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# Elimination of magnetic-susceptibility broadening in NMR using magic-angle sample spinning to measure chemical shifts in $NbH_x$

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Magnetic-susceptibility broadening of hydrogen NMR spectra in $NbH_x$ powders ($x = 0.10$ and 0.17) has been eliminated using magic-angle sample spinning. This has made it possible to measure two underlying hydrogen chemical-shift sites with shielding values of $\alpha_0 = -12.0 \pm 0.5$ ppm and $\beta_0 = +16.0 \pm 0.5$ ppm with respect to tetramethyl silane.

In the last decade various advances in nuclear magnetic resonance (NMR), such as multiple pulse techniques[1] and magic-angle sample spinning (MASS),[2–4] have created the field of high-resolution solid-state NMR by eliminating various spectral-broadening mechanisms, and revealing the underlying chemical shifts. Use of these techniques in concert has achieved spectral resolution in insulators approaching that in liquids, where such broadenings are averaged out by rapid isotropic motions. In systems such as powdered metals and metal hydrides, however, magnetic susceptibility has remained as a severe broadening mechanism, preventing the observation of the chemical shifts used in high resolution NMR as a finger print of the chemical environment of the nucleus. For nonellipsoidal sample shapes, the variation of the internal magnetic fields inhomogeneously broadens the NMR spectra. In this article, it is shown that MASS eliminates such suceptibility broadening, thus allowing the observation of two different chemically shifted proton sites in the $NbH_x$ system. We believe these sites result from protons in two structural phases of $NbH_x$, and can thus study the structural and motional parameters of protons in specific phases. To our knowledge this is the first example of high-resolution NMR in a system with severe magnetic susceptibility broadening.

Previous approaches to the problems of magnetic susceptibility broadening are often impractical or impossible. Since the susceptibility broadening results from the same nucleus-electron interaction as does the chemical shift, multiple-pulse techniques, so useful in eliminating homonuclear and heteronuclear broadening, cannot eliminate magnetic susceptibility broadening without eliminating chemical-shift information at the same time. Radio frequency skin depth problems preclude the use of large single crystals in systems of high conductivity. Making samples in the form of foils or wires is effective in reducing the susceptibility broadening, but powders give higher filling factors and thus higher signal-to-noise ratios. Further, in some materials it is not possible to make samples in the shape of foils or wires. Often the act of hydriding causes the sample to crumble or fracture. High surface area catalysts are generally amorphous with irregular geometry.

To our knowledge, the only method to date for reducing susceptibility broadening in powders[5] requires surrounding the irregularly shaped particles by a liquid of the same magnetic susceptibility as the powder. The irregular particle boundaries are effectively removed because the surrounding liquid has the same magnetic susceptibility, and the system as a whole has a magnetic boundary dictated by its container. If the container is ellipsoidal, the broadening should be eliminated. The technique suffers from two limitations. First, it cannot eliminate broadening if there are two material phases with different susceptibilities, or a single phase with an anisotropic susceptibility. However, this limitation could prove valuable as a way to measure different magnetic susceptibilities in the same system. Second, the susceptibilities of the liquid and solid particles in general have different temperature dependences, thus requiring different solutions for variable temperature experiments. Furthermore, from a practical standpoint, it is impossible to match susceptibilities well enough to achieve the resolution shown in this article using MASS.

Magic angle sample spinning means that the sample is physically being rotated at a rapid frequency about an axis with an angle $\Theta \approx 54.74°$ with respect to the Zeeman field in an NMR experiment. At this special angle, interactions which can be represented as second-rank symmetric tensors can be averaged to $\frac{1}{3}$ trace of the tensor, because at this angle the second-order spherical harmonic $(1-3\cos^2\Theta)$ is equal to zero.[1] The sample spinner used in this work was patterned after one by Zilm *et al.*[6]

In order to determine if magnetic susceptibility broadening can be narrowed by spinning, it is crucial to have a system where susceptibility is the main or, better still, the only broadening mechanism; $NbH_x$ is just such a system. The samples were prepared by taking high-purity Nb powders (−325 mesh, average particle size about 40 $\mu$m) and first heating them to 700 °C in vacuum for 2 h and then charging in hydrogen at 600 °C for 1 h. The amount of hydrogen uptake was determined by measuring the hydrogen overpressure before and after charging. At room temperature (all spectra in this article were taken at room temperature) the hydrogen is diffusing in $\alpha$ phase $NbH_x$ with a diffusion constant of about $10^{-5}$ $cm^2$/sec.[7] This is easily rapid enough to remove $^1H$-$^1H$ and $^1H$-$^{93}Nb$ dipolar broadening, thus, one would expect that if magnetic susceptibility broadening could be eliminated, one would observe a high-resolution chemical-shift spectrum.

The spectrum in Fig. 1(a) shows the Fourier-transformed free-induction decay (FTFID) hydrogen NMR signal (using a superconducting magnet and a hydrogen resonant frequency of 186.5 MHz) from the $NbH_{0.10}$ sample with a linewidth of about 13 kHz. The sample has relaxation times $T_1 \sim 75$ msec and $T_{1\rho} \sim 35$ msec, so we know that the 13-kHz linewidth is not lifetime broadened. The previous susceptibility matching work on the same system[5] proved that the 13-kHz linewidth must be due to the magnetic susceptibility of the powdered $NbH_{0.10}$. In addition, earlier work by Stalinkski and Zogal[8] on $NbH_x$ powders showed linewidths that were dominated by magnetic susceptibility broadening. The susceptibility of $NbH_x$ has been measured for various values of $x$,[9] and in particular it was found to be 200 ppm $cm^3$ $mole^{-1}$ for $x = 0.10$.

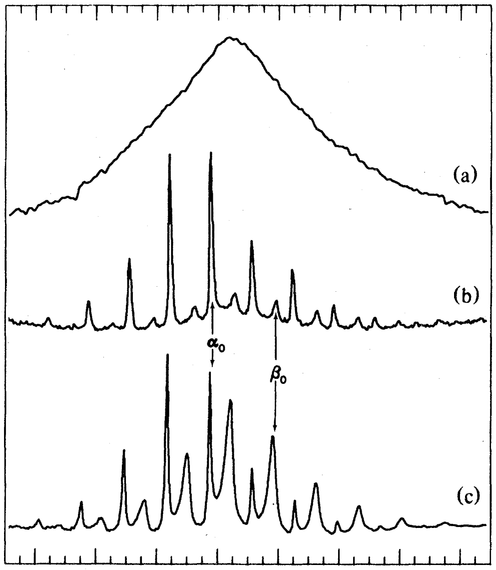

FIG. 1. Nonspinning and spinning hydrogen NMR spectra in $NbH_x$. Spectrum (a) is the magnetic susceptibility broadened hydrogen NMR spectrum from powdered $NbH_{0.10}$. Spectrum (b) is the spectrum from the same $NbH_{0.10}$ sample taken during magic angle sample spinning. Spectrum (c) is the hydrogen NMR spectrum from powdered $NbH_{0.17}$ during magic angle sample spinning. All three spectra have normalized amplitudes and the same horizontal scale. In (b) and (c) the $\alpha_0$ and $\beta_0$ indicate the center peaks, while the sets of sidebands are interleaved. Lower resonant frequencies are to the right, hence shielding increases to the right. Spectra (b) and (c) were taken with slightly different spinning frequencies, thus the sidebands are not perfectly aligned between (b) and (c), which is most pronounced for the highest harmonics.

Figure 1(b) shows a high-resolution spectrum which is the FTFID NMR signal from hydrogen in the $x = 0.10$ sample while the sample is undergoing MASS. The spectra in Figs. 1(a), 1(b), and 1(c) were all taken with the same horizontal scale. Thus the extreme narrowing from 13 kHz in Fig. 1(a) to 300 Hz in Fig. 1(b) is very apparent. The spectrum in Fig. 1(b) was taken with a spinning frequency of 3.38 kHz. It is possible to narrow a line much broader (in this case a factor of 4) than the spinning frequency only because the line broadening is inhomogeneous. In this case, though, there are a series of sidebands present which are separated by the spinning frequency. The plethora of spectral lines in Figs. 1(b) and 1(c) represent the full sideband set of only two spectral lines. This was sorted out by changing the spinning rate so that only the center lines did not move, but the sidebands did. From this process we were able to identify two distinct, highly resolved chemical shift sites we have denoted $\alpha_0$ and $\beta_0$. The sidebands are spaced equally on either side of these central peaks. The values for these chemical shieldings are $\alpha_0 = -12.0 \pm 0.5$ ppm and $\beta_0 = +16.0 \pm 0.5$ ppm with respect to tetramethyl silane (TMS). In Fig. 1 the spectra were all taken above resonance, so they all have the same convention, namely, shielding increases to the right.

To verify that the lines $\alpha_0$ and $\beta_0$ in Fig. 1(b) are really different chemical shift sites and not artifacts, the spectrum in Fig. 1(c) was taken from a sample with $x = 0.17$. Thus the spectrum in Fig. 1(c) is from a sample with 70% more hydrogen than Fig. 1(b). The relative size of the $\alpha_0$ and $\beta_0$ spectral lines has changed markedly, indicating that the 17 at. % sample has a larger fraction of its hydrogen at the $\beta_0$ site. The most plausible explanation for these two sites comes from the $NbH_x$ phase diagram.[10] Both the $x = 0.10$ and $x = 0.17$, $NbH_x$ samples are in a mixed-phase region of the Nb-H phase diagram. The $x = 0.10$ sample is close to being pure $\alpha$ phase (bcc solid solution) while the $x = 0.17$ sample has a substantial amount of $\beta$ phase (fc orthorhombic) also. Thus it is probable that the $\alpha_0$ and $\beta_0$ correspond to $\alpha$ and $\beta$ phases of NbH. Indeed, an estimate of the relative areas under the $\alpha_0$ and $\beta_0$ peaks of Fig. 1(c) agrees with the relative amounts of hydrogen in the $\alpha$ and $\beta$ phases present in $NbH_{0.17}$ according to the phase diagram (about 1 to 3).

We must next address the issue of two distinct peaks in the presence of rapid hydrogen motion. If the hydrogen were hopping between regions of $\alpha$ and $\beta$ phase rapidly compared to the inverse of the angular frequency difference between $\alpha_0$ and $\beta_0$ ($2\pi 5.22$ kHz), then we would observe only one peak with the average chemical shift. However, since two peaks are clearly visible, we then assume that the islands of $\beta$ phase are large enough that as the hydrogen diffuses rapidly throughout the sample, the frequency with which a hydrogen hops between regions of $\alpha$ and $\beta$ phase is small compared to the difference in frequency between the $\alpha_0$ and $\beta_0$ peaks.

A rough estimate of the minimum size of the $\beta$ phase islands can be made from,

$$D \sim l^2/\tau \ , \tag{1}$$

$$\tau >> 1/\Delta\omega \ , \tag{2}$$

$$l >> \sqrt{D/\Delta\omega} \ , \tag{3}$$

where $l$ is the size of the $\beta$ phase islands, $\Delta\omega$ is the angular frequency difference between $\alpha_0$ and $\beta_0$, $\tau$ is the correlation time for hopping between $\alpha$ and $\beta$ regions, and $D$ is the diffusion constant at room temperature for hydrogen in the $\beta$ phase ($2.8 \times 10^{-8}$ cm$^2$/sec), estimated from earlier NMR measurements of correlation times.[11] Equation (3) gives $l >> 0.01$ $\mu$m. If we furthermore allow for the existence of a free energy barrier for diffusion between the $\alpha$ and $\beta$ phases, then this estimate of $l$ could be reduced.

The experimental evidence presented here clearly indicates that magnetic susceptibility broadening can be narrowed by the use of magic-angle sample spinning. This was in general not suspected to be true because such broadening in irregularly shaped liquid samples, where there is rapid isotropic molecular motion, is not averaged to zero. MASS, however, effectively makes the samples spherical so that even without molecular motion the susceptibility broadening is removed. It is also well known that chemical shift tensors are averaged to $\frac{1}{3}$ trace by MASS, so one should suspect the same to be true for magnetic susceptibility, since both interactions are electron-nuclear dipolar in origin.

Even for spherical liquid samples, however, isotropic molecular motion does not totally average broadening due to an anisotropic magnetic susceptibility. By analogy we do not think that MASS is capable of eliminating all broadening due to an anisotropic magnetic susceptibility tensor,[12] and we will discuss this in more detail in a future paper. (Recent work in $^{13}C$ decoupling MASS, NMR experiments also indicates that anisotropic diamagnetic susceptibility limits spectral resolution in insulators.[13]) One bit of evidence for this is visible in Fig. 1(c). It is apparent that the $\beta_0$ line is about a factor of 2 broader than the $\alpha_0$ line. If the $\alpha_0$ and $\beta_0$ peaks correspond to $\alpha$ and $\beta$ phases, the $\alpha$ phase is bcc and would be expected to have an isotropic magnetic susceptibility tensor, but the $\beta$ phase which is fc orthorhombic might be expected to have an anisotropic tensor. Thus the broadening of the $\beta_0$ peak could be due to the anistropy of the $\beta$ phase magnetic susceptibility tensor.

This work shows that MASS in concert with the technique of susceptibility matching[5] should prove extremely useful for understanding microscopic structure in metals and hydrides using NMR. Pulsed-gradient diffusion studies using NMR are also hampered by susceptibility broadening, and several special pulse cycles have been proposed to alleviate the problem.[14, 15] MASS could instead be used to avoid the susceptibility broadening if the field gradients were arranged in such a manner that they would not be totally averaged by the spinning motion. Another possible application for this technique is in samples with ferromagnetic broadening, which should also be removed by MASS. By experiments such as these and by being able to measure relaxation parameters ($T_1$, $T_{1\rho}$, and $T_2$) of various chemically inequivalent sites, it is possible to learn much about the microscopic motion in metals and hydrides using NMR.

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