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Phase transitions and polymorphism in $LaH_{3.0}$ and $LaD_{3.0}$ at low temperatures

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The heat capacities of $LaH_{3.0}$ and $LaD_{3.0}$ have been measured in the temperature range from 1.2 to 300 K. Four sharp heat-capacity anomalies were found in $LaD_{3.0}$ at 211, 230.5, 233.5, and 274 K, indicating the existence of five phases. For $LaH_{3.0}$ two broad heat-capacity peaks were observed at 241 and 270 K, indicating the existence of three phases. The lowest transition in both $LaH_{3.0}$ and $LaD_{3.0}$ is thought to be a semiconductor-to-metal transition on warming, and the highest transition in $LaD_{3.0}$ to be a transition in which the deuterium atoms change locations from an off-centered position to the center of the tetrahedral site on warming. The intermediate transitions in $LaD_{3.0}$ and the upper transition in $LaH_{3.0}$ are probably transformations involving the rearrangement of the deuterium or hydrogen atoms, respectively, in different off-centered configurations. The thermodynamic functions for $LaH_{3.0}$ and $LaD_{3.0}$, respectively, are found to be as follows: $S^0_{298.15}=13.94$ and 16.58 J/g-at. K, $(H^0_{298.15}-H^0_0)/T=7.54$ and 9.36 J/g-at. K. The electronic specific-heat constant γ and Debye temperature Θ_D for $LaH_{3.0}$ and $LaD_{3.0}$, respectively, are $\gamma=0\pm0.04$ and 0 ± 0.06 mJ/g-at. K, $\Theta_D=241.5\pm0.8$ and 246.3 ± 0.2 K. The isotope effect in the heat capacity can be approximately accounted for by a shift of $1/\sqrt{2}$ in the frequency of the hydrogen optic modes in both octahedral and tetrahedral sites of $LaD_{3.0}$ relative to $LaH_{3.0}$.

I. INTRODUCTION

A continuous solid solution (based on a fcc metal lattice) exists for lanthanum hydride from $LaH_{1.9}$ to $LaH_{3.0}$ and for lanthanum deuteride from $LaD_{1.9}$ to $LaD_{3.0}$. The dihydride and dideuteride have the fcc CaF_2 ($C1$)-type structure. About 95% of the hydrogen and deuterium atoms occupy the tetrahedral interstices and the remaining 5% occupy the octahedral sites.[1] At the composition limits $LaH_{3.0}$ and $LaD_{3.0}$, all the tetrahedral and octahedral holes are occupied forming the $BiLi_3$ ($D0_3$)-type structure.

Neutron-diffraction[2,3] and nuclear-magnetic-resonance[4] (NMR) experiments have been carried out on the lanthanum trihydride and trideuteride. Fisher *et al.*[2] have proposed that the deuterium atoms in $LaD_{3.0}$ do not occupy the center of the octahedral interstices but are displaced in a random fashion along the $\langle 111 \rangle$ directions toward the nearest deuterium atom sites in the tetrahedral interstices at 295 K. In a more extensive neutron-diffraction study of $LaD_{3.0}$ Didisheim *et al.*[3] found several extra peaks in the low-temperature pattern and upon heating, according to the authors, the peaks disappear completely at about 230 K. However, the data presented in Fig. 3 of their paper show that it reappears between 240 and 270 K—more will be said about this in connection with our results. Didisheim *et al.* concluded that these results suggest the occurrence of a low-temperature second-order phase transition which is due to an ordering of the deuterium atoms on off-center positions in the octahedral interstices. However, they were unable to determine conclusively the arrangement of the deuterium atoms. NMR measurements[4] of LaH_x and LaD_x, $2.89 \leq x \leq 3.0$, indicated metallic behavior for $T \geq 210$ K, and semiconducting behavior characterized by a band gap, $E_g=0.1$ eV, for $T<210$ K. Photoemission studies[5] of LaH_x indicate a small-band-gap semiconducting behavior near $x=2.9$. Electrical-resistivity measurements[6] from 77 to 298 K on LaH_x indicated semiconducting behavior in the composition range $2.86 \leq x \leq 2.92$, while more recent measurements[7] on LaH_x (where $x=2.21$–2.85) indicated a semiconductor-to-metal transition on warming or a crystallographic transformation at low temperatures. Bieganski *et al.*[8,9] reported a λ-type heat-capacity anomaly in $LaH_{2.69}$ at 239 K which they attributed to a semiconductor-to-metal first-order transition.

X-ray-diffraction studies[3] of $LaH_{2.9}$ have shown that the lattice parameter of the cubic phase de-

TABLE I. Analyses of lanthanum metal (in atomic ppm). Most impurities were determined by using a spark-source mass spectrometer unless otherwise noted. Concentrations of impurities not listed were less than 1 ppm.

Impurity	Amount present
H[a]	275
C[b]	128
N[a]	30
O[a]	295
F[c]	146
Cl	3
Sc	1
Fe	10
Ni	2
Cu	10
Y	1.4
Ce	<2
Pr	<2
Gd	<7
Ta	3.4

[a] Determined by vacuum fusion.

[b] Determined by combustion-gas chromatography.

[c] Determined by the formation, distillation, and determination of fluosilicic acid.

creases between room temperature and about 200 K and increases at lower temperatures until it reaches the same value as it has at room temperature.

Low-temperature specific-heat measurements have been reported for $LaH_{2.03}$,[10] $LaH_{2.69}$,[8,9] and LaD_x (where $x = 2.53$, 2.76, and 2.91) (Ref. 11) but no measurements have been made on the trihydride or trideuteride. The heat capacities of $LaH_{3.0}$ and $LaD_{3.0}$ presented in this paper were measured to determine the electronic specific-heat constant, the Debye temperature, the heat effects associated with the phase transition(s), and the isotope effect in order to corroborate the findings obtained from NMR, neutron scattering, x-ray-diffraction, and electrical-resistivity measurements and band-structure calculations made by our associates at the Ames Laboratory. The anomalies observed in our heat-capacity measurements were studied by x-ray diffraction over the temperature range 30—300 K.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The samples used in this study were prepared in bulk form starting with the highest-purity Ames Laboratory polycrystalline La. Analyses of the starting lanthanum are given in Table I. After electropolishing, the solid piece of La metal was placed in a Pt boat and reacted with hydrogen or deuterium gas in a standard-pressure high-vacuum system using MMH_3 (MM = mischmetal) and UD_3 as gas sources. The system was pumped down to 2×10^{-7} Torr before heating the metal to 400 °C, and after this temperature was attained hydrogen or deuterium was admitted to the system. The quantity of hydrogen or deuterium which reacted was determined from the pressure change in the system of known volume. An excess pressure of hydrogen or deuterium was added to ensure complete formation of the trihydride or trideuteride composition. After hydriding or deuteriding the heat-capacity samples were loaded into the copper holders in a helium-filled dry box.

B. Heat-capacity measurements

The low-temperature calorimeters used in this work are of the usual isolation heat-pulse type with a mechanical heat switch. The sample was loaded into a gold-plated copper holder for the low-temperature [(1.2—20)-K] measurement. For the high-temperature [(20—300)-K] measurements the sample was placed in a copper holder and sealed under a helium atmosphere. A germanium resistance thermometer was used to measure the temperature in the (1.2—20)-K temperature range, a gold-cobalt-copper thermocouple was used in the (20—77)-K range, and a copper-Constantan thermocouple was used in the (70—300)-K range.

III. RESULTS

The results of heat-capacity measurements of $LaH_{3.0}$ and $LaD_{3.0}$ in the temperature range (1.2—300)-K are shown in Fig. 1. For $LaH_{3.0}$ two broad heat-capacity peaks I and II were observed at 241 and 270 K, respectively, indicating the existence of three phases: α-, β-, and γ-$LaH_{3.0}$. The entropy changes for the phase transitions $\alpha\rightarrow\beta$ and $\beta\rightarrow\gamma$ are listed in Table II. The temperature of peak I is nearly the same as the temperature of the heat-capacity anomaly reported for $LaH_{2.69}$ by Bieganski and Drulis.[8]

Four sharp heat-capacity anomalies, I, II, III, and IV, were found in $LaD_{3.0}$ at 211, 230.5, 233.5, and 274 K, respectively, indicating the existence of five phases: α-, β-, γ-, δ-, and ϵ-$LaD_{3.0}$. The entropy changes for the phase transitions $\alpha\rightarrow\beta$, $\beta\rightarrow\gamma$, $\gamma\rightarrow\delta$, and $\delta\rightarrow\epsilon$ are listed in Table II. The temperature of peak I corresponds to the metal-to-semiconductor transition temperature which was observed by NMR measurements.[4] The temperatures of peaks II and III are nearly the same as the temperature reported by Didisheim *et al.*[3] for a phase transition in which the deuterium atoms are thought to order in the off-center octahedral interstices as in-

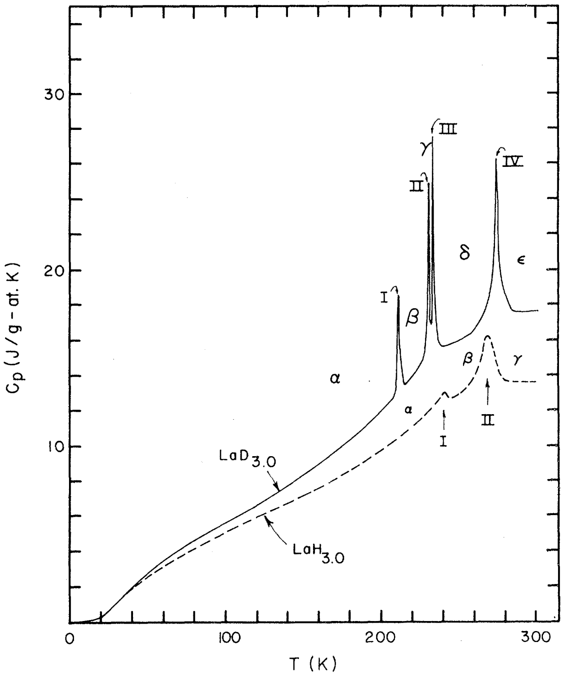

FIG. 1. Heat capacities of $LaH_{3.0}$ and $LaD_{3.0}$ from 1.2 to 300 K.

dicated by neutron-diffraction measurements. The smoothed heat capacities and thermodynamic functions for $LaH_{3.0}$ and $LaD_{3.0}$ are given in Tables III and IV, respectively. The thermodynamic functions for $LaH_{3.0}$ and $LaD_{3.0}$ were found to be $S^0_{298.15}=13.94$ and 16.48 J/g-at. K, $(H^0_{298.15}-H^0_0)/T=7.54$, and 9.36 J/g-at. K, respectively.

Some thermal-cycling experiments were made to see if some of the phase transitions would depend upon thermal treatment. After the initial heat-capacity measurements were made over the whole temperature range (20—300 K) on the high-temperature calorimeter, the sample was cooled below the lowest transformation (but not below 170 K), and heat-capacity measurements were repeated up to room temperature. The next cycle involved cooling the sample to a temperature between the first and second transformation temperatures before remeasuring the heat capacity. In the case of $LaD_{3.0}$ a fourth run was made in a similar manner as noted above but this time the starting temperature was between the third and fourth transformation temperatures. These results are shown in Figs. 2 and 3. For both samples the magnitude of the heat-capacity values decreased with higher starting temperatures, but the temperature and entropy of the specific anomalies are the same within the experimental precision of the measurements. These data show that the $LaD_{3.0}$ II peak completely disappears for the measurements made over the temperature range 220—300 K. This result indicates the γ-$LaD_{3.0}$ does not transform to β-$LaD_{3.0}$ upon cooling to 220 K. It is quite likely that β-$LaD_{3.0}$ only forms from α-$LaD_{3.0}$ and it (β-$LaD_{3.0}$) does not form reversibly from γ-$LaD_{3.0}$.

Figure 4 shows the C_p/T-vs-T^2 plots for $LaH_{3.0}$ and $LaD_{3.0}$ in the low-temperature region (1.2—4.1 K). The electronic specific-heat constant γ and Debye temperature Θ_D for $LaH_{3.0}$ and $LaD_{3.0}$ are $\gamma=0\pm0.04$ and 0 ± 0.06 mJ/g-at. K, $\Theta_D=241.5\pm0.8$ and 246.3 ± 0.2 K, respectively. Within the experimental precision there is no electronic contribution to the heat capacity of either material. These results are consistent with the NMR (Ref. 4) and photoemission[5] measurements.

A low-temperature x-ray investigation for $LaD_{3.0}$ has been carried out on a powder sample in the temperature range 30—300 K. Particular attention was paid to the line positions to see if there were any line

TABLE II. Transformation temperatures and entropies of transformation for $LaH_{3.0}$ and $LaD_{3.0}$.

Compound	Transformation	Type[a]	Transition temperature (K)	S_{tr} (J/g-at. K)
$LaH_{3.0}$	I ($\alpha\rightarrow\beta$)	$SC\rightarrow M$	241	0.040
	II ($\beta\rightarrow\gamma$)	$O_{0,0c}\rightarrow D_{0,0c}$ and $OC_{t,ap}\rightarrow OC_{t,p}$	270	0.109
$LaD_{3.0}$	I ($\alpha\rightarrow\beta$)	$SC\rightarrow M$	211	0.053
	II ($\beta\rightarrow\gamma$)	$O_{0,0c}\rightarrow D_{0,0c}$	230.5	0.083
	III ($\gamma\rightarrow\delta$)	$OC_{t,ap}\rightarrow OC_{t,p}$	233.5	0.112
	IV ($\delta\rightarrow\epsilon$)	$OC_{t,p}\rightarrow C_t$	274	0.176

[a] SC = semiconductor, M = metal, $O_{0,0c}$ = ordered, octahedral, and off-center sites, $D_{0,0c}$ = disordered (random), octahedral, and off-center sites, $OC_{t,ap}$ = tetragonal, off-center, and antiparallel sites, $OC_{t,p}$ = tetragonal, off-center, and parallel sites, and C_t = tetragonal, centered sites.

TABLE III. Smoothed values of the heat-capacity and thermodynamic functions of $LaH_{3.0}$ (J/g-at. K).

T (K)	C_p	S_T^0	$(H_T^0-H_0^0)/T$	$-(G_T^0-H_0^0)/T$
5	0.0167	0.0066	0.0047	0.0020
10	0.0853	0.0379	0.0270	0.0109
15	0.2051	0.0931	0.0649	0.0282
20	0.3434	0.1799	0.1261	0.0538
25	0.625	0.2882	0.1990	0.0592
30	1.044	0.4395	0.3053	0.1343
40	1.850	0.853	0.593	0.2599
50	2.525	1.342	0.916	0.4268
60	3.125	1.859	1.237	0.622
70	3.650	2.381	1.544	0.836
80	4.132	2.902	1.840	1.062
90	4.572	3.416	2.121	1.295
100	5.11	3.928	2.395	1.533
110	5.57	4.433	2.660	1.773
120	6.08	4.940	2.924	2.016
130	6.46	5.44	3.179	2.260
140	6.81	5.93	3.425	2.505
150	7.23	6.41	3.665	2.749
160	7.62	6.89	3.899	2.994
170	8.09	7.37	4.132	3.237
180	8.58	7.85	4.367	3.480
190	9.21	8.33	4.603	3.722
200	9.82	8.81	4.848	3.964
210	10.41	9.31	5.10	4.207
220	11.19	9.81	5.36	4.450
230	11.92	10.32	5.63	4.694
235	12.40	10.58	5.77	4.817
237.6	12.70	10.72	5.84	4.881
240.4	12.96	10.87	5.92	4.950
241.8	12.99	10.97	5.98	4.984
243.2	12.89	11.02	6.00	5.02
245	12.74	11.13	6.06	5.07
250	12.88	11.41	6.23	5.19
255	13.10	11.67	6.36	5.31
260	13.80	11.93	6.50	5.44
265	14.73	12.20	6.64	5.56
268.5	16.17	12.41	6.76	5.65
270.8	16.12	12.58	6.87	5.71
272.2	15.68	12.69	6.94	5.74
275	14.56	12.83	7.01	5.81
280	13.91	13.08	7.14	5.94
290	13.75	13.57	7.37	6.20
298.15	13.72	13.94	7.54	6.40
300	13.71	14.03	7.58	6.45

splittings in the lowest-temperature x-ray patterns, but only fcc peaks were observed and no evidence was found for a tetragonal or rhombohedral distortion of the cubic lines. The lattice parameter a_0 was determined from high-angle (531) and (600,442) reflections. As can be seen in Fig. 5 the lattice parameter of the fcc phase shows a normal temperature dependence. The linear thermal-expansion coefficient at 300 K derived from these data is 6.4×10^{-6} K^{-1}.

TABLE IV. Smoothed values of the heat-capacity and thermodynamic functions of $LaD_{3.0}$ (J/g-at. K).

T (K)	C_p	S_T^0	$(H_T^0-H_0^0)/T$	$-(G_T^0-H_0^0)/T$
5	0.0147	0.0054	0.0038	0.0016
10	0.0745	0.0257	0.0172	0.0085
15	0.1570	0.0621	0.0413	0.0208
20	0.2410	0.1067	0.0695	0.0373
25	0.753	0.1909	0.1314	0.0595
30	1.082	0.3150	0.2223	0.0927
40	1.963	0.786	0.583	0.2035
50	2.713	1.356	0.981	0.3749
60	3.413	2.039	1.449	0.589
70	4.088	2.586	1.748	0.839
80	4.600	3.051	1.963	1.088
90	5.11	3.624	2.285	1.338
100	5.60	4.188	2.593	1.595
110	6.08	4.747	2.890	1.856
120	6.60	5.30	3.179	2.120
130	7.15	5.85	3.461	2.386
140	7.70	6.40	3.744	2.653
150	8.27	6.95	4.027	2.921
160	8.96	7.50	4.315	3.190
170	9.62	8.07	4.607	3.460
180	10.29	8.64	4.905	3.732
190	11.06	9.21	5.21	4.005
200	11.86	9.80	5.52	4.280
208.2	12.68	10.40	5.90	4.507
210.3	13.43	10.57	6.00	4.567
211.3	18.52	10.67	6.07	4.596
212.0	17.32	10.72	6.10	4.616

IV. DISCUSSION

It is known that tantalum hydride, Ta_2H, undergoes an interstitial order-disorder transition in which hydrogen atoms order in the interstices of the bcc host lattice at low temperatures, and become disordered in a stepwise fashion with increasing temperature.[12–16] The heat-capacity measurements on Ta_2H show three sharp peaks with the upper two only 1.5 K apart. These results indicate the existence of four polymorphic forms.[13,16] Thus it is not too surprising that $LaH_{3.0}$ and $LaD_{3.0}$ have more than one transition and that some of these transformations may be due to transitions between two different ordered arrangements of hydrogen or deuterium atoms.

NMR measurements[4] on $LaD_{3.0}$ indicated semiconducting behavior for $T<210$ K and metallic behavior for $T>210$ K. These results are in good agreement with the results of our heat-capacity measurements in that the critical temperature of I is 211 K and there is no electronic contribution to the heat capacity ($\gamma=0$ mJ/g-at. K^2). It is possible that concomitant with the semiconductor-to-metal transition at 211 K there is a change in the ordered deuterium arrangements, but neutron-diffraction studies[3] seem to rule this out. Based on this evidence we have assumed that on warming transition I for $LaH_{3.0}$ is also a semiconductor-to-metal transformation. The zero value for γ for $LaH_{3.0}$ is in agreement with the band-structure calculations of Gupta and Burger[17] and Misemer and Harmon.[18]

Neutron-diffraction measurements[3] on $LaD_{3.0}$ have shown that several new peaks occur in the low-temperature pattern and that the peaks apparently disappear at about 230 K. This temperature corresponds to the critical temperatures II (230.5 K) or III (233.5 K). In the heat-capacity measurements from 220 to 300 K, peak II disappears completely. This result indicates that the β-$LaD_{3.0}$ phase was not formed when the sample was cooled to only 220 K. Thus the thermal history of the sample needs to be carefully documented before one can directly relate the two experimental results.

TABLE IV. *(Continued.)*

T (K)	C_p	S_T^0	$(H_T^0-H_0^0)/T$	$-(G_T^0-H_0^0)/T$
212.6	15.03	10.78	6.15	4.63
215	13.39	10.91	6.21	4.70
220	13.87	11.14	6.29	4.85
229	15.66	11.80	6.69	5.11
229.6	17.71	11.84	6.71	5.12
230.1	22.14	11.89	6.75	5.14
230.5	24.82	11.91	6.76	5.15
231.0	20.50	11.97	6.81	5.17
231.7	17.12	12.02	6.83	5.19
232.1	16.85	12.05	6.85	5.20
232.6	18.31	12.08	6.87	5.21
233.1	25.81	12.14	6.91	5.23
233.5	27.53	12.18	6.94	5.24
233.9	23.62	12.21	6.97	5.25
234.3	20.77	12.26	7.00	5.26
234.9	18.23	12.31	7.03	5.28
235	17.70	12.32	7.04	5.28
240	15.54	12.57	7.13	5.43
250	15.91	13.21	7.48	5.73
260	16.55	13.84	7.81	6.03
270	18.60	14.77	8.44	6.33
271.9	19.81	14.91	8.52	6.39
273.15	20.88	15.08	8.65	6.43
274.3	26.34	15.19	8.72	6.47
276.6	20.40	15.31	8.76	6.54
278.2	19.29	15.41	8.81	6.59
280.1	18.69	15.52	8.86	6.65
283	17.90	15.69	8.94	6.75
290	17.58	16.09	9.12	6.97
298.15	17.60	16.58	9.36	7.22
300	17.61	16.69	9.41	7.28

If the neutron scattering results are valid in that the deuterium atoms are located in the centers of the tetrahedral sites and in the off-center positions in the octahedral sites in a random arrangement at 295 K, then what is transformation IV (274 K) in $LaD_{3.0}$ due to? A closer examination of the neutron-diffraction data (Fig. 3 of Ref. 3) shows that the intensity of the peak at $2\theta=28°$ disappears for about a 10-K interval and then becomes observable again between about 240 and 270 K. The disappearance of the 2θ line at 28° between ~230 and ~240 K means that γ-$LaD_{3.0}$ does not have a diffraction peak at this angle but that both β-$LaD_{3.0}$ (also α-$LaD_{3.0}$) and δ-$LaD_{3.0}$ do. Thus it appears that the neutron-diffraction data are consistent with our heat-capacity results, and that, upon warming, transformation IV is due to the rearrangement of the deuterium atoms from the off-center position to the center of the tetrahedral interstitial site. Band-structure calculations[18] show that there is strong directional bonding between the hydrogen (deuterium) atoms in the tetrahedral sites and the metal atoms at the corners (and face centers), while weaker bonds exist between the lanthanum atoms and the hydrogen (deuterium) atoms in the octahedral sites. Thus the initial off centering of deuterium atoms on cooling would be expected to place in the tetrahedral sites rather than the ordering of atoms in the off-center octahedral sites. That is, in the δ phase the deuterium atoms in the off-center positions of the tetrahedral sites are directed toward the lanthanum atoms in the corners (and face centers), i.e., along $\langle 111 \rangle$ directions. Three possible (out of many) arrangements are shown in Fig. 6. This model is consistent with neutron scattering results which show that the octahedral-site deuterium atoms do not order until the temperature is ~35 K lower (i.e., ~230 K). Furthermore, since the entropy of transformation of the δ-ϵ transformation is about twice those of the two-lowest-temperature transfor-

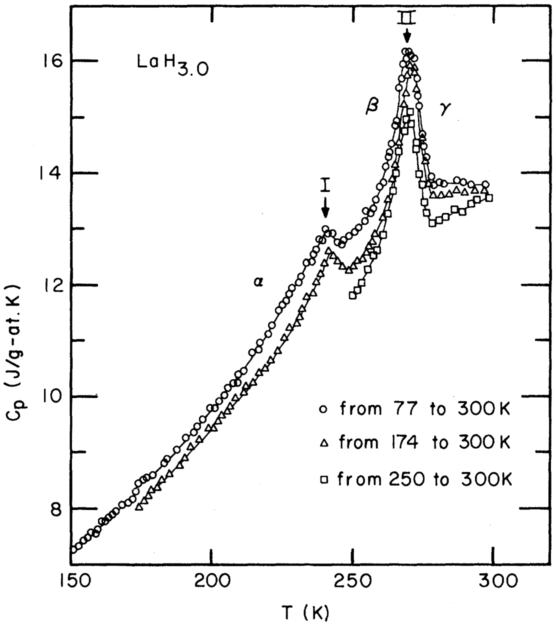

FIG. 2. Heat capacity of $LaH_{3.0}$ around the peak region (150—300 K) as a function of thermal cycling.

mations (α-β and β-γ) and about equal to that of the γ-δ transformation, this suggests that the tetragonal-site atoms are involved in this (δ-ϵ) transformation (and also the γ-δ) rather than the octahedral-site atoms since there are twice as many of the former atoms.

The absence of any change (e.g., discontinuity or kink) in the intensity-versus-temperature plot of the $2\theta=28°$ line at ~ 210 K indicates that the ordered arrangement of the deuterium atoms does not change when the sample undergoes the semiconductor-to-metal (α- to β-$LaD_{3.0}$) transition on warming at 211 K.

Having identified transitions I and IV in $LaD_{3.0}$ as the semiconductor-to-metal and an off-center—to—center transition of the tetrahedral-site atoms on warming, respectively, one wonders about the nature of transitions II and III. Transition III would be expected to involve the deuterium atoms in the tetrahedral sites from the entropy arguments given above. From the neutron-diffraction results,[3] the intensity of the $2\theta=28°$ line disappears for the γ phase suggesting that the off-center deuterium atoms go into an antiparallel arrangement of shifts along the $\langle 111 \rangle$ directions such that the intensity of this line is zero, e.g., Figs. 6(b) or 6(c) are possible arrangements which might satisfy such intensity-scattering—factor criteria. On the basis of the entropy arguments transition II is thought to involve the octahedral-site deuterium atoms which change upon cooling from a disordered arrangement of the off-centered atoms (γ-$LaD_{3.0}$) to an ordered arrangement of deuterium in the off-centered positions (β-$LaD_{3.0}$). Although this explanation reasonably accounts for transitions II and III, the exact ordered arrangements of deuterium atoms in δ- and γ-

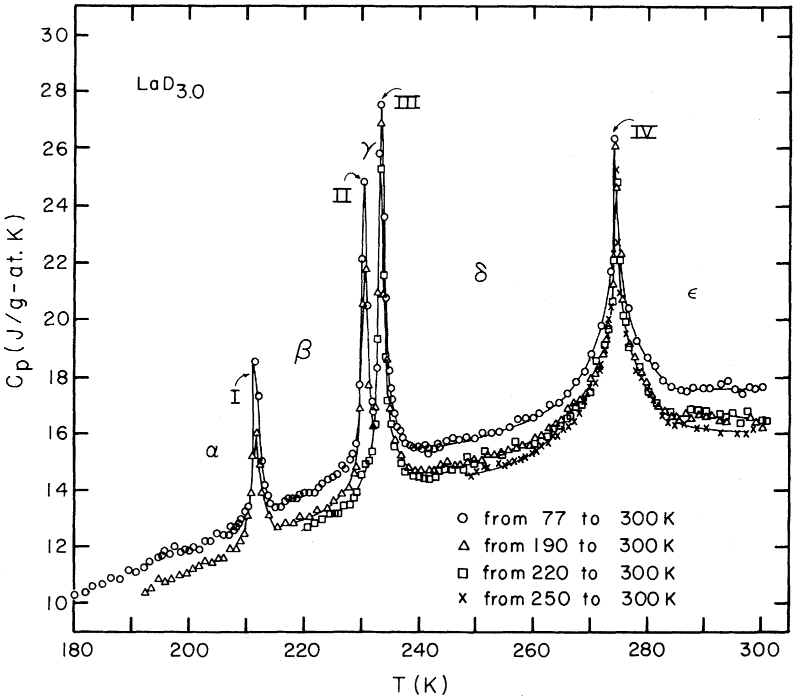

FIG. 3. Heat capacity of $LaD_{3.0}$ around the peak region (180—300 K) as a function of thermal cycling.

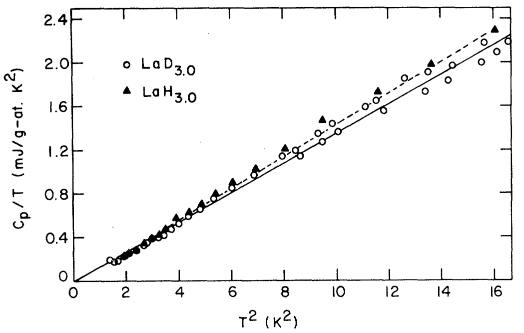

FIG. 4. Low-temperature heat capacity of $LaH_{3.0}$ and $LaD_{3.0}$. Lines are the result of a least-squares fit of the data to the equation $C_p/T=\gamma+\beta T^2$.

$LaD_{3.0}$ awaits experimental verification by careful neutron-diffraction studies.

The existence of only two peaks in $LaH_{3.0}$ compared to four in $LaD_{3.0}$ is unusual and difficult to accept. Assuming the lowest transition (I) in both $LaH_{3.0}$ and $LaD_{3.0}$ is the semiconductor-to-metal transition on warming, and transition II in $LaH_{3.0}$ is the same as II + III in $LaD_{3.0}$,[19] then one notes the corresponding transformation temperatures are $\sim 15\%$ ($T_{LaH_{3.0}}=1.14$ and $1.16T_{LaD_{3.0}}$, respectively) higher in $LaH_{3.0}$ than in $LaD_{3.0}$ and the corresponding entropies are 1.4 ($\sim\sqrt{2}$) times larger for $LaD_{3.0}$ than for $LaH_{3.0}$. If the β-γ transition in $LaH_{3.0}$ is an order-order transformation simultaneously involving the off centering of hydrogen atoms in the two interstitial sites, then the off-center—to—center transformation of the tetrahedral-site hydrogen atoms in $LaH_{3.0}$ upon warming is estimated to occur at $\sim$315 K with an entropy of transformation of 0.12 J/g-at. K. Since we did not make measurements above 300 K this tranformation was not detected.

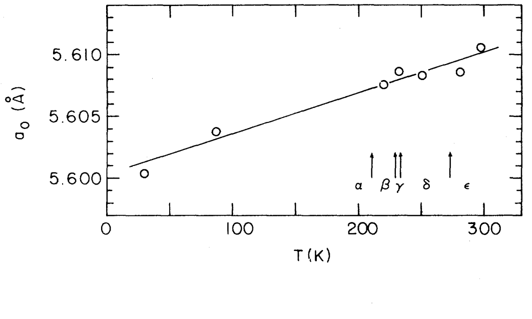

FIG. 5. Variation of the lattice parameter a_0 of $LaD_{3.0}$ with temperature. Arrows indicate the various transformation temperatures.

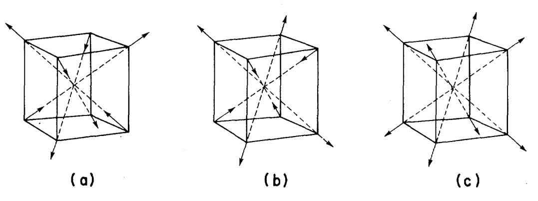

FIG. 6. Three possible shifts from the site centers of the tetrahedral H or D atoms along ⟨111⟩ directions. Cubes are not the entire unit cell of the LaH_3 (LaD_3) structure but only the three-dimensional lattice which connects the H (D) atoms in the tetrahedral sites.

Low-temperature x-ray-diffraction measurements on $LaD_{3.0}$ have shown that there is no crystal-structure transformation. However, x-ray measurements on $LaD_{2.78}$ revealed the occurrence of a fcc-to-tetragonal transformation at 254 K.[20] Heat-capacity studies[11] showed only one large peak ($S_{tr}\simeq 0.85$ J/g-at. K) at 251 K for $x=2.91$ and 2.76, i.e., the four peaks in $LaD_{3.0}$ disappeared when $x<3$.

The isotope effect in the heat capacity for $LaH_{3.0}$ and $LaD_{3.0}$ is similar to that found for YH_2 and YD_2. In the case of the yttrium compounds Flotow and co-workers[21] found that the difference in the heat capacities was due to the mass differences of the hydrogen isotopes which were assumed to vibrate as harmonic oscillators and thus contribute to the heat capacity according to the Einstein model. Following their approach, taking into account that there are three hydrogen (deuterium) atoms per mole instead of two, using $\nu_H=1047$ cm^{-1} and $\nu_D=\nu_H/\sqrt{2}=740$ cm^{-1}, and correcting the error in their Eq. (2), the calculated difference in the heat

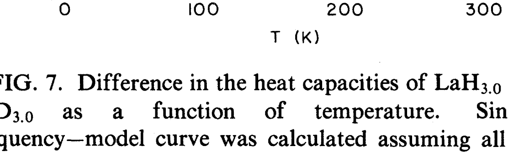

FIG. 7. Difference in the heat capacities of $LaH_{3.0}$ and $LaD_{3.0}$ as a function of temperature. Single-frequency—model curve was calculated assuming all the hydrogen (deuterium) atoms vibrate at a frequency of 1047 cm^{-1} (740 cm^{-1}). Two-frequency—model curve was calculated assuming the octahedral hydrogen (deuterium) atoms vibrate at a frequency of 650 cm^{-1} (460 cm^{-1}) and those in the tetrahedral site at 1200 cm^{-1} (849 cm^{-1}).

capacities was found to be in good agreement with the experimental ΔC_p from about 175 to 300 K (see Fig. 7—"single-frequency—model curve"). The agreement below 150 K was poor. This poor agreement is not unexpected since it was assumed that all the hydrogen (deuterium) atoms have the same vibrational frequencies. But since four hydrogen (deuterium) atoms per unit cell occupy the octahedral sites and eight occupy the tetrahedral sites, the first group of hydrogen (deuterium) probably vibrates at a much lower frequency because the force constant of the hydrogen in the octahedral site is weaker than that of the hydrogen in the tetrahedral site.[18] By assuming the hydrogen atoms which occupy the octahedral sites have $\nu_\mathrm{H}=650$ ($\nu_\mathrm{D}=460$) cm^{-1} while those in the tetrahedral sites have $\nu_\mathrm{H}=1200$ ($\nu_\mathrm{D}=849$) cm^{-1}, one obtains a reasonable fit over the entire temperature range (see Fig. 7—"two-frequency—model" curve). It is estimated that reasonable fits to the experimental results can be obtained for hydrogen octahedral vibrational frequencies in the range 625—675 cm^{-1} and for hydrogen tetrahedral frequencies between 1150 and 1250 cm^{-1}. Recently our colleagues[22] have measured the distribution of hydrogen vibrations in $\mathrm{LaH}_{2.99}$ and found two peaks (both of which are rather broad) at 65 meV (524 cm^{-1}) and 120 meV (968 cm^{-1}) which correspond to the vibrational frequencies of the hydrogen in the octahedral and tetrahedral holes, respectively. Although these values are significantly lower (by $\sim 24\%$) than the values required to fit the heat-capacity results the ratio of the tetragonal-site—to—octahedral-site frequencies are essentially identical, i.e., 1.85. Furthermore, in view of the complex frequency distribution[21] it is not all surprising that the model used to calculate the difference in heat capacities does not give quantitative agreement. The model, however, qualitatively explains the observed difference in the heat capacities. Also the fact that there are four transitions in $\mathrm{LaD}_{3.0}$ and two in $\mathrm{LaH}_{3.0}$ makes it difficult to determine the exact location of ΔC_p between 200 and 300 K.

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