

## Location of deuterium in $\alpha$ -yttrium

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Neutron-diffraction techniques have been used to assess the deuterium location in a single crystal of  $\alpha$ -yttrium. We find that in the  $\alpha$  phase of  $YD_x$  ( $x = 0.176$ ) the deuterium atoms occupy predominantly the tetrahedral sites of the hcp lattice. The isotropic temperature factor of yttrium, obtained in the present experiment, is found to be smaller than that of pure yttrium. This result indicates that the addition of deuterium hardens the phonon frequency spectrum of the host metal.

### I. INTRODUCTION

At sufficiently high temperatures transition metals form with hydrogen or deuterium a solid solution, the  $\alpha$  phase, where the atoms of the light elements are statistically distributed among the metallic interstices. Yttrium is a subgroup IIIA transition metal which, because of similar properties, is usually associated with the rare-earth metals. At room temperature the Y-H (or Y-D) system is in the  $\alpha$  phase<sup>1</sup> up to a concentration of approximately nineteen atomic percent of H (or D). Above this concentration the  $\alpha$  phase coexists at room temperature with the cubic (fcc)  $\gamma$  phase.

The properties of the cubic  $\gamma$  phase can be conveniently studied at room temperature for a hydrogen concentration close to that of the dihydride. The structure of this hydride is essentially that of  $CaF_2$ , with the metal atoms in an fcc lattice and the hydrogen atoms in the tetrahedral interstices. Recent neutron-diffraction measurements<sup>2</sup> on powdered samples of  $YD_{1.96}$  and  $YH_{1.98}$  showed, however, that a small fraction ( $\sim 5\%$ ) of the lighter element occupies the octahedral sites of the fcc lattice. Actually, this partial octahedral occupancy may be responsible for the low-energy, composition-dependent characteristics<sup>3,4</sup> of the optical absorptivity of  $YH_2$ .

In this paper we present the results of a neutron-diffraction study of the  $\alpha$  phase of the Y-D system. Deuterium instead of hydrogen was chosen in this investigation since neutron-diffraction measurements<sup>5</sup> on the  $\alpha$  phase of  $TiD_x$  indicated that a significant fraction of deuterium atoms occupy the octahedral sites. These results suggested<sup>5</sup> the possibility of an isotopic effect since neutron-diffraction measurements on the  $\alpha$  phase of both  $TiH_x$  (Ref. 6) and  $ZrH_x$  (Ref. 7) yielded no evidence of any significant occupation of the octahedral sites. Our measurements show that in the  $\alpha$  phase of  $YD_x$  the deuterium atoms

occupy predominantly the tetrahedral sites of the hcp lattice. The octahedral occupancy, if any, in the  $\alpha$  phase of  $YD_x$  is not significantly larger than that found in the  $\gamma$  phase.

### II. EXPERIMENTAL DETAILS

For the preparation of the samples, we used 99.9 at. % pure yttrium prepared<sup>8</sup> in the Ames Laboratory and 99.5 at. % pure deuterium purchased from Matheson Company. A single crystal of pure yttrium was prepared<sup>9</sup> by annealing an arc-melted sample at 1250°C for 24 h in a high-vacuum furnace and then cooling down to room temperature. The single-crystal sample, after careful electropolishing to remove any surface contamination, was placed in a platinum boat and heated to 600°C in a standard high-vacuum ( $2 \times 10^{-7}$  Torr) furnace before deuterium was admitted to the system. Approximately half of the required deuterium was then admitted to the system from a calibrated volume filled to a measured pressure with deuterium prepared by the thermal decomposition of  $UD_3$ . The  $YD_2$  layer formed on the surface of the crystal was allowed 100 h to decompose and the deuterium was allowed to diffuse into the crystal before admitting the remainder of the deuterium into the system. The crystal was then maintained at 600°C for three weeks to ensure complete decomposition of  $YD_2$  as well as homogeneous distribution of deuterium. Small crystallites on the surface of the crystal, formed probably by the formation and decomposition of  $YD_2$ , were removed by careful grinding. The deuterium concentration was estimated, from the pressure change of the calibrated volume of deuterium allowed to react with the crystal, to be  $15.0 \pm 0.2$  at. %.

The mosaic spread of the pure-Y single crystal was assessed by measuring the full width at half maximum (FWHM) of the rocking curve obtained using a monochromatic neutron beam from a Ge perfect crystal monochromator. No change in the

TABLE I. Atomic coordinates ( $x, y, z$ ), site occupancy ( $c$ ), and thermal parameters ( $\langle u_x^2 \rangle$ ,  $\langle u_z^2 \rangle$ ,  $B$ ) of  $YD_{0.176}$  at room temperature.  $\langle u_x^2 \rangle$  and  $\langle u_z^2 \rangle$  denote the mean square atomic displacements parallel and perpendicular to the basal plane, respectively, and  $B$  is the isotropic temperature factor. Measured lattice constants:  $a = 3.662 \pm 0.005$ ,  $c = 5.778 \pm 0.005$ .

Atom	$x$	$y$	$z$	$c$	$\langle u_x^2 \rangle$ ( $\text{\AA}^2$ )	$\langle u_z^2 \rangle$ ( $\text{\AA}^2$ )	$B$ ( $\text{\AA}^2$ )
Y	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1	$0.0077 \pm 0.0003$	$0.0108 \pm 0.0003$	$0.69 \pm 0.04$
D <sub>tetr.</sub>	$\frac{1}{3}$	$\frac{2}{3}$	$0.644 \pm 0.002$	$0.154 \pm 0.010$	$0.015 \pm 0.004$	$0.021 \pm 0.003$	$1.24 \pm 0.29$
D <sub>oct.</sub>	0	0	0	$0.016 \pm 0.010$	$0.10 \pm 0.30$	$0.06 \pm 0.10$	$6.8 \pm 18.1$

FWHM (approximately 10 min of arc) of the rocking curve of the crystal was detected after deuteration of the sample. The measured lattice constants of the deuterated sample were found to be consistent<sup>1</sup> with the deuterium concentration of the sample. Also, no evidence of any  $YD_2$  was found in the neutron-diffraction pattern of the deuterated crystal. In order to minimize the secondary extinction correction the measurements were performed using a pillar-shaped crystal (1 cm long with a  $2 \times 2$ -mm<sup>2</sup> base) cut from the original deuterated sample. The long axis of the pillar was chosen to be very close to the [110] direction.

The measurements were performed using the Ames Laboratory double-axis diffractometer at the 30-MW Oak Ridge Research Reactor. A monochromatic neutron beam ( $\lambda = 1.025 \text{ \AA}$ ) obtained from the (111) planes of a Ge monochromator was used to avoid corrections to the data arising from any  $\lambda/2$  component of the incident beam. The integrated reflectivities of forty ( $h0l$ )-type reflections were measured. The results obtained by measuring equivalent reflections were consistent to within experimental precision and their average was used in the analysis of the data.

### III. RESULTS AND DISCUSSION

In the present experiment the integrated reflectivities of forty reflections were measured at room temperature and the results were analyzed using the Busing-Martin-Levy crystallographic least-squares program.<sup>10</sup> In analyzing the data, the deuterium atoms were assumed to be randomly distributed among the tetrahedral ( $\frac{1}{3}, \frac{2}{3}, z$ ;  $\frac{2}{3}, \frac{1}{3}, -z$ ;  $\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z$ ;  $\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z$ ) and octahedral ( $0, 0, 0$ ;  $0, 0, \frac{1}{2}$ ) sites of the hcp lattice, and the scattering lengths of yttrium and deuterium were taken<sup>2</sup> to be  $0.667 \times 10^{-12}$  cm and  $0.765 \times 10^{-12}$  cm, respectively. The deuterium concentration  $c$  was varied in successive fits to the experimental results. The parameters listed in Table I provide

TABLE II. Comparison of observed and calculated square structure factors for  $YD_{0.176}$  at room temperature.

$hkl$	$ F_0 ^2$	$ F_c ^2$
002	$1243 \pm 23$	1343
004	$891 \pm 18$	892
006	$755 \pm 18$	727
008	$669 \pm 13$	661
100	$410 \pm 9$	404
200	$389 \pm 9$	371
300	$1260 \pm 24$	1291
400	$265 \pm 6$	254
500	$192 \pm 5$	189
101	$705 \pm 14$	780
201	$685 \pm 15$	720
401	$512 \pm 12$	519
501	$386 \pm 8$	405
102	$356 \pm 8$	344
202	$314 \pm 8$	308
302	$1021 \pm 22$	1028
402	$219 \pm 6$	208
502	$162 \pm 4$	157
103	$962 \pm 19$	969
203	$868 \pm 19$	881
403	$602 \pm 12$	603
503	$440 \pm 9$	455
104	$225 \pm 6$	207
204	$206 \pm 6$	193
304	$793 \pm 14$	690
404	$146 \pm 4$	142
105	$916 \pm 20$	883
205	$800 \pm 18$	799
405	$533 \pm 10$	538
106	$194 \pm 6$	181
206	$175 \pm 5$	166
306	$572 \pm 11$	569
406	$115 \pm 3$	117
107	$515 \pm 14$	532
207	$484 \pm 10$	485
108	$166 \pm 4$	159
208	$146 \pm 4$	144
308	$485 \pm 9$	496
109	$290 \pm 6$	297
209	$257 \pm 6$	273

the best fit to the experimentally determined integrated reflectivities. Notice that the values obtained for  $c$  and  $z$  are in good agreement with the estimated deuterium concentration in the sample (see Sec. II) and the geometrical position ( $z=0.634$  was obtained using the measured lattice constants) of the tetrahedral sites, respectively.

It can be seen from Table II and Fig. 1 that the experimentally determined intensities are in good agreement with the values calculated using the parameters listed in Table I. From an examination of Tables I and II and Fig. 1 it is evident that in the  $\alpha$  phase of  $YD_x$  the deuterium atoms occupy predominantly the tetrahedral sites of the hcp lattice. The octahedral occupancy, if any, is not significantly larger than that found<sup>2</sup> in the  $\gamma$  phase of  $YD_x$ . Notice also that our results for the tetrahedral and octahedral site occupancies (see Table I) are in excellent agreement with the values obtained from NMR measurements<sup>11</sup> on  $YH_{0.20}$  under the assumption that hydrogen occupies predominantly the tetrahedral sites. Neutron-diffraction measurements<sup>12</sup> performed on the  $\alpha$  phase of the hcp rare-earth metals showed directly that the H atoms occupy the tetrahedral sites and there is evidence from x-ray measurements<sup>13</sup> that this is also the case for the  $\gamma$  phase of Sc. Thus there

is considerable experimental evidence that in both the  $\alpha$  and the hydride phase of the subgroup IIIA transition elements the tetrahedral sites are energetically favorable. The situation is not as clear in the case of the IVA transition metals. Neutron-diffraction experiments on the  $\alpha$  phase of both  $TiH_x$  and  $ZrH_x$  again yielded no evidence of any significant occupancy of the octahedral sites. On the other hand, neutron-diffraction experiments<sup>5</sup> on  $TiD_x$  found significant occupancy of the octahedral sites in both the  $\alpha$  and  $\beta$  phase. If the discrepancy between the results obtained for the  $\alpha$  phase of  $TiH_x$  and  $TiD_x$  is due to an isotropic effect, our results show that there is no experimental evidence for such an effect in  $\alpha$ -yttrium.

Unfortunately, no neutron-diffraction measurements of the temperature factors of pure yttrium are currently available for a detailed comparison<sup>14</sup> with the results obtained in the present experiment. In the following discussion we will use the temperature factors obtained<sup>15</sup> by fitting the room-temperature dispersion curves of pure Y to a Born-von Kármán model (using the harmonic approximation and temperature-independent force constants); in such an analysis, effects on the temperature factors due to thermal expansion and

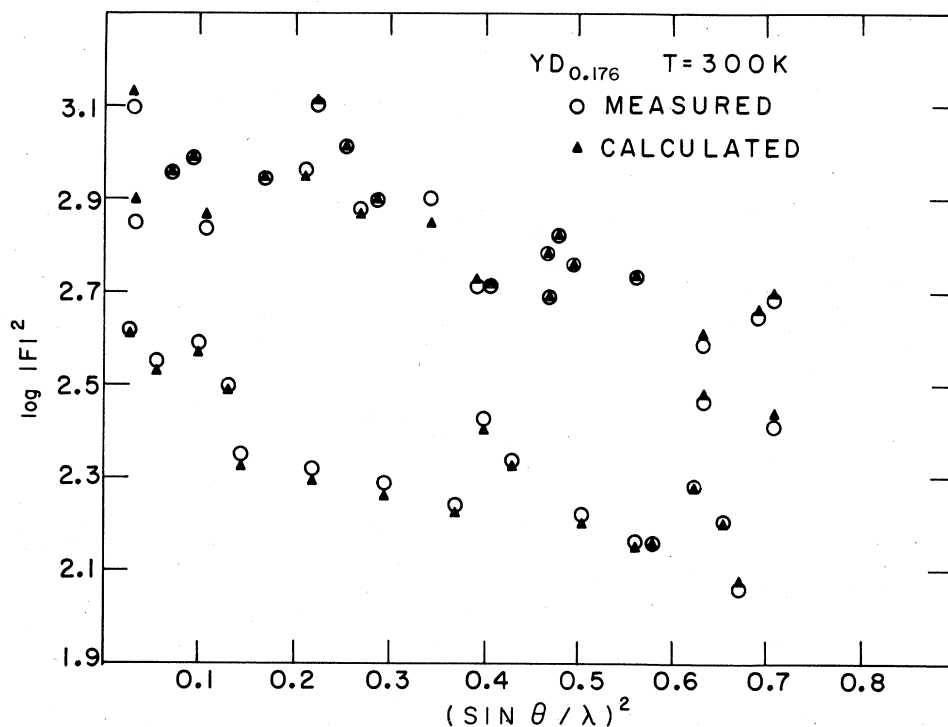


FIG. 1. Comparison of observed and calculated structure factors of  $YD_{0.176}$  at room temperature.

intrinsic anharmonic effects are ignored.

The yttrium isotropic temperature factor ( $0.69 \pm 0.04$ ) obtained from the analysis of our experimental results is somewhat smaller than the value 0.88 for pure yttrium.<sup>15</sup> This result indicates that in  $\alpha$ -yttrium the addition of deuterium hardens the phonon frequency spectrum of the host metal. This conclusion is consistent with the results of heat-capacity measurements<sup>16</sup> on the  $\alpha$  phase of  $\text{LuH}_x$ . This effect cannot be explained without a more complete understanding of the lattice dynamics and electronic properties of  $\alpha$ -yttrium than is currently available. However, it may be due partly to the decrease in the electronic screening of the lattice vibrations caused by a decrease in the electronic density of states at the Fermi level. In fact, heat-capacity measurements<sup>16</sup> on the  $\alpha$  phase of  $\text{LuH}_x$  showed a decrease in the coefficient ( $\gamma$ ) of the electronic specific heat with increasing H concentrations. It should also be pointed out that the results obtained in the present experiment indicate

that the anisotropy in the thermal motion of the yttrium atoms in  $\text{YD}_{0.176}$  is considerably larger than that in pure yttrium.<sup>15</sup> However, the calculations are not sufficiently sensitive to the anisotropy in the thermal motion of the yttrium atoms to allow us to draw a more definitive conclusion. Clearly, a detailed investigation of the phonon dispersion curves using inelastic neutron scattering techniques will contribute substantially to our understanding of the effect of H on the lattice-dynamical properties of the host metal. Such studies on  $\text{YD}_{0.176}$  are presently in progress in this laboratory.

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<sup>14</sup>A neutron-diffraction measurement of the temperature factors of pure Y would be of interest in itself since the lattice-dynamical calculations (Ref. 15) indicate that  $\langle u_x^2 \rangle > \langle u_y^2 \rangle$ , a result to be contrasted to that ( $\langle u_x^2 \rangle < \langle u_y^2 \rangle$ ) obtained in neutron-diffraction measurements (Ref. 17) on Be, for which  $c/a$  is also less than 1.633.

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