Supporting Information for

Elaborating the Crystal Structures of MgAgSb Thermoelectric Compound: Polymorphs and Atomic Disorders

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Table S1. Fractional coordinates and refined isotropic ADPs (U_{iso}) of α-MgAgSb at 400, 500 and 600 K.

Temperature (K)	Atom	Site	*x*	*y*	*z*	U_{iso} (Å^2)	*Occ* (%)
400	Mg1	16*i*	-0.0203(9)	0.2810(8)	0.1144(5)	0.013(2)	100
	Sb1	16*i*	0.2354(2)	0.4759(2)	0.1163(1)	0.017(1)	100
	Ag1	4*a*	0	0	0.25	0.061(3)	100
	Ag2	4*b*	0	0	0	0.017(1)	100
	Ag3	8*e*	0.2251(3)	0.2251(3)	0.25	0.017(1)	100
500	Mg1	16*i*	-0.0195(9)	0.2813(9)	0.1141(6)	0.023(3)	100
	Sb1	16*i*	0.2356(2)	0.4770(3)	0.1162(1)	0.020(1)	100
	Ag1	4*a*	0	0	0.25	0.059(3)	100
	Ag2	4*b*	0	0	0	0.024(2)	100
	Ag3	8*e*	0.2257(3)	0.2257(3)	0.25	0.022(1)	100
600	Mg1	16*i*	-0.0183(9)	0.2810(9)	0.1144(7)	0.028(3)	100
	Sb1	16*i*	0.2359(2)	0.4783(3)	0.1158(1)	0.024(1)	100
	Ag1	4*a*	0	0	0.25	0.069(4)	100
	Ag2	4*b*	0	0	0	0.028(2)	100
	Ag3	8*e*	0.2269(4)	0.2269(4)	0.25	0.029(2)	100

Table S2. Fractional coordinates and refined isotropic ADPs (U_{iso}) of β-MgAgSb at 700 K using the ordered structure (without the refinement of Ag and Sb occupancies) and disordered structure (with the refinement of Ag and Sb occupancies).

	Atom	Site	*x*	*y*	*z*	U_{iso} (Å^2)	□*Occ* (%)
Ordered structure	Mg1	2*c*	0.25	0.25	0.3222(9)	0.040(2)	100
	Ag1	2*a*	0.75	0.25	0	0.056(1)	100
	Sb1	2*c*	0.25	0.25	0.7253(2)	0.030(1)	100
Disordered structure	Mg1	2*c*	0.25	0.25	0.3173(9)	0.053(3)	100
	Ag1	2*a*	0.75	0.25	0	0.049(1)	87(1)
	Sb1	2*c*	0.25	0.25	0.7267(2)	0.037(1)	94(1)

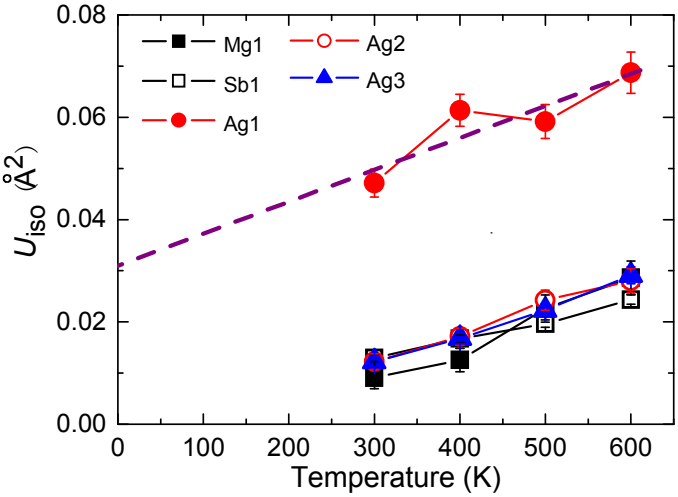

Figure S1. Temperature dependence of isotropic ADPs (U_{iso}) for different atoms. Extrapolation of the ADPs of Ag1 to 0 K suggests static disorder for the Ag1 atoms.

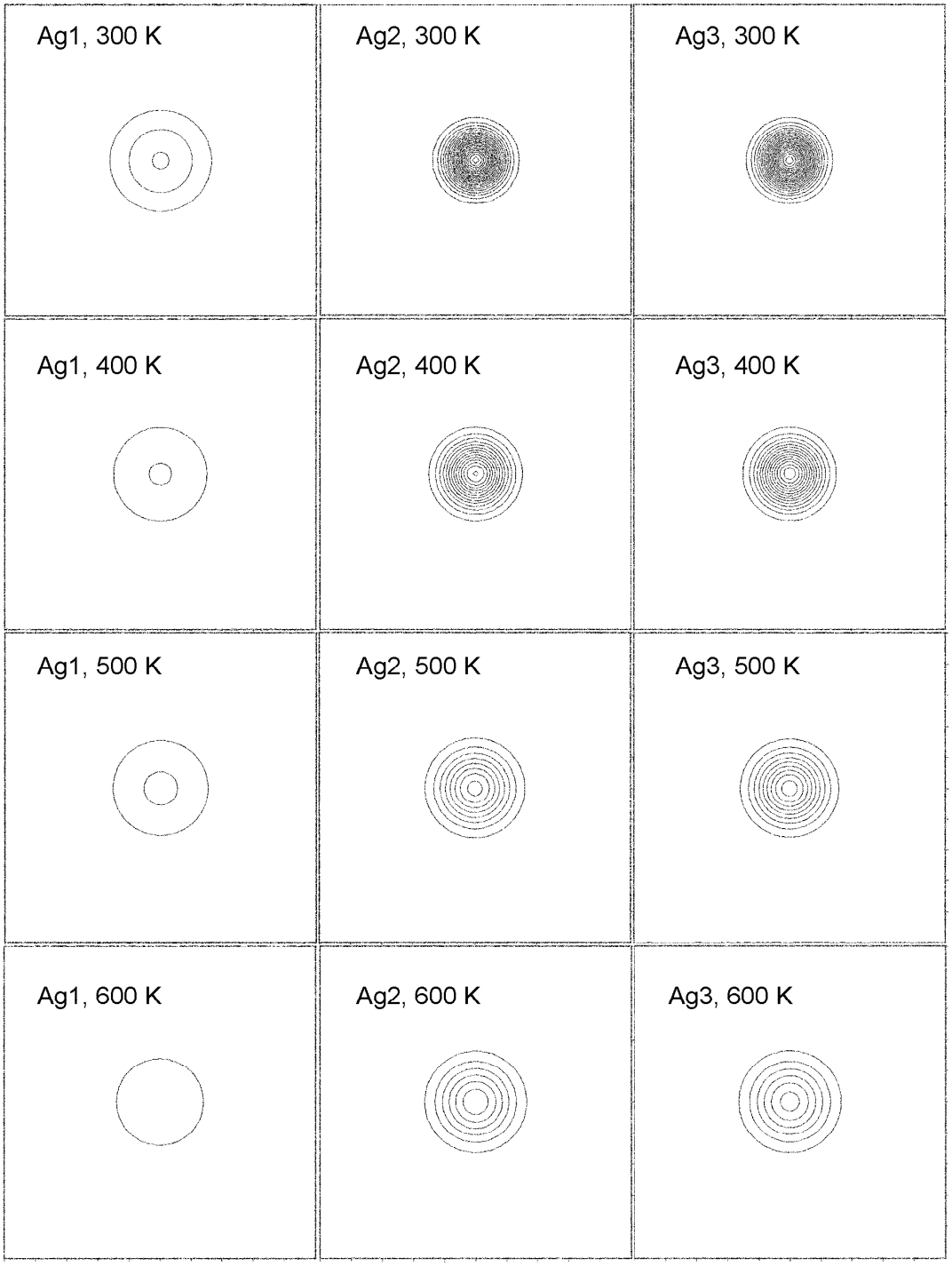

Figure S2. Probability density function maps of Ag1, Ag2, and Ag3 atoms of α-MgAgSb at different temperatures (positive contours = 2) obtained using Jana2006. The probability density function of Ag1 atom does not change very much with temperature indicating large static disorder.

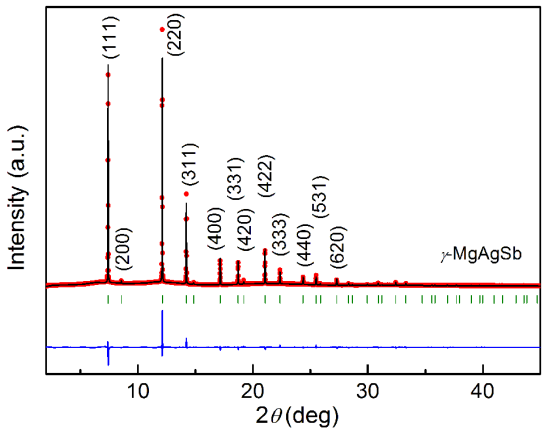

Figure S3. Observed (red) and calculated (black) diffraction patterns and the difference profile (blue) of MgAgSb (reflections given by green tick marks) at 800 K using the type II model where Mg, Ag, and Sb occupy 4*a*, 4*b* and 4*c*, respectively. R_P = 19.9%, R_{wp} = 15.8%, R_I = 8.53%, and R_F = 5.84%.

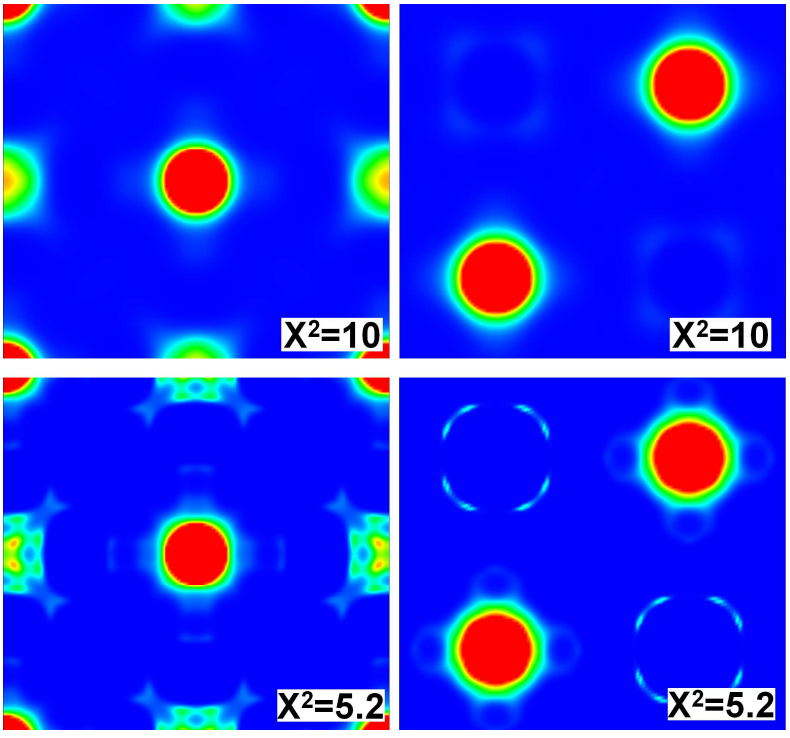

Figure S4. MEM charge densities at 800 K using structure factors extracted with the type II structural model at different χ^2 values (second minimum in the Rietveld refinement). In all maps the plane (001) is considered at z = 0.5 (left) and z = 0.25 (right) in fractional coordinates. The color scale is set from 0 (blue) to 15 eÅ^{-3} (red).

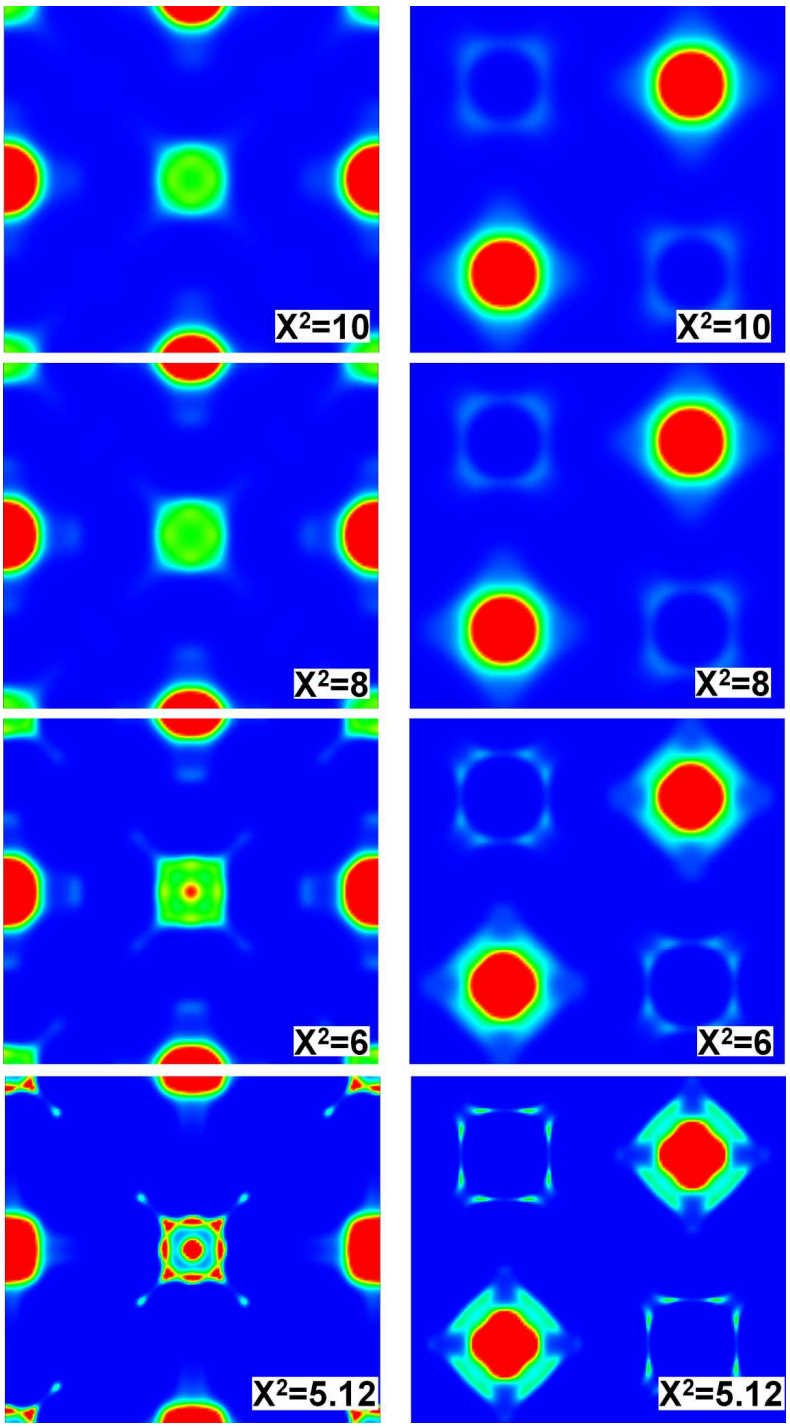

Figure S5. MEM charge densities at 800 K using structure factors extracted with the type I structural model at different χ^2 values. In all maps the plane (001) is considered at z = 0.5 (left) and z = 0.25 (right) in fractional coordinates. The color scale is set from 0 (blue) to 15 eÅ^{-3} (red).

Table S3. Refined occupancies (*occ*) of Mg and Ag for γ-MgAgSb at 700, 800, 900, and 1000 K using the type II model. The *occ* of Sb is fixed to 100% and the ADPs (U_{iso}) are fixed with values in table 3 of the type II model. R_P = 19.0%, R_{wp} = 14.7%, R_I = 6.05%, and R_F = 5.52% at 800 K.

Atom	Site	*x*	*y*	*z*	*Occ* (%) (700K)	*Occ* (%) (800K)	*Occ* (%) (900K)	*Occ* (%) (1000K)
Mg1	4*a*	0	0	0	118(2)	139(3)	150(4)	160(8)
Ag1	4*b*	0.5	0.5	0.5	80(2)	72(1)	63(2)	54(3)
Sb1	4*c*	0.25	0.25	0.25	100	100	100	100

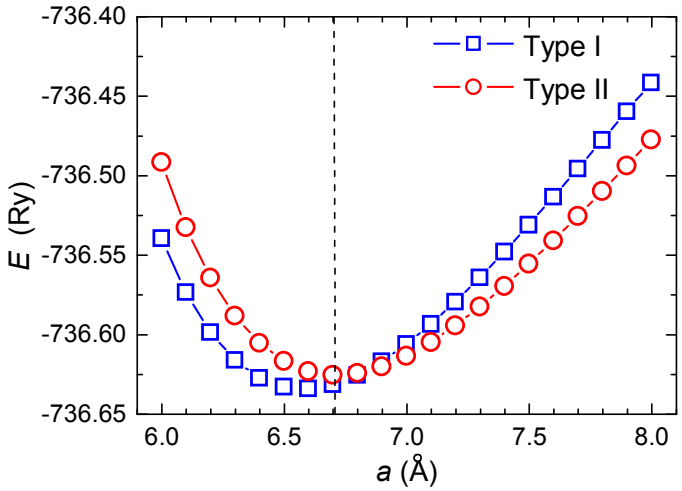

Figure S6. DFT energy vs unit cell parameter (*a*) in type I and type II γ-MgAgSb. The vertical dotted line indicates the experimental unit cell parameter at 800 K. The optimized lattice constants at 0 K are 6.59373 Å for type I and 6.71073 Å for type II. Although type I is more stable at 0 K, at the experimental geometries at T > 800 K the two type structural models are very close in energy inferring that type II is possible as well.

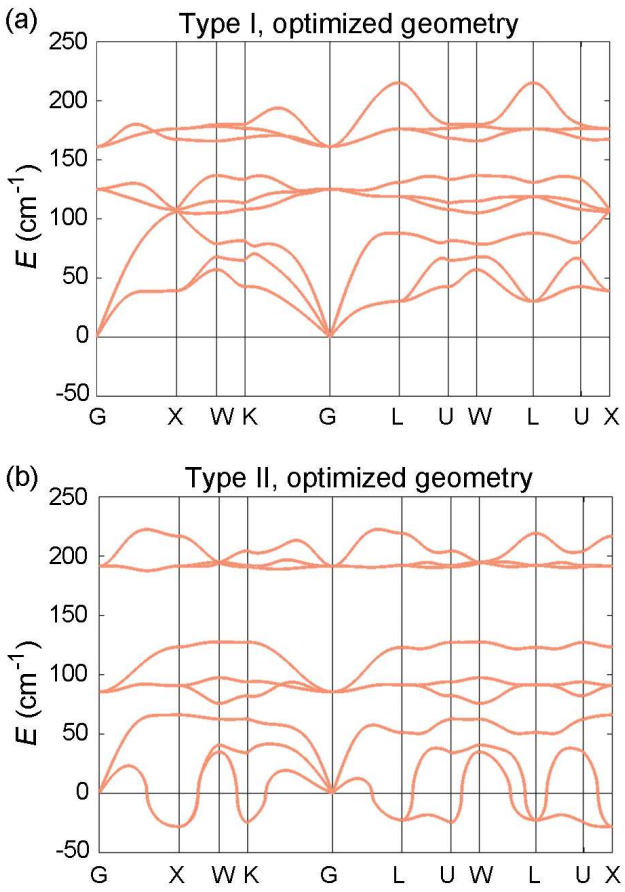

Figure S7. Phonon dispersion of γ-MgAgSb using type I (a) and type II (b) structural models at the optimized geometry. For type I no imaginary frequencies are found both performing phonon calculations at the optimized geometry and at the experimental geometry at 800 K, which points out that the structure is mechanically stable. Conversely, phonon calculations using the type II structural model point out that the structure is not mechanically stable both at the optimized geometry and at the experimental geometry at 800 K. Here phonon dispersions at the optimized geometries are reported.