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Crystal structure of $YD_{1.96}$ and $YH_{1.98}$ by neutron diffraction

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The crystal structure of $YD_{1.96}$ and $YH_{1.98}$ has been examined at room temperature and 11 K by neutron-diffraction techniques. Refinement of the data reveals the occupation of both tetrahedral and octahedral interstices of the fcc metal lattice. These results help to explain some features observed in the optical properties of YH_x.

I. INTRODUCTION

Yttrium, which has the hexagonal close-packed structure at room temperature, takes up hydrogen at elevated temperatures to form homogeneous cubic hydride phases with an approximate range of compositions from $YH_{1.80}$ to $YH_{2.04}$. In these hydrides, the basic structure is the CaF_2 structure, with the metal atoms in an fcc lattice, and the hydrogen atoms in the tetrahedral interstices. Until very recently, the H atoms were believed to be exclusively in tetrahedral sites, but it will be shown below that a significant fraction of the atoms occupy octahedral sites at compositions near YH_2. Yttrium can take up more hydrogen to form trihydride phases, but the lattice structure then transforms to hexagonal again.

Recently two companion papers[1,2] in this journal reported and discussed some low-energy, composition-dependent features in the optical absorptivity of YH_x. The features could not be interpreted in terms of self-consistent band-structure calculations[2] based on a perfect CaF_2 structure, in which hydrogen atoms occupy all available tetrahedral sites. Partial occupation of octahedral sites was suggested[1,2] to explain the observations. The present work, motivated by these recent results, is intended to clarify some uncertainties in their interpretation.

II. EXPERIMENTAL DETAILS

In order to have consistent results, the bulk samples were prepared from the same original materials and under the same conditions employed to prepare samples for optical measurements.[1] These bulk samples then were powdered for NMR and neutron-diffraction experiments. The $YD_{1.96}$ sample was enclosed in a cylindrical aluminum container 0.6 cm in diameter and 2.5 cm in length. For $YH_{1.98}$ a tetragonal container $0.2 \times 2.5 \times 3.5$ cm^3 was used. In this case, transmission geometry was used to minimize the absorption corrections. These samples, like some other hydrides, are reactive with moisture and oxygen from the air; all handling of the samples was therefore carried out in a glove box in an argon atmosphere. The hydrogen or deuterium concentration of the specimens was determined by a hot vacuum extraction method. The hydrogen was pumped from a weighed sample at about 1250 K into a calibrated volume. The accuracy and precision of this analytical technique is about one per cent.

The experiments were carried out on the Ames Laboratory two-axis diffractometer at the Oak Ridge Research Reactor. Data were collected over a range of 2θ from 15° to 123° using neutrons of wavelength 1.732 Å. The (311) planes of a germanium monochromator were employed at a take-off angle of 61°, yielding enough resolution to separate completely all peaks except for (420), which overlaps the aluminum (222) peak from the sample container. Since, in the case of $YH_{1.98}$, (420) is a strong peak, no problem was encountered in correcting for the Al(222) intensity. For $YD_{1.96}$ an accurate correction was not possible. Therefore, the sample was re-encapsulated in a vanadium container and the intensity of the (420) peak was measured again with more accuracy. The duration of a set of runs sufficient for one sample at a given temperature was about four days. Longer counting times were allowed for weak peaks and the intensities were normalized at the end of each run. The 11-K runs were made using a closed-cycle helium gas refrigerator.

III. RESULTS AND DISCUSSION

The data were analyzed using the Busing-Martin-Levy crystallographic least-squares program.[3] In this method one compares the integrated intensity of each peak with a calculated intensity, and minimizes an aggregate squared difference (WR defined in a footnote in Table I). For $YH_{1.98}$, an absorption correction was applied to the observed intensities. A satisfactory refinement of the data was achieved with a model,[4] based on the fluorite structure, but which allows variable octahedral as well as tetrahedral site occupation. The intensity structure factors are

TABLE I. Observed and calculated squared structure factors for $YD_{1.96}$ and $YH_{1.98}$ at 300 and 11 K, and measured lattice constants.

	$YD_{1.96}$ at 300 K			$YD_{1.96}$ at 11 K			$YH_{1.98}$ at 300 K			$YH_{1.98}$ at 11 K		
hkl	F_0^2	F_c^2	$\sigma(F_0^2)$[a]	F_0^2	F_c^2	$\sigma(F_0^2)$[a]	F_0^2	F_c^2	$\sigma(F_0^2)$[a]	F_0^2	F_c^2	$\sigma(F_0^2)$[a]
111	83	82	2	82	80	2	444	439	11	421	442	11
002	26	26	1	33	32	1	1268	1277	20	1343	1371	20
220	606	609	8	626	630	6	<0.1	0.1	0.5	<0.1	0.1	0.5
311	69	69	2	76	77	1	369	374	11	451	424	11
222	19	19	2	20	24	1	1116	1104	38	1346	1312	34
400	509	501	10	571	570	8	<0.1	0.0	0.5	<0.1	0.1	0.5
331	58	58	1	77	74	1	319	318	15	402	406	12
420	14	14	1				1002	954	51	1326	1256	40
422	412	412	5	521	516	5	<0.1	0.1	0.5	<0.1	0.1	0.5
333/511	50	50	3	68	72	3	269	271	19	388	389	16
WR[b]		0.008			0.021			0.014			0.036	
a(Å)		5.192 ± 0.002			5.188 ± 0.002			5.205 ± 0.002			5.197 ± 0.002	

[a] $\sigma(F_0^2)=F_0^2N^{1/2}/(N-N_b)$ where N is the total number of counts under a peak, and N_b is the number of background counts.

[b] WR is the weighted R factor defined by $\mathrm{WR}=[\Sigma W(F_0^2-F_c^2)^2]^{1/2}/(\Sigma WF_0^4)^{1/2}$, where $W=1/\sigma^2$.

shown in Table I and the fitted parameters are given in Table II. The scattering lengths of hydrogen and deuterium were taken to be -0.374×10^{-12} and 0.667×10^{-12} cm respectively.[5] For the scattering length of yttrium, the values 0.78×10^{-12} cm (Ref. 6) and 0.765×10^{-12} cm (Ref. 7) were tried; the latter was found to give more consistent results, and only these results are listed in the tables. Refinements based upon models in which the hydrogen or deuterium atoms are displaced from the octahedral $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ or the tetrahedral $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ sites were explored, but no such displacements could be detected. As one can see from Table II, except for $YD_{1.96}$ at 300 K, the values of the temperature factors for octahedral and tetrahedral sites were assumed to be the same.

In Table II the quoted errors are three times the calculated standard deviations. The larger errors and weighted R factors for the $YH_{1.98}$ sample arise from high background and associated statistical uncertainty due to the large incoherent cross section of hydrogen for thermal neutrons.

The results of this experiment, which are direct evidence for the premature (i.e., before complete filling of all tetrahedral sites) occupation of the octahedral sites, support the assumption made by Peterman *et al.*[2] in their explanation of the optical features observed by Weaver *et al.*[1] Occupation of octahedral sites in the presence of empty tetrahedral sites has also been reported by Titcomb *et al.*[4] for CeD_x, LaD_x, and PrD_x, but it is somewhat more surprising in YH_x, which does not form a fluorite-based trihydride. Other observations that should be made on the results of Table II are (i) the occupancy of octahedral sites is lower at 11 K than at 300 K, and (ii) the octahedral site occupancy is larger in $YH_{1.98}$ than in $YD_{1.96}$. Neither of these tendencies is far outside the quoted limits of error, and one should be wary of attaching too great a significance to them. Nonetheless, the first tendency is at least physically reasonable. One can easily imagine hydrogen atoms to move by thermal activation from lower-energy tetrahedral sites to higher-energy octahedral sites, thereby increasing octahedral occupancy at higher temperatures. However, we have no information on how quickly thermal equilibrium is reached, or whether our results are representative of samples in equilibrium. Weaver *et al.*[1] also observed that the low-energy feature in the absorptivity could be enhanced by quenching samples from high temperature, and our speculation

TABLE II. Occupation numbers and temperature factors for $YD_{1.96}$ and $YH_{1.98}$ at 300 and 11 K.

Sample	Occupancy		Temperature factors		
(Temperature)	$n_{\text{octahedral}}$	$n_{\text{tetrahedral}}$	$B(Y)$	B (D or H)$_{\text{octahedral}}$	B (D or H)$_{\text{tetrahedral}}$
$YD_{1.96}$(300 K)	0.088 ± 0.008	1.852 ± 0.028	1.15 ± 0.12	1.45 ± 0.09	1.41 ± 0.09
$YD_{1.96}$(11 K)	0.068 ± 0.032	1.940 ± 0.095	0.29 ± 0.10	0.91 ± 0.26	0.91 ± 0.26
$YH_{1.98}$(300 K)	0.136 ± 0.030	1.838 ± 0.083	1.10 ± 0.15	0.85 ± 0.56	0.85 ± 0.56
$YH_{1.98}$(11 K)	0.119 ± 0.066	1.895 ± 0.123	0.29 ± 0.27	0.30 ± 0.60	0.30 ± 0.60

that octahedral occupancy increases with temperature is consistent with their observations.

Our estimates of the octahedral site occupancy in $YH_{1.98}$ are in good agreement with recent NMR measurements[8] on the same sample, as described in the following paper.

IV. SUMMARY

The crystal structure of $YD_{1.96}$ and $YH_{1.98}$ has been examined at room temperature and 11 K by neutron-diffraction techniques. Refinement of the $YD_{1.96}$ ($YH_{1.98}$) structure shows that D(H) atoms are distributed over both tetrahedral and octahedral interstices of the fcc metal lattice. The results from $YD_{1.96}$ ($YH_{1.98}$) at room temperature reveal that 8.8 ± 0.8 (13.6 ± 3.0) percent of the octahedral sites are occupied at the expense of tetrahedral sites. Measurements at 11 K indicate about two per cent lower octahedral occupancy than at room temperature. These results provide direct evidence for the partial occupancy of the octahedral sites and help to explain[2] the observed[1] low-energy, composition-dependent optical features of YH_x. We have not observed any distortion or superlattice ordering at either temperature.

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