PROTON INTERACTIONS IN VICINITY OF A RARE EARTH
IMPURITY IN A HYDRIDE*

Peter M. Richards
Sandia Laboratories,[†] Albuquerque, NM 87185

ABSTRACT

MASTER

Recent rare-earth-impurity ESR in $\text{ScH}_x\text{:Er}$ has determined the fractions p_1 and p_2 of impurities which have 1 and 2 surrounding octahedral sites occupied by protons. In the absence of proton-proton interactions one expects $p_2 \propto p_1^2$, which is in gross disagreement with the data. We show that if only nearest neighbor interactions are included, p_2 should still be proportional to p_1^2 ; but satisfactory agreement can be obtained if both repulsive nearest-neighbor and longer range attractive interactions are included.

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*Work sponsored by the U.S. Dept. of Energy Under Contract No. DE-AC04-76-DPO0789.

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I. INTRODUCTION

Venturini and Richards [1,2] (referred to as VR) have shown that electron spin resonance (ESR) of the rare earth impurity Er^{3+} in a metal hydride can be used to identify proton occupation of octahedral (O) sites surrounding the impurity. For the case of ScH_x they were able to deduce the fractions p_1 and p_2 of sites with 1 and 2 surrounding O-sites occupied, respectively, relative to the number with no occupied O-sites. A lattice gas model was employed to relate p_1 and p_2 , which directly measure only properties in the neighborhood of an Er^{3+} impurity, to properties of the bulk ScH_x host lattice. We remarked there [1] that the combined behavior of p_2 and p_1 could be explained only by invoking interactions which extend at least beyond nearest neighbors, but we did not give any details. The present paper provides the details and explores the general feature of proton interactions required to fit the data. We find good agreement for a model in which nearest neighbor interactions are strongly repulsive hard-core like, but further distant ones are attractive, and probably quite long range.

Long range, elastic interactions have been recognized [3] as important features of metal-hydrogen systems. The recent discovery [4] that the α - α' phase transition of H in Nb is dependent on sample shape gives striking evidence for macroscopic scale interactions. The interpretation here, in quite a different context, is consistent with the view that the interaction must spread at least well beyond nearest neighbors.

II. THEORY

The lattice gas Hamiltonian [5] is written as

$$\mathcal{H} = \sum_i U_i P_i + \frac{1}{2} \sum_{ij} J_{ij} P_i P_j \quad (1)$$

where $P_i = 1$ if site i is occupied by a proton and $P_i = 0$ otherwise and U_i and

J_{ij} are site and interaction energies, respectively, which in general depend upon distance from the impurity as well as site type [O or tetrahedral (T)] and inter-proton separation. The premise that Eq. (1), which is equivalent to a spin $\frac{1}{2}$ Ising model in a field, is applicable to the system of interest rests on the energies being primarily determined by the presence or absence of protons at given sites, rather than on their vibrational states or other internal modes.

The ESR data are consistent with fully occupied T-sites surrounding an impurity but no more than 2 O-sites being occupied ($p_j = 0$ for $j > 2$). When two surrounding O-sites are occupied (p_2) the protons lie on a common axis with the impurity (shown in Fig. 1 as sites 1 and 2) as inferred from the axial-symmetry ESR pattern.

We specialize the Hamiltonian in Eq. (1) to account for these facts by writing it as

$$\begin{aligned} \mathcal{K} = & U'_0 \sum_{j=1}^6 O_j + \sum_{j=1}^6 \sum_k J_{jk} O_j P_k \\ & + \frac{1}{2} J_0 \sum_{j=1}^6 O_j O_{j'} + \mathcal{K}_0 \end{aligned} \quad (2)$$

where $O_j = P_j$ for the special case when j is one of the 6 O-sites surrounding an impurity (Fig. 1a). The 8 fully occupied T-sites surrounding the impurity (Fig. 1a) contribute either a constant term which can be ignored or may be lumped into an effective impurity-neighbor O-site interaction U'_0 . The interaction J_{jk} is between an impurity-neighbor O-site and an O or T-site which is not an impurity neighbor; and J_0 is between sites j and j' which lie on a common axis with the impurity (such as sites 1 and 2 in Fig. 1). We consider low impurity concentration so that it is sufficient to treat only the single-isolated-impurity Hamiltonian. The remaining $\mathcal{K}_0$ is as in Eq. (1) except that the sum excludes O and T-sites which are nearest neighbors of the impurity. It is not in general the host lattice Hamiltonian since U_i and J_{ij} may depend on the distance of sites i and j from the impurity.

The grand ensemble partition function is

$$z = \text{Tr} e^{-\beta[K-\mu n]} \quad (3)$$

where $n = \sum_i P_i$ and μ is the chemical potential determined from the condition $\langle n \rangle = Nx$ for N metal ions and hydrogen/metal ratio x where the triangular brackets indicate a thermal average over the ensemble (3) at temperature $T = 1/k_B\beta$.

The probability of an impurity having n neighbor O-sites occupied is proportional to the restricted partition function

$$z_n = \text{Tr}_n e^{-\beta[K-\mu n]} \quad (4)$$

where Tr_n indicates that only those sites for which $\sum_{i=1}^6 O_i = n$ are to be included. We therefore obtain for the relative probabilities

$$\begin{aligned} p_1 = z_1/z_0 &= 6e^{\beta(-U'_0+\mu)} \frac{\text{Tr} e^{-\beta \sum_K J_{1k} P_k} e^{-\beta F_0}}{\text{Tr} e^{-\beta F_0}} \\ &= 6e^{\beta(-U'_0+\mu)} \langle e^{-\beta \sum_K J_{1k} P_k} \rangle_0 \end{aligned} \quad (5a)$$

$$p_2 = z_2/z_0 = 3e^{-\beta J_0} e^{\beta(-2U'_0+2\mu)} \langle e^{-\beta \sum_K (J_{1k}+J_{2k}) P_k} \rangle_0 \quad (5b)$$

where $F_0 = K_0 - \mu \sum'_K P_k$ in which the prime indicates that impurity-neighbor O-sites are excluded from the summation, the factors 6 and 3 represent the number of ways of realizing states with one and two common-axis O-sites occupied, respectively, (sites 1 and 2 of Fig. 1) and $\langle \rangle_0$ indicates thermal average with respect to the distribution of non-impurity-neighbor sites. The interaction energy J_0 is assumed to be independent of x , so it is evident that $p_2 = Cp_1^2$ in the absence of interactions ($J_{jk}=0$) where C is a constant independent of x . This is in

striking disagreement with the data in VR as may be seen in Fig. 2, although p_1 itself can be fit to (5a) with $J_{jk} = 0$ [1,2,6].

We must therefore examine the interaction terms $\langle \rangle_0$ of Eqs. (5). If short-range order fluctuations are neglected so that $\langle P_i P_j \rangle_0 = \langle P_i \rangle_0 \langle P_j \rangle_0$ for $i \neq j$, one can factor the averages in Eqs. (5) and combine them to yield

$$p_2/p_1^2 = \frac{1}{12} e^{-\beta J_0 \prod_k R_k} \quad (6)$$

where

$$R_k = \frac{1 + [e^{-\beta(J_{1k} + J_{2k})} - 1] \langle P_k \rangle_0}{[1 + (e^{-\beta J_{1k}} - 1) \langle P_k \rangle_0][1 + (e^{-\beta J_{2k}} - 1) \langle P_k \rangle_0]} \quad (7)$$

and the product extends over all sites k which are not nearest O or T-site neighbors of the impurity. The justification for neglecting correlations is that the relative "magnetization" of the equivalent Ising model has magnitude $|\sigma| = |2\langle P \rangle - 1|$, and when $|\sigma| \approx 1$ it is well known that $\langle \sigma_i \sigma_j \rangle \approx \langle \sigma_i \rangle \langle \sigma_j \rangle$ for $i \neq j$, i.e. correlations are unimportant near full alignment away from the critical region. Here for x near 2, $\langle P_k \rangle_0 \approx 1$ if k is a T-site and $\langle P_k \rangle_0 \ll 1$ if k is an O-site other than a nearest-neighbor of the impurity, which is excluded from the averages $\langle \rangle_0$ in (5). In Eq. (7) we have used the identity $e^{-\lambda P} = 1 + P(e^{-\lambda} - 1)$ for any variable P which can only have the values 1 or 0.

The quantity $\langle P_k \rangle_0$ is the average for the Hamiltonian $\mathcal{H}_0$ which includes perturbed site and interaction energies due to the impurity. For sites k far from the impurity $\langle P_k \rangle_0 = x/2$ for T-sites and $\langle P_k \rangle_0 \approx 0$ for O-sites, since these are the assumed bulk values for ScH_x with $x \leq 2$. Near the impurity $\langle P_k \rangle_0$ is enhanced over its bulk value both for O and T-sites [1,2,7].

A mean field treatment gives

$$\langle P_k \rangle_0 = \left[\exp[\beta(\tilde{U}_k - \mu)] + 1 \right]^{-1} \equiv (A_k \epsilon + 1)^{-1} \quad (8)$$

with $A_k \equiv e^{\beta(\tilde{U}_k - \tilde{U}_T)}$, $\epsilon \equiv (2-x)/x$. Here $\tilde{U}_k$ is the effective energy, including mean field interactions, at site k and $\tilde{U}_T$ is the effective energy for a bulk T-site. We have eliminated μ by the relation $x/2 = \left[\exp[\beta(\tilde{U}_T - \mu)] + 1 \right]^{-1}$ valid for negligible bulk O-site occupation and small impurity concentration.

We note that $R_k = 1$ (i) if $J_{1k} = 0$ or $J_{2k} = 0$, or (ii) if $\langle P_k \rangle_0 = 0$ or 1. Condition (i) implies that the interactions must extend at least beyond nearest neighbors since site k must interact with both sites 1 and 2 in order to produce a deviation from $p_2 \propto p_1^2$; and (ii) shows that nearest neighbor T-sites, for which $\langle P_k \rangle_0 \approx 1$ ($A_k \ll 1$), and far away O-sites ($\langle P_k \rangle_0 \approx 0$, $A_k \gg 1$) are unimportant.

We assume that for the contributing T-sites, $1 - \langle P_k \rangle_0 \approx A_k^T \epsilon \ll \langle P_k \rangle_0 e^{-\lambda_k}$ where λ_k is either βJ_{1k} , βJ_{2k} or $\beta(J_{1k} + J_{2k})$. This is valid except for very strong repulsive interactions. Similarly for O-sites we take

$$\langle P_k \rangle_0 e^{-\lambda_k} \approx \frac{1}{A_k^O \epsilon} e^{-\lambda_k} \ll 1 - \langle P_k \rangle_0$$

which is valid except for very strong attractive interactions. (Note that $A_k^T \epsilon \ll 1$ and $A_k^O \epsilon \gg 1$ where the superscripts T and O denote the type of site.) It follows that

$$R_k^T \approx e^{\alpha_k \epsilon} \quad (9a)$$

and

$$R_k^O \approx e^{\gamma_k / \epsilon} \quad (9b)$$

where

$$\alpha_k = A_k^T (1 - e^{\beta J_{1k}}) (1 - e^{\beta J_{2k}}) \quad (10a)$$

$$\gamma_k = \frac{1}{A_k^O} (1 - e^{-\beta J_{1k}}) (1 - e^{-\beta J_{2k}}) \quad (10b)$$

The superscripts on R denote the site type and we have approximated $1 + \delta \approx e^\delta$ for any $\delta \ll 1$. Equations (9) and (6) predict the form

$$p_2/p_1^2 = C \exp[\alpha\epsilon + \gamma/\epsilon] \quad (11)$$

where $C = e^{-8J_0/12}$, $\alpha = \sum_{k_T} \alpha_k$, $\gamma = \sum_{k_O} \gamma_k$ with the sums in α and γ being over T and O-sites, respectively.

III. FIT TO DATA AND INTERPRETATION

Figure 2 shows a fit of Eq. (11) to the data of p_2/p_1^2 for $C = 4.7$, $\alpha = 31.3$, $\gamma = -5.0 \times 10^{-3}$. Our earlier work [1] had $\gamma = 0$, which clearly gives much poorer agreement because of the sizeable curvature of the $\ln(p_2/p_1^2)$ vs. ϵ plot in Fig. 2 which is adequately explained with a finite γ . These parameters may be interpreted as follows. From $C = 4.7$ we deduce that $8J_0 = -4.0$, the minus sign indicating an attractive interaction between the axial nearest neighbor O-sites 1 and 2 in Fig. 1. On the other hand, the fact that no ESR spectra is observed corresponding to two non-common-axis nearest neighbor sites such as 1 and 3 of Fig. 1 implies a repulsive interaction between these sites. Thus it is reasonable that the sign of J_{1k} varies with the location of site k . It is evident from Eqs. (10) that $\alpha > 0$ implies dominant contribution from T-sites where J_{1k} and J_{2k} have the same sign while $\gamma < 0$ means the major contributors are O-sites for which J_{1k} and J_{2k} have opposite sign. This is quite reasonable in view of the dependences of A_k^T and A_k^O on distance from the impurity. We expect $A_k^T \ll 1$ for T-sites in the vicinity of the impurity and $A_k^T = 1$ in the bulk. Thus α can be influenced significantly by sites well-removed from the impurity, and clearly J_{1k} and J_{2k} should have the same sign when $r_{1k}, r_{2k} \gg a$ where $a = r_{12}$ is the lattice constant. Hence $\alpha > 0$ is expected. But if we assume that A_k^O becomes very large (no O-site occupation) except in the immediate neighborhood of the impurity, it is possible to have J_{1k} and J_{2k} of opposite sign for γ .

For a specific model, assume that A_k^0 is impossibly large except for a next-nearest-neighbor O-site ($\frac{1}{2}\sqrt{3}a$) from the impurity, such as labeled "b" in Fig. 1b (nearest neighbor O-sites at distance $a/2$ are excluded from this consideration). Consistent with a strong repulsive J_{13} , we also assume a strong repulsive J_{1b} since both the pairs (1,3) and (1,b) are nearest neighbor O-sites to one another for which the interactions may be hard-core like. The further distant interactions, as J_0 , are taken to be attractive so that $J_{2b} < 0$. The result is that

$$\gamma \approx \frac{-8}{A_b^0} (e^{\beta|J_{2b}|} - 1) \quad (12)$$

for $e^{-\beta J_{1b}} \ll 1$. The factor 8 represents the total number of type b sites which must be included (4 each for sites 1 and 2).

One should have $|J_{2b}| < |J_0|$ and $A_b^0 > A_1^0$ where A_1^0 is the value for an O-site which surrounds the impurity. The VR data show $A_1^0 \sim 10^3$. Thus an upper limit for $|\gamma|$ is obtained by taking $A_b^0 = 10^3$ and $e^{\beta|J_{2b}|} = 55$ whereby $|\gamma| < 0.4$; so the observed $\gamma = -5 \times 10^{-3}$ is well within this limit and consistent with O-site occupation being confined to the immediate vicinity of the impurity, $A_b^0 \gg A_1^0$.

The interactions also affect p_1 . By applying the same reasoning which led to Eqs. (9) and (10) we predict

$$p_1 = (B/\epsilon) e^{-\frac{\gamma}{2\epsilon}} e^{\lambda\epsilon} \quad (14)$$

with

$$B = 6 \exp \beta [U_T + \sum_{kT} J_{jk} - U'_0 - \sum_{kT} J_{1k}] \quad (15a)$$

$$\lambda = - \sum_{kT} \beta (J_{jk} - A_k^T J_{1k}) + \frac{1}{2} \beta^2 \sum_{kT} A_k^T J_{1k}^2 \quad (15b)$$

where the origins j and l refer to a bulk T-site and a type 1 site of Fig. 1, respectively, mean field theory has been used for the bulk T-sites, and

$B|J_{1k}| \lesssim 1$ has been assumed. The quantity γ in Eq. (14) has the same value as in Eq. (12) as a consequence of the specific model which produced Eq. (13). (Note, however, that the exponent is $-\frac{\gamma}{2}$ in Eq. (15) rather than $+\gamma$, which also follows from the model.) Thus (14) contains only 2 new parameters. Figure 2 shows the fit obtained with $B = 1.6 \times 10^{-3}$, $\lambda = 16.1$ and, as before, $\gamma = -5.0 \times 10^{-3}$. It is about as good as, but no better than, the no-interaction fit [6] with $B = 2.9 \times 10^{-3}$, $\lambda = \gamma = 0$. Since $A_k^T \leq 1$ ($A_k^T \rightarrow 1$ for bulk sites), the fact that $\lambda > 0$ can be understood for attractive interactions or for the first sum in (16b) being negligible regardless of the sign of the interactions. The latter is a likely possibility for long range interactions since the first sum contains contributions only from short distances where $A_k^T \neq 1$ and the discrete nature of the lattice comes into play. If the first sum in (15b) is small, the fits $\lambda = 16$, $\alpha = 31$ imply that $\sum_{kT} J_{1k}^2$ and $\sum_{kT} J_{1k} J_{2k}$ are of comparable size [see Eq. (10a)], which once again is indicative of long range interactions.

IV. SUMMARY AND CONCLUSIONS

By considering the ESR data reported by Venturini and Richards [1] (VR) for both p_1 and p_2 , the relative number of impurities which have 1 and 2 occupied neighbor O-sites, we have inferred properties of proton-proton interactions in a metal hydride (ScH_x). Such inference is not possible from examination of p_1 alone since its behavior can adequately be fit to a model in which interactions are neglected. In the absence of interactions p_2 should be proportional to p_1^2 , in gross disagreement with the data. Further one can show that $p_2 \propto p_1^2$ is expected if the interactions are nearest neighbor only. We have been able to fit the data for both p_2/p_1^2 and p_1 according to a model which has the following features. (i) O-sites are occupied only if they are nearest or next nearest neighbors of the rare earth impurity (sites 1, 2, b of Fig. 1). (ii) O-O interactions are strongly repulsive between nearest neighbors (sites 1 and b of Fig. 1) but

attractive at longer distances (between sites 2 and b of Fig. 1). (iii) Interactions with T-sites are relatively long range so that $\sum_{kT} J_{1k}J_{2k}$ and $\sum_{kT} J_{1k}^2$ are comparable, i.e. terms for which $J_{2k} \approx J_{1k}$ contribute significantly to the sum, which clearly cannot be the case for short-range interactions.

Further evidence that the lack of proportionality between p_2 and p_1^2 is due to interactions comes from comparison of ScH_x and ScD_x [6]. There is a significant isotope effect in p_1 vs. x [6]. However, the curves of p_2/p_1^2 vs. x (not shown) are essentially the same for the hydride and deuteride. This is to be expected if p_1 itself depends on site energies, which [6] depend on isotope via zero-point levels, but p_2/p_1^2 depends only on interactions which are purely electrostatic in origin.

We have not investigated in detail the uniqueness of the form (12) which is a consequence of the simplifying assumptions of Eqs. (10). For example, a very strong attractive O-O interaction such that $A_k^0 \epsilon \ll e^{-\beta J_{1k}}$ or a very strong repulsive O-T one whereby $A_k^T \epsilon \gg e^{-\beta J_{1k}}$ would lead to $R_k \propto \epsilon^{-1}$ or $R_k \propto \epsilon$, respectively, and thus a power law rather than exponential form.

Although the good agreement exhibited in Fig. 2 may not be too surprising in view of the adjustable parameters, the signs of α , γ , λ are significant and consistent with the general features of the model. We feel that the importance of non-nearest-neighbor interactions has been demonstrated to give a satisfactory explanation to the otherwise peculiar behavior of p_2/p_1^2 .

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FIGURE CAPTIONS.

- Fig. 1 (a) Coordination of T (solid circles) and O (open circles) sites around an Er impurity in a fcc metal hydride lattice.
- (b) Typical octahedral sites (open circles) in vicinity of an impurity (large solid circle). Host metal ions shown as smaller solid circles.
- Fig. 2 Impurity-neighbor O-site occupation p_1 and p_2/p_1^2 vs. $\epsilon = (2-x)/x$ for $3cH_x:Er$. Solid curve is fit to Eq. (11) with $C = 4.7$, $\alpha = 31.3$, $\gamma = -5.0 \times 10^{-3}$. Dashed curve is fit to Eq. (14) with $B = 1.6 \times 10^{-3}$, $\lambda = 16.1$, $\gamma = -5.0 \times 10^{-3}$.

(a)

(b)

Fig 1

Fig 2