hole in the body of the vessel, designed to accept the 1/4” male pipe threads (MPT) of a Swagelok valve for gas handling purposes, failed to form a pressure-tight seal. As a hard metal, molybdenum machines like cast iron$^{ah,al}$ and is prone to tearing and chipping, especially in fine cuts. Forming the clean threads necessary for the metal-to-metal pipe thread seal is therefore difficult. An attempt to over-tighten the stainless steel (SS) valve into the molybdenum FPT hole resulted in the stripping of the SS threads by the much stronger molybdenum.

The pipe thread hole was bored out and plugged by a straight thread stainless steel bolt carrying a wall-sealing o-ring (so no metal-to-metal seal here). Then, an effort to create a built-in valve in the base of the cylindrical Mo vessel (open at one end only) was attempted. Unfortunately, a crack developed in the base of the vessel during initial test runs that rendered the vessel useless for ball milling under high pressure. The exact cause is unknown, but likely resulted from molybdenum's high ductile-brittle transition temperature (DBTT)$^{ah,as}$, the temperature at which a metal transitions from ductile to brittle behavior. Molybdenum, especially when heavily worked (similar to work hardening in many metals, e.g., copper), can have a DBTT as high as room temperature$^{ah}$ (see figure 2-4 below). It is possible that our vessel, which underwent extensive
machining (e.g., boring a 1.5” ID hole for the milling chamber; additional boring, drilling and tapping for the built-in valve), had a DBBT near room temperature, causing it to become brittle. During test runs under high pressure helium gas, the stress of the applied pressure and impact of the milling balls could have lead to the hairline fracture that resulted in the vessel's failure. Regardless of the cause, that vessel and the all-molybdenum design were scrapped in favor of a stainless steel pressure vessel paired with a molybdenum liner (the “molybdenum liner method”). The final version of this vessel, utilized for much of the work described in this thesis, is described in detail below.

![Graph showing the change in molybdenum's tensile ductility as a function of temperature.](image)

**Figure 2-4:** The change in molybdenum's tensile ductility as a function of temperature. Generally, the ductile-brittle transition temperature (DBTT) is defined as the value at which the ductility is reduced to half of its upper threshold value. For the particular example shown here, the DBTT is near 0 °C.
2.10 Molybdenum liner method
A cartoon graphic of the molybdenum liner method ball milling vessel is depicted in figure 2-5 below. The outer vessel is a cylindrical stainless steel (304L) pressure vessel open at both ends. Specially made fully-threaded stainless steel bolts served as the pressure vessel's end caps. A 1-1/16” OD, 15/16” ID molybdenum cylinder (length = 1”) open at both ends fits tightly (a press fit) into the ID of the SS pressure vessel and forms the wall of the milling chamber. Two molybdenum end caps serve as the end walls of the milling chamber. The molybdenum end caps have a 1/16” thick x 15/16” OD lip that extends into the milling chamber forming a powder tight (but not pressure tight) seal to the ID of the molybdenum cylinder (the Mo liner). The molybdenum end caps also carry an 1-1/16” o-ring (size 0-21) in a o-ring groove on their OD that forms a pressure tight seal to the ID of the stainless steel pressure vessel. Thus, the molybdenum end caps serve as pressure tight bulkheads while the stainless steel end caps prevent the molybdenum end caps from being ejected when the vessel is under pressure. Pedestals on the top of the molybdenum end caps house 10-32 threaded blanks, allowing the use of a machine bolt or threaded rod to remove the tight fighting end caps from the molybdenum liner.
Gas handling is accomplished by a 316 stainless steel Swagelok valve (model SS-1KM4-S4) pipe-threaded into the stainless steel pressure vessel's side wall. To accommodate the valve's threads, a 1” wide band with 2.5” OD was left about the pressure vessel's circumference. Compared to the rest of the pressure vessel with 1.6” OD, this thicker band afforded an extra 0.45” of wall thickness into which the valve could be safely and securely mounted. In addition, a
High Pressure Equipment Co. (Hi-P) AF1 port was placed in this thick band at a 60° angle (when viewed looking down the cylinder axis) from the Swagelok valve. The AF1 port served as a secondary pressure relief point, allowing the vessel to be depressurized should the Swagelok valve become jammed or blocked. To reduce the weight of the milling vessel and ensure that it fit into the SPEX mill, excess material from the 2.5” OD x 1” wide band was removed (until the OD ≈ 1.6”) except for a 120° section centered about the Swagelok valve and AF1 port (when viewed looking down the cylinder axis, see figure 2-6-A, top view, below).
Figure 2-6-A: Machine drawing of the stainless steel pressure vessel: side and top views.
Figure 2-6-B: Machine drawing of the stainless steel end caps: side, top and bottom views.
Two aluminum OD adapters were made to provide a tight fit for the vessel within the SPEX ball.

Figure 2-6-C: Machine drawing of all molybdenum pieces. The cylindrical molybdenum liner is shown (side and top/bottom views) above the dashed line. The molybdenum end caps (side, top, and bottom views) are shown below the dashed line.

Two aluminum OD adapters were made to provide a tight fit for the vessel within the SPEX ball.
mill's vessel mounting clamps. The clamps hold the vessel by the vessel's cylinder ends in a vice-like arrangement. The clamps of the vice are disc shaped with a small lip that has an ID of 2 1/4”. Thus, the 1.6” OD of the stainless steel pressure vessel is significantly undersized, resulting in considerable “walking” of the vessel during ball milling. This “walking” of the vessel, that is movement of the vessel within the vice-like clamp of the SPEX's vessel mount, damaged the rubber pads of the clamping surface and, more worrisome, allowed the vessel to come dangerously close to “slipping” the clamp's grip. The aluminum adapters effectively mated the smaller OD of the pressure vessel to the larger ID of the mill's clamps, eliminating this issue. A small set screw prevented the milling vessel from rotating with respect to the aluminum OD adapters, while the rubber pads on the mill's clamps prevented the OD adapters from rotating with respect to the clamp. A schematic of the SPEX’s vessel clamp is shown below (see figure 2-7) as are the machine drawings for the aluminum OD adapters (see figure 2-8).
Figure 2-7: (A) Schematic of the SPEX 8000 Mixer/Mill vessel clamp (in dashed red box). (B) Image of the high pressure milling vessel loaded into the SPEX's vessel mounting clamp. Here the aluminum OD adapters were not in place, so the vessel's OD is undersized compared to the clamp's ID and the rubber clamp pads are exposed (see red arrow).

Figure 2-8: Machine drawing of the aluminum OD adapters used to properly mate the undersized OD of the stainless steel pressure vessel's cylinder ends to the SPEX ball mill's vessel clamp. Side, top, and bottom views are shown.
Machine drawings with various views for the stainless steel pressure vessel, stainless steel end caps, molybdenum liner, and molybdenum end caps have already been provided above (see figure 2-6). Below, several pictures of the milling vessel are shown below.

![A and B](image)

**Figure 2-9:** Images of the stainless steel high pressure ball milling vessel. (A) The vessel without the aluminum OD adapters, and (B) the vessel with the OD adapters.

### 2.11 Strength considerations

An important design criteria was that this milling vessel be capable of supporting high H₂ and D₂ pressures within the ball milling chamber. Therefore, the structural strength, which depends on both the geometry of the vessel and the material used, was considered during the design process.

The milling vessel must withstand the load applied by the gas pressure in five critical areas: (1) the cylindrical walls of the stainless steel pressure vessel, (2) the screw threads of the stainless steel end caps, which support the molybdenum end caps, (3) the molybdenum end caps, which serve as a pressure-tight bulkhead at the ends of the cylindrical stainless steel pressure vessel, (4) the Swagelok valve and its pipe thread connection, and (5) the Hi-P AF1 secondary pressure relief port with Hi-P AM1 port plug.
2.12 Strength considerations – wall thickness

The stresses experienced by a thick-walled cylinder under internal and/or external pressures are given by the Lamé equations, which can be found in most introductory mechanical engineering textbooks. Geere, Hearn, and Roark were consulted here. This vessel may be considered “thick-walled” since the OD radius, $r_{OD}$, is not significantly greater than the wall thickness, $t$; here $t/r_{OD} \sim 0.34$. For a thick-walled cylindrical pressure vessel under internal pressure only, the stresses on the cylinder are shown in figure 2-10 below and the stresses (in the tangential, longitudinal, and radial directions) for internal and external cylinder walls are given in equations 2-2 through 2-7.

![Figure 2-10: Stresses on a thick walled cylinder under internal pressure only. A radial and side view are both shown. The maximum stress, $\sigma_{\theta-ID}$, occurs in the tangential direction (the hoop stress) on the inner cylinder wall.](image)
Internal wall

\[
\sigma_{\theta-ID} = P \frac{OD^2 + ID^2}{OD^2 - ID^2} \quad (2-2)
\]

\[
\sigma_{Z-ID} = P \frac{ID^2}{OD^2 - ID^2} \quad (2-3)
\]

\[
\sigma_{r-ID} = -P \quad (2-4)
\]

External wall

\[
\sigma_{\theta-OD} = 2P \frac{ID^2}{OD^2 - ID^2} \quad (2-5)
\]

\[
\sigma_{Z-OD} = P \frac{ID^2}{OD^2 - ID^2} = \sigma_{Z-ID} \quad (2-6)
\]

\[
\sigma_{r-OD} = 0 \quad (2-7)
\]

It can be demonstrated that the maximum stress is experienced in the tangential direction at the surface of the vessel's internal wall (\(\sigma_{\theta-ID}\)). For example,
\[
\frac{\sigma_{\theta-ID}}{\sigma_{\theta-OD}} = \frac{P \frac{OD^2 + ID^2}{OD^2 - ID^2}}{2P \frac{OD^2 + ID^2}{OD^2 - ID^2}}
= \frac{1}{2} \left(\frac{OD^2}{ID^2} + 1\right)
\]

Since OD > ID, then \(\frac{OD}{ID} > 1\) and \(\frac{OD^2}{ID^2} = \left(\frac{OD}{ID}\right)^2 > 1\)

\[\Rightarrow \frac{1}{2} \left(\frac{OD^2}{ID^2} + 1\right) > 1\]
\[\Rightarrow \left(\frac{\sigma_{\theta-ID}}{\sigma_{\theta-OD}}\right) > 1\]
\[\Rightarrow \sigma_{\theta-ID} > \sigma_{\theta-OD}\]

Thus, by choosing a material, OD, and ID such that the vessel can withstand the maximum internal wall tangential stress (also known as the hoop stress or circumferential stress) assures that the design will withstand all other wall stresses induced by the internal pressure.

The expression for the internal wall hoop stress (equation 2-2) can be reformulated to provide an equation for determining the maximum internal pressure a vessel of given ID, OD, and tensile strength \(S_T\) can support.

\[P_{\text{max}} = \sigma_{\theta-ID_{\text{max}}} \left(\frac{OD^2 - ID^2}{OD^2 + ID^2}\right)\]  
(2-8)
Since the tangential stress is a tensile stress, the maximum tangential stress, $\sigma_{\theta-ID_{\text{max}}}$, is equal to the tensile strength ($S_T$) of the cylinder material. Therefore, equation 2-8 becomes:

$$P_{\text{max}} = S_T \left( \frac{OD^2 - ID^2}{OD^2 + ID^2} \right) \quad (2-9)$$

The vessel material here is 304L stainless steel with $S_T = 81.8 \text{ kPSI}_{\text{aw,ax,ay}}$, 1.6” OD, and 1 1/16” = 1.00625” ID, giving:

$$P_{\text{max}} = 31.7 \text{ kPSI}$$

Using a safety factor of 2.5, the vessel's max operating pressure is

$$P_{\text{max}} / 2.5 = 12.7 \text{ kPSI}$$, well above the intended operating pressure of ~2 kPSI.

However, it is worth considering the maximum pressure based on the yield strength. The yield strength is the stress at which a material will no longer deform elastically. In effect, if a load is applied that is greater than a material's yield strength, the material will be permanently deformed. We want to avoid permanent deformations to ensure the milling vessel operates as intended. Thus, the maximum pressure the vessel walls can support without permanent deformation is given by equation 2-9 with $S_T$, the yield strength, substituted for $S_T$, the tensile strength. For 304L stainless steel, the yield strength is 30.5 kPSI$^{\text{aw,ax,ay}}$ so that:

$$P_{\text{max}} = 11.8 \text{ kPSI}$$
With a safety factor, the maximum safe operating pressure of the high pressure ball milling vessel becomes 4.72 kPSI, still more than double the maximum intended operating pressure.

2.13 Strength considerations – screw threads

The next consideration is the load that the stainless steel end caps can support. There are two primary stresses that a threaded fastener will experience: tensile and shear. By convention, a threaded fastener is designed to fail in tension (that is the bolt will tear apart) before the threads (both male and female) fail in shear. Here, we are using a custom fully-threaded bolt, so it is important that we determine the tensile and shear strength of the stainless steel end caps and the internal female threads that accept the caps on the stainless steel pressure vessel (see figure 2-5 above for reference). The load supported by the stainless steel end caps is the outward force applied on the molybdenum end caps with pressure-tight o-ring seals by the H₂ or D₂ gas pressure in the milling chamber. See figure 2-11 for a depiction of the load applied to the stainless steel end caps.
The tensile load that can be supported by a threaded fastener is given by:

\[ \text{Load}_{\text{max}} = S_T \times A_T \]  \hspace{1cm} (2-10)

where \( \text{Load}_{\text{max}} \) is the maximum load the fully-threaded bolt can support in tension, \( S_T \) is the tensile strength of the material, and \( A_T \) is the tensile stress area of the end cap, which is determined by its geometry. The tensile stress area of a bolt can be found tabulated in many places (e.g., Fastenal.com) for most standard size threads. It can also be calculated using the semi-empirical formula.\[^{35}\]
\[ A_T = 0.7854 \left( D - \frac{0.9743}{n} \right)^2 \]  

(2-11)

where \( D \) is the nominal (basic) diameter of the threaded bolt and \( n \) is the number of threads per inch. Here, the 1-1/4” – 12 threads have \( D = 1.25" \) and \( n = 12 \) so that:

\[ A_T = 1.073 \text{ in}^2 \]

and

\[ \text{Load}_{T_{\text{max}}} = 32.7 \times 10^3 \text{ lbf} \]

Generally, an acceptable load for a screw thread is defined as \( 0.6 \times \text{Load}_{T_{\text{max}}} \). Including a safety factor of 2.5, the maximum safe operating load is then:

\[ \text{Load}_{T_{\text{safe}}} = 7.85 \times 10^3 \text{ lbf} \]

The maximum safe pressure based on the maximum safe tensile load for the threaded stainless steel end caps can be determined by:

\[ P_{SS-\text{End-Caps-Tensile}_{\text{safe}}} = \frac{\text{Load}_{T_{\text{safe}}}}{A_{ID}} \]  

(2-12)

where \( A_{ID} \) is the area of the circle formed by the ID of the stainless steel pressure vessel. \( A_{ID} = 0.887 \text{ in}^2 \) so that:

\[ P_{SS-\text{End-Caps-T}_{\text{safe}}} = 8.85 \text{ kPSI} \]

more than 4x the intended operating pressure of the ball milling vessel.
The maximum safe pressure calculated above evaluates the tensile load capability of the stainless steel end caps. However, the shear strength of the threads, both internal and external, that hold the end caps in place, must also be considered. Similar to the tensile load calculation above, the maximum shear load that can be supported by a given thread is:

\[
\text{Load}_{S_{\text{max}}} = S_S \times A_S
\]  

where \( \text{Load}_{S_{\text{max}}} \) is the maximum shear load, \( S_S \) is the shear strength of the material, and \( A_S \) is the shear stress area of the threads. For stainless steel, \( S_S \sim 0.577 \times S_Y \sim 17.6 \text{kPSI} \). The shear stress area of a straight-threaded piece is given by:

\[
A_{S-\text{EXT}} = \pi n L_e K_{n_{\text{max}}} \left( \frac{1}{2n} + 0.57735 \left( E_{s_{\text{min}}} - K_{n_{\text{max}}} \right) \right) \tag{2-14}
\]

**External threads**

\[
A_{S-\text{INT}} = \pi n L_e D_{s_{\text{min}}} \left( \frac{1}{2n} + 0.57735 \left( D_{s_{\text{min}}} - E_{n_{\text{max}}} \right) \right) \tag{2-15}
\]

**Internal threads**

where

\( n \) = threads per inch

\( L_e \) = thread engagement length

\( K_{n_{\text{max}}} \) = maximum minor diameter of the internal thread

\( E_{s_{\text{min}}} \) = minimum pitch diameter of the external thread
\[ D_{s-min} = \text{minimum major diameter of the external thread} \]
\[ E_{n-max} = \text{maximum pitch diameter of the internal thread} \]

Here, the 1-1/4” – 12 threads have:

\[ n = 12 \quad E_{s-min} = 1.1941” \]
\[ L_e = 0.8” \text{ (see figure 2-6-B, side)} \quad D_{s-min} = 1.2368” \]
\[ K_{n-max} = 1.178” \quad E_{n-max} = 1.2039” \]

which are provided by American Society of Mechanical Engineers\textsuperscript{ba} and American National Standards Institute\textsuperscript{bb}, and can be found on many websites such as https://www.engineersedge.com. The shear stress area for the external and internal threads are:

\[ A_{S-EXT} = 1.889 \text{ in}^2 \]
\[ A_{S-INT} = 2.358 \text{ in}^2 \]

Therefore, the maximum shear load that can be sustained by the threads of the stainless steel pressure vessel and stainless steel end caps is:

\[ Load_{s麻辣} = S_S \times \text{minimum}(A_{S-EXT}, A_{S-INT}) = 33.2 \times 10^3 \text{ lbf} \]

which is quite close the maximum tensile load the stainless steel end caps can support.

Again, an acceptable load for a screw thread is considered \( 0.6 \times Load_{s麻辣} \). With a safety factor of 2.5, the maximum safe shear load that the threads can accommodate becomes 7.97
Similar to equation 2-12 above, the maximum safe operating pressure for shear loading of the threads can be calculated.

\[
P_{SS-End-Caps-Shear_{safe}} = \frac{Load_{S_{safe}}}{A_{ID}} = 9.0 \text{ kPSI}
\] (2-16)

In summary, the maximum safe operating pressure for the high pressure ball milling vessel, based upon the strength of the stainless steel end caps and the threaded connection between the end caps and the pressure vessel is:

\[
P_{SS-End-Caps-Tensile_{safe}} = 8.85 \text{ kPSI}
\]

and

\[
P_{SS-End-Caps-Shear_{safe}} = 9.0 \text{ kPSI}
\]

For both types of loading, the maximum safe operating pressure is more than four times the intended operating pressure.

### 2.14 Strength considerations – molybdenum end caps

The next consideration is the strength of the molybdenum end caps, which carry the o-ring seals and serve as a form of pressure bulkhead. The molybdenum end caps can be modeled as a simply supported circular plate under uniform load. While this model is not an accurate depiction of the our system (e.g., here the molybdenum end caps are supported by the thick stainless steel fully-threaded bolts), it does provide the maximum possible stress that the molybdenum end caps would experience for a given pressure. For example, for a given geometry and applied pressure,
the stress experienced by a simply supported circular flat plate is greater than that experienced by an edge clamped circular flat plate.\textsuperscript{am, au, av, az} A schematic of the model system is shown below:

\textbf{Figure 2-12:} The stress experienced by the molybdenum end cap due to the applied load of the internal gas pressure. The molybdenum end cap is modeled as simply supported circular flat plate. The maximum stress occurs at the center of the plate and is indicated by the red arrow in the figure.

From Roark\textsuperscript{av}, the maximum stress of a simply supported plate is experienced at the center of the plate and is given by:

\[
\sigma_{\text{max}} = \frac{3(3 + \nu)r^2}{8t^2}P
\]  

(2-17)
\( \nu = \text{Poisson's ratio} = 0.31 \) for molybdenum

\( r = \text{radius of the surface under pressure, here } r = \text{ID} / 2 = 0.53125'' \)

\( t = \text{thickness of the circular plate, here } t = 0.1870'' \)

Thus, the max stress experienced by the molybdenum end cap under the applied pressure from the \( \text{H}_2 \) or \( \text{D}_2 \) gas in the milling chamber is:

\[
\sigma_{\text{max}} = 10.02 \times P
\]

The maximum allowable pressure is then given by:

\[
P_{\text{max}} = \frac{\sigma_{\text{max}}}{10.02} = \frac{S_T}{10.02}
\]  \hspace{1cm} (2-18)

As done previously, the maximum allowed stress has been set to the tensile strength, \( S_T \), of the material under consideration (molybdenum). For molybdenum, \( S_T \) is 120 kPSI\(^a\) so that the maximum allowable operating pressure is:

\[
P_{\text{max}} = 11.98 \text{ kPSI}
\]

With a safety factor of 2.5, the maximum safe operating pressure becomes:

\[
P_{\text{safe}} = 4.8 \text{ kPSI}
\]

more than double the intended operating pressure.

The force applied to the molybdenum end caps due to the gas pressure will cause the end caps to
deflect. The maximum deflection, $\delta_{\text{max}}$, which occurs at the end caps' center points, is:

$$
\delta_{\text{max}} = \frac{(5 + \nu) \cdot 12 \cdot (1 - \nu^2) r^4}{64 \cdot (1 + \nu) \cdot E \cdot t^3} P
$$

where:

$$
E = \text{Young's modulus, for molybdenum, } E_{\text{Mo}} = 4.77 \times 10^7 \text{ PSI}
$$

$\nu$, $r$, and $t$ are the same as in equation 2-17 above.

At the maximum allowable operating pressure ($P_{\text{max}} = 11.98 \text{ kPSI}$):

$$
\delta_{\text{max}} = 0.0021 \text{ in}
$$

or a bend angle of:

$$
\theta_{\text{bend-max}} = \arctan\left(\frac{\delta_{\text{max}}}{\text{ID}/2}\right) = 0.15^\circ
$$

At the maximum safe operating pressure, $P_{\text{safe}} = 4.8 \text{ kPSI}$,

$$
\delta_{\text{safe}} = 0.00084 \text{ in}
$$

and

$$
\theta_{\text{bend-safe}} = 0.091^\circ
$$

2.15 Strength considerations – Swagelok valve and Hi-P port

The stainless steel Swagelok valve (model SS-1KM4-S4) is rated to 5,000 PSI at room
temperature and 3,435 PSI at 232 °C by the manufacturer. The High Pressure Company AF1 port
and AM1 plug are each rated to 15,000 PSI at room temperature. In both cases, the safe operating
pressures, as determined by the manufacturers, are more than double the intended operating pressure for the high pressure ball milling vessel.

In summary, all components of the high pressure vessel are designed to operate safely (includes safety factor) at more than double the intended operating pressure of 2,000 PSI. The table below summarizes the maximum safe operating pressure of the components discussed above.

<table>
<thead>
<tr>
<th>Component</th>
<th>$P_{safe}$ (PSI)</th>
<th>$P_{safe} / P_{intended}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS Wall</td>
<td>4,720</td>
<td>2.4</td>
</tr>
<tr>
<td>SS End Caps</td>
<td>8,850</td>
<td>4.4</td>
</tr>
<tr>
<td>Mo End Caps</td>
<td>4,800</td>
<td>2.4</td>
</tr>
<tr>
<td>Swagelok Valve</td>
<td>5,000</td>
<td>2.5</td>
</tr>
<tr>
<td>Hi-P Port / Plug</td>
<td>15,000</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Maximum safe operating pressure for various components of the high pressure ball milling vessel. The lowest safe maximum operating pressure is more than double the intended operating pressure of 2,000 PSI.

Before initial operations, the high pressure ball milling vessel was pressure tested at 4,000 PSI using a hydraulic pump with hydraulic oil (so no stored energy unlike a compressed gas). The vessel was held at this elevated test pressure overnight to ensure the absence of any fatigue related failures.

### 2.16 Concrete enclosure
A masonry block enclosure was built to house the ball milling setup. The cubic enclosure
consisted of 3-block-long sides that were 3 blocks high. Total dimensions were nominally 48” W x 48” L x 48” H (outer) and 32” W x 32” L x 24” H (inner). The blocks were supported by a lumber frame composed of 4 x 4 posts and 2 x 4 cross beams. The cross beams, which formed the enclosure's roof, were covered with 16” L x 8” W x 4” H masonry bricks, and the entire enclosure was covered with 1/8” thick steel sheet, courtesy of the Physics Department Machine Shop scrap pile. Two fans, one for ventilation and one for fresh air intake, were added to the enclosure to provide aid air exchange. The SPEX mill was removed from its standard housing and placed within the enclosure. To power the mill, a special adapter to mate the SPEX's AMP circular plastic connector (CPC) to a standard 3-prong electrical plug was made. The adapter included a 10-amp “slow-blow” fuse to replace this safety mechanism that is a part of the circuit board included in the mill's standard housing. The enclosure and milling setup is depicted in the image below.
The enclosure provides several benefits. First, it eliminates the issue of the high pressure milling vessel's Swagelok valve impacting the walls of the SPEX's original housing. The valve protrudes radially from the vessel's body several inches (see figure 2-9: A and B) and is thus exposed to being slammed against the housing walls in the standard setup (a tight fit with dimensions 21” L x 22” W x 14” H, see figure 2-7-A).

In addition, the larger volume, improved air flow from the two fans, and the large thermal mass of the concrete blocks act to considerably reduce the significant sample and vessel heating during ball milling commonly found in typical commercial ball mills. See Suryanarayana\textsuperscript{e} and Takacs and McHenery\textsuperscript{bc} for in-depth discussions of sample heating during ball milling. While the vessel
temperature was not monitored during milling, the vessel was cool to the touch within moments of the cessation of ball milling, even after extended milling runs (several hours). Furthermore, the air temperature within the enclosure, monitored by thermocouple, did not register a notable temperature increase (< 5 °C) during milling runs, even runs of > 24 hours.

More importantly, the enclosure adds an element of safety to the high pressure ball milling operation by surrounding the ball mill and high pressure milling vessel with energy absorbing materials (concrete and steel). Unfortunately, the critical importance of safety when working with hydrogen gas, especially when pressurized, has been reinforced by recent hydrogen explosions at the University of Hawaii\textsuperscript{bd} and at Ames Laboratory\textsuperscript{bc, bf}.

2.17 Gas manifold
A gas manifold composed of Swagelok and High Pressure Equipment Company parts was constructed for gas handling purposes. A rough vacuum was provided by a mechanical vacuum pump. The manifold and milling vessel's internal volumes were calibrated using helium gas and pressure vessels of known volumes. By calibrating the vessel and manifold volumes, the D\textsubscript{2} uptake by the Mg-Ti powders during high pressure ball milling could be monitored. The manifold was designed to minimize waste of D\textsubscript{2} gas (expensive, ∼$300 per 50 L STP) when pressurizing the vessel and monitoring deuterium uptake.

2.18 Safety considerations
As noted above, safety is critical when working with hydrogen gas. Various steps, like the masonry block and steel enclosure discussed above, have been taken to minimize the risks
associated with high pressure ball milling under $H_2$ or $D_2$ atmospheres. In addition, the energy of the high pressure ball milling system, which includes the energy supplied by kinetic energy of the milling balls, the energy stored in the pressurized gas, and the chemical potential energy of the $H_2/D_2$ gas as well as that of the exothermic hydriding reactions for MgH$_2$ and TiH$_2$, has been minimized by design.

The energy added to the system (here, the pressurized milling vessel and the sample, milling balls, and gas contained within) can be roughly approximated by the kinetic energy of the milling balls. The milling vessel transcribes a figure eight pattern every cycle of the mill, which operates at 1,060 cycles per minute.$^{bg}$ During a cycle, a milling ball will travel (by some complex path) from one end of the vessel and back. Thus, the minimum distance traveled during a cycle is double the interior length of the milling cavity (here, $L_{\text{interior}} = 7/8''$). Typically, a ball-to-powder by weight ratio (BPR) of 10:1 was used. For a standard 0.5 g sample, this BPR corresponds to a total mass of all the milling balls present of $\sim 5$ g. The kinetic energy of the milling balls (as a group) is then $\sim 2.2$ mJ at each impact (see below).

$$v = \frac{\Delta x}{\Delta t}, \quad \Delta x = 2 \cdot L \cdot 1,060, \quad \Delta t = 60 \text{ s}, \quad KE = \frac{1}{2} mv^2$$

This impact energy corresponds to a power supplied to the system by the mill of $P_{\text{mill}} \sim 80$ mW: 2.2 mJ/collision, $2 \times 1,060$ collisions per minute. This energy, some of which is absorbed by the sample, is quickly dissipated as heat (the system has high thermal conductivity) that is efficiently vented to the surroundings. Hence, the lack of significant temperature increase for the vessel during milling. Ignoring heat dissipation, in one hour (3,600 seconds) $< 300$ J is added to
the system by the mill. More detailed discussions of the energy associated can be found in Takacs and McHenry, Manai et al, Balaz, Maurice and Courtney, Magini et al, and Suryanarayana. Of special note, Maurice and Courtney found the energy per collision to be of the order of 1 – 10 mJ for the SPEX.

2.19 Stored energy of the H\textsubscript{2}/D\textsubscript{2} gas

There is energy stored in a compressed gas. Indeed, compressed gas is often paired with wind and solar energy generation to provide energy storage when these sources are overproducing and later meet energy needs when generation alone cannot. The explosive energy, referred to as the “burst energy”, due to the pressure of a compressed gas in a pressure vessel is given by the Brode equation:

\[
E_{\text{Brode}} = \frac{(P_0 - P_{\text{ambient}}) V}{\gamma - 1} \tag{2-20}
\]

where:

\(P_0\) = the pressure of the gas in the pressure vessel

\(P_{\text{ambient}}\) = the pressure of the gas (air) outside the pressure vessel

\(V\) = the internal volume of the pressure vessel

\(\gamma\) = the heat capacity ratio of the gas = \(\frac{C_p}{C_v}\)

here:

\(P_0 = 2,000\) PSI = \(13.8 \times 10^6\) Pa

\(P_{\text{ambient}} = 1\) atm = \(1.013 \times 10^5\) Pa

\(V = 11.12\) cm\(^3\) = \(1.112 \times 10^{-5}\) m\(^3\)
\( \gamma = 1.405 \) for H\(_2\)

So, the burst energy due to the compression of H\(_2\) or D\(_2\) gas for the high pressure milling vessel is:

\[
E_{\text{Brode}} \approx 364 \text{ J}
\]

Note, the Brode energy is simply the work required to adiabatically (no heat transfer) compress the gas from ambient pressure to the given pressure.

As can be seen, the energy stored in the compressed H\(_2\)/D\(_2\) gas of the high pressure ball milling vessel is quite small due to the design choice to have a small milling chamber (and thus internal volume), greatly reducing the effect of the relatively high gas pressure. A standard sized milling vessel for the SPEX has internal dimensions of ~1.5” ID x 1.5” L, four times the internal volume of our vessel implying ~4x the stored energy in a similarly pressurized vessel.

However, by far, there is more energy stored as chemical potential energy in the H\(_2\)/D\(_2\) gas. Given a spark, H\(_2\) (or D\(_2\)) will react exothermically with O\(_2\) (present in air) to form water and release 242 kJ/mol H\(_2\) of energy.\(^{19}\) Thus, the bigger concern is the rupture or failure of the pressure vessel, releasing H\(_2\) to the air where it can combine with the O\(_2\) present. The number of moles of H\(_2\) or D\(_2\) present in the milling vessel is given by the ideal gas law multiplied by the compressibility factor, Z, for H\(_2\) gas:

\[
n = \frac{PV}{RTZ} \quad \text{(2-21)}
\]
At room temperature and 2,000 PSI, \( Z_{H_2}(298 \text{ K}, 2,000 \text{ PSI}) \approx 1.1 \) so that \( n = 54 \text{ mmol} \) H\(_2\) (or D\(_2\)). Reacting this quantity of H\(_2\) with excess O\(_2\) would result in the release of \( \sim 13 \text{ kJ} \) of energy, more than 40x the energy stored as pressure in the compressed H\(_2\). Again, this energy is an important reminder of the care required when working with H\(_2\) or D\(_2\) gas. For comparison, one gram of TNT releases \( \sim 4.2 \text{ kJ} \) of energy.\(^{bq}\) By designing a high pressure milling vessel with \( \sim 1/4 \) the internal volume of a standard SPEX milling vial, the overall potential energy of the system is reduced. Here the chemical potential energy of the H\(_2\) or D\(_2\) gas is proportional to the number of moles of gas, which is in turn proportional to the volume of the milling vessel (see equation 2-21 above).

### 2.20 Chemical potential energy of the exothermic hydriding reactions

Finally, consider the energy released by the exothermic hydriding reactions for Mg and Ti:

\[
\text{Mg}_\text{(s)} + H_2\text{(g)} \Leftrightarrow MgH_2\text{(s)} + \Delta H_f
\]  

\[
\text{Ti}_\text{(s)} + H_2\text{(g)} \Leftrightarrow TiH_2\text{(s)} + \Delta H_f
\]

For both reactions, the enthalpy of formation, \( \Delta H_f \), is negative (-74.4 kJ/mol for MgH\(_2\) and -144.25 kJ/mol for TiH\(_2\))\text{\( ^{\text{m,at}} \)} indicating a release of energy upon hydrogen uptake.

By converting these \( \Delta H_f \)'s to the heat of formation per unit mass and using the maximum expected sample mass intended to be milled, the maximum energy release due to the
hydrogenation of Mg or Ti can be determined (assuming an excess of H₂ or D₂ gas). Note, isotope effects on ΔHᵢ are small and thus ignored. The mass heats of formation for MgH₂ and TiH₂ are 3.06 kJ/g and 3.01 kJ/g respectively. Thus a one gram sample (double the standard 0.5 gram sample amount) releases ~3.1 kJ by hydriding (or deuteriding) during high pressure ball milling. Once again, the design decision to use a smaller milling vessel and in turn ball mill smaller quantities of sample powders serves as a safety mechanism by setting a low maximum for the possible energy released by the system during ball milling under H₂ or D₂ pressure.

In summary, the milling vessel design resulted in a small H₂/D₂ gas volume and small sample sizes that in turn reduce the magnitude of possible energy release (vessel rupture, H₂ + O₂ reaction, or hydriding reaction for the metal powders), serving as a safety mechanism. Indeed, it can be shown that under the maximum energy release situation (H₂ + O₂ → H₂O), the temperature of the vessel (should the reaction occur within the confines of its volume) would be raised negligibly by the absorption of the reaction energy. Assuming that the total energy released is absorbed as heat by the vessel (E_released = Q_total), then:

\[ Q_{total} = Q_{SS} + Q_{Mo} \quad \text{(2-24)} \]

Where \( Q_{SS} \) is the heat absorbed by the stainless steel pressure vessel and end caps while \( Q_{Mo} \) is the heat absorbed by the molybdenum liner and end caps. In addition, since the molybdenum liner and stainless steel pressure vessel are in close thermal contact and both have high thermal conductivities (\( k_{SS} = 16.2 \text{ W/m*K}, k_{Mo} = 138 \text{ W/m*K} \)), it is assumed that the change in temperature upon absorption of the reaction energy is equal for both materials. That is:
\[ \Delta T_{SS} = \Delta T_{Mo} \]  

(2-25)

By combining equations 2-24 and 2-25, and recalling that:

\[ Q = cm \Delta T \]  

(2-26)

where \( c \) is the specific heat and \( m \) the mass of the material under consideration, we can determine the expected change in temperature upon the absorption of a given amount of heat (energy), \( Q_{total} \):

\[ Q_{SS} = Q_{total} \frac{c_{SS} m_{SS}}{c_{SS} m_{SS} + c_{Mo} m_{Mo}} \]  

(2-27)

and similarly

\[ Q_{Mo} = Q_{total} \frac{c_{Mo} m_{Mo}}{c_{SS} m_{SS} + c_{Mo} m_{Mo}} \]  

(2-27)

Here,

\[ c_{SS} = 0.5 \text{ J/g*K} \]

\[ m_{SS} = 1,060 \text{ g} \]

\[ c_{Mo} = 0.25 \text{ J/g*K} \]

\[ m_{Mo} = 110.5 \text{ g} \]

If we assume a heat release of double the expected maximum energy release (\( E_{max} \approx 13 \text{ kJ} \), see above), so 26 kJ of energy absorbed by the liner and pressure vessel as heat, the change in temperature of the vessel and liner is: 

59
\[ \Delta T_{\text{max}} \approx 47 \, ^{\circ}C \]

which is well below the level of heating required to significantly weaken the SS pressure vessel, melt the buna-N o-rings, or significantly increase the pressure (< 400 PSI increase). So, the relatively large thermal mass of the milling vessel adequately handles the energy release from ball milling, the hydriding reactions, or (should it occur) an \( \text{H}_2 + \text{O}_2 \) reaction.

On a related note, the relatively high thermal conductivity of hydrogen gas (0.187 W/m*K)\(^{br}\) compared to standard milling atmospheres (e.g., Ar: \( k = 0.0177 \, \text{W/m*K} \), air: \( k = 0.0262 \, \text{mW/m*K} \), air is a good thermal insulator!\(^{br}\))\(^{br}\) improves the heat dissipation during ball milling by aiding in the heat exchange between the powder sample and the vessel. See Huot et al\(^{ag}\) for a more detailed description of this phenomenon.

### 2.21 Benefits of the molybdenum liner method

The original approach, the all-molybdenum high pressure milling vessel, may seem like the more elegant design. However, the molybdenum liner method employed in the work of this thesis has several key benefits. As discussed above, there were several safety mechanisms that resulted from the stainless steel pressure vessel’s dimensions; namely the minimization of potential energy release from a vessel rupture, the metal hydriding reactions, or the reaction of \( \text{H}_2/\text{D}_2 \) with \( \text{O}_2 \). In some ways, this benefit was forced upon us by the use of a stainless steel pressure vessel with a molybdenum liner. Molybdenum has a much higher tensile strength than stainless steel, that could have allowed for an increased internal volume (milling chamber) while maintaining the necessary pressure worthiness (structural strength). Indeed, our original all-molybdenum
vessel had inner dimensions closely matching those of the larger, commercially available SPEX milling vials (roughly 1.5” ID, 1.5” inner length).

Furthermore, stainless steel is significantly cheaper than molybdenum. The 2.5” OD x 4.8” L molybdenum rod ordered for the all-molybdenum vessel cost $625.00 (6/2015) (supplier: Eagle Alloys\textsuperscript{a}). The 1.25” x 3” L molybdenum rod needed for the first molybdenum liner and end caps cost $155 (Eagle Alloys\textsuperscript{a}) in 2/2016. A second molybdenum rod of the same dimensions (1.25” OD x 3” L) was $175 (Eagle Alloys\textsuperscript{a}) in 1/2017 (the joys of inflation). However, the high-strength 2.5” OD x 6” L 304L stainless steel rod required for the SS pressure vessel was ~$50 (supplier McMaster-Carr\textsuperscript{b}, 3/2018 cost = $55.87). The all-in materials cost for the thin liner method was ~$205 compared to the $625 for the all-molybdenum approach.

By far, the greater expense was in the work that went into the vessels (a special thank you to Todd, Tony, Denny, and Nathan who all, at various points, contributed to this project). Again, the molybdenum liner approach proves advantageous. First, the majority of the work is on stainless steel as opposed to molybdenum. Molybdenum, due to its hardness, is notoriously difficult to machine, especially fine cuts like the threads or narrow, deep holes.\textsuperscript{ah,al} It is true that stainless steel is itself not trivial to machine, but its widespread use lends a familiarity to the material. In general the machining is significantly faster for stainless steel than molybdenum (perhaps 2x, based on anecdotal evidence), greatly reducing the cost of the vessel. Furthermore, the low material cost perhaps permits the work to be pressed forward at a more rapid pace since a failed piece wastes only the time cost, but a negligible material cost.
In addition, the aggressive, high energy nature of ball milling leads to significant wear of the ball milling surfaces over time. See, for example, figure 2-14 below depicting fresh molybdenum end caps compared to end caps after ~300 hours of use and several resurfacings. Note, the majority of material loss, as evidenced by the decrease in height of the Mo insertion, is the result of resurfacing, which removes material until a smooth, flat layer can be formed.

![Image of fresh and worn end caps]

*Figure 2-14: Wear of the ball milling surface on the molybdenum end caps. The end cap on the left is freshly made, while the end cap on the right has experienced ~300 hours of ball milling and has been resurfaced several times.*

The end caps bear the brunt of the ball milling action. Fortunately, the cylindrical molybdenum liner shows little wear even after several hundred hours of milling.

The ball milling surface of the molybdenum end caps can be resurfaced a few times to extend their life, allowing ~300 hours of total milling time before too little material remains to form a powder tight seal between the end caps and the cylindrical liner. At that point, the molybdenum end caps must be completely replaced.
However, the material and work costs for new end caps is relatively small (~$30 for the 1.25” OD x 0.5” L Mo rod, plus the machine shop time) so that the ongoing cost of the work (i.e., maintenance of the milling vessel) is inexpensive. The all-molybdenum approach would have led to significantly higher materials cost, labor cost, and time cost when dealing with the ever-present wear that results from ball milling. Here, the expensive (labor-wise) piece, the stainless steel pressure vessel, shows no indications of wear, even after several hundred (~500 – 1,000) hours of ball milling under high pressure.

2.22 Suggestions for future improvements

While this thesis signals the likely end of this work, the following are several suggestions for future improvements to the high pressure ball milling vessel should the work be continued at a later date.

First, the o-ring seals should be moved from the molybdenum end caps to a stainless steel (or other high strength, H\textsubscript{2}/D\textsubscript{2} compatible material). Moving the o-rings removes all critical machining work from molybdenum. While the o-ring grooves were comparatively easy to produce (according to the machinists), they still suffered from the tendency of molybdenum to tear while being machined. This tearing is slightly visible in the o-ring groove of the freshly made molybdenum end cap depicted on the left in figure 2-14 above.

In addition, one of the slowest components of creating a new sample was checking the pressure-tightness of the o-ring seals. The seals were always tested before loading a new sample.
However, to load a sample, at least one molybdenum end cap must be removed. While it may seem trivial, on several occasions, the o-ring seals passed muster on the initial, empty vessel test, but failed after subsequent loading of the vessel with powder. The tight fit of the molybdenum end caps and liner often led to tearing and pulling of the o-rings upon insertion or removal of the molybdenum end caps into or out of the stainless steel pressure vessel. Having a reliable seal, would greatly increase the work flow (sample generation) of this project by reducing time spent insuring the leak-tightness of the o-ring seals before the start of milling for each new sample. Furthermore, removing the o-ring seals from the molybdenum end caps would reduce the amount of the expensive molybdenum needed for the end caps and extend the usable life of the end caps since they could be resurfaced a greater number of times for a given length of end cap. There is no need to leave space for an o-ring groove.

In the same vein, having multiple molybdenum liners, especially paired with moving the o-ring seals from the molybdenum end caps, would significantly increase the throughput of sample generation for this work. The majority of time was spent in sample synthesis-related tasks: checking the o-ring seals on the empty vessel, packing a vessel with a sample in the glove bag, rechecking the o-ring seals with a sample packed inside, ball milling (passive time, no user input required), unpacking the sample from the vessel in the glove bag (time consuming), cleaning the molybdenum liner (also time intensive), repeat. By having several molybdenum liner and end cap sets, one could imagine simply sliding the “used” set (with ball milled sample inside) out of the stainless steel pressure vessel, replacing with a new liner and end cap set (previously loaded with a fresh sample) and starting the next round of ball milling while the time intensive tasks of
unpacking the milled sample and cleaning the used molybdenum liner and end cap set was proceeding in parallel. In addition, having multiple molybdenum liner and end cap sets reduces down time when the end caps need resurfacing.
2.23 References


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Chapter 3: Experimental Techniques

3.1 Sample preparation
Magnesium-titanium-deuteride (Mg-Ti-D) samples were prepared by ball milling magnesium (Mg), titanium (Ti), magnesium hydride (MgH₂), and titanium hydride (TiH₂) powders in various ratios under high pressure deuterium (D₂) gas. Magnesium (-325 mesh, Reagent Plus, 99.5% purity) and titanium (-100 Mesh, 99.7% purity) powders were obtained from Sigma Aldrich. TiH₂ (Sigma Aldrich) and MgH₂ (Alfa Aesar) powders were already on hand from previous work. A custom built, high pressure, molybdenum-lined milling vessel was developed for the high pressure ball milling. The vessel was previously discussed in detail in chapter 2, but a graphic of the vessel is shown below for reference.
Powder samples were loaded into the custom milling vessel inside a nitrogen gas flow-through glove bag (Aldrich AtmosBag, Sigma Aldrich). Nitrogen gas was supplied by liquid nitrogen (LN$_2$) boil-off from the Physics Department's bulk LN$_2$ dewar. The nitrogen atmosphere is necessary to protect these oxygen and moisture sensitive samples. All sample storage and handling was performed in an inert (usually N$_2$) atmosphere.

Generally, 500 mg of total sample of various Mg(H$_2$):Ti(H$_2$) ratios by mol was loaded into the
vessel. Approximately 13 yttria-stabilized zirconia (YSZ) milling balls were added to the chamber as well so that the ball to powder ratio by weight (BPR) was approximately 10:1. The YSZ balls were spherical in shape with a 5 mm diameter and supplied by Inframat Advanced Materials. Loading of the powder and YSZ balls into the vessel was accomplished by a glass funnel to prevent accumulation of powder on the o-ring sealing surface of the stainless steel pressure vessel. The mass of the powders, the mass of the YSZ balls, and the number of YSZ balls was recorded.

The milling vessel, with sample inside, was sealed before removal from the glove bag. The vessel was then connected to a high pressure gas manifold and evacuated using a mechanical roughing vacuum pump. Prior to ball milling, the vessel was pressurized with argon gas (Ultra High Purity, PurityPlus 5.0, Cee Kay Supply, Inc.) to 2,100 PSI. The pressure in the vessel was monitored for ~30 minutes to confirm it was leak tight, then the vessel was evacuated and refilled with D₂ gas at 1,000 – 2,000 PSI. Deuterium gas (50 L per bottle, 99.8% purity) was purchased from Cambridge Isotope. The volumes of the high pressure gas manifold and milling vessel were calibrated at the outset of this work using the ideal gas law, a pressure transducer, and a pressure vessel of known volume. With the volumes known, and the pressure of the vessel recorded before and after ball milling, the uptake of deuterium gas could be monitored. The gas manifold is discussed briefly in chapter 2. Deuterium uptake by the samples is discussed in chapter 4.

After being pressurized with D₂, the milling vessel's valve was closed and the vessel was
disconnected from the manifold (the vessel is thus still under D₂ pressure). Ball milling was carried out by a SPEX 8000 Mixer/Mill, a commercially available, laboratory scale, bench-top shaker-type ball mill. The SPEX was the property of Professor Eric Majzoub's research group at the University of Missouri – St. Louis and was generously loaned to us for the duration of our experiments. Details of the customized SPEX setup and the homebuilt high pressure ball milling vessel were discussed in chapter 3.

Typically, samples were initially milled for one hour. The vessel then sat for ~15 minutes, before the vessel was removed from the ball mill and reconnected to the gas manifold. The manifold was evacuated (up to the vessel's valve) and closed, then the vessel's valve was opened, venting the vessel to the closed, evacuated manifold. Thus, the pressure in the vessel could be sampled ex-situ after 1 hr of milling, and, by the ideal gas law, the deuterium absorbed by the sample could be determined. Of course, corrections for deuterium's non-ideal behavior at higher pressures (i.e., the compressibility factor) must be considered. Generally, full deuterium uptake was accomplished within one hour of ball milling. A complete discussion of deuterium uptake during ball milling is provided in chapter 4.

After sampling the milling vessel pressure, the vessel was re-pressurized (to 1,000 – 2,000 PSI) with a fresh bolus of D₂ gas, the vessel valve was closed, and the vessel disconnected from the gas manifold. Milling was resumed for an additional period of time ranging from 3 hours up to 160 hours (minimum total milling time = 4 hours, max = 170 hours).
At the completion of milling, the vessel was allowed to cool for approximately 15 minutes and then the gas pressure in the vessel was monitored as described above. Typically, the pressure was found to have decreased by 10 – 50 PSI during the second, extended milling run, a negligible amount compared to the 500 – 1,000 PSI drops observed as the result of deuterium uptake during the first round of milling.

The pressure in the vessel was vented until only a few atmospheres of D$_2$ pressure remained (so a small positive pressure in the vessel). The vessel was returned to the N$_2$ glove bag where the remaining D$_2$ pressure was released and the ball milled sample was unpacked. The mass of the recovered powder sample and the mass and number of the recovered YSZ balls was recorded.

When not in use, samples were stored in sealed glass vials, kept in sealed ziplock bags filled with indicating Drierite (to reduce moisture exposure). As stated previously, the sample containers were stored in the N$_2$ glove bag at all times.

Prior to reuse, the molybdenum liner and end caps (from the high pressure milling vessel, see figure 3-1 above) were cleaned; first with soap and water, then with acetone or ethanol. Usually, an ultrasonic bath was employed as part of the cleaning process. After cleaning, the molybdenum liner and end caps were baked out in a vacuum oven at ~100 °C overnight. The end caps were then examined for wear, and taken to the machine shop for resurfacing of the ball milling surface if required.
The stainless steel pressure vessel (see figure 3-1 above) required little maintenance between milling operations. Generally, wiping the inner surfaces with acetone to remove vacuum grease and o-ring residue was sufficient. Occasionally, the valve stem and tip from the vessel's Swagelok valve (model SS-1KM4-S4) required cleaning and re-lubrication or replacement. Fortunately, an update to the molybdenum liner design, which made the liner powder tight (but not gas leak tight), all but eliminated this valve maintenance.

3.2 Sample characterization - XRD
Most ball milled Mg-Ti-D samples were characterized by Powder X-Ray Diffraction (XRD) on a Bruker d8 Advance X-ray Diffractometer in the department of Earth and Planetary Sciences at Washington University in St. Louis. The d8 Advance operates in the Bragg-Brentano geometry and uses a Cu X-ray tube (Cu Kβ radiation is removed by an inline Ni filter so that only Cu Kα remains). Powder samples from ball milling were first ground using a mortar and pestle (in the N₂ glove bag) to create a homogeneous powder. Note, ball milling leads to small crystallite sizes (here ~10 nm), but agglomeration of crystallites during ball milling creates large, heterogeneous particles (groups of multiple crystallites). Ground powders were loaded onto a custom-made Plexiglas XRD sample holder (see figure 3-2 below). Approximately 100 mg of sample powder was needed to adequately fill the XRD sample holder.
A thin layer of petroleum jelly was applied to the top surface of the sample holder (indicated by the red dashed circle in figure 3-2 above) and a single layer of plastic wrap (PVC film) was placed over the slide (the petroleum jelly acts as a sealant) to protect the air sensitive samples during XRD measurements.

Packed XRD samples were transported to the XRD facility in sealed ziplock bags (so a nominally N$_2$ environment) to reduce air exposure prior to measurements. Typically, XRD spectra were collected using a step size of 0.02° 2θ, at a scan rate of 0.5 s/step over a range from 20° – 90° 2θ.

The Plexiglas sample holder and plastic wrap covering contributed a small, but consistent background signal to the observed XRD pattern (see figure 3-3 below). Acquired spectra underwent background subtraction and had the Cu Kα2 contribution stripped before undergoing
further analysis such as phase identification, peak fitting, and Reitveld Refinement. XRD spectra analysis was usually performed using the Bruker Eva and Topas software packages.

Figure 3-3: XRD powder patterns for the empty Plexiglas sample holder (black), the empty sample holder with the thin plastic film covering in place (red), MgO powder with the plastic film covering in place (blue), and MgO powder with no plastic film covering (magenta). The stick pattern for MgO is shown in dark cyan. The large apparent intensity for the background signal (black and red patterns) results from the x-ray beam being directly incident on the sample holder. When the x-rays are incident on a powder sample, the background signal is almost negligible. Care must be taken to not mistake the relatively sharp plastic film peak near 22° 2θ as originating from the sample. Note, a large Mg(OH)₂ impurity (marked by gray stick pattern) as well as other unidentified impurities are present in this sample. The key point is that the background signal from the sample holder is small with a sample in place, but the single, sharp peak from the saran wrap film must not be confused for a reflection from the sample under study.
3.3 Sample characterization - NMR

The primary characterization technique employed to analyze the ball milled Mg-Ti-D samples was deuterium Magic Angle Spinning Nuclear Magnetic Resonance ($^2$H MAS NMR). Powder samples were first mixed with aluminum oxide (Al$_2$O$_3$) powder (Sigma Aldrich) that had been previously baked out under dynamic vacuum at 350 °C for ~8 hours to remove moisture from the hydroscopic powder. The research sample and Al$_2$O$_3$ were mixed in a 1:1 ratio by weight (~3.6 MgD$_2$·Al$_2$O$_3$, ~2 TiD$_2$·Al$_2$O$_3$, and ~2.5 {1 MgD$_2$·TiD$_2$ by mol}·Al$_2$O$_3$, all by mol) by mortar and pestle. The Al$_2$O$_3$ prevents the formation of large, electrically conductive chains for non-insulating powders (note, Ti(H/D)$_2$ is metallic and thus conductive). Large, conductive particles inhibit RF penetration (skin depth or skin effect, $\delta_{RF} \propto 1/\sqrt{\omega\sigma}$) and impede sample rotation for MAS via the dynamo effect. Approximately 100 mg of research sample powder was required (so 200 mg with Al$_2$O$_3$) for NMR measurements.

Sample powder with Al$_2$O$_3$ was packed in 5 mm OD zirconia pencil rotors with PCTFE (Kel-F) drive tips and PTFE (Teflon) end caps. Usually, a small Teflon spacer was inserted behind the drive tip to minimize the amount of sample required, reduce the mass of the packed rotor (better sample spinning for MAS), and contain the sample to the region of the NMR coil. All rotors were packed with powder samples in a N$_2$ glove bag.

Rotor spinning was accomplished using N$_2$ bearing and drive gas to minimize exposure of the oxygen and moisture sensitive samples. N$_2$ gas was supplied by a liquid nitrogen dewar equipped with a pressure building circuit capable of maintaining a stable head space pressure via LN$_2$ boil-off of at least 100 PSI, much greater than the ~30 PSI needed for stable sample spinning at 9
kHz. Before being sent to the MAS air controller, the N\textsubscript{2} boil-off passed through a set of copper heat exchanger coils located on the body of the LN\textsubscript{2} dewar that warmed the gas to room temperature, eliminating any significant sample cooling. For 9 kHz spinning, the head space pressure was regulated to 50 PSI, which allowed for approximately 32 hours of stable spinning with a freshly filled LN\textsubscript{2} dewar (~400 lbs of LN\textsubscript{2}).

Most NMR measurements were performed on a 7.034 T (\textsuperscript{1}H frequency 299.67 MHz, \textsuperscript{2}H frequency 46.001 MHz) Oxford superconducting magnet. A home constructed NMR spectrometer was utilized. A frequency synthesizer supplied the RF carrier frequency and drove a gated LPI-10 1 kW RF amplifier. To minimize off-resonant frequency noise, a shorted (to ground) 52.28 MHz quarter-wave (\textit{λ/4}) coaxial cable was placed in a “T” with the output of the RF amplifier. An additional homemade low-pass 200 MHz filter was used inline on the RF amplifier output to reduce high frequency noise (note, the NMR MAS probe circuit is doubly resonant, with a high frequency (299.67 MHz) \textsuperscript{1}H NMR channel.

A 54 MHz \textit{λ/4} coaxial cable was connected between the transmit-receive “T” and the first set of crossed diodes to ground on the receiver side (towards the pre-amplifier) within the transmit-receive switch (T-Box). This \textit{λ/4} cable puts the receiver at the “wrong” electrical distance from the transmitter to receive the high powered RF pulses when the transmitter is on.

In all cases, the transmitter (TX) power was attenuated by an inline step attenuator between the frequency synthesizer and the input of the RF amplifier. A TX attenuation of 8 dB was generally employed and resulted in a π/2 pulse length of 3 μs for \textsubscript{D}\textsubscript{2}O, the standard deuterium NMR tune-
up sample. An example $^2$H NMR nutation curve for D$_2$O is shown in figure 3-4 below. A 3 μs $\pi/2$ pulse length corresponds to $B_1 \approx 83$ kHz (~127 G) in the rotating frame. The $\pi$ pulse length was found to be slightly less than the expected ($2\tau_{\pi/2}$) and was ~5.5 μs.

The receiver gain was left at a constant setting of 650 (range 0 – 1,000). Note, the gain is not linear as a function of knob setting over this range, but the gain vs. setting is well documented by previous users. Instead, the inline step attenuator on the receiving chain was used to adjust the receiver voltage and prevent saturation of the signal digitizer. The observed NMR signal is proportional to the number of deuterium spins present. The ball milled Mg-Ti-D samples under study can be considered isotopically enriched (100% deuterium). The high deuterium density in

![Figure 3-4: D$_2$O nutation curve for various transmitter (TX) attenuation settings. For most of results discussed in this thesis, a TX attenuation of 8 dB was used.](image)
these ~100% deuterated solids leads to strong NMR signals even though deuterium is a comparatively weak NMR nucleus since the NMR signal is proportional to the gyromagnetic ratio, $\gamma$, and $\gamma_D / \gamma_H \approx 1/7$. Therefore, 4 – 10 dB of receiver attenuation was used during signal acquisition. The specific receiver attenuation used depended on the sample because the density of deuterium spins was impacted by the relative presence of impurities (from ball milling) and the exact mixing ratio of the sample with the insulating $\text{Al}_2\text{O}_3$ powder.

A receiver muting time of 6 $\mu$s was utilized to limit the saturation of the signal digitizer by the high voltage LC circuit ring down following an RF pulse. Thus, the first 6 $\mu$s of the NMR signal during acquisition were dumped to ground before the signal was allowed to pass to the digitizer.

A Chemagnetics 5 mm, 2-channel (HX) MAS NMR probe was used to acquire all deuterium NMR data. The magic angle was adjusted by observing $^{79}\text{Br}$ NMR on a powder potassium bromide (KBr) sample packed in a zirconia rotor. Details of the magic angle adjustment are recorded in my lab notebook (book 3, pages 25 and 29) and on a reference sheet kept with the 300 MHz magnet. In general, when spinning at ~6 kHz, spun echoes, resulting from the refocusing of the quadrupole interaction by sample rotation about the magic angle, were observed to have a height of >10 mV at 6.2 ms when the KBr $^{79}\text{Br}$ FID was observed shot-to-shot on the spectrometer's oscilloscope. The magic angle was checked occasionally, but was found to be stable unless the probe and its mount were completely removed from the magnet (e.g., for maintenance or to free the magnet for usage with other NMR probes).
Room temperature shims were employed to increase the homogeneity of the $B_0$ magnetic field. With the shims, the full-width at half maximum (FWHM) for D$_2$O was $\sim$9 Hz ($\sim$0.2 ppm). The shims were tested at the start of each $^2$H NMR session by observing the line shape and FWHM of D$_2$O, which was found to vary by less than 1 Hz. The specific room temperature shim settings are recorded in my lab notebook (book 3, page 27) as well as on a reference sheet kept with the 300 MHz magnet. The shims are stable over time and rarely required adjustment.

The D$_2$O resonant frequency was 46,001,82X Hz. It was recorded at the start of each $^2$H NMR session and all $^2$H spectra presented in this thesis have been referenced to the chemical shift of D$_2$O. That is, the chemical shift of D$_2$O is set to 0 Hz (0 ppm) and all spectra are referenced to D$_2$O at zero shift.

3.4 Acoustic coil disease and signal acquisition techniques
Due to its low natural abundance (~0.015% of all hydrogen atoms)$^9$, little deuterium background signal is expected or observed. However, a strong, spurious electrical signal (acoustic coil disease), resulting from the interaction of the coil with the external magnetic field, was present. See Fukushima and Roeder$^{fg}$ or Buess and Peterson$^h$ for detailed discussions on acoustic ringing in NMR. The acoustical ringing led to an electrical signal near the carrier frequency that overwhelmed the NMR signal for the first 100 $\mu$s of signal acquisition. Figure 3-5 below details the magnetic field effect on this spurious signal. Here, the time domain signal for a simple pulse-acquire pulse sequence on an empty probe is shown for the probe at various positions in the magnetic field corresponding to different magnetic field strengths. Of note, if the signal were simply background deuterium signal it should not be present at the “down” position (red) where
the carrier frequency remained constant (46.001 MHz), but the magnetic field strength, and therefore the deuterium Larmor frequency, should be significantly reduced since the coil is no longer at the center (strongest, most homogeneous part) of the magnetic field. The Larmor frequency is given as:

\[ \omega_L = -\gamma_{\text{Deuterium}} B_0 \]  

(3-1)
Figure 3-5: Spurious acoustical ringing signal from the empty probe for various probe positions corresponding to different external magnetic field strengths. (A) The full time domain signal where the LC circuit ring down clearly dominates. The LC ringing is magnetic field independent and thus is constant for the 3 probe positions (magnetic fields) shown. (B) Zoom of the time domain signal from 15 μs to 200 μs. The periodic signal visible in the black and red time domain data is acoustic coil ringing. As the probe position is changed (magnetic field reduced) the acoustic ringing is decreased. The ringing is $\propto B^2$. 
The acoustical ringing signal is proportional to $B^2$. Therefore, when the MAS probe is completely lowered out of the bore of the magnet, the signal (blue curve) all but disappears (see figure 3-5-B). Here, the magnetic field is $< 1$ T corresponding to a $(1/7)^2 \sim 98\%$ reduction of the effect. Note, the large signal present for all probe positions from $\sim 6 – 15 \ \mu s$ is LC circuit ring down. This signal is magnetic field independent and thus appears constant for all probe positions (see figure 3-5-A).

Also of note, the phase of the spurious signal matches that of the RF pulse that produces it. So, a simple phase-cycled single pulse experiment (Bloch Decay) is not sufficient to remove the coil disease. Instead, a two pulse phase-cycled experiment must be utilized with a minimum of two steps where the phase of the second pulse is held constant, but the phase of the NMR signal (either FID or echo) is shifted by $180^\circ$ (see figure 3-6 below). Then, the two steps are subtracted from each other so that the NMR signals, which are $180^\circ$ out of phase, add. Meanwhile, the spurious ringing from the second pulse, which has the same phase in both steps, cancels out, leaving only the NMR signal.
Figure 3-6: Example of a 2-step, phase-cycled pulse sequence to remove acoustic coil disease. The phase of the second pulse ($\varphi_2 = x$) is kept constant for both steps. The spurious acoustical ringing signal (red) therefore has the same phase for both steps in the resulting time domain signal. However, the phase of the first pulse ($\varphi_1$) is changed so that the resulting NMR signal (blue) from pulse 2 has a 180° phase difference between the two steps. The two steps are subtracted from each other, causing the spurious signal to cancel out while the NMR signal adds.

Pulse sequences that take advantage of this 2-pulse, 2-step (or more) phase cycling include the blinking-180 (180°$\varphi$ – $\tau$ – 90°$\varphi$ – Acquire($\varphi$+π$\varphi$)), solid echo (90°$\varphi$ – $\tau$ – 90°±(π$\varphi$/2) – Acquire$\varphi$), and the Hahn echo (90°$\varphi$ – $\tau$ – 180°±(π$\varphi$/2) – Acquire$\varphi$). A comparison of the time domain signal for the blinking-180 pulse sequence as well as the time domain signal for the single pulse-acquire and 4-step phase-cycled pulse-acquire (90°$\varphi$ – Acquire$\varphi$) sequences for the empty probe in the center of the magnetic field are shown in figure 3-7 below. $\varphi$ in the above pulse sequence refers to the phase of the RF pulse and is usually specified as x, y, $\bar{x}$, $\bar{y}$ or as 0°, 90°, 180°, or 270°.
In general, the 8-step, phase-cycled Hahn echo yielded the best $^2$H MAS NMR spectra. Not only does this pulse sequence eliminate the spurious acoustical ringing signal, it also shifts the NMR signal out in time from the pulse, eliminating receiver dead time effects. For the $90^\circ - \tau - 180^\circ$ pulse sequence, a spin echo (or Hahn echo) will form at time $2\tau$ ($\tau$ after the middle of the $180^\circ$ pulse). The echo will fully reproduce the FID (with slightly smaller amplitude, depending on the pulse delay $\tau$). Thus, by left shifting to the peak (center) of the echo, a clean, acoustical ringing

**Figure 3-7:** Spurious acoustical coil disease signal for various pulse sequences on the empty probe. The time domain data begins at 15 $\mu$s so that the large LC circuit ring down is not shown (see figure 3-5-B). Notice that the 2-pulse, phase-cycled blinking-180 sequence effectively cancels out the spurious ringing signal. The 2-pulse, phase-cycled Hahn echo and solid echo sequences (not shown) provides similar cancellation of the unwanted signal.
and dead time free FID can be obtained. Provided $\tau$ is short compared to the spin-spin relaxation time ($T_2$) for all deuterium signals present, the effect of the echo on the resulting NMR spectrum will be negligible. The Hahn echo can reproduce the exact NMR spectrum that would be obtained by the more quantitative short-pulse Bloch decay technique. In general, $\tau$ was chosen to synchronize the 180° pulse with the completion of a rotor cycle (rotor synchronization) so that $\tau \sim 1/f_s \sim 110 \mu$s. A comparison of acquisition techniques is shown in figure 3-8-a (time domain) and 3-8-b (frequency domain) below for an example research sample (1 MgH$_2$ : 1 TiH$_2$ ball milled 4 hours under 1.5 kPSI D$_2$).
Figure 3-8: (a) Time domain signal for an example research sample (1 MgH$_2$: 1 TiH$_2$ ball milled under 1.5 kPSI D$_2$ for ~4 hours). Several pulse sequences are used. The inset shows the early time data (0 – 200 μs). Notice that for all acquisitions techniques, the first ~15 μs of data is lost due to receiver dead time (LC circuit ring down). (b) Fourier transforms of the time domain data shown in (a).
Compared to the single pulse techniques and the blinking-180, the echo techniques show a flatter baseline in the frequency domain spectra. The improved baseline results from shifting the NMR signal out in time by $\tau$ away from the preceding pulse. For the single pulse techniques and the blinking-180, the FID follows immediately from the “inspection” pulse. Usually the first $\sim 15 \mu s$ of the FID were therefore lost due to LC circuit ringing. See the corresponding time domain signal (figure 3-8-a) for the various pulse sequences that generated the frequency domain spectra of figure 3-8-b.

While left shifting the time domain data by $\sim 15 \mu s$ would result in a flat baseline in the frequency domain spectra for the single-pulse acquisition techniques, it would also introduce phase distortions between the various $^2$H signals (corresponding to different deuterium chemical environments) that have different resonant frequencies. For example, the TiD$_2$ signal, with $f \approx -7$ kHz, will acquire $\sim \{2\pi \times -7 \text{kHz} \times 15 \mu s\} = 0.21\pi$ radians of phase, while the MgD$_2$ signal, with $f \approx 0$ Hz, would acquire almost no phase. If the spectrum was composed entirely of narrow lines, it would be possible to left shift the time domain data to a point where all signals present had acquired an integer multiple of $2\pi$ worth of phase and therefore minimize any spectral distortion introduced by the left shift. Determining the exact point to which to left shift to need to be perfect since small offsets can be corrected with first order phase corrections. However, the spectra here are in general composed of broad lines with distributions of resonant frequencies so that no such zero-phase-distortion point exists (except in the case of the spectra of single chemical species, e.g., bulk MgD$_2$ and bulk TiD$_2$).
Instead, the loss of early time signal must be dealt with by setting the value of the early time points to zero. See figure 3-9 below for the effect of zeroing the first ~15 μs of the time domain signal for the single-pulse and blinking-180 pulse sequences.

**Figure 3-9:** (a) Time domain signal for an example research sample (1 MgH$_2$ : 1 TiH$_2$ ball milled under 1.5 kPSI $D_2$ for ~4 hours) acquired with a 4-step, phase-cycled pulse-acquire (bottom signal, solid lines) and a 2-step, phase-cycled blinking-180 (top signal, dashed lines). Various processing techniques for dealing with the early time issues are shown: raw data in black, setting initial 20 μs of data to zero shown in red, and left shifting 20 μs shown in blue. (b) Fourier transforms of the time domain signals from (a). A dashed (lower) and dotted (upper) horizontal red line have been added as a guide to the eye. Left shifting reduces the rolling baseline, but results in phase distortions. Zeroing the initial points minimizes phase twists, but leads to the rolling baseline.
Effectively, this process is equivalent to multiplying the FID by a step function. When the FID is then Fourier transformed, the resulting spectrum is a convolution of the Fourier transform of the FID and the Fourier transform of the step function. So a convolution of the FID Fourier transform and the Sinc function, resulting in the observed rolling baseline. Fukushima and Roeder provide a good discussion in II.B.6.

Therefore, the Hahn echo, which faithfully reproduced the single pulse spectrum without the addition of the rolling baseline, was chosen as the standard acquisition technique. The solid echo (90°ϕ – τ – 90°±(ϕ+π/2)) also eliminated the rolling baseline issue. However, the solid echo seemed to reproduce the Hahn echo results, but with half the intensity (the length of pulse 2 for the solid echo is half that of pulse 2 for the Hahn echo). See figure 3-8-b for a comparison of the spectra that result from the two pulse sequences. While the solid echo will refocus the quadrupolar evolution, if the quadrupolar anisotropy is relatively small, this refocusing is already well provided by magic angle spinning. The Hahn echo will not refocus the spin evolution due to the quadrupolar interaction, but will refocus the evolution due to magnetic field inhomogeneity. If quadrupolar evolution is adequately refocused by MAS, then the Hahn echo adds additional refocusing of other interactions.

Generally, an 8-step, phase-cycled Hahn echo was used. The phase table for the pulse sequence is shown in table 3-1 below. To reiterate, this pulse sequence was found to reliably reproduce the single pulse, small tip angle spectrum while simultaneously removing the spurious acoustic coil ringing signal and receiver dead time effect (LC circuit ringing), eliminating the resulting rolling
baseline issue. Generally, $\tau_{\text{HE}}$, the delay between the $\pi/2$ and $\pi$ pulses was set to equal one rotor period: $\sim 110 \, \mu$s for the usual $f_s = 9 \, \text{kHz}$ rotor spinning rate employed here. Acquisition of the received signal was triggered on the second ($\pi$) pulse and generally 8,192 points with a dwell time per point of 1.5 $\mu$s (so $\sim 12 \, \text{ms}$ of data) were collected. A minimum of 8 transients, up to 32 transients, were normally acquired. Note, the signal-to-noise ratio (SNR) increases as $\sqrt{N}$, with $N$ being the number of acquisitions. By collecting 32 transients, the SNR is doubled compared to that of the minimum number of acquisitions dictated by the 8-step phase cycle.

<table>
<thead>
<tr>
<th>Step</th>
<th>Pulse 1</th>
<th>Pulse 2</th>
<th>Receiver</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0°</td>
<td>90°</td>
<td>0°</td>
</tr>
<tr>
<td>2</td>
<td>0°</td>
<td>270°</td>
<td>0°</td>
</tr>
<tr>
<td>3</td>
<td>90°</td>
<td>0°</td>
<td>90°</td>
</tr>
<tr>
<td>4</td>
<td>90°</td>
<td>180°</td>
<td>90°</td>
</tr>
<tr>
<td>5</td>
<td>180°</td>
<td>90°</td>
<td>180°</td>
</tr>
<tr>
<td>6</td>
<td>180°</td>
<td>270°</td>
<td>180°</td>
</tr>
<tr>
<td>7</td>
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</tr>
<tr>
<td>8</td>
<td>270°</td>
<td>180°</td>
<td>270°</td>
</tr>
</tbody>
</table>

Phase table for the 8-step, phase-cycled Hahn echo, the primary pulse sequence used in this work.

3.5 $T_1$ considerations
In NMR, the longitudinal relaxation time, $T_1$, details the time required for the spin system to reach its equilibrium state. In the equilibrium state, the sample under study exhibits a net magnetization in the $B_0$ (z) direction known as the longitudinal magnetization $M_z$. When the spin system is perturbed by an applied $\pi/2$ RF pulse, the net longitudinal magnetization is transferred to the transverse (x-y) plane so that immediately following the pulse $M_z = 0$. 

95
The longitudinal magnetization will the recover to its equilibrium value $M_{z-0}$, such that the longitudinal magnetization at time $t$ after a $\pi/2$ pulse is given by:

$$M_z(t) = M_{z-0}(1 - e^{-t/T_1})$$  \hspace{1cm} (3-2)

After $1 \times T_1$, \quad $M_A(1 \times T_1) \approx 0.6321 \times M_{z-0}$

After $2 \times T_1$, \quad $M_A(2 \times T_1) \approx 0.8647 \times M_{z-0}$

After $5 \times T_1$, \quad $M_A(5 \times T_1) \approx 0.9933 \times M_{z-0}$

After $10 \times T_1$, \quad $M_A(10 \times T_1) \approx 0.99995 \times M_{z-0}$

Therefore, if a second transient is collected while allowing only a single $T_1$ of time following the first transient, the signal amplitude of the second transient will be 63% of that of the first transient.

Different chemical species present in the samples under study (e.g., MgD$_2$, TiD$_2$) may recover their longitudinal magnetization at different rates ($R_1 = 1/T_1$). That is, $T_1$ is chemical species specific, and the NMR spectrum of a sample with multiple deuterium-bearing chemical species
may exhibit a variety of $T_1$'s corresponding to the different deuterium signals. Care must therefore be taken to ensure that the recycle time (the time between collection of successive transients) is sufficiently long to allow equal (or full) recovery of all signals in the spectrum. Failure to do so can lead to artificial weighting in favor of signals (chemical species) with faster longitudinal relaxation rates (shorter $T_1$'s) over those with longer $T_1$'s.

An example is instructive. In many cases, the MgD$_2$ signal was found to have a $T_1$ of 1 s while the TiD$_2$ signal had a $T_1$ of $\sim$10 s. For a sample that was 1 MgD$_2$ : 1 TiD$_2$ by mol, we would expect the area of the MgD$_2$ peaks to be equal to the area of the TiD$_2$ peak(s) in the observed deuterium MAS NMR spectrum. For NMR, the area under the curve is proportional to the number of spins present. Assuming 96 transients were collected and a 1 s recycle delay were utilized, then for MgD$_2$, the signal collected would be proportional to $M_{Z=0, MgD_2}$ for the first transient and $0.63 \times M_{Z=0, MgD_2}$ for all 95 subsequent transients (see equation 3-2 above, with $t = 1$ s = $1 \times T_1$). The total signal acquired for MgD$_2$ would be

$$\left(1+0.63 \times 95\right) \times M_{Z=0, MgD_2} = 60.85 \times M_{Z=0}$$

where

$$M_{Z=0, MgD_2} = M_{Z=0, TiD_2} = M_{Z=0}$$

since we have equal numbers of MgD$_2$ and TiD$_2$ deuterium spins present in the sample.
For TiD₂, the chosen recycle delay of 1 s is \(0.1 \times T_1\) (TiD₂ has \(T_1 = 10\) s). Thus, we will gain \(M_{Z,0}\) for the first transient collected, but only

\[
\left(1 - e^{-0.1T_1/T_1}\right) M_{Z,0} = 0.0952 \times M_{Z,0}
\]

for each of the successive 95 transients, so that the total signal acquired would be

\[
\left(1 + 95 \times 0.0952\right) M_{Z,0} = 10.04 \times M_{Z,0}
\]

for the TiD₂. If we were careless, we would think that the sample had \(~6\) times more MgD₂ than TiD₂ based on the observed peak areas. It is critical that proper recycle delays be used that allow for full (~5 \(\times\) \(T_1\)) relaxation of all signals present to accurately compare the phase presence of the various deuterium-bearing chemical species. This type of analysis is discussed in detail in chapter 4.

Therefore, the \(T_1\) of each chemical species present was measured at the outset for each sample studied. The Hahn echo pulse sequence previously discussed was modified to include a saturation comb (denoted “III”), a series of \(~20\) \(\pi/2\) pulses of various phases separated by 10 ms (\(\gg T_2^*\) for the signals present). The pulse comb was followed by a recovery period, \(\tau_R\), which was in turn followed by the standard Hahn echo pulse sequence. The \(T_1\) measurement sequence is shown below. In III.D.2, Fukushima and Roeder¹ give a thorough discussion of the saturation-
The area under the curve (peak area) for each chemical species present is proportional to $M_z$ for that species. By measuring the peak area (obtained by integrating the NMR spectrum) as a function of recovery time, $\tau_R$, a $T_1$ recovery plot, like the example shown in figure 3-10 below, could be generated.

\[
III - \tau_R - \left(\frac{\pi}{2}\right)_{\phi} - \tau_{HE} - \pi_{\phi \pm (\pi/2)} - ACQ_{\phi}
\]
The peak area “A” for a given deuterium signal, which is proportional to $M_z$, was plotted as a function of $\tau_R$ and fit to equation 3-2 above to determine $T_1$ for each peak present in the

Figure 3-10: (a) Sample Hahn echo spectra for a research sample (1 MgH$_2$ : 1 TiH$_2$ ball milled under 1.5 kPSI D$_2$ for ~4 hours) as a function of recovery time ($\tau_R$) between subsequent acquisitions. The shaded regions indicate the areas integrated to obtain the peak areas for TiD$_2$ (blue region) and MgD$_2$ (grey regions). (b) The peak areas are plotted as a function of $\tau_R$ and fit to an exponential decay to extract $T_1$ for each chemical species.
The fully recovered spectra reported in this thesis were all acquired using a recycle delay (delay time between collecting subsequent transients) of at least $5 \times T_1$. Generally, recycle delays of 50 s – 60 s were used.

Of note, bulk MgD$_2$ is known to have an extremely long $T_1$ (~7 hours). But, $$(1 - e^{100 \text{s}/25,200 \text{s}}) \approx 0.004$$ so even a 100 s recycle delay would completely suppress NMR signals from chemical species with such long $T_1$'s. To check for the presence of long $T_1$ signals, a “poor man's $T_1$” (1 scan per point, 3 – 6 different recovery times) was run overnight for each research sample. For example, an overnight run might consist of $\tau_R = 20 \text{ min}, 40 \text{ min}, 1 \text{ hr}, 2 \text{ hr}, 5 \text{ hr}, 7 \text{ hr}$ (the linear part of the exponential build-up curve for $T_1 \sim 7 \text{ hr}$) with a single transient collected per $\tau_R$ (no phase cycling used). In all ball milled samples, no extremely long $T_1$ signals were found, consistent with previous findings for $^1$H NMR on ball milled MgH$_2$.$^1$

The general spectra processing routine was as follows. The collected time domain signal was baselined (to remove DC offset) by calculating the average value of the last 25% of the collected time domain points (data from ~ 9 – 12 ms) and subtracting this value from all points in the time domain signal. The time domain signal was then left shifted to the center (maximum value) of
the spin echo located at $\sim \tau_{IE}$ (the acquisition was triggered on the $\pi$ pulse). To increase the frequency resolution of the resulting NMR spectrum, a series of zero amplitude points was added to the end of the time domain signal (zero filling). Normally, the time domain signal was zero filled so that the resulting file size increased from 8,192 points ($\sim 12$ ms, $\Delta f = 81$ Hz/point) to 131,072 points ($2^{17}$ points, $\sim 197$ ms, $\Delta f = 5$ Hz/point) The time domain signal was then Fourier transformed and the resulting frequency spectrum underwent a zero-order phase correction (see Fukushima and Roeder$^f$, Levitt$^e$, or Keeler$^k$ for details) so that all peaks in the real spectrum were absorptive. The phase-corrected spectrum was then windowed so that only signal between $\pm 50$ kHz was saved, reducing the final file size by $\sim 85\%$ while retaining only the region of interest as well as the enhanced frequency resolution (step size) that results from the zero filling technique.
3.6 References


(c) Griffiths, D. J. *Introduction to Electrodynamics*; Pearson: Boston, 2013.


Chapter 4: Results and Discussion

4.1 Introduction

The reaction kinetics for the MgH$_2$ hydriding reaction are important for the successful implementation of a magnesium hydride-based hydrogen storage system. The details of this criteria have been discussed in the introduction chapter. It has been previously shown that hydrogen diffusion through the bulk metal/metal hydride is a key rate limiting step to the overall reaction kinetics, the so call “hydrogen blockade” problem.\textsuperscript{a–h} Thus, improving hydrogen diffusion through the bulk metal and hydride phase is an important target for improving the hydrogen storage properties of magnesium hydride.

In addition, it has been demonstrated that the crystal structure of the metal hydride plays a significant role in the overall hydrogen diffusion through the metal hydride crystal lattice. In fact, a cubic, fluorite (CaF$_2$ motif) structure has been shown to significantly improve hydrogen diffusion in the bulk metal hydride. This effect has been demonstrated experimentally by our group (Conradi et al)\textsuperscript{i} as well as Notten and coworkers\textsuperscript{j} for a magnesium-scandium hydride alloy and was discussed in brief in the introduction chapter of this thesis. The results from those works are prime motivating factors for this current work. The improvement of hydrogen diffusion through the lattice for fluorite structured materials has also been investigated theoretically.\textsuperscript{k, l, m} These theoretical studies suggest that the availability of octahedral interstitial sites in the fluorite structure reduce the energy barrier to hydrogen lattice diffusion.

Therefore, a magnesium hydride with bulk fluorite (fcc) structure is desired for the expected improvements in hydrogen diffusion through the metal hydride lattice. The improvement of H
diffusion results in significant kinetic enhancement for the magnesium hydride hydriding/dehydriding reaction.

The intent here is to study the local atomic structure of magnesium-titanium deuterides prepared by high pressure ball milling under D₂ gas using deuterium magic angle spinning nuclear magnetic resonance (²H MAS NMR). The hope is to find cubic structured MgD₂ upon ball milling magnesium with titanium under high deuterium pressure.

²H MAS NMR is sensitive to the local atomic structure surrounding the deuterium atoms in the sample under observation through the nuclear quadrupole interaction.

\[
H_Q = \frac{eQ}{2I(I - 1)\hbar} \hat{I} \cdot \vec{V} \cdot \hat{I} \tag{4-1}
\]

where

\( eQ \) is the quadrupole moment of the nuclei under study, for deuterium,

\( eQ = 0.286 \times 10^{-28} \text{ m}^2 \)

\( I \) is the spin quantum number, for deuterium, \( I = 1 \).

\( \hat{I} \) is the quantum spin operator

\( \vec{V} \) is the electric field gradient (EFG) tensor at the site of the deuterium nucleus:

\[
\vec{V} = \begin{pmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{pmatrix} \tag{4-2}
\]
and

\[ V_{ij} = \frac{\partial^2 \phi}{\partial x_i \partial x_j} \]  \hspace{1cm} (4-3)

where

\[ \phi \] is the electric potential

The term \( \hat{I} \cdot \vec{V} \cdot \hat{I} \) leads to both a magnitude and orientation dependence upon the electric field gradient for the quadrupole interaction. The orientation is relative to the direction of the EFG tensor principal axis and the external magnetic field, \( B_0 \). Since all other terms are constant, the quadrupole interaction, \( H_Q \), depends on the magnitude and orientation of the EFG. The electric field gradient, in turn, depends on the local atomic structure since it results from the electric fields generated by surrounding atoms. Thus, the electric field gradient is a direct probe of the local atomic structure that induces it. Since the quadrupole interaction depends on the magnitude and orientation of the EFG, the quadrupole interaction is dependent on the local atomic structure. It is through the quadrupole interaction that NMR is sensitive to crystal structure.

In the other direction, the observed deuterium MAS NMR signal is dependent upon the nuclear quadrupole interaction. This chain of information is summed up schematically in figure 4-1 below.
The intention here is to follow this process in reverse; that is start with the observed $^2$H MAS NMR spectrum and work back to the local structure. To do so, first consider an ensemble of isolated deuterium spins. With no magnetic field present, the energy levels of the spin states are degenerate (see figure 4-1-A below). When placed in an external magnetic field, the energy levels of the nuclear spin states are split by the applied field, resulting in the Zeeman splitting. For deuterium, with $I = 1$, this results in three states (see figure

**Figure 4-1**: Schematic detailing the connection between the observed $^2$H MAS NMR spectrum and the underlying local atomic structure. The charged nuclei and electrons of the atoms in a crystal lattice result in electric fields. If these electric fields are nonuniform, then they have an electric field gradient (EFG). The EFG interacts with the quadrupole moment of a nucleus with spin $I > \frac{1}{2}$. Thus, the nuclear quadrupole interaction (HQ) affects the observed deuterium NMR spectrum. Graphics used in the making of this schematic were sourced from references (m) and (o).
The energy difference between the states is given by $\omega^0 = \omega_L$, the Larmor frequency, with $\omega^0 = \omega_L = -\gamma B_0$. For deuterium, at 7.04 T, $\omega^0/2\pi = 46.001 \text{ MHz}$ (for D$_2$O). In NMR, we observe the transition of the spins between the various Zeeman energy states. So here, with only the Zeeman interaction present (figure 4-2-B above) we would observe a single resonance at $\omega = 2\pi \times 46.001 \text{ MHz}$ as shown in figure 4-3-A below.
However, when the quadrupole interaction is included, there is a shift in the energy levels so that the splitting between each level is no longer equal (see figure 4-2-C above).

\( \omega_Q \), the quadrupolar coupling in frequency units, depends on the magnitude and orientation of the electric field gradient as discussed previously. Suppose then, that a single crystal specimen was observed. Here, \( \omega_Q \) would have a single value, since the EFG is constant throughout the sample. That is, the local structure surrounding the observed nucleus is consistent throughout the sample (which is a single phase crystal) implying that the magnitude of the EFG is also constant for all observed nuclei within the sample. Furthermore, because the specimen is a single crystal and not

---

**Figure 4-3:** Observed deuterium NMR signal for (A) the Zeeman interaction only, (B) a single-valued quadrupolar coupling, \( \omega_Q \), such as for a single crystal or a liquid crystal, and (C) powder with randomly oriented crystallites, and thus EFGs, so that \( \omega_Q \) has a distribution of values. Graphic adopted from reference (o).
a powder, a single orientation is present for this sample (ignoring significant $B_0$ magnetic field inhomogeneities). Since the magnitude and orientation are single valued, $\omega_Q$ is also single valued. Therefore, we would observe two resonances (one for each transition) in the observed deuterium NMR spectrum: one at $\omega = \omega_L + (1/2)\omega_Q$ and one at $\omega = \omega_L - (1/2)\omega_Q$ (see figure 4-3-B). This scenario would also be the case for a liquid crystal where the liquid crystal’s director would align with the external magnetic field leading to a single orientation for the EFG and a single value for $\omega_Q$.

Finally, the case of a powder sample, which is the case for the samples used in this work, must be considered. In a powder, the magnitude of the EFG is constant, assuming the powder is made up of homogeneous crystallites, but the orientation of the EFG is not. If the crystallite orientation is isotropic, then all orientations will be sampled and there will be a continuous distribution of energy level shifts. Each shift will correspond to a crystallite with a particular orientation, and therefore a particular EFG orientation resulting in a specific $\omega_Q$. Of note, and possibly contrary to intuition, there is not an equal probability for all orientations and the observed line shape is not a continuous distribution from $\omega = \omega_L - (1/2)\omega_Q$ to $\omega = \omega_L + (1/2)\omega_Q$.

In fact, the probability distribution of the orientations is related to the surface area of a sphere (an isotropic distribution of orientations). $\omega_Q$ depends on the angle between $B_0$ (so z-axis) and the principal axis of the EFG tensor, $\theta$. The number of crystallites with a particular orientation $\theta$ is proportional to the surface area of a sphere between $\theta$ and $d\theta$ integrated over $0 \leq \varphi \leq 2\pi$ and $r = r$ (see figure 4-4 below).
Clearly the number of crystallites oriented along the field \((\theta = 0)\) or anti-aligned with the field \((\theta = \pi)\) is minimum, while the number of crystallites oriented perpendicular to the field \((\theta = \pi/2)\) is maximum.

To first order, the orientation dependence of \(\omega_Q\) is given by:

\[
3\cos^2(\theta) - 1 - \eta_Q \sin^2(\theta) \cos(2\phi)
\]  

(4-4)

where \(\eta_Q\) is the quadrupole asymmetry parameter defined as:

\[
\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}
\]  

(4-5)
and takes on values between 0 and 1.

The strength of the quadrupole splitting is given by the quadrupolar coupling constant, $C_Q$:

$$C_Q = \frac{eQV_{zz}}{h}$$

So that, to first order, the quadrupolar coupling is given as:

$$\omega_Q = \frac{3\pi eQV_{zz}}{2I(I-1)}h\left[3\cos^2(\theta) - 1 - \eta_Q\sin^2(\theta)\cos(2\phi)\right]$$

$$= \frac{3}{2} \pi C_Q \times \left[3\cos^2(\theta) - 1 - \eta_Q\sin^2(\theta)\cos(2\phi)\right]$$

(4-7)

for deuterium with spin $I = 1$.

Note, by convention, the principal components of electric field gradient tensor, $V_{xx}$, $V_{yy}$, and $V_{zz}$, are defined such that:

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

(4-8)

An example of the static $^2$H NMR spectrum for a powder sample is shown in figure 4-3-C. Here, $\eta_Q = 0$, a common case for deuterium\(^\text{p}\), so that the resulting lineshape is the familiar Pake pattern made famous by George Pake in his study of isolated dipolar-coupled spin-$\frac{1}{2}$ pairs.\(^\text{q}\)

Therefore, the observed line shape, which depends on $\omega_Q$, provides insight into the local atomic structure surrounding the deuterium nuclei under observation since $\omega_Q$ depends on the electric field gradient at the site of the deuterium nucleus, which in turn depends on the local atomic structure. In essence, we are starting at the end of the flow chart shown in figure 4-1, and working backwards from the observed $^2$H MAS NMR spectrum to the underlying atomic
structure that leads to it.

4.2 Sample rotation
For the work here, magic angle spinning (MAS) has been employed. In MAS, a powder sample is packed in a rotor, a cylindrical, pencil-shaped sample holder, and rotated about the cylinder axis at a high rate, usually several kilohertz. Here, the typical spinning rate was 9 kHz. The cylindrical axis of the rotor is oriented with respect to the static, external magnetic field so that

$$\theta_{\text{rotor}} = \theta_{\text{magic}} = \arccos \left( \frac{1}{\sqrt{3}} \right) \approx 54.7^\circ .$$

For a randomly oriented crystallite in the powder sample, the time averaged orientation of the principal axis of the crystallite’s electric field gradient will align along the rotor’s cylinder axis. If the magic angle is well set, this rotation will time average the first order quadrupolar interaction to zero, collapsing the broad powder pattern lineshape to a single, sharp resonance if the spinning rate is sufficiently high (usually, the spinning rate, $f_s$, must be greater than $\omega_{Q\text{-max}}/2\pi$ for full line narrowing). For many deuterium systems, $\omega_{Q\text{-max}}/2\pi \sim 100$ kHz, well above the maximum spinning rates for most MAS NMR probes. When the spinning rate is too low to completely time average out the first order quadrupolar interaction, the sample rotation instead results in the refocusing of the quadrupolar interaction every $n$ rotor cycles (360° rotation of the sample rotor about the rotor's cylinder axis). This refocusing is similar to the spin coherence refocusing achieved through RF pulses by the spin echo technique for NMR interactions that can be reversed (e.g., the chemical shift interaction and magnetic field
inhomogeneity). Indeed, like the spin echo, MAS results in “spun” echoes, which are spaced out at integer multiples of the rotor period, \( \tau_{\text{Rotor}} = 1/f_s \), in the time domain signal. When Fourier transformed, these spun echoes result in sharp peaks at \( \pm \) integer multiples of the spinning rate \( f_s \), known as spinning sidebands (SSBs), and outline the static powder pattern. Therefore, the information on local atomic structure that can be derived from the observed static pattern can in a similar fashion be obtained from the \(^2\text{H} \) MAS NMR spectrum through the observed spinning sideband manifold. In general, the time domain signal \( S(t) \) is complicated since it depends on the time dependence of the orientation of the electric field gradient's principal axis system with respect to the static external field. The behavior of the spun echoes is not directly apparent from the MAS time domain function. However, the time domain signal can be understood as a frequency modulated signal similar to that found in FM radio. The precession frequency of the spins is time dependent due to the modulation of the quadrupolar coupling \( \omega_Q \) that results from sample rotation. An insightful description of the effect of MAS on the NMR time domain signal is given by Jian and Harper. Marciq and Waugh were early developers of the theory of NMR in rotating samples. In their 1979 paper, “NMR in rotating solids”, they tackle the calculation of the time domain signal for deuterium MAS NMR (ignoring other interactions), and, by Fourier transform, the resulting \(^2\text{H} \) MAS spectrum. Their work links the observed \(^2\text{H} \) MAS sideband manifold to the underlying nuclear quadrupolar interaction, and, by the use of the Van Vleck method of moments, they determine \( C_Q \) and \( \eta_Q \) based upon the spinning sideband intensities. In general, the moments of the lineshape are calculated based upon the SSB intensities. The calculated moments are then used to
determine $C_Q$ and $\eta_Q$. The details of these calculations are not critical to the work here. Moreover, direct application of that specific analysis is often limited to special cases, making it difficult to apply to heterogeneous systems like the ball milled Mg-Ti-D powders under study here. For us, the important result of Marciq and Waugh's theoretical development, and similar analysis and application by many others\textsuperscript{p,u,y}, is that the observed $^2$H MAS NMR spinning sideband intensities are directly related to the underlying nuclear quadrupole interaction (parametrized by $C_Q$ and $\eta_Q$), which in turn depends directly on the electric field gradient at the site of the deuterium nuclei, establishing the connection between the SSBs and the local atomic structure. For those interested, a brief, but detailed discussion on the method of moments can be found in Fukushima IV.A.2\textsuperscript{c}

Thus, for our purposes, there is no need to exactly determine $C_Q$ and $\eta_Q$, a task made difficult by the complexity of the ball milled powders. Instead, the spinning sideband manifold in the deuterium MAS NMR spectra of the ball milled samples can be qualitatively examined, allowing for approximate assessment of the quadrupolar coupling, and thus the relative symmetry of the local atomic structure surrounding the deuterium atoms in the Mg-Ti-D powders. A broad static powder pattern leads to a more intense and extended spinning sideband manifold for a given MAS spinning rate, indicating a strong quadrupolar interaction (large $\omega_Q$) and thus a large EFG (so low site symmetry). Conversely, a narrow static powder pattern results in less intense spinning sidebands manifesting over a smaller frequency range for a given MAS spinning rate signaling a weak quadrupole interaction and a small EFG (high site symmetry). Qualitative analysis of the observed spinning sideband manifold can provide sufficient information on the
site symmetry of the deuterium atoms in the ball milled samples.

One question that might occur is that if the information on the electric field gradient at the site of the deuterium nucleus is already available in the static $^2$H NMR spectrum, why complicate matters by spinning the sample? There are two good reasons for magic angle spinning. First, in NMR the area under the curve (in the frequency domain) is conserved (it is proportional to the number of spins present). Under MAS, the broad powder pattern from static deuterium NMR collapses to a series of sharp spikes at $\pm n \times f_s$ ($n$ integer). Since the area under the curve is conserved, the amplitude (height) of the SSBs is increased to compensate for the reduced frequency distribution of the spectrum. Said another way, the intensity, which was spread across a broad, continuous frequency range when the sample was static, is now focused into a few sharp peaks at discrete frequencies under MAS. The signal-to-noise ratio (SNR) of the spectrum is related to the height of the observed peaks compared to the random baseline noise. By focusing the conserved intensity of the $^2$H frequency spectrum into several sharp peaks, MAS effectively increases the SNR of the resulting spectrum. In addition, and more importantly here, MAS allows the chemically inequivalent deuterium sites and/or the species (e.g., MgD$_2$ and TiD$_2$) to be separated by means of chemical (or Knight) shift. In the static condition, the quadrupolar-broadened lineshapes overlap. This interaction, paired with other smaller sources of line broadening, like the dipole-dipole interaction, results in lineshapes, from chemically inequivalent deuterium atoms that cannot be adequately separated. Under MAS, the collapse of the broad line into sharp peaks allows for easy separation between MgD$_2$ and TiD$_2$ signals based on frequency shift.
A demonstration of this qualitative analysis is shown below in figure 4-5. Here (in the right panel), the $^3$H MAS NMR spectra for several deuterium bearing compounds are shown ($f_s \sim 9$ kHz, $\omega_0/2\pi = 46.001$ MHz for all cases). The site symmetry of the deuterium atoms in the compounds increases significantly as you move from spectrum A (biphenyl, C$_{12}$D$_{10}$) to spectrum C (TiD$_2$). The increase in site symmetry, which is a probe of the local atomic structure surrounding the deuterium atoms, results in a decrease of the electric field gradient at the site of the deuterium nucleus. This decrease in the EFG in turn results in a weaker quadrupole interaction, leading to a smaller maximum value for $\omega_Q$ and a narrower $^3$H MAS NMR spinning sideband manifold. In the left panel of figure 4-5 the unit cell for each compound is shown, and the deuterium coordination environment is highlighted.
**Figure 4-5:** Left panel – unit cells for several example deuterium bearing compounds. Right panel – $^2$H MAS NMR ($f_s \sim 9$ kHz, $\omega_0/2\pi = 46.001$ MHz) spectra for the compounds of the left panel. (a) Deuterated biphenyl ($C_{12}D_{10}$) has D in a low symmetry environment resulting in a large $\omega_Q$ and an intense, extended SSB manifold. The red circles indicate various coordinations shells surrounding the D atom. The D atoms in $C_{12}D_{10}$ have a single carbon nearest neighbor and a complex arrangement of next nearest neighbors resulting in a strong EFG at D atom positions. (b) MgD$_2$ with D atoms coordinated by 3 surrounding Mg atoms resulting in a much higher symmetry environment (as compared to biphenyl) and a weaker quadrupole interaction. For biphenyl, $C_Q \sim 190$ kHz, while for MgD$_2$, $C_Q \sim 35$ kHz, hence the sideband manifold for MgD$_2$ while intense, extends over a much smaller frequency range. (c) TiD$_2$ with cubic (fluorite, fcc) structure has D atoms at sites of high symmetry. Each D atom is coordinated with 4 Ti atoms in a tetrahedral fashion resulting in a uniform electric field (EFG = 0) at the D atom sites. The absence of the EFG results in $\omega_Q = 0$, so that a single sharp resonance is observed for TiD$_2$. The sharp lines at $\pm 52.5$ kHz are noise from the spectrometer. The unit cell depiction for biphenyl was adopted from reference (aa) and the MgD$_2$ unit cell depiction was adopted from reference (ab). The TiD$_2$ unit cell depiction was generated using Vesta$^*$. 
For biphenyl \((C_{12}D_{10}, \text{figure 4-5, right panel, A})\) each D atom has a single carbon atom nearest neighbor and a complex coordination environment beyond this nearest neighbor resulting in a low symmetry D environment with a large EFG, and therefore a large \(\omega_Q\). Note, \(C_Q\) for deuterated biphenyl is \(\sim 191 \text{ kHz}\) with \(\eta_Q \sim 0.07\) (from CASTEP\textsuperscript{ae} and Quantum ESPRESSO\textsuperscript{ad} (QE) calculations, not discussed here). This large EFG results in the intense, extended spinning sideband manifold observed in the \(^2\text{H} \text{ MAS NMR}\) spectrum shown.

Bulk \(\text{MgD}_2\) has a tetragonal (rutile) crystal structure as shown in figure 4-5 (left panel, B) with each deuterium atom coordinated by three Mg atoms. This D coordination environment results in a much smaller EFG, as compared to biphenyl, at the site of the deuterium nucleus. For \(\text{MgD}_2\), \(C_Q \sim 35 \text{ kHz}\) and \(\eta_Q \sim 0.65\) so that the spinning sideband manifold for the \(^2\text{H} \text{ MAS NMR}\) spectrum of \(\text{MgD}_2\) extends over a much smaller frequency range: \(\pm 30 \text{ kHz}\) for \(\text{MgD}_2\) compared to \(\pm 100 \text{ kHz}\) for biphenyl, see figure 4-5 (right panel, A and B).

Finally a high symmetry deuterium site is presented in the \(\text{TiD}_2\) crystal structure shown in figure 4-5 (left panel, C). In \(\text{TiD}_2\), the D atoms are coordinated by four Ti atoms in a tetrahedral, cubic fashion. The cubic structure has high symmetry \((x = y = z)\) so that the EFG at the site of the deuterium atom is zero. A quick proof of the absence of an electric field gradient at a site of cubic symmetry is as follows.

Laplace's equation from electrostatics tells us that:
\[ \nabla^2 \phi = 0 \]  
(4-9)

where

\[ \nabla^2 \phi = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \]  
(4-10)

and

\( \phi \) is the electric potential

Laplace's equation (as opposed to Poisson's equation) is valid here because the EFG is evaluated at the site of the nucleus. The only charge present is the nucleus's own charge, resulting in a self-interaction. Thus the interaction does not depend on the spin orientation and does not impact the NMR signal.

Recall from equation 4-3 that these terms are the principal values of the electric field gradient tensor so that:

\[ V_{xx} + V_{yy} + V_{zz} = 0 \]  
(4-11)

Cubic symmetry means that:

\[ x = y = z \]  
(4-12)

so that:

\[ V_{xx} = V_{yy} = V_{zz} \]  
(4-13)

Substituting equation 4-13 into equation 4-10 results in

\[ V_{xx} + V_{xx} + V_{xx} = 0 \]

\[ \Rightarrow V_{xx} = 0 \]

\[ \Rightarrow \vec{V} = 0 \]
Therefore, atomic sites with cubic symmetry have no EFG.

The cubic, high symmetry site for deuterium in TiD$_2$ results in no electric field gradient at the site of the D nuclei and therefore the absence of the quadrupolar interaction (recall from equation 4-1 above that $H_Q \propto \vec{V}$). Thus, the $^2$H MAS NMR spectrum for bulk TiD$_2$, shown in figure 4-5 (right panel, C) is a single sharp peak (no SSBs), just like the case discussed above for a deuterium spin in the absence of a quadrupolar interaction (e.g., D$_2$O in the liquid state). As has been demonstrated, the nuclear quadrupolar interaction in deuterium MAS NMR manifests itself as spinning side bands. The more intense and more extended (over the frequency range) the spinning sideband manifold, the stronger the quadrupolar interaction. A strong quadrupole interaction is indicative of deuterium local structure with low symmetry, like the deuterated biphenyl example shown above in figure 4-5 (right panel, A). In contrast, the absence of spinning sidebands, or the presence of only weak SSBs that manifest over a small frequency range, indicates a weak quadrupole interaction and therefore a small EFG. A small or zero EFG implies deuterium sites of high symmetry (cubic) as in the case of TiD$_2$ discussed above and shown in figure 4-5 (right panel, C).

In summary, while more complex methods of analysis exist, like that of Marcq and Waugh discussed previously, these approaches are highly dependent on the system under study. Here, the heavily treated systems (by ball milling) result in significant heterogeneity in the final Mg-Ti-D powders that cannot often be described by one single NMR parameter (one $C_Q$ and $\eta_Q$ for the entire composite material). Magusin, Notten, and coworkers present several good discussions on
this issue for $^2$H MAS NMR measurements on Mg-Sc-D and Mg-Ti-D samples.\textsuperscript{af–ai} For instance, in their 2010 work on Mg-Sc-D and Mg-Ti-D, they note that the Mg-Sc-D $^2$H NMR lineshape (both static and MAS) can be accurately described by several values of $C_Q$ with $\eta_Q$ ranging from 0 to 1. However, the variation in $C_Q$ was relatively small, \textasciitilde 1 – 5 kHz, so that qualitative lineshape assessment still provided good insight into the deuterium site symmetry. It is this qualitative approach that is taken to analyze the $^2$H MAS NMR spectra of the Mg-Ti-D powders studied here.

Defects in the crystal structure introduced by ball milling would lead to a large EFG at the site of the D atom even in a cubic crystal structure. However, since NMR is a bulk technique that has low sensitivity, D atoms in sites with defects nearby would to need to account for a significant fraction of all D atoms present to be discernible by NMR.

### 4.3 Spinning sideband amplitude ratios

For consistent analysis, the spinning sideband amplitude ratios for the $^2$H MAS NMR spectra of all samples studied have been measured. The side band amplitude ratios have been defined in terms of the average sideband amplitude, $a_x$, as follows:

$$a_x = \text{the average amplitude of sidebands } m = \pm x = \frac{H\{m=+x\} + H\{m=-x\}}{2}$$

(4-14)

where:

“$m=x$” is the spinning sideband at frequency $= x*f_s$, and $x$ is integer

$H(m=+x)$ is the height (amplitude) of the spinning sideband located at $f = x*f_s$.
\( f_s \) is the MAS spinning rate; generally, \( f_s \sim 9 \text{ kHz} \)

Note, \( a_0 = H(m=0) \), is the height of the centerband

Thus, \( a_1 \) is the average amplitude (height) of the \( m=\pm 1 \) and \( m=\pm 1 \) spinning sidebands; so the average height of the sidebands located at \( \pm f_s \). “\( m \)” is often called the sideband order.

The spinning sideband intensity ratio has been defined as:

\[
R_x = \frac{a_x}{a_2}
\]  

(4-15)

where:

- \( a_x \) is the average sideband amplitude (height) for the \( m = \pm x \) sidebands as discussed above
- \( a_2 \) is the average height of the \( m=\pm 2 \) sidebands
- \( R_x \) is the spinning sideband amplitude ratio of the \( m=\pm x \) sidebands

The \( m=\pm 2 \) sidebands were chosen to be the normalization reference since they were usually present in the \( ^2\text{H} \) MAS NMR spectra for all Mg-Ti-D samples examined and usually had a strong enough amplitude to be well resolved above the baseline noise level. Furthermore, the \( m=\pm 2 \) sidebands are “thrown out” far enough in the spectrum (so to greater magnitude frequency shifts) that overlap with other \( ^2\text{H} \) signals is nonexistent.

For each sample, the spinning sideband amplitude ratios were measured and are reported as “\( R_0, R_1, R_2, R_3 \)” Note, \( R_2 = 1 \) by definition. An example of this type of analysis is shown for the spectrum of bulk MgD\(_2\) in figure 4-6 below. The spinning sideband intensity ratio measurements...
for several samples will be discussed in detail later. In general, larger values for $R_3$ paired with smaller values for $R_1$ and $R_0$ indicate a larger $C_Q$ and therefore a strong quadrupole interaction suggesting a low symmetry deuterium site. Large values for $R_0$ and $R_1$ paired with small values for $R_3$ instead point to a small $C_Q$ and weak quadrupole interaction indicating deuterium atoms at sites of high symmetry (trending towards cubic structure).

4.4 $^2\text{H}$ MAS NMR relative peak areas
As has been mentioned previously, the area under the curve in a NMR spectrum is proportional to the number of spins. This property provides an excellent measure of the relative phase presence of deuterium bearing species in the ball milled Mg-Ti-D samples. For example, the $^2\text{H}$ MAS NMR spectrum for a ~ 2 Mg : 1 Ti by mol (starting material) ball milled under 1,250 PSI
$D_2$ for $\sim 5$ hours is shown in figure 4-7 below.

![Figure 4-7: $^3$H MAS NMR spectrum for $\sim 2$ Mg : 1 Ti ball milled under 1,250 PSI $D_2$ for $\sim 5$ hours. The relative amounts of the MgD$_2$ and TiD$_2$ phases have been determined by integration of the peak areas for the two phases. Peaks associated with the rutile MgD$_2$ phase have been labeled “A”. The peak associated with the TiD$_2$ phase has been labeled “B”. The relative peak areas are reported as Area (MgD$_2$) : Area (TiD$_2$). In addition, the spinning sideband amplitude ratios for the MgD$_2$ phase (peaks A) have been reported as “$R_0, R_1, R_2, R_3$” in the upper left corner of the plot. The SSB amplitude ratios are reported as discussed in section 4.3 above.](image)

The sharp centerband near zero frequency as well as the sharp peaks at

$$\pm n \times f_s \approx \pm n \times 9 \text{ kHz}$$

with $n$ integer, correspond to the rutile MgD$_2$ phase (peaks labeled “A” in figure 4-7 above),
while the broad, shifted peak near -7 kHz with no associated spinning sidebands (if present, they would appear at -7 kHz $\pm n \times f_s$) is the cubic, metallic TiD$_2$ peak (labeled “B” in figure 4-7 above). By integrating the peak areas of the rutile MgD$_2$ centerband and all visible spinning sidebands (peaks “A”), and comparing this area to the integrated area of the lone, broad TiD$_2$ peak (peak “B”), the relative presence of deuterium in the rutile MgD$_2$ phase versus the fluorite TiD$_2$ phase can be obtained.

The relative phase presence would be expected to match the as mixed molar ratio since both Mg and Ti uptake two deuterium atoms per metal atom upon the formation of the deuteride phase. That is, the integrated area of the MgD$_2$ peaks (centerband and all sidebands) should be double that of the integrated area of the broad, shifted TiD$_2$ peak (recall there is twice as much Mg here as Ti). For this particular sample, this is approximately what is observed: as mixed, Mg : Ti = 1.93; as measured by $^2$H MAS, MgD$_2$ : TiD$_2$ = 1.9. In fact, the spectrum looks like a simple superposition of the coarse-grained (bulk) MgD$_2$ $^2$H MAS NMR spectrum from figure 4-5 (right panel, B) with that of a broad TiD$_2$-like peak (no spinning sidebands, large frequency shift).

As a reminder, for correct deuterium phase analysis, the $^2$H MAS NMR spectrum for the sample under study must be collected using a recycle delay (the time between collection of subsequent NMR transients) allowing for full $T_1$ recovery ($\sim 5 \times T_1$). If not, an artificial weighting of one phase (e.g., MgD$_2$) over another can result, leading to incorrect values for the relative phase presence of the MgD$_2$ and TiD$_2$ peaks. This phenomenon was discussed in detail in the experimental chapter. The relative presence of the deuterium phases reported in this chapter were
all obtained from fully T\textsubscript{1}-recovered spectra.

4.5 Results of SSB amplitude ratio and relative peak area ratio measurements

The \textsuperscript{2}H MAS NMR spectra for several samples studied are shown starting in figures 4-8 below. The samples include bulk MgD\textsubscript{2} and bulk TiD\textsubscript{2} powders, ball milled single phase materials (ball milled MgD\textsubscript{2} and ball milled TiD\textsubscript{2}), metal hydrides (MgH\textsubscript{2} – TiH\textsubscript{2}) ball milled under D\textsubscript{2} gas, as well as metal powders (Mg-Ti) ball milled under D\textsubscript{2} gas. The bulk MgD\textsubscript{2} and TiD\textsubscript{2} powders were synthesized by high temperature (450 °C) and high pressure (~2,000 PSI D\textsubscript{2}) reaction of bare metal powders (Mg and Ti) with D\textsubscript{2} gas.

For ball milled samples, to the right of each spectra, the initial powder mixture (by mol) and milling time are shown. “1 MgH\textsubscript{2} : 1 TiH\textsubscript{2}” indicates a one-to-one mixture of MgH\textsubscript{2} to TiH\textsubscript{2} by mol (starting with hydrides) was initially loaded into the milling vessel. “1 Mg : 1 Ti” indicates a one-to-one mixture by mol of magnesium and titanium powder (so bare metals) was loaded into the milling vessel. The time listed, \(t_m\), is the total ball milling time. In all cases, D\textsubscript{2} gas at \sim 1,000 – 2,000 PSI was used as the ball milling atmosphere. Also in all cases, the ball to powder weight ratio (BPR), so the mass of the YSZ milling balls compared to the mass of the powder to be milled, was \sim 10:1.

To the left of each spectrum, the spinning sideband amplitude ratios, given as “\(R_0, R_1, R_2, R_3\)” (see equations 4-14 and 4-15 above) as well as the relative peak area ratio of the rutile MgD\textsubscript{2}-like peaks to the cubic TiD\textsubscript{2}-like peak(s), given as \text{Area(MgD\textsubscript{2})} : \text{Area(TiD\textsubscript{2})}, are provided.
4.6 Bulk and ball milled MgD\(_2\)

The spectra for bulk (un-milled, coarse-grained) MgD\(_2\), previously shown in figures 4-5 (right panel, B) and 4-6, is reproduced along with MgD\(_2\) ball milled for 4 hours under ~1,500 PSI D\(_2\) in figure 4-8 below. In both spectra, the strong sideband manifold is present and spans a ±30 kHz frequency range. Sideband amplitude ratio analysis (shown to the left of each spectra) indicates that ball milling of the un-doped MgD\(_2\) (for a short period of time) has little effect on the local atomic structure based upon the close match of the sideband intensity ratios between the two spectra. This set of sideband intensity ratios, \(R_0, R_1, R_2, R_3\sim 2.0, 2.0, 1.0, 0.3\), seems to be indicative of rutile MgD\(_2\) and can be used as a fingerprint for identifying the presence of the tetragonal magnesium deuteride phase in more complex spectra. This approach is especially useful when considering the sideband intensity ratio \(R_3\) since it corresponds to the sidebands furthest out (to ±f) in the spectrum, so little signal overlap exists, and the \(m=±3\) sideband intensities would be first to decrease upon a reduction in \(C_Q\) due to a change to a more symmetric deuterium environment. Note, for the MgD\(_2\) spectra shown here and the TiD\(_2\) spectra shown below, no relative peak area ratio is provided since these samples consist of single deuterium-bearing phases. Recall, the relative peak area ratio is the ratio of the peak area for the MgD\(_2\)-like component (large SSB manifold, no frequency shift) to the TiD\(_2\)-like component (no or only weak SSBs, large frequency shift) as discussed in section 4.4 above,
4.7 Bulk and ball milled TiD$_2$

The $^2$H MAS NMR spectra for bulk, coarse-grained TiD$_2$ previously shown in figure 4-5 (right panel, C), titanium powder ball milled under ~ 2,000 PSI D$_2$ for 4 hours, as well as titanium powder ball milled under ~ 2,000 PSI D$_2$ for 75 hours are shown in figure 4-9 below. Bulk TiD$_2$ has been briefly discussed above. Important to the analysis here, bulk TiD$_2$ shows up as a single, sharp resonance at ~ -7 kHz under MAS. The absence of spinning sidebands is due to the high symmetry of the deuterium atom sites within the TiD$_2$ crystal structure (fcc, fluorite structure). The cubically symmetric sites have no electric field gradient so that the nuclear quadrupole
interaction is absent ( $H_q \propto \vec{V}$ ). The large shift (away from zero frequency) is the well known Knight shift for TiD$_2$ and serves as an excellent identifier for the TiD$_2$ species. The Knight shift results from the interaction of the nuclear spin with the electron spins of the conduction band in metallic materials. Thus TiD$_2$ is metallic and exhibits a large frequency shift. Note, chemical shifts for deuterium are usually 1 – 10 ppm (so 0 – 460 Hz here). The much larger Knight shift, ~150 ppm, easily distinguishes TiD$_2$ from other deuterium bearing species. Indeed, like the sideband intensity ratios for bulk MgD$_2$, the large Knight shift serves as a form of fingerprint for identifying TiD$_2$-like deuterium species. It is supplemented by the absence, or near absence, of spinning sidebands due to the cubic environment of the deuterium site. Together, the TiD$_2$ $^2$H MAS NMR spectrum indicates a metallic (large frequency shift) deuterium bearing species with deuterium at cubically symmetric sites (absence of spinning sidebands). These qualitative assessments will be important for interpreting the more complex spectra of the mixed-phase Mg-Ti-D powders discussed later.
Upon ball milling, there is a significant change in the lineshape. The TiD$_2$ resonance line is broadened considerably: the full width at half maximum (FWHM) for the bulk powder is ~160 Hz while for the ball milled powders the FWHM ~2,200 Hz. The Knight shift for the ball milled powders, determined by the center of the resonance peak, is less shifted (~ -114 ppm) compared to the bulk material (~160 ppm). Finally, for the ball milled TiD$_2$ powders, small, m=±1 spinning

Figure 4-9: $^2$H MAS NMR spectra for bulk TiD$_2$ (black) and bare titanium powder ball milled under D$_2$ for 4 hours (red) and 75 hours (blue). The Knight shift (in ppm) of the peak center, the peak width (FWHM), and $T_1$ are reported for each spectra in the table located in the upper left corner of the plot. The red dashed vertical lines are for reference to different ppm frequency shift values.
sidebands are present at ~ +4.5 kHz and -13 kHz.

The appearance of the low intensity, \( m = \pm 1 \) SSBs is likely the result of lattice strain introduced by ball milling. The deuterium sites must still occupy highly symmetric sites or the observed spinning sidebands would have much higher intensity. The low intensity of the sidebands and their presence only to order \( m = \pm 1 \) suggests a weak quadrupolar interaction for the deuterium atoms in TiD\(_2\) indicating only a slight deviation from perfect cubic site symmetry. Such a deviation could indicate the presence of defects in the crystal structure (e.g., a missing Ti atom) or the presence of lattice strain.

The change in peak position (Knight shift) and the broadening of the resonance line for the milled TiD\(_2\) are likely manifestations of the same underlying cause. A study of the ball milled TiD\(_2\) lineshape as a function of echo time, \( \tau_{HE} \), revealed that the broad line was easily refocused by the Hahn echo pulse sequence (see the experimental chapter for a description of the Hahn Echo acquisition technique). This result suggests that the “broad” line is not actually a single, broadened resonance, but a distribution of many narrow lines. That is, the TiD\(_2\) peak in the ball milled materials appears to exhibit a distribution of Knight shifts.

It is well known that the Knight shift in Ti(H/D)\(_2\) is dependent on the hydrogen/deuterium concentration, ranging from ~ -50 ppm at low D concentrations (~TiD\(_1\)) to ~150 ppm at higher deuterium concentrations (~TiD\(_{1.7}\)).\(^{ak}\) The H concentration dependence of the Knight shift (\( K \)) for Ti-H is shown in figure 4-10 below. Since titanium will form non-stoichiometric hydrides, the
finding of a mixture of titanium deuterides with varying concentrations of deuterium (TiDₙ) in the heterogeneous ball milled Ti-D powders is perhaps not surprising.

In addition, the difference in T₁ values for the ball milled samples versus the bulk sample (see figure 4-9) perhaps supports the conclusion of a distribution of D concentrations. For lower D concentrations, the T₁ should increase as shown in the lower curve of figure 4-10. There, the relaxation rate R₁ = 1/T₁ is plotted as a function of H concentration. Note, in figure 4-10, the value shown is \( \sqrt{R₁/T} \) since the Koringa T₁ is temperature dependent. At a constant temperature, here room temperature, the 1/T dependence can be thought of as a scaling factor. Importantly, R₁ is smaller (T₁ is longer) at low D concentrations suggesting that the ball milled Ti-D samples, with T₁ ~ 10 s, are TiDₓ as compared to the bulk TiD₂ sample, with T₁ ~ 6 s.

Figure 4-10: The hydrogen concentration (x) dependence (top curve) of the Knight shift (K) for titanium hydride at room temperature from reference (ak). Titanium hydride, which is a non-stoichiometric hydride, readily assumes TiHₓ. The lower curve details the H concentration dependence of the 'H T₁ for TiHₓ. The Knight shift and T₁ behavior for D in TiDₓ is the same though the absolute value of the shift (in frequency units) and T₁ are isotope dependent.

In addition, the difference in T₁ values for the ball milled samples versus the bulk sample (see figure 4-9) perhaps supports the conclusion of a distribution of D concentrations. For lower D concentrations, the T₁ should increase as shown in the lower curve of figure 4-10. There, the relaxation rate R₁ = 1/T₁ is plotted as a function of H concentration. Note, in figure 4-10, the value shown is \( \sqrt{R₁/T} \) since the Koringa T₁ is temperature dependent. At a constant temperature, here room temperature, the 1/T dependence can be thought of as a scaling factor. Importantly, R₁ is smaller (T₁ is longer) at low D concentrations suggesting that the ball milled Ti-D samples, with T₁ ~ 10 s, are TiDₓ as compared to the bulk TiD₂ sample, with T₁ ~ 6 s.
However, if this were truly the case, one might expect the most shifted portion of the broad peak (near -7 kHz), which has the highest D concentration, to recover faster (have a shorter $T_1$) than the least shifted portion of the broad peak (near -2 kHz). But, when the ball milled Ti-D spectrum is plotted as a function of recovery time (not shown here), this behavior is not observed. Instead, the broad, Gaussian lineshapes of the ball milled Ti-D samples recover uniformly suggesting that this behavior is not simply the result of a distribution of D concentrations ($x$ values) for TiD$_x$ crystallites in the milled samples.

Moreover, the lack of significant difference between the $^2$H MAS spectrum for the sample milled for 4 hours compared to that of the sample milled for 75 hours is surprising. If there were a distribution deuterium concentrations for the Ti-D particles in the powder sample, one might expect that additional ball milling time (under high pressure deuterium gas) would tend to tighten the concentration distribution as more and more Ti-D particles approached the upper limit of TiD$_2$ (fully deuterated).

It has also been shown by Latroche and coworkers$^{al}$ and confirmed by our own study, that bare titanium quickly uptakes deuterium, approaching the stoichiometric limit of TiD$_2$ within 20 minutes of ball milling under high pressure (~1,000 PSI) D$_2$ gas. The D$_2$ uptake of the ball milled bare metal powders will be discussed later in this chapter.

Another possible explanation is that the distribution of Knight shifts results from a distribution of crystallite sizes for the TiD$_2$ crystallites in the ball milled Ti-D powder. The Knight shift can be
thought of as a measure of the metallic character of a system. A large Knight shift corresponds to more metallic character. This can be qualitatively seen in the Knight shift formula from Slichter:

\[
K = \frac{8\pi}{3} \left\langle |u_k(0)|^2 \right\rangle_{E_f} \chi_e^S
\]  

(4-16)

where

- \(u_k(0)\) is the electron wave function at the site of the nucleus evaluated at the Fermi energy
- \(\chi_e^S\) is the total spin susceptibility of the electrons

The important take-away from equation 4-16 is that the Knight shift depends upon the band structure of the TiD$_2$ crystallite. As the crystallite size is reduced, the surface-to-volume ratio is increased so that more deuterium atoms are located near the grain boundary instead of in the bulk. The electronic band structure of the surface is likely different compared to that of the bulk and it is possible that the surface has a lower metallic character compared to the bulk. Therefore, the observed distribution of Knight shifts could result from the distribution of particle sizes in the ball milled Ti-D powder.

Of relevance, it has been shown that for Mg-Ti-H powders, the crystallite size is quickly reduced upon ball milling to a terminal value of ~ 10 nm.\textsuperscript{10} The terminal average crystallite size is reached in approximately 4 hours of ball milling (see figure 4-11 below), with no further reduction even with extended milling times (~ 60 hours). If the distribution of Knight shifts for the ball milled Ti-D samples does result from a crystallite size effect, then little change would be
expected in the observed $^3$H MAS lineshape with increased ball milling time beyond ~5 hours. Of note, the crystallite size versus ball milling time plot shown in figure 4-11 below is from Rousselot and coworkers$^{am}$ who ball milled various mixtures of Mg, Ti, MgH$_2$, and TiH$_2$ using a SPEX 8000 Mixer/Mill (same ball mill as used here). The reduction in particle size upon ball milling was not tracked extensively here. However, when it was measured from the XRD powder patterns collected on ball milled Mg-Ti-D powders, the average crystallite size behavior generally matched the results of previous Mg-Ti-H ball milling work.$^{am \cdot aq}$

In summary, the absence of spinning sidebands (cubic structure) and large frequency shift (metallic) act as unique signatures for TiD$_2$ in deuterium MAS NMR. Upon ball milling, little change in these signatures is found, even after extensive ball milling (75 hours). Though weak, order $m=\pm 1$ spinning sidebands appear for ball milled Ti-D, their low intensity suggests only a slight deviation from perfect cubic structure for the deuterium atom sites in ball milled TiD$_2$. The

Figure 4-11: Crystallite size in nanometers as a function of ball milling time for ball milled MgH$_2$ – TiH$_2$. Crystallite sizes were determined by the Scherrer method from the XRD powder patterns of the milled MgH$_2$ – TiH$_2$ samples. The behavior of crystallite size versus milling time appears to be consistent for many ball milled Mg-Ti-H samples and ball milling setups, with particle size quickly reduced to a terminal value within the first several hours of ball milling. Figure adapted from reference (am)
appearance of a broad line, as opposed to the narrow, single resonance in bulk TiD$_2$, results from a distribution of Knight shifts in the heterogeneous ball milled powder. This distribution could result from a variation in deuterium concentration for individual Ti-D crystallites within the milled powder or could be the manifestation of a distribution of crystallite sizes.

4.8 Ball milled MgH$_2$ – TiH$_2$

The $^2$H MAS NMR spectra for three MgH$_2$ – TiH$_2$ samples ball milled for 4 hours under ~1,500 PSI D$_2$ are shown in figure 4-12 below. The ratio of MgH$_2$ to TiH$_2$ for the starting powders was varied: the bottom spectrum in figure 4-12 is MgH$_2$-rich, the middle spectrum is equal parts MgH$_2$ and TiH$_2$, and the top spectrum is TiH$_2$-rich. Interestingly, the spinning sideband manifold for the MgD$_2$ (at zero frequency and with SSBs) signal deviates significantly from that of bulk MgD$_2$ and ball milled MgD$_2$ shown in figure 4-8. First, the frequency span of the spinning sideband manifold for the ball milled hydrides (~ ±20 kHz) is about two-thirds that of single-phased MgD$_2$ (~±30 kHz), indicating a reduction in the strength of the nuclear quadrupole interaction. This reduction is further evidenced by the spinning sideband intensity ratio, $R_0$, which is ~5x greater for the milled hydrides ($R_0 ~ 8 - 10$) as compared to the single-phased case ($R_0 ~ 2.1 – 2.4$). However, the first and third sideband intensity ratios ($R_1$ and $R_3$) for the milled hydrides ($R_1 ~ 2.4 – 2.9$, $R_3 ~ 0 – 0.32$) do not deviate significantly from those measured for bulk or ball-milled MgD$_2$ ($R_1 ~ 2.2 – 2.4$, $R_3 ~ 0.31 – 0.35$).
One interpretation is that two MgD\textsubscript{2} phases exist in the ball milled hydrides. One phase has been converted to a nearly cubic structure so that its lineshape consists of a single, sharp line and perhaps some weak first order SSBs (similar to the sidebands present in ball milled TiD\textsubscript{2} discussed above). This single, sharp resonance line, is then superimposed over the \textsuperscript{2}H MAS
NMR spectrum for standard, rutile MgD
2. The rutile MgD
2 spectrum has the expected spinning sideband manifold that extends over ±30 kHz. In this scenario, the centerband intensity, composed of the rutile MgD
2 centerband and the single peak of the cubic MgD
2, would be much higher than expected for rutile MgD
2 only. Thus, \( R_0 \) for the spectrum would be higher than that of bulk MgD
2. But the intensity of higher order spinning sidebands would primarily result from the standard rutile MgD
2 signal. Therefore, the spinning sideband ratios from higher order sidebands (\( R_x, x > 0 \)) would be expected to closely match those measured for coarse-grained MgD
2; exactly the case here.

Also important, the resonance frequency of the rutile-like MgD
2 and cubic-like MgD
2 is near zero frequency so that both phases behave as insulating powders (no Knight shift); the same as the bulk case. Based on the spinning sideband manifold, ball milling of MgH
2 – TiH
2 powders under high pressure deuterium gas results in two MgD
2 phases: one with cubic-like site symmetry for deuterium sites (no or minimal SSBs) and one with standard tetragonal structure for deuterium sites (strong quadrupole interaction with full SSB pattern). Both phases are non-metallic since they exhibit no Knight shift.

Measurement of the peak area ratios for the MgD
2-like phases (both rutile-like and cubic-like) as well as the TiD
2-like phase reveal a significant deviation from the as-mixed values. The relative peak area ratios are shown to the left of the spectra in figure 4-12. In all cases, more deuterium spins are associated with the broad, shifted TiD
2-like peak than the unshifted, MgD
2-like peak. Recall, that the area under the curve is proportional to the number of deuterium spins. Thus, for
the deuterium spins present in the ball milled MgH$_2$ – TiH$_2$ samples, more than double the expected amount (based on the ratio of the starting powders) of deuterium nuclei are in the TiD$_2$-like phase. This deviation in the relative peak area ratios is accompanied by a change in the lineshape for the TiD$_2$-like signal. The TiD$_2$ resonance exhibits the line broadening similar to that found for ball milled Ti-D. A hint of extremely weak first order sidebands is present in the spectrum of the 1 MgH$_2$ : 2 TiH$_2$ sample (figure 4-12, blue spectrum) as well as that of of the 1 MgH$_2$ : 1 TiH$_2$ sample (figure 4-12, red spectrum), but to a lesser extent. For both those cases, the peak location is shifted to a smaller Knight shift value as compared to the MgH$_2$-rich and bulk TiD$_2$ cases.

It is worth taking a moment to carefully state what these $^2$H MAS NMR spectra tell us. Each spectrum is composed of two distinct peak sets. The first is composed of a sharp centerband and a series of narrow spinning sidebands. The presence of sidebands indicates that deuterium atoms in this species are at lower symmetry sites in the crystal structure resulting in a non-zero EFG and a non-zero nuclear quadrupole interaction. It is possible, as discussed above, that this signal is actually composed of two separate phases: one, a cubic structured phase with no or only weak spinning sidebands, and the other, a lower symmetry structure phase that resembles bulk, rutile MgD$_2$. Regardless, this peak set corresponds to deuterium atoms in non-cubic symmetry atom sites (presence of SSBs) that is non-metallic. The other peak set consists of deuterium atoms in a metallic compound (large Knight shift) with high, cubic-like symmetry for the deuterium atom sites (no or only very weak spinning sidebands).
Thus, the unexpected peak area ratios could indicate the transformation of some MgD\textsubscript{2} from its standard, rutile crystal structure (insulating, so no Knight shift, and lower symmetry, so full spinning sideband manifold) to a metallic MgD\textsubscript{2} (Knight shift) with cubically symmetric deuterium sites (no spinning sidebands). The peak area ratios and lineshape changes could even indicate the formation of a metallic Mg-Ti-D alloy. In that case, MgD\textsubscript{2} is consumed (resulting in less signal from rutile MgD\textsubscript{2}) by TiD\textsubscript{2} forming a Mg-Ti-D compound that is metallic (Knight shift), cubic (no spinning sidebands), and accounts for the excess relative deuterium signal in the broad, shifted TiD\textsubscript{2}-like peak.

One caveat is that the extent of hydrogen and deuterium exchange during ball milling is unclear. For all samples, an excess of D was provided as overpressure (D\textsubscript{2} gas) in the milling vial compared to the H present in the metal hydride starting powders, so that the ratio of moles of D (from the gas) to moles of H (from the starting powders) was $D/H > 2$. In addition, for these samples, ball milling was interrupted after ~1 hour and the vessel was evacuated and filled with a fresh bolus of D\textsubscript{2} gas.

Still, if the deuterium atoms are not equally distributed over the hydrogen/deuterium bearing compounds, the analysis discussed above is subject to artificial weighting for species that preferentially exchange hydrogen for deuterium. Since it is very difficult to measure the D/H ratio in the ball milled hydrides, the promising results, in terms of finding MgD\textsubscript{2} with deuterium in cubic-like sites and possibly the formation of a Mg-Ti-D alloy as discussed above, must be viewed with caution. Indeed, this uncertainty motivated the use of bare magnesium and titanium
powders for additional samples.

4.9 Ball milled Mg – Ti
Several Mg-Ti-D samples were prepared by ball milling magnesium and titanium powders under high pressure D₂ gas. By starting with bare metals, any confusion related to preferential hydrogen-deuterium exchange that may have been present for the samples that started as hydrides is removed. In fact, the work here, as well as that of Latroche et al⁴, shows that the bare metal powders rapidly uptake deuterium during ball milling under high pressure, with full uptake within approximately 1 hour of ball milling. D₂ uptake during ball milling will be briefly discussed later in this chapter. The ²H MAS NMR spectra for several of these samples are shown in figure 4-13 below. In addition to the standard ball milling treatment with total milling time of ~4 hours, several samples were treated with extended ball milling runs of up to ~175 hours in total. For figure 4-13, the spectra have been plotted so that the total milling time increases from top to bottom.
The ~ 2 Mg : 1 Ti (1.93 Mg : 1 Ti by mol) as-mixed sample (top spectrum shown) has been previously discussed (see figure 4-7). For this Mg : Ti ratio and milling time, little effect on the MgD$_2$ crystal structure is apparent. Indeed, the $^2$H MAS NMR spectrum seems to be a simple

Figure 4-13: $^2$H MAS NMR spectra for several Mg-Ti-D samples prepared by milling bare Mg and Ti under high pressure D$_2$. All spectra are normalized to the MgD$_2$ centerband. The milling time increases from the top spectrum (dark cyab) to the bottom (black) spectrum. The spinning sideband amplitude ratios for the MgD$_2$-like peaks as well as the relative peak area ratio for the MgD$_2$-like to TiD$_2$-like peaks are shown to the left of each spectrum. To the right of each spectrum, the initial ratio of Mg to Ti is shown along with the total ball milling time. MgD$_2$-like peaks have been labeled with a “*”, TiD$_2$-like peaks are labeled with a “#”, and trapped D$_2$ gas peaks are marked with a “!”.

The ~ 2 Mg : 1 Ti (1.93 Mg : 1 Ti by mol) as-mixed sample (top spectrum shown) has been previously discussed (see figure 4-7). For this Mg : Ti ratio and milling time, little effect on the MgD$_2$ crystal structure is apparent. Indeed, the $^2$H MAS NMR spectrum seems to be a simple
superposition of ball milled MgD\textsubscript{2} and ball milled TiD\textsubscript{2}, and the spinning sideband intensity ratios and relative peak areas suggest that this is in fact the case. This result is in stark contrast to those of the ball milled metal hydrides shown if figure 4-12.

The magenta spectrum (2\textsuperscript{nd} from the top) is for a 1 Mg : 2 Ti as-mixed sample. Here, the ball milling time was increased by \(\sim 2.5\times\) to 10.5 hours. The resulting spectrum is relatively similar to its starting as hydrides counterpart shown in figure 4-12 (blue spectrum). Both spectra show similar values for the first order sideband intensity ratio, \(R_1\), and also have similar relative peak areas (0.2 – 0.3 : 1). In addition, both show a similar broad, shifted, asymmetric peak associated with the TiD\textsubscript{2} phase that has muted, but present, first order spinning sidebands (\(m=\pm 1\)). The broad, shifted peak extends nearly to 0 frequency in both the hydride and bare metal case. This could be the result of insulating MgD\textsubscript{2} dissolving into the TiD\textsubscript{2} lattice, diminishing the resulting solid solution's metallic character and leading to the reduction in the peak area ratio. The large value of \(R_0\) (3.24 here compared to 2.2 – 2.4 for single-phased MgD\textsubscript{2}) suggests the presence of a cubic (so SSBs), insulating (no Knight shift) MgD\textsubscript{2} superimposed on a standard, rutile MgD\textsubscript{2} spectrum (with large SSB manifold) similar to what was found for the starting as hydrides case.

When the milling time is dramatically increased to \(\sim 72\) hours, as in the 1 Mg : 1 Ti sample shown in the blue spectrum (3\textsuperscript{rd} from the top), a significant effect is observed in the deuterium MAS spectrum. Like the 1 MgH\textsubscript{2} : 1 TiH\textsubscript{2} sample discussed above and shown in figure 4-12 (red spectrum), the sideband amplitude ratios indicate a reduction in the nuclear quadrupole interaction for the MgD\textsubscript{2} signal suggesting a transformation to a cubic-like structure that results
in a decrease in the electric field gradient at the site of the deuterium nuclei. The sideband amplitude ratios can also be described in terms of a nearly cubic MgD$_2$ signal with a single, sharp peak near zero frequency superimposed upon the standard, full spinning sideband pattern of rutile MgD$_2$ as discussed above.

More startling is the significant change in the broad, shifted peak normally associated with TiD$_2$. Here, the broad, hump-like peak extends even into the positive shift range. The strange lineshape, paired with the relative peak area ratio which deviates considerably from the as mixed ratio, strongly suggest the formation of a Mg-Ti-D compound with a reduced metallic character as compared to pure TiD$_2$ (but still somewhat metallic due to the large frequency shifts). In addition, this Mg-Ti-D compound has D atoms at sites with nearly cubic symmetry as evidenced by the very weak spinning sidebands. The small m=±1 sidebands near +6 kHz and -12 kHz suggest a portion of the deuterium spins reside in sites that deviate slightly from perfect cubic symmetry. It is also clear, that these spins correspond to only one component (near -3 kHz) of the broad, shifted peak.

The new peak, the sharp peak just to the right of the normal centerband and located at ~ -680 Hz, is believed to be trapped D$_2$ gas. The long milling time used here led to significant molybdenum contamination, ~25% by mass of the recovered powder. It is believed that the additional, narrow peak is deuterium gas that has been trapped in the lattice of molybdenum, an effect which has been seen previously. The peak has a lightning fast $T_1$ (full recovery within 10 ms) and is very narrow, both of which suggest D$_2$ gas. In addition the peak is only present in samples that were
ball milled for extended periods (> 50 hours) and where a significant amount of molybdenum contamination resulted as in the red and black spectra of figure 5-13 above, with milling times of 163 and 170 hours respectively. Note, for the bottom three spectra of figure 5-13, each with the D$_2$ gas peak present, the calculated peak area ratios do not include the gas peak. Instead, the measured area is that of the rutile MgD$_2$-like centerband and associated weak spinning sidebands and that of the broad, shifted TiD$_2$-like peak and associated spinning sidebands if present.

Interestingly, ball milling for even longer times (160 – 170 hours), but with Mg-rich starting powders as in the red and black spectra of figure 4-13, does not lead to as dramatic of an effect as seen in the 1 Mg : 1 Ti case (blue spectrum). For both the 4.3 Mg : 1 Ti (red) and 1.94 Mg : Ti (black) spectra, the spinning sideband intensity ratios indicate either the reduction in the quadrupolar interaction, so a transition to a more cubic-like crystal structure, or the superposition of a deuterium signal from cubic structured MgD$_2$ with no spinning sidebands and a deuterium signal from rutile MgD$_2$ with the usual spinning sideband manifold. Note the deviation of $R_0$ and $R_1$ from the bulk MgD$_2$ values in both spectra. For both cases, the relative peak areas are reduced compared to the as mixed values. In addition, a broad secondary peak is discernible near -3 to -4 kHz for both spectra, suggesting the presence of a Mg-Ti-D phase with less metallic character (smaller Knight shift) than pure TiD$_2$, but with cubic deuterium site symmetry (no spinning sidebands). Unlike the 1 Mg : 2 Ti (magenta) and the 1 Mg : 1 Ti (blue) spectra, there is no distortion to the cubic symmetry of the deuterium sites contributing to the broad, shifted peak (with peak center maximum near – 7 kHz) and thus no weak m=±1 spinning sidebands.
The top (dark cyan) and bottom (black) spectra of figure 4-13 are of Mg-rich starting materials with the same initial composition, but ball milled for different times, allowing for a rudimentary probe of the effect of milling time. Several key differences in the $^2$H MAS spectrum result from the extended milling time. First, the zero and first order spinning sideband intensity ratios are greater for the sample that underwent longer milling (bottom, black spectrum). Larger $R_0$ and $R_1$ imply a smaller quadrupole coupling and thus a smaller EFG at the site of the deuterium nucleus, which in turn indicates some level of transition to a cubically symmetric structure. Additionally, comparisons of the relative peak area ratios shows that for the short milled sample, the measured peak area ratio matches the as-mixed value implying that for that system, standard rutile MgD$_2$ and standard TiD$_2$ were present and completely phase segregated. For the long milled sample, the relative peak area ratio is about 70% of the as-mixed ratio. Furthermore, there is an additional broad, shifted, cubically symmetric (no associated SSBs) peak near -3 kHz, which suggests the presence of a newly formed Mg-Ti-D phase that did not form when the sample was ball milled for a short period of time.

4.10 Effect of MgH$_2$ – TiH$_2$ / Mg – Ti ratio
Due to the limited number of samples and the large parameter space, it is difficult to draw any firm conclusions concerning the effect of the starting ratio between MgH$_2$ and TiH$_2$ for the hydride case or the ratio between Mg and Ti for the bare metals case. However, for both the starting with hydrides and the starting with bare metal powders methods, the 1 Mg(H$_2$) : 1 Ti(H$_2$) sample exhibited rather striking behavior when compared to other samples. Interestingly, Rousselot and coworkers, who ball milled several Mg, Ti, MgH$_2$, and TiH$_2$ powders for extended lengths of time using a SPEX ball mill, reported the best results, in terms of hydrogen
storage properties, for the 1 MgH$_2$ – 1 TiH$_2$ sample. In addition, they argue that their heavily ball milled 1 MgH$_2$ – 1 TiH$_2$ sample possessed a fluorite crystal structure. In the future, it would likely be worthwhile to explore more 1-to-1 samples (e.g., versus milling time, BPR, vessel filling factor, etc.).

**4.11 Molybdenum contamination**
Significant contamination, from the molybdenum liner and end caps was found in several ball milled samples, especially those that had been ball milled for lengthy periods of time. As discussed previously in the apparatus chapter, molybdenum was specifically chosen due to its chemical inertness to hydrogen, magnesium, and titanium. It appears that the molybdenum impurity plays no role in the behavior of the ball milled Mg-Ti-D powders. When samples with high molybdenum impurity content were examined by XRD, the molybdenum phase was clearly identifiable and segregated from the Mg-Ti-D phase. An example XRD pattern of a sample with high molybdenum impurity is discussed later and shown in figure 4-15 below.

**4.12 D$_2$ uptake**
Recently, Latroche and coworkers performed ball milling experiments similar to those described in this thesis. They ball milled magnesium and titanium powders under ~1,000 PSI D$_2$ using a Fristch Pulverisette ball mill and a Evico-magnetics high pressure milling vial. The milling vial was equipped with pressure and temperature sensors as well as a radio relay so that the pressure and temperature inside the milling vessel could be monitored in real time during ball milling. By tracking the pressure in the vessel as a function of time, they found that the Mg and Ti powders rapidly absorbed D$_2$ during ball milling under high pressure (see figure 4-14 below).
The ball milling setup used here did not allow for real-time monitoring of the pressure inside the ball milling vessel. However, the pressure inside the vessel was measured at start and cessation of each milling session. Since the volumes of the vessel and the gas manifold used to supply the vessel with D\textsubscript{2} gas were determined at the outset of this work, the pressure inside the vessel at the end of ball milling could be determined via the ideal gas law after accounting for deuterium's non-ideal behavior (the compressibility factor, $Z$). For all ball milled bare metal powder samples, the pressure drop inside the vessel was greater than 90\% of the expected dropped based on full deuterium uptake within the first hour of ball milling. At the 1 hour mark, milling was stopped, the vessel pressure was checked, and the vessel was re-pressurized with a fresh bolus of D\textsubscript{2} gas before milling was resumed. At the end of milling, the pressure in the vessel was measured and found to have dropped by less than 50 PSI in all cases.

**Figure 4-14:** Deuterium uptake during ball milling of Mg-Ti powders. The various curves correspond to different Mg\textsubscript{1-y}Ti\textsubscript{y} starting powders. The hydrogen uptake is plotted in terms of the hydrogen to metal ratio (H/M), which should approach 2 for full uptake. This plot is reproduced from reference (al).
4.13 XRD
Powder x-ray diffraction (XRD) measurements were made on several of the ball milled Mg-Ti-D powders. In general, the information offered by XRD was limited due to the nanosized crystallites that result from heavy ball milling. The Scherrer equation relates the crystallite size to the observed XRD peak widths:

\[ \tau = \frac{K \lambda}{\beta \cos \theta} \]  

(4-17)

where

- \( \tau \) is the average crystallite size
- \( K \) is the shape factor
- \( \lambda \) is the x-ray wavelength
- \( \theta \) is the Bragg angle
- \( \beta \) is the full width at half maximum for the XRD peak at angle \( \theta \)

Smaller crystallites result in broader lines, making phase identification very difficult in samples with multiple phases present like the Mg-Ti-D powders studied here. Such identification becomes especially difficult when there is strong overlap between the peaks for each phase as is the case for MgH\(_2\) and TiH\(_2\) (and even the molybdenum present as contamination) In addition, if the crystallite size is reduced sufficiently, a phase may not yield any XRD reflections (the phase is “XRD amorphous”) even though it is present. For these samples, the reflections related to the rutile MgD\(_2\) quickly disappear after short milling times. If XRD alone were used for analyzing
the samples, we might erroneously conclude that no rutile MgD$_2$ was present. However, NMR, which is not affected by the crystallite size, clearly indicates the presence of a rutile MgD$_2$-like phase in nearly all ball milled Mg-Ti-D samples studied.

An example XRD pattern for the 1 Mg : 1 Ti sample (blue spectrum from figure 4-13) discussed above is shown in figure 4-15 below. This sample had ~25% by mass molybdenum contamination. The molybdenum phase clearly shows up in the XRD pattern, while no rutile MgD$_2$ reflections are present.

![Figure 4-15](image)

**Figure 4-15:** XRD pattern for the 1 Mg : 1 Ti sample with $^2$H MAS NMR spectrum shown in figure 4-13 (blue spectrum). XRD reveals only TiH$_2$-like and molybdenum phases. This sample had heavy molybdenum impurity due to the length of ball milling (72 hr).
For some samples, Rietveld refinement was performed using the Bruker Topas software. The refinement technique allowed the relative presence of XRD active phases to be determined along with the average crystallite size for a given phase. In addition, as shown in the example in figure 4-16 below, Rietveld refinement could be used to measure a change in lattice parameter indicated by shifts to lower 2θ angles of the XRD reflections for a given phase. Figure 4-16 shows the Rietveld refinement of the XRD pattern for the 1 Mg : 1 Ti sample shown in figure 4-15 above.
The noticeable increase in the lattice parameter $a$ for the fcc TiD$_2$ phase could be explained by the dissolution of Mg into the TiD$_2$ lattice as argued by Latroche et al.$^{[a]}$. Such an effect matches the $^2$H MAS results for this sample (figure 5-13, blue spectrum) which indicated an excess of D.

Figure 4-16: Reitveld refinement of the XRD pattern for the ball milled 1 Mg : 1 Ti sample discussed previously. The black curve is the experimental XRD pattern while the red curve is the fit to the data after refinement. The blue curve is the difference between the experimental data and the refined pattern. The phase presence of the TiH$_2$-like and molybdenum phases is indicated in the upper right corner. In addition, the unit cell parameter “$a$” and the average crystallite size for each phase are reported. Notice, for the TiH$_2$-like phase, an increase in the lattice parameter “$a$” results from the extensive ball milling (~ 75 hours). The increase suggests a possible substitution of Mg into the TiD$_2$ unit cell as discussed in detail in reference (a$^m$).
spins in the broad, shifted TiD$_2$-like phase along with a distortion of the TiD$_2$ lineshape.

4.14 Summary
The results of the spinning sideband amplitude ratios and relative peak area ratio measurements for each of the samples discussed in this chapter are summarized in table 4-1 below. Importantly, the amplitude of the centerband relative to the heights of the other spinning sidebands ($R_0$) is increased in nearly all ball milled samples as compared to bulk MgD$_2$. For the bulk powder, $R_0 = 2.12$ and only a slight increase is found upon ball milling of undoped MgH$_2$ (under D$_2$ gas) where $R_0 = 2.38$. However, in many of the ball milled MgH$_2$ – TiH$_2$ and Mg – Ti samples, $R_0$ is significantly increased, up to $R_0 = 6.0$ for the 1 Mg : 1 Ti sample and up to $R_0 = 10.7$ for the 1 MgH$_2$ : 1 TiH$_2$ sample. However, in nearly all cases, the relative height of the m = ±3 sideband to the m = ±2 sideband ($R_3$) matches the values measured for the bulk MgD$_2$ and milled MgD$_2$ cases. This result suggests that the MgD$_2$ component (no frequency shift and spinning sideband manifold present) of the observed $^2$H MAS NMR spectra for the ball milled MgH$_2$ – TiH$_2$ (figure 4-12) and Mg – Ti powders (figure 4-13) is actually composed of two signals. One signal is that of standard, rutile MgD$_2$ with a non-vanishing EFG at the deuterium nucleus that results in the spinning sideband manifold observed in bulk MgD$_2$ (figure 4-8). Superimposed over this signal, is a single, sharp resonance with no spinning sidebands indicating cubic symmetry and no electric field gradient at the site of the D atom; a fluorite-structured MgD$_2$. The presence of fluorite MgD$_2$ explains the deviation of the m = 0 spinning sideband amplitude ratio ($R_0$) in the ball milled samples from that of bulk MgD$_2$. The agreement of the measured m = ± 3 spinning sideband ratio ($R_3$) for bulk MgD$_2$ with those measured for the ball milled samples indicates that some standard rutile MgD$_2$ remains in nearly all cases. That is, a complete conversion of rutile
MgD₂ to cubic MgD₂ is not achieved. The degree of the conversion to cubic structure is indicated by \( R_0 \). A larger \( R_0 \) represents more fluorite MgD₂ relative to rutile MgD₂. From table 4.1, \( R_0 \) appears to increase with both Ti (or TiH₂) content as well as with milling time. For example, for the 2 Mg : 1 Ti sample, \( R_0 = 2.27 \) when the powder is milled for a short period (~ 5.5 hours). But, \( R_0 \) is increased to 3.91 when the powder is milled for a much longer period of time (~ 170 hours). When the Ti content is increased so that the starting powder is 1 Mg : 2 Ti, but the milling time is relatively short (~ 10 hours), \( R_0 \) is increased to 3.24. Similarly, when the milling time is long (~ 163 hours), but the Mg content of the starting powder is increased to 4.27 Mg : 1 Ti (Ti content is decreased), \( R_0 \) is only 3.0, much less than the \( R_0 = 3.91 \) found for a similar milling time (~ 170 hours) but lower Mg content (higher Ti content) in the ~ 2 Mg : 1 Ti sample.
The trends are less clear for the samples that start as hydrides. However, for these samples there is a question as to how much of the sample is visible to deuterium NMR. That is, do the starting as hydride samples fully and equitably exchange H for D during ball milling under D\textsubscript{2} gas. If one component of the sample preferentially exchanges H for D, it will be overweighted in the observed \textsuperscript{2}H MAS NMR spectrum. Thus, the results of the measurements on the ball milled MgH\textsubscript{2} – TiH\textsubscript{2} powders should be considered suggestive, but not conclusive.

Also summarized in table 4-1 are the results of the relative peak area ratio measurements for the \textsuperscript{2}H MAS NMR spectra reported in this chapter. Again, a similar trend is apparent and suggests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Milling time (hr)</th>
<th>Spectrum</th>
<th>$R_0$</th>
<th>$R_3$</th>
<th>Relative Peak Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk MgD\textsubscript{2}</td>
<td>N/A</td>
<td>4-8, magenta</td>
<td>2.12</td>
<td>0.35</td>
<td>1 : 0</td>
</tr>
<tr>
<td>Milled MgH\textsubscript{2}</td>
<td>4</td>
<td>4-8, black</td>
<td>2.38</td>
<td>0.31</td>
<td>1 : 0</td>
</tr>
<tr>
<td>1 MgH\textsubscript{2} : 1 TiH\textsubscript{2}</td>
<td>4</td>
<td>4-12, red</td>
<td>10.72</td>
<td>0.32</td>
<td>0.33 : 1</td>
</tr>
<tr>
<td>3.6 MgH\textsubscript{2} : 1 TiH\textsubscript{2}</td>
<td>4</td>
<td>4-12, black</td>
<td>8.83</td>
<td>0.00</td>
<td>0.9 : 1</td>
</tr>
<tr>
<td>1 MgH\textsubscript{2} : 2 TiH\textsubscript{2}</td>
<td>4</td>
<td>4-12, blue</td>
<td>7.43</td>
<td>0.00</td>
<td>0.2 : 1</td>
</tr>
<tr>
<td>1.93 Mg : 1 Ti</td>
<td>5.5</td>
<td>4-13, dark cyan</td>
<td>2.27</td>
<td>0.35</td>
<td>1.9 : 1</td>
</tr>
<tr>
<td>1 Mg : 2.02 Ti</td>
<td>10.5</td>
<td>4-13, magenta</td>
<td>3.24</td>
<td>0.32</td>
<td>0.30 : 1</td>
</tr>
<tr>
<td>1 Mg : 1 Ti</td>
<td>72</td>
<td>4-13, blue</td>
<td>6.00</td>
<td>0.33</td>
<td>0.26 : 1</td>
</tr>
<tr>
<td>4.27 Mg : 1 Ti (long mill)</td>
<td>163</td>
<td>4-13, red</td>
<td>3.00</td>
<td>0.33</td>
<td>3.1 : 1</td>
</tr>
<tr>
<td>1.94 Mg : 1 Ti (long mill)</td>
<td>170</td>
<td>4-13, black</td>
<td>3.91</td>
<td>0.32</td>
<td>1.33 : 1</td>
</tr>
</tbody>
</table>

Summary of the results of the spinning sideband amplitude ratios and relative peak area ratio measurements for the \textsuperscript{2}H MAS NMR spectra reported in this chapter. Only the $R_0$ and $R_3$ spinning sideband amplitude ratios are summarized here, but all ratios have been previously reported in the chapter. The spinning sideband amplitude ratio was discussed in section 4.3. The relative peak area ratio is given in terms of Area(MgD\textsubscript{2}-like) : Area(TiD\textsubscript{2}-like) and was discussed in section 4.4. The samples are listed in order of shortest milling time to longest milling time.
that longer milling times and higher Ti content lead to a greater presence of the TiD$_2$-like phase than would be expected based upon the ratio (by mol) of the starting powders. For the ~ 2 Mg : 1 Ti sample discussed above, the measured peak area ratio of the MgD$_2$-like signal (no frequency shift, SSB manifold) to that of the TiD$_2$-like signal (large Knight shift, no or only weak SSBs) was ~ 1.9 MgD$_2$-like : 1 TiD$_2$-like when the sample was ball milled for a short period of time (~5.5 hours). This result is exactly as expected based upon the starting ratio of the Mg and Ti powders. However, when the sample was milled for an extended length of time (~170 hours), the relative peak area ratio decreased to 1.33 MgD$_2$-like : 1 TiD$_2$-like, a ~ 30% reduction when compared to the expected value. The reduction of MgD$_2$-like signal (cubic or rutile) can be explained by the dissolution of Mg into the TiD$_2$ lattice as briefly discussed above in section 4.13 and in detail in reference (aq). Such an occurrence would constitute the formation of a Mg-Ti-D alloy that is metallic (large frequency shift) and cubic (no or only weak spinning sidebands).

Since the results for the ball milled MgH$_2$ – TiH$_2$ samples are clouded by the question of H → D exchange during ball milling, the results of the relative peak area ratio measurements should not be treated as certain.

In conclusion, two effects are observed to result from ball milling MgH$_2$ – TiH$_2$ and Mg – Ti powders under high pressure deuterium gas. First, there is some conversion of the MgD$_2$ from its standard rutile crystal structure to a cubic fluorite structure as evidenced by analysis of the spinning sideband amplitude ratios. The conversion to fluorite structure is enhanced by higher titanium content and longer milling times, but is not complete in any samples studied. Second, there is evidence of the formation of a Mg-Ti-D alloy based upon analysis of the relative peak
area ratios. The peak area ratios indicated more deuterium spins in a metallic (large frequency shift), fluorite-structured (no or only weak SSBs) TiD$_2$-like phase than would be expected from the Mg to Ti ratio of the starting powders. Both effects are enhanced to varying degrees by longer ball milling times and higher titanium content. However, more samples (e.g., Mg : Ti ratio held constant, but milling time varied) are needed to more precisely elucidate these trends.
4.15 References


(g) Barkhordarian, G.; Klassen, T.; Bormann, R. Kinetic Investigation of the Effect of Milling Time on the Hydrogen Sorption Reaction of Magnesium Catalyzed with Different Nb$_2$O$_5$ contents.


(m) Dai, J.H.; Song, Y.; Yang, R. Intrinsic Mechanisms on Enhancement of Hydrogen


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Chapter 5: Conclusions

This dissertation details the synthesis of Mg-Ti-D powders by high pressure ball milling and subsequent measurement by $^2$H MAS NMR. Chapter 1 discussed the motivation for this work, namely the formation of a fluorite (cubic) structured MgH$_2$. As previously covered, magnesium hydride is a candidate material for onboard hydrogen storage, but its use is limited by the slow kinetics of the reversible hydriding and dehydriding reaction shown in equation 1-1. The fluorite structure has been previously shown to improve hydrogen diffusion through the lattice, often the rate limiting step for the hydriding/dehydring reaction. Previous work demonstrated enhanced hydrogen lattice diffusion and the formation of an fcc (fluorite) Mg-Sc-H hydride when Mg was alloyed with Sc. However, scandium is too rare and expensive for large scale implementation. Thus, the formation of a cubic Mg-Ti-H alloy is desired, but Mg and Ti do not alloy. Special, non-equilibrium processing techniques like ball milling have been used to form Mg-Ti-D composites. For the work of this dissertation, the ball milling technique has been augmented so that Mg and Ti powders could be ball milled under high pressure deuterium gas.

Chapter 2 details the custom, molybdenum-lined high pressure ball milling vessel specifically developed for this project. The vessel had several important design criteria, including the capability to support high D$_2$ overpressure and the exclusion of any impurities that were either magnetic or reactive with Mg, Ti, or D. The resulting high pressure ball milling vessel was used to prepare the Mg-Ti-D powders discussed in the results and discussion chapter of this dissertation (Chapter 4).
Deuterium magic-angle spinning nuclear magnetic resonance was utilized to study the crystal structure of the ball-milled Mg-Ti-D samples. Deuterium NMR is sensitive to the local atomic structure surrounding the deuterium atoms in the Mg-Ti-D samples through the nuclear quadrupole interaction, the interaction of the deuterium's quadrupole moment with the electric field gradient generated by surrounding atoms. For nearly all of the ball milled samples, some conversion of MgD$_2$ from its standard, rutile crystal structure to a fluorite (fcc) structure is observed as evidenced by the spinning sideband amplitude ratios measurement and analysis. An increase in the centerband ($m = 0$) height relative to the heights of the other sidebands (SSB ratio $R_0$) indicated the formation of cubic MgD$_2$. However, the consistency of the higher order spinning sideband amplitude ratios, specifically $R_3$, with that measured for bulk (rutile) MgD$_2$ signals that the conversion to cubic structure is not complete and that some rutile MgD$_2$ remains. Therefore, the observed MgD$_2$ signal is actually two overlapping signals: a signal from fluorite MgD$_2$ superimposed over that from rutile MgD$_2$. In each case, the observed MgD$_2$ is phase segregated from TiD$_2$ (so it is not Mg-Ti-D) and non-metallic (no large Knight shift). The relative amount of fluorite MgD$_2$ as compared to rutile MgD$_2$ was found to increase with both increasing Ti content and increasing ball milling time.

Analysis of the relative peak areas of the MgD$_2$-like peaks (no frequency shift, SSB manifold) to that of the TiD$_2$-like peak(s) (large Knight shift, no or only weak SSBs) suggests that some formation of a Mg-Ti-D alloy also occurs. The formation is evidenced by the increase in relative peak area of the broad, shifted TiD$_2$-like peak when compared to the expected, as-mixed value. The Mg-Ti-D alloy has a nearly cubic structured based upon the presence of only very weak
spinning sidebands and the alloy is metallic based upon its large frequency shift. This conclusion was supported by Reitveld refinement of the XRD patterns for these samples that an increase in lattice parameter (so a growth in unit cell size) in some cases. Like the conversion of rutile MgD₂ to fluorite MgD₂, the formation of the Mg-Ti-D was found to increase with increasing Ti content and increasing ball milling time. However, more samples must be synthesized and studied to elucidate this behavior.