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Proton NMR line shapes in ZrH_x

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The second moments (M_{2D}) were obtained from magic-echo measurements of the proton line shapes for high-purity polycrystalline ZrH_x. Contrary to previous reports of anomalously large M_{2D} values in ZrH_x, the present results are in excellent agreement with the calculated dipolar moments which assume random occupancy of protons on only tetrahedral interstitial sites.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) has proven to be a very valuable technique to evaluate the hydrogen site occupancies, electronic properties, and diffusion behavior in numerous metal-hydrogen systems.[1,2] Since protons are spin-$\frac{1}{2}$ nuclei without a nuclear quadrupole moment, the line shapes of the proton spectra are usually dominated by the well-understood[1,2] nuclear dipolar interactions as long as strong local magnetic moments such as those occurring in ferromagnetic materials are absent. In particular, the second moments (M_{2D}) of proton line shapes measured in the rigid-lattice limit (i.e., when the various diffusion motions become sufficiently slow) have often been directly related[3–6] to the arrangement of the H atoms in a host metal lattice. The hydrogen locations are identified by comparing the experimental M_{2D} for a powder metal-hydride sample with a theoretical value calculated using the dipolar expressions[1,2] for a model arrangement of H atoms that considers stoichiometry and the host-metal-lattice structure. This comparison is most straightforward when the proton-metal dipolar term is small due to either small gyromagnetic moments or low isotopic abundance of magnetic metal nuclei (e.g., Ti, Cr, Y, Zr, Pd, etc.).

The proton M_{2D} have generally yielded hydrogen arrangements[3–6] that were in excellent agreement with independent elastic and inelastic neutron scattering measurements. However, two previous broadline (cw) NMR studies[7,8] of the proton spectra in δ-phase (fcc) and ϵ-phase (fct) ZrH_x gave experimental M_{2D} values that greatly exceeded the calculated dipolar values. These results are summarized in Table I. Since ZrH_x does not exhibit any other unusual elec-

TABLE I. Summary of previously published proton M_{2D} parameters for δ-phase (fcc) and ϵ-phase (fct) ZrH_x.

Sample composition	ν_H (MHz)	T (K)	Experimental M_{2D} (G^2)	Calculated M_{2D} (G^2)	Ratio $\left(\frac{\text{experimental}}{\text{calculated}}\right)$	Fe content[a] (wt. %)	Reference
δ-$ZrH_{1.54}$	?	300	29[b]	12.3	2.4	~0.2	7
ϵ-$ZrH_{1.99}$	?	300	32[b]	16.9	1.9	~0.2	7
δ-$ZrH_{1.60}$	16	300(?)	18.1 ± 0.4	13.1	1.38	0.09	8
ϵ-$ZrH_{1.88}$	16	300(?)	20.3 ± 0.4	15.8	1.29	0.09	8
ϵ-$ZrH_{1.98}$	16	300(?)	17.3 ± 0.4	16.6	1.04	0.09	8
ϵ-$ZrH_{1.98}$	8	300(?)	17.1 ± 0.4	16.6	1.03	0.09	8

[a] In starting Zr metal as reported in reference.

[b] From rigid-lattice linewidth assuming Gaussian lineshape.

trical or magnetic properties[9,10] (in fact, ZrH_x can be considered a prototype transition-metal hydride), these anomalously large experimental M_{2D} values are completely unexpected considering the very good agreement between the measured and calculated M_{2D} values[3,8,11] for isostructural and isoelectronic γ-phase TiH_x. Nakamura[8] has reported the experimental M_{2D} values were sample dependent for ZrH_x, but not for TiH_x, and he concluded that impurities probably contributed to the line broadening in the ZrH_x phases. Because no subsequent investigation has apparently attempted to clarify the anomalous proton linewidths for ZrH_x, the magic-echo pulse sequence[11] has been utilized to determine the proton M_{2D} values for four samples of ZrH_x prepared from high-purity Zr metal. In contrast to the previous studies,[7,8] the present experimental M_{2D} values are in good to excellent agreement with the dipolar values calculated, assuming random occupancy in only the tetrahedral sites.

II. EXPERIMENTAL DETAILS

The ZrH_x samples were prepared by the direct reaction between zone-refined Zr metal as 254-μm-thick foils[12] and hydrogen gas that had been purified by diffusion through a Pd-Ag tube. To minimize oxygen on the surfaces, narrow strips of the Zr foil were sandblasted, which was followed by a 3- to 5-min ultrasonic cleaning in acetone. Each sample of about a dozen cleaned strips was weighed and placed into a molybdenum boat prior to insertion in a quartz reaction tube. The loaded reactor was quickly evacuated and flushed several times with purified hydrogen prior to heating to 600 °C under dynamic vacuum of about 10^{-4} Pa. The desired quantity of hydrogen was stored in a calibrated stainless-steel cylinder. After isolating the reactor from vacuum, the hydrogen gas was admitted. After 20 min at 600 °C, the temperature was adjusted to between 450 to 650 °C to give an approximate equilibrium pressure of 500 Pa. After remaining at this temperature overnight, the reactor was cooled at a rate of 20 °/h until the pressure fell below 10 Pa when final cooling occurred during an air quench. The hydrided ZrH_x foils were removed from the reactor, weighed, and quickly sealed in evacuated glass tubes. The ZrH_x compositions are $x = 1.60$, 1.80, 1.90, and 2.00 where the volumetric analyses of absorbed hydrogen and weight gains agree within $x = \pm 0.01$.

The glass tubes containing the ZrH_x foils were passed into a glovebox that circulated a purified argon atmosphere. Each tube was opened and the brittle ZrH_x foils removed. The foils were ground in an agate mortar and pestle to produce a powder that passes a 200-mesh sieve (i.e., corresponding to a 74-μm particle size). Weighed amounts of each ZrH_x powder were loaded into 5-mm-o.d. NMR sample tubes, which were evacuated and torch sealed.

Powder x-ray diffraction measurements confirmed that each ZrH_x sample was single phase with the following lattice constants:

$$\delta\text{-}ZrH_{1.60}[a_0 = 4.7775(8)\ \text{Å}] ;$$

$$\epsilon\text{-}ZrH_{1.80}[a_0 = 4.954(6)\ \text{Å},\quad c_0 = 4.50(2)\ \text{Å}] ;$$

$$\epsilon\text{-}ZrH_{1.90}[a_0 = 4.986(22)\ \text{Å},\quad c_0 = 4.461(37)\ \text{Å}] ;$$

$$\epsilon\text{-}ZrH_{2.00}[a_0 = 4.971(5)\ \text{Å},\quad c_0 = 4.426(6)\ \text{Å}] .$$

The proton line shapes for the ZrH_x samples were obtained using the simplified magic-echo pulse sequence described elsewhere.[11] The proton resonance frequency (ν_H) was 56.4 MHz and the transient NMR spectrometer and measurement procedures have been discussed.[11] Since well-resolved echo maxima were obtained for the ZrH_x samples, the zero-time point[2,11] for the proton line shapes was easily established. Gaussian plots of the initial portion of this decay of the magic-echo signal were used to determine the M_{2D} parameters. The magic-echo sequence has been found[11] to yield very reliable M_{2D} values in γ-$TiH_{1.98}$ as well as several other metal-hydrogen systems.

III. RESULTS AND DISCUSSION

The proton M_{2D} parameters for the high-purity ZrH_x ($x = 1.60$, 1.80, 1.90, 2.00) polycrystalline samples are summarized in Table II. The experimental values have been derived from analyses of the magic-echo line shapes. The calculated values are obtained using the expression[1,5]

$$M_{2D} = M_2(\text{H-H}) + M_2(\text{H-Zr}) , \tag{1}$$

where

$$M_2(\text{H-H}) = \tfrac{3}{5}\hbar^2\gamma_H^2 I(I+1) f_I \sum_i r_i^{-6} , \tag{2}$$

$$M_2(\text{H-Zr}) = \tfrac{4}{15}\hbar^2\gamma_S^2 S(S+1) f_S \sum_k r_k^{-6} . \tag{3}$$

Here, γ_H and γ_S are the gyromagnetic moments of protons and ^{91}Zr, respectively; I and S are the spin quantum numbers; f_I is the isotopic abundance of ^{91}Zr; $\hbar$ is Planck's constant divided by 2π; $\sum_i r_i^{-6}$ is the H-H lattice sum for occupancy on only tetrahedral sites; and $\sum_k r_k^{-6}$ is the H-Zr lattice sum centered on a proton site. These lattice sums were computed by direct summations over a radius of about 40 Å for both the fcc and fct lattices. The experimental lattice constants for the ZrH_x samples were used. For the fcc structure, the present summations converged to the values of Gutowsky and McGarvey.[13] Although the M_2(H-Zr) term has been included in the calculated M_{2D} values shown in Table II, it is very small (i.e., $\sim 0.1\ G^2$); hence, $M_{2D} \cong M_2$(H-H)

TABLE II. Proton M_{2D} parameters for high-purity (i.e., 0.002 wt.% Fe) ZrH_x from magic-echo line shapes at $\nu_H = 56.4$ MHz.

Sample composition	T (K)	Experimental M_{2D} (G^2)	Calculated dipolar M_{2D} (G^2)	Ratio $\left(\frac{\text{experimental}}{\text{calculated}}\right)$
δ-$ZrH_{1.60}$	291	12.4[a]	13.1	0.946
	187	12.5	. . .	. . .
	89	12.6	. . .	. . .
ε-$ZrH_{1.80}$	291	14.6	14.7	0.995
	187	15.1	. . .	. . .
	89	14.9	. . .	. . .
ε-$ZrH_{1.90}$	291	15.3	15.6	0.981
ε-$ZrH_{2.00}$	291	16.7	16.9	0.988
	187	16.8	. . .	. . .
	89	16.9	. . .	. . .

[a] Experimental error is ±0.4 G^2.

within the accuracy of both the experiments and the calculations.

In contrast to the anomalously large M_{2D} parameters measured by Hon[7] and Nakamura[8] and shown in Table I, the ratios of experimental M_{2D} to the theoretical dipolar values given in Table II are found to lie between 0.95 and 1.00. Hence, the proton line shapes for δ- and ε- phase ZrH_x are accurately represented by only rigid-lattice dipolar interactions—providing the ZrH_x samples are sufficiently pure. Although the source of the earlier anomalous M_{2D} values[7,8] cannot be definitely established, the rather large Fe content in these samples, as shown in Table I, appears to be the obvious choice. This view is further supported by the field-dependent magnetic susceptibilities for ZrH_x as reported by Ducastelle *et al.*[9] (about 40-ppm Fe) and Nemchenko and Charnetskii[10] (<160-ppm Fe). Since the Fe content was only 20 ppm in the starting Zr metal and none should have been inadvertently introduced in preparing the ZrH_x powder samples, the present proton line shapes measurements gave only the expected dipolar values for M_{2D} that are completely analogous to the behavior for γ-TiH_x (Refs. 3, 8, and 11) as well as many other metal-hydrogen systems.[4–6]

The experimental M_{2D} values in Table II are actually systematically slightly smaller than the calculated dipolar values. A small loss in hydrogen content from the initial synthesis compositions can easily account for this difference. However, the experimental and calculated M_{2D} values are generally within their combined uncertainty of about ±5%. If there were disordering of protons from the tetrahedral sites to octahedral sites, which has been reported for the fcc hydrides LaH_x (Ref. 4) and YH_x (Ref. 6), the experimental M_{2D} would be larger than the values calculated, assuming only occupancy on tetrahedral sites.[4,6] Hence, the present proton M_{2D} experiments imply only tetrahedral site occupancy in both δ- and ε-ZrH_x. This conclusion is consistent with elastic and inelastic neutron scattering studies[14,15] on ZrD_x and ZrH_x. The M_{2D} comparisons have only been made at 291 K in Table II since the low-temperature lattice constants are unavailable. However, the experimental M_{2D} values become larger as the temperature decreases. This is consistent with smaller lattice constants at the lower temperatures.

Finally, Soviet workers[16–18] have reported experimental evidence that both δ- and ε-phase ZrH_x undergo phase transitions below 230 K. Naskidashvili[19] has proposed that hydrogen ordering to form either δ-$ZrH_{1.50}$ (3 transitions) or ε-$ZrH_{1.75}$ (1 transition) superlattices in the tetrahedral sites causes these transitions. Table III summarizes the predicted proton dipolar M_{2D} parameters for δ-$ZrH_{1.50}$ and ε-$ZrH_{1.75}$ for random hydrogen occupancy of the tetrahedral sites as well as the four superlattices of Naskidashvili.[19] It would be very difficult to make any definite statements concerning models II and III for δ-$ZrH_{1.50}$ and model IV for ε-$ZrH_{1.75}$ since the differences with random occupancy are quite small. However, model I for δ-$ZrH_{1.50}$ predicts a rather large decrease in M_{2D}, whereas the experimental values for δ-$ZrH_{1.60}$ in Table II are seen to increase slightly between 291 and 89 K. Hence, the proton M_{2D} parameters in Table II do not provide any support to Naskidashvili's mechanism. Furthermore, no superlattices were found by neutron-diffraction measurements[14] when $ZrD_{1.82}$ was cooled to liquid-nitrogen temperature. Thus no structural technique has yet verified

TABLE III. Theoretical M_{2D} parameters for rigid-lattice dipolar interactions in ZrH_x. Only tetrahedral sites are occupied by protons and M_2(H-Zr) term is included.

Composition	Nature of tetrahedral site occupancy	M_{2D} (G^2)	Model
δ-$ZrH_{1.50}$[a]	Random	12.29	. . .
	Ordered (Fig. 1 of Ref. 19)	11.23	I
	Ordered (Fig. 2 of Ref. 19)	11.91	II
	Ordered (Fig. 3 of Ref. 19)	12.36	III
ϵ-$ZrH_{1.75}$[b]	Random	14.49	. . .
	Ordered (Fig. 4 of Ref. 19)	14.24	IV

[a] $a_0 = 4.7745$ Å.

[b] $a_0 = 4.9338$ Å, $c_0 = 4.5027$ Å.

that hydrogen atoms can order in δ- or ϵ-ZrH_x to form superlattices on tetrahedral sites.[19]

IV. CONCLUSIONS

The experimental M_{2D} parameters for the proton line shapes of both δ- (fcc) and ϵ- (fct) phase ZrH_x are accurately given by only rigid-lattice dipolar interactions contrary to earlier measurements[7,8] on lower-purity ZrH_x samples. The protons occupy only tetrahedral interstitial sites and probably do not form ordered superlattices at low temperatures.

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