Electronic Supplementary Information

Highly Anisotropic and Ultra-Diffusive Vacancies in α-Antimonene

Ning Lu,[1,] Xin Hu,[1] Jiaxin Jiang,[1] Hongyan Guo,[1] Gui Zhong Zuo,[2] Zhiwen Zhuo,[1,]* Xiaojun Wu[3] and Xiao Cheng Zeng[4]**

[1]Anhui Province Key Laboratory of Optoelectric Materials Science and Technology, Key Laboratory of Functional Molecular Solids Ministry of Education, Anhui Laboratory of Molecule-Based Materials, and Department of Physics, Anhui Normal University, Wuhu, Anhui, 241000, China.

[2]Institute of Plasma Physics, HIPS, Chinese Academy of Sciences, Hefei, 230031, China.

[3]Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Materials for Energy Conversion, and School of Chemistry and Materials Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China.

[4]Department of Materials Science & Engineering, City University of Hong Kong, Kowloon, 999077, Hong Kong.

Corresponding Author

*Email: luning@ahnu.edu.cn

*Email: zhuozw@ustc.edu.cn

*Email: xzeng26@cityu.edu.hk

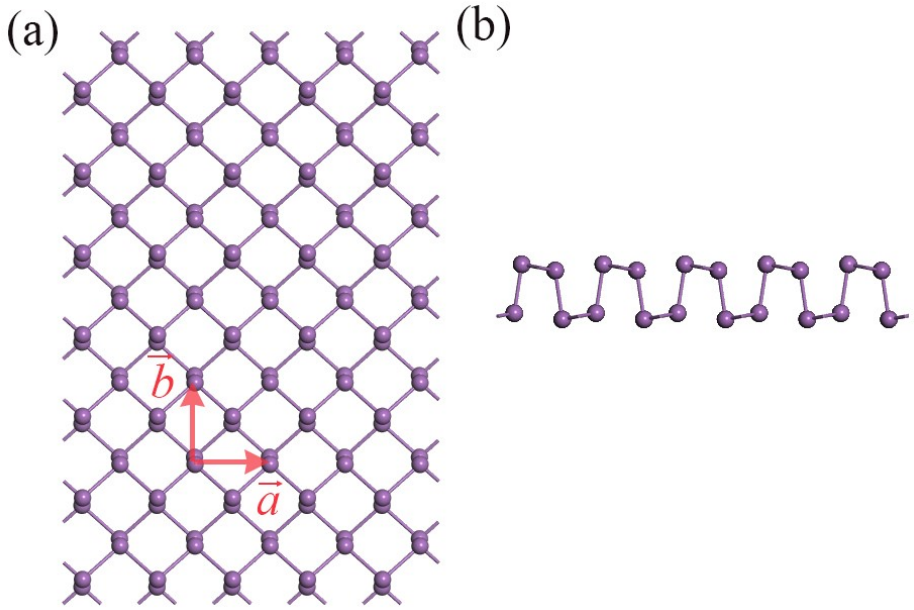

Fig. S1 (a) Top and (b) side view of the optimized α-antimonene structure. The unit cell is marked with red arrows.

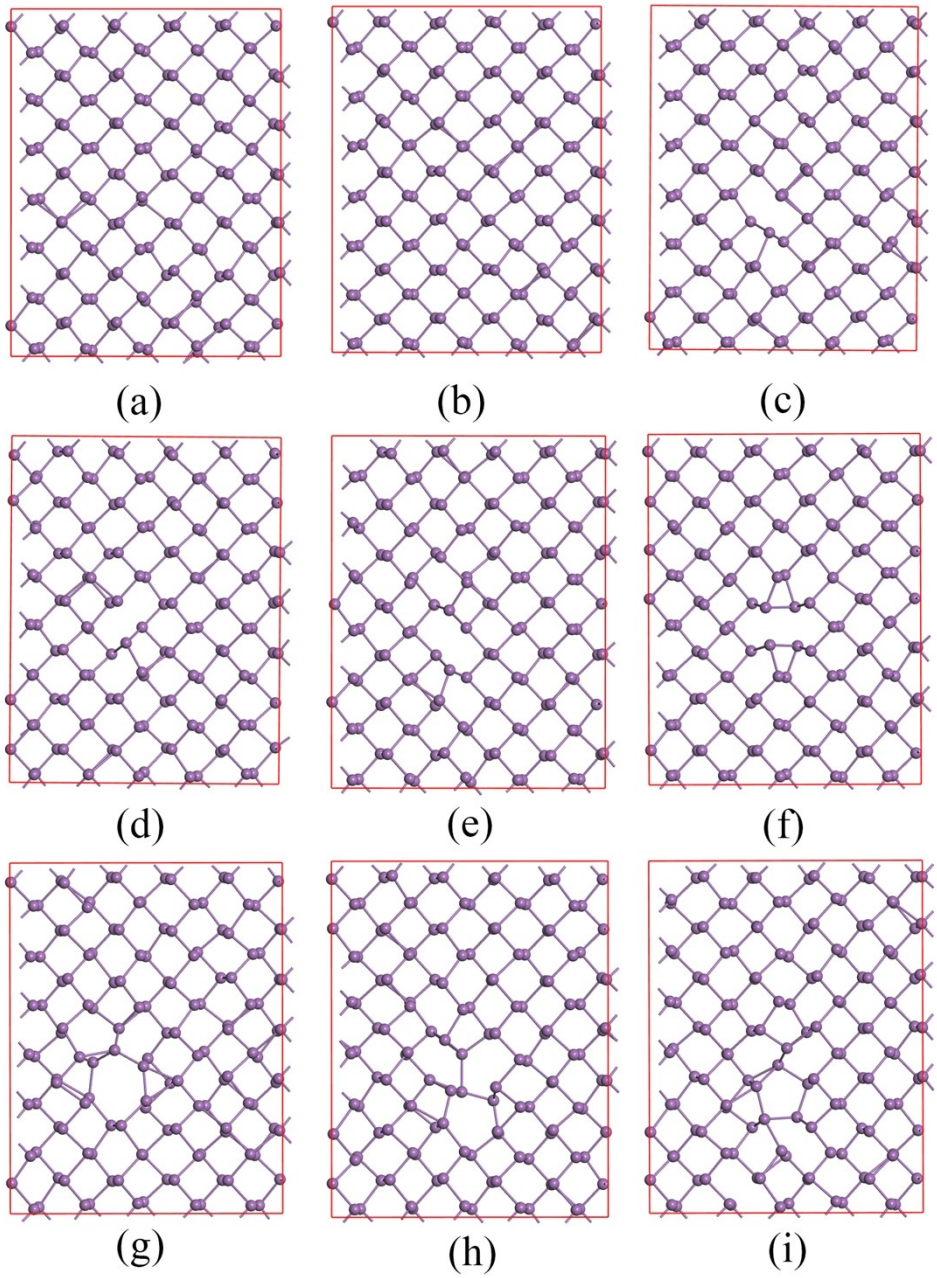

Fig. S2 Snapshots of defect containing α-antimonene structure after 5 ps AIMD simulations at 300 K: (a) SW-1, (b) SW-2, (c) SV-(5|9), (d) SV-(55|66), (e) DV-(5|8|5), (f) DV-(4|10|4), (g) DV-(555|777)-1, (h) DV-(555|777)-2, and (i) DV-(555|777)-3.

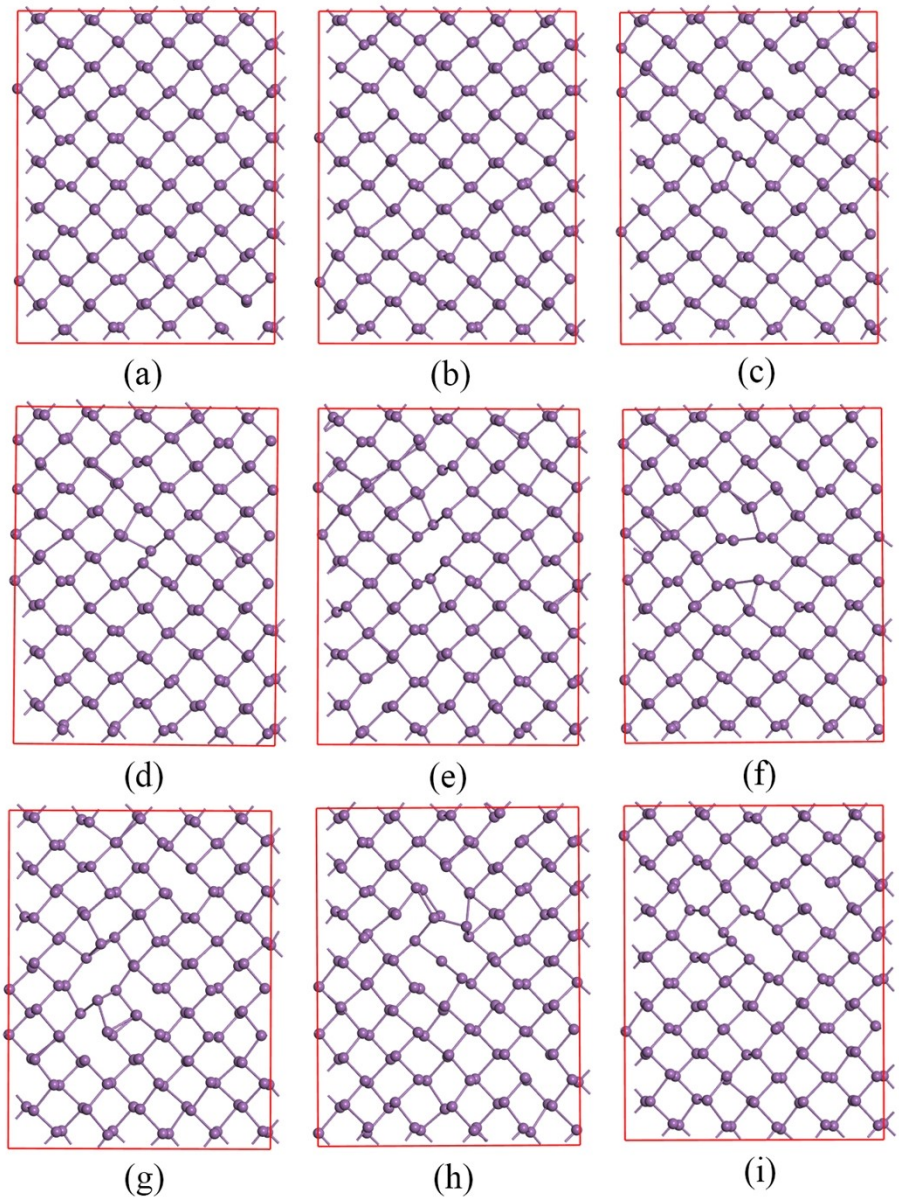

Fig. S3 Snapshots of defect containing α-antimonene structure after 5 ps AIMD simulations at 400 K: (a) SW-1, (b) SW-2, (c) SV-(5|9), (d) SV-(55|66), (e) DV-(5|8|5), (f) DV-(4|10|4), (g) DV-(555|777)-1, (h) DV-(555|777)-2, and (i) DV-(555|777)-3.

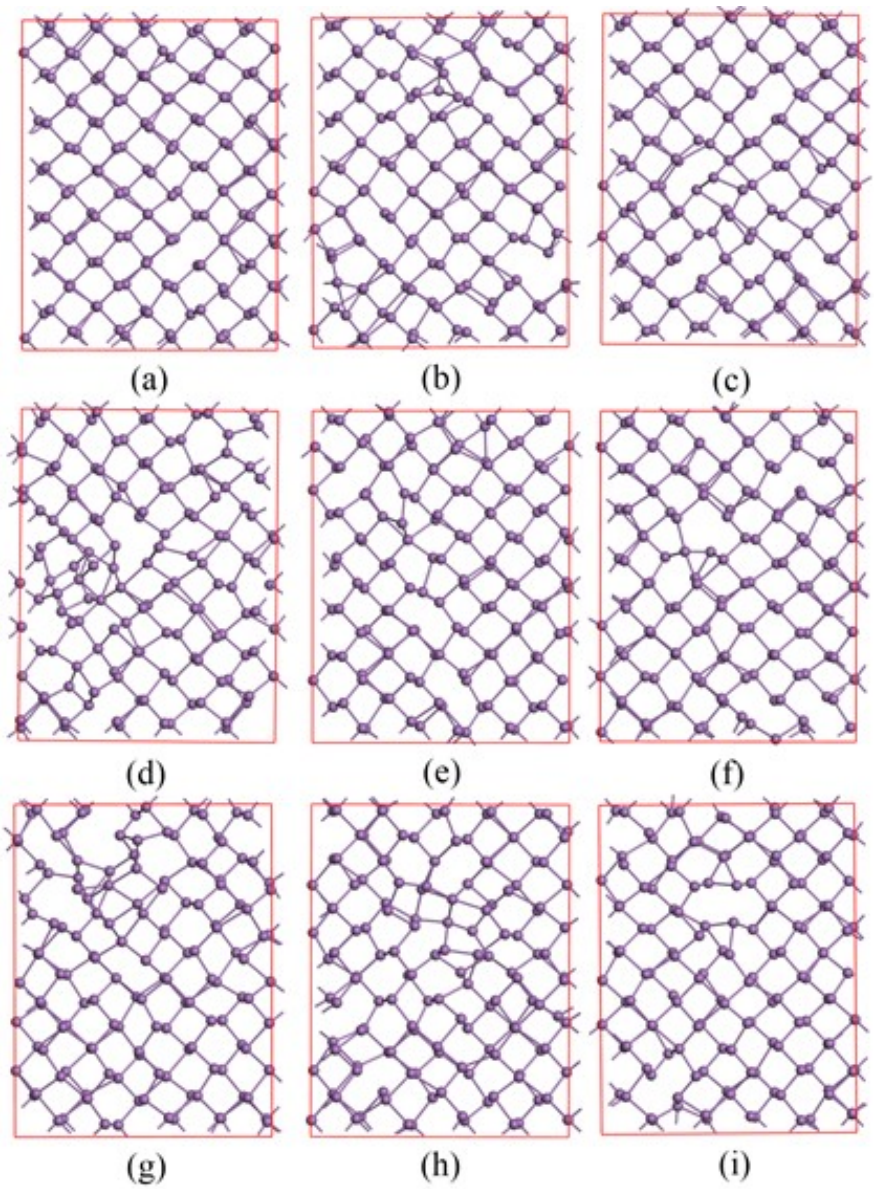

Fig. S4 Snapshots of defect containing α-antimonene structure after 5 ps AIMD simulations at 800 K: (a) SW-1, (b) SW-2, (c) SV-(5|9), (d) SV-(55|66), (e) DV-(5|8|5), (f) DV-(4|10|4), (g) DV-(555|777)-1, (h) DV-(555|777)-2, and (i) DV-(555|777)-3.

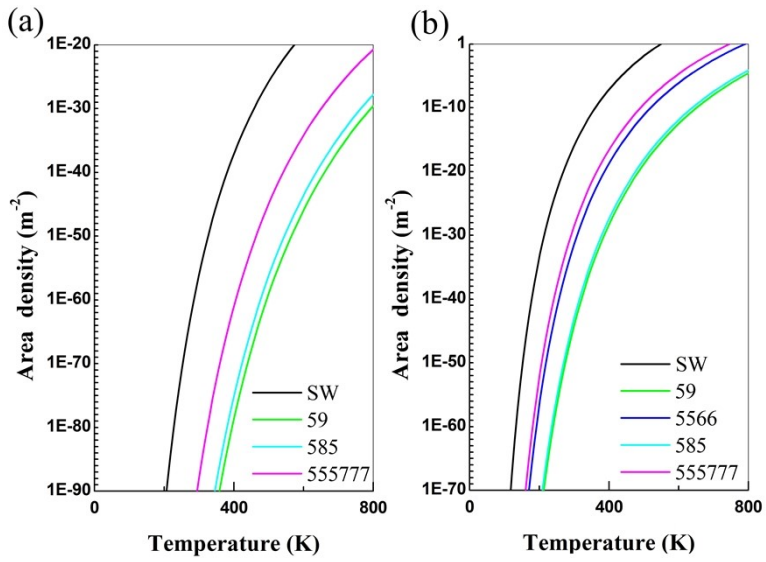

Fig. S5 Computed area density of atoms versus temperature. (a) graphene and (b) silicene with various types of point defects (SW, SV-(5|9), SV-(55|66), DV-(5|8|5), DV-(555|777) and DV-(4|10|4)). For perfect structures, the area density of atoms is $N_{perfect}$(graphene) = 3.79×10^{19} atom/m^2, $N_{perfect}$(silicene) = 1.55×10^{19} atom/m^2.

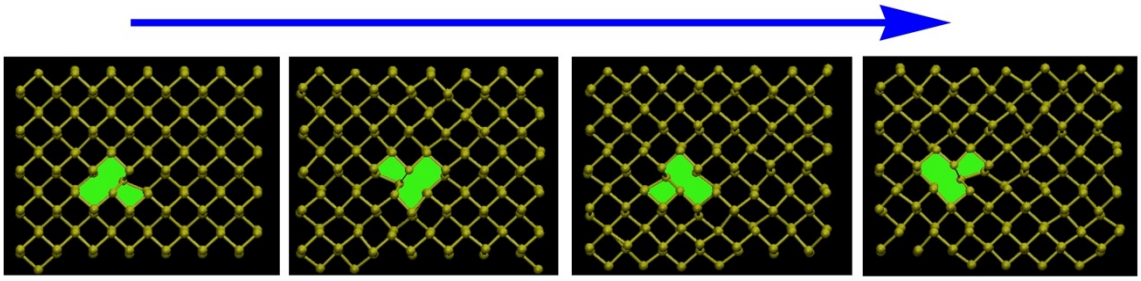

Fig. S6 Snapshots of α-antimonene with SV-(5|9) defect after 5 ps AIMD simulations at 300 K, revealing the hopping events along the zigzag direction.

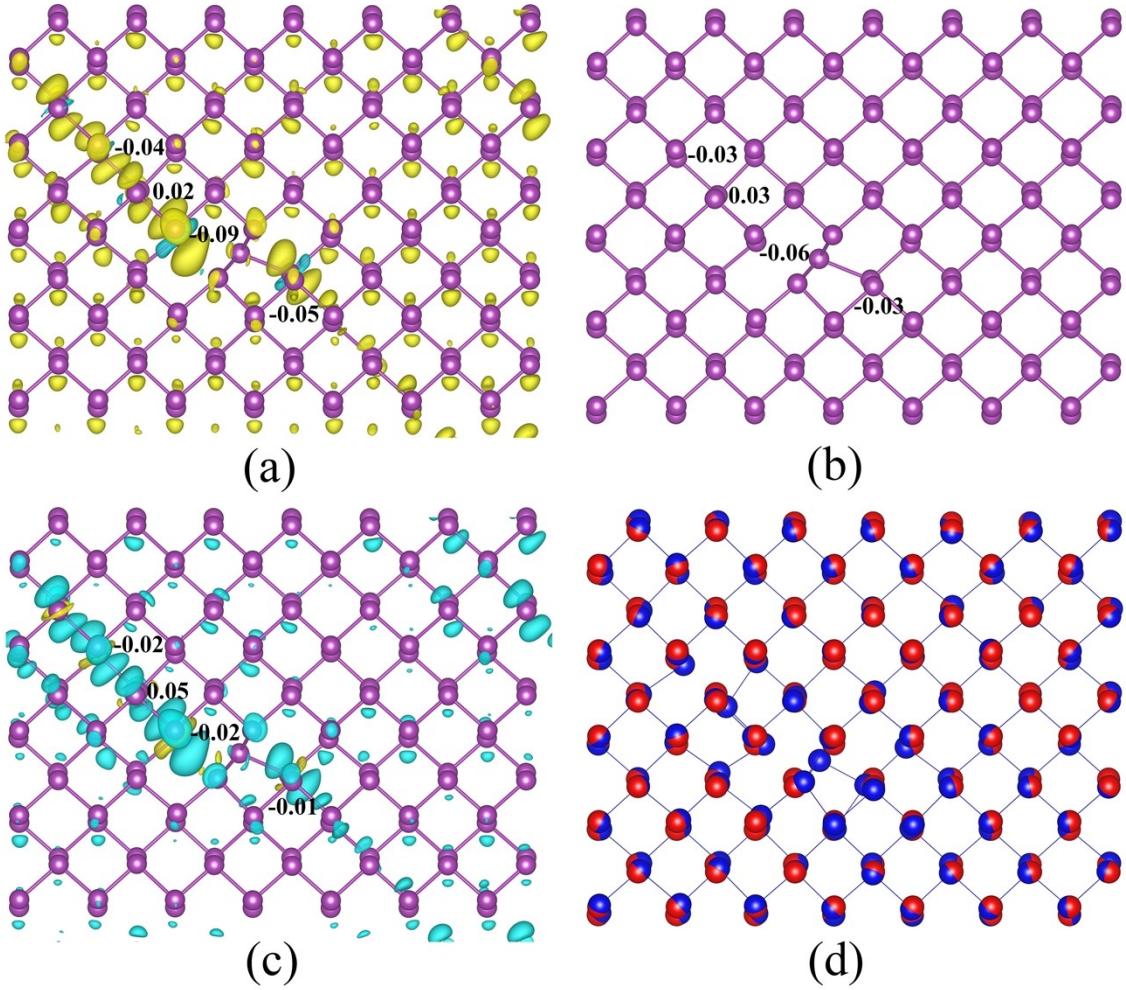

Fig. S7 (a) Computed Bader charge and charge density difference between SV- (5|9) defect with an extra electron and neutral SV-(5|9) defect, e.g. $\Delta\rho = \rho(+1e) - \rho(+0e)$ (isosurface: 0.0001 e Bohr^{-3}). Yellow and blue contours represent electron density accumulations and depressions, respectively.; (b) The Bader charge analysis of neutral SV-(5|9) defect. (c) Bader charge and charge density difference between neutral SV-(5|9) defect and SV-(5|9) defect with an extra hole, e.g. $\Delta\rho = \rho(-1e) - \rho(+0e)$ (isosurface: 0.0001 e Bohr^{-3}). (d) The change of atomic position between SV-(5|9) defective and perfect α-antimonene, and the red and the blue spheres represent the Sb atom of defective and perfect α-antimonene, respectively. The Bader charge values marked in (a)-(c) are with the same unit of e.

Calculation of the optical absorption coefficient:

The frequency-dependent dielectric function is calculated first by vasp5.4 code:[1, 2]

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$$

According to the dielectric function, the absorption coefficient can be calculated by[3]:

$$\alpha(\omega)=\frac{\sqrt{2\omega}}{c}\left\{\left[\varepsilon_1^{\,2}(\omega)+\varepsilon_2^{\,2}(\omega)\right]^{\frac{1}{2}}-\varepsilon_1(\varepsilon)\right\}^{\frac{1}{2}}$$

Here the vaspkit code is used to calculate the absorption coefficient.[4] The absorption coefficients are calculated for incident light polarized in the x ($\alpha_{//x}$), y ($\alpha_{//y}$), and z ($\alpha_{//y}$) direction, respectively. Here, the x and y directions are parallel to the α-antimonene plane, and the z direction is perpendicular to the α-antimonene plane.

Table S1. Comparison results of computed cohesive energy E_c (eV/atom) of the perfect α-antimonene, phosphorene, graphene, and silicene with the computed formation energy of defect, E_f (eV). The cohesive energy of the perfect α-antimonene is calculated by $E_c = (E_{total} - 4 \times E_{atom})/4$, where E_{total} is the total energy of the perfect α-antimonene cell with 4 Sb atoms, and E_{atom} is the energy of a single Sb atom.

Reference	α-Antimonene this work	Phosphorene Ref 27	Graphene Ref 18	Silicene Ref 19
E_c (perfect)	2.62	3.48	7.90	3.96
E_f (SW)	1.12-1.61	1.01-1.32	4.50	2.09
E_f (SV-(5|9))	0.97	1.63	7.80	3.77
E_f (SV-(55|66))	0.99	2.03		3.01
E_f (DV-(5|8|5))	1.16	1.91-3.04	7.52	3.70
E_f (DV-(555|777))	2.33-2.65	2.08-2.61	6.40	2.84
E_f (DV-(4|10|4))	1.07	2.13		

Table S2. Calculated area density (N_{defect}) (m^{-2}) of SV-(59) defect in α-antimonene, phosphorene, graphene and silicene versus temperature.

T (K)	N_{defect}(α-antimonene)	N_{defect}(phosphorene)	N_{defect}(graphene)	N_{defect}(silicene)
200	7.00E-06	2.79E-22	1.53E-94	1.55E-76
250	5.41E-01	4.36E-14	7.29E-72	1.55E-57
300	9.83E+02	1.27E-08	9.59E-57	7.20E-45
350	2.09E+05	1.01E-04	6.05E-46	8.03E-36
400	1.17E+07	8.54E-02	7.61E-38	4.90E-29
450	2.66E+08	1.61E+01	1.52E-31	9.29E-24
500	3.24E+09	1.07E+03	1.66E-26	1.55E-19

Supplementary Reference

1. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
2. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
3. B. Peng, H. Zhang, H. Shao, Y. Xu, R. Zhang and H. Zhu, *J. Mater. Chem. C*, 2016, **4**, 3592-3598.
4. V. Wang, N. Xu, J.-C. Liu, G. Tang and W.-T. Geng, *Comput. Phys. Commun.*, 2021, **267**, 108033.