Supplemental Information

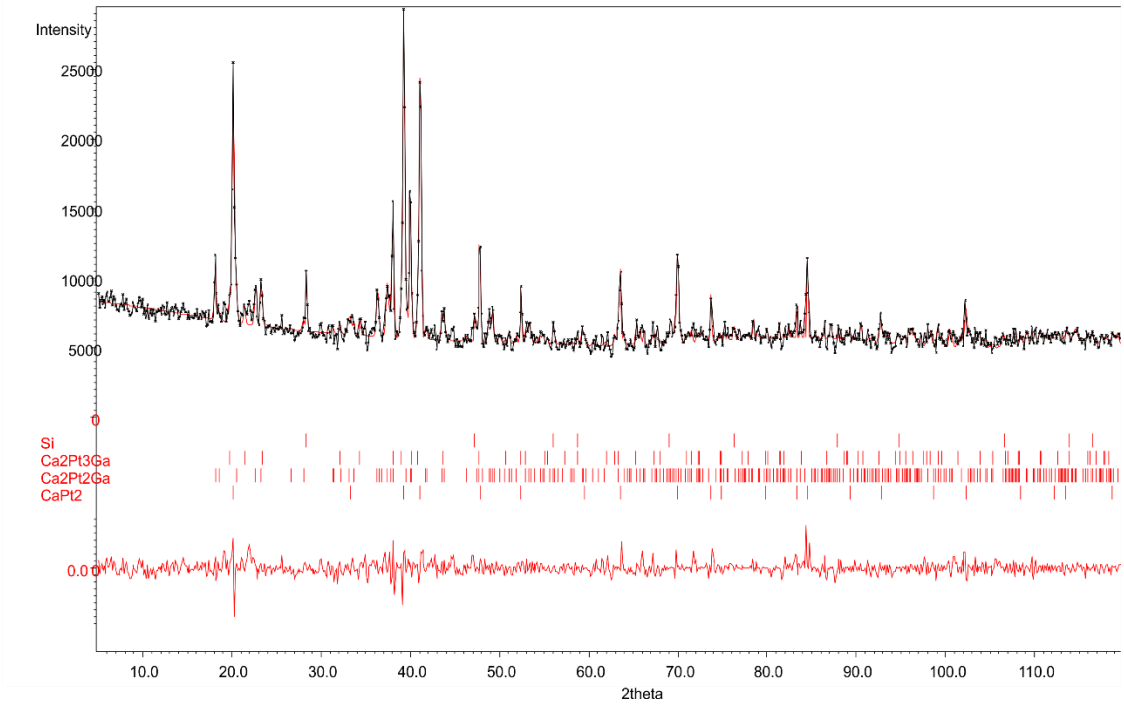


Figure S1. Peak fitting performed with Jana. Relative percentages of compounds are $CaPt_2$ (50%), Ca_2Pt_2Ga (30%), Ca_2Pt_3Ga (15%), and Si (5%).

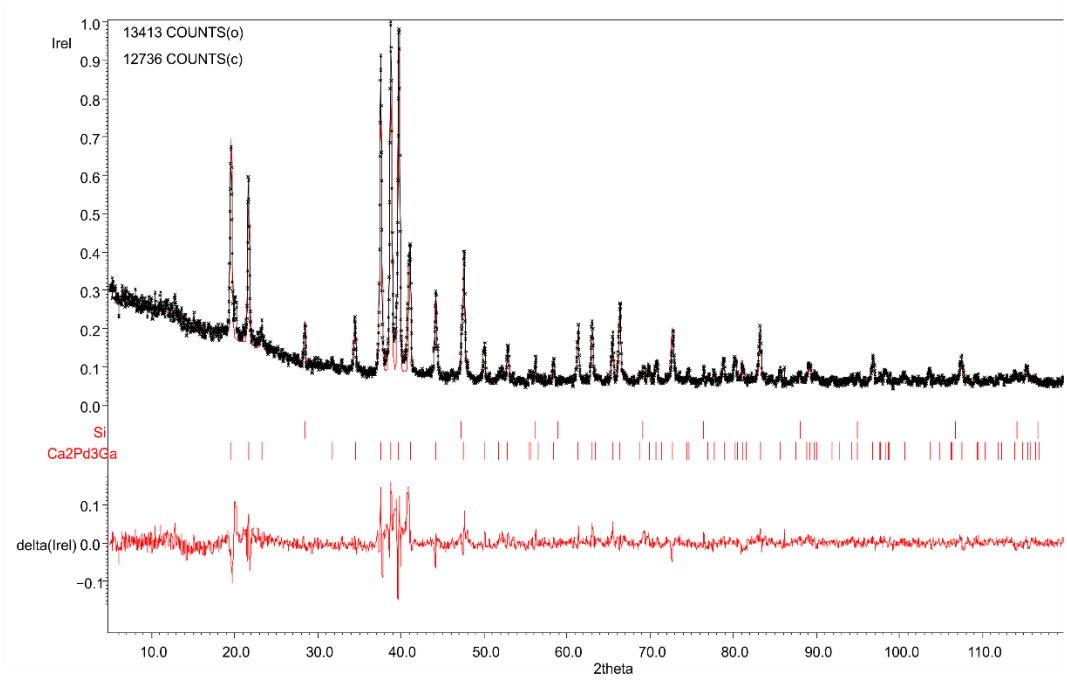


Figure S2. Rietveld refinement of Ca_2Pd_3Ga.

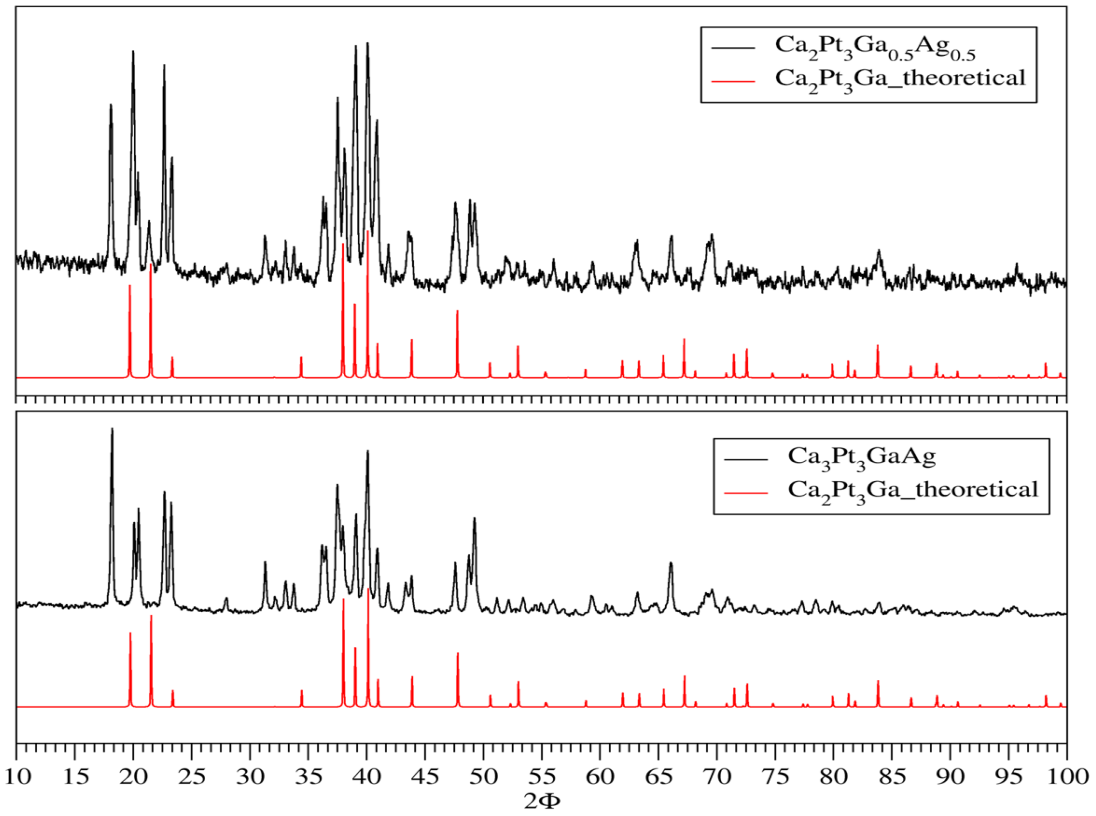


Figure S3. Powder patterns with loadings of $Ca_2Pt_3Ga_{0.5}Ag_{0.5}$ (upper) and Ca_3Pt_3GaAg (lower).

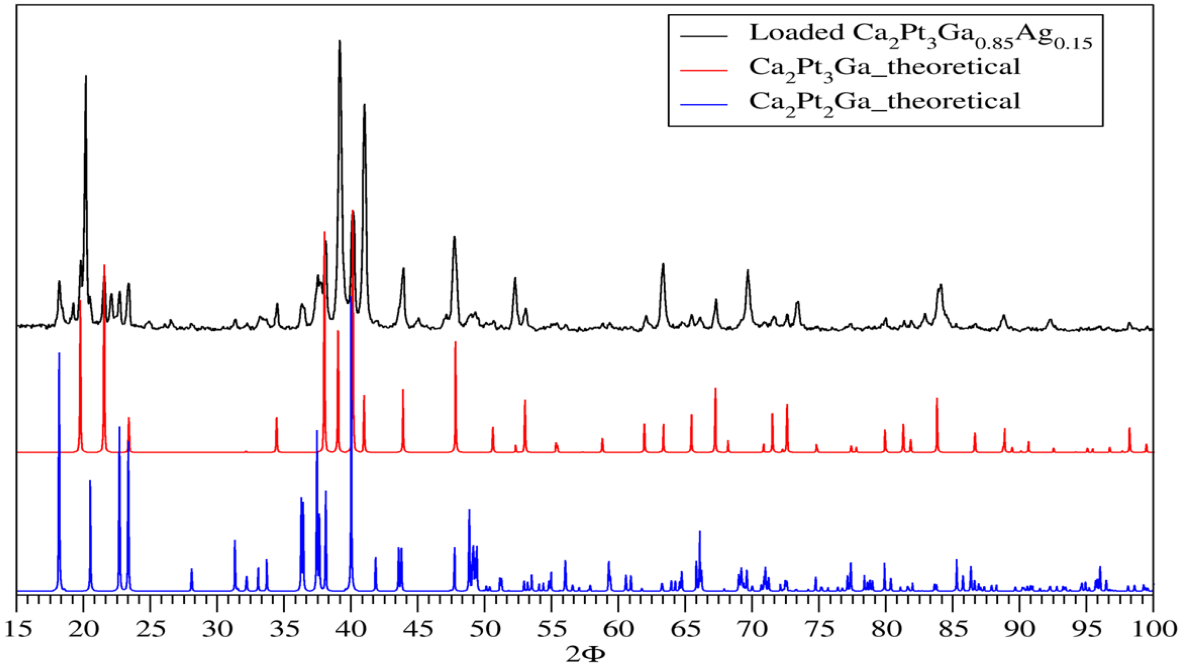


Figure S4. Powder pattern of another loaded sample of $Ca_2Pt_3Ga_{0.85}Ag_{0.15}$.

	x	y	z	U^{11}	U^{22}	U^{33}
Ca	0	0	0.3722(1)	0.012(1)	0.012(1)	0.012(1)
Pd	½	0	½	0.010(1)	0.007(1)	0.010(1)
Ga	0	0	0	0.009(1)	0.009(1)	0.008(1)

Table S1. Atomic coordinates and anisotropic displacement parameters ($Å^2$x10) for Ca_2Pd_3Ga.

	x	y	z	U^{11}	U^{22}	U^{33}
Ca	0	0	0.3750(2)	0.007(1)	0.007(1)	0.008(1)
Pt	½	0	½	0.008(1)	0.006(1)	0.006(1)
Ga	0	0	0	0.007(1)	0.007(1)	0.005(1)

Table S2. Atomic coordinates and anisotropic displacement parameters ($Å^2$x10) for Ca_2Pt_3Ga.

Sample	Ca_2Pt_3Ga	Ca_2Pt_3Ga	Ca_2Pd_3Ga	Ca_2Pd_3Ga
Space Group	*R*-3*m*	*R*-3*m*	*R*-3*m*	*R*-3*m*
Unit Cell Dim.	*a* = 5.571(7) Å *c* = 12.38(2) Å	*a* = 5.565(4) Å *c* = 12.367(8) Å	*a* = 5.666(8) Å *c* = 12.39(2) Å	*a* = 5.62(2) Å *c* = 12.27(4) Å
Volume	332.7(9) $Å^3$	331.7(1) $Å^3$	344.3(1) $Å^3$	336.(3) $Å^3$
Z	3	3	3	3
Theta range for data collection	4.534 to 28.837°	4.539 to 31.202 °	4.495 to 28.878 °	4.505 to 31.033 °
Index ranges	–7<=*h*<=7, –7<=*k*<=7, –16<=*l*<=16	–8<=*h*<=7, –7<=*k*<=7, –17<=*l*<=17	–7<=*h*<=7, –7<=*k*<=7, –17<=*l*<=17	–8<=*h*<=8, –8<=*k*<=8, –17<=*l*<=17
Reflections Collected	1548	1305	2654	1741
Independent Reflections	125[R(int)=0.0348]	153[R(int)=0.0322]	147[R(int)=0.0224]	154[R(int)=0.0585]
Data/restraints/parameters	125 / 0 / 11	153 / 0 / 11	147 / 0 / 1	154 / 0 / 11
Goodness-of-fit	1.204	1.179	1.282	1.236
Final R indices [I>2sigma(l)]	R1 = 0.0138, wR2 = 0.0318	R1 = 0.0196, wR2 = 0.0463	R1 = 0.0171, wR2 = 0.0416	R1 = 0.0157, wR2 = 0.0320
R indices (all data)	R1 = 0.0138, wR2 = 0.0318	R1 = 0.0200, wR2 = 0.0466	R1 = 0.0173, wR2 = 0.0417	R1 = 0.0174, wR2 = 0.0331
Extinction Coefficient	0.0037(2)	n/a	n/a	0.0030(3)
Largest diff. peak and hole	1.617 and –1.288 e·$Å^{-3}$	1.942 and –4.014 e·$Å^{-3}$	1.582 and –3.261 e·$Å^{-3}$	2.348 and –1.470 e·$Å^{-3}$

Table S3. X-ray diffraction data on additions crystals for Ca_2Pt_3Ga and Ca_2Pd_3Ga.

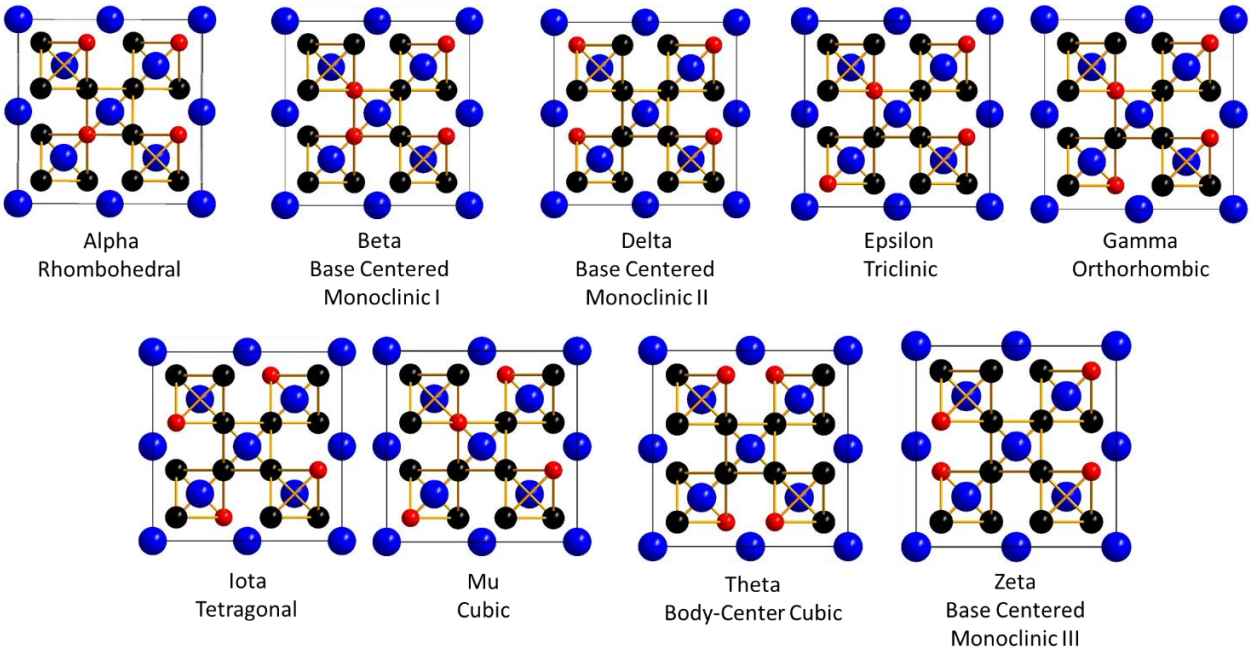


Figure S5. Coloring Models and respective symmetries.

	Ca_2Pd_3Ge		
Model	**Ge-Ge distance (Å)**	**meV non-optimized**	**meV optimized**
Alpha	5.280	0	+0.0
Beta	2.810	+29.8	+66.6
Delta	2.846	+55.1	+110.1
Epsilon	2.881	+36.7	+74.1
Gamma	4.785	+84.2	+31.7
Iota	3.137	+66.9	+102.0
Mu	4.723	+21.6	+43.9
Theta	3.091	+180.9	+217.4
Zeta	2.937	+88.8	+137.1

Table S4. Total energies and nearest Ge-Ge contact for theoretical models of Ca_2Pd_3Ge.

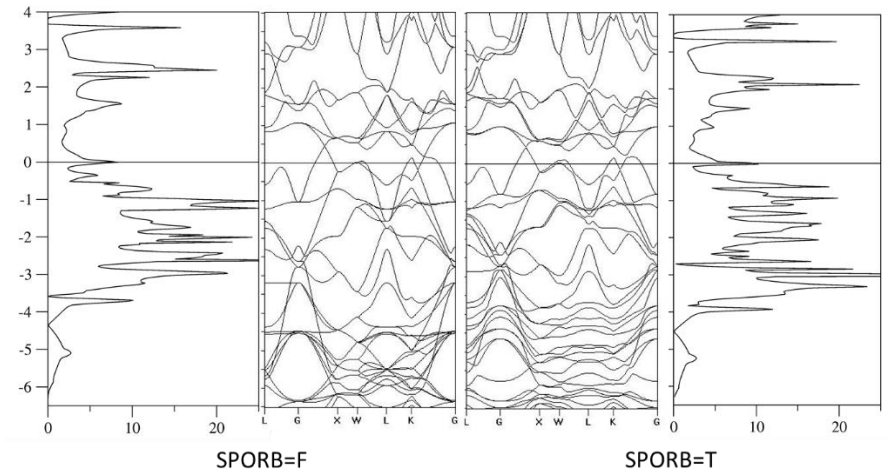


Figure S6. DOS and Band structures for $CaPt_2$ without (left) and with (right) spin-orbit coupling. Degeneracies in the band structure at Gamma are lifted at -4.5, -3, -2.5, and -1 eV along with degeneracies at L at -5.5 and 4.5 eV by spin-orbit coupling

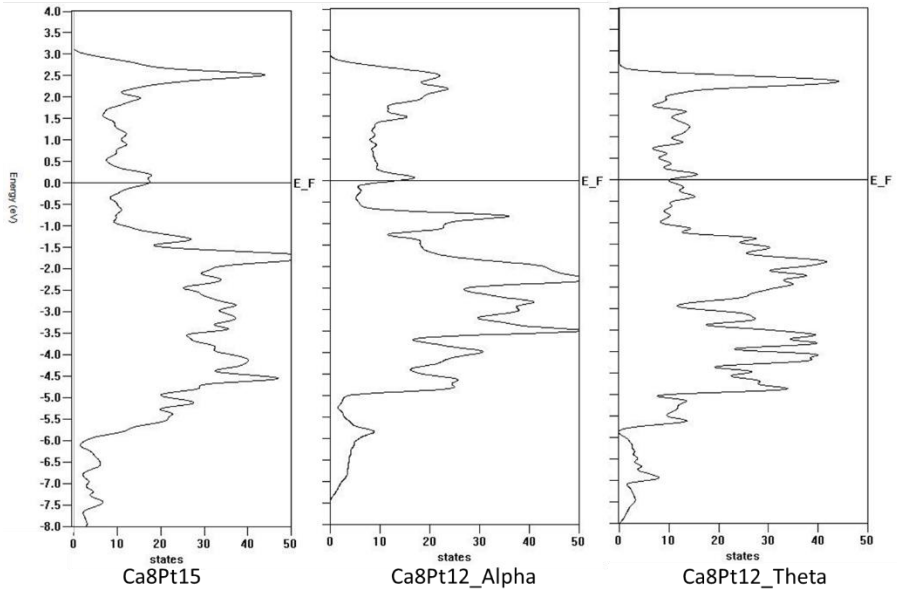


Figure S7. VASP calculated DOS for Ca_8Pt_{15} and two models of Ca_8Pt_{12}. Alpha has the vacancies as far apart in the structure as possible while theta has the vacancies as close together which removes one of the tetrahedra from the structure.

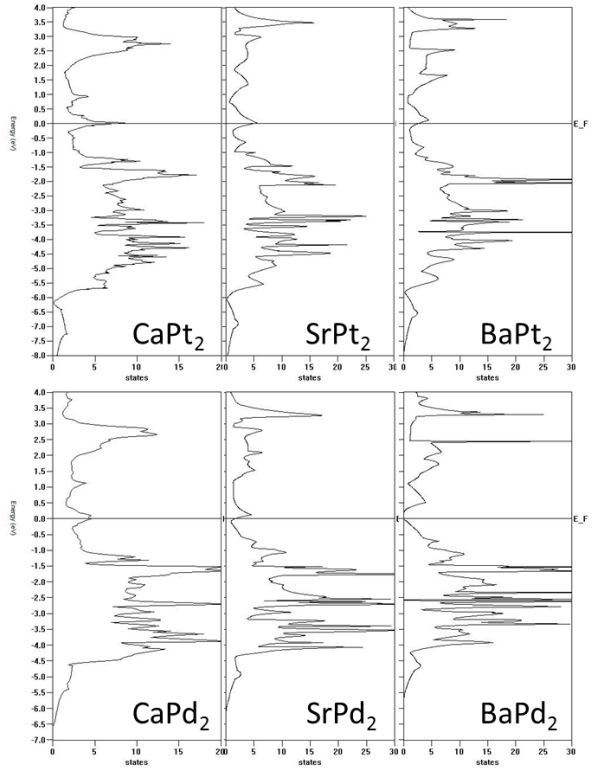
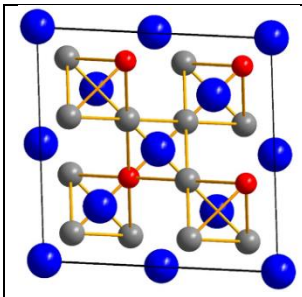
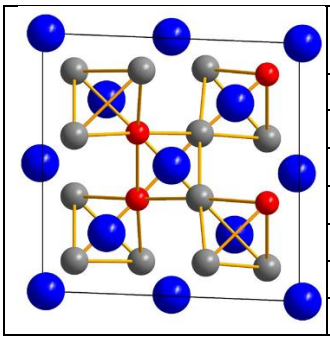


Figure S8. DOS calculated for AEM_2 (AE=Ca, Sr, Ba M=Pt, Pd). As the alkaline-earth metal gets larger and heavier the DOS starts to shift away from the Fermi level.



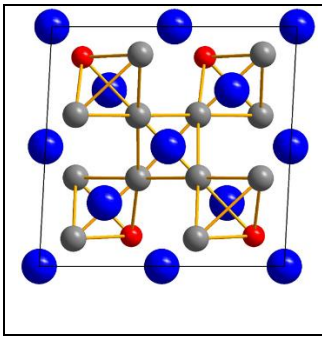
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.837	2.810	24	a (Å)	7.7511	7.7077
M-Ga	2.641	2.638	24	b (Å)	7.7511	7.7077
Ga-Ga	n/a	n/a	0	c (Å)	7.7511	7.7077
Ca-Ca	3.175 3.415	3.119 3.407	4 12	α (°)	94.0958	93.6062
Ca-Ga	3.311	3.286	24	β (°)	85.9042	86.3938
Ca-M	3.035 3.251	3.066 3.213	24 48	γ (°)	85.9042	86.3938

Table S5. Optimized Alpha structure with lattice constants and interatomic distances.



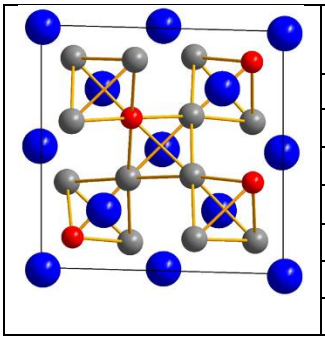
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.757-2.905	2.736-2.876	25	a (Å)	7.7657	7.7411
M-Ga	2.572-2.717	2.569-2.695	22	b (Å)	7.7657	7.7411
Ga-Ga	2.731	2.755	1	c (Å)	7.7031	7.6391
Ca-Ca	3.140-3.542	3.091-3.419	16	α (°)	92.1501	91.956
Ca-Ga	3.173-3.368	3.160-3.357	24	β (°)	87.8499	88.044
Ca-M	2.983-3.340	3.020-3.319	72	γ (°)	86.5066	87.097

Table S6. Optimized Beta structure with lattice constants and interatomic distances.



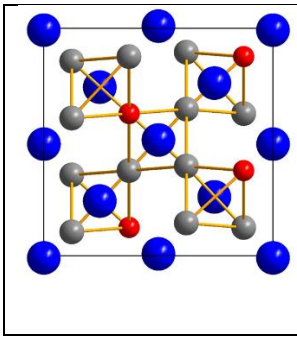
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.728-2.866	2.710-2.852	26	a (Å)	7.8794	7.8819
M-Ga	2.582-2.787	2.579-2.777	20	b (Å)	7.6739	7.6101
Ga-Ga	2.775	2.811	2	c (Å)	7.6959	7.6526
Ca-Ca	3.285-3.545	3.262-3.285	16	α (°)	90	90
Ca-Ga	3.223-3.375	3.205-3.397	24	β (°)	86.9465	87.5532
Ca-M	3.079-3.336	3.086-3.337	72	γ (°)	90	90

Table S7. Optimized Delta structure with lattice constants and interatomic distances.



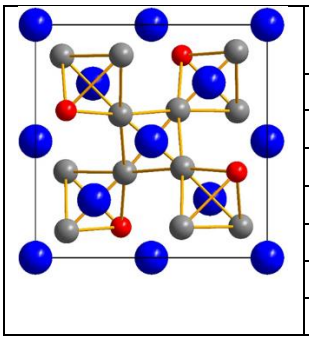
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.761-2.910	2.734-2.869	25	a (Å)	7.6727	7.6312
M-Ga	2.578-2.722	2.589-2.705	22	b (Å)	7.7939	7.7799
Ga-Ga	2.800	2.808	1	c (Å)	7.7508	7.6972
Ca-Ca	3.161-3.584	3.134-3.431	16	α (°)	91.5298	91.3602
Ca-Ga	3.209-3.369	3.194-3.361	24	β (°)	89.9967	89.8574
Ca-M	3.054-3.340	3.050-3.313	72	γ (°)	87.9109	88.3982

Table S8. Optimized Epsilon structure with lattice constants and interatomic distances.



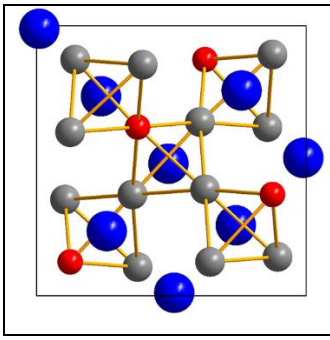
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.823-2.840	2.802-2.816	24	a (Å)	7.7343	7.7243
M-Ga	2.639-2.643	2.625-2.658	24	b (Å)	7.7343	7.7243
Ga-Ga	n/a	n/a	0	c (Å)	7.7343	7.6371
Ca-Ca	3.150-3.455	3.119-3.427	16	α (°)	90	89.9998
Ca-Ga	3.205-3.314	3.196-3.287	24	β (°)	90	90.0002
Ca-M	3.046-3.264	3.069-3.238	72	γ (°)	86.1127	86.9369

Table S9. Optimized Gamma structure with lattice constants and interatomic distances.



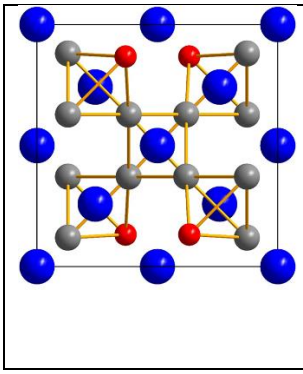
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.765-2.884	2.750-2.883	26	a (Å)	7.5721	7.5281
M-Ga	2.596-2.650	2.604-2.630	20	b (Å)	7.8370	7.8003
Ga-Ga	2.922	2.931	2	c (Å)	7.8370	7.8003
Ca-Ca	3.186-3.431	3.156-3.408	16	α (°)	90	90
Ca-Ga	3.211-3.330	3.185-3.337	24	β (°)	90	90
Ca-M	3.054-3.365	3.028-3.341	72	γ (°)	90	90

Table S10 Optimized Iota structure with lattice constants and interatomic distances.



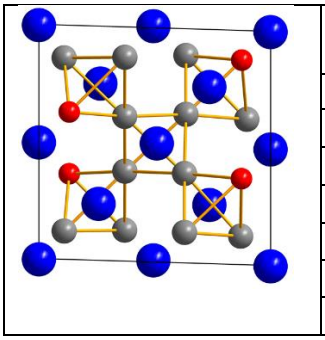
Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.793	2.8154	24	a (Å)	7.7740	7.6900
M-Ga	2.591	2.632	24	b (Å)	7.7740	7.6900
Ga-Ga	n/a	n/a	0	c (Å)	7.7740	7.6900
Ca-Ca	3.199-3.572	3.246-3.590	16	α (°)	90	90
Ca-Ga	3.226	3.258	24	β (°)	90	90
Ca-M	3.059-3.202	3.106-3.234	72	γ (°)	90	90

Table S11. Optimized Mu structure with lattice constants and interatomic distances.



Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.727-2.832	2.707-2.809	30	a (Å)	7.5980	7.7532
M-Ga	2.633	2.606	12	b (Å)	7.5980	7.7532
Ga-Ga	2.909	2.950	6	c (Å)	7.5980	7.7532
Ca-Ca	3.254-3.405	3.224-3.404	16	α (°)	90	90
Ca-Ga	3.207-3.338	3.195-3.353	24	β (°)	90	90
Ca-M	3.190-3.277	3.179-3.274	72	γ (°)	90	90

Table S12. Optimized Theta structure with lattice constants and interatomic distances.



Bond	Distance		#/unit cell	Unit Cell Parameters		
	Ca_2Pd_3Ga	Ca_2Pt_3Ga			Ca_2Pd_3Ga	Ca_2Pt_3Ga
M-M	2.722-2.931	2.706-2.929	27	a (Å)	7.7868	7.7557
M-Ga	2.588-2.786	2.583-2.782	18	b (Å)	7.7868	7.7557
Ga-Ga	2.798-2.913	2.824-2.922	3	c (Å)	7.6855	7.6535
Ca-Ca	3.211-3.537	3.180-3.538	16	α (°)	91.7224	91.3708
Ca-Ga	3.177-3.353	3.182-3.369	24	β (°)	88.2776	88.6292
Ca-M	3.052-3.311	3.075-3.281	72	γ (°)	89.5669	89.6874

Table S13. Optimized Zeta structure with lattice constants and interatomic distances.

Bond	Distance	#/formula unit	ICOHP Ry	ICOHP eV	Total	%
Ca-Ca	3.29	2	-0.01003	-0.13646	-0.27292	1.468672
Ca-Pt	3.15	12	-0.0405	-0.551	-6.61203	35.58198
Pt-Pt	2.686	6	-0.1433	-1.9496	-11.6976	62.94935

Table S14. COHP interactions in $CaPt_2$

Bond	Distance	#/formula unit	ICOHP Ry	ICOHP eV	Total	%
Ca-Ca	3.313	2	-0.01089	-0.14816	-0.29632	2.121318
Ca-Pd	3.172	12	-0.03377	-0.45944	-5.51329	39.46938
Pd-Pd	2.705	6	-0.09995	-1.35982	-8.15892	58.4093

Table S15. COHP interactions in $CaPd_2$

Bond	Distance	#/formula unit	ICOHP Ry	ICOHP eV	ICOHP/f.u.	%	% by Type
Ca-Ca	3.092	1	-0.01265	-0.1721	-0.1721	0.504105	1.82
	3.374	3	-0.01103	-0.15006	-0.45019	1.318642	
Ca-Ga	3.254	6	-0.0243	-0.3306	-1.98361	5.810154	5.81
Ca-Pt	3.036	6	-0.04967	-0.67576	-4.05456	11.87615	30.68
	3.183	12	-0.03933	-0.53508	-6.42102	18.80768	
Pt-Ga	2.613	6	-0.1327	-1.80538	-10.8323	31.7287	31.73
Pt-Pt	2.782	6	-0.12528	-1.70443	-10.2266	29.95457	29.95

Table S16. COHP interactions in Ca_2Pt_3Ga

Bond	Distance	#/formula unit	ICOHP Ry	ICOHP eV	ICOHP/f.u.	%	% by Type
Ca-Ca	3.145	1	-0.01444	-0.19646	-0.196456	0.68512	2.42
	3.389	3	-0.01216	-0.16544	-0.496310	1.730829	
Ca-Ga	3.287	6	-0.02772	-0.37713	-2.262783	7.891216	7.89
Ca-Pd	3.005	6	-0.04405	-0.5993	-3.595801	12.53997	31.56
	3.225	12	-0.03341	-0.45454	-5.454516	19.02204	
Pd-Pd	2.816	6	-0.08572	-1.16622	-6.997323	24.40242	24.40
Pd-Ga	2.617	6	-0.11848	-1.61192	-9.671522	33.7284	33.73

Table S17. COHP interactions in Ca_2Pd_3Ga

$CaPt_2$	–16.8947 eV
Pt	–6.0954 eV
Ca_2Pt_3Ga*	–30.4912 eV
Ca_2Pt_3Ga**	–30.5797 eV
Ca_2Pt_3Ga	–30.9045 eV
$CaPd_2$	–14.4409 eV
Ca_2Pd_3Ga*	–26.8363 eV
Ca_2Pd_3Ga**	–26.8787 eV
Ca_2Pd_3Ga	–27.1779 eV
Pd	–5.2156 eV
Ga	–2.9122 eV

Table S18. Specific total energies (eV/formula unit) for each component used to calculate ΔEs presented in **Table 4.**