Supporting Information

(Journal of Physical Chemistry C)

Structure and Deuterium Desorption from $Ca_3Mg_2Ni_{13}$ Deuteride: A Neutron Diffraction Study

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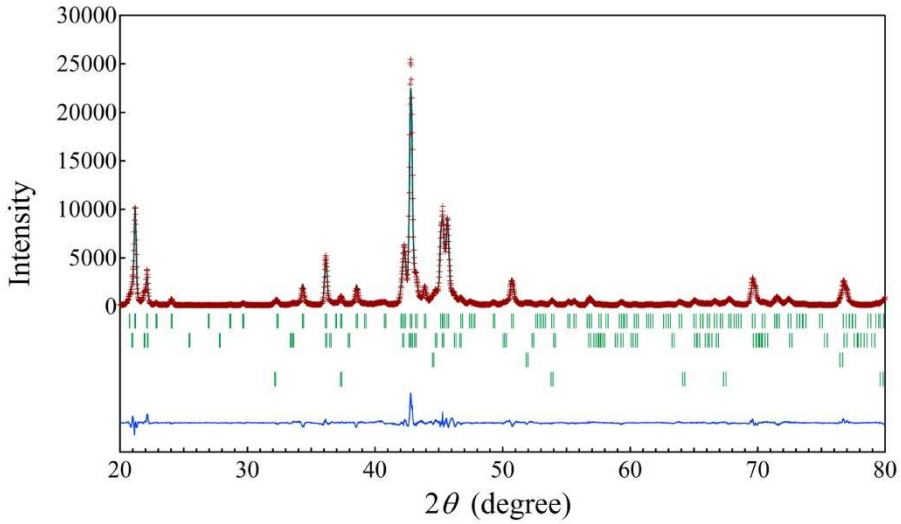

Figure S1. Rietveld refinement of the observed XRD pattern for the as-prepared $Ca_3Mg_2Ni_{13}$ alloy. Reflection markers (from above) are for the phases $Ca_3Mg_2Ni_{13}$ (85 wt%), Ca_2MgNi_9 (12 wt%), Ni (2 wt%) and CaO (1 wt%), respectively.

Table S1. Atomic coordinates, isotropic thermal parameters and occupation numbers for $Ca_3Mg_2Ni_{13}$ refined from X-ray powder diffraction data. Space group $R\bar{3}m$ (No. 166); cell parameters: a = 4.9615(5) Å and c = 36.066(3) Å; Z = 3. R_{wp} = 12.67%, R_p = 9.40%, R_I = 2.67%, S = 3.37.

Atoms	**Sites**	***g***	***x***	***y***	***z***	***B*** **(Å^2)**
Ca1	3*b*	1	0	0	1/2	3.1(3)
Ca2/Mg2	6*c*	0.45/0.55(3)	0	0	0.043(1)	2.0(3)
Ca3/Mg3	6*c*	0.53/0.47(3)	0	0	0.404(1)	0.4(2)
Ni1	6*c*	1	0	0	0.1658(2)	1.0(2)
Ni2	6*c*	1	0	0	0.2786(2)	0.5(1)
Ni3	9*e*	1	1/2	0	0	1.2(1)
Ni4	18*h*	1	0.4983(3)	–*x*	0.4441(1)	1.4(2)

Table S2. Possible crystallographic sites for hydrogen atoms in $Ca_3Mg_2Ni_{13}$ structure

Units	**No.**	**Wyckoff position**	**Site symmetry**	***x***	***y***	***z***
Within $[CaNi_5]$ unit	1	6*c*	Ni_4	0	0	z_1
	2	6*c*	Ni_4	0	0	$z_2 \approx z_1 - 1/3$
	3	18*h*	$CaNi_3$	x_3	$-x_3$	z_3
	4	18*h*	$CaNi_3$	$x_4 \approx 1 - x_3$	$-x_4$	$z_4 \approx z_3$
	5	18*h*	Ca_2Ni_3	x_5	$-x_5$	z_5
At the $[CaNi_5]/[CaMgNi_4]$ border	6	18*h*	$Ca(Ca/Mg)Ni_2$	x_6	$-x_6$	$z_6 \approx z_{Ni4}$
	7	18*h*	$Ca(Ca/Mg)Ni_2$	$x_7 \approx 1 - x_6$	$-x_7$	$z_7 \approx z_6$
Within $[CaMgNi_4]$ unit	8	6*c*	Ni_4	0	0	z_8
	9	6*c*	$(Ca/Mg)Ni_3$	0	0	$z_9 \approx z_8 - 1/3$
	10	6*c*	Ni_4	0	0	z_{10}
	11	6*c*	$(Ca/Mg)Ni_3$	0	0	$z_{11} \approx z_{10} - 1/3$
	12	18*h*	$(Ca/Mg)_2Ni_2$	x_{12}	$-x_{12}$	z_{12}
	13	18*h*	$(Ca/Mg)Ni_3$	$x_{13} \approx 1 - x_{12}$	$-x_{13}$	$z_{13} \approx z_{12}$
	14	18*h*	$(Ca/Mg)_2Ni_2$	x_{14}	$-x_{14}$	z_{14}
	15	18*h*	$(Ca/Mg)Ni_3$	$x_{15} \approx 1 - x_{14}$	$-x_{15}$	$z_{15} \approx z_{14}$
	16	36*i*	$(Ca/Mg)_2Ni_2$	x_{16}	y_{16}	z_{16}
	17	36*i*	$(Ca/Mg)_2Ni_2$	x_{17}	y_{17}	z_{17}
At the $[CaMgNi_4]/[CaMgNi_4]$ border	18	18*h*	$(Ca/Mg)_2Ni_2$	x_{18}	$-x_{18}$	$z_{18} \approx z_{Ni3}$

Table S3. Interatomic distances (Å) of the occupied interstices in $Ca_3Mg_2Ni_{13}D_{15.6}$ structure

Interstitial sites	Bonds	Distance	Interstitial sites	Bonds	Distance
Ni_4 in $CaNi_5$ unit	D1—Ni1	1.65(2)	(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D8—(Ca/Mg)2	2.19(3)
	D1—3Ni4	1.66(3)		D8—Ni2	1.66(3)
Tetragonal pyramid Ca_2Ni_3 in $CaNi_5$ unit	D2—2Ca1	2.70(3)		D8—2Ni3	1.61(2)
	D2—Ni1	1.61(4)	$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D9—(Ca/Mg)2	2.04(3)
	D2—Ni1	1.64(4)		D9—(Ca/Mg)3	2.08(3)
	D2—Ni4	1.63(5)		D9—2Ni4	1.64(4)
Ca(Ca/Mg)Ni_2 at $CaNi_5$/$CaMgNi_4$ border	D3—Ca1	2.63(2)	(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D10—(Ca/Mg)3	2.05(3)
	D3—(Ca/Mg)3	2.05(2)		D10—Ni2	1.68(3)
	D3—2Ni4	1.62(3)		D10—2Ni4	1.68(3)
Ca(Ca/Mg)Ni_2 at $CaNi_5$/$CaMgNi_4$ border	D4—Ca1	2.63(2)	$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D11—(Ca/Mg)2	2.10(4)
	D4—(Ca/Mg)3	2.05(2)		D11—(Ca/Mg)3	2.20(4)
	D4—2Ni4	1.61(3)		D11—Ni2	1.62(5)
Ni_4 in $CaMgNi_4$ unit	D5—Ni2	1.61(2)		D11—Ni3	1.61(3)
	D5—3Ni3	1.62(2)	$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D12—(Ca/Mg)2	2.03(4)
(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D6—(Ca/Mg)2	2.08(2)		D12—(Ca/Mg)3	2.14(4)
	D6—3Ni4	1.63(3)		D12—Ni2	1.63(3)
$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D7—(Ca/Mg)2	2.19(3)		D12—Ni4	1.67(4)
	D7—(Ca/Mg)3	2.19(3)	$(Ca/Mg)_2Ni_2$ at $CaMgNi_4$/$CaMgNi_4$ border	D13—2(Ca/Mg)2	2.24(3)
	D7—2Ni3	1.61(2)		D13—2Ni3	1.62(2)

Table S4. Values of the distances between the neighbouring D sites (less than 2 Å) in $Ca_3Mg_2Ni_{13}D_{15.6}$ structure. Such neighbouring sites cannot be simultaneously filled by D atoms.

Bonds	**Distance (Å)**	**Bonds**	**Distance (Å)**
D1—3D2	1.77(2)	D9—D6	1.16(2)
D1—3D4	1.83(2)	D9—2D9	1.91(2)
D2—D1	1.77(2)	D9—2D12	1.38(2)
D2—D2	1.08(1)	D10—D4	1.08(1)
D3—2D4	1.37(2)	D10—D10	1.91(2)
D3—D6	1.76(2)	D10—D12	1.12(1)
D3—D9	1.01(1)	D10—D12	1.80(2)
D4—D1	1.83(2)	D11—D5	1.78(2)
D4—2D9	1.92(2)	D11—D7	1.36(2)
D4—D10	1.08(1)	D11—D8	1.10(1)
D4—D12	1.86(2)	D11—D8	1.82(2)
D5—2D7	1.74(2)	D11—D11	1.14(1)
D5—3D8	1.12(1)	D11—D11	1.80(2)
D5—6D11	1.78(2)	D11—D12	1.38(2)
D5—2D13	1.77(2)	D11—D12	1.94(2)
D6—2D3	1.76(2)	D11—D13	1.82(2)
D6—3D9	1.16(2)	D11—D13	1.94(2)
D7—D5	1.74(2)	D12—D4	1.86(2)
D7—D7	1.85(2)	D12—D9	1.38(2)
D7—2D11	1.36(2)	D12—D10	1.12(1)
D7—D13	1.07(1)	D12—D11	1.38(2)
D8—D5	1.12(1)	D12—D11	1.94(2)
D8—2D8	1.85(2)	D12—D12	1.03(1)
D8—2D11	1.10(1)	D13—D5	1.77(2)
D8—2D11	1.82(2)	D13—D7	1.07(1)
D8—D13	1.07(1)	D13—D8	1.07(1)
D9—D3	1.01(1)	D13—2D11	1.82(2)
D9—2D4	1.92(2)	D13—2D11	1.94(2)

Table S5. Occupation numbers (*g* values) of D atoms for minor $Ca_3Mg_2Ni_{13}D_{0.4}$ refined from the neutron diffraction data of Sample 2. Space group $R\bar{3}m$ (No. 166); cell parameters: a = 4.9799(6) Å and c = 36.453(4) Å; Z = 3. R_{wp} = 2.25%, R_p = 1.74%, R_I = 3.17%, S = 1.11. To limit the number of refined parameters, other parameters were fixed as those of $Ca_3Mg_2Ni_{13}D_{15.6}$ in Sample 1.

Atoms	**Sites**	***g***	***x***	***y***	***z***	***B*** **(Å^2)**
Ca1	3*b*	1	0	0	1/2	2.8
Ca2/Mg2	6*c*	0.45/0.55	0	0	0.045	1.1
Ca3/Mg3	6*c*	0.53/0.47	0	0	0.404	2.9
Ni1	6*c*	1	0	0	0.163	1.3
Ni2	6*c*	1	0	0	0.279	2.4
Ni3	9*e*	1	1/2	0	0	0.3
Ni4	18*h*	1	0.499	–*x*	0.445	2.3
D1	6*c*	0.07(1)	0	0	0.205	1.5
D2	18*h*	0.04(1)	0.174	–*x*	0.847	1.5
D3	18*h*	0	0.851	–*x*	0.443	1.5
D4	18*h*	0	0.149	–*x*	0.443	1.5
D5	6*c*	0	0	0	0.680	1.5
D6	6*c*	0	0	0	0.098	1.5
D7	18*h*	0	0.783	–*x*	0.978	1.5
D8	18*h*	0	0.217	–*x*	0.978	1.5
D9	18*h*	0	0.213	–*x*	0.578	1.5
D10	18*h*	0	0.787	–*x*	0.580	1.5
D11	36*i*	0	0.625	0.035	0.038	1.5
D12	36*i*	0	0.946	0.697	0.262	1.5
D13	18*h*	0	0.851	–*x*	0	1.5

Table S6. Occupation numbers (*g* values) of D atoms for minor $Ca_2MgNi_9D_{7.2}$ refined from the neutron diffraction data of Sample 2. Space group $R\bar{3}m$ (No. 166); cell parameters: a = 5.1879(7) Å and c = 25.298(5) Å; Z = 3. R_{wp} = 2.25%, R_p = 1.74%, R_I = 1.12%, S = 1.11. To limit the number of refined parameters, the atomic coordinates were fixed as those of $La_2MgNi_9D_{13}$,[S1] and the B values for metal and D atoms were constrained as 1 and 1.5, respectively.

Atoms	**Sites**	***g***	***x***	***y***	***z***	***B*** **(Å^2)**
Ca1	3*a*	1	0	0	0	1.0
Ca2/Mg2	6*c*	0.5/0.5	0	0	0.1468	1.0
Ni1	3*b*	1	0	0	1/2	1.0
Ni2	6*c*	1	0	0	0.3306	1.0
Ni3	18*h*	1	0.4967	–*x*	0.0832	1.0
D1	18*h*	0.29(1)	0.494	–*x*	0.0196	1.5
D2	6*c*	0.21(1)	0	0	0.390	1.5
D3	18*h*	0	0.145	–*x*	0.084	1.5
D4	18*h*	0.15(1)	0.854	–*x*	0.0843	1.5
D5	18*h*	0.35(2)	0.4868	–*x*	0.1485	1.5
D6	18*h*	0.21(1)	0.798	–*x*	0.1191	1.5
D7	6*c*	0.06(1)	0	0	0.235	1.5
D8	6*c*	0.31(2)	0	0	0.4429	1.5

(S1) Denys, R. V.; Yartys, V. A.; Webb, C. J. Hydrogen in $La_2MgNi_9D_{13}$: The Role of Magnesium. *Inorg. Chem.* **2012**, *51*, 4231–4238. (The same below).

Table S7. Occupation numbers (*g* values) of D atoms for minor $Ca_2MgNi_9D_{0.8}$ refined from the neutron diffraction data of Sample 2. Space group $R\bar{3}m$ (No. 166); cell parameters: a = 5.1026(7) Å and c = 24.804(6) Å; Z = 3. R_{wp} = 2.25%, R_p = 1.74%, R_I = 10.28%, S = 1.11. To limit the number of refined parameters, the atomic coordinates were fixed as those of $La_2MgNi_9D_{13}$,[S1] and the B values for metal and D atoms were constrained as 1 and 1.5, respectively.

Atoms	**Sites**	***g***	***x***	***y***	***z***	***B*** **(Å^2)**
Ca1	3*a*	1	0	0	0	1.0
Ca2/Mg2	6*c*	0.5/0.5	0	0	0.1468	1.0
Ni1	3*b*	1	0	0	1/2	1.0
Ni2	6*c*	1	0	0	0.3306	1.0
Ni3	18*h*	1	0.4967	–*x*	0.0832	1.0
D1	18*h*	0.13(1)	0.494	–*x*	0.0196	1.5
D2	6*c*	0	0	0	0.390	1.5
D3	18*h*	0	0.145	–*x*	0.084	1.5
D4	18*h*	0	0.854	–*x*	0.0843	1.5
D5	18*h*	0	0.4868	–*x*	0.1485	1.5
D6	18*h*	0	0.798	–*x*	0.1191	1.5
D7	6*c*	0	0	0	0.235	1.5
D8	6*c*	0	0	0	0.4429	1.5

Table S8. Interatomic distances (Å) of the occupied interstices in $Ca_3Mg_2Ni_{13}D_{5.9}$ structure

Interstitial sites	Bonds	Distance	Interstitial sites	Bonds	Distance
Ni_4 in $CaNi_5$ unit	D1—Ni1	1.55(3)	(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D8—(Ca/Mg)2	2.10(3)
	D1—3Ni4	1.58(3)		D8—Ni2	1.63(3)
Tetragonal pyramid Ca_2Ni_3 in $CaNi_5$ unit	D2—2Ca1	2.62(2)		D8—2Ni3	1.58(2)
	D2—Ni1	1.54(3)	$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D9—(Ca/Mg)2	1.96(3)
	D2—Ni1	1.60(3)		D9—(Ca/Mg)3	2.01(3)
	D2—Ni4	1.56(3)		D9—2Ni4	1.60(3)
(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D6—(Ca/Mg)2	2.00(3)	(Ca/Mg)Ni_3 in $CaMgNi_4$ unit	D10—(Ca/Mg)3	2.01(3)
	D6—3Ni4	1.59(3)		D10—Ni2	1.56(3)
$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D7—(Ca/Mg)2	2.09(3)		D10—2Ni4	1.61(3)
	D7—(Ca/Mg)3	2.04(3)	$(Ca/Mg)_2Ni_2$ in $CaMgNi_4$ unit	D11—(Ca/Mg)2	2.04(3)
	D7—2Ni3	1.60(2)		D11—(Ca/Mg)3	2.12(3)
				D11—Ni2	1.60(3)
				D11—Ni3	1.54(3)

Table S9. Occupation numbers (*g* values) of D atoms for minor $Ca_2MgNi_9D_{0.7}$ refined from the neutron diffraction data of Sample 3. Space group $R\bar{3}m$ (No. 166); cell parameters: a = 5.0988(7) Å and c = 24.696(6) Å; Z = 3. R_{wp} = 3.52%, R_p = 2.68%, R_I = 5.26%, S = 1.64. To limit the number of refined parameters, the B values for metal and D atoms were constrained as 1 and 1.5, respectively; other parameters were fixed as those of $La_2MgNi_9D_{13}$.[S1]

Atoms	**Sites**	***g***	***x***	***y***	***z***	***B*** **(Å^2)**
Ca1	3*a*	1	0	0	0	1.0
Ca2/Mg2	6*c*	0.5/0.5	0	0	0.1468	1.0
Ni1	3*b*	1	0	0	1/2	1.0
Ni2	6*c*	1	0	0	0.3306	1.0
Ni3	18*h*	1	0.4967	–*x*	0.0832	1.0
D1	18*h*	0.12(1)	0.494	–*x*	0.0196	1.5
D2	6*c*	0	0	0	0.390	1.5
D3	18*h*	0	0.145	–*x*	0.084	1.5
D4	18*h*	0	0.854	–*x*	0.0843	1.5
D5	18*h*	0	0.4868	–*x*	0.1485	1.5
D6	18*h*	0	0.798	–*x*	0.1191	1.5
D7	6*c*	0	0	0	0.235	1.5
D8	6*c*	0	0	0	0.4429	1.5

Table S10. Interatomic distances (Å) of the occupied interstices in $Ca_3Mg_2Ni_{13}D_{0.3}$ structure

Interstitial sites	**Bonds**	**Distance**	**Interstitial sites**	**Bonds**	**Distance**
Ni_4 in $CaNi_5$ unit	D1—Ni1	1.53(3)	Tetragonal pyramid Ca_2Ni_3 in $CaNi_5$ unit	D2—2Ca1	2.55(2)
	D1—3Ni4	1.57(3)		D2—Ni1	1.53(3)
				D2—Ni1	1.53(3)
				D2—Ni4	1.50(2)