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TITLE TEMPERATURE AND CONCENTRATION DEPENDENCE OF HYDROGEN SITE
OCCUPANCY IN SEVERAL RARE-EARTH DIHYDRIDES

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TEMPERATURE AND CONCENTRATION DEPENDENCE OF HYDROGEN SITE OCCUPANCY IN
SEVERAL RARE-EARTH DIHYDRIDES

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Neutron inelastic scattering and diffraction techniques were used to study the hydrogen site distribution in several rare earth dihydrides as a function of temperature and concentration. For Y, La, and Ce the fraction of hydrogen on octahedral sites is approximately a constant from 15K to 200K followed by a decrease with increasing temperature. A model is presented which qualitatively explains this behavior.

1. Introduction

The preferential occupation of interstitial sites by hydrogen in the rare earth dihydrides has been the subject of considerable interest[1-12]. Most rare earth hydrides(REH_x) have a cubic CaF_2 structure (space group $Fm3m$) near $x=2$ which contains two tetrahedral(t) and one octahedral(o) interstitial sites per metal atom. Under normal conditions of pressure and temperature, hydrogen first fills the t sites. However, dual site occupancy has been observed for $x < 2.0$, i.e. before all the t-sites are filled, particularly in those REH_x which can be loaded well beyond $x=2$. The fraction of o-sites occupied at $x=2.0$ has been defined as the intrinsic disorder[9].

In order to study the systematics of site occupation in the rare earth dihydrides, we have extended our previous work[11] on YH_x to include the similar systems LaH_x and CeH_x . Inelastic neutron scattering studies were again carried out over a concentration range of $1.9 < x < 2.0$ for temperatures

between 15K and 490K. A powder diffraction experiment was also performed in LaH_{2.1} to provide more detailed structural results. As in the previous work the o-site occupancy was found to be approximately constant between 15K and 200K and then decrease with further increase in temperature in agreement with the model developed earlier[11]. A further consideration of this model is presented here which correctly predicts the abrupt drop to zero occupancy of o-sites near x=1.9.

2. Experimental Method

The binary hydrides used in this study were prepared by the direct reaction of hydrogen gas and each metal in a quartz reaction tube of a modified Sievert's hydriding system. Each metal hydride was weighed to compare hydrogen loading ratios from pressure-volume and weight gain. Typical agreement was better than 0.25%. Exposure to air was avoided during all handling and no evidence of oxidation was observed with this handling procedure.

Neutron diffraction and inelastic incoherent neutron scattering experiments were performed on the time-of-flight instruments at the pulsed spallation neutron source (LANSCE) at the Los Alamos National Laboratory. Diffraction data at 15 and 300 K were taken on the general purpose diffractometer[13]. Only the high resolution (0.45% $\Delta\lambda/\lambda$) detector bank was analyzed using a Reitveld profile refinement code appropriate for pulsed sources[14].

The inelastic measurements were performed on two inverted geometry spectrometers for which the final flight time (sample to detector) is fixed by selecting a particular energy band from the scattered neutron beam, the

filter difference spectrometer(FDS) [15] and the crystal analyzer spectrometer (CAS)[16]. Inelastic data on these samples were taken at temperatures from 15 to 490K. The data were corrected for background, and intensities were normalized by the incident spectrum. Data were converted to the scattering function $S(Q,\omega)$ by correcting for the Debye-Waller factor, the thermal occupation, and the Jacobian for the time to energy conversion so that the area under the optic mode peak is proportional to the number of hydrogen atoms.

3. Results

Inelastic incoherent neutron scattering spectra for La and Ce hydrides are shown in figures 1-2. The yttrium data has been previously published(see fig 1, of ref. 11). The large structured peak observed at ~100 meV and above is the vibrational spectrum of t-site hydrogens. The width and structure of this peak is believed to be the result of dispersion in the optic modes as was observed in measurements of the phonon dispersion relations on the system[12] $\text{CeD}_{2.12}$. The much weaker peak evident at 70-80 meV is characteristic of the o site hydrogen vibrations. Phonon dispersion measurements again on $\text{CeD}_{2.12}$ have shown this to be dispersionless. This distinct separation of the t-site and o-site hydrogen vibrations allows inelastic incoherent scattering to be employed to determine relative occupation by hydrogen on the two sites. This is invaluable as neutron diffraction techniques take considerably more time due to the hydrogen background. In samples which contain o site hydrogen, a shoulder develops with increasing hydrogen concentration on the high energy side of the

tetrahedral peak. The origin of this shoulder is believed to lie in interactions between o-site and t-site hydrogen.

Powder diffraction data on Y and La were analyzed with the CaF_2 structure (Fm3m) allowing the hydrogen occupation at the o-sites (position b at $1/2, 1/2, 1/2$) and the t-sites (positions c at $1/4, 1/4, 1/4$) to vary. The low temperature patterns were also analyzed by allowing o-site hydrogen to be displaced along [111] in accordance with the results of diffraction studies on several closely related hydride systems. No significant improvement in the Rietveld powder refinement was obtained.

From both the inelastic scattering and neutron diffraction data, the fraction of hydrogen atoms occupying o-sites can be extracted. Figure 3 shows the fraction of hydrogen atoms on o-sites (half the value of intrinsic disorder) for $\text{YH}_{2.0}$, $\text{CeH}_{2.1}$, $\text{LaH}_{2.0}$, and $\text{LaH}_{2.1}$. The inelastic spectra of $\text{CeH}_{2.1}$ and $\text{LaH}_{2.0}$ broadened severely at the high temperatures, which prevented a reasonable determination of the o-site occupancy.

4. Discussion

No evidence of o-site occupation was found in the $\text{LaH}_{1.9}$, $\text{CeH}_{1.9}$, and $\text{CeH}_{2.0}$ samples. Furthermore the o-site peak is seen to be split near 78K in La and Ce, which may be the result of a lowering of the site symmetry of the o-site. Since it is known from X-ray data that the metal lattice remains fcc (thereby ruling out a crystallographic distortion), one may assume that o-site hydrogen atoms move off the site with full cubic symmetry. The diffraction data on $\text{LaH}_{2.1}$ confirm this assumption. While the room temperature data could be fit well with the CaF_2 structure and the hydrogens on

their high symmetry site, the 13K data could not. Upon allowing the H-atoms to move along the [111] direction, t-site hydrogen atoms were found to move only slightly off while the o-site hydrogen atoms were displaced by 0.137(9)Å. This new site (x,x,x) has two significantly different nearest neighbor H-La distances and can therefore easily account for the splitting of the o-site vibration peak. No previous evidence for a phase transition at this concentration has been reported to the authors' knowledge. This shift in the o-site position increases the number of available sites in the lattice by a factor of eight and may account for the constancy in the relative occupation of o-sites at lower temperatures. A determination of the exact nature of the low temperature phase transition requires further study on deuterated samples.

In the simple lattice gas model[17], the intrinsic disorder is expected to increase with temperature, so it is remarkable that the disorder is lower at 900K than at 300K. If the intrinsic disorder were given by this model, the disorder should reach its saturation value well below 900K. An attempt to reconcile this inconsistency led to a model which invoked proton-proton repulsion in the excited vibrational states to prevent nearest neighbor o-site and t-site occupation. This model however required a decrease in the o-site occupation at lower temperature (<400K) not observed in the data. Modifications to this basic model were proposed to include vibration of the metal lattice (acoustic modes) and proton-proton interactions[11]. These additions to the model show that a decrease in entropy occurs when hydrogen moves from the t-site to the o-site so that total entropy increases with increasing temperature even though the site disorder decreases.

A curious feature of the data is that o-site occupation is not seen in the La sample with $x=1.9$ (see fig. 2a) although there is considerable disorder at $x=2.0$. Simple theory[18] predicts that the intrinsic disorder should only be reduced to about 0.05 at $x=1.9$ if it is 0.1 at $x=2.0$ and thus be appreciable. This can be understood in terms of our previously published model using the same interaction parameters. It was noted there that at low temperature, there are two solutions for the intrinsic disorder (eq.1 of ref 11); and one must choose the one which gives the lower free energy. It can be shown that the chemical potential corresponding to the two roots x_1 and x_2 satisfy:

$$2(u_1 - u_2)/k_B T = \ln [(x_1/\delta + x_1)/(x_2/\delta + x_2)] - \Gamma(x_1 - x_2)$$

where $\delta = 2-x$ and Γ is related to the interactions as discussed in detail in ref 11. With $\Gamma > 0$ the larger value is the correct root a (lower u) for $\delta \leq 0$, consistent with ref. 11 which was confined to $\delta=0$. However, the condition changes to the other root when δ is sufficiently positive. For typical values of the parameter[11] the cross-over occurs for $\delta > 0.02$ and the lower root has intrinsic disorder ~ 0.001 . Thus the same model which described the anomalous temperature dependence also correctly predicts negligible o-site occupation for $x < 2.0$.

5. Conclusions

The intrinsic disorder (octahedral site occupation) has been shown to decrease monotonically with increasing temperature for three rare earth

hydrogen systems (Ce, La, Y) and also decrease to zero for $x=1.9$. Both these observations have been qualitatively explained by the same model which is based on detailed entropy calculation. The lack of o-site occupation occupancy at $x=1.9$ can also be explained by selection of the proper root of the disorder equation.

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References:

- [1] D. J. Peterman, B. N. Harmon, J. Marchiando & J. H. Weaver, Phys. Rev. B19 (1979) 4867.
- [2] J. H. Weaver, R. Rosei & D. T. Peterson, Phys. Rev. B19 (1979) 4855.
- [3] D. Khatamian, W. A. Kamitakahara, R. G. Barnes & D. T. Peterson, Phys. Rev. B21 (1980) 2622.
- [4] D. L. Anderson, R. G. Barnes, D. T. Peterson & D. R. Torgeson, Phys. Rev. B21 (1980) 2625.
- [5] E. L. Venturini & P. M. Richards, Phys. Lett. 76A (1980) 344.
- [6] E. L. Venturini in: Electronic Structure and Properties of Hydrogen in Metals P. Jena and C. B. Satterwaite, eds. (Plenum Press, New York 1983) p.97.
- [7] P. G. Dantzer & O. J. Kleppa, J. Chem. Phys. 73 (1980) 5259.
- [8] W. L. Korst & J. C. Warf, Inorg. Chem. 10 (1966) 1719.
- [9] G. G. Libowitz in: Solid State Chemistry of Binary Metal Hydrides, (Benjamin, New York, 1965) p.119.
- [10] P. G. Dantzer & O. J. Kleppa, J. Solid State Chem. 35 (1980) 34.
- [11] J. A. Goldstone, J. Eckert, P. M. Richards & E. L. Venturini, Solid State Comm. 49 (1984) 475.
- [12] C. J. Glinka, J. M. Rowe, J. J. Rush, G. G. Libowitz & A. Maeland, Solid State Comm. 22 (1977) 541.; P. Voderwisch, S. Hauteclier & W. D. Teuchert, Solid State Comm. 25 (1978) 213.
- [13] A. K. Soper, A. I. P. Conference Proceedings, Vol 89 "Neutron Scattering-1981" (1982) p23.
- [14] R. B. Von Dreele, J. D. Jorgenson & C. G. Windsor, J. Appl. Cryst. 15 (1982) 581.
- [15] A. D. Taylor, E. J. Wood, J. A. Goldstone & J. Eckert, Nucl. Inst. Meth. 221 (1984) 408.
- [16] J. Eckert, J. A. Goldstone, D. Tonks & D. Richter, Phys. Rev. B27, (1983) 1980.
- [17] P. M. Richards, J. Solid State Chem. 43 (1982) 5.
- [18] E. L. Venturini, J. Less Comm. Metals 74 (1980) 45.

Figure 1: Inelastic incoherent neutron scattering spectrum of $\text{CeH}_{2.1}$ at 12K. The broad peak at 103 meV is due to t-site hydrogen and the one at 70 meV to o-site hydrogen.

Figure 2: Inelastic incoherent neutron scattering spectrum of $\text{LaH}_{1.9}$ at 15K(a). The broad peak at 98 meV is due to t-site hydrogen and no o-site occupation is evident. Inelastic incoherent neutron scattering spectrum of $\text{LaH}_{2.1}$ at 15K(b) and 175K(c). The broad peak at 98 meV is due to t-site hydrogen and the one at 72 meV to o-site hydrogen. Note the change in the peak shape of the o-site vibrational mode from 15K to 175K.

Figure 3: The fraction of hydrogen atoms on o-sites as a function of temperature and concentration. The solid curve is the model fit to the $\text{YH}_{2.0}$ data (see text and ref. 11). $\odot$ - $\text{YH}_{2.0}$ ND; $\boxplus$ - $\text{LaH}_{2.1}$ ND; $\bullet$ - $\text{YH}_{2.0}$ IINS; $\blacktriangle$ - $\text{LaH}_{2.0}$ IINS; $\blacksquare$ - $\text{LaH}_{2.1}$ IINS; $\blacktriangledown$ - $\text{CeH}_{2.1}$ IINS; $\circ$ - YH_x [7]; $\times$ - LaH_x [8-10]; $*$ - $\text{LaH}_{2.0}$ ESR[6]; ∇ - $\text{YH}_{2.0}$ ESR[5]; $\triangle$ - YH_x NMR[4]; $\square$ - YH_x ND[3]; where ND = neutron diffraction, IINS = incoherent inelastic neutron scattering, and symbols without references are our data.

FIGURE 1

$S(Q, \omega)$ (arb units)

ENERGY TRANSFER (meV)

FIGURE 2

SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH

FRACTION OF HYDROGEN ON O-SITES

FIGURE 3