

ISOTOPE EFFECT ON HYDROGEN SITE ENERGIES FOR TWO METAL DIHYDRIDES*

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MASTER

The change in hydrogen site energy with isotope for dihydrides and dideuterides of Sc and Y has been indirectly determined using electron spin resonance (ESR) of dilute Er ions in these face-centered-cubic hosts. The ESR spectra measure the distribution of hydrogen adjacent to the Er, and the variation in this distribution with isotope and with hydrogen to metal ratio has been studied for several samples of both host metals. These data are accurately described by a lattice-gas model which yields the energy difference for protons or deuterons on octahedral and tetrahedral sites, both adjacent to the Er impurities and in the bulk host lattice. This energy difference is 10% greater for deuterons, and the change with isotope can be attributed primarily to the mass dependence of the vibrational part of the total energy associated with each site.

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1. INTRODUCTION

Hydrogen has two available sites in the face-centered-cubic group IIIB metal dihydrides which are denoted as octahedral (O) and tetrahedral (T) from the arrangement of nearest-neighbor metal ions.[1] There are two T-sites and one O-site per metal atom with the O-sites having a higher total energy than the T-sites. This leads to the formation of a metal dihydride with very few O-sites occupied at low temperatures. At low temperature the site energy of a hydrogen ion consists of an electronic and a vibrational part, i. e., well depth plus zero point energy, and to a first approximation only the vibrational part changes with isotope, varying as the inverse square root of the mass.

Using electron spin resonance (ESR) of dilute Er ions in Sc and Y dihydride and deuteride hosts, we have measured the occupation of O-sites adjacent to the Er as a function of hydrogen and deuterium loading. The experimental details are presented in the next section, while in the third section we outline a simple lattice-gas calculation which explains the ESR data and yields site energy differences for the hydrogen isotopes both next to the Er impurity ions and in the bulk hydride/deuteride. This energy difference is approximately 10% larger for deuterium in both Sc and Y host lattices. In the final section we estimate the change in the vibrational part of the site energies with isotope mass using published inelastic neutron data, and show that the change in total site energy as measured by the Er ESR data is explained by the mass dependence of the vibrational energy for each site. This result supports a suggestion that the electronic part of the site energy is nearly independent of hydrogen isotope [2], and allows extrapolation to find total site energies in metal tritides.

2. EXPERIMENTAL DETAILS

The samples used in this study were prepared by arc-melting 0.1 atomic percent Er into specially purified Sc or Y, followed by hydrogen or deuterium loading in a modified Sieverts' apparatus, and then grinding the brittle metal hydride into a

fine powder for the ESR measurements. The loading ratio for each sample was determined both volumetrically and gravimetrically, the former method yielding a more accurate number while both agreed to better than 1%. The hydrogen to metal ratio ranged from 1.89 to 1.995 in the scandium samples, and from 1.90 to 2.10 for yttrium. The yttrium samples with the highest loading had a very small amount of the trihydride phase, while all other samples were single phase within the accuracy of our measurements.

In Fig. 1 we show derivative ESR absorption spectra for 0.1 atomic percent Er in samples of $YH_{1.99}$ and $YD_{1.99}$ powder. These data were taken at 9.6 GHz and 2 K, the low temperature yielding narrower resonance lines and a better signal/noise ratio. Both spectra reveal two distinct sites for the Er ions, one with cubic symmetry and one with axial symmetry. Similar spectra [3,4] are observed for Er in Sch_x . The Er ESR data in Fig. 1 are dominated by a large isotropic resonance with a g-factor of 6.781 ± 0.003 , consistent with a Γ_7 doublet ground state for Er^{3+} in a cubic crystal field.[5] This field is produced by the configuration shown in the inset in Fig. 1, where the Er ion is surrounded by a cube of eight nearest-neighbor T-site protons (solid circles), and the next-nearest-neighbor O-sites (open circles) are vacant. The Γ_7 ground state indicates that these protons are negatively charged.[5] There are eight hyperfine lines approximately centered on the large isotropic resonance due to those Er ions in a cubic site with a nuclear spin of 7/2 (23% of the Er has this nuclear spin). The hyperfine line positions are indicated at the bottom of Fig. 1.

In addition to the cubic Er ESR signal and its eight hyperfine lines, the spectra in Fig. 1 have a resonance at higher field labelled g_{\perp} and a barely distinguishable peak at lower field shown as g_{\parallel} . These two signals arise from Er ions in a distinct axial site: in a powder sample a magnetic ion with axial surroundings produces an ESR spectrum with a positive peak and a "normal" derivative resonance at g_{\parallel} and g_{\perp} , respectively, where g_{\parallel} is the g-factor with the applied

magnetic field along the symmetry direction and g_{\perp} is the g-factor with the field normal to this axis.[6] The hyperfine lines arising from those Er ions with a nuclear spin on an axial site are too weak to be resolved.

The strength of the axial Er resonance increases with increasing hydrogen loading for both Sc and Y host hydrides, and we associate this signal with an Er ion surrounded by eight T-site protons plus one and only one proton on an adjacent O-site.[4] There is no evidence for Er ions with less than eight adjacent T-site protons in any ESR spectrum studied to date. This is consistent with a lowered T-site energy for hydrogen adjacent to an impurity compared with bulk sites. In the case of Er in ScH_x or ScD_x there is a second distinct axial resonance which is attributed to Er ions with two adjacent O-site protons on opposite sides of the Er.[4] This second axial signal has not been observed for Er in YH_x or YD_x , and will not be considered here. The spectra in Fig. 1 have been analyzed via least-squares computer fit [3,5] to determine the number of Er ions with a neighboring O-site occupied compared to those on a cubic site, and the results are shown versus loading in Figs. 2 and 3.

The ESR signal in Fig. 1 attributed to Er with one occupied neighboring O-site is larger in intensity for $\text{H}_{1.99}$ than for $\text{D}_{1.99}$, but it appears at the same magnetic field value ($g_{\perp} = 5.00 \pm 0.01$) for both samples. Similarly, the axial Er signal in a ScH_x sample is larger than that in a ScD_x sample for a given hydrogen to metal ratio, but occurs at the same g-factor ($g_{\perp} = 5.44 \pm 0.01$). These results indicate that the effective charge on the hydrogen ion and its distance from the Er do not vary significantly with isotope. This is consistent with the small change in lattice constant for a hydride and deuteride of the same metal.[1] It also supports the assumption that the electronic properties of these materials are relatively insensitive to isotope.[2]

3. LATTICE-GAS CALCULATION

In a previous paper [7] we presented a lattice-gas model for the hydrogen in

these samples. This model assumes that the Er ions are well separated in the host lattice, and that the proton arrangement around one Er is independent of all other Er ions. The face-centered-cubic dihydride lattice has four metal atoms per cubic cell, and at 0.1 atomic percent Er the impurities are separated by six cells on the average. We have studied samples with both more and less Er, and the ESR linewidth increases linearly with concentration, indicating isolated impurity ions.

Furthermore the ratio of Er ions in cubic sites to those in axial sites did not vary significantly with Er concentration, supporting our model of independent impurity ions. This allows a distinction between those protons or deuterons on a site adjacent to an Er ion (nearest or next-nearest neighbors) and those on sites in the bulk host lattice.

Three site energies for hydrogen ions are involved: U_T is the energy for hydrogen on a bulk T-site, U_O is the bulk O-site energy, and U_O' is the energy of an O-site next to an Er impurity. Neglecting proton-proton interactions [8], the probability p_1 of an Er impurity having one and only one adjacent O-site occupied normalized to the probability of all O-sites being vacant is given by [7]

$$p_1(x) = A[x - c_O(x)]/[2 - x + c_O(x)] \quad (1)$$

where x is the hydrogen to metal ratio, $c_O(x)$ is the probability that a bulk O-site is occupied, and $A = 6 \exp[(U_T - U_O')/k_B T]$ (there are six equivalent O-sites). The bulk O-site occupation probability is [7]

$$c_O(x) = x - 4x/[2 + x + B(1-x) + \sqrt{6B + \{2 - x - B(1-x)\}^2}] \quad (2)$$

where $B = \exp[(U_T - U_O)/k_B T]$.

Since the samples are single phase and the lattice spacing is relatively constant for the concentrations studied here, we make the simplifying assumption

that the site energies U_T , U_0 and U_0' are independent of the hydrogen to metal ratio x . This neglects any mean-field contributions of hydrogen-hydrogen interactions to the effective site energies. Hence there are two adjustable parameters, A and B , for fitting Eq. (1) to our ESR data.

In Fig. 2 the experimental impurity O-site occupation probability $p_i(x)$ is plotted versus x for Er in ScH_x (solid circles) and ScD_x (open circles). The curves are calculated from Eq. (1) with $A = 0.0029$ and $B = 0$ for ScH_x , $A = 0.0017$ and $B = 0$ for ScD_x , corresponding to a 7% increase in site energy difference $U_0' - U_T$ for the heavier isotope. (The value of A given here for ScH_x is slightly smaller than that reported earlier [4,7] using a less sophisticated fitting routine.) When $B = 0$, the probability of bulk O-site occupation $c_0(x)$ is zero for $x < 2$ from Eq. (2). The error bar on our hydrogen to metal ratio x is ± 0.005 , and this sets an upper limit on B of 10^{-5} for both ScH_x and ScD_x .

In Fig. 3 the experimental p_i data for YH_x (solid circles) and YD_x (open circles) are shown. In contrast to the Sc data which rise rapidly as x approaches 2, the Y data vary smoothly from $x = 1.9$ to 2.1. This means that $c_0(x)$ for the Y samples is not negligibly small as it was for Sc. The curve for YH_x was calculated from Eq. (1) with $A = 0.020$ and $B = 0.0040$. The values for YD_x are $A = 0.011$ and $B = 0.0025$. This corresponds to a 10% increase in the site energy difference $U_0' - U_T$ for the heavier isotope, and a 9% increase in the bulk difference $U_0 - U_T$.

As discussed elsewhere [7], the temperature T which appears in Eqs. (1) and (2) is a "freezing" temperature T_f below which the hydrogen ions cannot establish equilibrium among the available sites on our experimental time scale. The ESR data are taken at 2 K, and each sample is cooled from room temperature at between 2 and 5 degrees per minute, so a reasonable estimate for T_f is the temperature at which the proton jump time is one minute. Proton motion in metal hydrides is characterized by activation energies of 400 to 500 meV, which makes the jump time a strong function of temperature. Using proton NMR diffusion data [9] for ScH_x , the jump times are

estimated (by extrapolation) to be 1 second at 150 K and 1 hour at 135 K, and we choose $T_f = 150$ K (one minute jump time). This value for T_f will vary with isotope mass and host metal, but for the discussion below these changes are not important, and we use a single freezing temperature for all samples.

With $T_f = 150$ K the values for A and B given above for the four host materials yield the site energy differences listed in Table 1. The bulk site energy difference for the two Y hosts can be substituted into Eq. 2 to obtain the octahedral site occupation fraction at room temperature for a hydrogen to metal ratio of 2: $c_0(x=2)$ is 0.28 in YH_2 and 0.25 in YD_2 . For T below the freezing temperature, these numbers are 0.08 and 0.07, respectively. Note that these latter occupation fractions are obtained directly by applying Eqs. (1) and (2) to the ESR data in Fig. 3, and are independent of the actual value of T_f (assuming it is higher than the experimental 2 K).

4. VIBRATIONAL ENERGY SHIFT AND CONCLUSIONS

From Table 1 the bulk site energy difference $U_O - U_T$ increases from 71 to 78 meV upon substituting deuterons for protons in the Y system. If the choice of 150 K for the freezing temperature were in error by 50 K, this increase would change by 2 meV. Hence we must explain a site energy shift of 5 to 9 meV with isotope in the Y samples.

The site energy for a hydrogen ion in these materials can be divided into an electronic and a vibrational part, i. e., well depth plus zero point motion. This is shown schematically in Fig. 4 for a T-site where the well depth or electronic part of the total site energy is $-E_T$, and the vibrational part is $3\hbar\omega_T^H/2$ for a proton and $3\hbar\omega_T^D/2$ for a deuteron. Hence the T-site energy for a proton is $U_T^H = -E_T + 3\hbar\omega_T^H/2$ with a similar expression for T-site deuterium. The energy of protons and deuterons on O-sites can be divided into an electronic and vibrational part in an identical manner.

The electronic energy for either an O-site or a T-site is expected to be

relatively insensitive to isotope from energy band considerations.[2] In addition our ESR results show that the axial g-factor splitting of an Er ion due to an adjacent O-site proton or deuteron is independent of isotope, indicating a similar effective charge and lattice spacing. Hence we look to the change in vibrational energy with mass to explain the 5 to 9 meV shift determined by impurity ESR.

Recent inelastic neutron scattering results [10,11] give a direct measure of the proton vibration energy on a T-site in YH_x : $\hbar\omega_T^H = 116 \pm 2$ meV. Unfortunately, no direct measurement of the corresponding O-site vibrational energy has been reported. We can estimate this energy from inelastic neutron scattering data [12,13] on isomorphic hydrides and deuterides (using the published lattice constants to scale the vibration frequencies), obtaining a value for $\hbar\omega_O^H$ of 85 ± 5 meV for O-site protons.[14] Data for deuterons show that the vibrational energy varies as the inverse square root of the isotope mass as expected.[10,13]

Using these values, the vibrational T-site energy is approximately 46 meV higher than the vibrational O-site energy for protons. Our lattice-gas model estimates that the total T-site energy U_T is 71 meV lower than the O-site energy U_O for protons. Hence the electronic part of the site energy ($-E$ in Fig. 4) must be roughly 117 meV lower for protons on T-sites compared to O-sites.

Using the inverse square root mass dependence, the T-site vibrational energy is approximately 33 meV higher than the O-site value for deuterons. If the electronic site energies are independent of isotope, this means that the total site energy difference should be $46 - 33 = 13$ meV greater in YD_x than in YH_x . This is in reasonable agreement with the shift of 7 ± 2 meV obtained from impurity ESR assuming a freezing temperature $T_f = 150$ K. The discrepancy may be due to a small change in the electronic energy with isotope, a value for T_f that is too low, or a higher O-site vibrational energy than our estimate of 85 meV. If the latter explanation holds, the O-site vibrational energy in YH_x is 95 to 100 meV, but this seems high.

In summary, ESR measurements of the proton and deuteron distribution around dilute Er ions in samples of Sc and Y hydrides and deuterides together with a lattice-gas model yield total site energy differences for the hydrogen isotopes both adjacent to the Er and in the bulk host lattice. Inelastic neutron data provide the vibrational part of the site energies for H and D, and there is reasonable agreement between the isotope dependence of the total site energy and that from the vibrational motion alone. This supports the assertion that the electronic part of the energy is relatively insensitive to the particular hydrogen isotope. As discussed elsewhere [8] the hydrogen-hydrogen interactions deduced from the ESR data for ScH_x and ScD_x also appear to be isotope independent.

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Table 1. Site energy differences for a freezing temperature $T_f = 150$ K using the parameters A and B which fit the lattice-gas model to the ESR p_1 data.

Sample	$U_0' - U_T$	$U_0 - U_T$
ScH _x	98 meV	>150 meV
ScD _x	106	>150
YH _x	74	71
YD _x	81	78

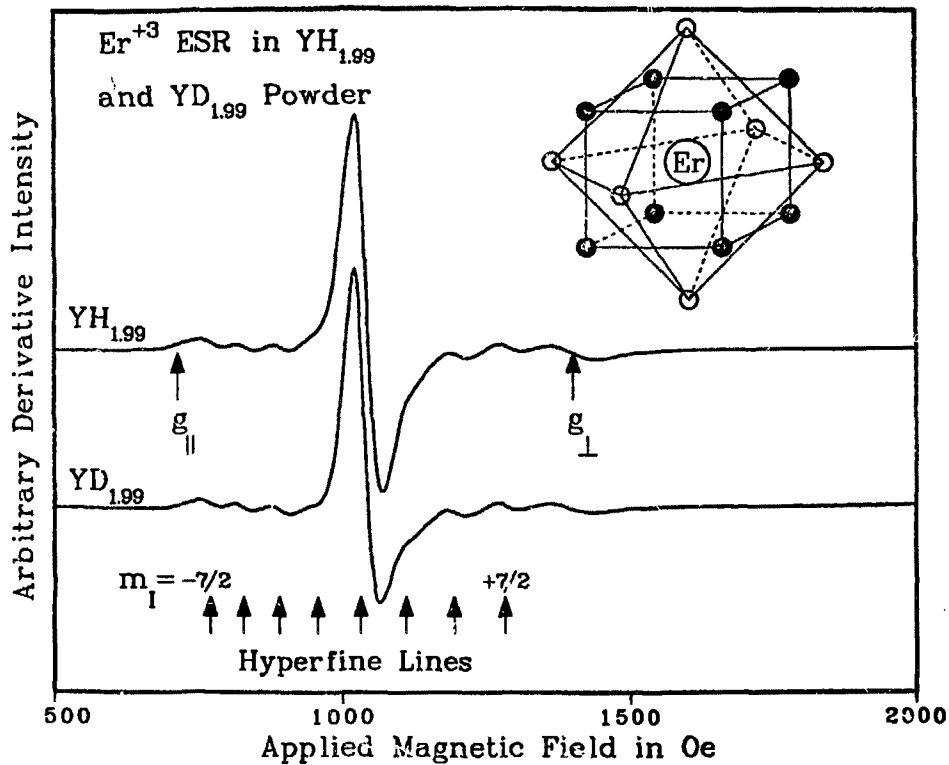
FIGURE CAPTIONS

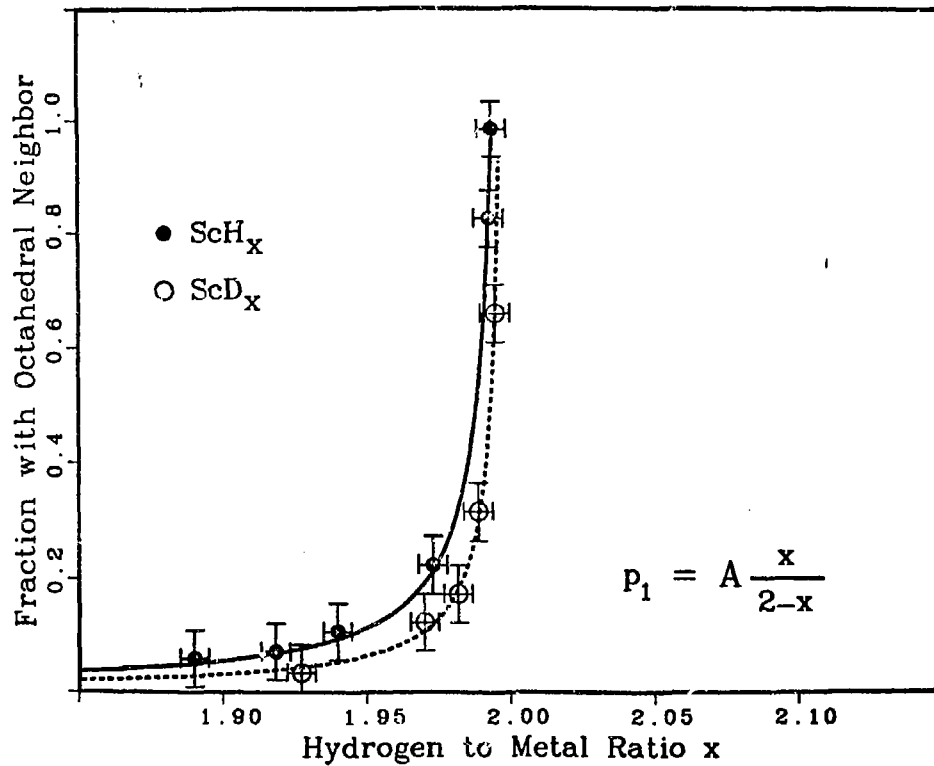
Fig. 1. ESR absorption derivative versus applied magnetic field for Er in $\text{YH}_{1.99}$ and $\text{YD}_{1.99}$. Inset shows tetrahedral (solid) and octahedral (open) hydrogen sites surrounding Er in the face-centered-cubic host lattice.

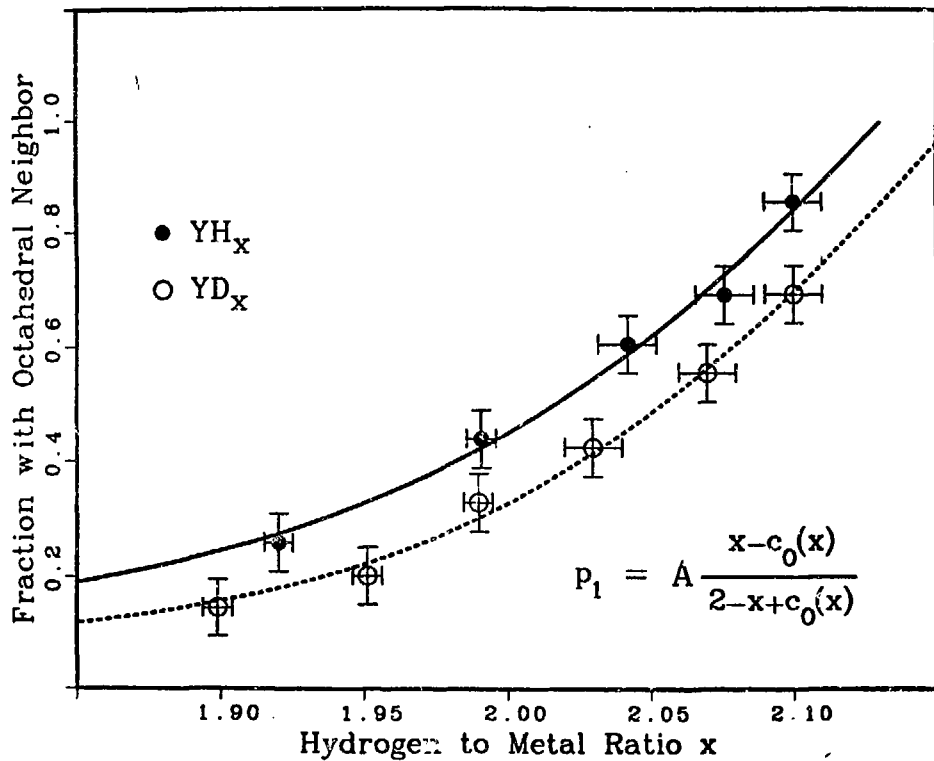
Fig. 2. Fraction of Er ions with one adjacent octahedral hydrogen ion versus proton (solid circles) and deuteron (open circles) concentration for Sc host metal. Curves from relation shown with $A = 0.0029$ for ScH_x and $A = 0.0017$ for ScD_x (see text).

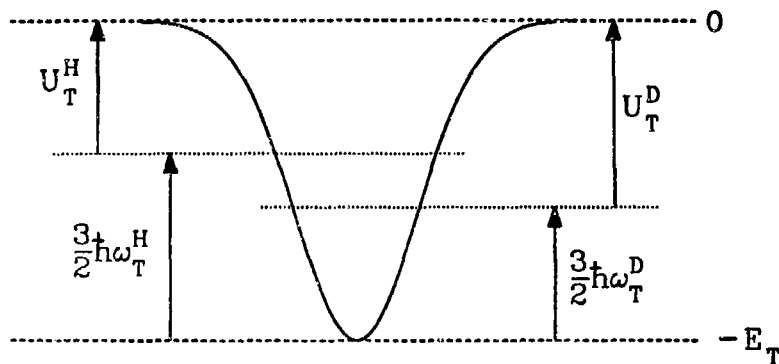
Fig. 3. Fraction of Er ions with one adjacent octahedral hydrogen ion versus proton (solid circles) and deuteron (open circles) concentration for Y host metal. Curves from relation shown with $A = 0.0020$ and $B = 0.0040$ for YH_x , $A = 0.011$, $B = 0.0025$ for YD_x (see text).

Fig. 4. Schematic representation of various energies associated with protons and deuterons on a tetrahedral site in the bulk host lattice. The site energy U_T is the difference between the electronic energy $-E_T$ and the vibrational energy $3\hbar\omega_T/2$.









Venturini/Fig. 4