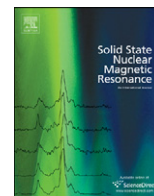




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Lightweight hydrogen-storage material $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_2$ studied with ^2H and $^2\text{H}\text{-}\{^{45}\text{Sc}\}$ MAS NMR exchange spectroscopy

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ABSTRACT

Using double-quantum ^2H MAS NMR with ^{45}Sc recoupling and Bloch–Siegert compensated $^2\text{H}\text{-}\{^{45}\text{Sc}\}$ TRAPDOR we have identified the overlapping NMR signals of deuterium with and without scandium neighbors in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_2$, a candidate lightweight material for hydrogen storage. At room temperature we also observe a third type of mobile deuterium. Deuterium mobility among the three NMR-distinct sites has been investigated by means of one- and two-dimensional exchange spectroscopy (Exsy). Complete deuterium exchange within 0.1 s is observed, which indicates that the three NMR-distinct sites are close together in the crystal lattice. The weak temperature- and MAS-rate dependences observed in Exsy are indicative for a combination of chemical exchange and spin diffusion.

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1. Introduction

Lightweight metal hydrides represent an interesting class of materials with potential application for chemical storage of hydrogen. ^1H and ^2H MAS NMR spectroscopy are powerful characterization tools for these materials, because NMR can directly detect hydrogen or deuterium in metal hydrides or deuterides, respectively. NMR provides information about the local structure at the hydrogen sites, as well as about hydrogen mobility [1–7]. This is relevant for the potential application of metal hydrides as hydrogen-storage materials. Since crystallinity is not required for NMR, the technique can also “see” hydrogen inside XRD-amorphous parts of metal hydrides. Although the isotope ^1H has higher NMR frequency and sensitivity, ^2H nuclei tend to have relatively narrower resonances in MAS NMR spectra of metal deuterides compared to the corresponding metal hydrides. This results from the weaker dipole coupling between ^2H nuclei than between ^1H nuclei.

Magnesium is a lightweight metal capable of safely storing large amounts of hydrogen, but its adsorption and desorption kinetics has to be improved. Our group is currently investigating the sorption boost caused by alloying magnesium with transition metals, such as scandium and titanium [8–10]. We have previously investigated deuterium absorbed in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_2$ by means of MAS ^2H NMR and reported the first results in a letter [5].

Using double-quantum ^2H NMR and $^2\text{H}\text{-}\{^{45}\text{Sc}\}$ TRAPDOR we were able to distinguish between deuterium at tetrahedral sites with or without scandium atoms in the first coordination sphere. Quantitative analysis of the data suggested that about half of the deuterium atoms were located at Mg_4 sites and the others at $\text{Mg}_n\text{Sc}_{4-n}$ ($n \neq 4$) sites. On the basis of the 50% fraction of Mg_4 sites in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_2$ we proposed that the material was segregated into Mg-rich and Sc-rich nanodomains. The size of these nanodomains should be in the order of a few crystal unit cells, because we observed complete deuterium exchange at a sub-second timescale between the Mg-rich and Ti-rich sites in two-dimensional exchange ^2H NMR spectra even at 213 K. Such small nanodomain size is also consistent with the fact that the material looks homogeneous in the earlier X-ray and neutron diffraction studies.

Following our earlier study [5] we have further investigated deuterium exchange in $\text{Mg}_{0.65}\text{Sc}_{0.35}\text{D}_2$ using one-dimensional exchange spectroscopy (1D Exsy). Compared to two-dimensional exchange spectroscopy (2D Exsy), 1D Exsy is less model-free, but also less time consuming. Thus, once a suitable model has been chosen on the basis of a few 2D exchange spectra, 1D Exsy can be employed to systematically investigate deuterium exchange at varied timescales and temperatures.

2. Theory

Let us consider deuterium chemical exchange in a deuteride compound with N NMR-distinct types of deuterium sites with

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relative occurrences f_n and occupation θ_n . In Boltzmann equilibrium the individual spin polarization is the same at all sites and the relative NMR intensities I_n^{eq} associated with the respective site types are equal to the deuterium fractions g_n at those sites:

$$I_n^{eq} = g_n = \frac{f_n \theta_n}{\sum f_n \theta_n} \quad (1)$$

with $n=1, \dots, N$. Deuterium exchange between the sites is expressed in terms of fluxes J_{mn} defined as the relative number of deuterium atoms moving from type- n to type- m sites per time unit. The deuterium fluxes J_{mn} may depend in any way on the occurrence and occupation of the various sites. The essential point here is that in dynamic equilibrium the fluxes are constant, and equal in opposite direction:

$$J_{mn}^{eq} = J_{nm}^{eq} \quad (2)$$

By assumption, deuterium atoms leaving any site n between time t and $t+dt$ carry the average intensity $\delta I_n = I_n/g_n$ independently of their individual history prior to time t . In dynamic equilibrium the change in the NMR intensities I_n caused by chemical exchange and spin-lattice relaxation after an initial polarization perturbation is then given by the linear differential equation:

$$\frac{d}{dt} \vec{I} = -\underline{X} \vec{I} - \underline{R}(\vec{I} - \vec{I}^{eq}) \quad (3)$$

where \vec{I} and \vec{I}^{eq} denote the vectors $(I_1, I_2, \dots, I_{N-1}, I_N)$ and $(I_1^{eq}, I_2^{eq}, \dots, I_{N-1}^{eq}, I_N^{eq})$, respectively. \underline{R} is the Redfield relaxation matrix here assumed to be diagonal, $R_{nn} = 1/T_{1n}$ with T_{1n} the spin-lattice relaxation time associated with the type- n sites. \underline{X} is the exchange matrix with elements:

$$X_{mn} = -J_{mn}^{eq}/g_n \quad \forall m \neq n \quad (4a)$$

$$X_{mm} = \sum_k J_{mk}^{eq}/g_m \quad (4b)$$

This structure of \underline{X} ensures that in combined dynamic and spin-polarization equilibrium \vec{I}^{eq} is indeed a steady-state solution. It also follows from Eqs. (3) and (4) that in the absence of relaxation, $\underline{R}=0$, the sum of all NMR intensities $\sum I_n$ is conserved. This reflects the conservation of spin polarization under chemical exchange alone. These two features of chemical exchange, i.e. (1) homogenizing the spin polarization and (2) conserving the total spin polarization, are also properties of spin exchange, which may also show up in Exsy. It can be readily incorporated into the exchange matrix \underline{X} by adding a polarization-exchange rate $-k_{mn}/g_n$ to the off-diagonal elements X_{mn} , and $\sum k_{mk}/g_m$ to the diagonal elements X_{mm} , with $k_{mn} = k_{nm}$. Since chemical exchange and spin diffusion generally have a different temperature dependence one can vary the temperature to distinguish between the two.

Because \vec{I}^{eq} belongs to the kernel of \underline{X} we can rewrite Eq. (3) as a homogeneous differential equation in terms of $\Delta \vec{I} = \vec{I} - \vec{I}^{eq}$:

$$\frac{d}{dt} \Delta \vec{I} = -(\underline{X} + \underline{R}) \Delta \vec{I} \quad (5)$$

In fact, it is this deviation $\Delta \vec{I}$ of the NMR intensities from their thermal-equilibrium values, which is actually monitored in our one-dimensional exchange experiments.

A simple phenomenological model for deuterium motion between sites with and without scandium neighbors in $Mg_{0.65}Sc_{0.35}D_2$, or between sites with immobile and mobile deuterium is two-site exchange. Such model is similar to the one we have proposed earlier for sorbate motion in zeolite ZK-5 [11]. For the case of two sites the exchange-relaxation matrix in

Eq. (5) becomes

$$\underline{X} + \underline{R} = \begin{pmatrix} (J/g_1) + R_1 & -J/g_2 \\ -J/g_1 & (J/g_2) + R_2 \end{pmatrix} \quad (6)$$

where $J = J_{12}^{eq} = J_{21}^{eq}$ and $R_n = 1/T_{1n}$. If chemical exchange is fast compared to spin-lattice relaxation, $J \gg R_n$, the two eigenvalues $\underline{X} + \underline{R}$ are approximately given by

$$\lambda_1 = g_1 R_1 + g_2 R_2 \quad (7a)$$

$$\lambda_2 = J/g_1 + J/g_2 + g_2 R_1 + g_1 R_2 \quad (7b)$$

The first eigenvalue λ_1 reflects the weight-averaged relaxation rate expected for fast chemical exchange on the spin-lattice relaxation timescale. For $J \gg R_n$, the effect of relaxation on λ_2 is negligible. The corresponding approximate ‘‘slow-relaxation’’ solutions for $\Delta I_1(t)$ and $\Delta I_2(t)$ are given by the bi-exponential decays:

$$\Delta I_1(t) = g_1 \Delta I_{tot}(0) e^{-\lambda_1 t} + \{\Delta I_1(0) - g_1 \Delta I_{tot}(0)\} e^{-\lambda_2 t} \quad (8a)$$

$$\Delta I_2(t) = g_2 \Delta I_{tot}(0) e^{-\lambda_1 t} + \{\Delta I_2(0) - g_2 \Delta I_{tot}(0)\} e^{-\lambda_2 t} \quad (8b)$$

with

$$\Delta I_{tot}(0) = \Delta I_1(0) + \Delta I_2(0) \quad (8c)$$

If the polarization of the deuterium spins at sites 1 and 2 are equally perturbed at time $t=0$, their initial intensities $\Delta I_1(0)$ and $\Delta I_2(0)$ are equal to respective fractions g_1 and g_2 of $\Delta I_{tot}(0)$. Then, there is no fast decay component visible in Exsy and both signal intensities decay with the average relaxation rate λ_1 . If the spins at type-1 sites are initially more perturbed than those at sites 2, $\Delta I_1(t)$ shows a fast initial decay with rate λ_2 followed by a slow decay with rate λ_1 . Simultaneously, the intensity $\Delta I_2(t)$ of the relatively less perturbed spins at site 2 initially increases with rate λ_2 and then decays slowly to zero with rate λ_1 . At long time values with rate $\lambda_2 t > 1$, the ratio $I_1(t):I_2(t)$ equals the Boltzmann-equilibrium ratio $I_1^{eq}:I_2^{eq}$. This is as expected for the homogeneously mixed polarization resulting from chemical exchange. Finally, the sum polarization $I_1(t) + I_2(t)$ decays in a mono-exponential way at the average relaxation rate.

In reality, multiple types of deuterium sites exist within $Mg_{0.65}Sc_{0.35}D_2$. Theoretically this results in more complex multi-exponential exchange behavior. In the slow-relaxation limit, however, the intensity decays may still have a pseudo-bi-component character with a slow component reflecting the average relaxation and a fast component comprising the decay components at the chemical-exchange timescale. Eq. (8a) can be readily generalized for multiple-site exchange:

$$\Delta I_1(t) = g_1 I_{tot}(0) e^{-\lambda_1 t} + \{\Delta I_1(0) - g_1 I_{tot}(0)\} h(t) \quad (9)$$

where λ_1 is approximately equal to the average relaxation rate, and the total polarization is now summed over the multiple sites. The difference between Eqs. (8a) and (9) is that the fast decay component $h(t)$ represents a multi-exponential sum involving the other eigenvalues λ_k ($k \geq 2$):

$$h(t) = \frac{\sum A_k(0) e^{-\lambda_k t}}{\sum A_k(0)} \quad (10)$$

where the factors $A_k(0)$ depend on the specific perturbation of the deuterium spins at $t=0$. In practice, it may be difficult to distinguish $h(t)$ from a mono-exponential decay with effective decay rate:

$$\lambda_{eff} = \frac{\sum A_k(0) \lambda_k}{\sum A_k(0)} \quad (11)$$

If not from a significant deviation from bi-exponential behavior, multiple-site exchange can thus be recognized from the

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