Supporting Information

Polarity-extended 8–N^{eff} rule for semiconducting main-group compounds with the TiNiSi type of crystal structure

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Table S1. Lattice parameters, cell volume per formula unit (*f.u.*) and calculated band gaps for *AA'E* compounds studied.

Compound *AA'E*	Experimental			Relaxed			Band gap (eV)
	a, b, c (Å)		*V* (Å³ *f.u.⁻¹*)	*a, b, c* (Å)		*V* (Å³ *f.u.⁻¹*)	
Be_2C ‡ [1]	4.340(2)		20.44	4.341		20.45	1.16
Mg_2C ‡ [2]	5.4480(4)		40.42	5.460		40.69	0.74
Mg_2Sn ‡ [3]	6.76648(2)		77.45	6.816		79.16	0.00
Ba_2Ge ‡	*hypothetic*		–	8.006		128.29	0.04
Ca_2Si † [4]	7.6910(3) 4.8174(1) 9.0477(3)		83.81	7.614 4.821 9.038		82.94	0.29
Ca_2Ge † [5]	7.734(7) 4.834(4) 9.069(9)		84.76	7.675 4.857 9.090		84.71	0.31
Sr_2Si † [6]	8.11(2) 5.15(2) 9.54(2)		99.61	8.120 5.143 9.595		100.17	0.36
Sr_2Ge † [7]	8.13(2) 5.20(6) 9.58(2)		101.25	8.178 5.188 9.653		102.39	0.39
Ba_2Si † [8]	8.43(2) 5.40(2) 9.88(2)		112.44	8.448 5.375 10.096		114.61	0.07
Ba_2Ge † [9]	8.38(2) 5.48(2) 10.04(2)		115.26	8.487 5.433 10.169		117.22	0.05
Ba_2Pb [10]	8.651(1) 5.691(2) 10.618(2)		130.69	8.768 5.763 10.759		135.91	0.05
CaMgSi † [11]	7.4825(3) 4.4319(2) 8.3133(3)		68.92	7.474 4.433 8.318		68.90	0.04
CaMgGe † [12]	7.62(2) 4.42(2) 8.34(2)		70.22	7.529 4.464 8.418		70.73	0.00
CaMgSn † [12]	7.86(2) 4.66(2) 8.74(2)		80.03	7.875 4.720 8.818		81.94	0.02
SrMgGe [12]	7.80(2) 4.56(2) 8.55(2)		76.03	7.874 4.631 8.635		78.72	0.12
CaLiAs † [13]	7.233(3) 4.313(1) 7.895(3)		61.57	7.253 4.311 7.976		62.35	1.19
CaLiSb [13]	7.643(1) 4.632(1) 8.292(1)		73.39	7.663 4.639 8.336		74.08	0.65
CaLiBi † [13]	7.7294(9) 4.7134(6) 8.422(1)		76.71	7.813 4.735 8.530		78.89	0.55
SrLiAs † [14]	7.6458(2) 4.5158(1) 8.0403(3)		69.40	7.647 4.519 8.152		70.43	1.13
NaLiSe † [15]	7.174(4) 4.249(2) 7.716(2)		58.80	7.206 4.270 7.779		59.84	2.44
NaLiTe † [16]	7.740(1) 4.624(2) 8.406(1)		75.21	7.720 4.598 8.358		74.17	2.30
KNaSe † [16]	8.063(2) 4.817(1) 8.651(2)		84.00	8.149 4.833 8.798		86.62	2.01

† TiNiSi structure type; ‡ CaF_2 structure type;

Table S2. Atomic (according to the periodic table of the elements PTE) and ELI-D core populations $N_{core}^{PTE}(X)$ and $N_{core}^{ELI}(X)$, respectively, for each atomic species in $A^1 A'^1 E^{14}$ compounds, and the corresponding the valence shell defects $N_{vdef}^{ELI}(X)$.

Compound	Species X	$N_{core}^{PTE}(X)$	$N_{core}^{ELI}(X)$	$N_{vdef}^{ELI}(X)$
CaMgSi †	Ca	18	18.29	−0.29
	Mg	10	10.07	−0.07
	Si	10	10.07	−0.07
CaMgGe †	Ca	18	18.29	−0.29
	Mg	10	10.07	−0.07
	Ge	28	27.72	+0.28
CaMgSn †	Ca	18	18.29	−0.29
	Mg	10	10.06	−0.06
	Sn	46	45.77	+0.23
SrMgGe †	Sr	36	36.30	−0.30
	Mg	10	10.07	−0.07
	Ge	28	27.73	+0.27

† TiNiSi-type (optimized)

Table S3 Atomic (according to the periodic table of the elements PTE) and ELI-D core populations $N_{core}^{PTE}(X) and N_{core}^{ELI}(X)$, respectively, for each atomic species in $A^2A'^1E^{15}$ compounds, and the corresponding valence shell defects $N_{vdef}^{ELI}(X)$.

Compound	Species X	$N_{core}^{PTE}(X)$	$N_{core}^{ELI}(X)$	$N_{vdef}^{ELI}(X)$
CaLiAs †	Ca	18	18.29	−0.29
	Li	2	2.04	−0.04
	As	28	27.76	+0.24
CaLiSb †	Ca	18	18.28	−0.28
	Li	2	2.04	−0.04
	Sb	46	45.76	+0.24
CaLiBi †	Ca	18	18.29	−0.29
	Li	2	2.04	−0.04
	Bi	78	77.65	+0.35
SrLiAs †	Sr	36	36.29	−0.29
	Li	2	2.04	−0.04
	As	28	27.76	+0.24

† TiNiSi-type (optimized)

Table S4. Atomic (according to the periodic table of the elements PTE) and ELI-D core populations $N^{PTE}_{core}(X)$ and $N^{ELI}_{core}(X)$, respectively, for each atomic species in $A^2A'^2E^{16}$ compounds, and the corresponding valence shell defects $N^{ELI}_{vdef}(X)$.

Compound	Species X	$N^{PTE}_{core}(X)$	$N^{ELI}_{core}(X)$	$N^{ELI}_{vdef}(X)$
	Na	10	10.04	–0.04
NaLiSe †	Li	2	2.04	–0.04
	Se	28	27.78	+0.22
	Na	10	10.05	–0.05
NaLiTe †	Li	2	2.04	–0.04
	Te	46	45.74	+0.26
	K	18	18.10	–0.10
KNaSe †	Na	10	10.05	–0.05
	Se	28	27.78	+0.22

† TiNiSi-type (optimized)

Table S5. Atomic (according to the periodic table of the elements PTE) and ELI-D core populations $N^{PTE}_{core}(X)$ and $N^{ELI}_{core}(X)$, respectively, for each atomic species in $A^2_2E^{14}$ compounds, and the corresponding valence shell defects $N^{ELI}_{vdef}(X)$.

Compound	Species X	$N^{PTE}_{core}(X)$	$N^{ELI}_{core}(X)$	$N^{ELI}_{vdef}(X)$
	Ca1	18	18.29	–0.29
Ca_2Si †	Ca2	18	18.27	–0.27
	Si	10	10.07	–0.07
	Ca1	18	18.30	–0.30
Ca_2Ge †	Ca2	18	18.28	–0.28
	Ge	28	27.73	+0.27
	Sr1	36	36.31	–0.31
Sr_2Si †	Sr2	36	36.29	–0.29
	Si	10	10.07	–0.07
	Sr1	36	36.31	–0.31
Sr_2Ge †	Sr2	36	36.29	–0.29
	Ge	28	27.73	+0.27
	Ba1	54	54.50	–0.50
Ba_2Si †	Ba2	54	54.46	–0.46
	Si	10	10.07	–0.07
	Ba1	54	54.50	–0.50
Ba_2Ge †	Ba2	54	54.46	–0.46
	Ge	28	27.74	+0.26
	Ba1	54	54.47	–0.47
Ba_2Pb †	Ba2	54	54.43	–0.43
	Pb	78	77.79	+0.21

† TiNiSi-type (optimized)

Table S6. ELI-D core population for each atomic species in $A^2_2E^{14}$ compounds with the $cF12$-CaF_2 structure, together with the valence shell defects.

Compound	Species X	$N_{core}^{PTE}(X)$	$N_{core}^{ELI}(X)$	$N_{vdef}^{ELI}(X)$
Be$_2$C ††	Be	2	2.06	–0.06
	C	2	2.11	–0.11
Mg$_2$C ††	Mg	10	10.07	–0.07
	C	2	2.10	–0.10
Mg$_2$Sn ††	Mg	10	10.07	–0.07
	Sn	46	45.76	+0.24
hyp-Ba$_2$Ge ††	Ba	54	54.45	–0.45
	Ge	28	27.73	+0.27

†† anti-CaF$_2$-type type (optimized)

Table S7. Position-space bonding results for each constituting atoms of the targeted compounds **without** the application of the **PSC0 correction**. QTAIM effective charges and volumes, which are not affected by this correction, are listed in the main text.

| Compound | ELIBON | | | $N_{acc}^{ELI}(C^E)$ | $N_{val}^{ELI}(E)$ | $N_{cb}(E)$ | $N_{lp}(E)$ |
	A	A'	E				
NaLiSe †	+0.95	+0.96	−1.91	8.13	7.88	0.25	3.82
NaLiTe †	+0.95	+0.96	−1.91	8.17	7.92	0.25	3.84
KNaSe †	+0.90	+0.95	−1.85	8.07	7.76	0.31	3.72
CaLiAs †	+1.71	+0.96	−2.67	7.92	7.39	0.53	3.43
CaLiSb †	+1.72	+0.96	−2.67	7.91	7.38	0.54	3.42
CaLiBi †	+1.71	+0.96	−2.67	8.03	7.48	0.56	3.46
SrLiAs †	+1.71	+0.96	−2.67	7.91	7.35	0.55	3.40
CaMgSi †	+1.71	+1.93	−3.64	7.57	6.58	0.99	2.79
CaMgGe †	+1.71	+1.93	−3.64	7.91	6.88	1.03	2.92
CaMgSn †	+1.71	+1.93	−3.64	7.88	6.80	1.08	2.86
SrMgGe †	+1.70	+1.93	−3.63	7.90	6.77	1.13	2.82
Ca$_2$Si †	+1.73	+1.71	−3.44	7.36	6.36	1.00	2.68
Ca$_2$Ge †	+1.73	+1.70	−3.43	7.71	6.69	1.02	2.84
Sr$_2$Si †	+1.71	+1.69	−3.40	7.34	6.25	1.09	2.58
Sr$_2$Ge †	+1.71	+1.69	−3.40	7.68	6.56	1.12	2.72
Ba$_2$Si †	+1.55	+1.50	−3.05	6.98	5.89	1.10	2.39
Ba$_2$Ge †	+1.55	+1.50	−3.05	7.31	6.19	1.12	2.54
Ba$_2$Pb †	+1.57	+1.53	−3.10	7.32	6.13	1.19	2.47
Be$_2$C ††	+1.94	–	−3.88	7.77	7.14	0.63	3.26
Mg$_2$C ††	+1.93	–	−3.87	7.77	6.96	0.81	3.07
Mg$_2$Sn ††	+1.93	–	−3.87	8.11	7.00	1.11	2.95
hyp-Ba$_2$Ge ††	+1.55	–	−3.09	7.36	6.28	1.07	2.60

† TiNiSi-type (optimized), †† anti-CaF$_2$-type (optimized)

Table S8a. Data referred to ELI-D valence basins for ternary phases **after PSC0**.

Compound	ELI-D basin (B_i)	Atomicity	$\bar{N}(B_i)$	$p(B_i^E)$	cc	lpc	$p(B_i^{A'})$	$\sum_j p(B_i^{A_j})$
NaLiSe †	d1	(Se; Li; 4Na)	2.0796	0.9590	0.0820	0.9180	0.0171	0.0237
	d2	(Se; Li; 4Na)	2.1547	0.9565	0.0871	0.9129	0.0180	0.0250
	d2	(Se; Li; 4Na)	2.1753	0.9565	0.0870	0.9130	0.0180	0.0250
	d3	(Se; Li; 3Na)	1.5932	0.9585	0.0831	0.9169	0.0227	0.0185
NaLiTe †	d1	(Te; Li; 4Na)	2.0301	0.9598	0.0803	0.9197	0.0179	0.0221
	d2	(Te; Li; 4Na)	2.1225	0.9576	0.0849	0.9151	0.0179	0.0239
	d2	(Te; Li; 4Na)	2.1394	0.9575	0.0850	0.9150	0.0180	0.0239
	d3	(Te; Li; 3Na)	1.7093	0.9563	0.0873	0.9127	0.0207	0.0224
KNaSe †	d1	(Se; Na; 4K)	1.9536	0.9407	0.1186	0.8814	0.0265	0.0324
	d2	(Se; Na; 4K)	2.1996	0.9406	0.1189	0.8811	0.0247	0.0346
	d2	(Se; Na; 4K)	2.2177	0.9406	0.1188	0.8812	0.0246	0.0347
	d3	(Se; Na; 3K)	1.6327	0.9452	0.1096	0.8904	0.0320	0.0225
CaLiAs †	d1	(As; Li; 4Ca)	2.0596	0.8881	0.2238	0.7762	0.0200	0.0916
	d2	(As; Li; 4Ca)	2.4396	0.8907	0.2187	0.7813	0.0193	0.0892
	d2	(As; Li; 4Ca)	2.4591	0.8915	0.2171	0.7829	0.0193	0.0884
	d3	(As; Li; 3Ca)	1.0462	0.9101	0.1797	0.8203	0.0368	0.0512
CaLiSb †	d1	(Sb; Li; 4Ca)	2.3102	0.8884	0.2232	0.7768	0.0190	0.0925
	d2	(Sb; Li; 4Ca)	2.2158	0.8894	0.2211	0.7789	0.0216	0.0880
	d2	(Sb; Li; 4Ca)	2.2002	0.8906	0.2189	0.7811	0.0214	0.0870
	d3	(Sb; Li; 3Ca)	1.2769	0.9071	0.1859	0.8141	0.0292	0.0618
CaLiBi †	d1	(Bi; Li; 4Ca)	2.2376	0.8854	0.2293	0.7707	0.0198	0.0946
	d2	(Bi; Li; 4Ca)	2.5708	0.8869	0.2262	0.7738	0.0185	0.0930
	d2	(Bi; Li; 4Ca)	2.5899	0.8866	0.2269	0.7731	0.0186	0.0932
	d3	(Bi; Li; 3Ca)	0.6083	0.9287	0.1426	0.8574	0.0591	0.0082
SrLiAs †	d1	(As; Li; 4Sr)	1.6570	0.8893	0.2213	0.7787	0.0240	0.0860
	d2	(As; Li; 4Sr)	2.4868	0.8851	0.2299	0.7701	0.0195	0.0951
	d2	(As; Li; 4Sr)	2.5086	0.8852	0.2296	0.7704	0.0195	0.0950
	d3	(As; Li; 3Sr)	1.3521	0.9035	0.1929	0.8071	0.0263	0.0688
CaMgSi †	d1	(Si; Mg; 4Ca)	1.9743	0.8290	0.3419	0.6581	0.0786	0.0920
	d2	(Si; Mg; 4Ca)	2.3221	0.8320	0.3360	0.6640	0.0703	0.0970
	d2	(Si; Mg; 4Ca)	2.3411	0.8311	0.3378	0.6622	0.0708	0.0974
	d3	(Si; Mg; 3Ca)	1.3632	0.8310	0.3380	0.6620	0.1052	0.0613
CaMgGe †	d1	(Ge; Mg; 4Ca)	2.0017	0.8245	0.3511	0.6489	0.0819	0.0933
	d2	(Ge; Mg; 4Ca)	2.3121	0.8285	0.3431	0.6569	0.0745	0.0964
	d2	(Ge; Mg; 4Ca)	2.3324	0.8269	0.3462	0.6538	0.0750	0.0975
	d3	(Ge; Mg; 3Ca)	1.3579	0.8180	0.3640	0.6360	0.1156	0.0620
CaMgSn †	d1	(Sn; Mg; 4Ca)	2.1293	0.8204	0.3592	0.6408	0.0846	0.0945
	d2	(Sn; Mg; 4Ca)	2.2612	0.8239	0.3522	0.6478	0.0800	0.0952
	d2	(Sn; Mg; 4Ca)	2.2776	0.8234	0.3532	0.6468	0.0807	0.0951
	d3	(Sn; Mg; 3Ca)	1.3361	0.8102	0.3796	0.6204	0.1254	0.0606
SrMgGe †	d1	(Ge; Mg; 4Sr)	1.7658	0.8081	0.3838	0.6162	0.0967	0.0950
	d2	(Ge; Mg; 4Sr)	2.3377	0.8121	0.3758	0.6242	0.0822	0.1053
	d2	(Ge; Mg; 4Sr)	2.3571	0.8108	0.3785	0.6215	0.0827	0.1061
	d3	(Ge; Mg; 3Sr)	1.5430	0.8179	0.3643	0.6357	0.1090	0.0708

† TiNiSi-type (optimized)

Table S8b. Data referred to ELI-D valence basins for binary phases **after PSC0**.

Compound	ELI-D basin (B_i)	Atomicity	$\bar{N}(B_i)$	$p(B_i^E)$	cc	lpc	$\sum_l p(B_i^{A1_l})$	$\sum_j p(B_i^{A2_j})$
Ca$_2$Si †	d1*	(Si; 3Ca1; 2Ca2)	1.7458	0.7771	0.4457	0.5543	0.1437	0.0746
	d2*	(Si; 3Ca1; 3Ca2)	3.1165	0.8114	0.3773	0.6227	0.0880	0.0993
	d2*	(Si; 3Ca1; 3Ca2)	3.1392	0.8123	0.3753	0.6247	0.0886	0.0977
Ca$_2$Ge †	d1*	(Ge; 3Ca1; 2Ca2)	1.8002	0.7735	0.4531	0.5469	0.1464	0.0753
	d2*	(Ge; 3Ca1; 3Ca2)	3.0879	0.8103	0.3795	0.6205	0.0887	0.0995
	d2*	(Ge; 3Ca1; 3Ca2)	3.1184	0.8089	0.3822	0.6178	0.0886	0.1010
Sr$_2$Si †	d1*	(Si; 3Sr1; 2Sr2)	1.8470	0.7602	0.4797	0.5203	0.1570	0.0812
	d2*	(Si; 3Sr1; 3Sr2)	3.0691	0.7976	0.4048	0.5952	0.0931	0.1083
	d2*	(Si; 3Sr1; 3Sr2)	3.0895	0.7988	0.4024	0.5976	0.0933	0.1071
Sr$_2$Ge †	d1*	(Ge; 3Sr1; 2Sr2)	1.8413	0.7550	0.4899	0.5101	0.1593	0.0839
	d2*	(Ge; 3Sr1; 3Sr2)	3.0632	0.7962	0.4076	0.5924	0.0942	0.1087
	d2*	(Ge; 3Sr1; 3Sr2)	3.0920	0.7949	0.4101	0.5899	0.0944	0.1098
Ba$_2$Si †	d1*	(Si; 3Ba1; 2Ba2)	1.8456	0.7103	0.5795	0.4205	0.1915	0.0982
	d2*	(Si; 3Ba1; 2Ba2)	2.0761	0.7562	0.4876	0.5124	0.1313	0.1125
	d2*	(Si; 3Ba1; 2Ba2)	2.0906	0.7551	0.4898	0.5102	0.1315	0.1135
	d3*	(Si; 4Ba1; 3Ba2)	1.9920	0.7516	0.4969	0.5031	0.0767	0.1704
Ba$_2$Ge †	d1*	(Ge; 3Ba1; 2Ba2)	1.8570	0.7048	0.5904	0.4096	0.1930	0.1021
	d2*	(Ge; 3Ba1; 2Ba2)	1.9860	0.7498	0.5006	0.4994	0.1340	0.1163
	d2*	(Ge; 3Ba1; 2Ba2)	1.9953	0.7506	0.4987	0.5013	0.1339	0.1154
	d3*	(Ge; 4Ba1; 3Ba2)	2.1661	0.7526	0.4949	0.5051	0.0803	0.1661
Ba$_2$Pb †	d1*	(Pb; 3Ba1; 2Ba2)	1.8225	0.6971	0.6058	0.3942	0.1914	0.1111
	d2*	(Pb; 3Ba1; 2Ba2)	2.0909	0.7461	0.5078	0.4922	0.1321	0.1217
	d2*	(Pb; 3Ba1; 2Ba2)	2.0974	0.7471	0.5058	0.4942	0.1323	0.1206
	d3*	(Pb; 4Ba1; 3Ba2)	1.9806	0.7673	0.4655	0.5345	0.0767	0.1543

† TiNiSi-type (optimized)

Table S8c. Data referred to ELI-D valence basins for binary phases with the $cF12$-CaF_2 structure **after PSC0**.

Compound	Atomicity	$N(B_i)$	$p(B_i^E)$	cc	lpc	$\sum_l p(B_i^{A1_l})$
Be$_2$C ††	(C; Be)	1.0005	0.9055	0.1891	0.8109	0.0933
	(C; Be)	1.0006	0.9054	0.1893	0.8107	0.0933
	(C; Be)	1.0009	0.9061	0.1878	0.8122	0.0934
	(C; Be)	1.0008	0.9057	0.1887	0.8113	0.0934
	(C; Be)	1.0011	0.9054	0.1892	0.8108	0.0937
	(C; Be)	1.0012	0.9062	0.1876	0.8124	0.0938
	(C; Be)	1.0018	0.9059	0.1883	0.8117	0.0937
	(C; Be)	1.0035	0.9049	0.1901	0.8099	0.0945
Mg$_2$C ††	(C; Mg)	0.9999	0.8823	0.2355	0.7645	0.1171
	(C; Mg)	0.9999	0.8823	0.2355	0.7645	0.1171
	(C; Mg)	0.9999	0.8822	0.2357	0.7643	0.1172
	(C; Mg)	0.9999	0.8826	0.2349	0.7651	0.1171
	(C; Mg)	1.0000	0.8822	0.2357	0.7643	0.1171
	(C; Mg)	0.9999	0.8826	0.2349	0.7651	0.1172
	(C; Mg)	1.0008	0.8821	0.2359	0.7641	0.1177
	(C; Mg)	1.0008	0.8819	0.2363	0.7637	0.1177
Mg$_2$Sn ††	(Sn; Mg)	0.9996	0.8450	0.3101	0.6899	0.1550
	(Sn; Mg)	1.0002	0.8449	0.3103	0.6897	0.1551
	(Sn; Mg)	0.9999	0.8450	0.3100	0.6900	0.1550
	(Sn; Mg)	1.0002	0.8446	0.3107	0.6893	0.1553
	(Sn; Mg)	1.0002	0.8448	0.3105	0.6895	0.1551
	(Sn; Mg)	1.0001	0.8448	0.3103	0.6897	0.1552
	(Sn; Mg)	1.0002	0.8448	0.3105	0.6895	0.1552
	(Sn; Mg)	1.0002	0.8448	0.3105	0.6895	0.1552
hyp-Ba$_2$Ge ††	(Ge; 4Ba)	1.3220	0.7509	0.4982	0.5018	0.2491
	(Ge; 4Ba)	1.3314	0.7526	0.4947	0.5053	0.2473
	(Ge; 4Ba)	1.3316	0.7525	0.4949	0.5051	0.2474
	(Ge; 4Ba)	1.3227	0.7506	0.4987	0.5013	0.2494
	(Ge; 4Ba)	1.3433	0.7538	0.4924	0.5076	0.2461
	(Ge; 4Ba)	1.3433	0.7538	0.4924	0.5076	0.2461

†† anti-CaF$_2$-type (optimized)

Table S9a. Data referred to ELI-D valence basins for ternary phases **without PSC0**.

Compound	ELI-D basin (B_i)	Atomicity	$\bar{N}(B_i)$	$p(B_i^E)$	cc	lpc	$p(B_i^{A'})$	$\sum_i^{s_x} p(B_i^A)$
NaLiSe †	d1	(Se; Li; 4Na)	2.1123	0.9705	0.0591	0.9409	0.0124	0.0171
	d2	(Se; Li; 4Na)	2.1904	0.9684	0.0633	0.9367	0.0130	0.0182
	d2	(Se; Li; 4Na)	2.2105	0.9681	0.0638	0.9362	0.0130	0.0183
	d3	(Se; Li; 3Na)	1.6213	0.9700	0.0600	0.9400	0.0164	0.0133
NaLiTe †	d1	(Te; Li; 4Na)	2.0726	0.9708	0.0584	0.9416	0.0130	0.0161
	d2	(Te; Li; 4Na)	2.1682	0.9689	0.0622	0.9378	0.0130	0.0175
	d2	(Te; Li; 4Na)	2.1862	0.9687	0.0626	0.9374	0.0131	0.0176
	d3	(Te; Li; 3Na)	1.7466	0.9683	0.0633	0.9367	0.0150	0.0161
KNaSe †	d1	(Se; Na; 4K)	1.9665	0.9607	0.0785	0.9215	0.0195	0.0196
	d2	(Se; Na; 4K)	2.2164	0.9608	0.0785	0.9215	0.0183	0.0208
	d2	(Se; Na; 4K)	2.2353	0.9606	0.0788	0.9212	0.0184	0.0209
	d3	(Se; Na; 3K)	1.6519	0.9621	0.0758	0.9242	0.0238	0.0137
CaLiAs †	d1	(As; Li; 4Ca)	2.0279	0.9314	0.1373	0.8627	0.0155	0.0528
	d2	(As; Li; 4Ca)	2.4101	0.9326	0.1348	0.8652	0.0149	0.0516
	d2	(As; Li; 4Ca)	2.4306	0.9323	0.1354	0.8646	0.0150	0.0519
	d3	(As; Li; 3Ca)	1.0472	0.9405	0.1190	0.8810	0.0277	0.0298
CaLiSb †	d1	(Sb; Li; 4Ca)	2.2769	0.9304	0.1392	0.8608	0.0149	0.0545
	d2	(Sb; Li; 4Ca)	2.1881	0.9305	0.1390	0.8610	0.0168	0.0516
	d2	(Sb; Li; 4Ca)	2.1741	0.9309	0.1383	0.8617	0.0167	0.0514
	d3	(Sb; Li; 3Ca)	1.2754	0.9394	0.1212	0.8788	0.0224	0.0362
CaLiBi †	d1	(Bi; Li; 4Ca)	2.2361	0.9288	0.1425	0.8575	0.0154	0.0556
	d2	(Bi; Li; 4Ca)	2.5757	0.9295	0.1410	0.8590	0.0143	0.0547
	d2	(Bi; Li; 4Ca)	2.5951	0.9292	0.1416	0.8584	0.0144	0.0549
	d3	(Bi; Li; 3Ca)	0.6276	0.9463	0.1074	0.8926	0.0438	0.0061
SrLiAs †	d1	(As; Li; 4Sr)	1.6349	0.9294	0.1413	0.8587	0.0187	0.0511
	d2	(As; Li; 4Sr)	2.4515	0.9281	0.1438	0.8562	0.0152	0.0565
	d2	(As; Li; 4Sr)	2.4728	0.9277	0.1445	0.8555	0.0153	0.0567
	d3	(As; Li; 3Sr)	1.3480	0.9374	0.1251	0.8749	0.0200	0.0412
CaMgSi †	d1	(Si; Mg; 4Ca)	1.8639	0.8689	0.2621	0.7379	0.0743	0.0564
	d2	(Si; Mg; 4Ca)	2.1925	0.8716	0.2569	0.7431	0.0661	0.0617
	d2	(Si; Mg; 4Ca)	2.2100	0.8707	0.2586	0.7414	0.0666	0.0620
	d3	(Si; Mg; 3Ca)	1.3002	0.8618	0.2764	0.7236	0.0973	0.0382
CaMgGe †	d1	(Ge; Mg; 4Ca)	1.9728	0.8706	0.2587	0.7413	0.0744	0.0546
	d2	(Ge; Mg; 4Ca)	2.2850	0.8736	0.2529	0.7471	0.0671	0.0588
	d2	(Ge; Mg; 4Ca)	2.3037	0.8727	0.2546	0.7454	0.0676	0.0591
	d3	(Ge; Mg; 3Ca)	1.3524	0.8556	0.2888	0.7112	0.1030	0.0370
CaMgSn †	d1	(Sn; Mg; 4Ca)	2.0901	0.8645	0.2711	0.7289	0.0786	0.0564
	d2	(Sn; Mg; 4Ca)	2.2244	0.8669	0.2662	0.7338	0.0738	0.0585
	d2	(Sn; Mg; 4Ca)	2.2417	0.8659	0.2682	0.7318	0.0744	0.0589
	d3	(Sn; Mg; 3Ca)	1.3256	0.8449	0.3102	0.6898	0.1147	0.0365
SrMgGe †	d1	(Ge; Mg; 4Sr)	1.7403	0.8531	0.2939	0.7061	0.0892	0.0576
	d2	(Ge; Mg; 4Sr)	2.3030	0.8589	0.2821	0.7179	0.0751	0.0656
	d2	(Ge; Mg; 4Sr)	2.3211	0.8580	0.2840	0.7160	0.0757	0.0658
	d3	(Ge; Mg; 3Sr)	1.5366	0.8557	0.2887	0.7113	0.0979	0.0442

† TiNiSi-type (optimized)

Table S9b. Data referred to ELI-D valence basins for binary phases **without PSC0**.

Compound	ELI-D basin (B_i)	Atomicity	$\bar{N}(B_i)$	$p(B_i^E)$	cc	lpc	$\sum_l p(B_i^{A1_l})$	$\sum_j p(B_i^{A2_j})$
Ca$_2$Si †	$d1^*$	(Si; 3Ca1; 2Ca2)	1.6017	0.8383	0.3234	0.6766	0.1047	0.0521
	$d2^*$	(Si; 3Ca1; 3Ca2)	2.8690	0.8716	0.2569	0.7431	0.0592	0.0677
	$d2^*$	(Si; 3Ca1; 3Ca2)	2.8937	0.8714	0.2573	0.7427	0.0595	0.0676
Ca$_2$Ge †	$d1^*$	(Ge; 3Ca1; 2Ca2)	1.7204	0.8418	0.3163	0.6837	0.1024	0.0507
	$d2^*$	(Ge; 3Ca1; 3Ca2)	2.9807	0.8755	0.2490	0.7510	0.0570	0.0660
	$d2^*$	(Ge; 3Ca1; 3Ca2)	3.0059	0.8754	0.2493	0.7507	0.0571	0.0660
Sr$_2$Si †	$d1^*$	(Si; 3Sr1; 2Sr2)	1.6841	0.8247	0.3507	0.6493	0.1151	0.0585
	$d2^*$	(Si; 3Sr1; 3Sr2)	2.8169	0.8592	0.2817	0.7183	0.0639	0.0759
	$d2^*$	(Si; 3Sr1; 3Sr2)	2.8399	0.8592	0.2817	0.7183	0.0641	0.0758
Sr$_2$Ge †	$d1^*$	(Ge; 3Sr1; 2Sr2)	1.7518	0.8269	0.3463	0.6537	0.1127	0.0586
	$d2^*$	(Ge; 3Sr1; 3Sr2)	2.9505	0.8630	0.2741	0.7259	0.0620	0.0741
	$d2^*$	(Ge; 3Sr1; 3Sr2)	2.9750	0.8629	0.2742	0.7258	0.0621	0.0740
Ba$_2$Si †	$d1^*$	(Si; 3Ba1; 2Ba2)	1.6680	0.8187	0.3626	0.6374	0.1197	0.0616
	$d2^*$	(Si; 3Ba1; 2Ba2)	1.8189	0.8555	0.2891	0.7109	0.0775	0.0670
	$d2^*$	(Si; 3Ba1; 2Ba2)	1.8302	0.8553	0.2894	0.7106	0.0775	0.0671
	$d3^*$	(Si; 4Ba1; 3Ba2)	1.9944	0.8540	0.2919	0.7081	0.0421	0.1028
Ba$_2$Ge †	$d1^*$	(Ge; 3Ba1; 2Ba2)	1.6680	0.8187	0.3626	0.6374	0.1197	0.0616
	$d2^*$	(Ge; 3Ba1; 2Ba2)	1.8189	0.8555	0.2891	0.7109	0.0775	0.0670
	$d2^*$	(Ge; 3Ba1; 2Ba2)	1.8302	0.8553	0.2894	0.7106	0.0775	0.0671
	$d3^*$	(Ge; 4Ba1; 3Ba2)	1.9944	0.8540	0.2919	0.7081	0.0421	0.1028
Ba$_2$Pb †	$d1^*$	(Pb; 3Ba1; 2Ba2)	1.6398	0.8012	0.3976	0.6024	0.1261	0.0722
	$d2^*$	(Pb; 3Ba1; 2Ba2)	1.9147	0.8443	0.3115	0.6885	0.0801	0.0755
	$d2^*$	(Pb; 3Ba1; 2Ba2)	1.9240	0.8440	0.3121	0.6879	0.0803	0.0757
	$d3^*$	(Pb; 4Ba1; 3Ba2)	1.8431	0.8540	0.2920	0.7080	0.0463	0.0978

† TiNiSi-type (optimized)

Table S9c. Data referred to ELI-D valence basins for binary phases with the *cF*12-CaF2 structure **without PSC0**.

Compound	Atomicity	$N(B_i)$	$p(B_i^E)$	cc	lpc	$\sum_l p(B_i^{A1_l})$
Be₂C ††	(C; Be)	0.9708	0.9190	0.1619	0.8381	0.0797
	(C; Be)	0.9710	0.9189	0.1623	0.8377	0.0797
	(C; Be)	0.9712	0.9197	0.1606	0.8394	0.0798
	(C; Be)	0.9711	0.9193	0.1615	0.8385	0.0798
	(C; Be)	0.9715	0.9190	0.1620	0.8380	0.0801
	(C; Be)	0.9716	0.9197	0.1606	0.8394	0.0801
	(C; Be)	0.9722	0.9194	0.1613	0.8387	0.0801
	(C; Be)	0.9738	0.9185	0.1631	0.8369	0.0810
Mg₂C ††	(C; Mg)	0.9709	0.8957	0.2087	0.7913	0.1037
	(C; Mg)	0.9709	0.8957	0.2087	0.7913	0.1037
	(C; Mg)	0.9709	0.8957	0.2089	0.7911	0.1038
	(C; Mg)	0.9709	0.8960	0.2081	0.7919	0.1037
	(C; Mg)	0.9710	0.8956	0.2089	0.7911	0.1037
	(C; Mg)	0.9709	0.8960	0.2080	0.7920	0.1038
	(C; Mg)	0.9718	0.8955	0.2091	0.7909	0.1043
	(C; Mg)	0.9718	0.8953	0.2095	0.7905	0.1043
Mg₂Sn ††	(Sn; Mg)	1.0130	0.8636	0.2729	0.7271	0.1364
	(Sn; Mg)	1.0134	0.8634	0.2731	0.7269	0.1366
	(Sn; Mg)	1.0132	0.8636	0.2728	0.7272	0.1364
	(Sn; Mg)	1.0134	0.8633	0.2733	0.7267	0.1367
	(Sn; Mg)	1.0133	0.8634	0.2732	0.7268	0.1366
	(Sn; Mg)	1.0134	0.8634	0.2731	0.7269	0.1366
	(Sn; Mg)	1.0135	0.8633	0.2733	0.7267	0.1367
	(Sn; Mg)	1.0135	0.8633	0.2733	0.7267	0.1367
hyp-Ba₂Ge ††	(Ge; 4Ba)	1.2171	0.8535	0.2930	0.7070	0.1465
	(Ge; 4Ba)	1.2260	0.8546	0.2909	0.7091	0.1454
	(Ge; 4Ba)	1.2262	0.8544	0.2911	0.7089	0.1456
	(Ge; 4Ba)	1.2178	0.8532	0.2936	0.7064	0.1468
	(Ge; 4Ba)	1.2352	0.8545	0.2910	0.7090	0.1455
	(Ge; 4Ba)	1.2352	0.8545	0.2910	0.7090	0.1455

†† anti-CaF₂-type (optimized)

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