

Supporting information

**First Germanium Doped Titanium Disulfides Polytypes :
Crystal Structure and Metal-Metal Interactions**

**Premier Dopage au Germanium de Polytypes de disulfure de Titane :
Structure Cristalline et Interactions Métal-Métal**

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for the T- M_1S_2 , 12R- $M_{1,111}S_2$, 12R-super $M_{1,206}S_{1.91}$, $(4H)_2$ - $M_{1,244}S_{1.945}$ ($M = \text{Ge/Ti}$) polytypes.

Polytype	Atoms	Position	x/a	y/b	z/c	U_{ed}	Occupancy Ge/Ti	
1T- M_1S_2	M1	1a	0	0	0	0.0047(5)	0.015(6)/ 0.968(6)	
	M2	1b	0	0	0.5	0.0047(5)	0.002(3)/ 0.013(3)	
	S1	2d	1/3	-1/3	0.25017(10)	0.0036(4)	1	
12R- $M_{1,111}S_2$	M1	3a	0	0	0	0.0123(3)	0.035(8)/ 0.937(8)	
	M2	3b	1/3	2/3	1/6	0.0113(3)	0.057(8)/ 0.897(8)	
	M3	6c	0	0	0.08878(8)	0.0094(11)	0.038(5)/ 0.109(5)	
	S1	6c	-2/3	-1/3	0.041743(17)	0.0098(3)	1	
	S2	6c	2/3	1/3	0.124836(16)	0.0102(3)	1	
12Rsuper $M_{1,206}S_{1.91}$	M1	1a	1	1	0	0.0046(7)	0.08(4)/0.84(4)	
	M2	2c	1/3	2/3	0	0.0039(5)	0.06(2)/ 0.87(2)	
	M3	2e	0	0	0.0895(2)	0.0039(5)	0.055(17)/0.198(17)	
	M4	4h	2/3	1/3	0.08928(16)	0.0023(5)	0.055(12)/0.195(12)	
	M5	6k	0.3327(3)	0.3327(3)	0.83320(3)	0.0042(3)	0.044(15)/0.955 (15)	
	M6	6k	0.3253(8)	0	0.75554(12)	0.0023(5)	0.081(10)/0.161(10)	
	M7	6k	0.3334(3)	0	0.66685(4)	0.0058(4)	0.945(10)	
	M8	6k	0.3487(7)	0	0.57759(11)	0.0023(5)	0.029(10)/0.275(10)	
	M9	2c	0	0	0.502(4)	0.002(5)	0.09(2)/0.81(2)	
	M10	2d	2/3	1/3	1/2	0.125(19)	0.17(7) / 0.17(7)	
	S1	6k	0.3330(4)	0.3330(4)	0.95764(5)	0.0049(4)	1	
	S2	6k	0.3337(3)	0	0.87580(5)	0.0035(5)	1	
	S3	2e	0	0	0.20857(12)	0.0070(9)	0.93(3)	
	S4	4h	1/3	-1/3	0.79125(7)	0.0048(4)	1	
	S5	6k	0.6698(4)	0	0.70931(5)	0.0052(5)	1	
	S6	2e	0	0	0.37611(15)	0.0093(10)	0.89(3)	
	S7	4h	1/3	2/3	0.37525(7)	0.0039(5)	0.919(17)	
	S8	6	0.3356(4)	0.3356(4)	0.54241(6)	0.0049(4)	0.844(9)	
	$(4H)_2$ - $M_{1,244}S_{1.945}$	M1	4a	0.2283(7)	0.0837(3)	0.07030(15)	0.0176(10)	0.026(15)/ 0.910(15)
		M2	4a	0.7310(5)	0.2493(3)	0.06753(12)	0.0161(7)	0.071(17)/ 0.853(17)
M3		4a	0.2314(7)	0.4179(3)	0.07050(15)	0.0185(8)	1	
M4		4a	0.7728(8)	0.2510(3)	0.20462(18)	0.0061(6)	0.023(13)/0.694(13)	
M5		4a	0.9818(6)	0.0829(3)	0.31882(15)	0.0161(8)	1	
M6		4a	1.4671(6)	0.2512(5)	0.31829(17)	0.0255(10)	0.029(17)/0.846(17)	
M7		4a	0.4816(6)	-0.0819(3)	0.31881(14)	0.0124(8)	1	
M8		4a	1.1813(11)	0.4179(5)	-0.0618(3)	0.0117(17)	0.040(15)/0.411(15)	
M9		4a	1.1837(11)	0.0840(4)	-0.0635(2)	0.0190(16)	0.051(16)/0.512(16)	
S1		4a	0.5391(8)	0.0787(5)	0.0066(2)	0.0229(15)	1	

S2	4a	1.0456(7)	0.2500(6)	0.0069(2)	0.0158(12)	0.884(13)
S3	4a	0.5418(8)	0.4197(5)	0.00920(19)	0.0201(15)	1
S4	4a	0.9172(7)	0.0834(4)	0.13397(15)	0.0118(11)	1
S5	4a	0.4220(7)	0.2516(4)	0.13538(17)	0.0094(10)	0.941(14)
S6	4a	0.9148(7)	0.4191(4)	0.13422(16)	0.0117(11)	1
S7	4a	0.6214(9)	0.0760(4)	0.25541(16)	0.0229(13)	1
S8	4a	1.1294(5)	1.1294(5)	0.25642(13)	0.0110(9)	1
S9	4a	1.1209(8)	-0.0786(4)	0.25660(16)	0.0122(11)	1
S10	4a	1.3288(9)	0.0843(4)	0.3829(2)	0.0169(15)	0.937(12)
S11	4a	0.8342(8)	0.2481(4)	0.38058(16)	0.0097(9)	0.938(11)
S12	4a	0.8316(9)	-0.0806(4)	0.3861(2)	0.0207(15)	0.965(13)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensors.

Table S2. Anisotropic displacement parameters for the 1T-M₁S₂, 12R-M_{1,111}S₂, 12R-superM_{1,206}S_{1,91}, (4H)₂-M_{1,244}S_{1,945} (M = Ge/Ti) polytypes.

Polytype	Atoms	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
1T-M ₁ S ₂	M1	0.0044(6)	0.0044(6)	0.0059(8)	0.0020(3)	0	0
	M2	0.0044(6)	0.0044(6)	0.0059(8)	0.0020(3)	0	0
	S1	0.0032(5)	0.0032(5)	0.0045(6)	0.0016(3)	0	0
12R-M _{1,111} S ₂	M1	0.0111(4)	0.0111(4)	0.0146(5)	0.0056(2)	0	0
	M2	0.0103(4)	0.0103(4)	0.0134(5)	0.0052(2)	0	0
	M3	0.0084(14)	0.0084(14)	0.0114(17)	0.0042(7)	0	0
	S1	0.0088(4)	0.0088(4)	0.0117(5)	0.00439(19)	0	0
	S2	0.0089(4)	0.0089(4)	0.0129(5)	0.0045(2)	0	0
12RsuperM _{1,206} S _{1,91}	M1	0.0055(9)	0.0055(9)	0.0028(12)	0.0027(5)	0	0
	M2	0.0041(6)	0.0041(6)	0.0035(8)	0.0020(3)	0	0
	M3	0.0041(6)	0.0041(6)	0.0035(8)	0.0020(3)	0	0
	M4	0.0013(6)	0.0013(6)	0.0041(9)	0.0006(3)	0	0
	M5	0.0057(4)	0.0057(4)	0.0019(4)	0.0034(4)	0.0003(3)	0.0003(3)
	M6	0.0013(6)	0.0013(6)	0.0041(9)	0.0006(3)	0	0
	M7	0.0056(4)	0.0057(6)	0.0060(5)	0.0028(3)	0.0011(4)	0
	M8	0.0013(6)	0.0013(6)	0.0041(9)	0.0006(3)	0	0
	M9	0.0024(4)	0.0024(4)	0.001(16)	0.0012(2)	0	0
	M10	0.068(13)	0.068(13)	0.24(5)	0.034(7)	0	0
	S1	0.0053(4)	0.0053(4)	0.0054(5)	0.0037(5)	-0.0039(4)	-0.0039(4)
	S2	0.0032(5)	0.0038(7)	0.0037(6)	0.0019(3)	0.0002(4)	0
	S3	0.0063(11)	0.0063(11)	0.0084(16)	0.0031(6)	0	0
	S4	0.0054(5)	0.0054(5)	0.0036(7)	0.0027(3)	0	0
	S5	0.0056(5)	0.0041(7)	0.0056(6)	0.0021(3)	0.0023(5)	0
	S6	0.0060(12)	0.0060(12)	0.016(2)	0.0030(6)	0	0
	S7	0.0052(7)	0.0052(7)	0.0014(8)	0.0026(4)	0	0
	S8	0.0053(4)	0.0053(4)	0.0054(5)	0.0037(5)	-0.0039(4)	-0.0039(4)

(4H) ₂ -M _{1.244} S _{1.945}	M1	0.021(2)	0.0193(15)	0.0124(15)	0.0004(13)	0.0030(12)	0.0045(12)
	M2	0.0169(13)	0.0181(11)	0.0135(13)	-0.0012(16)	0.0026(8)	0.0032(14)
	M3	0.0155(17)	0.0195(13)	0.0204(14)	0.0001(12)	-0.0001(12)	0.0045(12)
	M4	0.0074(13)	0.0065(10)	0.0046(10)	-0.0019(17)	0.0009(8)	0.0038(12)
	M5	0.0165(17)	0.0142(12)	0.0182(14)	-0.0024(13)	0.0042(12)	0.0069(10)
	M6	0.021(2)	0.0350(18)	0.0192(16)	0.000(2)	-0.0081(12)	0.0171(15)
	M7	0.0156(17)	0.0114(11)	0.0110(12)	0.0007(12)	0.0051(11)	0.0075(9)
	M8	0.013(4)	0.013(2)	0.008(3)	-0.001(2)	-0.001(2)	-0.005(2)
	M9	0.029(4)	0.021(2)	0.008(2)	-0.002(2)	0.007(2)	-0.0024(18)
	S1	0.019(3)	0.028(2)	0.021(3)	0.000(2)	-0.001(2)	0.0104(17)
	S2	0.015(2)	0.0177(17)	0.016(2)	-0.001(2)	0.0056(15)	-0.0025(19)
	S3	0.025(3)	0.024(2)	0.012(2)	0.0002(19)	0.0019(18)	0.0080(15)
S4	0.017(2)	0.0076(15)	0.0107(19)	-0.0029(15)	0.0031(17)	0.0013(12)	
S5	0.0045(17)	0.0072(14)	0.017(2)	0.0000(19)	0.0021(14)	0.0028(15)	
S6	0.009(2)	0.0089(15)	0.017(2)	-0.0037(15)	-0.0024(16)	0.0026(13)	
S7	0.030(3)	0.029(2)	0.0090(18)	-0.003(2)	-0.0025(19)	0.0018(15)	
S8	0.0126(19)	0.0137(14)	0.0069(14)	-0.008(2)	0.0020(13)	-0.0009(15)	
S9	0.009(2)	0.0104(15)	0.0161(18)	-0.0035(15)	-0.0015(17)	-0.0006(13)	
S10	0.014(3)	0.011(2)	0.027(3)	0.0014(17)	0.011(2)	0.0013(15)	
S11	0.0120(18)	0.0091(13)	0.0090(14)	0.0038(19)	0.0065(12)	0.0026(15)	
S12	0.023(3)	0.0088(19)	0.029(3)	0.0035(17)	-0.007(2)	0.0048(15)	

Table S3. Selected bond distances (Å) for the 1T-M₁S₂, 12R-M_{1,111}S₂, 12R-superM_{1,206}S_{1,91}, (4H)₂-M_{1,244}S_{1,945} (M = Ge/Ti) polytypes. The distortion δ (Å) is the difference between the longest and shortest M-S bond distance.

Polytype	M (Ge/Ti)-S	Distances (Å)	M (Ge/Ti)-S	Distances (Å)
1T-M ₁ S ₂	M1-S1(x6)	2.4239(5)	M2-S1(x6)	2.4250(5)
12R-M _{1,111} S ₂	M1-S1 (x6)	2.4596(3)	M3-S1 (x3)	2.5722(19)
	M2-S2 (x6)	2.4614(3)	M3-S2 (x3)	2.3486(16)
			δ	0.224
12R-superM _{1,206} S _{1,91}	M1-S1 (x6)	2.4543(16)	M2-S1 (x6)	2.457(3)
	M3-S1(x3)	2.555 (6)	M4-S2(x3)	2.314 (3)
	M3-S2(x3)	2.312 (5)	M4-S1 (x 3)	2.552 (2)
	δ	0.243	δ	0.238
	M5-S2 (x2)	2.460 (2)	M6-S3	2.291(5)
	M5-S2	2.4621(18)	M6-S4(x2)	2.349(3)
	M5-S3	2.441(3)	M6-S5(x2)	2.511(4)
	M5-S4(x2)	2.449(2)	M6-S5	2.589(5)
	δ	0.0211	δ	0.298
	M7-S5	2.473 (3)	M8-S6	2.610 (5)
	M7-S5(x2)	2.451 (2)	M8-S7 (x2)	2.523 (3)
	M7-S7 (x2)	2.4507 (17)	M8- S8	2.231 (5)
	M7-S6	2.468 (3)	M8-S8 (x2)	2.365 (4)
	δ	0.0223	δ	0.38
	M9-S8 (x3)	2.43 (7)	M10-S8 (x4)	2.452 (3)
	M9-S8 (x3)	2.50 (7)	M10-S8 (x2)	2.452 (3)
δ	0.07			
(4H) ₂ -M _{1,244} S _{1,945}	M1-S2	2.448(8)	M2-S2	2.434(14)
	M1-S5	2.509(7)	M2-S5	2.518(13)
	M1-S3	2.412(7)	M2-S3	2.433(7)
	M1-S1	2.463(14)	M2-S1	2.472(8)
	M1-S6	2.453(7)	M2-S6	2.520(7)
	M1-S4	2.463(14)	M2-S4	2.495(7)
	δ	0.097	δ	0.087
	M3-S2	2.471(8)	M4-S5	2.519(17)
	M3-S5	2.487(7)	M4-S7	2.375(7)
	M3-S3	2.424(14)	M4-S9	2.355(7)
	M3-S1	2.440(8)	M4-S8	2.348(18)
	M3-S6	2.492(14)	M4-S6	2.569(6)
	M3-S4	2.452(7)	M4-S4	2.576(6)
	δ	0.068	δ	0.228
	M5-S10	2.436(17)	M6-S10	2.466(7)

M5-S11	2.435(6)	M6-S11	2.512(18)
M5-S7	2.494(18)	M6-S7	2.540(7)
M5-S12	2.510(7)	M6-S12	2.518(7)
M5-S9	2.395(6)	M6-S9	2.487(7)
M5-S8	2.458(6)	M6-S8	2.365(16)
δ	0.115	δ	0.175
M7-S10	2.490(7)	M8-S2	2.529(8)
M7-S11	2.471(6)	M8-S10	2.363(19)
M7-S7	2.389(6)	M8-S11	2.398(8)
M7-S12	2.491(17)	M8-S3	2.587(18)
M7-S9	2.480(18)	M8-S1	2.489(8)
M7-S8	2.466(6)	M8-S12	2.293(8)
δ	0.102	δ	0.294
M9-S2	2.546(8)	M9-S3	2.579(7)
M9-S10	2.342(8)	M9-S1	2.551(18)
M9-S11	2.383(7)	M9-S12	2.311(19)
		δ	0.268

Table S4. Bond valence calculation BVS of M atoms and selected M-M distances for the 1T-M₁S₂, 12R-M_{1,111}S₂, 12R-superM_{1,206}S_{1,91}, (4H)₂-M_{1,244}S_{1,945} (M = Ge/Ti) polytypes.

Polytype	Atom	BVS	M-M distances (Å)	Atom	BVS	M-M distances (Å)
1T-M ₁ S ₂	M1	3.768	M1-M2 = 2.8435(10)	M2	3.780	M1-M2 = 2.8435(10)
12R-M _{1,111} S ₂	M1	3.432	M1-M3 = 3.088(3)	M3	3.582	M2-M3 = 3.360(2)
	M2	3.414	M2-M3 = 3.360(2)			
12R-superM _{1,206} S _{1,91}	M1	3.480	M1-M2 = 3.4308(8)	M7	3.455	M8-M7 = 3.061(4)
	M2	3.458	M1-M3 = 3.068(8)	M8	3.887	M8-M10 = 3.290(3)
	M3	3.885	M4-M2 = 3.060(5)	M9	3.399	M8-M9 = 3.42(9)
	M4	3.882	M4-M3 = 3.4309(9)	M10	3.508	M8-M9 = 3.32 (9)
	M5	3.492	M4-M5 = 3.315(5)			M9-M10 = 3.431(2)
	M6	3.741	M5-M3 = 3.306(7)			
			M6-M5 = 3.303(4)			
			M6-M5 = 3.349(5)			
			M6-M7 = 3.040(4)			
(4H) ₂ -M _{1,244} S _{1,945}	M1	3.458	M1-M2 = 3.42(2)	M6	3.279	M7-M6 = 3.445(7)
	M2	3.275	M1-M2 = 3.46(2)	M7	3.404	M7-M6 = 3.37(2)
	M3	3.429	M1-M3 = 3.43(2)	M8	3.725	M7-M9 = 3.368(11)
	M4	3.582	M1-M3 = 3.455(5)	M9	3.658	M7-M8 = 3.360(7)
	M5	3.497	M2-M3 = 3.427(5)			M8-M5 = 3.410(11)
			M2-M3 = 3.46(2)			M8-M3 = 3.034(7)
			M4-M2 = 3.144(5)			M8-M6 = 3.421(8)
			M4-M5 = 3.305(7)			M8-M9 = 3.43(2)
			M4-M7 = 3.298(7)			M8-M9 = 3.452(7)
			M4-M6 = 3.318(11)			M9-M5 = 3.348(7)
			M5-M6 = 3.38(2)			M9-M8 = 3.46(3)
			M5-M7 = 3.44(2)			M9-M6 = 3.372(8)
			M5-M7 = 3.465(6)			M9-M1 = 3.069(6)

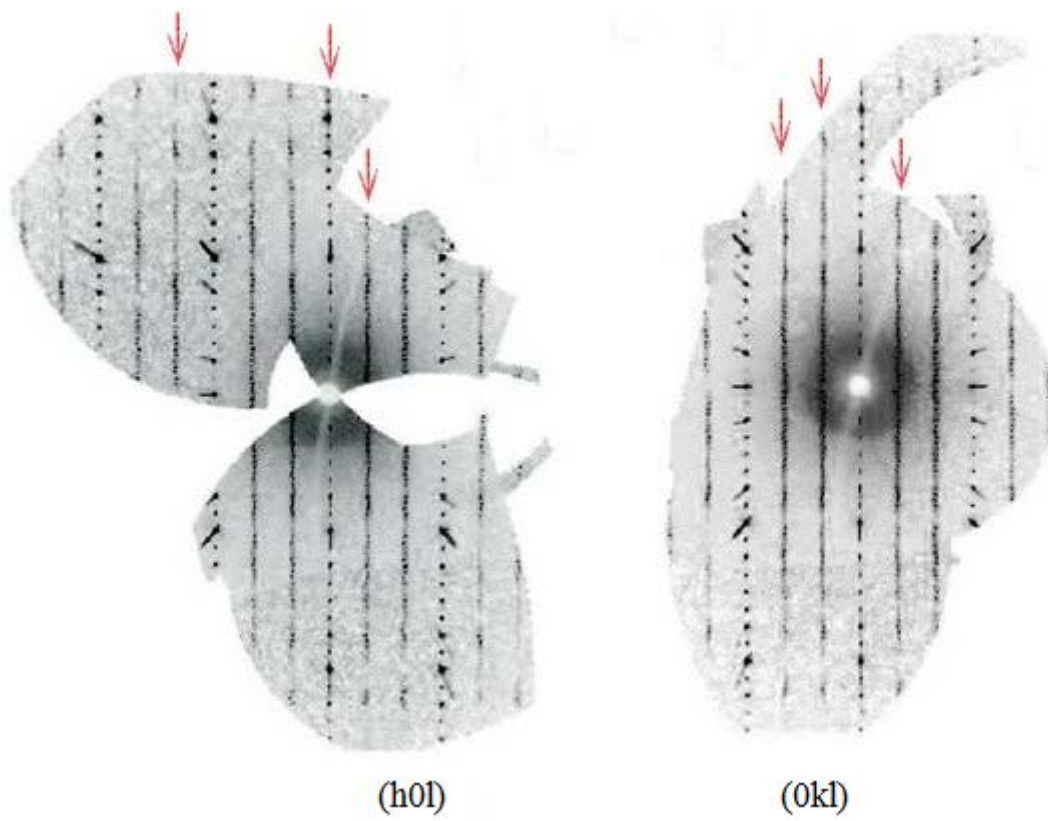


Fig. 1S. (h0l) and (0kl) sections of the reciprocal space of the crystal 12R-super $M_{1.206}S_{1.91}$ ($M = \text{Ge/Ti}$), showing reflections exhibited rod-shaped streaking along the c^* axis marked with red arrows.

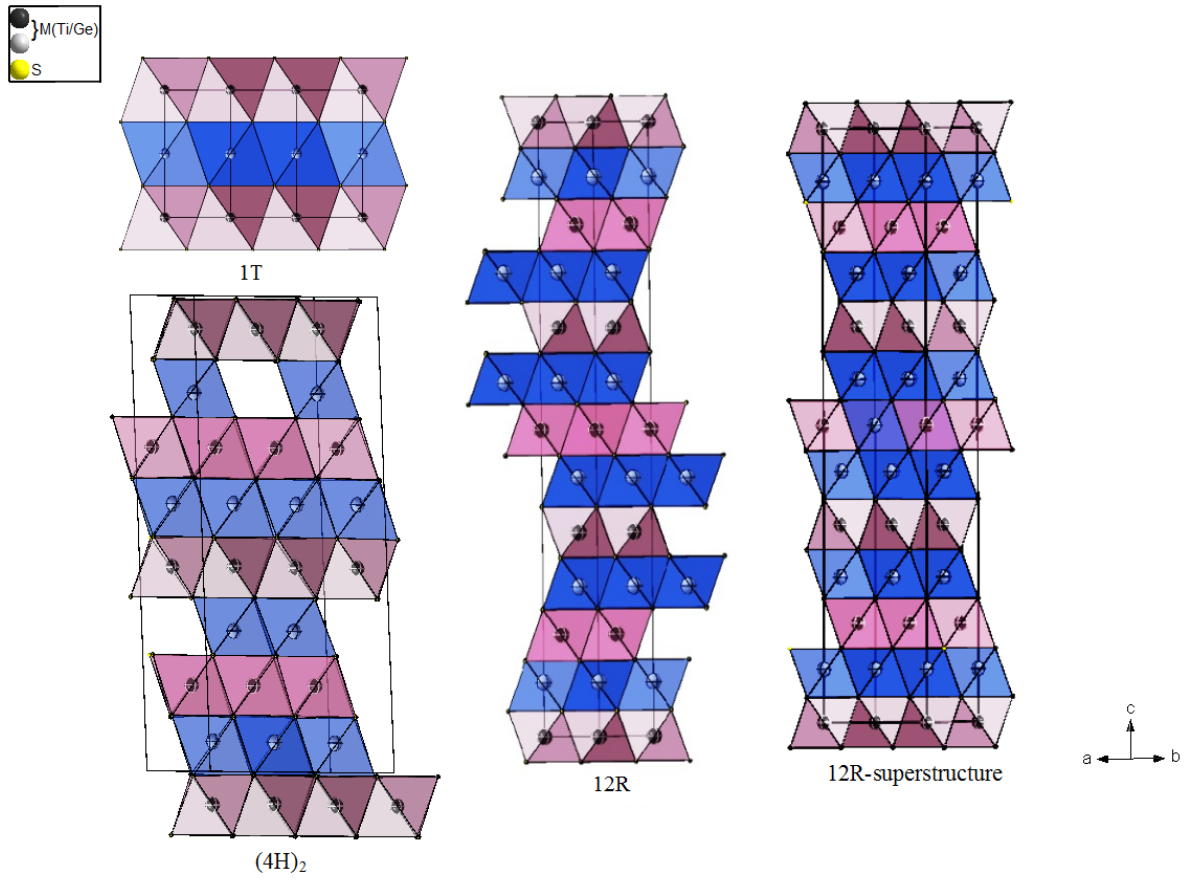


Fig. 2S. Projection of the crystal structures of the 1T- M_1S_2 , 12R- $M_{1.111}S_2$, 12R-super $M_{1.206}S_{1.91}$, $(4H)_2$ - $M_{1.244}S_{1.945}$ (M = Ge/Ti) polytypes, showing the zigzag MS_6 octahedral chain running along the c axis.

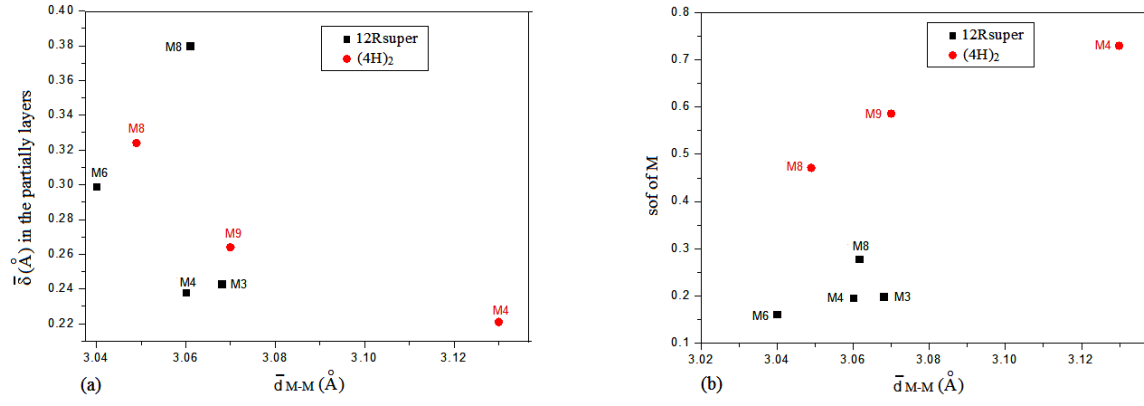


Fig. 3S. (a) Variation of the mean distortion $\bar{\delta}$ (Å) in the partially layers with the mean distance \bar{d} (M-M) (Å) in the 12R-super $M_{1,206}S_{1,91}$ and the $(4H)_2$ - $M_{1,244}S_{1,945}$ (M = Ge/Ti) polytypes. (b) Variation the mean distance \bar{d} (M-M) (Å) with the site occupation factor (*s.o.f*) of M atoms in the partially filled layers in the 12R-super $M_{1,206}S_{1,91}$ and the $(4H)_2$ - $M_{1,244}S_{1,945}$ (M = Ge/Ti) polytypes.

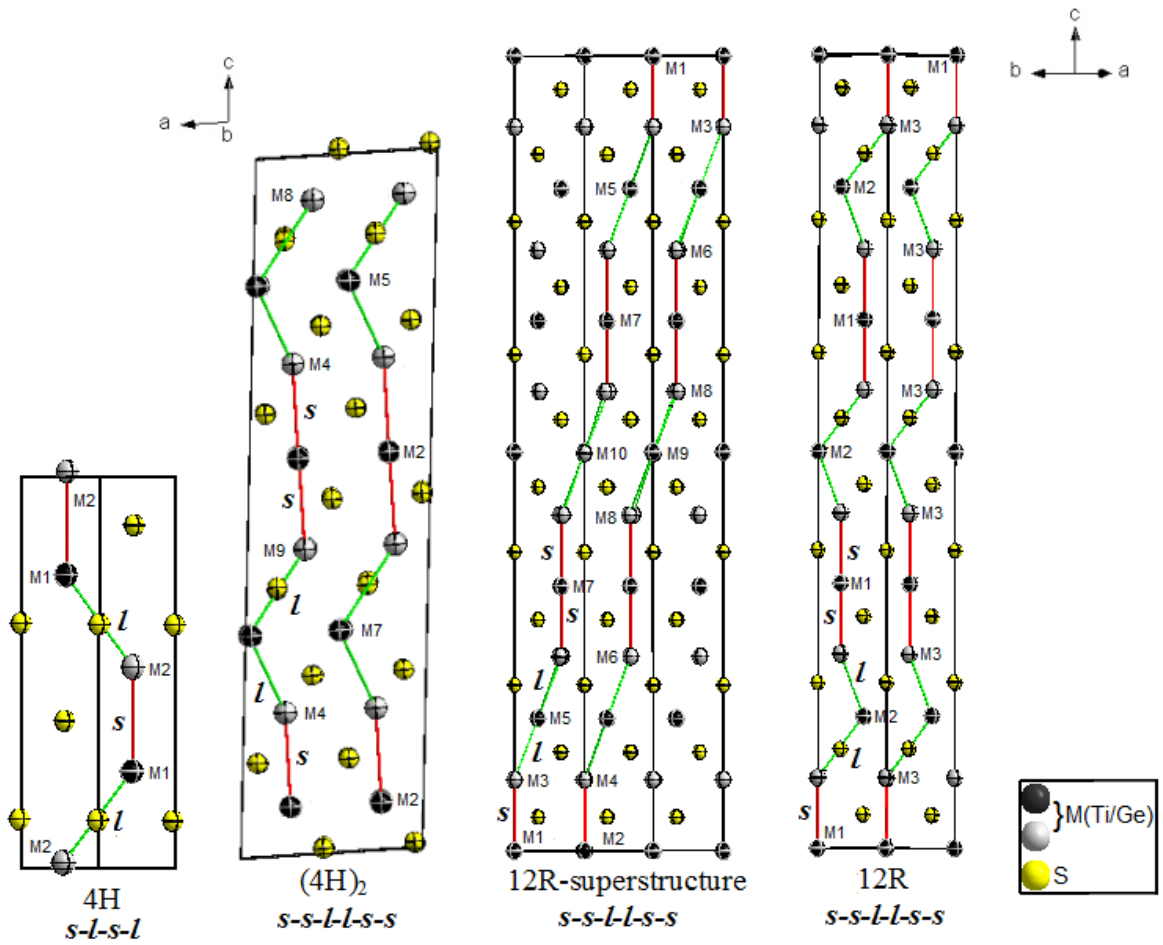


Fig. 4S. The M-M bond distances on parallel zigzag chains along the *c* direction in the 4H- $M_{1,225}S_2$ [55], 12R- $M_{1,111}S_2$, 12R-super $M_{1,206}S_{1,91}$ and the $(4H)_2$ - $M_{1,244}S_{1,945}$ ($M = \text{Ge/Ti}$) polytypes. The red and the green distances represent respectively the shortest (*s*) and the longest (*l*) M-M distances. Intermediate distances are omitted.