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Proton Location in Metal Hydrides Using Electron Spin Resonance[a)]

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ABSTRACT

Electron spin resonance (ESR) of dilute paramagnetic ions establishes the site symmetry of these ions. In the case of metal hydrides the site symmetry is determined by the number and location of neighboring protons. Typical ESR spectra for trivalent erbium in scandium and yttrium hydrides are presented and analyzed, and this technique is shown to be a versatile microscopic probe of the location, net charge and occupation probability of nearby protons.

INTRODUCTION

Microscopic information concerning the location, net charge, site energy, occupation probability and diffusion of protons in metals and metal hydrides is of fundamental importance in understanding these materials and improving their characteristics for specific applications. Several analysis techniques have been applied to this problem including nuclear magnetic resonance, Mossbauer spectroscopy, static magnetic susceptibility, low temperature specific heat, electrical resistivity, neutron diffraction and ion beam scattering. In this presentation we will show that electron spin resonance (ESR) is a sensitive microscopic probe which complements other methods. In particular ESR provides direct evidence of neighboring protons via their electrostatic fields. Each distinct proton configuration around the paramagnetic ion studied by ESR produces a distinguishable signal, and numerical analysis of the data yields the location, charge and occupation probability for the protons (the latter is related to the site energy).

Our discussion will be limited to ESR of dilute trivalent erbium substituted into the metal hydrides of two group IIIB elements, scandium and yttrium. These hydrides have the face-centered-cubic fluorite structure shown in Fig. 1 for a hydrogen-to-metal ratio x = 2. In the ideal dihydride the

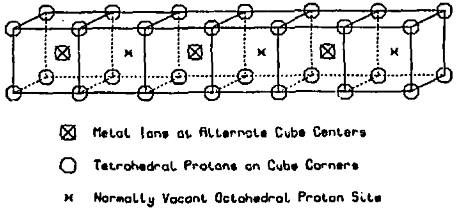

Figure 1. Ideal face-centered-cubic dihydride for group IIIB elements.

protons occupy all available tetrahedral sites forming a simple cubic network. The metal atoms (ions) fill alternate cube centers as shown. The other cube centers are octahedral sites for protons which are normally vacant for x less than 2. The nearest neighbors of a given metal atom are eight tetrahedral protons (simple cube). The six next-nearest neighbor sites (empty adjacent cube centers) form an octahedron.

The samples used in this work are prepared by first arc-melting measured quantities of either scandium or yttrium metal plus 0.1 atomic percent erbium on a water-cooled copper hearth in a purified argon atmosphere. The resulting ingot is then loaded with the desired amount of hydrogen in a modified Sieverts' apparatus. The metal hydride is ground into a fine powder, and placed in a microwave cavity for ESR measurements. By varying the erbium content of our samples we have determined that the erbium is randomly distributed on metal lattice sites throughout the hydride. Exposure to air at room temperature for long periods of time does not alter the ESR signals obtained with these materials.

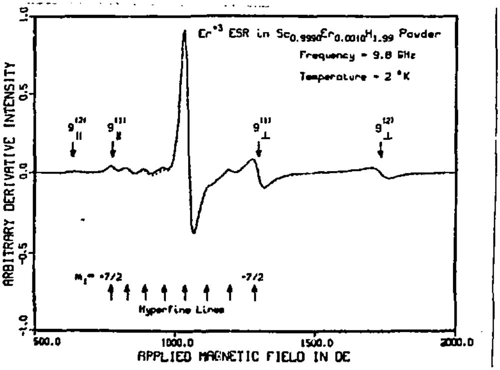

Figure 2. ESR spectrum for erbium in scandium hydride. Solid line is experimental data; dashed line is numerical fit (discussed in text).

In Fig. 2 we show the erbium ESR signal measured in a scandium hydride powder with x = 1.99±0.01 at 2 °K and 9.8 GHz. The derivative absorbed microwave power is plotted versus the static applied magnetic field in Oe. The solid line is the actual digitized data, and the dashed curve is a numerical fit. This spectrum is the sum of ESR signals from erbium ions in three distinct sites, one with cubic symmetry and the other two with uniaxial (tetragonal) symmetry. In the next section we will discuss each site and its associated ESR signal. In the third section we analyze the proton occupation probability determined from the strength of the different ESR signals versus the bulk hydrogen-to-metal ratio. Finally, we present ESR data for erbium in yttrium hydride which establishes a new proton configuration with biaxial (orthorhombic or lower) symmetry.

ERBIUM IN SCANDIUM HYDRIDE

The microwave power absorption shown in Fig. 2 is due to transitions within the ground state of the erbium ions in scandium hydride. A free trivalent erbium ion has eleven 4f electrons which couple to produce a total angular momentum J = 15/2. Thus the ground state for this free ion is sixteen-fold degenerate. This degeneracy is lifted when the erbium ion is located in a metal hydride lattice.

Consider an erbium ion surrounded by a simple cube of eight tetrahedral protons as shown in Fig. 3a. If these protons have a net charge, they will produce an electrostatic field with cubic symmetry at the erbium ion. The general problem of a rare earth ion in a cubic electrostatic field has been solved by Lea, Leask and Wolf (LLW).[1] They find that the sixteen degenerate levels of the free trivalent erbium ion are split into three four-fold degenerate levels (quartets) and two two-fold degenerate levels (doublets). If the charges on the cube corners are positive, a quartet is the ground state, while for negative charges a doublet is the lowest level in most situations.

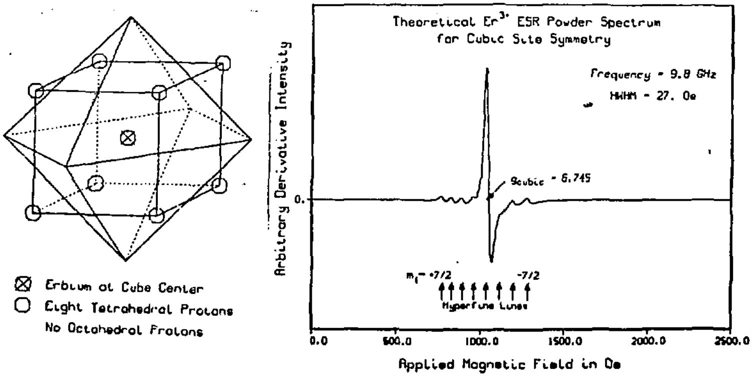

Figure 3. (3a) Erbium in a cubic site; (3b) theoretical ESR spectrum.

In discussing ESR it is convenient to define an effective g-factor given by the following relation:

$$g = h\nu/\beta H_{res} \quad (1)$$

where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton and H_{res} is the applied magnetic field for maximum power absorption. For the main (largest) derivative absorption signal shown in Figs. 2 and 3b the g-factor is 6.745, and this identifies the ground state as a doublet using the results of LLW. If the ground state is a doublet, the protons which produce the cubic electrostatic field must have a net negative charge. This result is termed the hydridic model, and it has been confirmed in numerous previous studies in these materials.

The g-factor is only one of four adjustable parameters in the theoretical lineshape shown in Fig. 3b. The lineshape is Lorentzian (determined by its agreement with the experimental data in Fig. 2), and contains an arbitrary amount of absorption plus dispersion. This is due to the metallic powder sample used for the measurements which has a skin depth comparable to the particle size at the microwave frequency used here. Hence one parameter is the relative amount of absorption and dispersion to best fit the data. A second parameter is the strength of the signal (the integrated intensity is proportional to the number of erbium ions in cubic sites). Finally, the half-width at half-maximum (HWHM) of the absorption is 27 Oe for the best agreement with the measurements. These parameters were used to calculate the theoretical lineshape shown in Fig. 3b for erbium in a cubic site.

There is one additional complication for erbium ESR. There are several stable isotopes of erbium, and one isotope with a natural abundance $c = 0.23$ has a nuclear spin $I = 7/2$ (the remaining isotopes have no nuclear spin). At the measurement temperature of 2 °K in an applied magnetic field of 1000 Oe this nuclear spin is almost evenly distributed among the eight available states from $m = +7/2$ to $-7/2$. This produces eight small subsidiary absorptions centered on the main resonance (referred to as hyperfine lines in Figs. 2 and 3b). These eight lines have an amplitude $c/[8(1-c)]$ compared with the main line (roughly 0.037 for $c = 0.23$). Since the electrostatic field has cubic symmetry for the site shown in Fig. 3a, the main line and its hyperfine lines have an isotropic g-factor (the angle of the applied magnetic field with respect to the cube axes does not alter the absorption energy).

Comparing the theoretical curve in Fig. 3b for erbium in a cubic site with the data in Fig. 2, we find four measured absorption signals which are not explained. There are two peaks at fields less than the main line in Fig. 2 labelled $g_{\parallel}$ with superscripts 1 and 2, and there are two signals at fields above the main line labelled $g_{\perp}$ 1 and 2. The sharp decrease in size of these four resonances as the hydrogen-to-metal ratio is lowered suggests that they are due to additional protons near some erbium ions. By their general shape, i.e., a positive peak at low field and a two-sided resonance at high field, we know that they arise from erbium ions in sites with axial (tetragonal or trigonal) symmetry.

Consider the proton configuration shown in Fig. 4a. The addition of one octahedral proton to the eight tetrahedral protons changes the erbium site symmetry from cubic to tetragonal. This introduces additional components into the electrostatic field acting on the erbium ion (assuming the octahedral proton has a net charge), and the isotropic g-factor defined in Eq. (1) for erbium in a cubic site now has an angular dependence:

$$g = \sqrt{g_{\parallel}^2 \cdot \cos^2\theta + g_{\perp}^2 \cdot \sin^2\theta} \qquad (2)$$

where θ is the angle between the applied magnetic field and a line connecting the erbium ion and the octahedral proton in Fig. 4a. The g-factor varies from $g_{\parallel}$ when θ is zero to $g_{\perp}$ when θ is $\pi/2$.

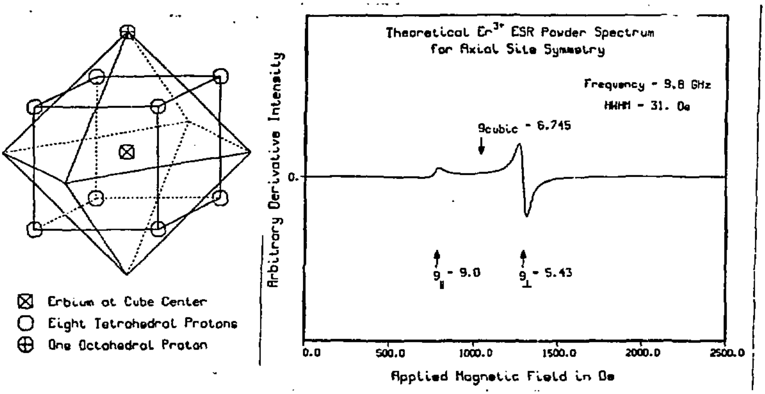

Figure 4. (4a) Erbium in an axial site; (4b) theoretical ESR spectrum.

The theoretical ESR spectrum for erbium in an axial site depends on the separation of magnetic fields corresponding to $g_{\parallel}$ and $g_{\perp}$ compared with the absorption HWHM. For erbium in the site shown in Fig. 4a we find the best agreement with the data when the g-values are 9.0 and 5.43, respectively, with a HWHM of 31 Oe. This produces the theoretical spectrum shown in Fig. 4b, where one uses the angular variation in Eq. (2) plus the appropriate intensity versus angle [2], and averages the calculated ESR signal over all angles for a powder sample. The assumptions implicit in this analysis are justified by the agreement with the measured data. The hyperfine lines which are clearly resolved for erbium in a cubic site are not observed after averaging over all angles for an axial site.

The site shown in Fig. 4a explains the signals in Fig. 2 labelled with a superscript 1. The remaining pair of signals with superscript 2 are also due to erbium in an axial site as shown in Fig. 5a. Here we have two octahedral protons on opposite sides of the erbium ion. As discussed in the next section, the erbium site shown in Fig. 5a has twice the axial electrostatic field as that in Fig. 4a. The theoretical spectrum in Fig. 5b is similar to that in Fig. 4b except that the g-values are now 11.0 and 4.05, and the HWHM is 50 Oe. The calculated curve shown as a dashed line in Fig. 2 is the sum of the three theoretical curves shown in Figs. 3b, 4b, and 5b.

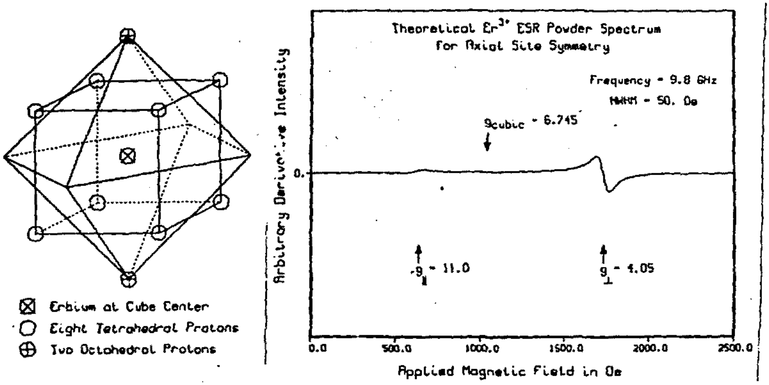

Figure 5. (5a) Erbium in axial site 2; (5b) theoretical ESR spectrum.

SITE OCCUPATION PROBABILITY

Two considerations support our suggestion that the proton configurations in Figs. 4a and 5a give rise to the axial ESR signals shown in Figs. 4b and 5b. First we discuss a calculation of g-factors for the ground state of an erbium ion in a cubic electrostatic field with a small axial perturbation. Then we consider the probability that a proton occupies the octahedral position next to an erbium ion versus the bulk hydrogen-to-metal ratio.

As mentioned above, the electrostatic field from the simple cube of tetrahedral protons can be treated as a perturbation on the sixteen-fold degenerate ground state of a free trivalent erbium ion. Treating the protons as point charges, one can write the field in terms of the erbium ion coordinates.[3] The problem is then rewritten using the Stevens' operator equivalent method [4], resulting in a Hamiltonian which lifts the sixteen-fold degeneracy of the ground state. This Hamiltonian contains terms with fourth and sixth order spin operators, and the entire problem involves two parameters, an overall energy splitting W and a ratio of fourth to sixth order terms r. The ESR signal associated with cubic site symmetry has a g-factor of 6.745 (Fig. 3b), and this identifies the ground state as a Γ_7 doublet. From this it follows that W must be positive, the net charge on the tetrahedral protons must be negative (hydridic model), and r must be between -0.5 and +0.6.[1]

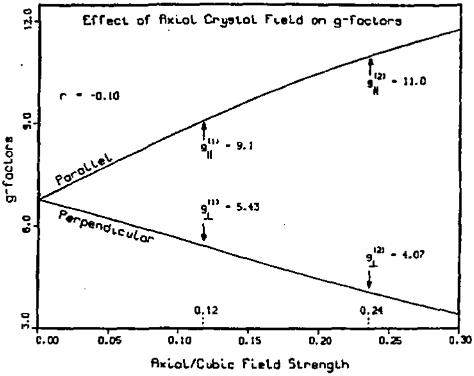

Figure 6. Splitting of erbium ground state g-factor in an axial field.

The addition of one octahedral proton as shown in Fig. 4a introduces new terms in the Hamiltonian. This problem has been studied by Yi and Choh [5] for interstitial fluorine in the calcium fluoride lattice which is isostructural with the dihydrides. The new ground state for the erbium ion in this axial site has two g-factors, $g_{\parallel}$ and $g_{\perp}$, which deviate from the cubic (isotropic) value as the strength of the axial field increases relative to the cubic field. We have calculated the g-factors for this ground state as shown in Fig. 6. Choosing the fourth to sixth order parameter $r = -0.10$, we find that an axial electrostatic field of some 12% of the cubic field energy yields axial g-factors of 5.43 and 9.1 in good agreement with those for the axial ESR signal labelled as superscript 1 in Fig. 2. With no adjustable parameters we simply double the axial field strength as a first approximation to the effect of the two octahedral protons shown in Fig. 5a compared to the single octahedral proton in Fig. 4a. This axial-to-cubic field ratio of 24% predicts ground state g-factors of 4.07 and 11.0 (Fig. 6) in excellent agreement with the measured values for the axial site labelled by superscript 2. This result strengthens our contention that octahedral protons are responsible for the axial erbium sites.

The effect of varying the bulk hydrogen-to-metal ratio x on the number of octahedral protons provides additional support for our choice of the axial site proton configuations in Figs. 4a and 5a. By comparing the integrated intensities of the ESR signals for the three distinct erbium sites, we can determine an occupation probability P(n) that there are n octahedral protons adjacent to a given erbium ion. P(0) is the number of erbium ions in cubic sites over the total number of erbium ions, P(1) is the relative number with one next-nearest-neighbor octahedral proton and P(2) is the relative number with two octahedral protons. Richards [6] has solved this problem using a one parameter model which assumes: (a) there are no octahedral protons in the bulk scandium hydride (in accord with the experimental fact that x does not exceed 2 for scandium hydride); (b) an erbium ion can have zero, one or two adjacent octahedral protons, but in the latter case they must be on opposite sides of the erbium; (c) the single parameter A depends on the difference in energy between a bulk tetrahedral proton and one in an octahedral site adjacent to an erbium ion divided by a "freezing" temperature below which the octahedral protons remain on a site. His result for the occupation probabilities can be expressed in terms of $z = A(2-x)/x$:

$$P(1)/P(0) = 1/z; \quad P(2)/P(0) = 1/(12z^2). \qquad (3a,b)$$

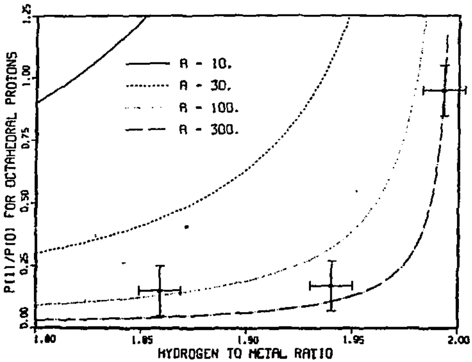

Figure 7. Relative number of single octahedral proton sites versus x.

In Fig. 7 we plot the experimental probability of one octahedral proton over zero octahedral protons (i.e., the number of erbium ions in axial site 1 over the number in a cubic site) versus the hydrogen-to-metal ratio x for three samples. We also show several theoretical curves using Eq. (3a) for four values of A. The dramatic increase in axial erbium ion sites observed experimentally as x approaches 2 is predicted by the simple model which is based on the octahedral proton picture in Figs. 4a and 5a, and thus strengthens our choice of these proton configurations to explain the data. A similar figure for the probability of two octahedral protons shows that the experimental data lies consistently above the values predicted by Eq. (3b). Although this discrepancy has not been resolved, we suggest that there is an attractive interaction between the two octahedral protons in Fig. 5a such that the probability for erbium ions in this site is enhanced.

ERBIUM IN YTTRIUM HYDRIDE

Yttrium hydride is isostructural with scandium dihydride for x between 1.9 and 2.2, while for larger x yttrium hydride has the hexagonal HoD_3 structure. In the latter case the metal ions have orthorhombic (biaxial) site symmetry, and one expects three distinct g-factors for the ground state. In Fig. 8 we show preliminary data for erbium ESR in two yttrium hydride samples. The top curve for x near 2 is remarkably similar to our results in scandium hydride. The main signal is for erbium in cubic sites, while there is at least one clearly resolved resonance from erbium in axial sites. The dependence of this signal on the hydrogen-to-metal ratio is under study.

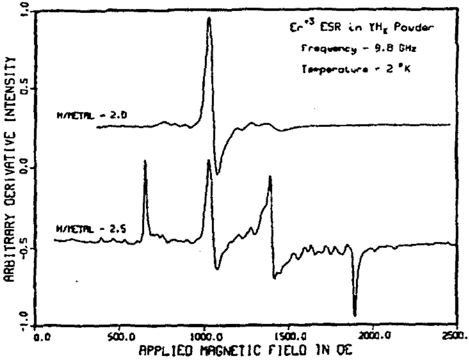

Figure 8. Erbium ESR data for two yttrium hydride powder samples.

The lower curve in Fig. 8 shows erbium ESR data in yttrium hydride with x = 2.5. The powder sample is probably a mixture of dihydride and trihydride phases, the signal near 1000 Oe associated with erbium in a cubic site in the dihydride while the three remaining strong lines indicate erbium in a biaxial site expected for the trihydride. This trace was taken at 2 °K, and as the temperature is increased the linewidth of the ESR signal from erbium in a cubic site broadens. This is expected for dilute ion ESR in a metallic host: the linewidth increases linearly with temperature due to spin relaxation via conduction electron scattering. The remarkable fact is that the linewidth for the remaining three resonances does not change appreciably from 2 to 10 °K. This would indicate that the erbium associated with these latter signals is in a nonmetallic host, and indeed yttrium trihydride is reported to be semiconducting.[7]

DISCUSSION AND CONCULSIONS

This brief presentation of an electron spin resonance study of dilute trivalent erbium ions in scandium and yttrium hydrides demonstrates its potential as a microscope probe for the location, net charge and site occupation probability of protons in these group IIIB metal hydrides. Although erbium is clearly a perturbation in the lattice, particularly in the case of scandium hydride, comparison of proton configurations around erbium versus bulk hydrogen loading in different host metal hydrides will yield basic information concerning site energies. We note that there is no evidence for more than two octahedral protons adjacent to erbium in scandium hydride, while in yttrium hydride we detect an ESR signal for erbium in a biaxial site which requires three or more octahedral protons. Clearly we are observing effects intimately related to the host lattice (and the interaction between protons in different sites) despite the use of a probe ion.

The analysis technique presented here is not restricted to group IIIB metal hydrides, although it does require the introduction of a dilute probe into a host material. One application that holds great promise is a study of hydrogen trapping at erbium atoms in the fcc metals. Erbium in silver is known to have a readily observed ESR signal, and our intent is to introduce hydrogen into silver:erbium foils and monitor trapping using ESR. The trapping and release of hydrogen in fcc metals and austenitic stainless steels is a great concern at present, and the use of ESR may allow new insight into this problem. Finally, we note that replacing hydrogen with tritium in metal hydrides allows us to monitor accumulation of helium by its effects on dilute ion ESR. This is an example where microscopic information is sparse, and the potential of the analysis technique outlined above is very intriguing.

ACKNOWLEDGEMENT

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