

## I. SUPPLEMENTARY MATERIAL

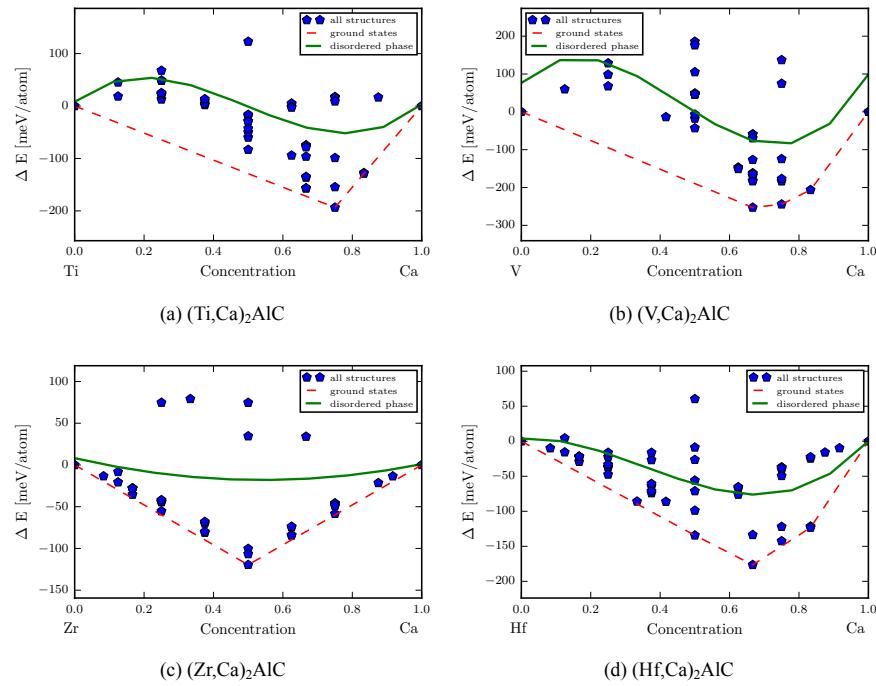


FIG. 1. Ground states at 0 K using cluster expansion for  $(\text{M1}, \text{Ca})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

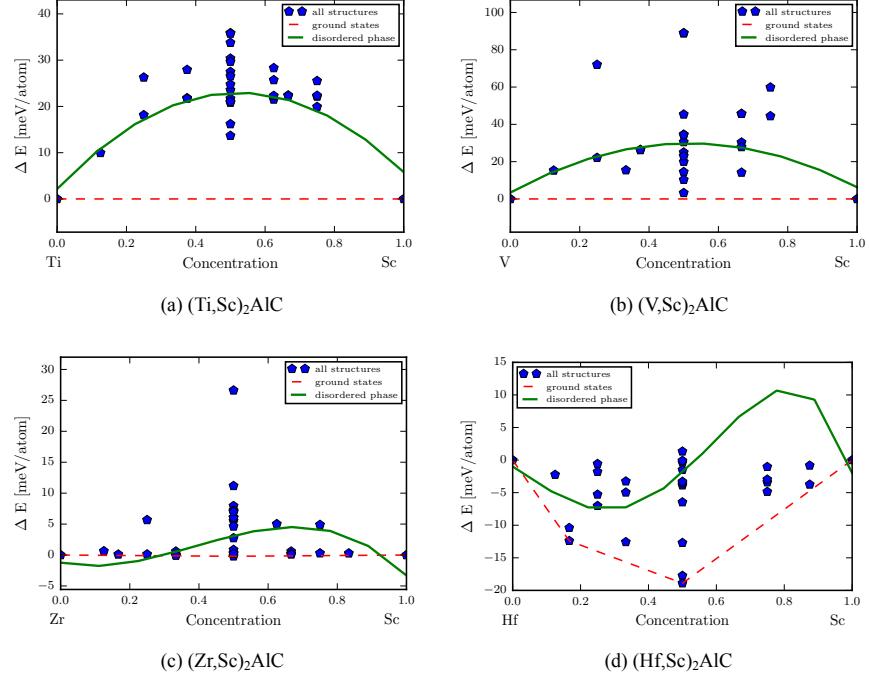


FIG. 2. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Sc})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

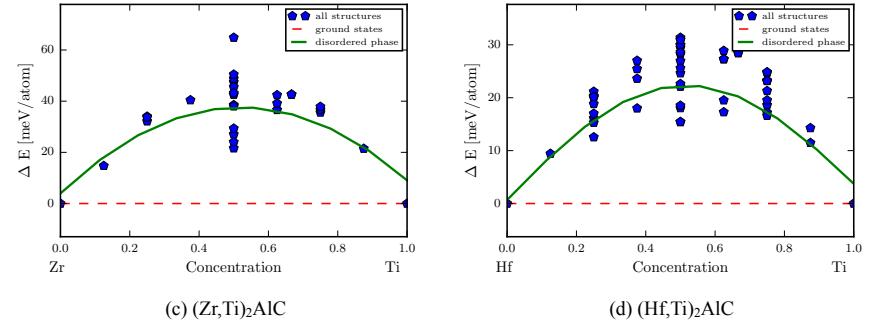


FIG. 3. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Ti})_2\text{AlC}$ , a)  $\text{M1}=\text{Zr}$ , b)  $\text{M1}=\text{Hf}$

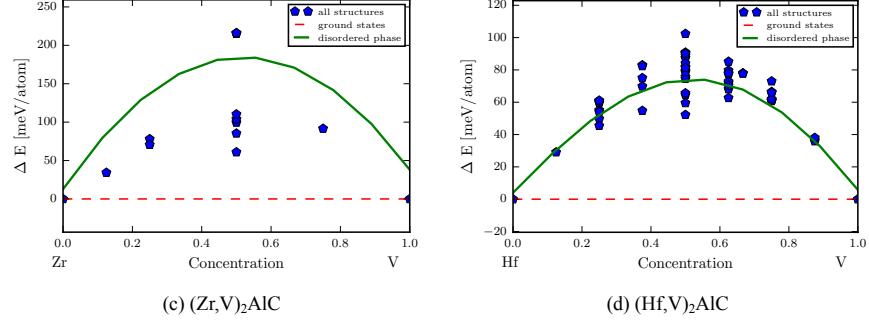


FIG. 4. Ground states at 0 K using cluster expansion for  $(M_1, V)_2\text{AlC}$ , a)  $M_1 = \text{Zr}$ , b)  $M_1 = \text{Hf}$

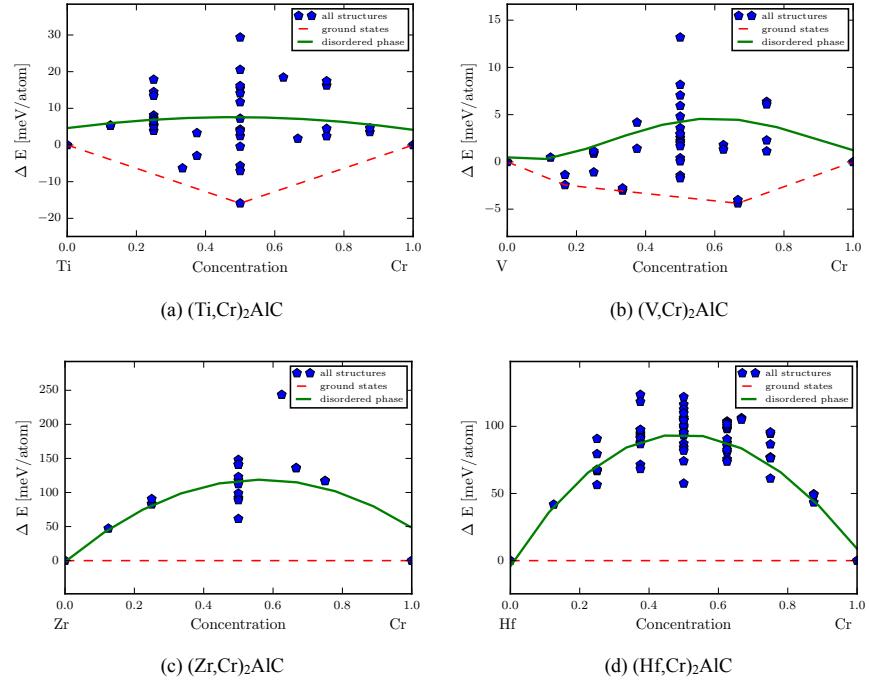


FIG. 5. Ground states at 0 K using cluster expansion for  $(M_1, \text{Cr})_2\text{AlC}$ , a)  $M_1 = \text{Ti}$ , b)  $M_1 = \text{V}$ , c)  $M_1 = \text{Zr}$  and d)  $M_1 = \text{Hf}$

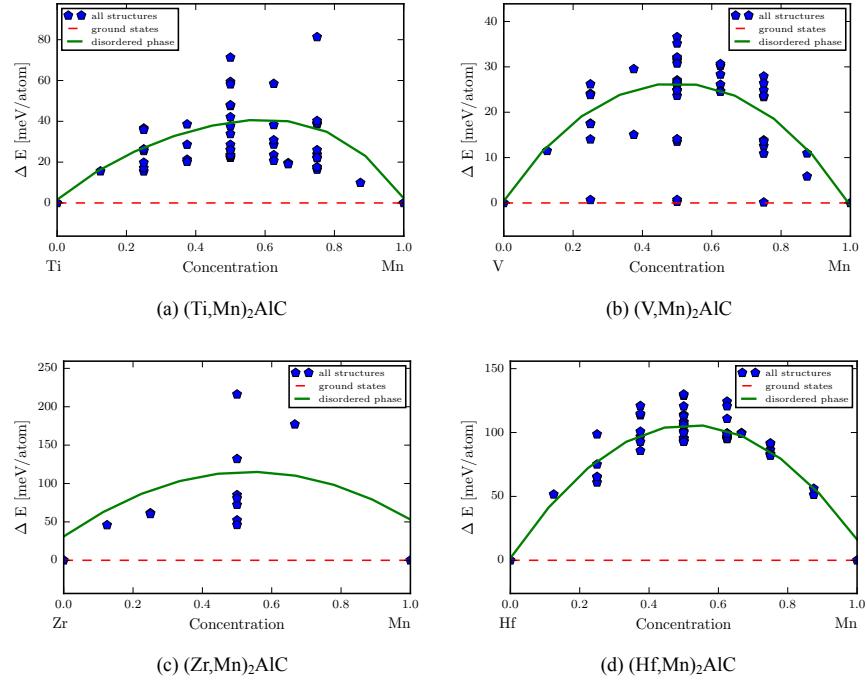


FIG. 6. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Mn})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

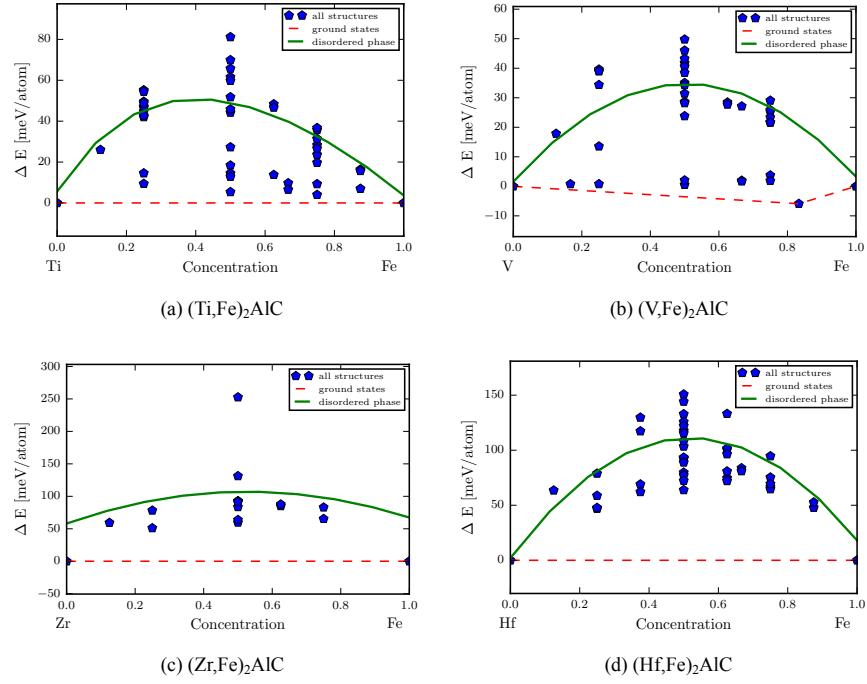


FIG. 7. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Fe})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

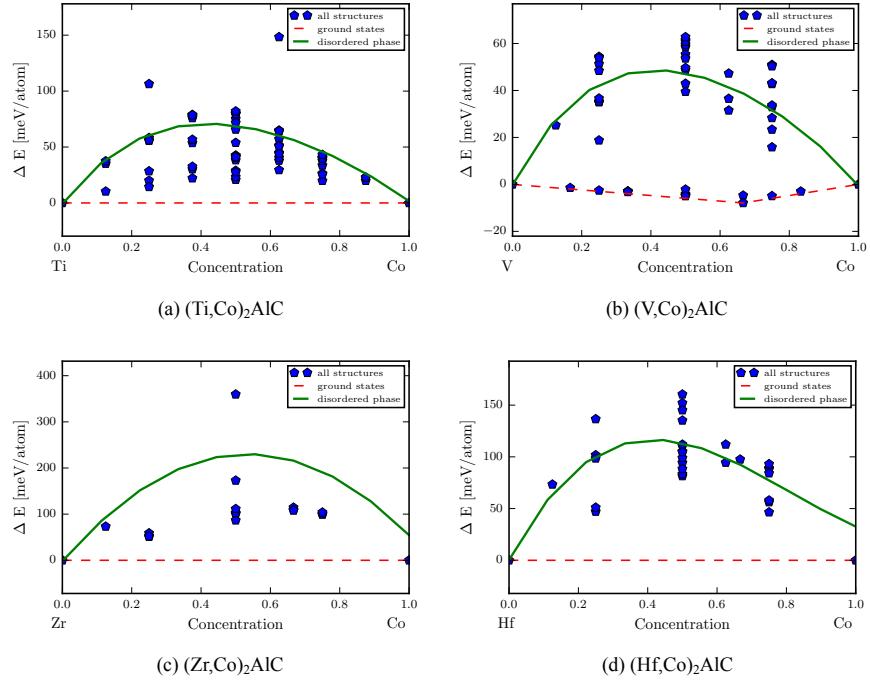


FIG. 8. Ground states at 0 K using cluster expansion for  $(\text{M}_1, \text{Co})_2\text{AlC}$ , a)  $\text{M}_1 = \text{Ti}$ , b)  $\text{M}_1 = \text{V}$ , c)  $\text{M}_1 = \text{Zr}$  and d)  $\text{M}_1 = \text{Hf}$

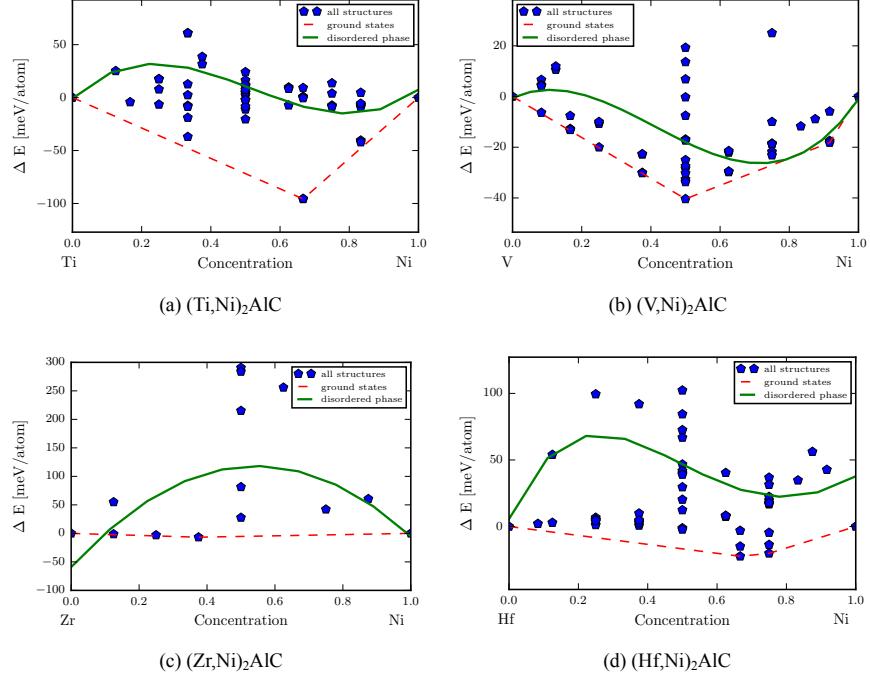


FIG. 9. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Ni})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

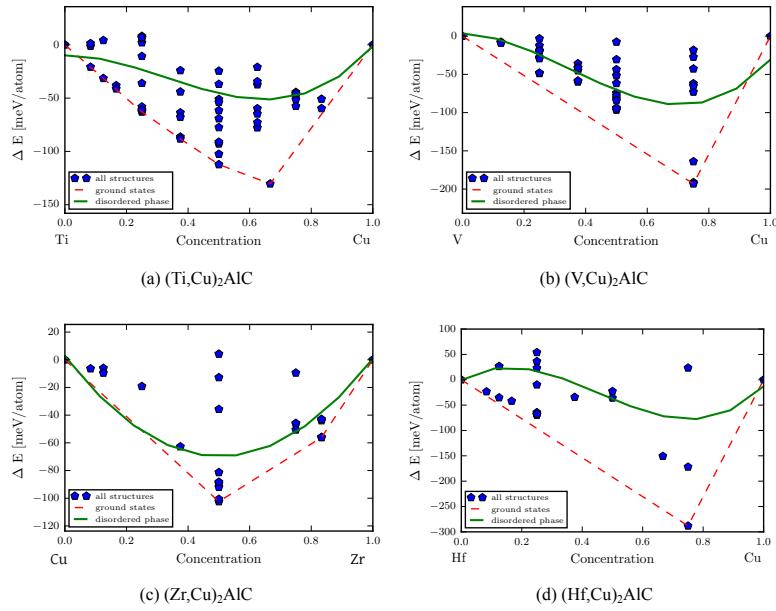


FIG. 10. Ground states at 0 K using cluster expansion for  $(\text{M1},\text{Cu})_2\text{AlC}$ , a)  $\text{M1}=\text{Ti}$ , b)  $\text{M1}=\text{V}$ , c)  $\text{M1}=\text{Zr}$  and d)  $\text{M1}=\text{Hf}$

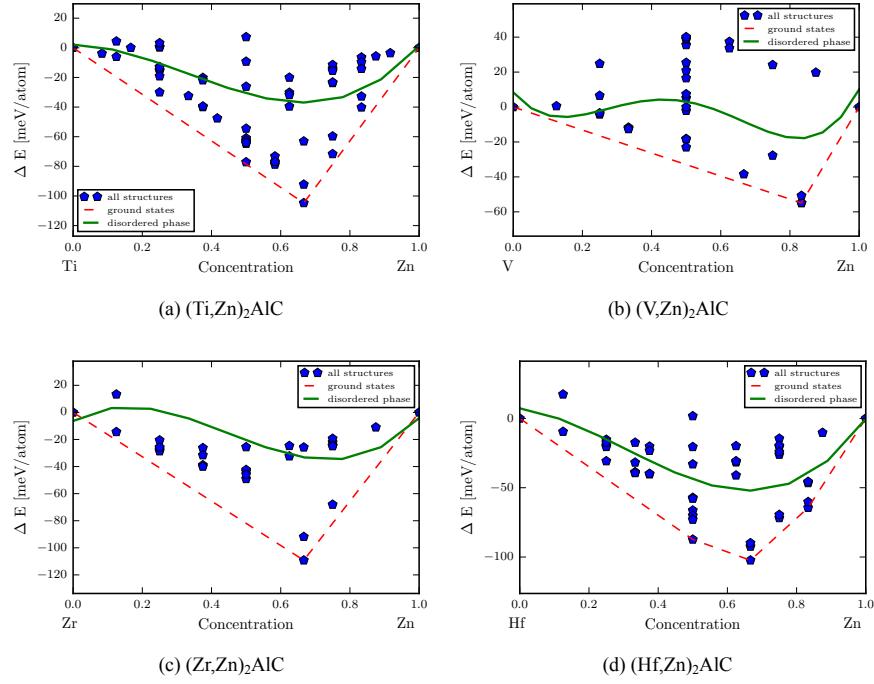


FIG. 11. Ground states at 0 K using cluster expansion for  $(M1, Zn)_2 AlC$ , a)  $M1=Ti$ , b)  $M1=V$ , c)  $M1=Zr$  and d)  $M1=Hf$

Sr. No	Composition	Space Group	a	b	c	$\alpha$	$\beta$	$\gamma$
1	(Ti <sub>0.25</sub> Ca <sub>0.75</sub> ) <sub>2</sub> AlC	31	3.79	7.19	13.18	90	90	90
2	(Ti <sub>0.5</sub> V <sub>0.5</sub> ) <sub>2</sub> AlC	62	2.97	5.17	13.48	90	90	90
3	(Ti <sub>0.5</sub> Cr <sub>0.5</sub> ) <sub>2</sub> AlC	59	2.93	5.14	13.18	90	90	90
3	(Ti <sub>0.33</sub> Ni <sub>0.67</sub> ) <sub>2</sub> AlC	15	5.22	12.12	12.12	78	78	60
4	(Ti <sub>0.75</sub> Cu <sub>0.25</sub> ) <sub>2</sub> AlC	156	3.10	3.10	13.08	90	90	120
5	(Ti <sub>0.625</sub> Cu <sub>0.375</sub> ) <sub>2</sub> AlC	156	3.12	3.12	25.34	90	90	120
6	(Ti <sub>0.50</sub> Cu <sub>0.50</sub> ) <sub>2</sub> AlC	186	3.15	3.15	12.25	90	90	90
7	(Ti <sub>0.33</sub> Cu <sub>0.66</sub> ) <sub>2</sub> AlC	63	8.28	8.28	12.00	90	90	158
8	(Ti <sub>0.34</sub> Zn <sub>0.66</sub> ) <sub>2</sub> AlC	8	8.06	8.06	13.87	104	104	23

TABLE I. Space group, lattice paramters ( a, b, c in angstrom units) and lattice angles (in degrees) of all identified ordered phases for M1=Ti

Sr. No	Composition	Space Group	a	b	c	$\alpha$	$\beta$	$\gamma$
1	(V <sub>0.17</sub> Ca <sub>0.83</sub> ) <sub>2</sub> AlC	155	15.96	15.96	15.96	22	22	22
2	(V <sub>0.25</sub> Ca <sub>0.75</sub> ) <sub>2</sub> AlC	1	15.50	15.19	15.64	23	22	23
3	(V <sub>0.34</sub> Ca <sub>0.66</sub> ) <sub>2</sub> AlC	15	13.09	13.09	13.09	22	22	22
4	(V <sub>0.34</sub> Cr <sub>0.66</sub> ) <sub>2</sub> AlC	9	13.10	13.10	13.10	24	24	24
5	(V <sub>0.83</sub> Cr <sub>0.17</sub> ) <sub>2</sub> AlC	189	5.03	5.03	13.00	90	90	120
6	(V <sub>0.83</sub> Fe <sub>0.17</sub> ) <sub>2</sub> AlC	194	2.85	2.85	37.18	90	90	90
7	(V <sub>0.34</sub> Co <sub>0.66</sub> ) <sub>2</sub> AlC	194	2.88	2.88	36.86	90	90	120
8	(V <sub>0.5</sub> Ni <sub>0.5</sub> ) <sub>2</sub> AlC	62	2.97	4.77	12.92	90	90	90
8	(V <sub>0.08</sub> Ni <sub>0.92</sub> ) <sub>2</sub> AlC	185	5.00	5.00	12.21	90	90	120
9	(V <sub>0.25</sub> Cu <sub>0.75</sub> ) <sub>2</sub> AlC	12	13.41	13.41	13.41	167	158	24
10	(V <sub>0.17</sub> Zn <sub>0.83</sub> ) <sub>2</sub> AlC	1	13.90	13.90	13.90	22	22	22

TABLE II. Space group, lattice paramters ( a, b, c in angstrom units) and lattice angles (in degrees) of all identified ordered phases for M1=V

Sr. No	Composition	Space Group	a	b	c	$\alpha$	$\beta$	$\gamma$
1	(Zr <sub>0.5</sub> Ca <sub>0.5</sub> ) <sub>2</sub> AlC	187	3.44	3.44	15.46	90	90	120
2	(Zr <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>2</sub> AlC	164	3.29	3.29	14.71	90	90	120
3	(Zr <sub>0.625</sub> Ni <sub>0.375</sub> ) <sub>2</sub> AlC	156	3.34	3.34	24.43	90	90	120
4	(Zr <sub>0.17</sub> Cu <sub>0.83</sub> ) <sub>2</sub> AlC	186	3.36	3.35	13.04	90	90	120
5	(Zr <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> AlC	186	3.42	3.42	11.20	90	90	120
6	(Zr <sub>0.67</sub> Zn <sub>0.33</sub> ) <sub>2</sub> AlC	63	8.31	8.31	13.57	90	90	157

TABLE III. Space group, lattice parameters ( a, b, c in angstrom units) and lattice angles (in degrees) of all identified ordered phases for M1=Zr

Sr. No	Composition	Space Group	a	b	c	$\alpha$	$\beta$	$\gamma$
1	(Hf <sub>0.16</sub> Ca <sub>0.84</sub> ) <sub>2</sub> AlC	189	6.31	6.31	16.08	90	90	120
2	(Hf <sub>0.34</sub> Ca <sub>0.66</sub> ) <sub>2</sub> AlC	155	16.26	16.26	16.26	21	21	21
3	(Hf <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>2</sub> AlC	59	3.43	6.23	15.10	90	90	90
4	(Hf <sub>0.83</sub> Ca <sub>0.17</sub> ) <sub>2</sub> AlC	155	14.84	14.84	14.84	22	22	22
5	(Hf <sub>0.85</sub> Ca <sub>0.5</sub> ) <sub>2</sub> AlC	38	5.69	5.69	16.67	90	90	120
6	(Hf <sub>0.34</sub> Ni <sub>0.66</sub> ) <sub>2</sub> AlC	12	8.06	8.06	12.55	111	111	23
7	(Hf <sub>0.75</sub> Ni <sub>0.25</sub> ) <sub>2</sub> AlC	26	3.05	5.00	12.47	90	90	90
8	(Hf <sub>0.25</sub> Cu <sub>0.75</sub> ) <sub>2</sub> AlC	156	3.29	3.29	13.25	90	90	120
9	(Hf <sub>0.875</sub> Cu <sub>0.125</sub> ) <sub>2</sub> AlC	187	3.28	3.28	23.64	90	90	120
10	(Hf <sub>0.5</sub> Zn <sub>0.5</sub> ) <sub>2</sub> AlC	12	8.10	8.10	14.85	110	110	23
11	(Hf <sub>0.16</sub> Zn <sub>0.84</sub> ) <sub>2</sub> AlC	155	13.37	13.37	13.37	24	24	24
12	(Hf <sub>0.34</sub> Zn <sub>0.66</sub> ) <sub>2</sub> AlC	63	8.31	8.31	13.71	90	90	157

TABLE IV. Space group, lattice paramters ( a, b, c in angstrom units) and lattice angles (in degrees) of all identified ordered phases for M1=Zr

No.	Ordered Phase	Competitive Phases	$\Delta H_f^O$	$\Delta H_f^D$	$\Delta H_f^O - \Delta H_f^D$
1	$(\text{Ti}_{0.33}\text{Zn}_{0.67})_2\text{AlC}$	$1.33 \text{ Zn} + 0.539 \text{ TiC}$ $+ 0.154 \text{ Al}_4\text{C}_3 + 0.128 \text{ TiAl}_3$	-0.29	-0.123	-0.167
2	$(\text{Ti}_{0.33}\text{Ni}_{0.67})_2\text{AlC}$	$0.5 \text{ AlNi} + 0.667 \text{ TiC}$ $+ 0.333 \text{ C} + + 0.167 \text{ Al}_3\text{Ni}_5$	-0.621	-0.24	-0.380
3	$(\text{Ti}_{0.33}\text{Cu}_{0.67})_2\text{AlC}$	$0.167 \text{ AlCu}_3 + 0.667 \text{ TiC}$ $+ 0.333 \text{ C} + 0.834 \text{ AlCu}$	-0.383	-0.184	-0.199
4	$(\text{V}_{0.25}\text{Cu}_{0.75})_2\text{AlC}$	$0.75 \text{ AlCu} + 0.583 \text{ C}$ $+ 0.25 \text{ AlCu}_3 + 0.0833 \text{ V}_6\text{C}_5$	-0.172	-0.05	-0.122
5	$(\text{Zr}_{0.5}\text{Cu}_{0.5})_2\text{AlC}$	$\text{AlCu} + \text{ZrC}$	-0.513	-0.256	-0.256
6	$(\text{Hf}_{0.75}\text{Cu}_{0.25})_2\text{AlC}$	$0.25 \text{ AlCu}_3 + 0.5 \text{ HfC}$ $+ 0.5 \text{ C} + 0.5 \text{ AlCu}_3$	-0.364	-0.170	-0.194
7	$(\text{Hf}_{0.33}\text{Zn}_{0.67})_2\text{AlC}$	$0.07 \text{ HfAl}_3 + 1.33 \text{ Zn}$ $+ 0.2 \text{ Hf}_3\text{Al}_3\text{C}_5 + 0.19 \text{ Al}$	-0.351	-0.036	-0.314

TABLE V. Phase decomposition analysis for the lowest energy ground states of systems showing strong ordering.  $\Delta H_f^O$  is the formation energy/atom of the ordered phase.  $\Delta H_f^D$  is the sum of the formation energies/atom for the competitive phases. A negative value for  $\Delta H_f^O - \Delta H_f^D$  indicates that at 0 K, the ordered phase is more stable than the possible competitive phases. All energies are in eV/atom

Element	Electronic configuration
C	[He]2s <sup>2</sup> 2p <sup>2</sup>
Al	[Ne]3s <sup>2</sup> 3p <sup>1</sup>
Ca	[Ar]4s <sup>2</sup>
Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>
Ti	[Ar]4s <sup>2</sup> 3d <sup>2</sup>
V	[Ar]4s <sup>2</sup> 3d <sup>3</sup>
Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>
Mn	[Ar]4s <sup>2</sup> 3d <sup>5</sup>
Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>
Co	[Ar]4s <sup>2</sup> 3d <sup>7</sup>
Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>
Cu	[Ar]4s <sup>1</sup> 3d <sup>10</sup>
Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>
Zr	[Kr]5s <sup>2</sup> 4d <sup>2</sup>
Hf	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup>

TABLE VI. Electronic configurations used in this work, used within the projector augmented-wave (PAW) pseudopotentials formalism, implemented in the VASP package.

M2 → Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
M1 ↓											
Ti	0.023	0.011		0.003	0.012	0.012	0.012	0.025	0.025	0.019	0.023
V	0.014	0.016	0.003		0.002	0.002	0.013	0.006	0.030	0.012	0.018
Zr	0.019	0.008	0.023	0.014	0.012	0.014	0.004	0.022	0.019	0.016	0.019
Hf	0.019	0.004	0.007	0.020	0.014	0.025	0.031	0.024	0.030	0.012	0.016

TABLE VII. Cross validation (CV) scores for all the systems.