Crystal structure of the deuteride $LaCu_5D_{3.2}$ studied by neutron powder diffraction

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Abstract

The crystal structure of the deuteride $LaCu_5D_{3.2}$ is investigated by neutron powder diffraction. Analysis of the diffraction pattern shows that the initial $CaCu_5$-type cell adopted by $LaCu_5$ is not preserved upon deuteration. The pattern of the deuteride can be indexed in a new *ortho*-hexagonal cell ($Pmma$ space group; $a' = 2a = 10.7647$ Å, $b' = c = 4.1493$ Å, $c' = 2a + b = 9.4445$ Å) leading to a cell volume four times larger than that of $LaCu_5$. All possible hydrogen sites derived from the original $CaCu_5$-type cell have been tested. Eight different sites have been found occupied by deuterium in 2c, 2e, two 4i and four 4j positions. At least 2.05 D atoms are found in tetrahedral positions and the remaining ones are in octahedral positions. The deuterium ordering is responsible for the symmetry lowering observed for the $LaCu_5$ compound upon hydrogenation. It induces small shifts of the metallic atoms compared to the $CaCu_5$-type structure leading to the supercell description. Finally, the impact of this structure on the unusual diffusion properties previously observed for $LaCu_5H_{3.4}$ during nuclear magnetic resonance (NMR) studies will be discussed.
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1. Introduction

Among the AB_5 family compounds (A: rare earths, B: transition metals) adopting the hexagonal $CaCu_5$-type structure ($P6/mmm$ space group) and absorbing hydrogen, most of the crystal structures of the resulting hydride phases have been previously determined [1–10]. In many cases, despite substantial volume expansions, the parent $CaCu_5$-type structure is preserved upon hydrogenation. However, superstructures related to hydrogen ordering appear for some compounds. For example, the compound $LaNi_5H_x$ ($5 < x < 6.7$ H/f.u.) exhibits a structural phase transformation due to a progressive ordering of the hydrogen atoms within the β phase [11]. This induces a symmetry reduction and the appearance of superstructure lines leading to a doubling of the *c*-axis with a new description in space group $P6_3mc$ and seven different interstitial sites for hydrogen. Similar behaviors are also reported for overstoichiometric $LaNi_{5+x}$ alloys with B/A ratio ranging between 5 and 5.4 [9]. As concerns

cobalt, the system RCo_5–H (R = rare earths) was investigated by Kuijpers [12]. For $LaCo_5$, two hydrides are formed with hydrogen contents 3.35 and 4.3 H/f.u., respectively. For the $CeCo_5$–H system, only one hydride is observed at 3 H/f.u. In both cases, a transformation from hexagonal to the *ortho*-hexagonal cell was observed upon hydrogenation. Similar structural change was also reported for the system $LaCo_{5x}Ni_{5-5x}$–H_y for $0.6 \leq x \leq 1$ [13] and for $PrCo_5D_4$ [2]. For this latter compound, small shifts of the metal atomic positions lead to a symmetry lowering into the space group $Cmmm$ with two sites (4e, 4h) almost fully occupied with hydrogen.

In the present work, the crystal structure of the deuteride $LaCu_5D_{3.2}$ is investigated by neutron powder diffraction. The impact of this structure on the unusual diffusion properties previously observed [14] for $LaCu_5H_{3.4}$ during nuclear magnetic resonance (NMR) studies will be also briefly discussed.

2. Experimental

A portion of the same $LaCu_5$ ingot previously used by Spada et al. [14] for their volumetric, X-ray diffraction (XRD) and NMR experiments was used in these studies. This $LaCu_5$ alloy had been made at the Ames Laboratory, Iowa State University (USA) by first arc melting a stoichiometric mixture of

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La (99.95%) and Cu (99.999%) metal followed by vacuum annealing at 973 K for 2 months. The present pieces had been stored in an evacuated glass tube for over 15 years with no indication of discoloration or degradation (e.g., oxidation) from their initial appearance. Powder XRD and electron probe micro-analysis (EPMA) were used in the present work to verify composition and homogeneity of this stored $LaCu_5$ material, which agreed very well with the original results by Spada et al. [14]. For powder ND analysis, about 7.5 g of crushed alloys were activated by five deuterium absorption–desorption cycles, transferred to a silica tube sample holder for the last absorption, deuterium loaded to full capacity to a pressure of 9.2 bar at room temperature (RT) and closed under controlled pressure to prevent any desorption effect during ND pattern acquisition. Neutron diffraction experiments were performed at the Institut Laue Langevin in Grenoble (France) on the diffractometer D1A. The wavelength was set to 1.911 Å. All diffraction patterns were refined using the program FULLPROF [15].

3. Results and discussion

Analysis of the sample using EPMA leads to $La_{1.02(8)}Cu_{4.98(8)}$ in fair agreement with the nominal stoichiometry. Beside the main phase, some precipitates possibly belonging to the $LaCu_6$-type phase may be present but only in very small quantities. The X-ray diffraction pattern of the intermetallic compound can be indexed in the $P6/mmm$ space group assuming a $CaCu_5$-type structure with $a = 5.1827(3)$ and $c = 4.1155(2)$ Å; $V = 95.733(9)$ Å in agreement with the data published by Spada et al. [14] and Dwight [16]. No lines belonging to the $LaCu_6$ phase could be observed. Results of the refinement are given in Table 1.

Table 1
Crystal structure of the intermetallic compound $LaCu_5$

Atoms	$P6/mmm$	Position	B_{iso} (Å²)
La	1a	(0, 0, 0)	0.68(7)
Cu	2c	(1/3, 2/3, 0)	0.61(6)
Cu	3g	(1/2, 0, 1/2)	0.61(6)

$R_p = 4.55\%$; $R_{\omega p} = 5.78\%$; $R_{exp} = 4.85\%$; $R_{Bragg} = 7.54\%$.

The deuteride was obtained by loading the sample to 3.2 D/f.u. under a pressure of 9.2 bar at RT. From the neutron diffraction pattern, it was clearly observed that the initial hexagonal cell is not preserved upon deuteration. First attempt to index the cell in the *ortho*-hexagonal cell ($a' = 2a + b$; $b' = a$; $c' = c$) gives some improvement but extralines remain non-indexed. All lines could be finally indexed by doubling the b' axis: ($b' = 2a$) leading to a cell volume $V' = 4V$. Among the different $P6/mmm$ subgroups, $Pbmm$ does correctly describe the structure. However, this space group in non-conventional and the conventional space group $Pmma$ have been chosen using the circular permutation: $x \rightarrow z \rightarrow y$. The new cell parameters are $a' = 10.7647(3)$ Å, $b' = 4.1493(1)$ Å, $c' = 9.4445(3)$ Å and $V' = 421.85(2)$ Å³. That gives a volume equal to 105.46 Å³ per $LaCu_5D_{3.2}$ corresponding to a ΔV of 9.73 Å³ for 3.2 D/f.u. and a volume expansion $\Delta V/V$ of 10.2%.

All the atomic positions from the original $CaCu_5$-type cell split into several as summarized in Table 2. All possible hydro-

Table 2
Crystal structure of the deuterated compound $LaCu_5D_{3.2}$ described in the *Pmma* space group

Atoms		$Pmma$	x	y	z	B_{iso} (Å²)	Occupied	% Occupied
La(1a)	La	2a	1/2	0	0	1.07(9)	2	100
	La	2e	1/4	0	0.5185(9)		2	100
Cu(2c)	Cu	2e	1/4	0	0.1335(11)	2.75(7)	2	100
	Cu	4i	0.5088(8)	0	0.3277(8)		4	100
	Cu	2e	3/4	0	0.1853(13)		2	100
Cu(3g)	Cu	4j	0.6263(9)	1/2	0.2452(10)		4	100
	Cu	4j	0.3710(9)	1/2	0.2375(9)		4	100
	Cu	2f	1/4	1/2	−0.0106(14)		2	100
	Cu	2d	0	1/2	1/2		2	100
D(3f)	D1	2c	0	0	1/2	2.7(2)	1.04(5)	52
	D2	2e	3/4	0	0.0149(23)		1.27(5)	63
	D3	4i	0.3735(13)	0	0.2523(13)		3.23(7)	81
	D4	4i	0.6183(34)	0	0.2314(29)		1.24(7)	31
Total D(3f)		12					6.6(3)	55
D(6m)	D5	4j	0.5055(12)	1/2	0.1308(8)	2.1(2)	3.24(7)	81
	D6	4j	0.6467(19)	1/2	0.4404(16)		1.77(8)	44
	D7	4j	0.3420(14)	1/2	0.4069(17)		2.14(8)	53
	D8	4j	0.3909(34)	1/2	0.0729(30)		1.03(7)	26
Total D(6m)		16					8.2(3)	51
Total D		28					14.8(6)	53
		a	10.7647(3) Å	R_p	4.03%			
		b	4.1493(1) Å	$R_{\omega p}$	5.32%			
		c	9.4445(3) Å	R_{exp}	1.39%			
		z	4	R_{Bragg}	8.5%			

The first column gives between brackets the equivalent positions of the atoms in the $CaCu_5$-type structure for comparison (*P6/mmm* space group).

gen sites (3f, 4h, 6m, 12n and 12o) derived from the original $CaCu_5$-type cell have been tested. The sites 4h and 12o were not found occupied. This is in agreement with the relative low deuterium concentration observed for this compound and with the fact that those two sites are usually the less occupied in other AB_5 hydrides. The site 6m splits into seven positions in space group *Pmma*. Only four of them are occupied with deuterium atoms, the remaining ones were found empty. The site 12n splits into six positions that have been also tested. However, after refinement analysis it was observed that the 12n atomic positions are shifted toward the equivalent 3f ones in the *P6/mmm* space group (it is worth to note that the 12n position (0.47; 0; 0.09) is close to the 3f one (0.50; 0; 0) in the $CaCu_5$-type structure). Accordingly, the 3f position that splits in four different sites was tested leading to more reliable refinement results.

Finally, 2.05 D atoms are found in tetrahedral positions in the equivalent 6m La_2Cu_2 sites and the remaining ones (1.65 D) are in octahedral positions in the equivalent 3f La_2Cu_4 sites. This deuterium ordering is assumed to be responsible for the symmetry lowering observed for the $LaCu_5$ compound upon hydrogenation. It also induces small shifts of the metallic atoms compared to the $CaCu_5$-type structure leading to the supercell description. The total D content obtained by NPD is 3.7(2) D/f.u., relatively higher than the composition measured by the Sievert's method (3.2 D/f.u.) but in rather good agreement. No anisotropic broadening of the diffraction lines could be observed in the present neutron data and it was therefore concluded that the strain-induced anisotropic broadening observed in some other $LaNi_5$-type deuterides [17–19] does not appear in this compound. The refined pattern is shown in Fig. 1 and results of the refinement are given in Table 2. Views of the octahedral and tetrahedral sites occupied by deuterium are shown in Fig. 2.

Hydrogen absorption properties observed in the present work are coherent with those reported by Spada et al. [14] who found 3.7 H/f.u. under 36 atm at 374 K. However, they report a C-centered monoclinic cell for the hydride phase whereas a reliable refinement is obtained in the present case with a double *ortho-*
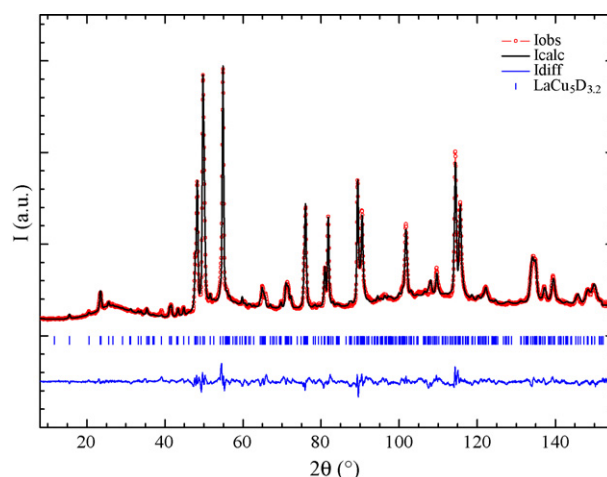

Fig. 1. Refined diffraction pattern (*Pmma* space group) of $LaCu_5D_{3.2}$ obtained from powder neutron diffraction analysis at RT (measured (dots), calculated (solid line) and difference curves (below); vertical bars correspond to line positions of the deuteride).

hexagonal cell. However, to avoid any H_2 desorption, Spada and co-workers investigated their sample with X-ray using specimens rapidly cooled down to 77 K and poisoned by exposure to air. In our case, the structural parameters are obtained by ND analysis on a sample at RT in a tight deuterium cell and it may happen that the monoclinic distortion observed by Spada and co-workers was triggered by the thermal treatment at 77 K. It is worth to note that a rapid X-ray diffraction pattern collected at room temperature on our deuteride can be successfully indexed in the double *ortho*-hexagonal cell confirming the current structure at least for the metallic framework.

As mentioned in Section 1 of this paper, prior NMR measurements [14] of the proton relaxation times for $LaCu_5H_{3.4}$ indicated very different hydrogen diffusion behavior than observed from $LaNi_5H_x$ and related Ni-substituted hydrides [20–22]. Namely, the apparent hydrogen mobility is much slower in $LaCu_5H_{3.4}$ with little evidence for rapid localized hop-
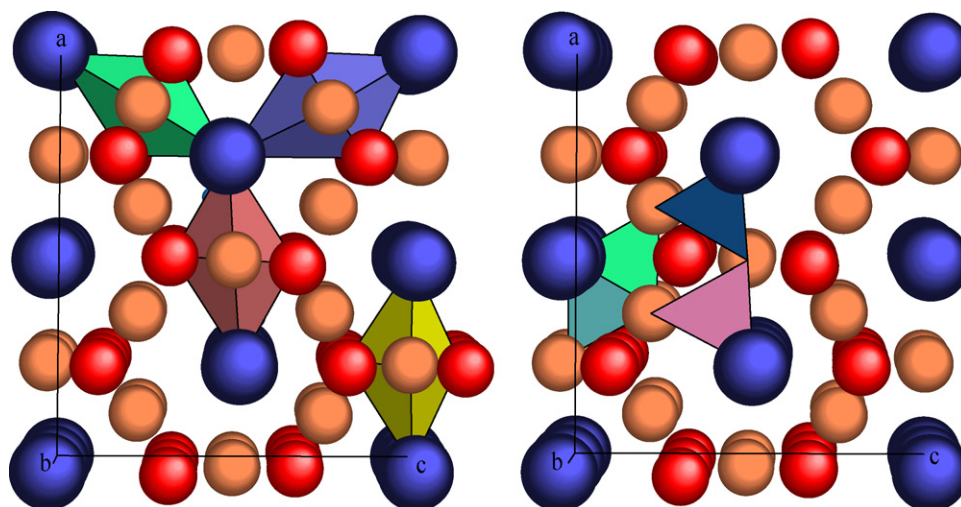

Fig. 2. Schematic view of the four octahedrons (left) equivalent to 3f position in $LaNi_5$ and four tetrahedrons (right) equivalent to 6m position in $LaNi_5$ and occupied in $LaCu_5D_{3.2}$ (structure projection perpendicular to the *b*-axis, La: large spheres; Cu: small spheres).

ping processes that are presumably allowed [21] in hexagonal lattices for LaNi$_5$D$_x$ [6,7], LaNi$_{5-y}$Al$_y$D$_x$ [3], LaNi$_4$BH$_{1.5}$ [21] and LaNi$_{5-y}$Sn$_y$D$_x$ [23]. Two independent localized hopping processes involving jumps within the 3f–12n clusters and 6m rings can become quite rapid [21] in these hexagonal structures that contribute to relatively fast long-range diffusion through the jump sequence 3f–12n–12o–6m–12o–12n [21,22]. In contrast, the absence of nominal 12n and 12o site occupancies and separation of both 3f and 6m into inequivalent and distorted sites in the *Pmma* structure for LaCu$_5$H$_x$ as reflected in Table 2 and Fig. 2 can dramatically increase the barriers for localized hopping to reduce significantly these rates. Thus, the structure differences between LaCu$_5$D$_x$ and the LaNi$_5$-based hexagonal hydrides would appear to be the primary source for slowed hydrogen motion found [14] for LaCu$_5$H$_{3.4}$. Unfortunately, the available proton relaxation time, especially for the thermally unstable [14] LaCu$_5$H$_{3.4}$, precludes a more quantitative assessment based upon just empirical results. Perhaps, future systematic theoretical first principles simulations of the short- and long-range diffusion processes in these AB$_5$ hydrides with hexagonal and *Pmma* structures will provide this information.

4. Conclusions

When hydrogenated, the LaCu$_5$ compound exhibits a structural transition from hexagonal to orthorhombic with a cell volume four times larger than that of the parent compound. Deuterium atoms are located in eight different sites split between tetrahedral and octahedral positions. The symmetry lowering is due to deuterium ordering and induces small shifts of the metallic atomic positions. It is hoped this determination of the multiple locations of the deuterium atoms in LaCu$_5$D$_{3.2}$, which are distinctively different from the structures for deuterides of LaNi$_5$ and its substituted alloys [3–12,23], will facilitate more detailed analyses that will compare apparent differences in the diffusion processes for these AB$_5$ hydride phases.

Acknowledgements

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