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Electronic Supplementary Information (ESI) for

Vibrational properties and bonding nature of Sb₂Se₃ and their implications for chalcogenide materials

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Supplementary methods

The data reported in the main text have been obtained in the local density approximation (LDA), not only due to its conceptual simplicity but also because the LDA has previously shown excellent performance in reproducing experimentally determined on-site force constants in the chemically related Sb₂Te₃.^{S1} Nonetheless, the results reported in the paper must be independent of one particular DFT method and be reproducible at other, higher levels of theory. **We show in this ESI document that this is indeed the case.**

For this purpose, supplementary computations were performed using the VASP package as described in the main text, with the following methods (and otherwise comparable computational parameters):

- The generalised gradient approximation (GGA)—that is, the second rung of Perdew's "ladder" of DFT functionals^{S2}—using, in particular,
 - o the Perdew–Burke–Ernzerhof (**PBE**) functional;^{S3}
 - the PBE functional revised for solids (**PBEsol**);^{S4}
 - o the Armiento–Mattsson (AM05) functional.^{S5}
- Dispersion corrections to GGA, which have been seen to be important for layered tellurides and might also improve the description of Sb₂Se₃ (see also the discussion in Ref. S6):
 - the "D3" scheme of Grimme and co-workers,^{S7} which is a pairwise *a posteriori* correction added to energies (and forces), both in the initially proposed zero-damping scheme (**D3** in the following) and
 - o using Becke–Johnson damping (BJ in the following);^{S8}
 - furthermore, the vdW-DF2 method of Langreth, Lundqvist, and co-workers (abbreviated as "DF2" in the following).^{S9}
- Finally, the meta-GGA functional after Tao, Perdew, Staroverov, and Scuseria (TPSS) was employed to explore the effect of a "third-rung" functional (that is, one exceeding LDA and GGA in formal and methodological scope).^{S10}

DFT methods beyond the LDA

Optimised lattice parameters. The structure of Sb₂Se₃ contains a range of "weak" interatomic contacts whose description is notoriously nontrivial for traditional DFT methods.^{S11} We thus start by assessing the computed lattice parameters at different levels of theory; the results (for cells fully optimised at the respective computational level) are provided in **Figure S1** below. Not surprisingly, the cell volume in particular is underestimated by LDA, and overestimated by the PBE functional; some of the methods can alleviate this, but there is no clear "failure" of the LDA among its competitors. It is also interesting to note that along the *b*-axis, the deviations are mainly very small—this is the direction in which the covalently bonded chains extend. Along the *a*-axis, where only weak stacking interactions occur, the deviations are generally more pronounced. Finally, we stress that the aim of these data is *not* to benchmark DFT methods or judge their merit (note, *e.g.*, that several other formulations of "vdW-DF"-type functionals exist, ^{S9} some of which will likely provide better lattice parameters).



Figure S1. Quality of structural descriptions as judged from the computed lattice parameters and their deviation from experiment (single-crystal X-ray diffraction; data from Ref. S12).

Atomic positions. In addition to the computed lattice parameters, it is worthwhile to quantify the description of the individual atoms' positions; this gives more detailed insight into how well interatomic distances are reproduced at the different levels of theory. For this purpose, it has been suggested to inspect the root mean square (rms) deviation of experimental and computed Cartesian coordinates;^{S13} later, this definition has been extended by George *et al.*^{S14} and decomposed according to the different spatial directions, which seems particularly useful for anisotropic structures. By definition, the *y* component (rms_{*y*}) equals zero because all atoms reside on Wyckoff sites with $y = \frac{1}{4}$ or $y = \frac{3}{4}$. The results for the other two spatial directions (which are most important as the "weak" contacts occur in these) are provided in **Figure S2**. Again, certain improvements are possible, but there is not a clear failure of LDA, and we note that a minor deviation remains even with the best methods.



Figure S2. Quality of structural descriptions as measured by the directionally resolved and overall root mean square deviation of Cartesian coordinates.^{S14}

Bond-projected force constants with different DFT methods. Among the key results of this study is a significant contrast in bond-projected force constants: they are large for the "classically" covalent bonds, but very low for the medium-range contacts. One might argue that more sophisticated formulations are required to capture properties of the latter, too, and hence we have repeated the phonon computations described in the main text at all levels of theory. The results—separated, for clarity, into two panels—are given below (**Figures S3** and **S4**), and they unambigously show that the conclusions obtained in the LDA hold also at the other DFT levels investigated.



Figure S3 (*as supplement to Figure 7 of the main text*). Bond-projected force constants, computed with different GGA functionals. The LDA data used in the main text are given by red triangles for comparison.



Figure S4 (*as supplement to Figure 7 of the main text*). Bond-projected force constants, computed with different dispersion-corrected DFT methods and at the meta-GGA (TPSS) level. The LDA data used in the main text are given by red triangles for comparison.

Supplementary results for bulk Sb₂Se₃



Figure S5 (*as supplement to Figure 5 of the main text*). Computed phonon band structure along the more comprehensive reciprocal-space pathway that had also been used for the electronic bands in Figure 2. No imaginary contributions are seen over the entire range.



Figure S6 (as supplement to Figure 5 of the main text). Computed partial density of phonon states, resolved according to symmetry-inequivalent antimony (*top*) and selenium (*bottom*) atoms. Note the pronounced contribution of both Sb(2) and Se(1) at around 200 cm⁻¹, corresponding to a stretching vibration of the shortest covalent bond. The large partial density of states of Se(1) at ≈ 120 cm⁻¹ also seems an interesting target for experimental investigation. The vibrations projected on the antimony atoms (top panel), which lie in the "interior" of the chains, are more evenly distributed over the range of wavenumbers.

Born effective charges. To better understand the bonding nature of the compound, we computed Born effective charges, using density-functional perturbation theory $(DFPT)^{S15}$ as implemented in VASP (settings: LEPSILON = .TRUE., LRPA = .FALSE.).^{S16} The analysis of Born effective charges also in comparison to experiment has recently proven a valuable tool to elucidate the nature of bulk and nanoscale oxides and heavier chalcogenides.^{S17} Here, doing so is especially interesting as it allows for comparison with recent results for Sb₂S₃.^{S18} The computed Born effective charges are listed in **Table S1**, and throughout, they are slightly larger than those of the lighter sulphide compound.^{S18}

	xx	уу	<i>ZZ</i> .	XZ	zx				
Sb(1)	3.07	5.92	8.17	0.25	1.87				
Sb(2)	2.98	7.45	4.87	0.46	0.20				
Se(1)	-2.02	-4.23	-4.71	1.19	1.11				
Se(2)	-1.84	-5.09	-4.98	-0.27	-0.13				
Se(3)	-2.16	-4.05	-3.37	-0.16	-1.62				

Table S1 (*as supplement to Figure 5 of the main text*). Nonzero elements of the Born effective charge tensor as computed here for Sb₂Se₃. The presentation is similar to that in Ref. S18, to ease comparison with the results for Sb₂S₃ given in the latter work.

Force constants and Badger's relation. Here, we provide raw data for the bond-projected force constants as discussed in the main text, and also supply additional data to further justify the hypothesis of low force constants in the "weak" Sb–Se bonds. According to Badger, the force constants ϕ and bond distances *d* in molecules obey^{S19}

$$\phi \times (d - d_0)^3 = \text{const.}$$

where d_0 is an element-specific constant. Plotting the cubic root of ϕ^{-1} hence yields a linear relationship if Badger's relation is satisfied. Doing so for the dataset obtained here for Sb₂Se₃ reveals that the short bonds within the 1D chains appear to follow a Badger-like relation, whereas the weaker bonds deviate because their force constants are lower (**Figure S7**).

Table S2 (as supplement to Figure 7 of the main text). Bond-projected force constants.

	$d_{\mathrm{opt}}(\mathrm{\AA})$	ф в (eV Å ^{−2})
Sb(2)-Se(1)	2.629	5.572
Sb(1)– $Se(3)$	2.714	3.500
Sb(1)– $Se(2)$	2.703	3.315
Sb(2)-Se(3)	2.771	2.545
Sb(2)–Se(1)'	2.977	0.306
Sb(1)– $Se(1)$	3.077	0.267
Sb(1)–Se(2)'	3.049	0.444
Sb(2)–Se(2)'	3.355	0.070
Sb(1)–Se(3)'	3.495	0.084



Figure S7 (*as supplement to Figure 7 of the main text*). Application of Badger's relation to the short and medium-range bonds in Sb₂Se₃.

Supplementary results for 1D chains

Dynamic stability of low-dimensional fragments. To further validate the results for 1D fragments cleaved from the crystal structure (Figure 6 in the main text), we have performed additional computations at the GGA (PBEsol) and dispersion-corrected GGA level (using Grimme's "D3" scheme). The resulting phonon band structures are collected in **Figure S8**. For the single wire characterised in panel (a), all three methods arrive at imaginary vibrational wavenumbers, qualitatively confirming the result of the LDA DPS; for the double wire in panel (b), all three methods evidence dynamic stability. For the chains bridged *via* longer interchain contacts, the PBEsol approach confirms the LDA result, albeit we note that a trace amount of imaginary modes does appear in the dispersion-corrected result.



Figure S8 (as supplement to Figure 6 of the main text). Phonon band structure for computations on 1D fragments as described in the main text, showing results for (a) a single wire, (b) a double wire bridged via the "primary inter-chain" bond as defined in the main text, and (c) a double wire bridged via the "secondary inter-chain" bond. Results from the LDA (red solid lines), the GGA functional PBEsol (blue dotted lines) and the dispersion-corrected PBE-D3 approach (green dashed lines) are provided.

The results provided so far have been obtained for structural fragments from the optimised crystal structure. However, subsequent optimisation of the 1D models is also an option: this alters the structural details compared to the bulk network, but it can provide additional insight regarding the dynamic stability. Results for these fully re-optimised models are given in **Figure S9**: again, a dynamic instability is observed for the single chain at all three levels of theory.



Figure S9 (as supplement to Figure 6 of the main text). Phonon band structures as before, but for fully re-optimised models at the respective level of theory. The double wire bridged via longer bonds relaxed into a distinctly different, but ultimately unstable structure; it is hence not considered here. In the double wire characterised in panel (b), on the contrary, the character of the "interchain" contacts remained similar, changing only from 2.977 Å to 2.960 Å (LDA), for example.

Structural raw data

Listing S1. Optimised structure of Sb₂Se₃ at the LDA-DFT level. Lattice vectors and coordinates are provided in VASP POSCAR format for convenience.

Antimony selenide LDA		
1.00000000000000		
11.53366664367613	84 0.000000000000	0.0000000000000000000000000000000000000
0.000000000000000	00 3.9601337536816	0.0000000000000000000000000000000000000
0.00000000000000	00 0.0000000000000000000000000000000000	11.2210518223176425
Sb Se		
8 12		
Direct		
0.1532363560821750	0.75000000000000000	0.9621619931950463
0.5187766115735997	0.25000000000000000	0.8283942748294990
0.0187766115735997	0.25000000000000000	0.6716057251705010
0.6532363560821750	0.75000000000000000	0.5378380068049537
0.3467636439178250	0.25000000000000000	0.4621619931950463
0.9812233884264003	0.7500000000000000	0.3283942748294990
0.4812233884264003	0.7500000000000000	0.1716057251705010
0.8467636439178250	0.25000000000000000	0.0378380068049537
0.6294130243619236	0.7500000000000000	0.9465496402764586
0.9448073833154211	0.7500000000000000	0.8673043928942263
0.2168040381329206	0.25000000000000000	0.8022423206686895
0.7168040381329206	0.25000000000000000	0.6977576793313105
0.4448073833154211	0.75000000000000000	0.6326956071057737
0.1294130243619236	0.75000000000000000	0.5534503597235414
0.8705869756380764	0.25000000000000000	0.4465496402764586
0.5551926166845789	0.25000000000000000	0.3673043928942263
0.2831959618670794	0.75000000000000000	0.3022423206686966
0.7831959618670794	0.75000000000000000	0.1977576793313105
0.0551926166845718	0.2500000000000000	0.1326956071057737
0.3705869756380764	0.25000000000000000	0.0534503597235414

Listing S2. As before, but at the PBE level.

Antimor	ny selenide PBE									
1.00	000000000000000000000000000000000000000									
12.	84895456790327	73	0.000	00000	00000	000	0.0	000000	000000	000
0.	. 0000000000000000	00	4.030	15061	62767	247	0.0	000000	000000	000
0.	. 0000000000000000	00	0.000	00000	00000	000	11.5	352420	140232	397
Sb	Se									
8	12									
Direct										
0.137	73604255775902	0.750	000000	00000	000	0.963	27180	448820)12	
0.535	56406967537808	0.250	000000	00000	000	0.831	98714	832838	805	
0.035	56406967537808	0.250	000000	00000	000	0.668	01285	167161	.95	
0.637	73604255775902	0.750	00000	00000	000	0.536	72819	551179	88	
0.362	26395744224098	0.250	00000	00000	000	0.463	27180	448819	941	
0.964	3593032462192	0.750	00000	00000	000	0.331	98714	832838	805	
0.464	13593032462192	0.750	000000	00000	000	0.168	01285	167161	.95	
0.862	26395744224098	0.250	000000	00000	000	0.036	72819	551179	88	
0.627	74410940012274	0.750	00000	00000	000	0.952	59403	577107	/80	
0.952	26080941564530	0.750	00000	00000	000	0.866	97047	228512	250	
0.204	10079922379832	0.250	00000	00000	000	0.809	14681	612739	951	
0.704	10079922379761	0.250	00000	00000	000	0.690	85318	387260)49	
0.452	26080941564530	0.750	00000	00000	000	0.633	02952	771487	/50	
0.127	74410940012203	0.750	00000	00000	000	0.547	40596	422892	20	
0.872	25589059987726	0.250	00000	00000	000	0.452	59403	577108	351	
0.547	73919058435470	0.250	00000	00000	000	0.366	97047	228512	250	
0.295	59920077620168	0.750	000000	00000	000	0.309	14681	612739	951	
0.795	59920077620239	0.750	000000	00000	000	0.190	85318	387260)49	
0.047	73919058435470	0.250	000000	00000	000	0.133	02952	771487	750	
0.372	25589059987797	0.250	000000	00000	000	0.047	40596	422891	.49	

Listing S3. As before, but at the PBEsol level.

Antimony selenide PBE	sol	
1.00000000000000		
11.78911006047657	93 0.000000000000	0.0000000000000000000000000000000000000
0.0000000000000	00 3.979774176708	0.0000000000000000000000000000000000000
0.0000000000000	0.0000000000000000000000000000000000000	0000 11.3175337334822466
Sb Se		
8 12		
Direct		
0.1502664476415774	0.75000000000000000	0.9628785179197905
0.5231093738531527	0.25000000000000000	0.8286296588467152
0.0231093738531527	0.25000000000000000	0.6713703411532848
0.6502664476415774	0.75000000000000000	0.5371214820802095
0.3497335523584226	0.25000000000000000	0.4628785179197905
0.9768906261468473	0.75000000000000000	0.3286296588467152
0.4768906261468473	0.75000000000000000	0.1713703411532848
0.8497335523584226	0.25000000000000000	0.0371214820802095
0.6293574757508864	0.75000000000000000	0.9480210106325728
0.9466475465424224	0.75000000000000000	0.8672883123855755
0.2147524380337984	0.25000000000000000	0.8040554669344786
0.7147524380337984	0.25000000000000000	0.6959445330655214
0.4466475465424224	0.75000000000000000	0.6327116876144245
0.1293574757508864	0.75000000000000000	0.5519789893674272
0.8706425242491136	0.25000000000000000	0.4480210106325728
0.5533524534575776	0.25000000000000000	0.3672883123855826
0.2852475619662087	0.75000000000000000	0.3040554669344786
0.7852475619662016	0.75000000000000000	0.1959445330655214
0.0533524534575776	0.25000000000000000	0.1327116876144174
0.3706425242491136	0.2500000000000000	0.0519789893674272

Listing S4. As before, but at the AM05 level.

Antimon	y selenide AMO	5											
1.00	000000000000												
12.	22115568794517	77	0.000	00000	000000	000	0	0.0	0000	0000	00000	000	
0.	0000000000000000000	00	3.976	57652	246593	393	2	0.0	0000	0000	00000	000	
0.	0000000000000000000	00	0.000	00000	000000	000	0 2	11.3	6478	32310	07411	163	
Sb	Se												
8	12												
Direct													
0.144	2912063034143	0.750	00000	00000	0000	0.	96439	9546	4351	18591	7		
0.530	1888777297421	0.250	00000	00000	0000	0.	82949	9989	6701	16056	5		
0.030	1888777297421	0.250	00000	00000	0000	0.	67050	0010	3298	33944	1		
0.644	2912063034143	0.750	00000	00000	0000	0.	53560	0453	5648	31403	3		
0.355	7087936965857	0.250	00000	00000	0000	0.	46439	9546	4351	18591	7		
0.969	8111222702579	0.750	00000	00000	0000	0.	32949	9989	6701	16056	5		
0.469	8111222702579	0.750	00000	00000	0000	0.	17050	0010	3298	33944	1		
0.855	7087936965857	0.250	00000	00000	0000	0.	03560	0453	5648	31403	3		
0.628	8892605501673	0.750	00000	00000	0000	0.	95008	8701	6762	22892	2		
0.950	4734426217496	0.750	00000	00000	0000	0.	86743	3952	4186	51532	2		
0.209	5061043178958	0.250	00000	00000	0000	0.	80742	2037	3110	07445	5		
0.709	5061043178958	0.250	00000	00000	0000	0.	6925	7962	6889	92555	5		
0.450	4734426217496	0.750	00000	00000	0000	0.	63256	6047	5813	38468	3		
0.128	8892605501815	0.750	00000	00000	0000	0.	54993	1298	323	77108	3		
0.871	1107394498327	0.250	00000	00000	0000	0.	45008	8701	6762	22821	L		
0.549	5265573782504	0.250	00000	00000	0000	0.	36743	3952	4186	51532	2		
0.290	4938956821042	0.750	00000	00000	0000	0.	30742	2037	3110	07445	5		
0.790	4938956821042	0.750	00000	00000	0000	0.	1925'	7962	6889	92555	5		
0.049	5265573782504	0.250	00000	00000	0000	0.	13256	6047	5813	38468	3		
0.371	1107394498185	0.250	00000	00000	0000	0.	04993	1298	323	77179)		

Listing S5. As before, but at the PBE-D3 (zero-damping) level.

Antimony selenide PBE-	-D3	
1.00000000000000		
12.047052363655018	30 0.00000000000	0.0000000000000000000000000000000000000
0.00000000000000000	4.018892546484	3619 0.000000000000000
0.00000000000000000	0.0000000000000000000000000000000000000	0000 11.4593148812205037
Sb Se		
8 12		
Direct		
0.1465231278037393	0.7500000000000000	0.9618922440694675
0.5267211888437373	0.2500000000000000	0.8295055370489237
0.0267211888437373	0.2500000000000000	0.6704944629510763
0.6465231278037322	0.7500000000000000	0.5381077559305325
0.3534768721962607	0.2500000000000000	0.4618922440694675
0.9732788111562627	0.7500000000000000	0.3295055370489237
0.4732788111562627	0.7500000000000000	0.1704944629510763
0.8534768721962678	0.2500000000000000	0.0381077559305325
0.6278611326473964	0.7500000000000000	0.9485748683935498
0.9467587725350484	0.75000000000000000	0.8675639325439377
0.2124412174909409	0.25000000000000000	0.8053437669114913
0.7124412174909409	0.25000000000000000	0.6946562330885087
0.4467587725350413	0.75000000000000000	0.6324360674560623
0.1278611326473964	0.75000000000000000	0.5514251316064502
0.8721388673526036	0.25000000000000000	0.4485748683935498
0.5532412274649516	0.25000000000000000	0.3675639325439377
0.2875587825090591	0.75000000000000000	0.3053437669114913
0.7875587825090591	0.75000000000000000	0.1946562330885087
0.0532412274649516	0.25000000000000000	0.1324360674560623
0.3721388673526036	0.2500000000000000	0.0514251316064502

Listing S6. As before, but at the PBE-D3 level using Becke–Johnson damping.

Antimony selenide PBE	-D3(BJ)	
1.00000000000000		
11.66096131529343	26 0.00000000000000000000000000000000000	0.0000000000000000000000000000000000000
0.00000000000000	3.9894602340440	0.0000000000000000000000000000000000000
0.00000000000000	0.0000000000000000000000000000000000000	0000 11.3468039010953223
Sb Se		
8 12		
Direct		
0.1518177384332944	0.75000000000000000	0.9605701407281018
0.5190404680656400	0.25000000000000000	0.8291023668929896
0.0190404680656400	0.25000000000000000	0.6708976331070104
0.6518177384332944	0.75000000000000000	0.5394298592718982
0.3481822615667056	0.25000000000000000	0.4605701407281018
0.9809595319343600	0.75000000000000000	0.3291023668929896
0.4809595319343600	0.75000000000000000	0.1708976331070104
0.8481822615667056	0.2500000000000000	0.0394298592718982
0.6287897735184060	0.75000000000000000	0.9467996737548745
0.9441757687545973	0.75000000000000000	0.8672849872254176
0.2162266264795818	0.2500000000000000	0.8014884017968456
0.7162266264795818	0.2500000000000000	0.6985115982031544
0.4441757687545973	0.7500000000000000	0.6327150127745824
0.1287897735184060	0.75000000000000000	0.5532003262451255
0.8712102264815940	0.2500000000000000	0.4467996737548745
0.5558242312454027	0.2500000000000000	0.3672849872254176
0.2837733735204182	0.7500000000000000	0.3014884017968456
0.7837733735204182	0.7500000000000000	0.1985115982031544
0.0558242312454027	0.2500000000000000	0.1327150127745824
0.3712102264815940	0.25000000000000000	0.0532003262451255

Listing S7. As before, but at the vdW-DF2 level.

Antimony selenide vdW	-DF2	
1.00000000000000		
12.86072383427952	03 0.00000000000	0000 0.000000000000000
0.00000000000000	00 4.179731538131	0387 0.000000000000000
0.00000000000000	00 0.00000000000	0000 12.1770930122101824
Sb Se		
8 12		
Direct		
0.1377869708752471	0.7500000000000000	0.9590881212288949
0.5387336950931427	0.2500000000000000	0.8315580085590213
0.0387336950931427	0.2500000000000000	0.6684419914409787
0.6377869708752471	0.7500000000000000	0.5409118787711051
0.3622130291247601	0.2500000000000000	0.4590881212288949
0.9612663049068573	0.7500000000000000	0.3315580085590213
0.4612663049068573	0.7500000000000000	0.1684419914409787
0.8622130291247529	0.2500000000000000	0.0409118787711051
0.6286120421170480	0.7500000000000000	0.9484307444578022
0.9467965129682199	0.7500000000000000	0.8703037768068285
0.2080969777661537	0.2500000000000000	0.8086130044735569
0.7080969777661537	0.2500000000000000	0.6913869955264431
0.4467965129682199	0.7500000000000000	0.6296962231931715
0.1286120421170409	0.7500000000000000	0.5515692555421978
0.8713879578829520	0.2500000000000000	0.4484307444578022
0.5532034870317801	0.2500000000000000	0.3703037768068285
0.2919030222338463	0.7500000000000000	0.3086130044735640
0.7919030222338463	0.7500000000000000	0.1913869955264360
0.0532034870317801	0.2500000000000000	0.1296962231931715
0.3713879578829591	0.2500000000000000	0.0515692555421978

Listing S8. As before, but at the TPSS level.

Antimony selenide TPS	S		
1.000000000000000			
12.23492863805010	0.0000000000000000000000000000000000000	0.0000000000000000000000000000000000000	
0.00000000000000	4.012488199360	0.0000000000000000000000000000000000000	
0.00000000000000	0.0000000000000000000000000000000000000	00000 11.5950078194070993	
Sb Se			
8 12			
Direct			
0.1453269833984692	0.75000000000000000	0.9639480175228883	
0.5312660554942497	0.25000000000000000	0.8284474713919678	
0.0312660554942497	0.25000000000000000	0.6715525286080322	
0.6453269833984692	0.75000000000000000	0.5360519824771117	
0.3546730166015379	0.25000000000000000	0.4639480175228883	
0.9687339445057503	0.75000000000000000	0.3284474713919678	
0.4687339445057503	0.75000000000000000	0.1715525286080322	
0.8546730166015308	0.25000000000000000	0.0360519824771117	
0.6288965432864515	0.75000000000000000	0.9475077438357431	
0.9503427503673905	0.75000000000000000	0.8697650177755847	
0.2100143911952301	0.25000000000000000	0.8074889714779587	
0.7100143911952230	0.25000000000000000	0.6925110285220413	
0.4503427503673905	0.75000000000000000	0.6302349822244153	
0.1288965432864515	0.75000000000000000	0.5524922561642569	
0.8711034567135485	0.25000000000000000	0.4475077438357431	
0.5496572496326095	0.25000000000000000	0.3697650177755847	
0.2899856088047699	0.75000000000000000	0.3074889714779587	
0.7899856088047770	0.75000000000000000	0.1925110285220413	
0.0496572496326095	0.25000000000000000	0.1302349822244153	
0.3711034567135485	0.25000000000000000	0.0524922561642569	

Supplementary references

- (S1) R. P. Stoffel, V. L. Deringer, R. E. Simon, R. P. Hermann and R. Dronskowski, J. Phys.: Condens. Matter, 2015, 27, 085402.
- (S2) J. P. Perdew and K. Schmidt, ed. V. Van Doren et al., American Institute of Physics, Editon edn., 2001, pp. 1-20.
- (S3) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- (S4) J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- (S5) R. Armiento and A. E. Mattsson, Phys. Rev. B, 2005, 72, 085108.
- (S6) M. R. Filip, C. E. Patrick and F. Giustino, *Phys. Rev. B*, 2013, 87, 205125.
- (S7) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- (S8) S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- (S9) (a) M. Dion, H. Rydberg, E. Schröder, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 2004, 92, 246401; (b) K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, *Phys. Rev. B*, 2010, 82, 081101(R); (c) J. Klimeš, D. R. Bowler and A. Michaelides, *Phys. Rev. B*, 2011, 83, 195131.
- (S10) J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
- (S11) T. Björkman, A. Gulans, A. V. Krasheninnikov and R. M. Nieminen, J. Phys.: Condens. Matter, 2012, 24, 424218.
- (S12) G. P. Voutsas, A. G. Papazoglou, P. J. Rentzeperis and D. Siapkas, Z. Kristallogr., 1985, 171, 261-268.
- (S13) J. van de Streek and M. A. Neumann, Acta Crystallogr., Sect. B, 2010, 66, 544-558.
- (S14) J. George, V. L. Deringer and R. Dronskowski, Inorg. Chem., 2015, 54, 956-962.
- (S15) S. Baroni, S. de Gironcoli, A. Dal Corso and P. Giannozzi, *Rev. Mod. Phys.*, 2001, 73, 515-562.
- (S16) M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller and F. Bechstedt, *Phys. Rev. B*, 2006, 73, 045112.
- (S17) (a) Q.-C. Sun, X. S. Xu, L. I. Vergara, R. Rosentsveig and J. L. Musfeldt, *Phys. Rev. B*, 2009, **79**, 205405; (b) Q.-C. Sun, X. Xu, S. N. Baker, A. D. Christianson and J. L. Musfeldt, *Chem. Mater.*, 2011, **23**, 2956-2960.

- (S18) Y. Liu, K. T. E. Chua, T. C. Sum and C. K. Gan, *Phys. Chem. Chem. Phys.*, 2014, **16**, 345-350.
- (S19) R. M. Badger, J. Chem. Phys., 1934, 2, 128-131.