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Studies of the Rare-Earth Hydrides
Technical Report VIII

CRYSTAL STRUCTURE OF THE RARE-EARTH HYDRIDES.
X-RAY DIFFRACTION BY RARE-EARTH HYDRIDE AMALGAMS

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THE CRYSTAL STRUCTURES OF THE HYDRIDES OF
LANTHANUM, CERIUM, PRASEODYMIUM
AND NEODYMIUM

Introduction

X-ray powder diffraction photographs of the hydrides of lanthanum, cerium, praseodymium, and neodymium obtained in the present investigation show that these hydrides all possess f.c.c. lattices, in agreement with previously-reported findings of other investigators. Hydrides having a composition slightly richer in hydrogen than $MH_{1.8}$ (the hydrogen-rich phase in the two-phase region) display the largest lattice constants. Addition of further hydrogen results in a slight contraction of these lattices. A plot of lattice constants versus compositions for the hydrides of these four metals is given in Figure 7. Individual values are tabulated in the following individual sections for the different metals.

Similar data have been obtained by Holley, Mulford, Allinger, Koehler, & Zachariasen (1955), who have published a similar plot, together with a table of lattice constants for the hydrides of compositions MH_2 . These values are in

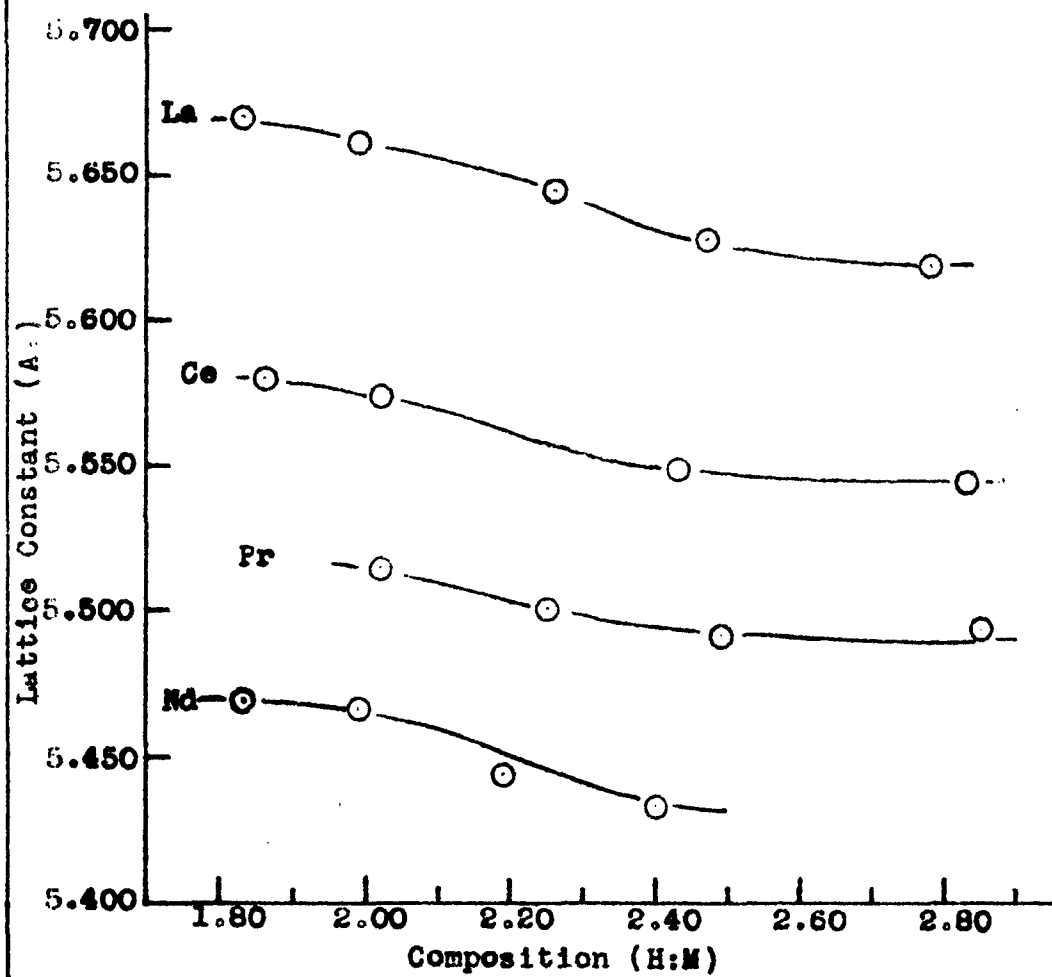


Figure 7

Variation in Hydride Lattice Constants with Composition

excellent agreement with the largest lattice constants found in the present work, that is, for compositions somewhat below MH_2 , in most cases. A table comparing these values is given below.

Holley, et al.		This work	
Hydride	a_0 (A.)	Hydride	a_0 (A.)
LaH_2	5.667 ± 0.001	$LaH_{1.86}$	5.670 ± 0.002
CoH_2	5.581 ± 0.001	$CoH_{1.83}$	5.580 ± 0.002
PrH_2	5.517 ± 0.001	$PrH_{1.02}$	5.515 ± 0.002
NdH_2	5.470 ± 0.001	$NdH_{1.83}$	5.469 ± 0.002

Diffraction patterns for some samples in the two-phase region have also been obtained. All of these show the presence of the hydrogen-rich phase, with lattice constants the same as those listed above. Together with this lattice there appeared in some cases a f.c.c. pattern giving a lattice constant within experimental error of that for the metal, presumably the hydrogen-poor phase of the two-phase region. The exact composition of this phase is not known, nor can it be definitely said that there is a difference between the lattice constants for it and for the metal itself in its f.c.c. modification. Some films also showed a f.c.c. pattern which has been attributed to a monoxide formed on the surface of the sample--other evidence for such a phase has been discussed above in Chapter IV, in connection with x-ray diffraction studies of the metals themselves.

Some comparative values for hydride and deuteride phases have been obtained, which indicate the deuterides to have slightly smaller lattice constants than the hydrides.

Experimental

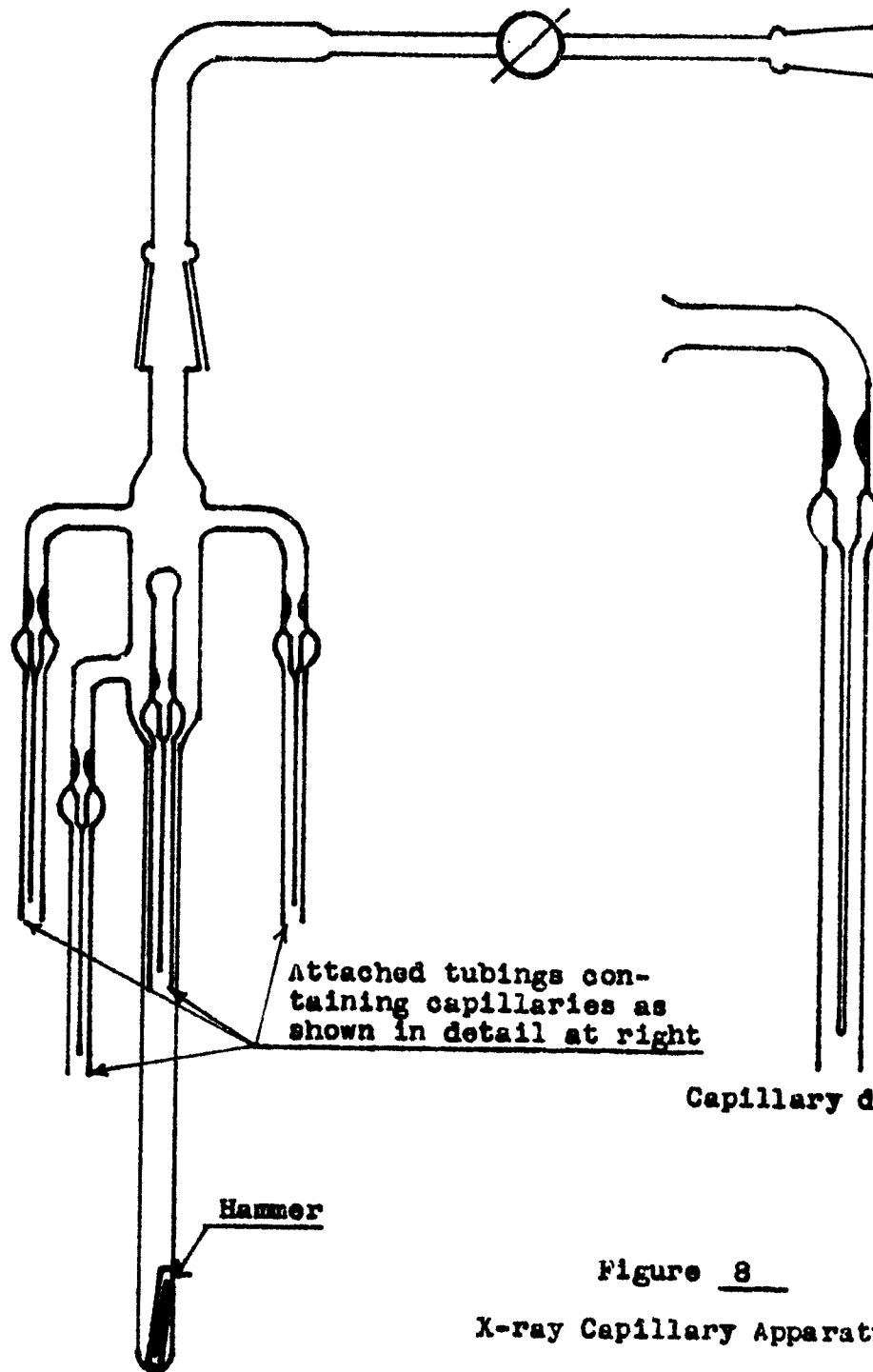
Apparatus

An apparatus was prepared which had the X-ray diffraction capillaries directly attached to it, so that the hydride samples could be shaken into them, and thus never come into contact with any atmosphere other than hydrogen. A sketch of the apparatus is given in Figure 8, and its construction will be described in some detail, since no very satisfactory description of such an apparatus could be found in the literature.

X-ray capillaries.--Capillaries were prepared from pyrex test tubes of about 19 mm. O. D., by drawing them down successively, first to a diameter of about 3 mm., and then to a diameter of about 0.5 mm. The capillaries were cut so that a short length at one end was of the larger diameter--this end was flanged, and after the small end of the capillary was sealed shut, the flanged end was sealed into a length of 7-mm. pyrex tubing in a small ring seal. The 7-mm. tubing had been previously prepared with the bulb

110

To
Vacuum
Line



Attached tubings con-
taining capillaries as
shown in detail at right

Capillary detail

Hammer

Figure 8

X-ray Capillary Apparatus

and thickened portion shown in the sketch, and the end was subsequently bent for sealing to the reaction vessel. Placement of the capillary within an outer tube in this manner gives it excellent protection.

Reaction vessel.--The reaction vessel consisted of a 12-cm. length of 13-mm. vycor tubing, attached to the same-sized pyrex tubing through a graded seal. Overall length of 13-mm. tubing was about 24 cm. The vycor end was sealed shut, and the pyrex end was sealed to an 8-cm. length of 22-mm. pyrex tubing, to the upper end of which was sealed half of a ground-glass joint. The capillaries described above were sealed to the 22-mm. section so that they paralleled the length of the vessel. The first was sealed near the bottom of this section, the next two opposite each other at 90° to the first, and about half-way up the section, and the final two at 90° to these, again opposite each other, and near the upper end of the section.

In some preparations a small molybdenum-foil cup was placed in the bottom of the vessel, fitting closely. The final addition to the vessel was a small hammer, constructed of a 4-cm. length of 5-mm. pyrex tubing sealed at both ends and containing a length of iron rod. The reaction vessel was attached to the vacuum line through a short length of tubing containing a stopcock, and having ground-

glass joints at both ends. "Varno-Cement" was used to seal these joints during the course of a preparation.

Procedure

Cleaning of the metal samples and purification of the hydrogen used were the same as described in Chapter III. Samples were outgassed at varying temperatures from 300-600° C. Subsequently, reaction usually began upon admission of hydrogen at room temperature from the gas buret. After the initial absorption was completed, the reactor was closed off, and hydrogen in the line was pumped into the gas buret, using the Toepler pump. The reactor, together with the section of tubing above it containing the stop-cock, was then removed from the line and placed on a shaker until the product was well pulverized by the action of the glass hammer. The reactor was then replaced on the vacuum line, and the sample was taken through several cycles of heating and cooling, to temperatures as high as 700° C. in some cases, to ensure completeness of reaction, and a homogeneous product. During such heating the pyrex hammer would be kept suspended out of the hot zone by a small magnet adjacent to the reaction vessel. In some cases the reactor was removed for additional shaking between such cycles. The initial pulverizing usually resulted in desorption of some gas, which was usually all reabsorbed after

several cycles of heating and cooling. The first sample was removed after pumping out the line and reactor into the gas buret, with the reaction vessel at room temperature. Composition was usually found to be about $\text{MH}_{2.8}$. The method of procedure was to remove the reactor from the line as described above, and tip it to shake some product into the first capillary. This was facilitated by adroit manipulation of the hammer with a magnet.

Subsequent samples were similarly removed after additional gas had been pumped into the buret, the hydride having been heated to produce an appreciable dissociation pressure. All gas was pumped out of the line and reactor and into the buret before each sample was removed, so that all hydrogen was either in the buret or in the solid product. The sample was always at room temperature during the latter part of this pumping. Heating before removal of the last sample in each case usually reached $700-800^{\circ}\text{C.}$, to produce a dissociation pressure high enough to make removal of gas with the Toepler pump feasible.

The capillaries were removed from the reactor by sealing them off at the thickened portion. The outer 7-mm. tubing was then marked with a file, and cracked with the heated end of a glass rod, leaving the capillary exposed, which could then be sealed off about 17 mm. from the end,

thus to give a capillary of suitable length for the X-ray camera.

The amount of the total product removed each time was neglected in calculating the compositions of samples removed subsequently. The average weight of a number of X-ray samples was found to be between 4 and 5 mg., while the metal sample used was usually of the order of 1000 mg. It may be easily shown that removal of five 5-mg. samples at approximately equal intervals of composition from $MH_{2.80}$ to $MH_{1.80}$ would result in a corrected composition of $MH_{1.79}$ for the last sample, while the uncorrected value would be $MH_{1.80}$. Intermediate samples would be less in error, and this is certainly negligible compared to other errors inherent in the system.

Most of the samples were annealed for approximately 48 hours at about $540^{\circ} C.$, to give films having better resolution. Films of the samples richest in hydrogen were first prepared without having annealed the samples, except for their having been cooled slowly in hydrogen while still on the vacuum line. The samples were then subjected to the same annealing treatment, and in some cases withstood it. Some loss of hydrogen owing to diffusion through the thin pyrex capillaries may have occurred during the annealing of the hydrogen-rich samples. This is especially thought to

have occurred for the $\text{LaH}_{2.78}$ sample, which reacted with the capillary, and is discussed below. Such reaction was not observed for the other hydrogen-rich samples which withstood the annealing. Samples less rich in hydrogen would not be expected to undergo any significant loss, as the pressure of hydrogen in the capillary owing to dissociation would not have been very high.

Structures of the Hydrides

Lanthanum hydride

Five samples of lanthanum hydride, progressively poorer in hydrogen, were prepared as described above in the experimental section, and the λ -ray diffraction pattern for each was obtained. The compositions of these samples, together with the corresponding f.c.c. lattice constants, are given in the following table.

<u>H:La</u>	<u>a_0 (Å.)</u>
2.78	5.619 ± 0.010
2.47	5.628 ± 0.005
2.26	5.645 ± 0.005
1.99	5.661 ± 0.005
1.83	5.670 ± 0.002

It is seen that the cell constants follow the general trend as described above. The data from which these values were derived are tabulated in Appendix III, Tables 28 and 29. The lattice constants for the samples poorer in hydrogen

are more accurate, as patterns for these samples were better resolved.

Another pattern for $\text{LaH}_{2.78}$ was obtained after the sample had been annealed 53 hours at 475°C. , a treatment the hydrogen-rich samples did not usually undergo without causing the containing capillary to burst. The data for this film are tabulated in appendix III, Table 30. The pattern showed lines for two f.c.c. lattices, with a_0 values of 5.297 ± 0.010 and $5.727 \pm 0.010 \text{ \AA.}$ Microscopic examination of the capillary showed that its inside wall had been attacked. No break in the capillary was evident, and the greater part of the sample retained its former black appearance. But there were some greyish-white flecks in the sample, and it is considered likely that some oxide and/or silicide had formed. The larger f.c.c. lattice probably corresponds to the strong lines of h.c.c. La_2O_3 , and to an actual h.c.c. lattice constant of approximately $11.45 \text{ \AA.}$ The smaller f.c.c. lattice constant is within experimental error of that for f.c.c. lanthanum, and corresponds to the metal or to the hydrogen-poor phase.

It is not clear why a metal phase should form from the hydride, unless there could have been considerable diffusion of hydrogen through the thin pyrex wall of the capillary. Though the sample probably contained only about

1 cc. (N.T.P.) of hydrogen before being annealed, the initial pressure in the capillary on heating would have been quite high (evidenced by bursting of other such hydrogen-rich samples). That diffusion may well have occurred is indicated by the findings of Busey & Ciaugue (1953) concerning the diffusion of hydrogen through pyrex glass. Errors introduced by such hydrogen loss have been discussed above.

In addition, samples of composition $\text{LaH}_{1.49}$ and $\text{LaH}_{0.33}$ were obtained from two of the dissociation pressure experiments. These samples were exposed to nitrogen in the line and CO_2 in a dry box, sealed into pyrex capillaries, and annealed at 540°C . for 12 and 20 hours, respectively. The diffraction pattern for the former corresponded to two f.c.c. lattices, while the latter displayed three f.c.c. lattices, as well as several unidentified lines. The lattice constants are tabulated below, while the diffraction data may be found in Appendix III, Tables 31 and 32.

$\text{LaH}_{1.49}$	$\text{LaH}_{0.33}$
$5.670 \pm 0.002 \text{ \AA}$.	$5.669 \pm 0.003 \text{ \AA}$.
$5.239 \pm 0.010 \text{ \AA}$.	$5.247 \pm 0.008 \text{ \AA}$.
	$5.292 \pm 0.010 \text{ \AA}$.

The largest value for each is doubtless that of the hydrogen-rich phase, of approximate composition $\text{LaH}_{1.8}$. The second value in each case most probably corresponds to

that of the lanthanum monoxide described in Chapter IV, the formation of which would have been caused by contact of the sample during the annealing with the small amount of CO_2 and perhaps air sealed into the capillaries. The third value for $\text{LaH}_{0.33}$ of 5.292 ± 0.010 Å. is within experimental error of that for f.c.c. lanthanum, and is considered to represent the hydrogen-poor phase of the two-phase region. Failure to observe the lines of the hydrogen-poor phase in the $\text{LaH}_{1.49}$ sample may be ascribed to the fact that the proportion of this phase present at this composition would be rather small.

On the other hand it is possible, though less likely, that the phase with a_0 of 5.292 Å. could represent a small proportion of a lanthanum nitride phase, LaN . This might be decided by intensity measurements, but they could not be made with sufficient accuracy for this film, since it was not too well resolved, and there was considerable overlap among the various lines.

The unidentified lines on the $\text{LaH}_{0.33}$ film appear to be ascribable to hexagonal La_2O_3 , though this cannot be certain.

In addition one sample of lanthanum deuteride of composition $\text{LaD}_{0.95}$ was obtained from a dissociation pressure experiment. This sample was prepared as were the hydride

samples described just above. Diffraction data are tabulated in appendix III, Table 33. Its diffraction pattern showed lines corresponding to two f.c.c. lattices, with cell constants of 5.251 ± 0.002 Å. and 5.662 ± 0.003 Å. The former probably corresponds to lanthanum monoxide, as discussed above, and the latter to the deuterium-rich phase of the two-phase region. It is seen that the deuteride phase displays a slightly smaller lattice parameter than the corresponding hydride phase. Similar observations have been reported for the hydrides and deuterides of lithium, uranium, and hafnium, and are summarized by Sidhu (1954).

Cerium hydride

Films were obtained for four samples of various compositions of cerium hydride, which were prepared as described above in the experimental section. The cell constants, tabulated below, follow the general trend as described above. The data from which the constants are derived may be found in appendix III, Tables 34 and 35.

<u>H:Ce</u>	<u>a_0 (Å.)</u>
2.83	5.545 ± 0.003
2.43	5.549 ± 0.002
2.02	5.574 ± 0.002
1.86	5.580 ± 0.002

In addition one sample of cerium deuteride of composition $\text{CeD}_{0.56}$ was obtained from the dissociation pressure

studies. This sample was exposed to nitrogen in the line and to CO_2 in the dry box, sealed into a pyrex capillary, and annealed 8 hours at about 540°C . Its diffraction pattern showed lines corresponding to two f.c.c. lattices, of $5.569 \pm 0.003 \text{ \AA}$. and $5.123 \pm 0.005 \text{ \AA}$. The diffraction data are in appendix III, Table 36. The larger lattice constant doubtless corresponds to the deuterium-rich phase of the two-phase region, while the smaller probably corresponds to that observed above in the case of the annealed metal sample, which is thought to be that of a monoxide.

Praseodymium hydride

Films were obtained for four samples of praseodymium hydride of various compositions, prepared as described above. The compositions of the samples, together with the corresponding f.c.c. lattice constants, are given in the following table.

<u>H:Pr</u>	<u>a_0 (Å.)</u>
2.85	5.495 ± 0.003
2.49	5.491 ± 0.005
2.25	5.501 ± 0.005
2.02	5.515 ± 0.002

The data from which these constants were derived are to be found in appendix III, Tables 37 and 38.

In addition one sample of composition $\text{PrH}_{0.79}$ was obtained from the dissociation pressure studies. This sample

was exposed to both nitrogen in the vacuum line and to CO_2 in a dry box, sealed off, and annealed for 20 hours at about 540°C . Its diffraction pattern showed lines corresponding to two different f.c.c. lattices, with cell constants of $5.518 \pm 0.005 \text{ \AA}$. and $5.14 \pm 0.01 \text{ \AA}$. Data from this photograph may be found in Appendix III, Table 39. The former value corresponds to that for the hydrogen-rich phase of the two-phase region, while the latter may be ascribed to the hydrogen-poor phase, or may be due to a monoxide.

Neodymium hydride

Films were obtained for four samples of various compositions of neodymium hydride, which were prepared as described above in the experimental section. The diffraction data are tabulated in Appendix III, Tables 40 and 41, and the cell constants derived therefrom are tabulated below.

<u>H:Nd</u>	<u>a_0 (Å.)</u>
2.40	5.433 ± 0.005
2.19	5.444 ± 0.003
1.99	5.467 ± 0.002
1.83	5.469 ± 0.002

In addition one sample of composition $\text{NdH}_{0.76}$ was obtained from the dissociation pressure studies. This sample was exposed to nitrogen in the line and CO_2 in the dry box, sealed into a pyrex capillary, and annealed approximately

9 hours at about 540° C. The diffraction data are tabulated in Appendix III, Table 42. The lines correspond to two f.c.c. lattices, of 5.466 ± 0.004 Å. and 5.693 ± 0.003 Å.

The former value doubtless corresponds to the lattice of the hydrogen-rich phase. The latter value probably corresponds to that observed above in the case of the annealed metal sample, which is thought to be that of a monoxide.

Discussion

It has been shown that the hydrides of the rare earth metals discussed in this chapter are considerably expanded over the parent metal structures. This expansion is a maximum for the hydrides of approximate composition $MH_{1.8}$, or slightly richer in hydrogen--apparently a maximum, therefore, for the hydrogen-rich phase of the two-phase region. A comparison of the lattice constants of the metals and hydrides is made below, and the percentage change in molecular volume is also given.

	<u>a_0 (Å.)</u>		
	<u>Metal</u>	<u>Hydride</u>	<u>ΔV (%)</u>
La	5.307	5.670	21.9
Ce	5.115	5.590	25.3
Pr	5.153	5.515	22.6
Nd(d.hsp)	3.655	5.469	19.9
c	11.796		

Further addition of hydrogen has been shown to result in a slight contraction of the lattice. This contraction

in volume for the hydride of approximate composition $MH_{2.8}$ relative to the hydride of approximate composition $MH_{1.85}$ ranges from 1.1% for the case of praseodymium to 2.6% for the case of lanthanum. These values must be considered only as approximate, however, as lattice constants for the hydrides having a higher content in hydrogen are less accurately known than those for the hydrogen-rich phase of the two-phase region.

Holley, et al. (1955) reported maximum lattice constants for samples of composition MH_2 , and a gradual decrease with increasing hydrogen content. Since these lattice constants agree well with those found in the present investigation for samples of approximate composition $MH_{1.85}$, which represents the hydrogen-rich phase of the two-phase region, and since Holley, et al. identify these samples as being the hydrogen-rich phase of the two-phase region, it is probable that the compositions of the hydrides considered to be MH_2 by Holley, et al. were actually somewhat lower in hydrogen.

This gradual contraction of the hydride with addition of hydrogen beyond the composition corresponding to the rich phase in the two-phase region can be correlated with the sharp rise in dissociation pressure which also occurs at compositions somewhat below MH_2 . Neutron diffraction work

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by Holley, et al. has been reported as demonstrating that the two hydrogen atoms in hydrides of composition MH_2 are situated in the tetrahedral positions, and that additional hydrogen enters the octahedral positions. Two samples of cerium hydride had been investigated using neutron diffraction, of reported compositions CeH_2 and $CeH_{2.48}$. Here again the composition of the phase described as CeH_2 was probably somewhat lower than this. The values $|F|/n$, where $|F|$ is the structure factor per unit cell and n is the number of molecules per unit cell, calculated on the basis of a fluorite-type structure of composition CeH_2 are listed below, together with observed values. Calculated values for a composition of $CeH_{1.85}$ are also listed. The agreement for the latter composition is certainly as good as for the composition CeH_2 .

<u>hkl</u>	<u>F /n</u>		
	<u>obs.</u>	<u>CeH_2(calc.)</u>	<u>$CeH_{1.85}$(calc.)</u>
111	0.58	0.46	0.46
200	1.23	1.22	1.16
220	0.10	0.30	0.24

The observed values of $|F|/n$ for the sample of composition $CeD_{2.48}$ are listed below, together with the values calculated for a) 2 atoms of deuterium per atom of cerium in the tetrahedral positions and the remainder in the octahedral positions, and b) 1.85 atoms of deuterium per atom

of cerium in the tetrahedral positions, and the remainder in the octahedral positions.

<u>hkl</u>	<u> F /n</u>		
	<u>obs.</u>	<u>CeD₂D_{0.48}(calc.)</u>	<u>CeD_{1.85}D_{0.63}(calc.)</u>
111	0.175	0.15	0.05
200	.368	.53	.33
220	1.95	2.07	2.07

The degree of accuracy of the observed values was not given. It does not appear that a very definite distribution of the deuterium atoms between tetrahedral and octahedral positions can be made on the basis of the observed data. It is unfortunate that observed values have been reported for only three diffraction maxima. Even though the octahedral positions begin to fill at a composition below MH_2 , it is possible that thereafter both sites continue to fill, until at a composition such as $CeH_{2.48}$ all tetrahedral positions would be filled. On the other hand it is possible that some tetrahedral positions remain unfilled until much higher compositions are reached.

Holley, et al. (1955) have given a brief discussion of the structures of the hydrides. They have concluded that two valence electrons of each metal atom participate in M-H bond formation in MH_2 , and that the metallic character of the hydrides is due to the presence of additional valence electrons. Metallic character and a subnormal

valence of two are also shown by monoxides and monosulfides of 4f and 5f elements, it was pointed out. However, these authors drew no further comparison other than this statement. They also showed that since the metal-hydrogen distances decrease more rapidly with the increasing atomic number of the metals than do the metallic radii (corrected for coordination number of 8), the radius of hydrogen cannot be constant if it is assumed that each metal-hydrogen distance is the sum of covalent radii of the metal and hydrogen.

Dialer (1948b), and Dialer & Rothe (1955a, b) have suggested that the first two hydrogens in the rare earth hydrides are bonded ionically. Gibb & Libowitz (1955) have advanced the theory that certain metallic hydrides, including the rare earth hydrides, are closely related to the salt-like hydrides, though possessing somewhat more covalent character. From a plot of effective hydride ion radius versus electronegativity of the metal for certain ionic hydrides, these authors derived effective hydride ion radii for hydrides of metals of different electronegativities. These radii for the rare earth hydrides varied from 1.33 Å. for lanthanum hydride to 1.30 for samarium hydride. The sum of this effective hydride ion radius and the radius of the trivalent cation (corrected for coordination number 8)

showed excellent agreement with the metal-hydrogen distance in each hydride of composition MH_2 .

The view taken by Gibb & Libowitz of the nature of the hydrogen was a somewhat ambiguous one. They stated that, at least in volume requirements, the hydrogen could be considered to be present as hydride anions. However, the possibility was left open for the electron pair of the hydride ion to participate to a limited extent in the electron system of the metallic product. At the same time they stated that this "pseudo hydride anion" could also be regarded as a proton closely associated with two electrons of a metallic system or alloy. The extra valence electrons of the metal were still considered to participate in weak metallic bonding.

Gibb & Libowitz drew no analogy between these hydrides on the one hand, and metallic monoxides and monosulfides on the other. Holley, et al., who did make this analogy, did not recognize the correspondence between the M-H distances in the hydrides and the sum of the trivalent cation radius and a nearly constant hydride ion radius. It has been pointed out by Landelli (1955) that the interatomic distances in the monochalcogenides of the first four rare earth metals agree with an ionic lattice consisting of positive trivalent and negative divalent ions, the metallic

bond being partially due to one free electron per metal atom. Conductivity and magnetic measurements by Eastman, Brewer, Bromley, Gilles & Lofgren, 1950a, b) have been interpreted as signifying that each metal atom in cerium monosulfide has one free unpaired f electron, and one d electron which is paired in metallic bonding. The sulfur atoms are presumed to take up two electrons apiece from the metal atoms, and the cerium sulfide lattice thus would be made up of dipositive and dinegative ions. The shortening of the bond relative to that expected for such ions was ascribed to the influence of the extra bonding due to the d electrons. These authors apparently did not notice that the radius of cerium in the monosulfide was approximately that of Ce^{+3} .

However, this is apparently fortuitous. In the case of ThS, which is not paramagnetic, two d electrons are presumed used in metallic bonding, and the radius of thorium in ThS is slightly shortened relative to that of Th^{+4} . In US, which has a paramagnetism corresponding to two unpaired, presumably f electrons, and therefore also has two d electrons used in metallic bonding, the radius of U is almost exactly that of U^{+6} . Thus the effective radius of the cation in any of these metallic sulfides does not appear to be

a genuine reflection of its valency, and it is probable that this is also the case for the hydrides.

The case of uranium furnishes further confirmation of similarity between the monosulfides and hydrides, since UH_3 apparently also displays paramagnetism corresponding to two unpaired 5f electrons (Rundle, 1951; Trzebiatowski, Śliwa, & Staliński, 1952, 1954), and the effective radius of U in UH_3 is also very close to that of U^{+6} , after being corrected for coordination number of 12. Presumably only one d electron would be available for metal-metal bonding in the hydride, however. There seems to be considerable basis, therefore, for considering the rare earth hydrides, as well as some other so-called "metallic" or "interstitial" hydrides, to be similar in nature to the monosulfides of these metals.

Therefore, to summarize the point of view suggested above as a plausible explanation of the nature of the rare earth hydrides, of composition close to MH_2 , the following may be stated:

- 1) Two electrons from each metal atom are taken up by hydrogen, and hydride anions are formed. It is not considered necessary to make the qualification made by Gibb & Libowitz, and suppose that these electrons still participate in the electron system of the metallic product,

although the metal-hydrogen bond doubtless does have some covalent character.

2) The third valence electron of each metal atom participates in metal-metal bonding, and is to be considered as a 5d electron. The metal-hydrogen distance is shortened by this metallic bonding relative to that expected for a divalent cation and a hydride anion, by an amount which makes the resulting distance almost exactly the sum of the radii of a trivalent cation and a hydride anion. This is not justification for considering the metal to be trivalent, however, on the basis of the evidence to the contrary cited above in the comparison of uranium hydride and uranium monosulfide.

3) The 4f electrons of the rare earth metals remain 4f electrons in the hydrides, and do not contribute to bonding, but do contribute to paramagnetism. The paramagnetism of gadolinium hydride reported by Trombe (1944) is evidence supporting this statement.

The question of the nature of additional hydrogen beyond a composition of MH_2 remains to be considered. The neutron diffraction work of Holley, et al. indicates that such hydrogen enters the octahedral holes in the lattice. Holley, et al. do not discuss this structure further, but limit their discussion to hydrides of composition MH_2 .

Neither do Gibb & Libowitz offer any discussion of rare earth hydrides of composition beyond MH_2 . Dialer & Rothe (1955a, b) considered the third hydrogen to be interstitial, on the basis of the smaller amount of energy evolved in its addition. If this third hydrogen were anionic, it would mean that the d electron of the metal previously used in metallic bonding now was transferred to hydrogen, making the metal ions trivalent. The metal-hydrogen distance is much larger for the third hydrogen atom than for the first two hydrogen atoms. Also involved here is a slight compression of the hydride ions in the tetrahedral positions, as the lattice contracts with additional hydrogen. This compression is probably a major factor in causing the amount of energy evolved upon addition of the third hydrogen to be so small. It is difficult to estimate the magnitudes of these effects, but there does not seem to be a good reason for assuming that the third hydrogen could not also be ionic, even though its addition involves less energy.

On the other hand, the decrease in metallic character of the hydride with addition of the third hydrogen atom indicates that the d electrons are being used in metal-hydrogen bonding. The resulting structure, if a composition of MH_3 were attained, would be of the bismuth trifluoride type

(Strukturbericht II, pp. 22, 290). Other ionic compounds having such a structure are also known. The persistence of the black color of the hydrides can be ascribed to residual metal-metal bonding, since the composition MH_3 does not appear to be attained. The hydrides of europium and ytterbium, which are apparently ionic, and made up of divalent cations and hydride anions, are also black in color--perhaps this is also due to a slight deficiency in hydrogen. These hydrides are discussed in Chapter VII.

X-ray diffraction pattern of a
lanthanum hydride "amalgam" sample

A pyrex capillary containing a sample of lanthanum hydride of composition $\text{LaH}_{1.99}$, which had been sealed when evacuated, was broken open under mercury. The mercury entered the capillary and formed a shiny "amalgam," like those described previously. The end of the capillary was closed with "Varno-Cement," to prevent access of air and decomposition of the preparation.

An X-ray powder diffraction photograph was taken using this sample immediately after its preparation. The

Lines of the pattern obtained were not too well-resolved, but a photograph prepared 60 days after preparation of the sample showed the same pattern, very well-resolved. Diffraction data from this pattern are tabulated in Appendix III, Table 43.

The pattern is quite complex, and there are indications that the unit cell may be orthorhombic. Unfortunately the unit cell could not be determined. The lines do not match those of lanthanum hydride, or of either modification of lanthanum metal. Nor do they match lines calculated for four different lanthanum-mercury compounds reported by Landelli & Ferro (1951).

The fact that a diffraction pattern which differs from that of lanthanum hydride is obtained from the "amalgam" indicates that some sort of reaction must occur between the hydride and mercury. Furthermore, this reaction occurs without evolution of any large proportion of hydrogen, as shown by the fact that the capillary did not burst, and also as indicated by the experiments discussed above concerning stability of the hydride "amalgams" on long standing. However, the question of the nature of this crystalline product remains unanswered.

APPENDIX III

X-RAY DIFFRACTION DATA

TABLE 28.--X-ray diffraction data for lanthanum hydride samples of various compositions. Cu radiation, Ni filter. See p. 115.

Σh_i^2	LaH _{2.47}		LaH _{2.26}		LaH _{1.99}	
	sin θ	a_0	sin θ	a_0	sin θ	a_0
3	0.23965	5.572	0.23733	5.626	0.23796	5.611
4	.27644	5.577	.27287	5.650	.27455	5.616
8	.38943	5.599	.38681	5.637	.38681	5.637
11	.45564	5.611	.45388	5.633	.45310	5.643
12	.47616	5.608	.47366	5.638	.47327	5.643
16						
19	.59828	5.619	.59583	5.640	.59443	5.653
20	.61361	5.618	.61102	5.642	.61031	5.649
24	.67206	5.619	.66947	5.641	.66800	5.654
27	.71216	5.625			.70816	5.657
32	.77497	5.6272*	.77308	5.6409*	.77025	5.6617*
35	.81068	5.6258*	.80841	5.6416*	.80578	5.6600*
36	.82155	5.6301*	.81885	5.6486*	.81729	5.6594*
40	.86672	5.6253*	.86369	5.6451*	.86099	5.6628*
43	.89796	5.6295*	.89548	5.6451*	.89309	5.6602*
44	.90865	5.6276*	.90594	5.6444*	.90291	5.6634*
48			.94562	5.6480*	.94329	5.6620*
51			.97538	5.6443*		
51 ₁	.97689	5.6308*			.97146	5.6623*
51 ₂					.97449	5.6588*
52 ₁					.98108	5.6614*
52 ₂					.98322	5.6632*

Average a_0 values computed using starred values are:

LaH_{2.47} 5.628 $\pm$ 0.005 Å.

LaH_{2.26} 5.645 $\pm$ 0.005 Å.

LaH_{1.99} 5.661 $\pm$ 0.005 Å.

TABLE 29. X-ray diffraction data for lanthanum hydride samples of different compositions. Mo radiation, Zr filter. See p. 115.

Σh_1^2	LaH _{2.78}		LaH _{1.83}	
	$\sin^2\theta$ obs.	a_0^2	$\sin^2\theta$ obs.	a_0
4	0.01662	31.803	0.03276	5.553
8	.03280	31.781	.04461	5.581
11	.04508	31.629	.04869	5.579
12	.04936	31.466	.06491	5.579
16			.07628	5.608
19	.07760	31.506*	.08035	5.606
20	.08154	31.542*	.09604	5.617
24	.09758	31.466*	.10774	5.625
27	.10957	31.586*	.12743	5.631
32	.12982	31.542*	.13917	5.635
35	.14173	31.575*	.14362	5.626
36	.14612	31.492*	.15941	5.629
40	.16142	31.645*	.17149	5.627
43	.17347	31.635*	.17464	5.640
44	.17747	31.635*	.19121	5.630
48	.19931	31.659*	.20222	5.643
51	.20593	31.561*	.20554	5.652
52	.20891	31.716	.22219	5.641
56	.22569	31.597*	.23378	5.645
59	.23802	31.552*	.95045	5.670*
243 α_1			.95482	5.669*
244 α_1			.96165	5.671*
243 α_2			.96631	5.669*
244 α_2			.97013	5.670*
248 α_1			.98166	5.671*
248 α_2				5.671*
251 α_1				

An absorption correction of $E \cos^2\theta \sin 2\theta$ was applied to the $\sin^2\theta$ values for the LaH_{2.78} sample (Buerger, 1942). An empirical value for E of 0.293 was obtained as the average for a number of films, on each of which the a_0 derived from lines at very large values of θ was assumed correct, and the best value of E was calculated. Average a_0 values computed using starred values are 5.619 ± 0.010 A. and 5.670 ± 0.002 A. for the two samples.

Buerger, M. J. (1942). X-ray crystallography. New York: John Wiley & Sons, Inc., p. 429.

TABLE 30.--X-ray diffraction data for lanthanum hydride sample of composition $\text{LaH}_{2.78}$, after annealing. Cu radiation, Ni filter. See p. 116.

$\sin \theta$	$\sum h_i^2$	a_0	$\sum h_i^2$	a_0
0 23266	3	5.739		
.25285			3	5.281
.26912	4	5.729		
.29162			4	5.287
.38151	8	5.715		
.41287			8	5.281
.44707	11	5.719		
.46646	12	5.724		
.48409			11	5.282
.50427			12	5.296
.53914	16	5.720		
.58698	19	5.725	16	5.253
.60182	20	5.730		
.63516			19	5.290
.65970	24	5.725		
.69913	27	5.730		
.75615			27	5.298
.79669	35	5.7246*		
.80897	36	5.7176*		
.84977	40	5.7376*		
.86111			35	5.2963*
.88296	43	5.7252*		
.89323	44	5.7247*		
.92042			40	5.2971*
.93229	48	5.7288*		
.96138	51	5.7267*		
.97029	52	5.7292*		

Average a_0 values computed using starred values are $5.727 \pm 0.010 \text{ \AA}$ and $5.297 \pm 0.010 \text{ \AA}$.

TABLE 31 --X-ray diffraction data for lanthanum hydride
sample of composition $\text{LaH}_{1.49}$. Cu radiation, Ni filter.
See p. 117.

$\sin \theta$	$\sum h_i^2$	a_0	$\sum h_i^2$	a_0
0.23902	3	5.587		
.25602			3	5.216
.27497	4	5.607		
.29514			4	5.224
.38761	8	5.625		
.41825			8	5.213
.45370	11	5.635		
.47347	12	5.640		
.48920			11	5.226
.54590	16	5.649		
.59478	19	5.650		
.61015	20	5.650		
.64124			19	5.2403*
.65820			20	5.2378*
.66768	24	5.656		
.70803	27	5.658		
.77041	32	5.660		
.80489	35 α_1	5.662		
.81593	36 α_1	5.664		
.86000	40 α_1	5.664		
.89143	43 α_1	5.666		
.90151	44 α_1	5.667		
.94747	48 α_1	5.668		
.97016	51 α_1	5.6700*		
.97245	51 α_2	5.6706*		
.97948	52 α_1	5.6707*		
.98197	52 α_2	5.6704*		

Average a_0 values computed using starred values are
5.670 $\pm$ 0.002 A. and 5.239 $\pm$ 0.010 A.

TABLE 32.---X-ray diffraction data for lanthanum hydride
sample of composition $\text{LaH}_{0.33}$. Cu radiation, Ni filter.
See p. 117.

$\sin \theta$	$\sum h_1^2$	a_0	$\sum h_1^2$	a_0	$\sum h_1^2$	a_0
0.23796	3	5.611				
.25534			3	5.230		
.27329	4	5.642				
.29511			4	5.224		
.38603	8	5.648				
.39369 ?						
.41172					8	5.296
.41692			8	5.230		
.44100 ?						
.45197	11	5.657				
.46636 ?						
.47292	12	5.647				
.48408					11	5.282
.48905			11	5.228		
.50462					12	5.292
.50990			12	5.237		
.58846			16	5.240		
.59516	19	5.646				
.60914	20	5.660				
.63514					19	5.2906*
.64121			19	5.241		
.65157					20	5.2911*
.65785			20	5.241		
.66770	24	5.656				
.67935 ?						
.70803	27	5.658				
.71387					24	5.2903*
.72028			24	5.243		
.75628					27	5.2967*
.76395			27	5.244		
.80515	35	5.664				
.81668	36	5.664				
.82394					32	5.2927*
.86090	40	5.663				
.86924			35	5.2468*		
.88213			36	5.2434*		
.89222	43	5.6658				
.90227	44	5.6674				
.96275			43	5.2507*		
.97037	51 α_1	5.6687*				
.97306	51 α_2	5.6671*				

TABLE 32.--Continued

<u>sin θ</u>	<u>Σh_1^2</u>	<u>a_0</u>	<u>Σh_1^2</u>	<u>a_0</u>	<u>Σh_1^2</u>	<u>a_0</u>
0.97958	$52\alpha_1$	5.6701*				
.98205	$52\alpha_2$	5.6700*				

Average a_0 values computed using starred values are:

$$5.669 \pm 0.003 \text{ A.}$$

$$5.247 \pm 0.008 \text{ A.}$$

$$5.292 \pm 0.010 \text{ A.}$$

TABLE 33.--X-ray diffraction data for lanthanum deuteride
sample of composition $\text{LaD}_{0.95}$, Cu radiation, Ni filter.
See p. 119.

$\sin \theta$	$\sum h_1^2$	a_0	$\sum h_1^2$	a_0
0.23897	3	5.588		
.25636			3	5.209
.27535	4	5.599		
.29632			4	5.203
.38756	8	5.626		
.41841			8	5.211
.45424	11	5.629		
.47440	12	5.629		
.48897			11	5.229
.51020			12	5.234
.54696	16	5.638		
.59618	19	5.636		
.61118	20	5.641		
.64184			19	5.235
.65814			20	5.238
.66862	24	5.648		
.70889	27	5.651		
.72022			24	5.244
.76362			27	5.246
.77147	32	5.653		
.80615	35	5.657		
.81789	36	5.655		
.83077			32	5.2492*
.86152	40	5.6593*		
.86811			35	5.2536*
.88085			36	5.2511*
.89258	43 α_1	5.6587*		
.90261	44 α_1	5.6605*		
.92744			40 α_1	5.2526*
.94250	48 α_1	5.6620*		
.96213			43	5.2496*
.97129	51 α_1	5.6633*		
.97364	51 α_2	5.6637*		
.98060	52 α_1	5.6642*		
.98285	52 α_2	5.6654*		

Average a_0 values computed using starred values are
5.662 $\pm$ 0.003 Å. and 5.251 $\pm$ 0.002 Å.

TABLE 34.--X-ray diffraction data for cerium hydride samples of various compositions. Cu radiation, Ni filter.
See p. 119.

Zn_1^2	CeH _{2.83}		CeH _{2.43}		CeH _{2.02}	
	sin θ	a_0	sin θ	a_0	sin θ	a_0
3			0.24412	5.470		
4			.28043	5.498		
8			.39587	5.508		
11			.46322	5.520		
12			.48365	5.522		
16						
19			.60738	5.5325		
20			.62306	5.5332		
24	0.61874	5.5396	.68238	5.5345		
27	.72309	5.5398	.72326	5.5385	0.71950	5.5675
32	.78640	5.5454*	.78656	5.5443	.78239	5.5738*
35	.82300	5.5416*	.82290	5.5422	.81829	5.5735*
36	.83427	5.5442*	.83369	5.5481*	.83019	5.5715*
40	.88010	5.5398*	.87857	5.5495*	.87468	5.5742*
43	.91170	5.5447*	.91091	5.5495*	.90682	5.5745*
44	.92167	5.5481*	.92143	5.5495*	.91723	5.5749*
48	.96277	5.5474*	.96237	5.5497*	.95792	5.5755*
51 α_1	.99171	5.5467*	.99180	5.5462*		

Average a_0 values computed using starred values are:

CeH_{2.83} 5.545 $\pm$ 0.003 A.

CeH_{2.43} 5.549 $\pm$ 0.002 A.

CeH_{2.02} 5.574 $\pm$ 0.002 A.

Lines at small values of θ were not always read, as in the cases of two films above, and other films as well, since such lines were not used in calculating the value of a_0 .

TABLE 35.--X-ray diffraction data for cerium hydride sample of composition $\text{CeH}_{1.86}$. Mo radiation, Zr filter. See p.119

$\sum h_i^2$	$\sin^2 \theta$	a_0^2
3	0.01285	
4	.01698	
8	.03350	
11	.04576	
12	.04987	
16	.06618	
19	.07829	
20	.08258	
24	.09903	
27	.11084	
32	.13167	
35	.14296	
36	.14759	
40	.16344	
43	.17559	
44	.17995	
48	.19552	
51	.20817	
52	.21139	
216 Δ 1	.87329	31.1065
219 Δ 1	.88469	31.1318*
227 Δ 1	.91704	31.1306*
243 Δ 1	.98163	31.1319*
244 Δ 1	.98563	31.1334*

Average value of a_0 computed using starred values is $5.580 \pm 0.002 \text{ \AA}$.

TABLE 36.---X-ray diffraction data for cerium deuteride sample of composition $\text{CeD}_{0.56}$. Cu radiation, Ni filter. See p. 120.

$\sin \theta$	$\sum h_i^2$	a_0	$\sum h_i^2$	a_0
0.39403	8	5.534		
.46268	11	5.526		
.48221	12	5.538		
.55702	16	5.536		
.60579	19	5.547	16	5.090
.62067	20	5.545		
.66039			19	5.088
.67986			20	5.071
.72116	27	5.555		
.73969			24	5.106
.78446	32	5.559	27	5.106
.81999	35	5.562		
.83161	36	5.562		
.87553	40 α_1	5.564		
.89014			35 α_1	5.1193*
.90741	43 α_1	5.5709	36 α_1	5.0931
.90942	43 α_2	5.5677*		
.91762	44 α_1	5.5679*		
.91969	44 α_2	5.5693*		
.95039			40 α_1	5.1258*
.95836	48 α_1	5.5683*		
.96095	48 α_2	5.5672*		
.98724	51 α_1	5.5718	43 α_1	5.1161
.98975	51 α_2	5.5715*		
.99629	52 α_1	5.5750	44 α_1	5.1282

Average a_0 values computed using starred values are 5.569 ± 0.003 A. and 5.123 ± 0.005 A.

TABLE 37.--X-ray diffraction data for praseodymium hydride samples of various compositions. Cu radiation, Ni filter.
See p. 120.

Σh_1^2	PrH _{2.85}		PrH _{2.49}		PrH _{2.25}	
	sin θ	a_0	sin θ	a_0	sin θ	a_0
3	0.24390	5.475	0.24624	5.423	0.24517	5.446
4	.28065	5.494	.28442	5.421	.28232	5.461
8	.39728	5.488	.39987	5.453	.39867	5.469
11	.46554	5.492	.46805	5.463	.46632	5.483
12	.48594	5.496	.48662	5.465	.48690	5.485
16	.56117	5.495	.56298	5.477		
19	.61153	5.495	.61395	5.473	.61205	5.490
20	.62750	5.494	.62989	5.473	.62802	5.490
24	.68762	5.492	.68949	5.477	.68753	5.493
27	.72873	5.497	.73076	5.482	.72921	5.493
32	.79438	5.490	.74986	5.486	.79348	5.496
35	.83009	5.4942*	.83126	5.486	.82975	5.496
36	.84161	5.4959*	.84299	5.487	.84128	5.498
40	.88723	5.4953*	.88799	5.4906*	.88634	5.5008*
43	.91992	5.4952*	.92057	5.4913*	.91900	5.5006*
44	.93023	5.4970*	.93115	5.4916*	.92968	5.5003*
48 α_1	.97121	5.4946*				

Average a_0 values computed using starred values are:

PrH_{2.85} 5.495 $\pm$ 0.003 A.

PrH_{2.49} 5.491 $\pm$ 0.005 A.

PrH_{2.25} 5.501 $\pm$ 0.005 A.

TABLE 38.--X-ray diffraction data for praseodymium hydride
sample of composition $\text{PrH}_{2.02}$. Mo radiation, Zr filter.
See p. 120.

$\sum h_i^2$	$\sin^2\theta$	a_0
3		
4	0.01736	5.395
8	.03435	5.423
11	.04686	5.445
12	.05108	5.446
16	.06771	5.462
19	.08032	5.465
20	.08452	5.466
24	.10123	5.472
27	.11370	5.476
32	.13472	5.477
35	.14673	5.488
36	.15097	5.487
40	.16745	5.492
43	.18032	5.487
44	.18383	5.498
48		
51	.21287	5.500
52	.21687	5.503
56	.23400	5.497
59	.24665	5.496
219 ₄₁	.90526	5.5158*
227 ₄₁	.93873	5.5146*

Average value of a_0 computed using starred values is
 5.515 ± 0.002 A.

TABLE 39.--X-ray diffraction data for praseodymium hydride
sample of composition $\text{PrH}_{0.79}$. Cu radiation, Ni filter.
See p. 121.

$\sin \theta$ obs.	$\sum h_i^2$	a_0	$\sum h_i^2$	a_0
0.24553	3	5.438		
.26330			3	5.071
.28182	4	5.471		
.30242			4	5.098
.39787	8	5.480		
.42638			8	5.114
.46574	11	5.490		
.48576	12	5.498		
.49890			11	5.125
.52149			12	5.121
.56132	16	5.494		
.61118	19	5.498		
.62700	20	5.498		
.65503			19	5.130
.67109			20	5.137
.68549	24	5.509		
.72789	27	5.503		
.73506			24	5.138
.82720	35	5.513		
.83882	36	5.514		
.84822			32	5.1412*
.88463	40	5.511	35	5.1555
.89869			36	5.1468*
.91561	43 $\frac{1}{2}$	5.5163*		
.92602	44 $\frac{1}{2}$	5.5174*		
.96680	48 $\frac{1}{2}$	5.5196*		
.99635	51 $\frac{1}{2}$	5.5346	44	5.1322

Average a_0 values computed using starred values are
5.518 $\pm$ 0.005 Å. and 5.14 $\pm$ 0.01 Å.

TABLE 40.--X-ray diffraction data for neodymium hydride samples of different compositions. Cu radiation, Ni filter. See p. 121.

$\sum h_i^2$	NdH _{2.40}		NdH _{2.19}	
	$\sin \theta$	a_0	$\sin \theta$	a_0
27	0.73848	5.4244		
32				
35	.84039	5.4269	0.83867	5.4380*
36	.85112	5.4345*	.85039	5.4392*
40	.89765	5.4315*	.89548	5.4447*
43	.93083	5.4307*	.92823	5.4460*
44	.94085	5.4350*	.93820	5.4503*

Average a_0 values computed using starred values are:

NdH_{2.40} 5.433 $\pm$ 0.003 Å.

NdH_{2.19} 5.444 $\pm$ 0.008 Å.

TABLE 41.--X-ray diffraction data for neodymium hydride samples of different compositions. Mo radiation, Zr filter. See p. 121.

$\sum h_i^2$	NdH _{1.99}		NdH _{1.83}	
	$\sin \theta$	a_0	$\sin \theta$	a_0
200 α_1	0.91771	5.4649	0.91778	5.4645
203 α_1	.92045	5.4680	.92463	5.4646
216 α_1	.95359	5.4656	.95349	5.4662
219 α_1	.95980	5.4678*	.95963	5.4688*
227 α_1	.97754	5.4658*	.97713	5.4681*
227 α_2	.98317	5.4672*	.98283	5.4692*

Average a_0 values computed using starred values are:

NdH_{1.99} 5.467 $\pm$ 0.002 Å.

NdH_{1.83} 5.469 $\pm$ 0.002 Å.

TABLE 42.--X-ray diffraction data for neodymium hydride
sample of composition $\text{NdH}_{0.76}$. Cu radiation, Ni filter.
See p. 122.

$\sin \theta$	$\sum h_i^2$	a_0	$\sum h_i^2$	a_0
0.24497	3	5.451		
.26443			3	5.050
.28040	4	5.499		
.30471			4	5.060
.39627	8	5.502		
.42916			8	5.081
.46302	11	5.522		
.50362			11	5.077
.52577			12	5.079
.60768			16	5.074
.61599	19	5.455		
.63239	20	5.452		
.66110			19	5.0829*
.67801			20	5.0847*
.69045	24	5.4698*		
.73285	27	5.4661*		
.74407			24	5.0756*
.78818			27	5.0823*
.83489	35	5.4626*		
.84743	36	5.4581*		
.85772			32	5.0843*
.89120	40	5.4708*		
.89688			35	5.0851*
.90964			36	5.0849*
.92413	43 α_1	5.4655*		
.92645	43 α_2	5.4654*		
.93478	44 α_1	5.4657*		
.95835			40 α_1	5.0832*

Average a_0 values computed using starred values are
5.466 $\pm$ 0.004 Å. and 5.083 $\pm$ 0.003 Å.

Film was of low contrast, with many diffuse lines.

TABLE 43.--X-ray diffraction data for lanthanum hydride "amalgam" sample, formed using a hydride sample of composition $\text{LaH}_{1.99}$. Cu radiation, Ni filter. See p. 148.

<u>Intensity</u>	<u>$\sin^2\theta$</u>
w	0.05774
s	.08733
m	.09208
m-s	.09604
vvw	.15197
w	.17843
w-m	.18723
vvs	.22618
vvw	.23818
vw	.27195
w	.27760
m	.28666
vs	.32067
vvw	.34303
vw	.35836
w	.37970
m	.50971
w-m	.53725
vw	.55598
m	.60435
vvw	.62776
w	.63409
vw	.66374
s	.88642
m	.91635
s	.99098

The last 3 lines are $K\alpha_2$ lines; others are $K\alpha_1$ lines

w: weak; m: medium; s: strong; v: very

See Technical Report I for references