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Supplementary Information

Understanding the Complex Electronic Structure of Mg_3Sb_2 and the Effect of Alloying Through First-Principles Tight-binding Models

Wenhao Zhang[1,2], Jean-François Halet[3,*] and Takao Mori[1,2,*]

[1] Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Tsukuba, Japan

[2] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan

[3] CNRS-Saint-Gobain-NIMS, Laboratory for Innovative Key Materials and Structures (LINK, IRL 3629), National Institute for Materials Science, Tsukuba, Japan

Supplemental Figures

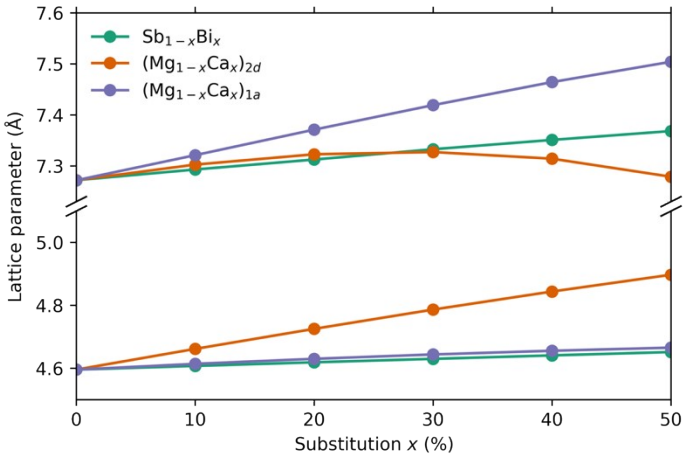

Fig S1. Change in lattice parameter a and c ($P\bar{3}m1$ space group, trigonal unit cell) as a function of the ratio of substitution from the VCA calculations. The two Mg sites are indicated by their corresponding Wyckoff letter.

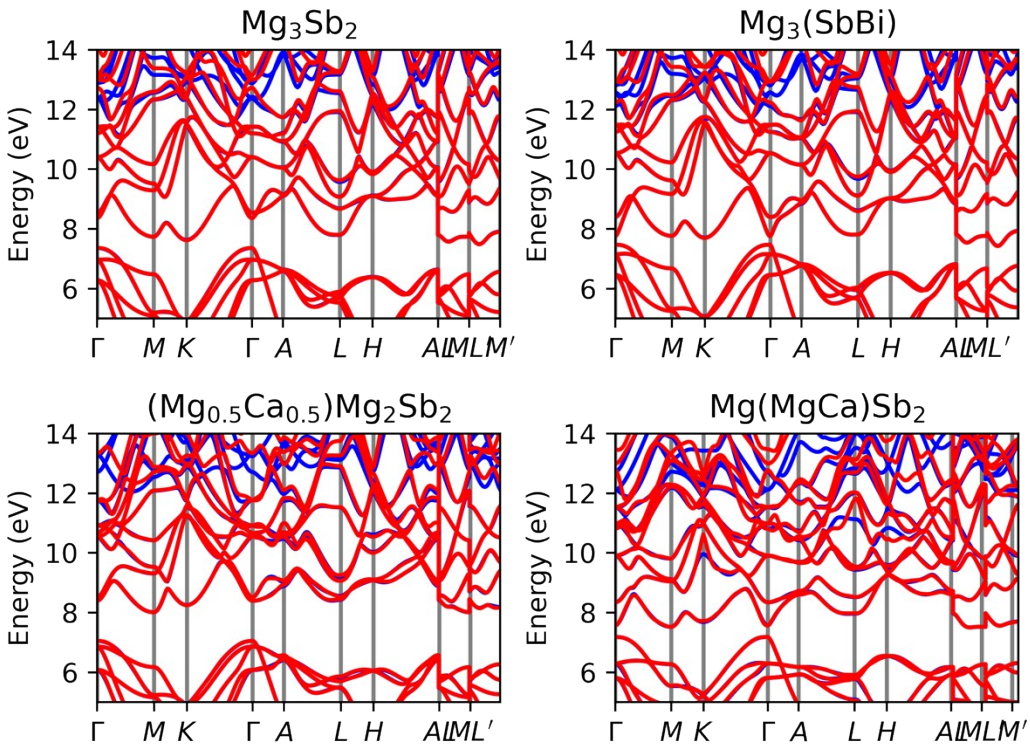

Fig S2. Comparison between the DFT band structure (blue) and the Wannier function projected tight-binding band structure (red) for the pristine and alloyed compounds.

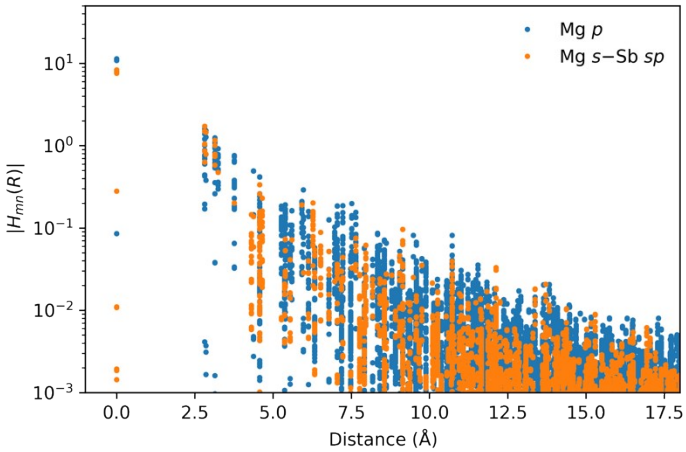

Fig S3. The absolute value of tight-binding interaction parameters $H_{nm}(R)$ as a function of interatomic distance. The two different colors separate interaction related to Mg p orbitals and the remaining interactions.

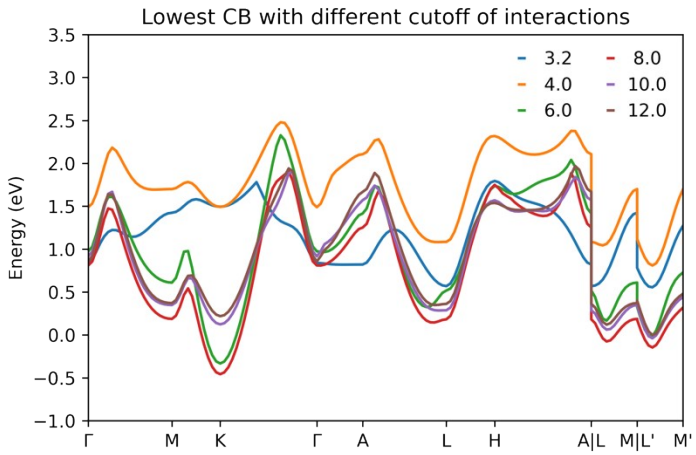

Fig S4. Shape of the lowest conduction band with different cutoffs (in Å) of the real space tight-binding interactions.

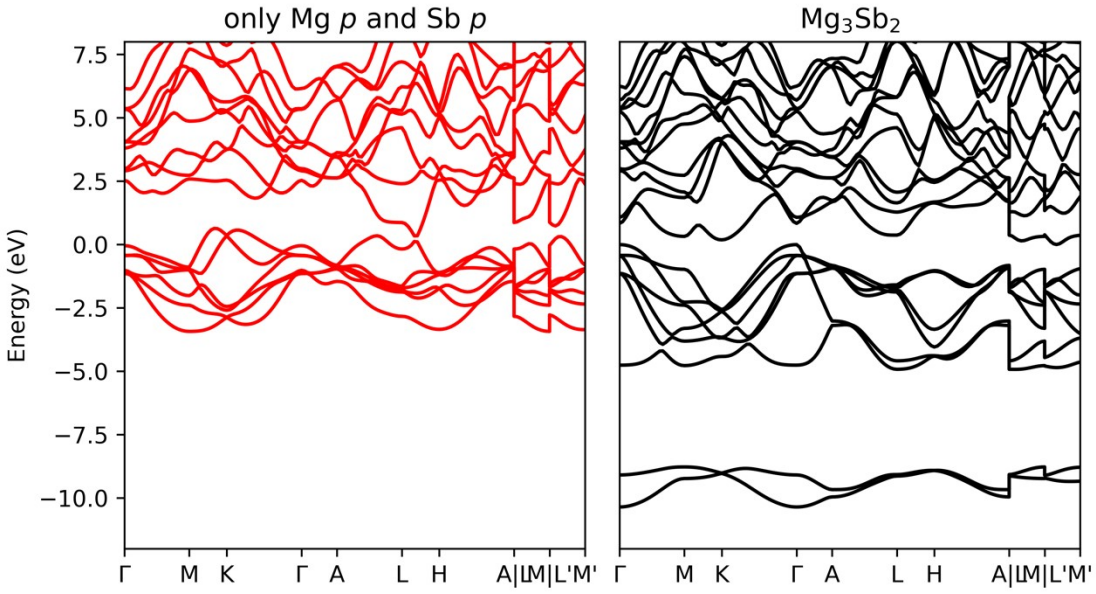

Fig S5. Left: calculated band structure in Mg_3Sb_2 only considering the p orbitals of the Mg and Sb atoms and their interactions, and right: the band structure of Mg_3Sb_2 considering all orbitals

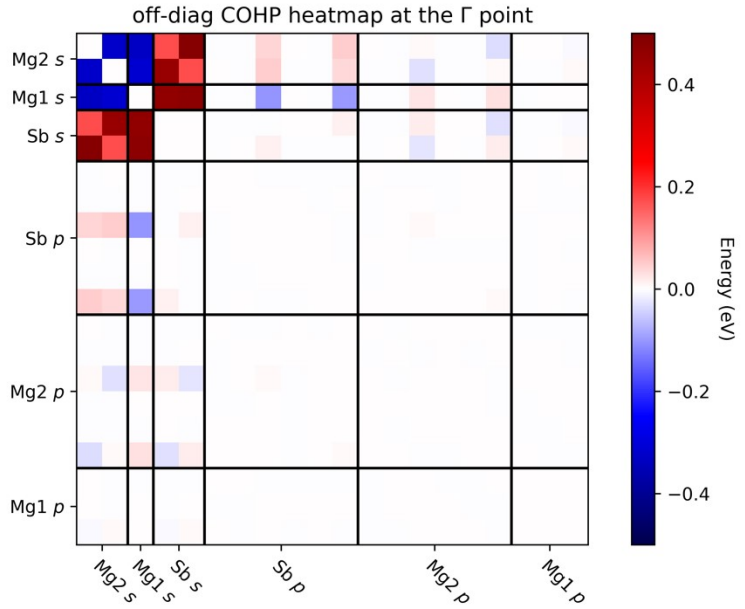

Fig S6. Off-diagonal part of the COHP matrix for the lowest conduction band at the Γ point. All diagonal components of COHP are set to zero.

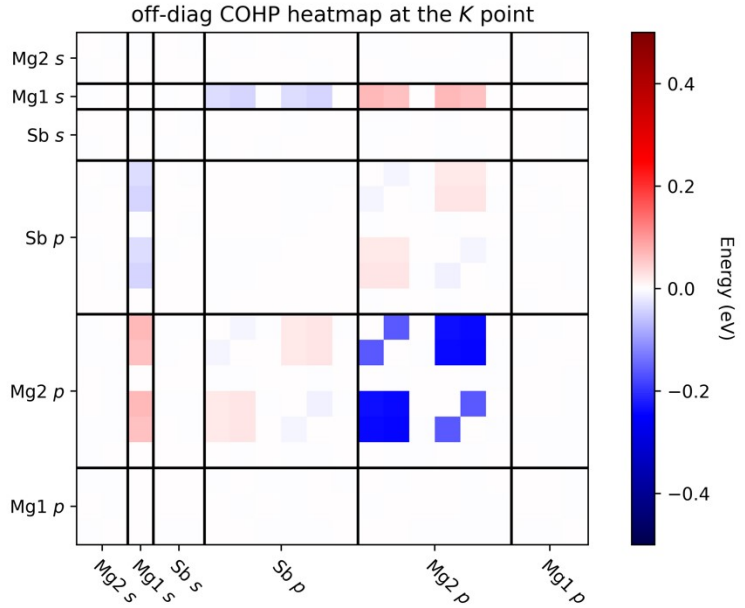

Fig S7. Off-diagonal part of the COHP matrix for the lowest conduction band at the *K* point.

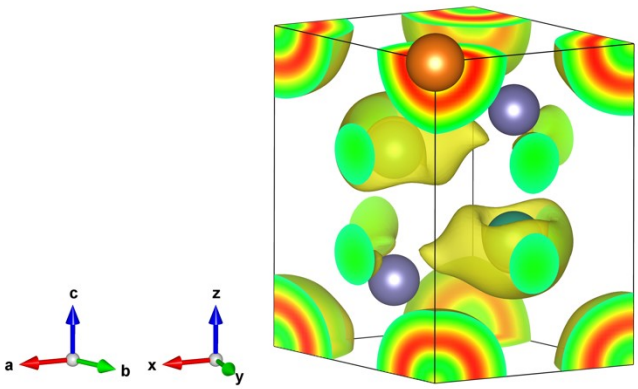

Fig S8. Local electron density of states in real space for the conduction band minimum. The main contribution to the conduction band minimum comes from Mg atoms localized at $1a$ site. Some Sb character can also be observed.

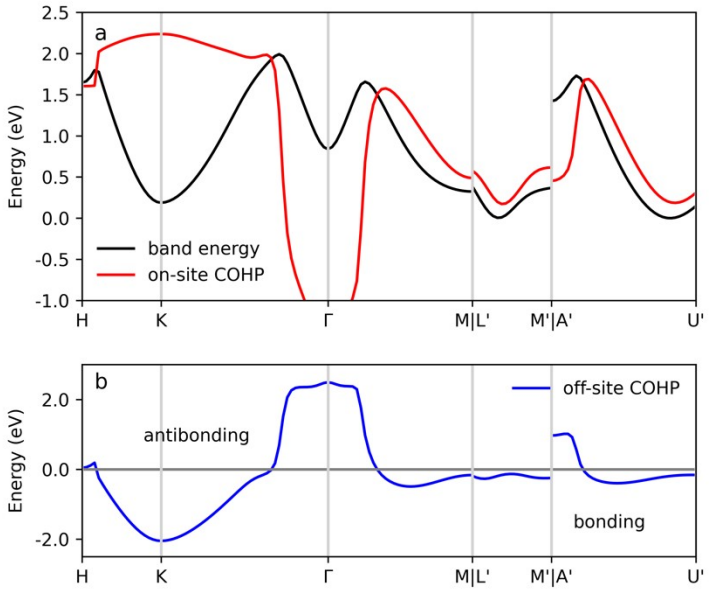

Fig S9. Decomposition of the lowest conduction band energy into on-site and off-site COHP.

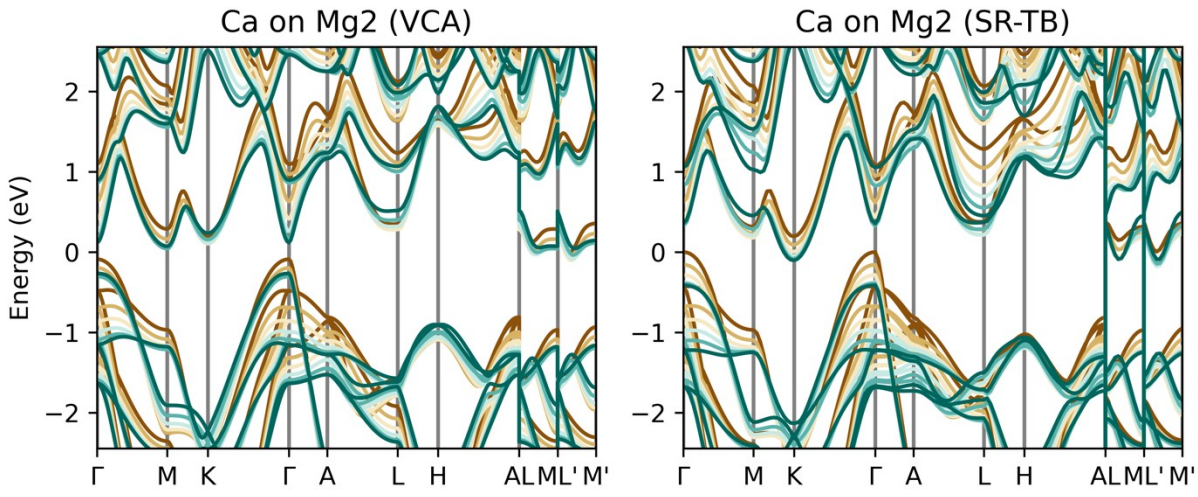

Fig S10. Band structure of Mg3Sb2 alloyed with Ca on Mg2 site obtained from VCA calculation and Wannier function tight-binding model with short range change.

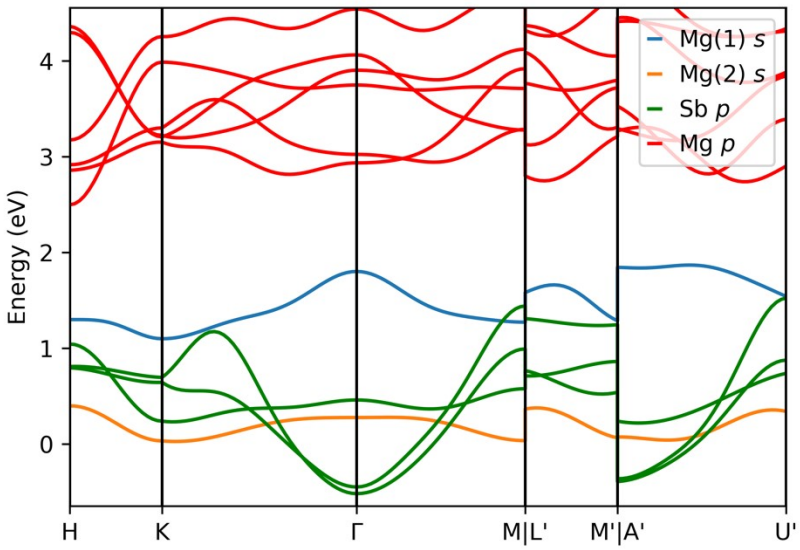

Fig S11. Energy dispersion of the Bloch functions as a function of wave vector k for Mg3Sb2 with 50% Ca alloying on the Mg1 site.

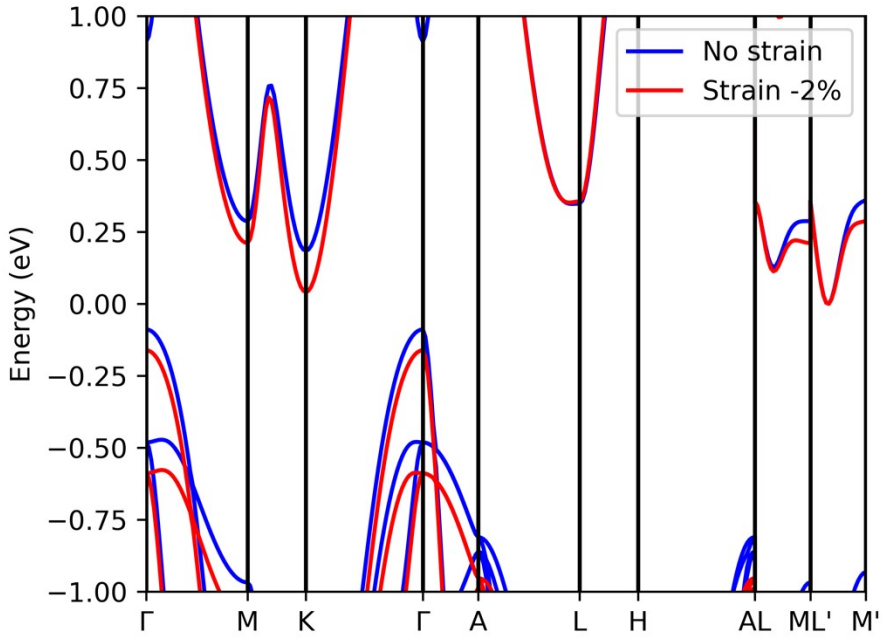

Fig S12. Band structure from DFT calculation for Mg_3Sb_2 with/without strain. The energy zero is aligned at the conduction band minimum for both band structures.

Table S1. Coordinates (k_x, k_y, k_z) of the conduction band minimum (CBM point) in the Brillouin zone for different alloyed compounds (x, substitution rate), with the change of conduction band minimum energy (E_{CBM}) compared to pristine Mg_3Sb_2.

	Bi on Sb				Ca on Mg1				Ca on Mg2			
x	k_x	k_y	k_z	E_{CBM}	k_x	k_y	k_z	E_{CBM}	k_x	k_y	k_z	E_{CBM}
0.0	0.420	0.0	0.339	0.0	0.420	0.0	0.340	0.0	0.420	0.0	0.339	0.0
0.1	0.416	0.0	0.340	-0.03	0.422	0.0	0.342	0.09	0.426	0.0	0.331	-0.08
0.2	0.416	0.0	0.340	-0.04	0.426	0.0	0.344	0.21	0.432	0.0	0.319	-0.12
0.3	0.414	0.0	0.340	-0.06	0.429	0.0	0.341	0.36	0.431	0.0	0.307	-0.09
0.4	0.415	0.0	0.339	-0.06	0.429	0.0	0.340	0.52	0.445	0.0	0.299	-0.04
0.5	0.414	0.0	0.338	-0.07	0.431	0.0	0.336	0.66	0.466	0.0	0.252	0.04

Table S2. Values of tight-binding interaction parameters for the onsite energy of each orbital and nearest-neighbor interactions related to Mg s orbitals. The column "vector" presents the relative position between the two atomic sites (from left to right in "Sites" column). The substitution ratio for each alloyed compound is 50%.

Term	Sites	vector	Mg_3Sb_2	Bi on Sb	Ca on Mg1	Ca on Mg2
E_s	Mg1	(0,0,0)	7.589	-0.028	1.328	-0.44
E_{py}	Mg1	(0,0,0)	11.341	0.084	0.045	-0.444
E_{pz}	Mg1	(0,0,0)	-1.074	0.004	0.077	0.21
E_s	Mg2	(0,0,0)	7.831	-0.024	-0.203	0.94
E_{pz}	Mg2	(0,0,0)	10.872	0.033	-0.192	-0.007
E_{py}	Mg2	(0,0,0)	10.896	0.055	-0.241	-0.105
E_s	Sb	(0,0,0)	0.28	-0.976	-0.136	-0.562
E_{pz}	Sb	(0,0,0)	8.322	0.201	-0.311	-0.938
E_{py}	Sb	(0,0,0)	8.05	0.143	-0.111	-0.692
V_{ss}	Mg1, Sb	(2.3, 1.3, 1.7)	-0.742	0.035	0.03	0.087
V_{spz}	Mg1, Sb	(2.3, -1.3, -1.7)	-0.789	0.025	-0.072	0.184
V_{spy}	Mg1, Sb	(0, -2.6, 1.7)	-1.163	-0.003	0.061	0.167
V_{ss}	Mg2, Sb(short)	(0, -2.6, 1.0)	-1.048	0.08	0.002	0.104
V_{ss}	Mg2, Sb(long)	(0, 0, -2.9)	-0.789	0.057	-0.07	0.098
V_{spz}	Mg2, Sb(short)	(2.3, -1.3, -1.0)	-0.631	0.003	0.064	0.139
V_{spy}	Mg2, Sb(short)	(0.0, 2.6, -1.0)	1.722	-0.051	-0.043	-0.227
V_{spz}	Mg2, Sb(long)	(0, 0, 2.9)	1.457	-0.046	0.001	-0.17