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Anomalous Site Disorder in Metal Hydrides*

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We point out that existing measurements in *fcc* metal hydrides LaH_x and YH_x of intrinsic disorder $x_0(2)$ (octahedral site occupation at the stoichiometric composition $x = 2$) appear to be highly inconsistent with one another by thermodynamic and spectroscopic techniques. The high-temperature thermodynamic data give $x_0(2) \sim 0.01$, while NMR, ESR, and neutron scattering have $x_0(2)$ an order of magnitude larger at room temperature, where conventional wisdom indicates it should be less. This is explained by a model in which large-amplitude hydrogen vibrations at high temperature prevent occupation of both a tetrahedral and neighbor octahedral sites. Hence $x_0(2)$ decreases at high temperature, and good agreement is found with reasonable values of the parameters.

I. Introduction

The attractiveness of metal hydrides for hydrogen storage has focused attention on the manner in which interstitial sites of the metal lattice are occupied by hydrogen atoms (*1*). For the *fcc* hydrides of concern here, tetrahedral (T) sites are more readily occupied than octahedral (O) ones. Since there are two T sites and one O site per metal ion, one has a simple explanation of why hydrides with a relatively small lattice constant, such as ScH_x, exist only for the hydrogen/metal ratio $x \leq 2$, while larger rare earths, such as LaH_x, can be formed up to $x = 3$. In the former, ScH_x, only T sites can be occupied, while the latter, LaH_x, can accommodate protons in both T and O sites.

A natural question is the extent to which O sites can be occupied at finite temperature for $x \leq 2$. This reflects the amount of disorder in the system, indeed a parameter called "intrinsic disorder" has been defined (*2*) as the fraction of O sites occupied at $x = 2$. The purpose of this paper is to point out that there exist two seemingly contradictory sets of data on the amount of intrinsic disorder in LaH_x and YH_x, but they can be explained by invoking large thermal motions of the protons at high temperature. These, when combined with repulsion at short distances, make the intrinsic disorder *decrease* with increasing temperature, θ, at sufficiently high θ.

Estimates of intrinsic disorder have been obtained by traditional thermodynamic measurements of pressure (p) vs composition (x) isotherms (*3–6*), and more recently by microscopic probes of NMR (*7*), ESR (*8*) (electron spin resonance), and neutron scattering (*9*). The thermodynamic data, which exist only in the range above about 870 K, are all consistent with intrinsic disorder $x_0(2) \leq 0.05$; the most recent results (*5, 6*) give $x_0(2) \approx 0.02$ and 0.01 in LaH_x

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and YH_x, respectively, at about 920 K. This is in stark contrast with the NMR, ESR, and neutron work, all performed at room temperature or lower, which indicate that $x_0(2)$ for YH_x is about 15% at 300 K. Optical absorption measurements (*10*) at low temperature also have indicated appreciable O site occupation for $x < 2$, but no numerical estimate of $x_0(2)$ was made. Since it is logical to expect $x_0(2)$ to increase rapidly with temperature, the discrepancy is extremely large. [Equation (5) below predicts that $x_0(2) = 5 \times 10^{-7}$ at 300 K if it is 0.01 at 900 K.] Definitive low-temperature spectroscopic data do not yet exist for LaH_x. However, earlier estimates (*11*) gave $x_0(2) \sim 5\%$ and the NMR appears to be qualitatively similar (*12*) to YH_x.

I propose that both sets of data are correct and can be explained by a model in which large thermal fluctuations cause $x_0(2)$ to be considerably less above 800 than at 300 K. Before presenting the model in Section III, I review the simple theory in Section II.

II. Simple Lattice Gas Theory

Disorder in metal hydrides has been successfully treated (*13*) by a simple noninteracting lattice gas model whose Hamiltonian is

$$H = -U_T \sum_{i_T} P_{i_T} - U_O \sum_{i_O} P_{i_O}, \quad (1)$$

where $P_i = 1$ or 0 depending on whether site i is occupied or vacant, respectively. U_T and U_O are binding energies at T and O sites, respectively. The constraint on the total number of protons,

$$2\langle P_{i_T}\rangle + \langle P_{i_O}\rangle = x, \quad (2)$$

is handled in the usual way by use of a grand canonical ensemble whereby

$$\langle P_{i_T}\rangle \equiv x_T = \{\exp[-\beta(U_T + \mu)] + 1\}^{-1}, \quad (3a)$$

$$\langle P_{i_O}\rangle \equiv x_o = \{\exp[-\beta(U_O + \mu)] + 1\}^{-1}, \quad (3b)$$

in which μ is the chemical potential, $\beta = 1/k_B\theta$, and triangular brackets indicate thermal average. Simultaneous solution of Eqs. (2) and (3) give the occupations x_o and x_T in terms of $\beta(U_T - U_O)$ and x. We are primarily concerned with small O site occupation for x near 2, whereby the approximations x_o, $1 - x_T \ll 1$ may be made and insertion of Eqs. (3) in Eq. (2) gives

$$-2e^{-\beta(U_T+\mu)} + e^{\beta(U_O+\mu)} = x - 2. \quad (4)$$

At $x = 2$ the intrinsic disorder is

$$x_0(2) = (2)^{1/2}e^{-\beta(U_T-U_O)/2}. \quad (5)$$

The calculation is readily extended to obtain the pressure vs concentration isotherms. Consider the hydride to be in equilibrium with H_2 gas at sufficiently low pressure for the ideal gas law to hold. The total number of molecules in the gas N_G is given by

$$N_G = e^{2\beta\mu} \sum_k e^{-\beta\varepsilon_k} \quad (6)$$

where the sum is over the energy levels ε_k of a gas molecule and the factor 2 in $e^{2\beta\mu}$ accounts for the diatomic molecule. It follows from the ideal gas law that

$$e^{\beta\mu} = Cp^{1/2}, \quad (7)$$

where C is a constant whose value is unimportant for our purposes. Use of Eq. (7) in (4) gives a Sievert's law form

$$Ap^{1/2} - Bp^{-1/2} = x - 2 \quad (8)$$

with A and B appropriate constants. A plot of p vs $(x - 2)p^{1/2}$ should therefore yield a straight line, which holds reasonably well for the tabulated data in Ref. (*3*). Using Eqs. (5), (7), and (8) with a little algebra one can show that

$$x_0(2) = Ap_2^{1/2} = 1/(d\ln p/dx)_{x=2}, \quad (9)$$

where p_2 is the equilibrium pressure at $x = 2$. In this manner one can extract the intrinsic disorder $x_0(2)$ from p vs x isotherms and conclude $x_0(2) \leq 0.05$ in LaH_x and YH_x above 870 K. Note that knowledge of the constant C is not necessary for this analysis. [It should be mentioned that $x_0(2)$ was obtained in Refs. (*5*) and (*6*) from consideration of the disorder entropy vs x. However, the entropy was obtained from analysis of the p vs x isotherm together with enthalpy data and the same lattice gas model used to derive the disorder contribution to entropy. Thus, in effect, they used the same treatment as presented here.]

A modified lattice gas model which accounts for the effect of an impurity metal ion was used to extract $x_0(2)$ from ESR of Er^{3+} impurities in YH_x. The NMR and neutron work do not rely on any lattice gas interpretation and thus, at least in this context, are more direct probes of bulk O site occupation.

III. Extended, High-Temperature Lattice Gas Model

The simple lattice gas model of Eq. (1) neglects both interactions and the possibility of multilevel structure at each site. Although interactions are obviously present, they do not appear to play an overly important role. This is evidenced by the facts that both the ESR and p vs x data can be described reasonably well by the simple noninteracting picture as long as one is in the single-phase hydride region. Thus, most of the effect of interactions can probably be lumped into effective-site energies for our purposes. Since typical vibrational energies (*14*) are 110 meV (~1300 K) and 75 meV (~850 K) for T and O sites, respectively, the occupation of higher energy levels is not likely to be important at and below room temperature, where the NMR, ESR, and neutron data exist. However, I argue that it plays a crucial role at higher temperatures. There is then considerable proton motion, and it may be more appropriate to view the hydride as a liquidlike superionic conductor. In such a picture there are site-to-site hopping and large anharmonic thermal factors (*15*).

The physical idea as sketched in Fig. 1 is that proton–proton repulsion at short distances forbids large-amplitude vibrations toward a site which is occupied. This is consistent with the accepted idea that hopping can occur only to a vacant site.

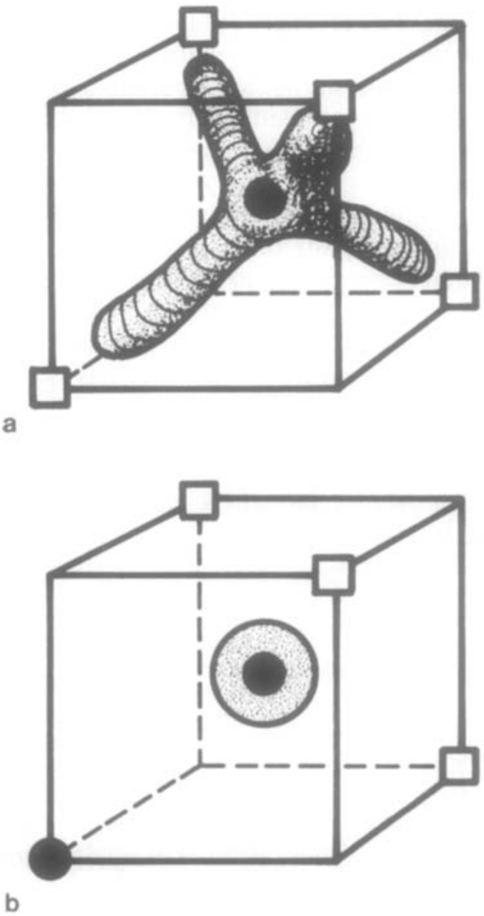

FIG. 1. (a) Occupied T site surrounded by four vacant O sites. In this case large-amplitude vibrations are possible at high temperature, as indicated by density map. Not shown are metal ions which distort density from spherical as indicated. (b) Same as (a) but with a surrounding O site occupied, which prevents large-amplitude motion at T site.

Also note that the metal ions prevent vibrations between T sites, once again consistent with the picture of diffusion taking place along T–O–T paths, so the dominant effect related to site occupation is the T–O interaction. As a consequence one can have all protons in high energy (large vibrational amplitude) states at $x = 2$ only if they are all confined to T sites. Thus O site occupation actually becomes less favorable at high temperature. (Since there are two T sites for each O site, but only one T site vacancy is created for each occupied O site, one cannot eliminate the repulsion at $x = 2$ by producing T site vacancies in the neighborhood of an occupied O site. This would be possible if there were equal numbers of O and T sites.) With large thermal amplitudes the distinction between whether a proton occupies a T site or an O site can become obscure on a microscopic picture. However, for consideration of entropy and thereby thermodynamic properties, the important thing is counting of states; and this is such that the maximum number of available high energy states at $x = 2$ is the same *as if* the protons were confined to T sites.

The above picture is quantified by a model Hamiltonian

$$H = \sum_{i_T} \sum_{\lambda} \epsilon_{T\lambda}\, n_{i_T\lambda} + \sum_{i_O} \sum_{\lambda} \varepsilon_{O\lambda}\, n_{i_O\lambda} + \sum_{i_T i_O}{}' \sum_{\lambda\lambda'} J_{\lambda\lambda'}\, n_{i_T\lambda}\, n_{i_O\lambda} \quad (10)$$

where $n_{i_T\lambda}$ is the occupation number (0 or 1) for a particle at a T site in the level λ with energy $\varepsilon_{T\lambda}$; similar definitions apply to $n_{i_O\lambda}$ and $\epsilon_{O\lambda}$. Since only one particle per site is allowed, we have $\sum_{\lambda} n_{i\lambda} = P_i$, where $P_i = 0$ or 1 is the total occupation used in Eq. (1). The levels are assumed to be bound harmonic oscillator states for energy less than zero and particle-in-a-box extended states for energy greater than zero. That is,

$$\begin{aligned} \varepsilon_{T\lambda} &= -U_T + \hbar\omega_T n_\lambda, && \varepsilon_{T\lambda} < 0, \\ &= \frac{\hbar^2}{2M} k_\lambda^2, && \varepsilon_{T\lambda} > 0, \end{aligned} \quad (11)$$

where $\hbar\omega_T$ is the T site vibrational energy; n_λ is an integer between 0 and the integer value of $U_T/\hbar\omega_T$, where $-U_T$ is the ground state T site energy, just as in Eq. (1); and $k_\lambda^2 = \pi^2(m_x^2 + m_y^2 + m_z^2)/L^2$, with m_x, m_y, m_z integers and L the size of the three-dimensional box in which a proton of mass M with $\varepsilon_{T\lambda} > 0$ is located. Similar definitions hold for O sites with the quantities U_0 and ω_0. For simplicity, we take the box size L to be the same for O and T sites. The interaction $J_{\lambda\lambda'}$ expresses the fact of increased repulsion for the large-amplitude states. We take it to be

$$\begin{aligned} J_{\lambda\lambda'} &= \infty, && \varepsilon_\lambda > 0 \text{ and/or } \varepsilon_{\lambda'} > 0, \\ &= 0, && \text{otherwise}, \end{aligned} \quad (12)$$

which is an obvious oversimplification but conveys the basic meaning that a large vibrational amplitude state is highly unfavorable unless neighbor sites are vacant. [The prime on the summation in Eq. (10) indicates that i_T and i_0 are nearest neighbors.] The partition functions for a T site are written as

$$z_{T\nu} = \sum_{\substack{\lambda \\ \epsilon_{T\lambda}<0}} e^{\beta(U_T - \varepsilon_{T\lambda})} = e^{\beta U_T}(1 - e^{-\beta\hbar\omega_T})^{-3}, \quad (13)$$

$$z_{TG} = \sum_{\epsilon_{T\lambda}>0} e^{-\beta(\hbar^2 k_\lambda^2/2M)} = (\theta/\theta_0)^{3/2}, \quad (14)$$

where $z_{T\nu}$ represents the bound state contribution and z_{TG} that of the gaslike states. In Eq. (13) we have assumed there are a sufficient number of levels of the truncated three-dimensional oscillator that the form for an infinite number can be used. In Eq. (14) the classical limit $\theta \gg \theta_0$ has been assumed where the characteristic temperature is

$$k_B\theta_0 = 2\pi\hbar^2/ML^2. \quad (15)$$

If there is no particle in a neighbor O site the grand partition function for a T site assumes its complete value

$$\bar{z}_T = 1 + (z_{T\nu} + z_{TG})\, e^{\beta\mu}, \tag{16}$$

but if a neighbor O site is occupied, it is restricted to

$$z'_T = 1 + z_{T\nu}\, e^{\beta\mu} \tag{17}$$

if the O site particle has $\varepsilon_{o\lambda} < 0$, and to unity (i.e., no T site occupation) if $\varepsilon_{o\lambda} > 0$.

To lowest order in the density of occupied O sites it is sufficient to consider a cluster containing a central O site and the eight surrounding T sites. According to the reasoning of Eqs. (16) and (17) the grand partition function for such a cluster is

$$z = \bar{z}_T^8(1) + z_T'^8\,(z_{0\nu}e^{\beta\mu}) + (1)(z_{0G}e^{\beta\mu}), \tag{18}$$

where $z_{0\nu}$ and z_{0G} are defined analogous to $z_{T\nu}$ and z_{TG} in Eqs. (13) and (14). This can be rewritten as

$$z = \bar{z}_o\bar{z}_T^8[1 - \Delta], \tag{19}$$

where, analogous to Eq. (16),

$$\bar{z}_o = 1 + (z_{0\nu} + z_{0G})e^{\beta\mu} \tag{20}$$

is the complete O site grand partition function, and

$$\begin{aligned}\Delta &= z_{0\nu}\, e^{\beta\mu}(\bar{z}_T^8 - z_T'^8)/(\bar{z}_o\bar{z}_T^8) \\ &\qquad + z_{0G}e^{\beta\mu}(\bar{z}_T^8 - 1)/(\bar{z}_o\bar{z}_T^8) \\ &= \bar{x}_{0\nu}(1 - z_T'^8/\bar{z}_T^8) + \bar{x}_{0G}(1 - \bar{z}_T^{-8}). \end{aligned} \tag{21}$$

The second equality in Eq. (21) comes from recognizing that the average occupation numbers of an O site by bound ($\varepsilon_{o\lambda} < 0$) and gaslike ($\varepsilon_{o\lambda} > 0$) states are $\bar{x}_{0\nu} = z_{0\nu}e^{\beta\mu}/\bar{z}_o$ and $\bar{x}_{0G} = z_{0G}e^{\beta\mu}/\bar{z}_o$, respectively, in the absence of interactions, just as the total average occupation number in the absence of interactions is $\bar{x}_o = (z_{0\nu} + z_{0G})e^{\beta\mu}/\bar{z}_o$. The total average occupation numbers x_o and x_T are obtained by noting that if z is expressed as

$$z = \sum_{n_o=0}^{1} f(n_o) \quad \text{or} \quad z = \sum_{n_T=0}^{8} g(n_T),$$

where n_o and n_T are the numbers of occupied O and T sites in the respective expansions, then

$$x_o = \sum_{n_o=0}^{1} n_o\, f(n_o) \Big/ \sum_{n_o=0}^{1} f(n_o)$$

and

$$x_T = \left(\frac{1}{8}\right) \sum_{n_T=1}^{8} n_T g(n_T) \Big/ \sum_{n_T=1}^{8} g(n_T).$$

We thereby obtain

$$x_o = (\bar{x}_o - \Delta)/(1 - \Delta), \tag{22}$$

$$x_T = \bar{x}_T \left[1 - \bar{x}_o + \bar{x}_{0\nu}\frac{\bar{x}_{T\nu}}{\bar{x}_T}\left(\frac{z'_T}{\bar{z}_T}\right)^7\right] \Big/ (1 - \Delta), \tag{23}$$

where $\bar{x}_T = (z_{T\nu} + z_{TG})e^{\beta\mu}/\bar{z}_T$ and $\bar{x}_{T\nu} = z_{T\nu}e^{\beta\mu}/\bar{z}_T$ are total and bound state T site occupations, respectively, in the absence of interactions.

In arriving at Eq. (23) use has been made of the fact that if $(1 + ye^{\beta\mu})^8 = \sum_{n=0}^{8} g(n)$, where $g(n)$ is the term containing $e^{n\beta\mu}$ and y is any constant, then

$$\frac{1}{8}\sum_{n=0}^{8} ng(n) \Big/ \sum_{n=0}^{8} g(n) = ye^{\beta\mu}/(1 + ye^{\beta\mu}).$$

For concentration x near 2 and small O site occupation the quantities x_o, $\bar{x}_o$, $\bar{x}_{0G}$, $1 - x_T$, $1 - \bar{x}_T$, $1 - \bar{x}_{T\nu}$ may all be taken as small. These imply $z_{o\alpha}\, e^{\beta\mu} \ll 1$, $z_{T\alpha}\, e^{\beta\mu} \gg 1$, where α stands for ν or G. Equation (22) is therefore approximated by

$$x_o = z_{0\nu}\,(1 + z_{TG}/z_{T\nu})^{-8}\, e^{\beta\mu} \equiv \tilde{z}_o e^{\beta\mu} \tag{24}$$

and (23) reduces to

$$x_T \approx \bar{x}_T = 1 - (z_{T\nu} + z_{TG})^{-1}\, e^{-\beta\mu}. \tag{25}$$

Comparison of Eqs. (24) and (25) with Eqs. (3) for $1 - x_T$, $x_o \ll 1$ shows that the only effect of the more complex model presented here is to replace $e^{\beta U_T}$ and $e^{\beta U_o}$ by $z_{T\nu} + z_{TG}$ and $\tilde{z}_o$, respectively. It follows that the form (8) remains valid for the p vs x isotherm and the intrinsic disorder becomes

$$x_0(2) = (2)^{1/2}[\tilde{z}_0/(z_{\mathrm{T}v} + z_{\mathrm{TG}})]^{1/2}. \qquad (26)$$

If the gas ($\epsilon > 0$) phases are negligible there is no major effect. But if $z_{\mathrm{TG}} \gg z_{\mathrm{T}v}$, Eq. (24) shows a sizable reduction in $\tilde{z}_0$ below z_{0v}, and hence a much smaller value of $x_0(2)$ results. Numerical examples are presented in the next section.

IV. Numerical Examples

The intrinsic disorder given by Eq. (26) is calculated for the following values of parameters which appear to be reasonable.

$U_{\mathrm{T}} - U_{\mathrm{O}} = 0.1$ eV [chosen to give $x_0(2) \sim 0.2$ at room temperature (*7*, *9*)].

$U_{\mathrm{T}} = 0.2$ eV [representative value for barrier height inferred from NMR activation energy for diffusion (*16*)].

$\hbar\omega_{\mathrm{T}} = 110$ MeV, $\hbar\omega_{\mathrm{O}} = 75$ MeV (neutron inelastic scattering (*14*) in LaH$_x$).

$L^3 = (1/8)a^3\ [1 - \pi/3(2)^{1/2}]$, with $a = 5.66$ Å, the lattice constant for LaH$_2$. [This corresponds to the available volume (volume of lattice minus volume of hard-sphere metal ions) per T site. Use of this figure in Eq. (15) gives $\theta_0 = 85$ K.]

The resulting variation of $x_0(2)$ with temperature is shown in Fig. 2, together with points taken from the various experiments mentioned earlier. The curve with ω_0, ω_{T}, and L for YH$_x$ is indistinguishable from that shown for LaH$_x$. Agreement is seen to be quite satisfactory. It should be mentioned, though, that the results are very sensitive to the value of U_{T}, since this barrier determines the amount of large-amplitude (gaslike) states. For $U_{\mathrm{T}} = 0.3$ eV, and the other parameters unchanged, $x_0(2)$ is increased to 0.20 at 1000 K.

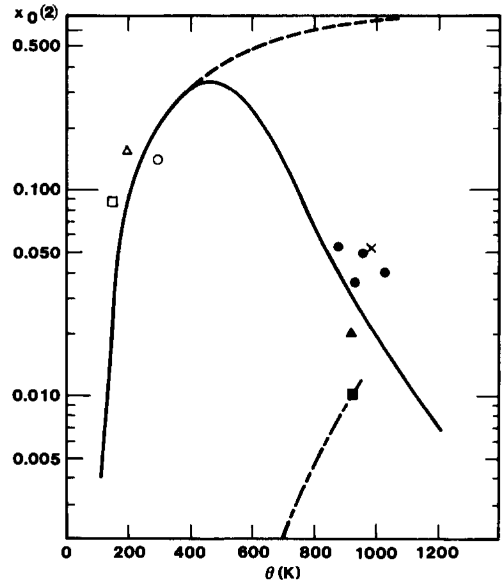

FIG. 2. Intrinsic disorder $x_0(2)$ vs temperature θ. Solid curve—Eq. (26) with parameters as given in Sect. IV. Dashed curve—Lattice gas result in neglect of extended states. Dash–short dash curve—Eq. (5) with parameters to fit 920 K data for YH$_x$, gives $x_0(2) = 5 \times 10^{-7}$ at 300 K. □—YH$_x$, Ref. (*8*); △—YH$_{1.98}$, Ref. (*7*); ○—YH$_{1.98}$, Ref. (*9*); ●—LaH$_x$, Ref. (*3*); ×—LaH$_x$, Ref. (*2*); ▲—LaH$_x$, Ref. (*5*); ■—YH$_x$, Ref. (*6*).

V. Conclusions

This paper has shown that the intrinsic disorder in an *fcc* hydride [$x_0(2) =$ O site occupation at the stoichiometric H/metal ratio $x = 2$] decreases with increasing temperature if proton–proton repulsions prevent large-amplitude vibrations between an O and a T site when both sites are occupied. Consequently, the discrepancy between high-temperature thermodynamic measurements which show a relatively small $x_0(2)$ and low-temperature spectroscopic ones which give an order of magnitude larger $x_0(2)$ is resolved. Quantitative agreement is very good for reasonable values of the parameters using a simple model in which the repulsion is taken to be infinite.

A more reasonable calculation would, of course, have a finite J, and also account might be taken of highly anisotropic vibrations instead of the simple particle in a cubic box employed here. Both of these would tend to diminish the effect. The calculation here implicitly assumes $\beta J \gg 1$; otherwise the large overlap of a T site vibration onto an occupied O site would not be so highly unfavorable. If the vibrations are anisotropic, one would not require *all* of the neighbor sites to be unoccupied. The qualitative effect illustrated here should nonetheless remain.

The theory predicts $x_0(2)$ to go through a maximum vs temperature, and it obviously would be desirable to have measurements to check this rather than having to rely on the fairly limited data presently available in which no one technique is used at both high and low temperature. Unfortunately, there are problems in attaining such data. Pressure vs composition measurements are difficult at low temperature because of the low equilibrium pressures and surface effects. NMR cannot be used to identify site occupation at high temperatures where the protons are diffusing or highly delocalized. Careful analysis of thermal parameters obtained from neutron scattering may provide the best hope.

Note added in proof. Since submission of this manuscript, new data have appeared which show $x_0(2) \approx 0.03$ between about 100 and 300 K for YH_2. These were obtained by neutron inelastic scattering (J. Goldstone *et al.*, International Symposium on Electronic Structure and Properties of Hydrogen in Metals, Richmond, Va., March 1982). At the same conference, E. L. Venturini reported $x_0(2) = 0.02$ in LaH_2 from impurity ESR at low temperature. These data fit the general pattern shown in Fig. 2 except for the fact that the new neutron data give no temperature variation between 100 and 300 K.

I have also kindly been informed by G. G. Libowitz of an earlier analysis (G. G. Libowitz and J. B. Lightstone, Proceedings, 6th Rare Earth Research Conference, 1967) of pressure composition isotherms in CeH_2 which showed $x_0(2) \approx 0.03$ with only a small temperature variation between 600 and 1100 K. Appropriate modification of the theory to include a finite J can reproduce these data. However, it does not seem possible to make $x_0(2)$ temperature independent below room temperature because only ground states of the potential wells should be occupied and the simple lattice gas model should therefore hold.

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