

Hydrogen location in yttrium dihydride by means of NMR measurements

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The proton magnetic resonance rigid-lattice second moment in $\text{YH}_{1.92}$ and $\text{YH}_{1.98}$ has been measured in the temperature range 160–200 K. From these the occupancy factors for hydrogen in the octahedral and tetrahedral interstitial sites of the fcc metal lattice have been determined. A significant fraction (≈ 10 –15%) of the octahedral sites are found to be occupied, consistent with features observed in the optical properties of YH_2 .

I. INTRODUCTION

As Khatamian *et al.*¹ have indicated in the preceding accompanying note, the work reported here was undertaken in an effort to determine the degree of octahedral site occupancy by hydrogen atoms in the yttrium-dihydride phase. The rigid-lattice second moment of the proton magnetic resonance is sensitive to the distribution of hydrogen atoms on the octahedral (O) and tetrahedral (T) interstitial sites of the fcc CaF_2 structure of YH_2 . This method was first utilized by Schreiber and Cotts² to estimate the fractional occupation of the O sites in lanthanum dihydride which also has the CaF_2 structure. In fact, YH_2 presents a more favorable case for this method than does LaH_2 because the contribution to the second moment from the metal nuclei (^{89}Y) is completely negligible due to the very small nuclear dipole moment of ^{89}Y (roughly 5% that of the proton). Consequently, hydrogen-hydrogen separations are completely responsible for the observed second moment of the resonance.

II. EXPERIMENTAL DETAILS

Samples were prepared from the same original materials and under the same conditions employed to prepare samples for recent optical measurements³ which motivated this investigation. The bulk samples were powdered to skin-depth dimensions for the NMR measurements, which were made on two compositions, $\text{YH}_{1.92}$ and $\text{YH}_{1.98}$. Following the NMR measurements, the $\text{YH}_{1.98}$ sample was also used in the neutron-diffraction measurements described in the accompanying note. Hydrogen concentrations were determined by hot vacuum extraction.

The NMR measurements were made with an induction spectrometer⁴ employing crystal-stabilized radio-frequency sources and a crossed-coil probe. Conventional 400-channel nuclear analyzers adapted for NMR use were used for signal aver-

aging.⁵ Resonance data were obtained at an operating frequency of 16 MHz, corresponding to a magnetic-field strength of 3.76 kOe. Signal-averaging periods of up to 3 hours were required for good resolution and signal-to-noise ratios, depending on spectrometer parameters. A gas-flow system was employed to maintain temperatures in the 160–200-K range.

III. RESULTS AND DISCUSSION

The rigid-lattice second moment M_2 was determined by direct numerical integration of the derivative recording at temperatures of 160 and 200 K, both of which are well within the rigid-lattice regime for these hydrogen concentrations. To ensure that a faithful representation of the line shape was obtained, slow-passage conditions as well as weak-field modulation amplitudes and low frequencies were employed. More importantly, it was found that the resonance exhibited both saturation-narrowing (at 160 K) and saturation-broadening (at 200 K) effects.⁶ On this account, it was necessary to maintain the amplitude H_1 of the rotating radio-frequency field at a very low value of approximately 2 mOe to ensure that undistorted line shapes were obtained. When these precautions were observed M_2 was temperature independent within the range 160–200 K. The M_2 values listed in Table I are the average of the 6 "best values" as determined from systematic variations in scan-rate, lock-in time constant, modulation frequency and amplitude, at $H_1 \approx 2$ mOe. The listed uncertainties are the standard deviations in these measurements.

To determine the fractional occupancies of the tetrahedral and octahedral sites, the measured M_2 was compared with the value calculated from the Van Vleck formula appropriate to a powder,⁷ as generalized by Stalinski *et al.*⁸ to take account of the contributions from inequivalent sites to the total M_2 . Letting α and β represent the probabilities of occupancy of O and T sites, respectively,

TABLE I. Measured proton-magnetic-resonance rigid-lattice second moments in yttrium dihydrides and octahedral and tetrahedral site-occupancy factors derived from these.

Hydride	Measured second moment (Oe) ²	Occupancy factors	
		Octahedral (α)	Tetrahedral (β)
YH _{1.92}	10.68 ± 0.26	0.105 ± 0.020	0.908 ± 0.010
YH _{1.98}	11.57 ± 0.35	0.155 ± 0.030	0.913 ± 0.015

M_2 may be written as

$$M_2 = \frac{Ca_0^{-6}}{2\alpha + \beta} (115.6\alpha^2 + 2643\alpha\beta + 1075.4\beta^2 + 1.42\beta + 0.46\alpha), \quad (1)$$

where $C = 3.568 \times 10^{-46}$ Oe² cm⁶ for protons, and $a_0 = 5.205$ Å is the lattice parameter of fcc YH₂. The last two terms of Eq. (1), which are the contributions from the yttrium nuclei, are seen to be negligible in comparison to the proton-proton terms.

Since the hydrogen to metal ratio, $H/Y = 2\alpha + \beta$, Eq. (1) yields values of α (or β) corresponding to the experimental M_2 values. The resultant values are listed in Table I, with the uncertainties in α and β based directly on the uncertainties in the M_2 values.

Comparison of the occupancy factors with the corresponding results from the neutron diffraction measurements of Khatamian *et al.*,¹ (note that $\alpha = n_{\text{octa}}$ and $2\beta = n_{\text{tetra}}$) shows that the NMR measurements yield slightly higher values of octahedral site occupancy. The differences are probably not significant and are certainly within the stated uncertainties. Taking, for example, $n_{\text{octa}} = \alpha = 0.136$ for YH_{1.98} from Ref. 1, we calculate from Eq. (1) an $M_2 = 11.28$ Oe², whereas the experimental value is 11.57 Oe² (Table I). The α values derived from Eq. (1) are quite sensitive to M_2 . Thus, whereas the uncertainty in the experimental M_2 value amounts to only ± 3%, the resulting uncertainty in α is ± 20%. In any event, both NMR and neutron measurements show that

octahedral site occupancy by hydrogen in yttrium-dihydride is significantly greater (by a factor between 2 and 3) than in lanthanum dihydride where $\alpha \cong 0.05$.²

Measurements of the activation energy for hydrogen diffusion in these samples, based both on the temperature dependence of the motional narrowing of the resonance⁹ and of the proton spin-lattice relaxation time¹⁰ are also consistent with a substantial and increasing O site occupancy as H/Y approaches 2. As in LaH₂ the activation energy decreases with increasing H/Y within the dihydride phase.

IV. CONCLUSIONS

The fraction of octahedral interstitial sites occupied by hydrogen in fcc yttrium dihydride has been shown on the basis of NMR measurements to be substantial, reaching a value of approximately 15% at YH_{1.98}. Alternatively, approximately 7.5% of the hydrogen in YH_{1.98} occupies octahedral sites. In addition, O site occupancy appears to increase with increasing hydrogen content (H/Y) within the dihydride phase.

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