

Supporting Information

Belonging to the manuscript

Fluorine Substitution in Magnesium Hydride as a Tool for Thermodynamic Control

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Table S1a. Quantitative Rietveld analysis of SR-XRD data for $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ solid solutions. Errors are in parentheses. The phases in shaded grey were used in the weight averaged calculations.

MgF ₂	wt%	Lattice Parameter (Å)				Axial Mg-H(F) bond distance (Å)		Equatorial Mg-H(F) bond distance		Refined H occupancy factor
		a	c	Wt. av. a	Wt. av. c		Wt. av.		Wt. av.	
1	0.72	4.558 22(5)	2.98699 (5)	4.62337 (5)	3.05214 (5)	1.95323(2)	1.98114 (2)	1.96041(2)	1.99700(2)	0.76
2	0.00	4.563 22(5)	2.99199 (5)			1.95537(2)		1.96322(2)		0.78
3	0.18	4.568 22(5)	2.99699 (5)			1.95751(2)		1.96603(2)		0.80
4	0.18	4.573 22(5)	3.00199 (5)			1.95966(2)		1.96884(2)		0.82
5	0.13	4.578 22(5)	3.00699 (5)			1.96180(2)		1.97164(2)		0.84
6	0.17	4.583 22(5)	3.01199 (5)			1.96394(2)		1.97445(2)		0.86
7	0.17	4.588 22(5)	3.01699 (5)			1.96608(2)		1.97726(2)		0.89
8	0.12	4.593 22(5)	3.02199 (5)			1.96823(2)		1.98007(2)		0.90
9	0.25	4.598 22(5)	3.02699 (5)			1.97037(2)		1.98287(2)		0.92
10	0.16	4.603 22(5)	3.03199 (5)			1.97251(2)		1.98568(2)		0.94
11	0.99	4.608 22(5)	3.03699 (5)			1.97465(2)		1.98849(2)		0.96
12	0.88	4.613 22(5)	3.04199 (5)			1.97680(2)		1.99130(2)		0.98
13	12.59	4.618 22(5)	3.04699 (5)			1.97894(2)		1.99411(2)		0.99
14	67.93	4.623 22(5)	3.05199 (5)			1.98108(2)		1.99692(2)		1.01
15	15.52	4.628 22(5)	3.05699 (5)			1.98322(2)		1.99973(2)		1.03
MgH _{0.95} F _{0.05}										
1	0.59	4.514 52(1)	3.01339 (1)	4.52458 (1)	3.02345 (1)		1.946(3)		1.964(2)	0.87
2	2.11	4.519 52(1)	3.01839 (1)			1.944(3)		1.961(2)		0.89
3	92.56	4.524 52(1)	3.02339 (1)			1.946(3)		1.964(2)		0.91
4	3.22	4.529 52(1)	3.02839 (1)			1.948(3)		1.967(2)		0.93

5	0.67	4.534 52(1)	3.03339 (1)						0.95
6	0.28	4.539 52(1)	3.03839 (1)						0.97
7	0.17	4.544 52(1)	3.04339 (1)						0.99
8	0.09	4.549 52(1)	3.04839 (1)						1.01
9	0.08	4.554 52(1)	3.05339 (1)						1.03
10	0.09	4.559 52(1)	3.05839 (1)						1.05
11	0.01	4.564 52(1)	3.06339 (1)						1.07
12	0.04	4.569 52(1)	3.06839 (1)						1.09
13	0.03	4.574 52(1)	3.07339 (1)						1.11
14	0.00	4.579 52(1)	3.07839 (1)						1.12
15	0.05	4.584 52(1)	3.08339 (1)						1.14
MgH_{0.85}F_{0.15}									
1	0.00	4.527 75(1)	3.01473 (1)	4.54284 (1)	3.02982 (1)		1.94663 7(4)	1.974027(4)	0.75
2	0.00	4.532 75(1)	3.01973 (1)						0.77
3	1.82	4.537 75(1)	3.02473 (1)			1.944456(4)		1.971164(4)	0.79
4	94.53	4.542 75(1)	3.02973 (1)			1.946598(4)		1.973976(4)	0.80
5	3.65	4.547 75(1)	3.03473 (1)			1.948741(4)		1.976787(4)	0.82
6	0.00	4.552 75(1)	3.03973 (1)						0.84
7	0.00	4.557 75(1)	3.04473 (1)						0.86
8	0.00	4.562 75(1)	3.04973 (1)						0.88
9	0.00	4.567 75(1)	3.05473 (1)						0.90
10	0.00	4.572 75(1)	3.05973 (1)						0.92
11	0.00	4.577 75(1)	3.06473 (1)						0.94
MgH_{0.70}F_{0.30}									
1	0.00	4.528 42(4)	3.00351 (3)	4.56514 (4)	3.04023 (3)		1.95619 (2)	1.98201(1)	0.46
2	0.00	4.533 42(4)	3.00851 (3)						0.48
3	0.00	4.538 42(4)	3.01351 (3)						0.50
4	0.00	4.543 42(4)	3.01851 (3)						0.52
5	0.00	4.548 42(4)	3.02351 (3)						0.54
6	0.00	4.553 42(4)	3.02851 (3)						0.56
7	46.96	4.558 42(4)	3.03351 (3)			1.95331(2)		1.97827(1)	0.57
8	22.22	4.563 42(4)	3.03851 (3)			1.95545(2)		1.98108(1)	0.59
9	10.39	4.568 42(4)	3.04351 (3)			1.95759(2)		1.98389(1)	0.61
10	7.19	4.573 42(4)	3.04851 (3)			1.95973(2)		1.98670(1)	0.63
11	4.98	4.578 42(4)	3.05351 (3)			1.96188(2)		1.98951(1)	0.65
12	3.38	4.583 42(4)	3.05851 (3)			1.96402(2)		1.99232(1)	0.67
13	2.33	4.588 42(4)	3.06351 (3)			1.96616(2)		1.99514(1)	0.69
14	1.11	4.593 42(4)	3.06851 (3)			1.96830(2)		1.99795(1)	0.71

15	1.47	4.598 40(4)	3.07351 (3)			1.97045(2)		2.00076(1)		0.73
MgH_{0.50}F_{0.50}										
1	0.00	4.531 71(3)	2.98387 (2)	4.59225 (3)	3.04441 (2)		1.9716(8)		1.9860(5)	0.16
2	0.00	4.536 71(3)	2.98887 (2)							0.18
3	0.00	4.541 71(3)	2.99387 (2)							0.20
4	0.00	4.546 71(3)	2.99887 (2)							0.22
5	0.00	4.551 71(3)	3.00387 (2)							0.24
6	0.00	4.556 71(3)	3.00887 (2)							0.26
7	0.00	4.561 71(3)	3.01387 (2)							0.28
8	0.00	4.566 71(3)	3.01887 (2)							0.30
9	0.00	4.571 71(3)	3.02387 (2)							0.32
10	0.00	4.576 71(3)	3.02887 (2)							0.34
11	0.00	4.581 71(3)	3.03387 (2)							0.36
12	12.56	4.586 71(3)	3.03887 (2)			1.9692(8)		1.9829(5)		0.38
13	66.89	4.591 71(3)	3.04387 (2)			1.9714(8)		1.9857(5)		0.40
14	17.71	4.596 71(3)	3.04887 (2)			1.9735(8)		1.9885(5)		0.41
15	2.83	4.601 71(3)	3.05387 (2)			1.9757(8)		1.9913(5)		0.43
MgH₂										
1	99.31	4.517 95(1)	3.02257 (1)	4.51795 (1)	3.02257 (1)	1.935973(6)	1.93597 3(6)	1.966804(5)	1.966804(5)	0.96
2	0.69	4.522 95(1)	3.02757 (1)							0.98
3	0.00	4.527 95(1)	3.03257 (1)							1.00
4	0.00	4.532 95(1)	3.03757 (1)							1.02
5	0.00	4.537 95(1)	3.04257 (1)							1.04
6	0.00	4.542 95(1)	3.04757 (1)							1.06
7	0.00	4.547 95(1)	3.05257 (1)							1.08
8	0.00	4.552 95(1)	3.05757 (1)							1.10
9	0.00	4.557 95(1)	3.06257 (1)							1.12
10	0.00	4.562 95(1)	3.06757 (1)							1.14
11	0.00	4.567 95(1)	3.07257 (1)							1.16
12	0.00	4.572 95(1)	3.07757 (1)							1.18
13	0.00	4.577 95(1)	3.08257 (1)							1.20
14	0.00	4.582 95(1)	3.08757 (1)							1.22
15	0.00	4.587 95(1)	3.09257 (1)							1.24

Table S1b. Atomic coordinates and thermal parameters of $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ solid solutions. Errors are in parentheses.

Sample	Mg coordinates (x, y, z)	H coordinates (x, y, z)	F coordinates (x, y, z)	Mg Thermal parameter (beq)	H Thermal parameter (beq)	F Thermal parameter (beq)
MgF₂	0, 0, 0	---	0.303, 0.303, 0	0.21(1)	---	0.52(2)
Mg(H_{0.5}F_{0.5})	0, 0, 0	0.303, 0.303, 0	0.303, 0.303, 0	0.97(1)	3	1.23(3)
Mg(H_{0.7}F_{0.3})	0, 0, 0	0.303, 0.303, 0	0.303, 0.303, 0	0.92(2)	3	2.38(8)
Mg(H_{0.85}F_{0.15})	0, 0, 0	0.303, 0.303, 0	0.303, 0.303, 0	1.215(7)	3	2.10(8)
Mg(H_{0.95}F_{0.05})	0, 0, 0	0.303, 0.303, 0	0.303, 0.303, 0	1.088(8)	3	2.7(2)
MgH₂	0, 0, 0	0.303, 0.303, 0	---	1.45(2)	3	---

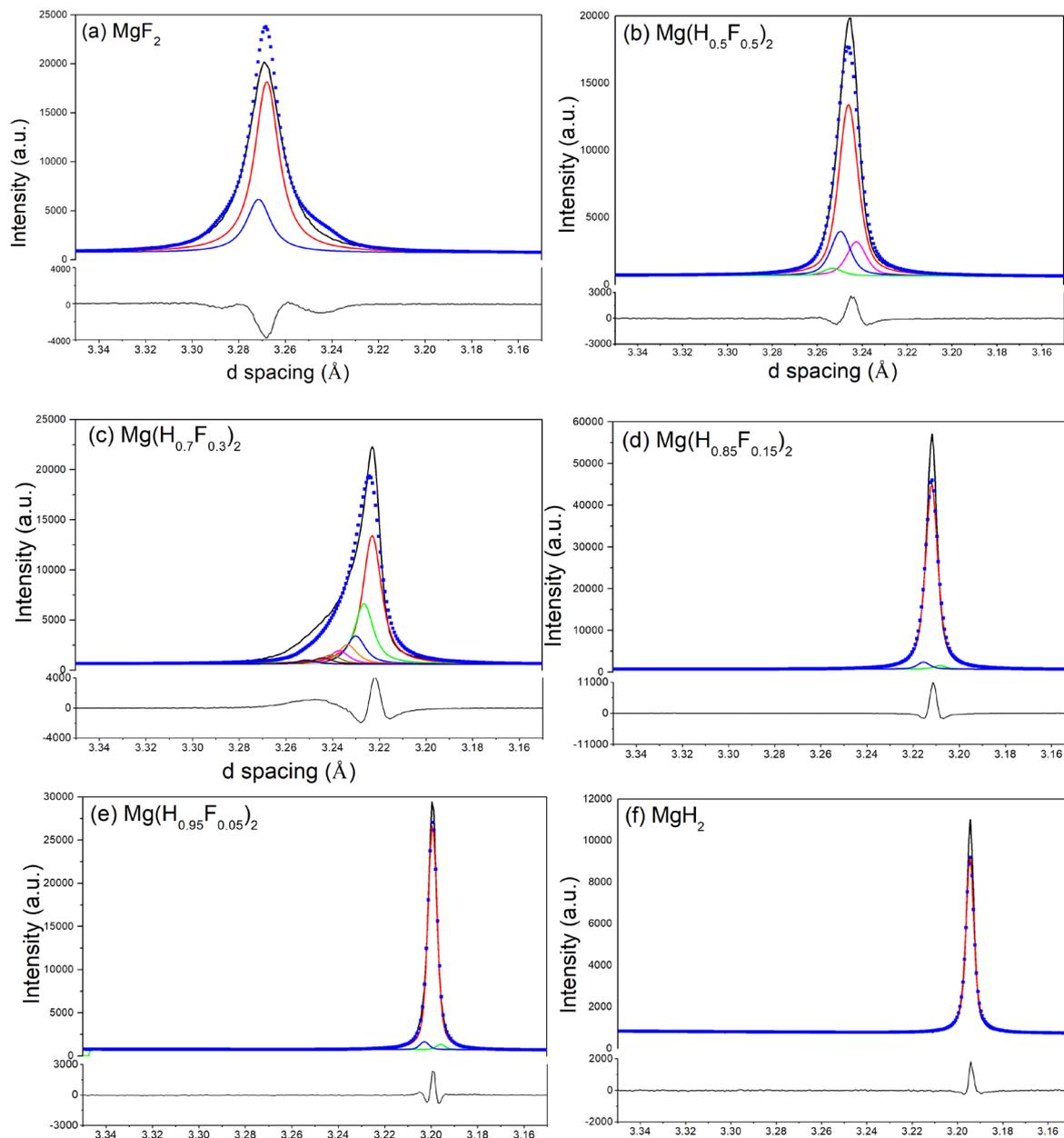


Figure S1. SR-XRD pattern, Phase distribution and Rietveld refinement plot of $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ solid solutions focused on the (110) Bragg peak. The Experimental data illustrated as black line, calculated diffraction pattern as blue squares, calculated phase distribution as multi-coloured lines and the difference plot in black at the bottom of the plot. $T = 27^\circ\text{C}$.

Table S2. Crystallographic parameters for $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ compounds optimized by DFT calculations. Percentage difference compared to experimental values given in parentheses.

Sample name	MgH_2	$\text{Mg}(\text{H}_{0.95}\text{F}_{0.05})_2$	$\text{Mg}(\text{H}_{0.90}\text{F}_{0.10})_2$	$\text{Mg}(\text{H}_{0.85}\text{F}_{0.15})_2$	$\text{Mg}(\text{H}_{0.80}\text{F}_{0.20})_2$	$\text{Mg}(\text{H}_{0.75}\text{F}_{0.25})_2$	$\text{Mg}(\text{H}_{0.70}\text{F}_{0.30})_2$	$\text{Mg}(\text{H}_{0.50}\text{F}_{0.50})_2$	MgF_2
Super cell size	1x1x1	1x1x5	1x1x5	1x1x5	1x1x5	1x1x5	1x1x5	1x1x1	1x1x1
Atoms in unit cell	6	30	30	30	30	30	30	6	6
Unit cell volume (Å ³)	61.07028	309.24927	311.51702	313.79404	315.95886	317.97643	319.55212	64.94474	67.27904
Volume/atom	10.17838 (1.01)	10.30831 (0.07)	10.3839 (N/A)	10.4598 (0.37)	10.53196 (N/A)	10.59921 (N/A)	10.65174 (1.31)	10.82412 (1.17)	11.21317 (3.08)
a (Å)	4.50589 (0.27)	4.52701 (0.06)	4.54044 (N/A)	4.55194 (0.2)	4.56547 (N/A)	4.57608 (N/A)	4.58461 (0.55)	4.61052 (0.4)	4.67321 (1.08)
c (Å)	3.00794	15.09009	15.11153	15.14244	15.15988	15.18472	15.20716	3.0579	3.0807
α (°)	90	90	89.9996	90.0006	89.9754	89.9763	89.9755	90	90
β (°)	90	90	89.9996	89.9982	90.019	90.0221	90.0175	90	90
γ (°)	90	89.6908	89.4224	89.7289	89.3277	89.6027	89.4074	87.6092	90
Average Mg-H(F) bond distance (Å)	1.94984 (0.08)	1.95653 (0.16)	1.95983 (N/A)	1.96521 (0.26)	1.96834 (N/A)	1.97319 (N/A)	1.97888 (0.65)	2.00472 (1.34)	2.01258 (1.17)

Table S3. Thermodynamics of $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ compounds determined by DFT calculations and physical measurements. ΔH_{form} is the enthalpy of formation of $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ determined by DFT calculations. ΔH_{des} is the enthalpy of desorption determined experimentally.

Sample (x)	ΔH_{form} DFT (kJ/mol compound)	ΔH_{des} measured (kJ/mol compound)	ΔS_{des} measured (J/K/mol compound)	ΔG_{des} measured (kJ/mol compound, @ 448 °C)
1	-204.4	74.06 ^a	133.4 ^a	-22.1
0.95	-250.7	---	---	---
0.9	-298.3	---	---	---
0.85 ^b	-346.0	62.6 ^b	112 ^b	-17.8
0.8	-393.7	---	---	---
0.75	-441.3	---	---	---
0.7	-489.3	---	---	---
0.5	-681.4	---	---	---
0	-1177.5	1124 ^c	57.17 ^d	---

^a Ref 1; ^b ref 2; ^c ref 3; ^dref 4.

NEXAFS

Near-Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy measurements were performed at the Soft X-ray (SXR) beamline of the Australian Synchrotron.⁵ All measurements were carried out at room temperature with the ultra-high vacuum (UHV) analysis chamber being maintained at a base pressure of $\leq 9 \times 10^{-10}$ mbar. Powdered samples were loaded in an argon-filled glovebox onto sample mounts and then transferred to the SXR beamline using a purpose-built vacuum transfer vessel. The vacuum transfer vessel is a sealed chamber that ensures that the samples are not exposed to air or moisture in the process of introducing them to the UHV chamber of the beamline. The NEXAFS spectra were recorded at the magnesium K-edge (1280 – 1360 eV). All spectra were obtained in total electron yield (TEY) mode and all NEXAFS spectra were processed and normalised using the QANT software program developed at the Australian Synchrotron.⁶ Intensities have been normalised with respect to impinging photon flux.

Figure S2 shows the NEXAFS data collected for the $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ samples with the MgF_2 pattern showing excellent agreement with literature data.⁷⁻⁸ MgF_2 has a relatively simple spectrum with two predominant peaks at 1313 and 1318 eV in the full multiple scattering region, followed by several minor features in the intermediate multiple scattering region (IMS).³⁹ The NEXAFS spectrum of MgH_2 in contrast, has a predominant peak at 1308 eV followed by a number of broad features at higher energy. The $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ spectra each bear resemblance to the parent MgH_2 and MgF_2 spectra and vary depending on the stoichiometry of the solid solution. It has been noted that the spectra of six-coordinate Mg compounds are the weighted sums of all the independent partial spectra generated by the absorber when located in each different environment within the investigated structure.⁸

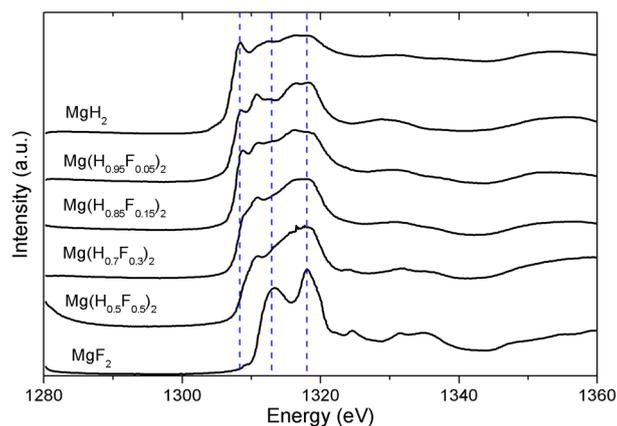


Figure S2. NEXAFS data collected near the magnesium *K*-edge for the $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ system.

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