

Vacancy ordering as a driving factor for structural changes in ternary germanides.

The new $R_2Zn_{1-x}Ge_6$ series of polar intermetallics (R = rare earth metal).

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Table S1. SEM/EDXS and XRPD characterization results for samples with nominal composition $R_{22.2}Zn_{11.1}Ge_{66.7}$ (* means that it was not possible to calculate accurate lattice parameters due to small amount of the phase).

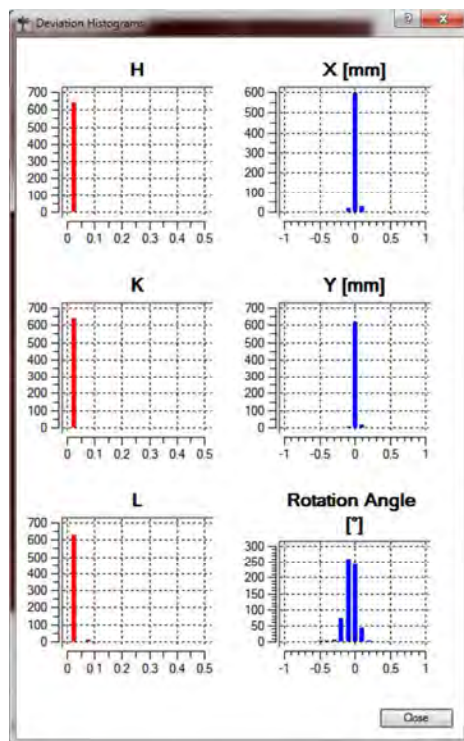
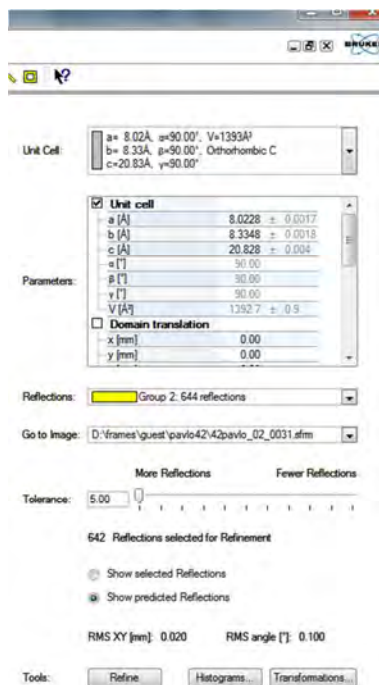
R	Phase	Crystal structure	Phase composition [at%]			Cell parameters [Å]			
			R	Zn	Ge	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]
La	La₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	22.7	11.0	66.3	8.729(3)	8.276(2)	21.426(9)	
	La ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	18.7	27.8	53.5	5.985(1)	24.909(4)	5.967(1)	
	LaGe _{2-x}	<i>oI12</i> –4x–GdSi _{1.4}	35.4	1.7	62.9	4.316(5)	4.38(2)	14.25(2)	
	Ge	<i>cF8</i> –C	0.0	0.0	100.0	5.6543(5)	5.6543(5)	5.6543(5)	
Ce	Ce₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	23.0	10.6	66.4	8.645(9)	8.227(8)	21.33(3)	
	Ce ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	18.8	26.9	54.3	5.956(2)	24.772(7)	5.947(4)	
	CeGe _{2-x}	<i>oI12</i> –4x–GdSi _{1.4}	36.2	0.9	62.9	4.329(2)	4.246(2)	14.112(3)	
Pr	Pr₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	21.0	10.6	68.4	8.601(3)	8.221(3)	21.197(7)	
	Pr ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	16.9	27.4	55.7	*	*	*	
	PrGe _{2-x}	<i>oI12</i> –4x–ThSi ₂	33.5	2.8	63.7	4.238(3)	4.238(3)	14.09(2)	
Nd	Nd₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	22.0	9.6	68.4	8.539(6)	8.15(1)	21.15(4)	
	NdGe _{2-x}	<i>oI12</i> –4x–ThSi ₂	35.3	0.4	64.3	4.2224(3)	4.2224(3)	13.938(1)	
Sm	Sm₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	22.0	9.4	68.6	8.452(8)	8.08(1)	20.94(2)	
	Sm ₂₇ Zn ₆ Ge ₆₇	unknown	27.5	5.8	66.7				
	Sm ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	18.1	26.8	55.1	5.85(1)	24.51(1)	5.86(1)	
	SmGe _{2-x}	<i>oI12</i> –4x–ThSi ₂	35.6	0.8	63.6	*	*	*	
	Ge	<i>cF8</i> –C	0.0	0.0	100.0	*	*	*	
Gd	Gd₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	23.0	7.7	69.3	8.36(1)	8.033(4)	21.22(3)	
	Gd ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	18.7	25.7	55.6	5.819(1)	24.459(5)	5.825(3)	
	Ge	<i>cF8</i> –C	0.0	0.0	100.0	5.655(3)	5.655(3)	5.655(3)	
Tb	Tb₂Zn_{1-x}Ge₆	<i>oS72</i>–Ce₂(Ga_{0.1}Ge_{0.9})₇	23.6	7.1	69.3	8.304(1)	8.005(1)	20.790(1)	
	Tb ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	18.9	25.3	55.8	5.773(2)	24.367(7)	5.770(4)	
	TbZn _x Ge ₂	unknown	30.1	7.6	62.3				
Dy	Dy₂Zn_{1-x}Ge₆	<i>mP36</i>–Dy₂Zn_{1-x}Ge₆	24.0	6.6	69.4	7.959(2)	8.236(2)	10.516(9)	100.92(4)
	Dy ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	19.0	24.8	56.2	5.746(3)	24.328(9)	5.753(3)	
	Ge	<i>cF8</i> –C	0.0	0.0	100.0	5.653(3)	5.653(3)	5.653(3)	
	DyZn _x Ge ₂	unknown	31.7	7.0	61.3				
Ho	Ho₂Zn_{1-x}Ge₆	<i>mP36</i>–Dy₂Zn_{1-x}Ge₆	23.6	5.7	70.7	7.924(5)	8.204(3)	10.489(5)	100.97(9)
	Ho ₂ Zn ₃ Ge ₆	<i>oS44</i> –La ₂ Zn ₃ Ge ₆	19.0	24.8	56.2	5.735(4)	24.27(2)	5.743(4)	
	Ge	<i>cF8</i> –C	0.0	0.0	100.0	5.6587(5)	5.6587(5)	5.6587(5)	
	HoZn _x Ge ₂	unknown	31.6	5.9	62.5				
Er	Ge	<i>cF8</i> –C	0.0	0.0	100.0	5.653(2)	5.653(2)	5.653(2)	
	ErZn _x Ge ₂	unknown	32.2	4.6	63.2				
Tm	Er ₄ Zn ₅ Ge ₆	<i>oS30</i> –Gd ₄ Zn ₅ Ge ₆	27.4	32.5	40.1	4.195(2)	18.430(3)	15.135(2)	
	TmGe _{2-x}	<i>oS12</i> –ZrSi ₂	34.1	2.4	63.5	4.033(4)	15.840(5)	3.900(5)	
	Tm ₄ Zn ₅ Ge ₆	<i>oS30</i> –Gd ₄ Zn ₅ Ge ₆	28.3	32.3	39.4	4.1900(3)	18.410(3)	15.090(3)	
	Ge	<i>cF8</i> –C	0	0	100	5.6576(3)			

Table S2. Interatomic distances for R₂Zn_{1-x}Ge₆ (R=La, Ce, Nd, Gd, Tb).

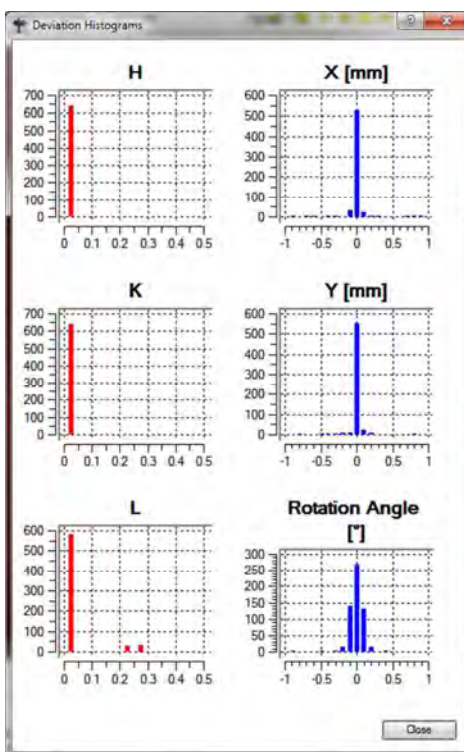
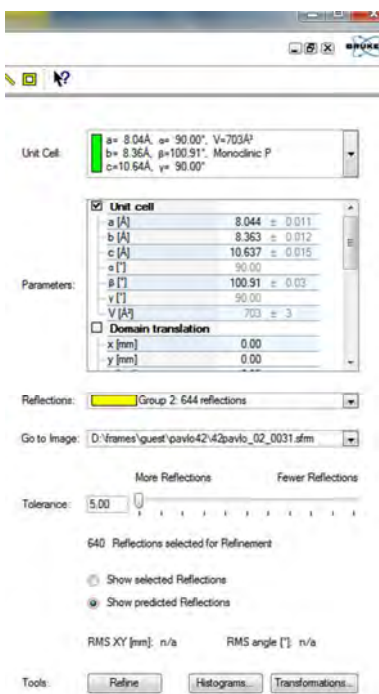
Atom 1	Atom 2	R=La <i>d</i> [Å]	R=Ce <i>d</i> [Å]	R=Nd <i>d</i> [Å]	R=Gd <i>d</i> [Å]	R=Tb <i>d</i> [Å]	Atom 1	Atom 2	R=La <i>d</i> [Å]	R=Ce <i>d</i> [Å]	R=Nd <i>d</i> [Å]	R=Gd <i>d</i> [Å]	R=Tb <i>d</i> [Å]
R	Ge1	3.144(1)	3.111(1)	3.071(1)	3.007(4)	2.989(1)	Ge3	Ge3	2.462(1)	2.464(1)	2.461(1)	2.449(2)	2.457(1)
	Ge1	3.159(1)	3.136(1)	3.097(1)	3.034(4)	3.016(1)		Ge2	2.551(1)	2.551(1)	2.546(1)	2.554(3)	2.572(2)
	Ge3	3.177(1)	3.156(1)	3.118(1)	3.059(3)	3.041(1)		Ge5	2.553(1)	2.552(1)	2.544(1)	2.568(3)	2.561(2)
	Ge3	3.185(1)	3.160(1)	3.126(1)	3.062(3)	3.042(1)		Zn	2.671(1)	2.643(1)	2.595(1)	2.489(2)	2.459(1)
	Ge4	3.187(1)	3.164(1)	3.125(1)	3.056(4)	3.035(1)		R	3.177(1)	3.156(1)	3.118(1)	3.059(3)	3.041(1)
	Ge4	3.228(1)	3.210(1)	3.176(1)	3.087(4)	3.066(1)		R	3.185(1)	3.160(1)	3.126(1)	3.062(3)	3.042(1)
	Ge2	3.250(1)	3.216(1)	3.175(1)	3.100(2)	3.079(1)		Ge5	3.464(1)	3.428(1)	3.369(1)	3.229(3)	3.207(2)
	Ge5	3.259(1)	3.227(1)	3.189(1)	3.114(2)	3.089(1)		Ge2	3.466(1)	3.428(1)	3.367(1)	3.243(3)	3.196(2)
	Ge4	3.282(1)	3.250(1)	3.216(1)	3.192(1)	3.182(1)	Ge4	Ge4	2.527(2)	2.519(2)	2.507(1)	2.504(6)	2.505(2)
	Zn	3.329(1)	3.300(1)	3.261(1)	3.204(3)	3.193(2)		Zn	2.554(2)	2.514(2)	2.480(1)	2.396(3)	2.376(2)
	Zn	3.343(1)	3.312(1)	3.274(1)	3.218(3)	3.201(2)		Ge1	2.569(2)	2.571(2)	2.557(1)	2.552(6)	2.552(2)
	Ge1	3.427(1)	3.414(1)	3.392(1)	3.331(1)	3.315(1)		2R	3.187(1)	3.164(1)	3.125(1)	3.056(4)	3.035(1)
								2R	3.228(1)	3.210(1)	3.176(1)	3.087(4)	3.066(1)
								2R	3.282(1)	3.250(1)	3.216(1)	3.192(1)	3.182(1)
Ge1	Ge4	2.569(2)	2.571(2)	2.557(1)	2.552(6)	2.552(2)	Ge5	Ge2	2.478(2)	2.485(2)	2.483(1)	2.481(3)	2.490(2)
	Ge1	2.627(2)	2.634(2)	2.628(1)	2.608(5)	2.608(2)		2Ge3	2.553(1)	2.552(1)	2.544(1)	2.568(3)	2.561(2)
	2R	3.144(1)	3.111(1)	3.071(1)	3.007(4)	2.989(1)		Zn	2.587(2)	2.569(2)	2.535(1)	2.431(4)	2.412(3)
	2R	3.159(1)	3.136(1)	3.097(1)	3.034(4)	3.016(1)		2R	3.259(1)	3.227(1)	3.189(1)	3.114(2)	3.089(1)
	2R	3.427(1)	3.414(1)	3.392(1)	3.331(1)	3.315(1)		2Ge3	3.464(1)	3.428(1)	3.369(1)	3.229(3)	3.207(2)
Ge2	Ge5	2.478(2)	2.485(2)	2.483(1)	2.481(3)	2.490(2)	Zn	Ge2	3.474(2)	3.487(2)	3.479(1)	3.513(4)	3.530(2)
	2Ge3	2.551(1)	2.551(1)	2.546(1)	2.554(3)	2.572(2)		Ge4	2.554(2)	2.514(2)	2.480(1)	2.396(3)	2.376(2)
	Zn	2.584(2)	2.570(2)	2.530(1)	2.442(4)	2.403(3)		Ge2	2.584(2)	2.570(2)	2.530(1)	2.442(4)	2.403(3)
	2R	3.250(1)	3.216(1)	3.175(1)	3.100(2)	3.079(1)		Ge5	2.587(2)	2.569(2)	2.535(1)	2.431(4)	2.412(3)
	2Ge3	3.466(1)	3.428(1)	3.367(1)	3.243(3)	3.196(2)		2Ge3	2.671(1)	2.643(1)	2.595(1)	2.489(2)	2.459(1)
	Ge5	3.474(2)	3.487(2)	3.479(1)	3.513(4)	3.530(2)		2R	3.329(1)	3.300(1)	3.261(1)	3.204(3)	3.193(2)
								2R	3.343(1)	3.312(1)	3.274(1)	3.218(3)	3.201(2)

Table S3. Interatomic distances for Dy₂Zn_{1-x}Ge₆.

Atom 1	Atom 2	<i>d</i> [Å]	Atom 1	Atom 2	<i>d</i> [Å]	Atom 1	Atom 2	<i>d</i> [Å]
Dy1	Ge7	2.980(1)	Ge3	Zn2	2.245(6)	Ge8	Zn2	2.238(7)
	Ge9	2.998(2)		Ge6	2.515(2)		Ge5	2.492(2)
	Ge1	3.006(1)		Ge7	2.577(2)		2Ge4	2.583(1)
	Ge8	3.022(1)		2Dy2	2.978(1)		2Ge9	2.981(1)
	Ge3	3.026(1)		2Dy1	3.026(1)		2Dy1	3.022(1)
	Ge4	3.045(1)		2Dy2	3.243(1)		Ge1	3.594(2)
	Ge6	3.046(1)	Ge4	Ge4	2.459(1)	Ge9	Zn2	2.306(2)
	Ge10	3.099(1)		Zn1	2.545(1)		Ge9	2.477(1)
	Ge6	3.118(1)		Ge8	2.583(1)		Ge5	2.578(1)
	Zn2	3.179(5)		Ge2	2.585(1)		Ge10	2.579(1)
	Zn1	3.180(1)		Dy1	3.045(1)		Ge2	2.978(1)
	Ge1	3.303(1)		Dy2	3.054(2)		Ge8	2.981(1)
Dy2	Ge1	2.961(1)	Ge5	Ge5	3.336(1)		Dy1	2.998(2)
	Ge3	2.978(1)		Ge10	3.336(1)		Dy2	2.999(1)
	Ge7	2.986(1)		Ge4	3.488(1)	Ge10	Ge2	2.493(1)
	Ge9	2.999(1)		Ge1	3.557(1)		Zn1	2.505(2)
	Ge2	3.035(1)		Ge8	2.492(2)		2Ge9	2.579(1)
	Ge6	3.048(1)		Zn1	2.506(2)		2Dy1	3.099(1)
	Ge4	3.054(2)	Ge6	2Ge9	2.578(1)		Ge5	3.286(2)
	Ge5	3.092(1)		2Dy2	3.092(1)		2Ge4	3.336(1)
	Zn1	3.177(1)		Ge10	3.286(2)		Ge7	3.532(2)
	Zn2	3.190(5)		2Ge4	3.336(1)	Zn1	Ge6	2.442(2)
	Ge3	3.243(1)		Ge7	3.545(2)		Ge10	2.505(2)
	Ge7	3.282(1)		Zn1	2.442(2)		Ge5	2.506(2)
				Ge3	2.515(2)		2Ge4	2.545(1)
Ge1	Ge6	2.529(2)	Ge7	Ge1	2.529(2)	Zn2	2Dy2	3.177(1)
	Ge7	2.600(2)		2Dy1	3.046(1)		2Dy1	3.180(1)
	2Dy2	2.961(1)		2Dy2	3.048(1)		Ge2	2.237(6)
	2Dy1	3.006(1)		2Dy1	3.118(1)		Ge8	2.238(7)
	2Dy1	3.303(1)		Ge3	2.577(2)		Ge3	2.245(6)
	Ge2	3.549(2)		Ge1	2.600(2)		2Ge9	2.306(2)
	2Ge4	3.557(1)		2Dy1	2.980(1)		2Dy1	3.179(5)
	Ge8	3.594(2)		2Dy2	2.986(1)		2Dy2	3.190(5)
Ge2	Zn2	2.237(6)		2Dy2	3.282(1)			
	Ge10	2.493(1)		Ge10	3.532(2)			
	2Ge4	2.585(1)		Ge5	3.545(2)			
	2Ge9	2.978(1)						
	2Dy2	3.035(1)						
	Ge1	3.549(2)						

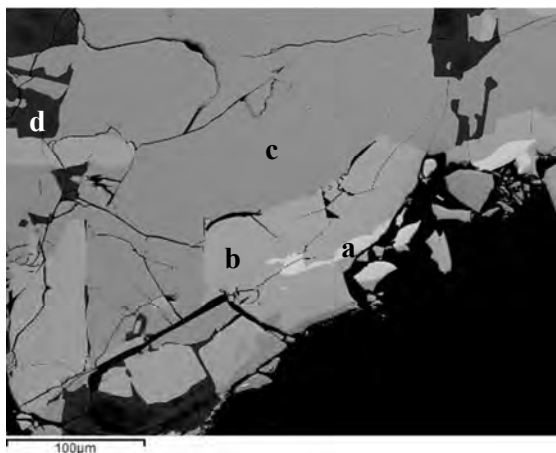


a)



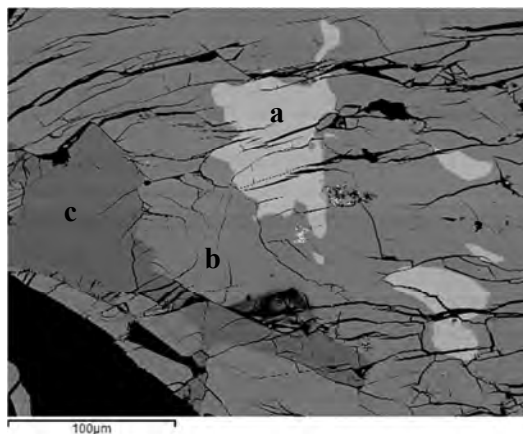
b)

Figure S1. Deviation histograms refined on 644 reflections for orthorhombic (a) and monoclinic (b) unit cells chosen for $\text{Gd}_2\text{Zn}_{1-x}\text{Ge}_6$ single crystal data.



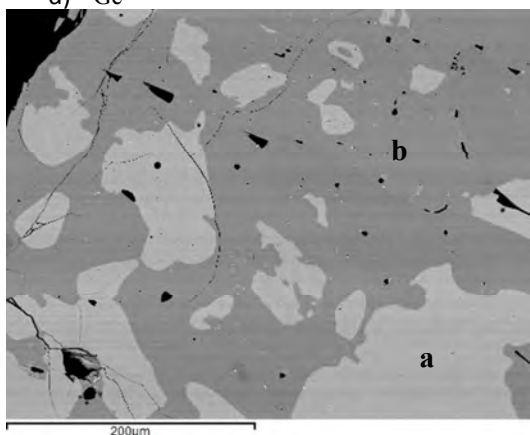
Sample $\text{La}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) LaGe_{2-x}
- b) $\text{La}_2\text{Zn}_{1-x}\text{Ge}_6$
- c) $\text{La}_2\text{Zn}_3\text{Ge}_6$
- d) Ge



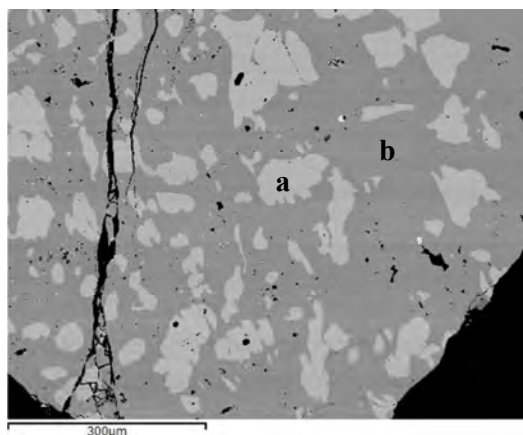
Sample $\text{Ce}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) CeGe_{2-x}
- b) $\text{Ce}_2\text{Zn}_{1-x}\text{Ge}_6$
- c) $\text{Ce}_2\text{Zn}_3\text{Ge}_6$



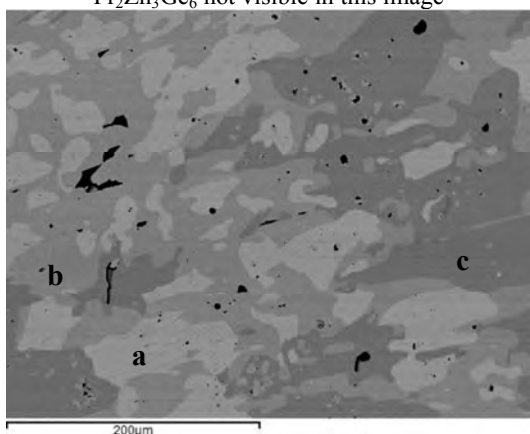
Sample $\text{Pr}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) PrGe_{2-x}
- b) $\text{Pr}_2\text{Zn}_{1-x}\text{Ge}_6$
- $\text{Pr}_2\text{Zn}_3\text{Ge}_6$ not visible in this image



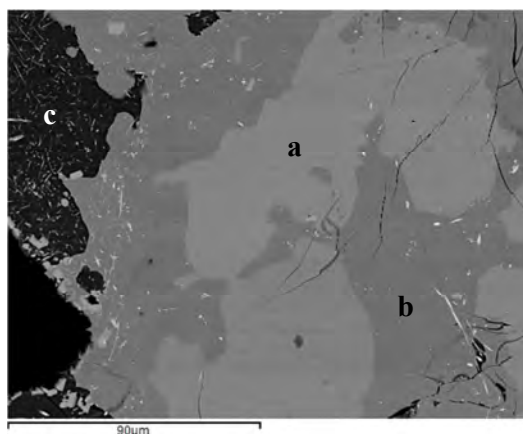
Sample $\text{Nd}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) NdGe_{2-x}
- b) $\text{Nd}_2\text{Zn}_{1-x}\text{Ge}_6$



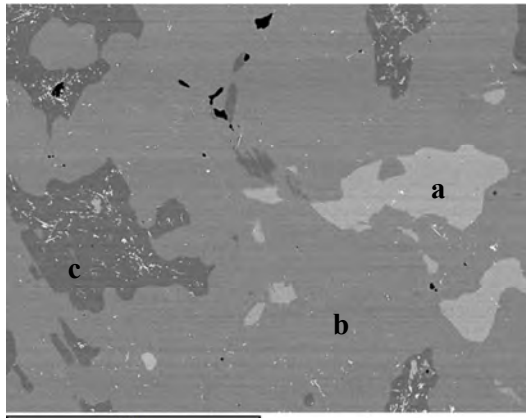
Sample $\text{Sm}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) SmGe_{2-x}
- b) $\text{Sm}_{27}\text{Zn}_6\text{Ge}_{67}$
- c) $\text{Sm}_2\text{Zn}_{1-x}\text{Ge}_6$
- $\text{Sm}_2\text{Zn}_3\text{Ge}_6$, SmZn_xGe_2 and Ge not visible in this image



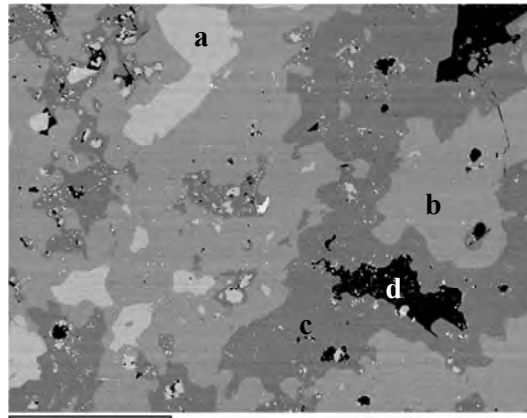
Sample $\text{Gd}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) $\text{Gd}_2\text{Zn}_{1-x}\text{Ge}_6$
- b) $\text{Gd}_2\text{Zn}_3\text{Ge}_6$
- c) Ge



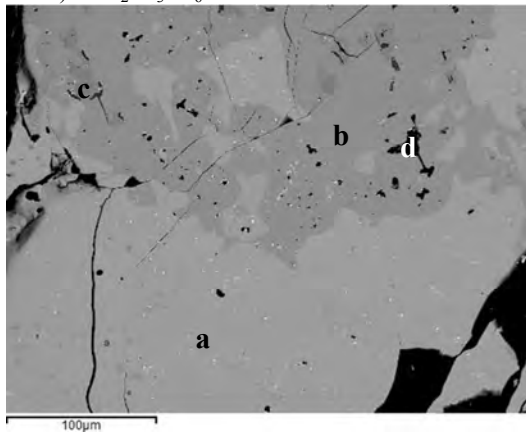
Sample $\text{Tb}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) TbZn_xGe_2
- b) $\text{Tb}_2\text{Zn}_{1-x}\text{Ge}_6$
- c) $\text{Tb}_2\text{Zn}_3\text{Ge}_6$



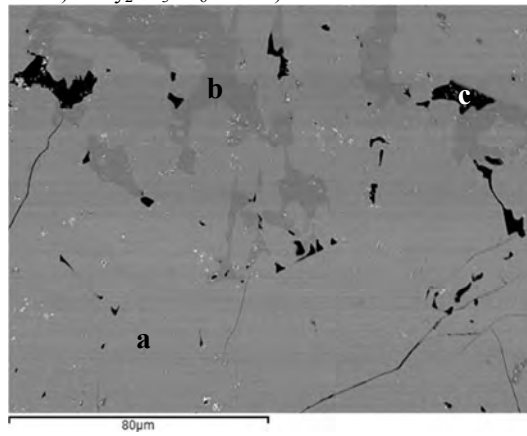
Sample $\text{Dy}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) DyZn_xGe_2
- b) $\text{Dy}_2\text{Zn}_{1-x}\text{Ge}_6$
- c) $\text{Dy}_2\text{Zn}_3\text{Ge}_6$
- d) Ge



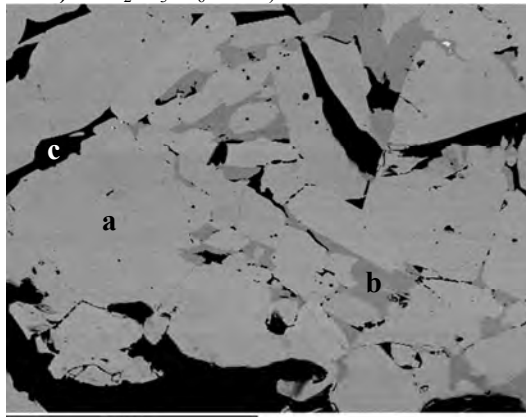
Sample $\text{Ho}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) HoZn_xGe_2
- b) $\text{Ho}_2\text{Zn}_{1-x}\text{Ge}_6$
- c) $\text{Ho}_2\text{Zn}_3\text{Ge}_6$
- d) Ge



Sample $\text{Er}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) $\text{Er}_4\text{Zn}_5\text{Ge}_6$
- b) ErZn_xGe_2
- c) Ge



Sample $\text{Tm}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$:

- a) TmGe_{2-x}
- b) $\text{Tm}_4\text{Zn}_5\text{Ge}_6$
- c) Ge

Figure S2. Representative SEM microphotographs (BSE image mode) of samples of nominal composition $\text{R}_{22.2}\text{Zn}_{11.1}\text{Ge}_{66.7}$

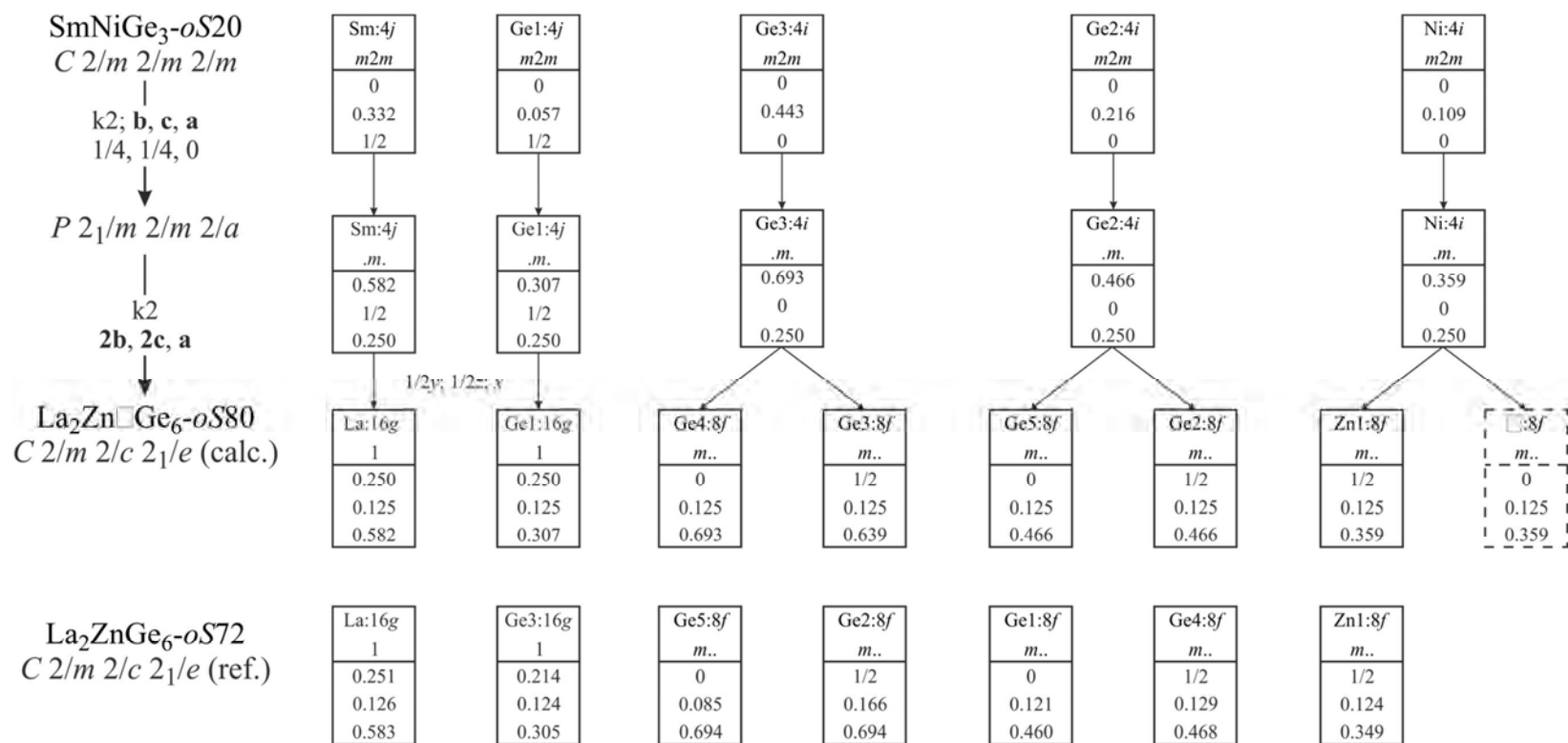


Figure S3. Group-subgroup relation in the *Bärnighausen* formalism between the SmNiGe_3 aristotype and $\text{La}_2\text{Zn}\square\text{Ge}_6$. The indexes of the symmetry reductions and the evolution of the atomic parameters are given.

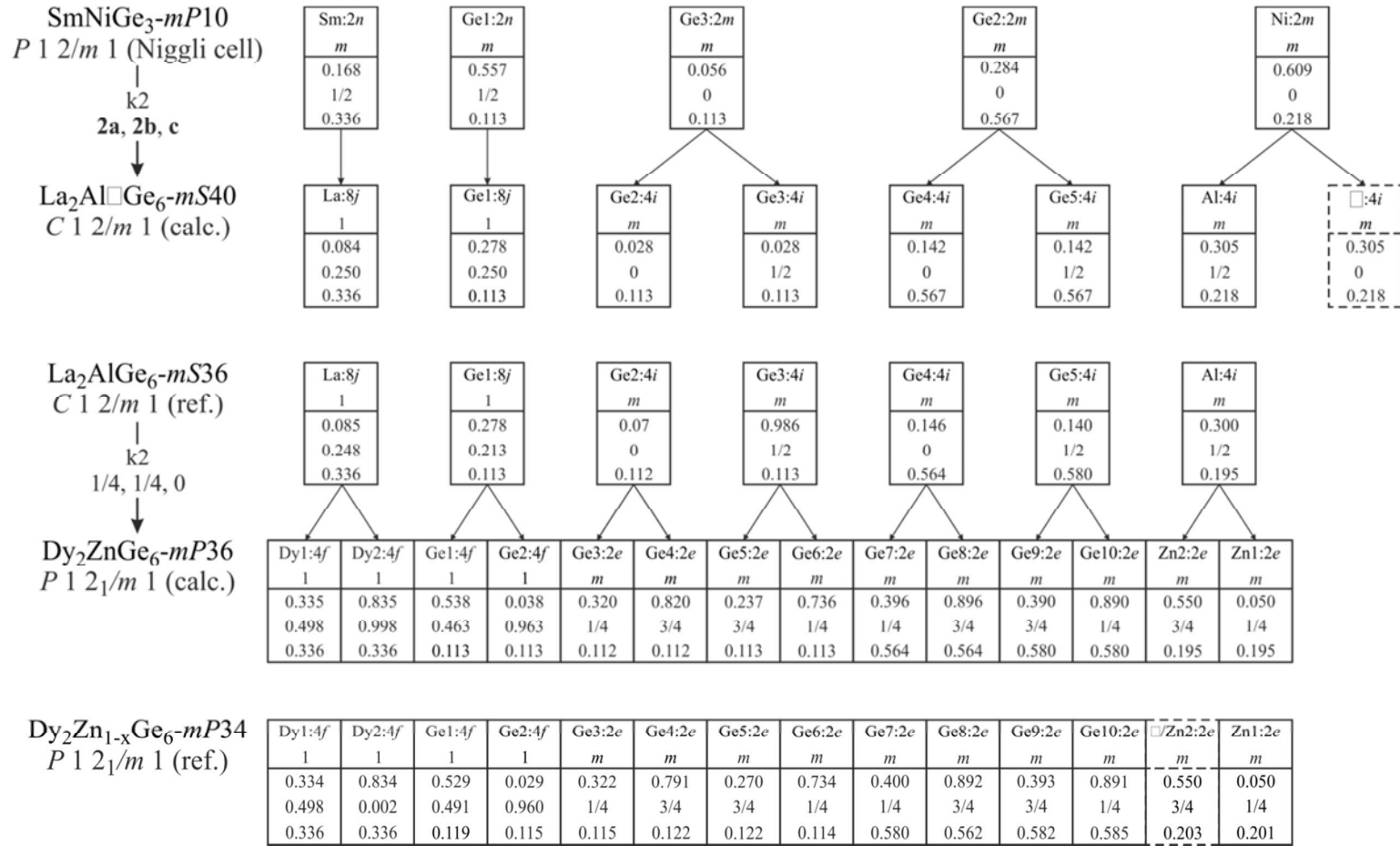


Figure S4. Group-subgroup relation in the *Bärnighausen* formalism between the SmNiGe₃ aristotype and Dy₂Zn_{1-x}Ge₆. The indexes of the symmetry reductions and the evolution of the atomic parameters are given.

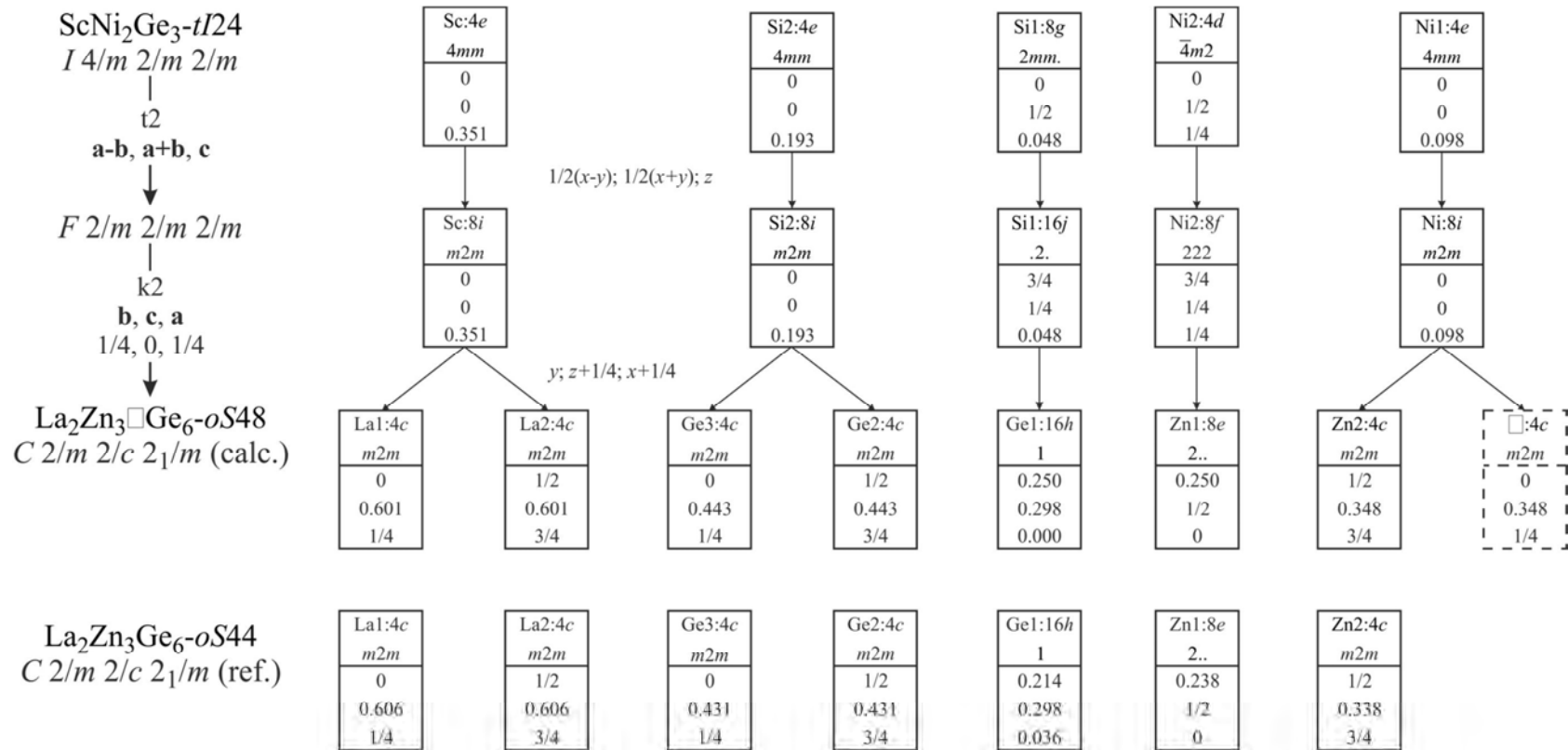


Figure S5. Group-subgroup relation in the *Bärnighausen* formalism between the ScNi₂Ge₃ aristotype and La₂Zn₃□Ge₆. The indexes of the symmetry reductions and the evolution of the atomic parameters are given.

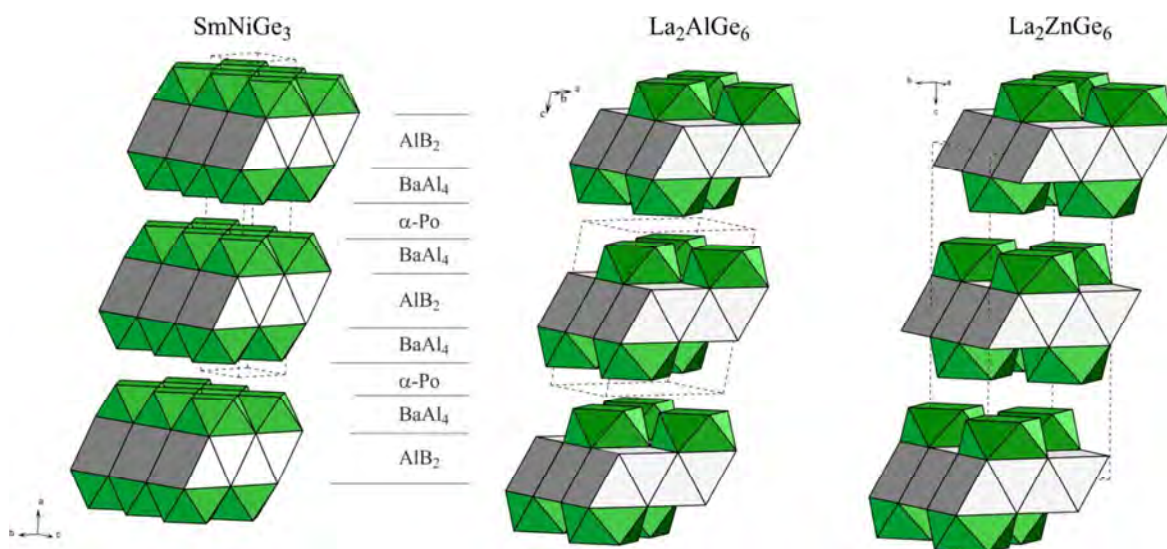


Figure S6. SmNiGe_3 , La_2AlGe_6 and La_2ZnGe_6 structures in terms of linear intergrowth representation.

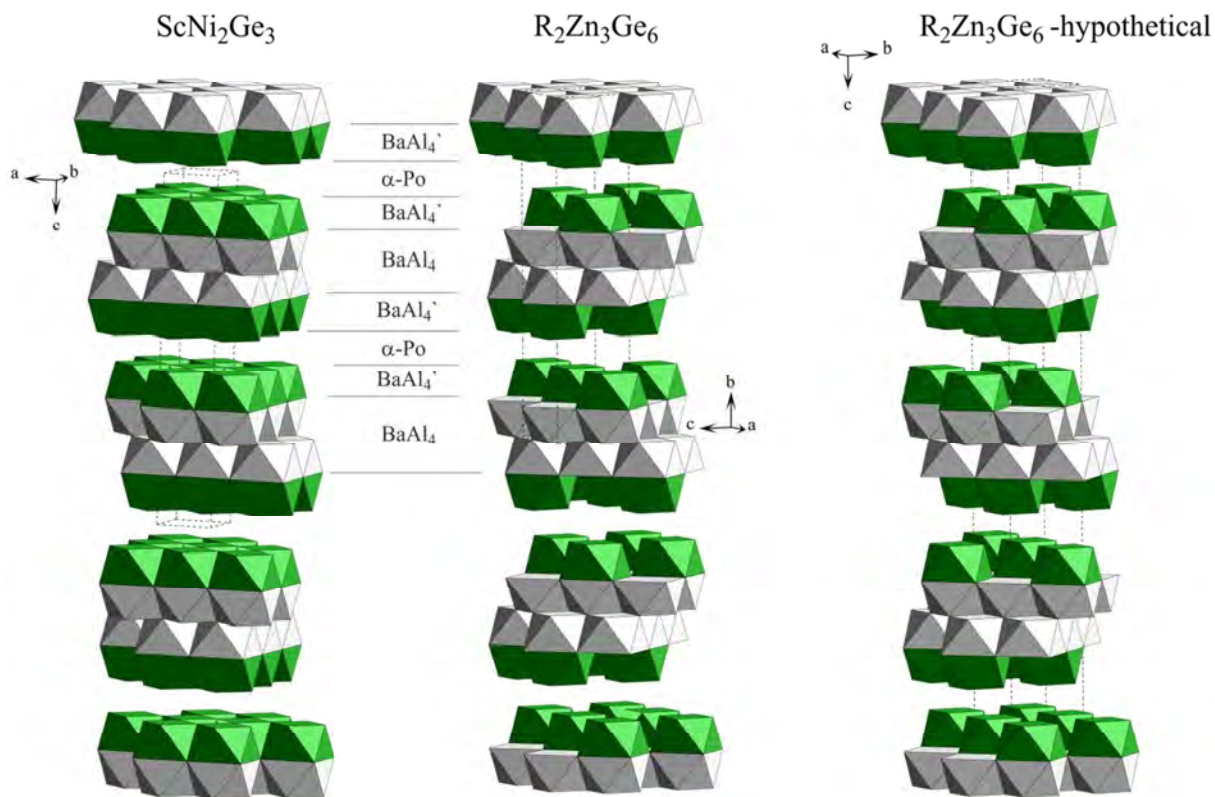


Figure S7. ScNi_2Ge_3 and $\text{R}_2\text{Zn}_3\text{Ge}_6$ (real and hypothetical) structures in terms of linear intergrowth representation.

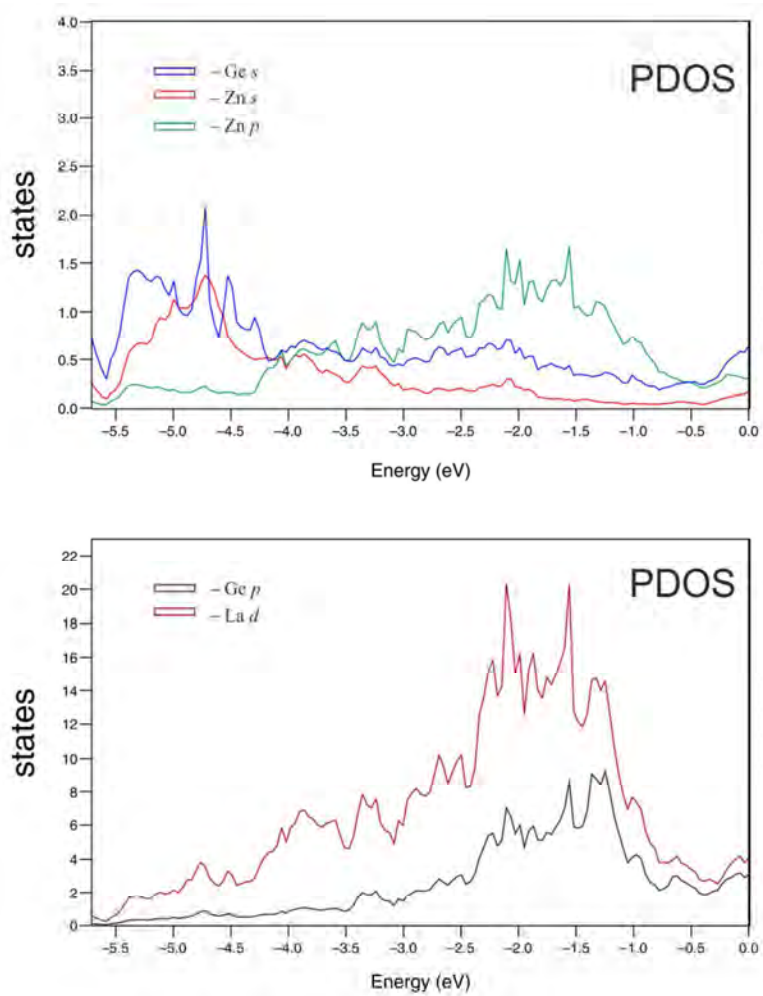


Figure S8. Partial DOS curves for La_2ZnGe_6 .

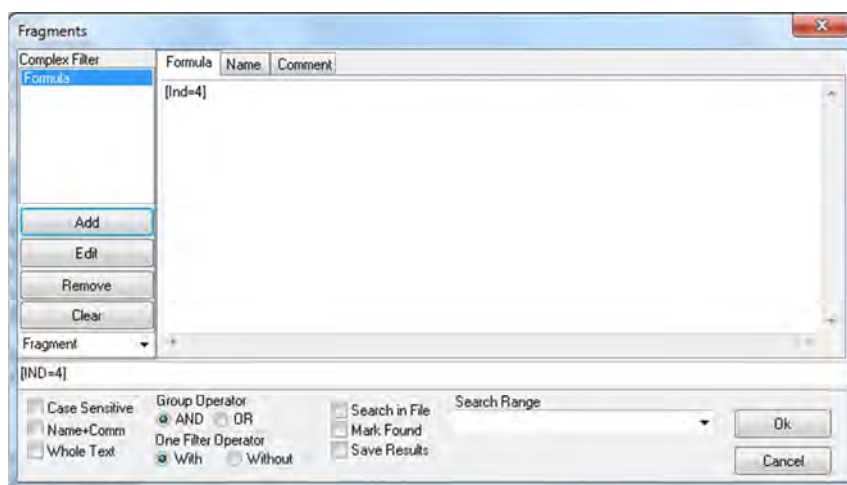
Modeling of vacancy ordering in the 2:1:6 family starting from the SmNiGe₃ aristotype using ToposPro

Algorithm

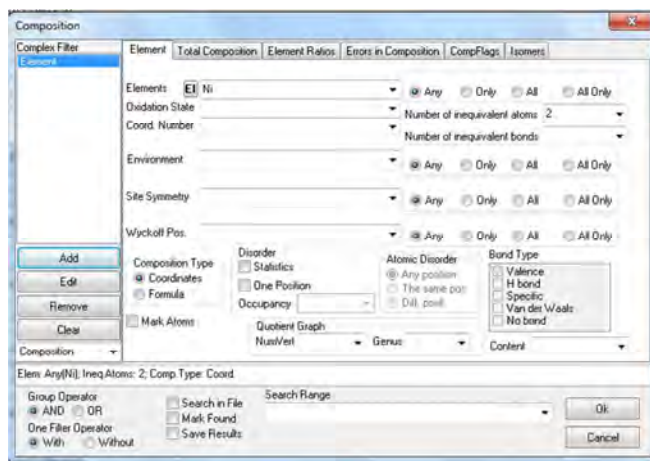
- 1) Open the database containing the aristotype (SmNiGe₃.cmp). Check if the adjacency matrix is computed for this compound.
- 2) Open the **Representation Parameters** window (**Compound/Copy representations**). Specify the options as shown below:



- 3) To retain only the subgroups of order 4 open the **Fragments** window (**Filter** menu). Specify the options as shown below.



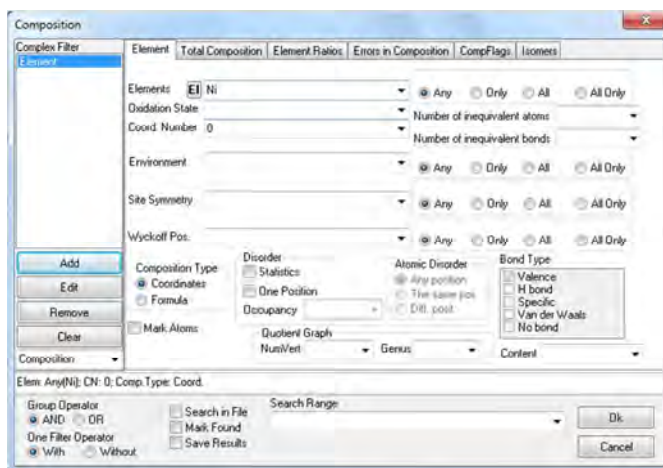
- 4) To retain only the models where the original Ni position is split in two, open the **Composition** window (**Filter** menu). Specify the options as shown below.



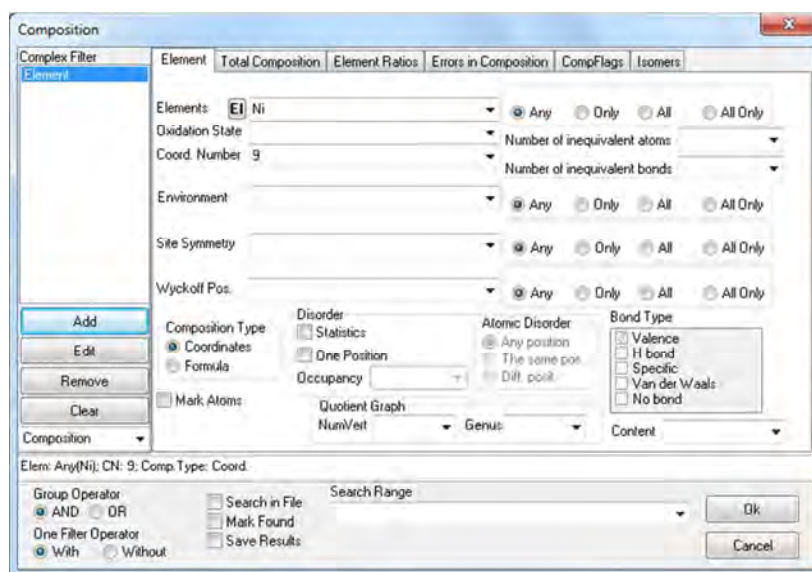
- 5) The modeling of vacancy “formation” should be done in several steps:
- Open the **Representation Parameters** window (**Compound/Copy representations**), specify the options as shown below:



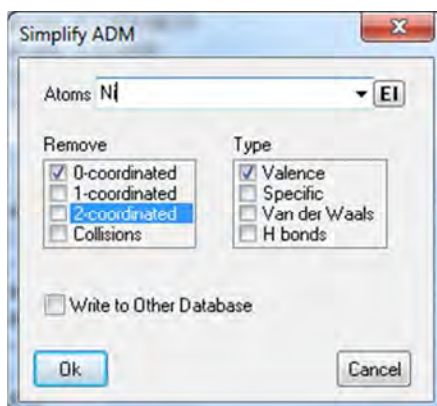
- Open the **Composition** window (**Filter** menu). Specify the options as shown below.



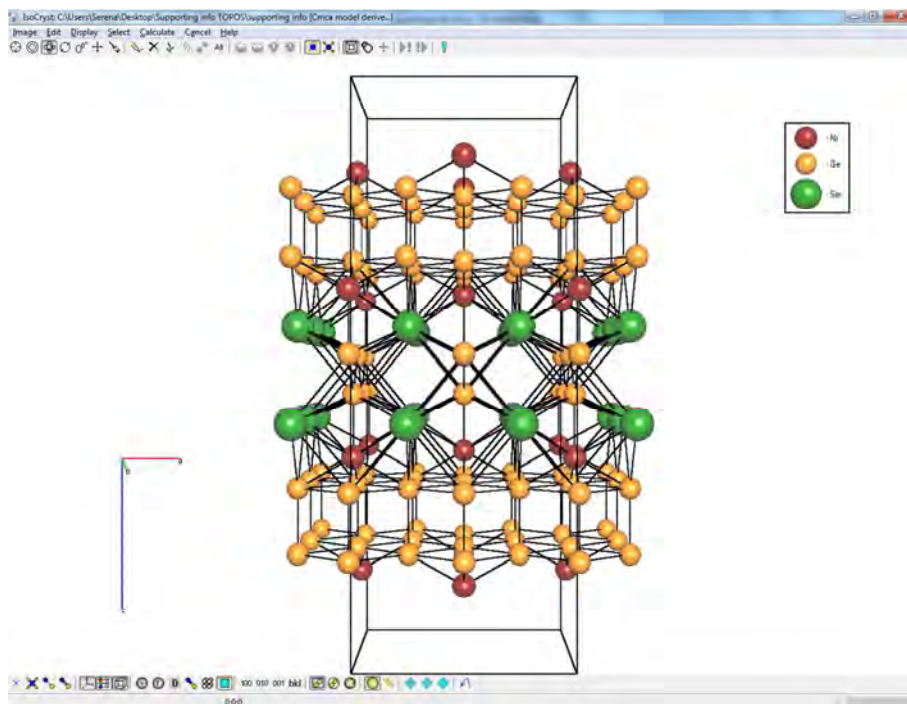
- Open the **Composition** window (**Filter** menu). Specify the options as shown below.



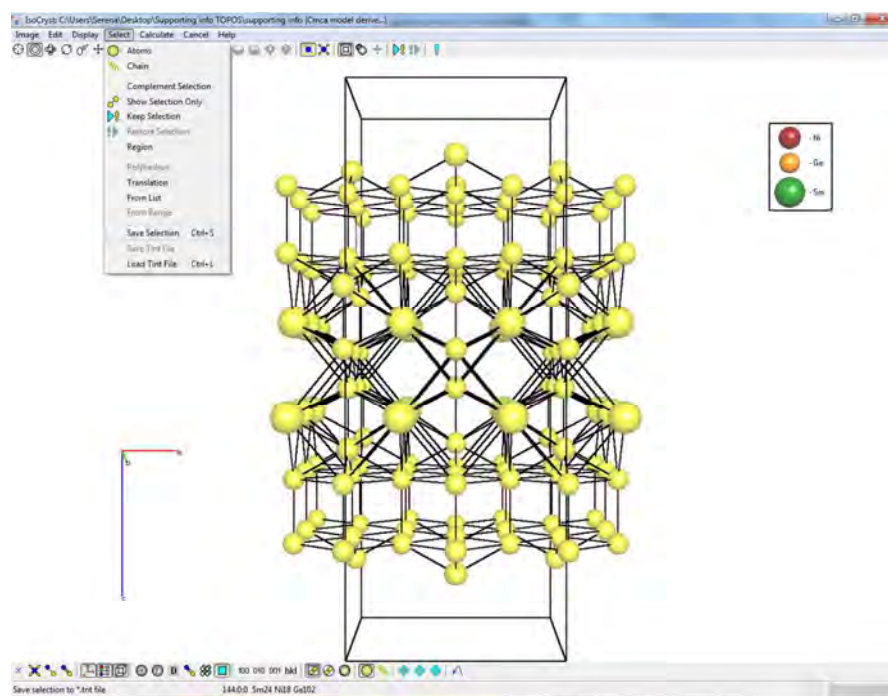
- d) Remove 0-coordinated Ni atoms (vacant positions). (**Compound/Auto Determine/Simplify ADM**). Specify the options as shown below:



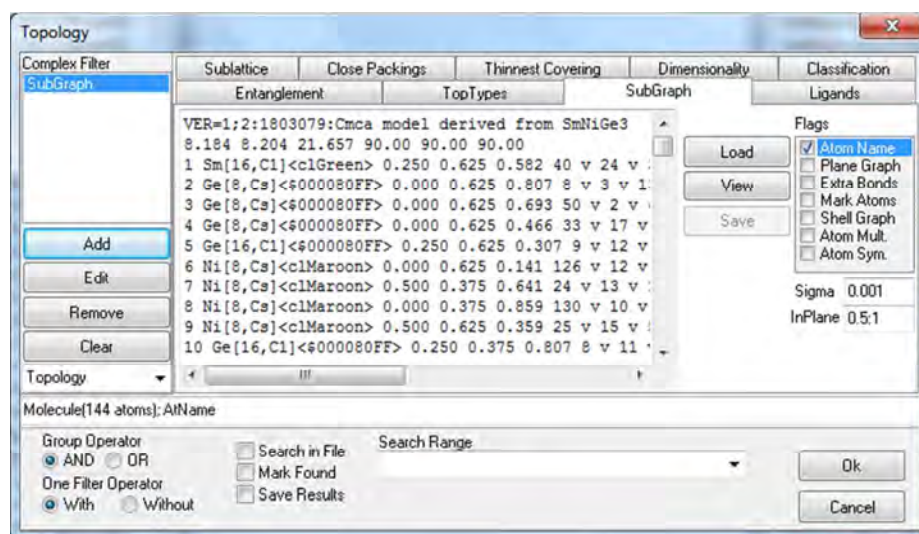
- e) Save the generated models in a new database
- 6) Select the fragment of the local topology to be searched in IsoCryst (structure named “Cmca model derived from SmNiGe₃” in the ToposPro database provided as Supporting material). The fragment chosen by us is shown below (of composition Sm₂₄Ni₁₈Ge₁₀₂).



Save the selected fragment as file .gph



- 7) To search for this fragment open the database created at the 5e) step, and then open the **Topology** window (**Filter** menu). Click “Load” and select the file .gph created during step 6, then specify the options as shown below:



At the end of this step the desired models are obtained. We obtained 8 models (4 equivalent in the Cmca space group and 4 equivalent in the C2/m space group).