# X-ray diffraction study of the cubic-to-tetragonal structural transformation in substoichiometric lanthanum trihydride and trideuteride

P. Klavins, R. N. Shelton, R. G. Barnes, and B. J. Beaudry

Ames Laboratory-U.S. Department of Energy and Department of Physics, Iowa State University, Ames, Iowa 50011

(Received 18 July 1983)

A low-temperature powder x-ray diffraction study of 13 compounds in the series  $LaH_x$  and  $LaD_x$ (2.50  $\leq x \leq$  3.00) indicates the presence of a cubic-to-tetragonal distortion of the lanthanum sublattice for a limited concentration range centered about x=2.75. Transformation temperatures occur from 197 to 256 K, with a maximum distortion from cubic symmetry of about 1%. Possible influence on the metal sublattice from the hydrogen (deuterium) sublattices is considered. Precision room-temperature lattice parameters are also reported for 22 samples in the extended series  $LaH_x$ and  $LaD_x$  (2.00  $\leq x \leq$  3.00).

### INTRODUCTION

The early lanthanides lanthanum, cerium, praseodymium, and neodymium form nonstoichiometric homogeneous hydride and deuteride phases<sup>1</sup> with an apparent range of composition from  $LH_{1.9}$  to  $LH_3$ . The dihydrides all have the cubic fluorite structure with the hydrogen (deuterium) occupying predominantly the tetrahedral (*T*) interstitial sites. Further increase of the hydrogen concentration results in filling the octahedral (*O*) interstitial sites in this structure. The dihydrides,  $LH_2$ , exhibit metallic conductivity due to the occurrence of overlapping energy bands, but as the ratio [H]/[L] approaches 3 the bands are shifted considerably, and semiconducting behavior is expected.<sup>2,3</sup>

Recent NMR studies of the lanthanum hydrides and deuterides<sup>4</sup> found a metallic shift (Knight shift) of the <sup>139</sup>La resonance at all compositions up to and including LaH<sub>3</sub> and LaD<sub>3</sub> at 300 K, with the transition to semiconducting behavior, defined by the disappearance of the Knight shift, occurring at about 200 K. Earlier measurements of the resistivity of cerium hydrides indicated the metal-semiconductor (M-S) transition occurred at 250 K in CeH<sub>2.81</sub>.<sup>5</sup> In addition, x-ray diffraction measurements<sup>5</sup> on CeH<sub>2.75</sub> revealed the onset of a tetragonal distortion of the Ce sublattice at about the same temperature, apparently accompanying the M-S transition. In contrast, both xray<sup>6</sup> and deuteron NMR (Ref. 7) attempts to detect such a tetragonal distortion of the lanthanum lattice in LaH<sub>3</sub> and LaD<sub>3</sub> were unsuccessful, although neutron diffraction has shown the existence of superlattice reflections below about 250 K.<sup>6</sup> A further puzzling feature of these materials is the occurrence of two proton NMR signals in LaH<sub>x</sub> samples  $(2.5 \le x \le 3.0)$  at temperatures below about 250 K.<sup>8</sup>

Accordingly, we report the results of x-ray powder diffraction measurements on polycrystalline specimens of lanthanum hydrides and deuterides,  $LaH_x$  and  $LaD_x$  $(2.5 \le x \le 3.0)$  in the temperature range  $30 \le T \le 295$  K, undertaken in an effort to clear away some of this confusion. These measurements show that a crystallographic transformation, consistent with a tetragonal distortion of the La sublattice, occurs only within a restricted composition range, roughly  $2.65 \le x \le 2.90$ . The measurements also confirm the earlier observations that this distortion does not occur in LaH<sub>3</sub>.

#### **EXPERIMENTAL SETUP**

The lanthanum hydride and deuteride samples used in these measurements are identical to ones previously employed in NMR and neutron-diffraction studies.<sup>4,6</sup> These samples were all prepared from the highest purity Ames Laboratory lanthanum metal which had been analyzed by spark source mass spectrometry and shown to contain only very small concentrations (<0.0002 at. %) of impurities such as Fe, Cu, Ta, Ni, and rare earths. Preparation procedures for the hydrides and deuterides have been described in detail in an earlier report.9 For roomtemperature lattice parameter determination, each one of the complete set of 22 samples was loaded into its own 0.3-mm-diam Pyrex capillary in a helium-filled glove box. The capillary was then sealed with vacuum grease, removed from the glove box, and fused closed with a flame. The diffraction pattern was taken with a 114.6-mm-diam Debye-Scherrer camera using Cu  $K\alpha$  radiation. Doublet lines  $(\alpha_1, \alpha_2)$  in the back reflection region were measured and the results were computer fit using a Nelson-Riley extrapolation function to calculate the lattice parameter. Thirteen of these samples were used in the lowtemperature x-ray diffraction studies. Once again, all samples were handled in an inert gas atmosphere to prevent reaction with air. Finely powdered samples were mounted on a copper block which was in thermal equilibrium with the cold finger of a closed-cycle helium refrigerator. For each sample, this unit was mounted on the horizontal goniometer of the powder diffractometer and a complete x-ray pattern of intensity versus  $2\theta$  was taken at both 295 and 30 K. These complete patterns were taken using Cu  $K\alpha$  radiation and a diffracted beam graphite monochromator over the  $2\theta$  range of  $20^{\circ}$  to  $140^{\circ}$  at a step scan rate of 0.6° per min. with a step size of 0.01°. If comparison of these two x-ray patterns indicated the occurrence of a crystallographic phase transformation, then



FIG. 1. Room-temperature cubic lattice parameters vs concentration for lanthanum hydride and deuteride.

the profiles of high-angle reflections [e.g., (422), (511) and (333), (531), (600), and (442)] were determined as a function of temperature. The sample temperature, as measured by a Chromel versus gold 0.07% iron thermocouple mounted on the cold finger was stabilized by a combination of a heater on the cold finger and the refrigerator power. A series of peak profiles taken at small tempera-



FIG. 2. Temperature dependence of the lattice parameters for  $LaH_{2.80}$ . The cubic-to-tetragonal transformation at 248 K is evident.



FIG. 3. Temperature dependence of the lattice parameters for  $LaD_{2.78}$ . The cubic-to-tetragonal transformation at 254 K is evident.

ture intervals about the transition temperature resulted in an accurate and reproducible determination of the transformation temperature associated with the cubic-totetragonal phase change. The process of step scanning through these high-angle peaks was done with a step size of  $0.004^{\circ}$  at a rate of  $0.06^{\circ}$  per min. All lattice parameters were determined by a least-squares-fitting procedure.

## **RESULTS AND DISCUSSION**

Room-temperature cubic lattice parameters as determined by the Debye-Scherrer method for the entire series of 22 lanthanum hydrides and deuterides are presented in Fig. 1. For the hydrides a relatively rapid decrease in lattice parameter for hydrogen concentrations less than 2.60 is followed by a small plateau region and then a continued, but slower decrease as hydrogen content is increased. A roughly similar behavior is found for the deuterides; the plateau region is broader and extends from  $x \approx 2.40$  to  $x \approx 2.60$  and for  $2.65 \le x \le 2.70$  the lattice parameter increases slightly with increasing deuterium concentration. Our results are somewhat different than those of Müller *et al.*<sup>10</sup> who reported no variation in the cubic lattice parameter for  $x \ge 2.40$ . The quality of the initial lanthanum



FIG. 4. Concentration dependence of the magnitude of the tetragonal distortion for lanthanum hydrides.



FIG. 5. Lattice transformation temperature vs hydrogen concentration in lanthanum hydrides.

may be the main cause of this small discrepancy.

Figures 2 and 3 show the dependence of the lattice parameters on temperature for  $LaH_{2.80}$  and  $LaD_{2.78}$ , respectively. These two samples show the maximum distortion from cubic symmetry. In both cases the onset of the tetragonal phase occurs sharply at approximately 250 K. In contrast to the case of CeH<sub>2.75</sub>, there is little indication of any gradual growth in strength of the tetragonal distor-

tion with decreasing temperature.<sup>5</sup> The transition also exhibits negligible hysteresis.

In Fig. 4 we show the dependence of the tetragonality of the low-temperature phase, i.e., (c/a-1), on hydrogen concentration in LaH<sub>x</sub>. The maximum distortion is 1.0%, in the vicinity of x=2.75-2.80, to be compared with 0.75% observed in CeH<sub>2.75</sub>.<sup>5</sup> No indication whatever of the transition could be detected in LaH<sub>2.92</sub>, and as shown in Fig. 4, the effect is very weak, on the order of 0.25%, in LaH<sub>2.60</sub> and LaH<sub>2.68</sub>.

Figure 5 shows the dependence of the onset temperature on hydrogen concentration for the  $LaH_x$  series of samples. This temperature increases sharply from x=2.70 to 2.80. However, as already remarked, for x > 2.86 the transition can no longer be detected. In order to provide quantitative information, we list the lattice parameters and transformation temperature in Table I for all samples investigated.

There is prior evidence for a slight tetragonal distortion of the metal sublattice in  $\text{CeD}_{2.75}$ .<sup>5</sup> However, our work is the first low-temperature x-ray diffraction study of an entire rare-earth hydride or deuteride series. This complete study enables us to ascertain the effects of hydrogen (deuterium) concentration on the rare-earth metal sublattice. These measurements show clearly that the tetragonal distortion of the La lattice occurs only within a rather narrow range of hydrogen concentration centered at approximately [H]/[La]=2.75. They also confirm that the distortion does not occur (i.e., is not detectable) at the trihydride composition. At the higher hydrogen concentrations the onset temperature coincides with that of the

Composition	$a_{\text{cubic}}$ (Å)	$a_{\text{tet}}$ (Å)	$c_{\text{tet}}$ (Å)	c/a	$T_L$ (K)
LaH <sub>2.00</sub>	5.6656(4)				a
LaH <sub>2.15</sub>	5.6638(6)				а
LaH <sub>2.27</sub>	5.6498(4)				а
LaH <sub>2.46</sub>	5.6367(6)				а
LaH <sub>2.53</sub>	5.6270(4)				b
$LaH_{2.60}$	5.6239(5)	5.604	5.619	1.003	197±4
LaH <sub>2.66</sub>	5.6243(2)				a
LaH <sub>2.68</sub>	5.6236(4)	5.602	5.611	1.002	$202 \pm 6$
LaH <sub>2.76</sub>	5.6229(4)	5.597	5.649	1.009	$242 \pm 4$
LaH <sub>2.80</sub>	5.6218(4)	5.598	5.654	1.010	$248 \pm 2$
LaH <sub>2.86</sub>	5.6193(4)	5.615	5.623	1.001	248±4
$LaH_{2.92}$	5.6186(5)				b
$LaD_{2,28}$	5.6295(6)				а
$LaD_{2,41}$	5.6164(3)				a
$LaD_{2.50}$	5.6168(8)				b
$LaD_{2.62}$	5.6157(6)				b
$LaD_{2.65}$	5.6170(3)				a
$LaD_{2.70}$	5.6176(4)	5.600	5.616	1.003	256+4
$LaD_{2.76}$	5.6134(2)				a
LaD <sub>2.78</sub>	5.6111(4)	5.587	5.649	1.011	254±2
$LaD_{2.91}$	5.6100(5)				b
LaD <sub>3.00</sub>	5.6064(5)				b

TABLE I. Lattice parameters and transformation temperatures for  $LaH_x$  and  $LaD_x$  compounds. For  $a_{tet}$  and  $c_{tet}$ , low-temperature lattice parameters determined at 30 K.

<sup>a</sup>Sample was not investigated below room temperature.

<sup>b</sup>No crystallographic transformation observed above 30 K.

peak of the heat capacity anomaly obtained in recent measurements in this laboratory on  $LaD_{2.76}$  and  $LaD_{2.91}$ .<sup>11</sup> Moreover, in those measurements no indication of an anomaly was detected in  $LaD_{2.53}$ , consistent with these x-ray observations.

Because the tetragonal distortion is so weak, it is difficult to determine from these powder diffraction measurements if both the cubic and tetragonal phases coexist over an appreciable temperature range. Coexistence of two proton resonances having different linewidths was observed in the first NMR study of lanthanum hydrides.<sup>8</sup> This has been confirmed by a more recent investigation<sup>12</sup> which has shown that the two resonances have both different linewidths and spin-lattice relaxation times  $(T_1)$ 's) over a rather wide temperature range. For the most recent proton  $T_1$  measurements,<sup>13</sup> analysis of the two distinct signals appears to indicate that the low-temperature phase is semiconducting while the high-temperature phase is metallic. The coexistence of two proton resonances has also been observed in substoichiometric cerium trihydride.<sup>14</sup> A striking departure from the x-ray results is the fact that this two-phase character of the proton NMR occurs at compositions up to and including the trihydride limit. Moreover, recent heat capacity measurements of LaD<sub>3</sub> show the occurrence of four  $\lambda$ -type anomalies in the temperature range 210-275 K.9 Based on this lowtemperature x-ray diffraction study, these four heat capacity anomalies cannot be associated with crystallographic distortions of the metal sublattice.

The origin or driving mechanism responsible for the tetragonal distortion is difficult to identify at this point. The fact that the distortion occurs only in the neighbor-



FIG. 6. Projection onto the (001) plane of the atomic arrangement for ordering of octahedral site hydrogen on (420) planes in LaH<sub>2.80</sub>. Only octahedral sites are indicated.

hood of [H]/[La]=2.75 suggests that it may be associated with an ordering of the remaining vacancies on the O-site sublattice. Ordering of the O-site hydrogen (deuterium) at x=2.50 leading to a tetragonal superlattice was first detected by neutron-diffraction measurements.<sup>15</sup> These were later confirmed by deuteron NMR which also indicated that a different ordered superstructure existed at x = 2.25.<sup>7</sup> However, both deuteron and <sup>139</sup>La NMR were unable to detect superlattice formation at x = 2.75.<sup>4,7</sup> Two distinct types of superlattices also have been confirmed by neutron-diffraction studies<sup>16</sup> for CeD<sub>2.26</sub> and CeD<sub>2.43</sub>. Recent neutron-diffraction studies of LaD<sub>3</sub> detected superlattice reflections whose intensity increases at temperatures below  $\sim 250$  K.<sup>6</sup> However, it has not been possible to index these reflections to determine the underlying structure.

An alternative possibility may be formulated in analogy with the model Blaschko et al.<sup>17</sup> used for deuterium ordering in  $PdD_x$ . In this model, Blaschko and co-workers consider an ordering of octahedral-site D atoms on (420) planes, identical to the long-range ordered state in Ni<sub>4</sub>Mo.<sup>18,19</sup> This type of ordering along (420) planes is already evident in LaH<sub>x</sub> where the superlattice at x=2.5corresponds to NiMo. For  $PdD_{0.8}$  this model yields four consecutive (420) planes with filled O-site deuterium followed by a fifth plane with all D sites vacant. A similar structure (see Fig. 6) can be generated in the LaH, and  $LaD_x$  systems where the ordering of O-site deuterium along (420) planes for x = 2.8 would correspond directly to Ni<sub>4</sub>Mo in the Ni-Mo system. It is interesting to note that we observe the maximum tetragonal distortion of the metal sublattice at the compositions  $LaH_{2,80}$  and  $LaD_{2,78}$ , that is, exactly the concentration favored by ordering on (420) planes. The small tetragonal distortion ( $\sim 1\%$  maximum) is consistent with a hydrogen (deuterium) sublattice ordering driving the heavier lanthanum sublattice distortion. Neutron scattering off a single crystal of LaH<sub>2.80</sub> would be one experimental test of these models; however, the difficulties of sample preparation may preclude this measurement for some time.

The key result of this paper is the first systematic determination of the cubic-to-tetragonal distortion of the lanthanum sublattice in  $LaH_x$  and  $LaD_x$  compounds. The distortion is small in magnitude with a maximum deviation of ~1% from a cubic cell for  $x \cong 2.8$  and is limited to hydrogen (deuterium) concentrations near 2.75. The cause of this crystallographic transformation is not clear, but it is possible that ordering of hydrogen (deuterium) on (420) planes in analogy to the PdD<sub>x</sub> system may provide the driving force for the metal sublattice transformation.

## ACKNOWLEDGMENTS

Ames laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This research was supported by the Director of Energy Research, Office of Basic Sciences, U.S. Department of Energy, under Grant No. WPAS-KC-02-02-02.

- <sup>1</sup>W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides* (Academic, New York, 1968), p. 395.
- <sup>2</sup>A. C. Switendick, Solid State Commun. <u>8</u>, 1463 (1970).
- <sup>3</sup>D. K. Misemer and B. N. Harmon, Phy. Rev. B <u>26</u>, 5634 (1982).
- <sup>4</sup>R. G. Barnes, B. J. Beaudry, R. B. Creel, D. R. Torgeson, and D. G. de Groot, Solid State Commun. <u>36</u>, 105 (1980).
- <sup>5</sup>G. G. Libowitz, J. G. Pack, and W. P. Binnie, Phys. Rev. B <u>6</u>, 4540 (1972).
- <sup>6</sup>J. J. Didisheim, K. Yvon, P. Fischer, W. Hälg, and L. Schlapbach, Phys. Lett. <u>78A</u>, 111 (1980).
- <sup>7</sup>D. G. de Groot, R. G. Barnes, B. J. Beaudry, and D. R. Torgeson, J. Less-Common Met. <u>73</u>, 233 (1980).
- <sup>8</sup>D. L. Schreiber and R. M. Cotts, Phys. Rev. <u>131</u>, 1118 (1963).
- <sup>9</sup>T. Ito, B. J. Beaudry, K. A. Gschneider, Jr., and T. Takeshita, Phys. Rev. B <u>27</u>, 2830 (1983).
- <sup>10</sup>Horst Müller, P. Knappe, and O. Greis, Z. Phys. Chem. <u>114</u>, 45 (1979).
- <sup>11</sup>T. Ito, B. J. Beaudry, and K. A. Gschneidner, Jr., J. Less-

Common Met. <u>88</u>, 425 (1982).

- <sup>12</sup>R. G. Barnes, B. J. Beaudry, R. B. Creel, T.-T. Phua, and D. R. Torgeson, Bull. Am. Phys. Soc. <u>26</u>, 377 (1981).
- <sup>13</sup>D. R. Torgeson, T.-T. Phua, R. G. Barnes, R. J. Schoenberger, and E. F. W. Seymour, Bull. Am. Phys. Soc. <u>28</u>, 409 (1983).
- <sup>14</sup>D. Zamir, R. G. Barnes, N. Salibi, R. M. Cotts, T.-T. Phua, D. R. Torgeson, and D. T. Peterson, Phys. Rev. B <u>29</u>, 61 (1984).
- <sup>15</sup>C. G. Titcomb, A. K. Cheetham, and B. E. F. Fender, J. Phys. C 7, 2409 (1974).
- <sup>16</sup>V. K. Fedotov, V. G. Fedotov, M. E. Kost, and E. G. Ponyatovskii, Fiz. Tverd. Tela (Leningrad) <u>24</u>, 2201 (1982) [Sov. Phys.—Solid State <u>24</u>, 1252 (1982)].
- <sup>17</sup>O. Blaschko, P. Fratzl, and R. Klemencic, Phys. Rev. B <u>24</u>, 277 (1981).
- <sup>18</sup>P. R. Okamoto and G. Thomas, Acta Metall. <u>19</u>, 825 (1971).
- <sup>19</sup>D. de Fontaine, Acta. Metall. <u>23</u>, 553 (1975); in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73.