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Synthesis and crystal structure of tetragonal $LnMg_2H_7$ (Ln=La, Ce), two Laves phase hydride derivatives having ordered hydrogen distribution

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Abstract

$LaMg_2H_7$, $CeMg_2H_7$ and their deuterides were synthesized by hydrogenation (deuteration) of binary $LnMg_2$ at 373 K (Ln=La) and 423 K (Ln=Ce) and 100 bar hydrogen (deuterium) pressure and characterized by X-ray and neutron powder diffraction at room temperature. Their metal substructure represents a new tetragonal distortion variant of the cubic C15 Laves phase structure, space group $P4_12_12$ (No. 92); cell parameters for $LaMg_2H_7$: $a=6.4054(2)$ Å, $c=9.5994(3)$ Å; $LaMg_2D_7$: $a=6.3900(2)$ Å, $c=9.5782(4)$ Å; $CeMg_2H_7$: $a=6.3663(3)$ Å, $c=9.5226(5)$ Å; $CeMg_2D_7$: $a=6.3501(3)$ Å, $c=9.4957(5)$ Å; $Z=4$. The hydrogen (deuterium) distribution consists of four symmetry independent, fully occupied sites having triangular $[Ln_2Mg]$ and tetrahedral $[Ln_2Mg_2]$ and $[Mg_4]$ metal coordinations with distances in the range La–D=2.39–2.55 Å; Ce–D=2.36–2.51 Å; Mg–D=1.92–2.13 Å (La), 1.91–2.18 Å (Ce). The hydrogen-to-metal ratio, H/M=7/3, is the highest reported so far for Laves phase hydride derivatives.

Keywords: Laves phase; Crystal structure; Neutron diffraction; Hydrogen ordering

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1. Introduction

Transition metal compounds crystallizing with the cubic Laves phase (C15, $MgCu_2$) structure constitute a class of commercially available hydrogen storage materials, whose structural and physical properties are well established [1]. Their hydrogen concentrations reach values of up to 6 H atoms per formula unit (f.u.), a limit which is thought to be determined mainly by geometrical constraints [2]. The hydrogen atoms in the metal host structure occupy tetrahedral interstices and are usually disordered at room temperature. By contrast, little is known about the hydriding properties of Laves phases containing no transition elements. Some of these compounds react with hydrogen such as $LaMg_2$ and $CeMg_2$, which were found to absorb hydrogen to concentrations of up to 6.8 (6.2) H f.u.$^{-1}$ at room temperature [3]. The hydrides formed were described as crystallizing with a body-centered tetragonal cell having the parameters $a=6.386$ (6.362) Å and $c=9.583$ (9.343) Å; space group and atomic coordinates, however, were not determined. In this paper we report on the synthesis and the crystal structure of these two hydrides. It is shown that both have ordered hydrogen distribution at room temperature, in which hydrogen occupies not only centers but also faces of metal tetrahedra. The hydrogen content of 7 H f.u.$^{-1}$ is significantly higher than that of other known members of this class of compounds.

2. Experimental details

2.1. Synthesis

All steps of synthesis and sample preparation for X-ray and neutron diffraction were carried out under dry argon atmosphere. $LaMg_2$ and $CeMg_2$ alloys were prepared by arc melting stoichiometric mixtures of the elements (La, Ce: Johnson Matthey, 99.99%, Mg: Cerac, 99.6%). The ingots were remelted several times and ground to fine powders. The powders were placed in an autoclave and put under a hydrogen (deuterium) pressure, which was slowly increased to 100 bar at room temperature. Under these conditions, the compounds absorbed considerable amounts of hydrogen (deuterium) without decomposing into the binary hydrides (deuterides). The reaction was completed by increasing the temperature to 373 K ($LaMg_2$) and 423 K ($CeMg_2$) and annealing the samples under 100 bar pressure for three days. The resulting products had a

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brownish grey colour and were sensitive to air and moisture. A rapid increase of pressure at room temperature and/or higher sintering temperatures favoured segregation into binary hydrides (deuterides).

2.2. X-ray diffraction

In contrast to previous results [3], our X-ray powder patterns showed that the hydride structures were primitive tetragonal and not body-centered tetragonal (cell parameters, $LaMg_2H_7$: $a=6.4054(2)$ Å, $c=9.5994(3)$ Å; $LaMg_2D_7$: $a=6.3900(2)$ Å, $c=9.5782(4)$ Å; $CeMg_2H_7$: $a=6.3663(3)$ Å, $c=9.5226(5)$ Å; $CeMg_2D_7$: $a=6.3501(3)$ Å, $c=9.4957(5)$ Å; $Z=4$). The a parameter corresponds to one half of the face diagonal of the fcc cell of $LnMg_2$. The lattice expansion of $LaMg_2$ during hydrogenation (deuteration) is very anisotropic: c increases by 9.4% (9.2%), while a increases by only 3.2% (3.0%). The volume expansion is 16.6% (15.8%). A starting model for the metal atom positions was obtained by transforming the C15-type structure (space group $Fd\bar{3}m$) to the primitive tetragonal cell described above. Preliminary structure refinements in space group $P\bar{4}m2$ converged, but could not explain the intensity of the (012) reflection, which violates the extinction rule for body centering. Further investigation of the reflection list revealed as a possible extinction condition $00l$: $l=4n$. Therefore, profile fittings were calculated in the space groups containing a 4_1 screw axis ($P4_1$, $P4_122$ and $P4_12_12$). Finally, the metal structure was refined in space group $P4_12_12$, which was found to be the correct space group from neutron data. The refinement converged to $R_B=10.9\%$, $R_P=4.1\%$, $R_{WP}=5.8\%$, $S=2.68$ for $LaMg_2H_7$. A similar refinement was performed on the Ce sample. No indications for impurity phases were found.

2.3. Neutron diffraction:

The hydrogen positions were determined from neutron powder diffraction data of deuterated samples. $LaMg_2D_7$ was measured on the high resolution neutron powder diffractometer (HRNPD) [4] at the high flux beam reactor at Brookhaven National Laboratory (focusing Ge(511) monochromator, $\lambda=1.8857$ Å, $2\theta_{max}=160°$, step size $\Delta 2\theta=0.05°$, $T=295$ K, total measuring time 12 h). The $CeMg_2D_7$ data were collected on the D1A diffractometer at Institut Laue Langevin (Ge(511) monochromator, $\lambda=1.9090$ Å, $2\theta_{max}=160°$, step size $\Delta 2\theta=0.05°$, $T=295$ K, total measuring time 24 h). Both samples ($LaMg_2D_7$: 7 g; $CeMg_2D_7$: 7.5 g) were enclosed in cylindrical vanadium containers of 9 mm inner diameter. Profile fitting on the $LaMg_2D_7$ data with the Program FULLPROF [5] in space group $P4_1$ showed that the assumption of a fourfold screw axis was correct and that the sample was single-phase. Further refinements showed the presence of additional 2_1 screw axes, leading to the final space group $P4_12_12$. Starting with the two metal sites obtained from X-ray powder data, the following structure model was refined: Deuterium was distributed over four interstitial sites, three (D1, D2, D3) corresponding to the centers of $[La_2Mg_2]$ tetrahedra (6 $f.u.^{-1}$) and one (D4) to the center of $[Mg_4]$ tetrahedra (1 $f.u.^{-1}$). Preliminary refinements (program DBWS-9006PC [6]) showed that the occupancies of these sites did not differ significantly from unity and that all other interstitial sites (including the $[LaMg_3]$ type sites) were empty, leading to an ordered structure of composition $LaMg_2D_7$. The refinements also showed that D1 was shifted towards the triangular face shared by an empty $[La_2Mg_2]$ tetrahedron and thus had triangular $[La_2Mg]$ coordination. The following 29 parameters were allowed to vary in the final refinement: one scale factor, one zero correction, three peak shape, one mixing, one asymmetry, two cell parameters, fourteen positional and six isotropic displacement parameters. Six additional parameters were refined for the $CeMg_2D_7$ sample, namely one scale factor, two cell parameters, one positional and two isotropic displacement parameters for the impurity phase MgD_2. Scattering lengths were taken from [7]. The refinement results are summarized in Tables 1 and 2, the observed, calculated and difference neutron powder diffraction patterns are shown in Figs. 1 and 2. The metal–deuterium and deuterium–deuterium distances are given in Table 3.

Table 1
Refinement results on neutron powder diffraction data for $LaMg_2D_7$ ($T=295$ K; estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} (Å^2)
La	4*a*	0.2683(3)	*x*	0	0.0101(5)
Mg	8*b*	0.0258(3)	0.2618(4)	0.3519(2)	0.0130(5)
D1	8*b*	0.0319(4)	0.0320(4)	0.1294(3)	0.0285(5)
D2	8*b*	0.0709(4)	0.4332(4)	0.1809(2)	0.0227(5)
D3	8*b*	0.3052(3)	0.1611(3)	0.2542(3)	0.0276(5)
D4	4*a*	0.7585(4)	*x*	0	0.0224(7)

Space group $P4_12_12$ (No. 92).
Cell parameters (X-rays) $a=6.3900(2)$ Å, $c=9.5782(4)$ Å, $V=391.10(3)$ Å^3, $Z=4$. $R_B=5.1\%$, $R_P=4.1\%$, $R_{WP}=5.4\%$, $S=2.70$ for 163 reflections.
Form of the temperature factor: $T=\exp[-8\pi^2U_{iso}(\sin\theta/\lambda)^2]$.

Table 2
Refinement results on neutron powder diffraction data for $CeMg_2D_7$ ($T=295$ K; estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} (Å^2)
Ce	4*a*	0.2718(4)	*x*	0	0.0027(9)
Mg	8*b*	0.0260(3)	0.2584(4)	0.3524(2)	0.0142(5)
D1	8*b*	0.0346(4)	0.0311(4)	0.1274(3)	0.0241(4)
D2	8*b*	0.0776(4)	0.4337(4)	0.1822(2)	0.0241(4)
D3	8*b*	0.3082(3)	0.1583(3)	0.2541(3)	0.0245(5)
D4	4*a*	0.7541(4)	*x*	0	0.0226(6)

Space group $P4_12_12$ (No. 92).
Cell parameters (X-rays) $a=6.3501(3)$ Å, $c=9.4957(2)$ Å, $V=382.90(4)$ Å^3, $Z=4$. $R_B=5.4\%$, $R_P=3.8\%$, $R_{WP}=5.0\%$, $S=3.20$ for 157 reflections.
Form of the temperature factor: $T=\exp[-8\pi^2U_{iso}(\sin\theta/\lambda)^2]$.

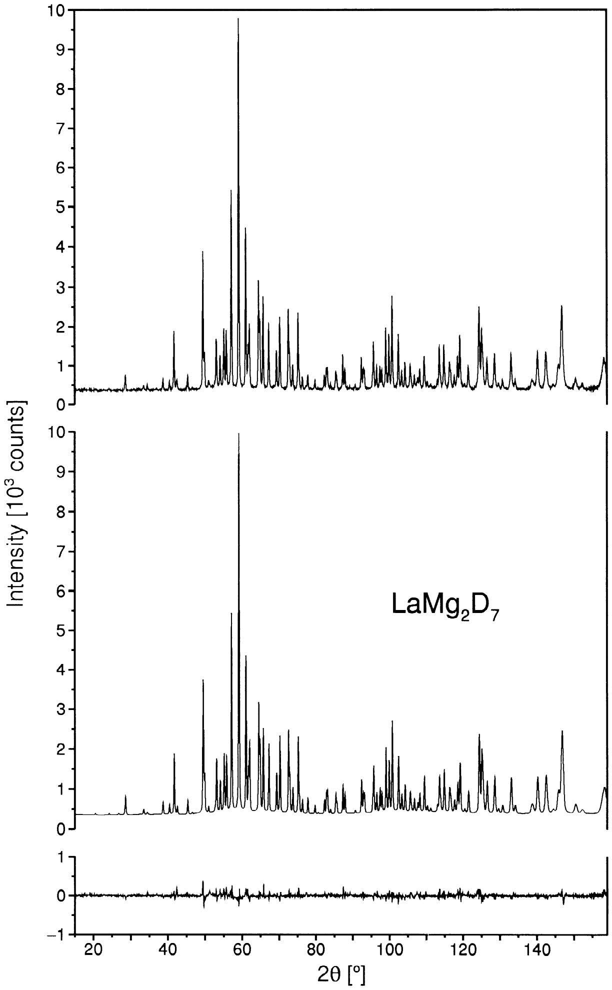

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder diffraction pattern of $LaMg_2D_7$ (HRNPD data, $\lambda = 1.8857$ Å).

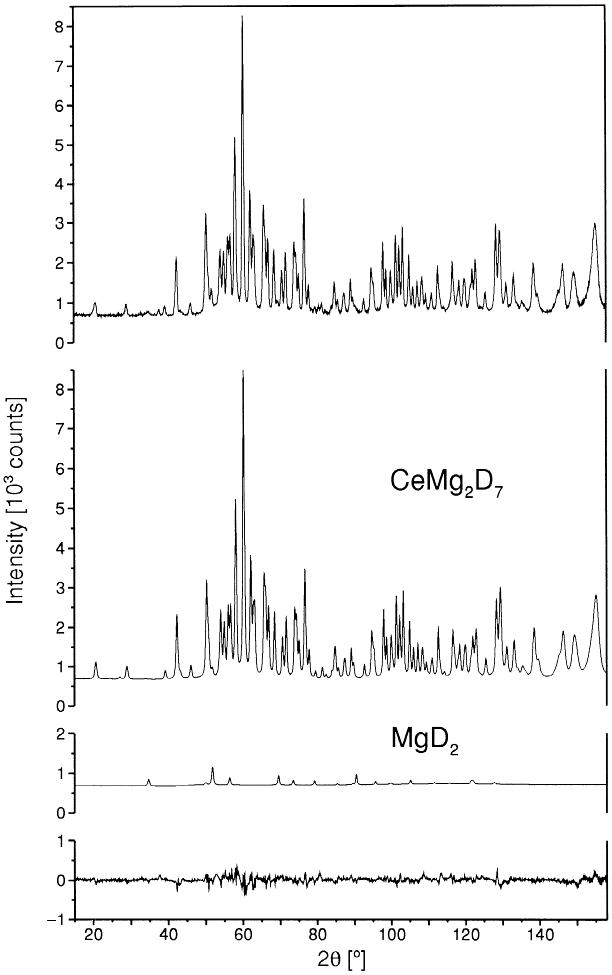

Fig. 2. Observed (top), calculated (middle) and difference (bottom) neutron powder diffraction pattern of $CeMg_2D_7$ containing MgD_2 as impurity (D1A data, $\lambda = 1.9090$ Å).

2.4. Desorption measurements

The thermal stability was estimated by thermal desorption measurements on a Sartorius microbalance M25D-P at 1 bar H_2 and a heating rate of 1 K min^{-1}. Surprisingly, both $LaMg_2H_7$ and $CeMg_2H_7$ started to decompose only at temperatures above 573 K, which is significantly higher than the reaction temperature necessary for their synthesis and the desorption temperatures reported (508 K at 1 bar H_2 [8]). In order to check the absolute temperature scale of the microbalance, MgH_2 was measured as a standard under the same experimental conditions and found to decompose at 630 K. This value is also much higher than the reported desorption temperature of 557 K [9]; the difference is presumably due to a temperature gradient in the balance, indicating that the true decomposition temperature of the ternary hydrides is around 500 K. The reaction products after desorption were not investigated, but the weight loss of the sample (4 H atoms $f.u.^{-1}$) and the analysis of the various reaction products obtained during synthesis suggests the presence of binary LaH_3 and elemental Mg.

3. Results and discussion

The title compounds provide new insight into the hydrogenation behaviour of Laves phases. Firstly, their hydrogen-to-metal ratio, $H/M = 7$, is the highest one achieved so far for C15-type metal host structures. This ratio considerably exceeds that observed [1] and predicted (AB_2H_6 [2]) for C15-type hydride phases. The predictions were made by assuming that the structure retains cubic symmetry and that hydrogen occupies the centers of tetrahedral interstices. The present result shows that these assumptions are not justified and that higher hydrogen concentrations can be obtained by allowing the metal structure to distort and hydrogen to shift away from the center of the metal tetrahedra. Fig. 3 shows the distorted metal structure of $LnMg_2D_7$ (a) compared to the structure

Table 3
Selected interatomic distances (Å) for $LnMg_2D_7$ (Ln = La, Ce; estimated standard deviations in parentheses).

		La	Ce			La	Ce
Ln–	2 D2	2.388(3)	2.360(3)	D2–	Mg	1.991(3)	1.990(3)
	2 D1	2.409(3)	2.362(3)		Mg	2.131(4)	2.179(4)
	2 D2	2.466(3)	2.437(4)		D3	2.319(3)	2.301(3)
	2 D1	2.470(3)	2.463(3)		Ln	2.388(3)	2.360(3)
	2 D3	2.540(3)	2.529(3)		D3	2.400(3)	2.381(3)
	2 D3	2.554(3)	2.507(3)		D3	2.427(3)	2.385(3)
					Ln	2.466(3)	2.437(4)
Mg–	D1	1.921(4)	1.905(4)		D4	2.473(4)	2.480(4)
	D4	1.982(3)	1.980(3)		2 D2	2.551(3)	2.545(3)
	D2	1.991(3)	1.990(3)				
	D3	2.032(3)	2.012(3)	D3–	Mg	2.032(3)	2.012(3)
	D4	2.062(3)	2.027(3)		Mg	2.116(3)	2.118(3)
	D3	2.116(3)	2.118(3)		D1	2.271(4)	2.262(3)
	D2	2.131(4)	2.179(4)		D2	2.319(3)	2.301(3)
	D1	2.588(4)	2.579(4)		D2	2.400(3)	2.381(3)
					D2	2.427(3)	2.385(3)
D1–	Mg	1.921(4)	1.905(4)		D4	2.444(3)	2.433(3)
	D3	2.271(4)	2.262(3)		Ln	2.540(3)	2.529(3)
	D1	2.381(4)	2.402(4)		Ln	2.554(3)	2.507(3)
	Ln	2.409(3)	2.362(3)				
	Ln	2.470(3)	2.463(3)	D4–	2 Mg	1.982(3)	1.980(3)
	D1	2.479(4)	2.420(4)		2 Mg	2.062(3)	2.027(3)
	Mg	2.588(4)	2.579(4)		2 D3	2.444(3)	2.433(3)
					2 D2	2.473(4)	2.480(4)

of $LnMg_2$ (b). Secondly, the compounds are the first C15-type derivative deuterides whose deuterium distributions are found to be ordered at room temperature. All other AB_2 deuterides are disordered at room temperature with deuterium occupying mainly $[A_2B_2]$ and $[AB_3]$-type, and rarely $[B_4]$-type interstices (for a review see Ref. [1]; see also $UTi_2D_{4.5}$ [10]). A C15-type derivative deuteride having an ordered distribution near room temperature is HfV_2D_4 [11]. Its deuterium atoms order at 278 K by occupying $\frac{1}{3}$ of the $[Hf_2V_2]$-type interstices, which leads to a tetragonal distortion different from that in the present structure. Finally, the compounds show a novel metal coordination for deuterium. As shown in Fig. 4, D1 is located in the center of a $[Ln_2Mg]$ triangle; the deviation from the plane defined by these three metal neighbours is only 0.08 Å. The Mg–D1 distance in this triangle (La: 1.92 Å; Ce: 1.91 Å) is the shortest Mg–D distance of the structure. The two Mg atoms completing a trigonal bipyramidal configuration are much further away (La: 2.59 and 3.27 Å). The displacement of D1 away from the center of the $[Ln_2Mg_2]$ tetrahedra is presumably due to repulsive interactions with its close deuterium neighbours (La: D1–D3 = 2.27 Å; D1–D1 = 2.38 Å). The metal–deuterium distances in the tetrahedral $[Ln_2Mg_2]$ interstices (La–D = 2.39–2.55 Å, Ce–D = 2.36–2.51 Å, Mg–D = 1.98–2.13 (La), 1.98–2.18 Å (Ce)) and the $[Mg_4]$ interstices (Mg–D = 1.98 and 2.06 (La); 1.98 and 2.03 (Ce)) are consistent with those in LaD_3 (La–D = 2.43–2.59 Å [12]), CeD_3 (Ce–D = 2.40–2.58 Å [13]) and MgD_2 (Mg–D = 1.95 Å [14]). As expected, the metal deuterium distances in the Ce compound are generally shorter than those in the La compound; an exception is the Mg–D2 distance which is significantly longer (La: 2.13 Å; Ce: 2.18 Å). The shortest D–D distances (2.27 Å (La); 2.26 Å (Ce)) are in the range found for other ternary deuterides. The shortest distances between the metal atoms are Mg–Mg = 3.23 Å (La), 3.21 Å (Ce), La–Mg = 3.55 Å; Ce–Mg = 3.48 Å, compared to Mg–Mg = 3.10 Å (La), 3.09 Å (Ce), La–Mg = 3.64 Å, Ce–Mg = 3.62 Å in the binary alloys. Surprisingly, the Ln–Mg distances in the deuterides are shorter than those in the binary compounds. Other examples for a strengthening of metal–metal bonds during hydrogenations are given in Ref. [1].

The hydrogen storage efficiencies are 3.6 wt.% and 116 (La) and 118 (Ce) g H l^{-1}. Despite these favourable values and the fact that the binary alloys react with hydrogen already at room temperature, the compounds do not appear to be of interest for storage applications because their decomposition appears to be irreversible within useful temperature and pressure ranges.

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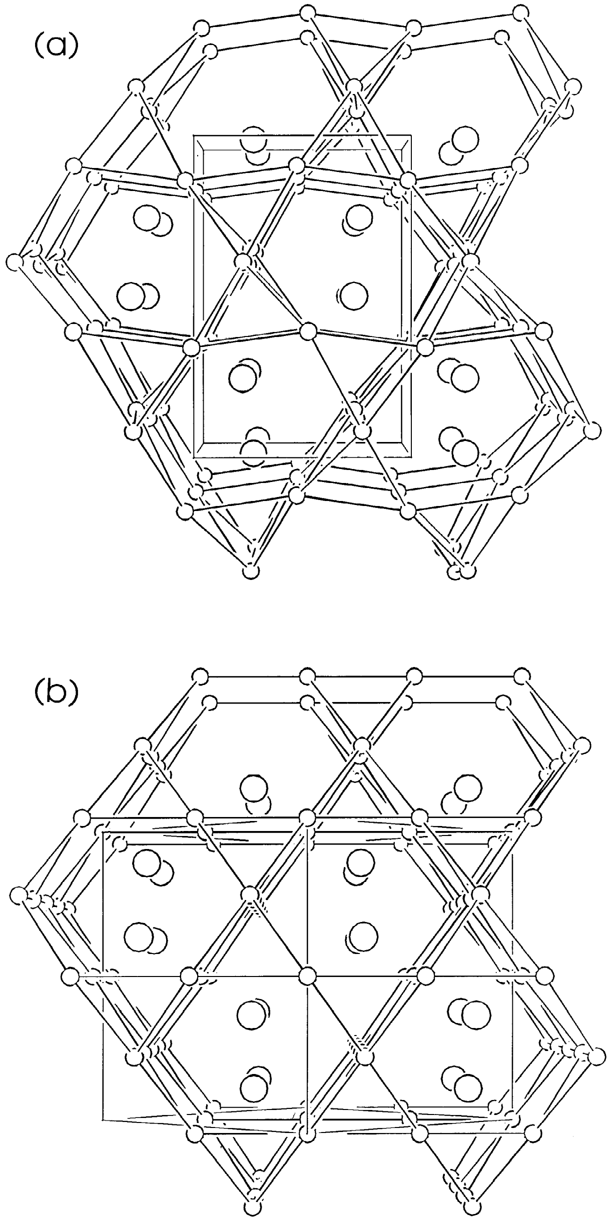

Fig. 3. Metal structure of tetragonal $LnMg_2D_7$ viewed along $[\underline{0}10]$: (a) compared to the structure of cubic $LnMg_2$; (b) viewed along $[\bar{1}10]$.

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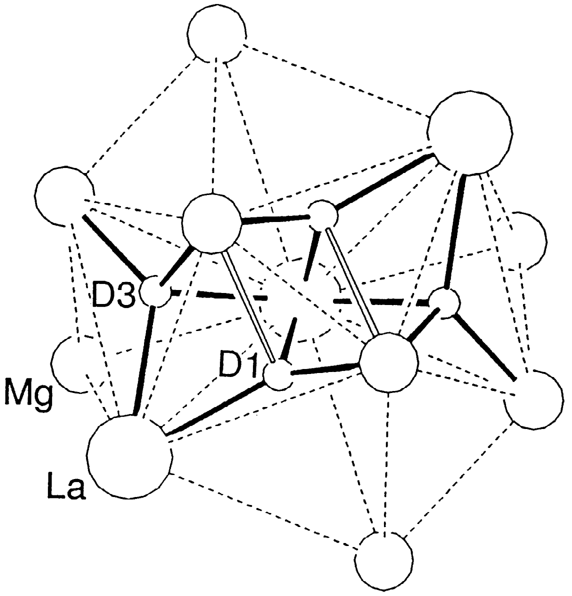

Fig. 4. Structure detail of $LnMg_2D_7$ (Ln=La, Ce) viewed along the twofold axis, showing the triangular coordination of D1 and the tetrahedral coordination of D3.

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