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1. Introduction

Since the discovery of graphene,¹ a lot of two-dimensional (2D) materials have been experimentally synthesized and theoretically predicted with many fascinating properties, showing great potential for various applications.^{2–8} As compared to the widely studied 2D metal oxides and carbides, much less effort has been devoted to the nitrogen analogues, metal nitrides (MNs). Among the recently studied 2D MNs, the sheets can be in very distinct geometry configurations.⁹⁻¹⁶ For instance, the Ti₄N₃ sheet has a MXene like geometric structure with multi-atomic layers and atomic N,⁹ while the tetra-MoN₂ sheet has a square lattice with a single-atomic thickness and atomic N,¹⁷ and the O-YN₂ sheet possesses a buckled monolayer where the metal atoms are sandwiched between the top and bottom layers of N₂ dimers.18 Additionally, previous studies reported that the penta-AlN₂ sheet has a buckled Cairo pentagonal tiling geometry with N₂ dimers,¹⁹ whereas the BeN₂ sheet is in distorted honeycomb lattice containing N₄ cluster units.²⁰ These studies demonstrate that the geometric structures of 2D MNs sensitively depend on the metal species and the atomic ratio of metal/N, exhibiting complexities and diversities.

Moreover, the diverse and flexible bonding features of a metal with N/N_2 lead to rich physical and chemical properties

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2D planar penta-MN₂ (M = Pd, Pt) sheets identified through structure search

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Two-dimensional (2D) metal dinitrides have attracted increasing attention because of their diverse geometry configurations and extraordinary properties. Using the particle swarm optimization (PSO)-based global structure search method combined with first principles calculations, we have identified 2D metal dinitride MN_2 (M = Pd, Pt) sheets containing N_2 dimers, penta- MN_2 , which are planar and composed entirely of pentagons. These pentagonal sheets are not only dynamically, thermally and mechanically stable, but also energetically more favorable over the experimentally synthesized pyrite MN_2 monolayers. In particular, penta- PtN_2 can withstand a temperature as high as 2000 K, showing its potential as a refractory material. In addition, due to its unique atomic configuration, penta- MN_2 exhibits intriguing electronic properties. Penta- PdN_2 is metallic, while penta- PtN_2 is semiconducting with a direct band gap of 75 meV and an ultrahigh carrier mobility. This study expands the family of 2D metal nitrides, and provides new insight into finding new materials using a reliable structure search algorithm rather than chemical and physical intuition.

of MNs. For example, the H-MoN₂ sheet displays a robust ferromagnetism with a Curie temperature over 420 K,²¹ the metallic O-YN₂ sheet shows promising potential as an anode material for potassium (K) ion batteries with high K capacity,¹⁸ and the penta-AlN₂ sheet is a half-metal and presents ferromagnetism as well.¹⁹ These advances inspire us to carry out the present study focusing on 2D MN_2 (M = Pd, Pt) systems by using the global structure search method and first principles calculations. Our results show that the most stable monolayers are composed of pure pentagons, thus named penta-MN₂. They are totally planar, differing from the other hitherto reported 2D pentagon-based materials which have buckled structures.8,20,22-29 We further systematically investigated their physical properties, including melting points, in-plane Young's modulus, ideal strength, band structure, charge distribution, and carrier mobility. In particular, penta-PtN₂ possesses ultrahigh melting point over 2000 K and carrier mobility comparable with that of graphene.

2. Computational methods

We use the Crystal structure AnaLYsis by Particle Swarm Optimization $(CALYPSO)^{30}$ code to search for the ground state structures of 2D PdN₂ and PtN₂, and this method has been successfully employed to predict numerous structures ranging from elemental crystals to binary and ternary compounds.³¹ In the global search, the PSO algorithm is used with thirty generations and population size up to thirty, which means a total of 900 structures are produced including the symmetry *P4/mbm*, *Pmmm*

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and so on. It reaches convergence quickly after 14 generations. The unit cells containing 6 atoms and the buffering thickness is set to 0.15 Å to accommodate the buckling of the structures.

Density functional theory (DFT) based first-principles calculations are further performed to study the structural and electronic properties as implemented in the Vienna ab initio Simulation Package (VASP)³² with the projector augmented wave potential $(PAW)^{33}$ to treat the ion-electron interactions. The generalized gradient approximation (GGA)³⁴ with the Perdew-Burke-Ernzerhof (PBE) functional³⁵ is used to describe the exchange and correlation energy. All atoms of system are relaxed with the convergence criteria for the force and total energy set to be 10^{-2} eV Å⁻¹ and 10^{-4} eV, respectively. The kinetic energy cutoff is set to be 600 eV for all calculations. The Monkhorst–Pack k-mesh³⁶ is employed to the sample kpoint of the first Brillouin zone. The k-point grids are set as $9 \times 9 \times 1$ and $25 \times 25 \times 1$ for the geometry optimization and electronic structure calculations, respectively. For eliminating the interaction between adjacent cells in the vertical orientation, a vacuum distance of 20 Å is used. The PHONOPY package is adopted to calculate the phonon dispersion of the structures and verify their dynamic stability.³⁷

In 2D materials, the carrier mobility can be calculated by using the deformation potential (DP) theory³⁸ and given by the expression:

$$\mu_{\rm 2D} = \frac{eh^3 C_{\rm 2D}}{(2\pi)^3 k_{\rm B} T m_{\rm e}^* m_{\rm d} E_{\rm l}^2} \tag{1}$$

where m_e^* is the carrier effective mass, and m_d is the carrier average effective mass defined by $m_d = \sqrt{m_{ex}^* m_{ey}^*}$. *T* is the temperature, which is set to be 300 K in our calculations. E_1 represents the deformation potential constant defined as $E_1 = \Delta E / (\Delta l_x / l_x)$. ΔE is the energy change of the *i*th band under proper structure compression or dilatation, l_x is the lattice constant along the deformation direction and Δl_x is the amount of the deformation. C_{2D} is the elastic modulus of the longitudinal strain in the propagation directions of the longitudinal acoustic wave given by $(E - E_0)/S_0 = C_{2D}\delta^2/2$, where *E* is the total energy and S_0 is the area of the cell and δ is the applied uniaxial strain.

3. Results and discussion

3.1 Geometric structures

By performing global structure search, we obtain some lowenergy structures of 2D MN_2 (M = Pt, Pd). Among them, three energetically most stable isomers are displayed in Fig. 1, where the relative energies of the structures are also listed. The ground-state structures of 2D PdN_2 and PtN_2 are shown in the bottom panel of Fig. 1. They both have tetragonal structures and P4/mbm symmetry (space group no. 127). From the top views of the structures, one can see that the MN_2 monolayers are composed entirely of pentagons, which form a Cairo pentagonal tiling,³⁹ thus the monolayers are termed penta- MN_2 . While the side views show that the penta- MN_2 monolayers



Fig. 1 The geometrical structures of low-lying (a) PdN_2 and (b) PtN_2 and their relative energy. The total energy of the lowest-energy structure (the bottom panel) is set as 0 eV.

are in ideal planar forms which are rare in previously reported pentagonal structures. The optimized lattice constants of penta-PdN₂ are a = b = 4.873 Å, while those of penta-PtN₂ are a = b = 4.826 Å. In penta-MN₂, all N atoms are in dimers and form the N–N bonds. The N–N bond lengths in penta-PdN₂ and penta-PtN₂ are 1.225 Å and 1.260 Å, respectively, both showing the double bond characters. Specifically in penta-MN₂ sheets, the planar geometry structures and the bond angles $\theta_{N-M-N} = 90^{\circ}$ and $\theta_{N-N-M} = 120^{\circ}$ indicate the square hybridization configurations of M atoms and the regular triangle hybridization configurations of N atoms.

3.2 Stability

To evaluate the energetic stability, we calculate the cohesive energy of penta-MN₂ by following the formula: $E_{\rm coh} = (2E_{\rm M} + 4E_{\rm N} - E_{\rm MN_3})/6$ $(E_{\rm M}, E_{\rm N}, \text{ and } E_{\rm MN_2}$ are the total energies of a single M atom, a single N atom, and one unit cell of the penta-MN₂ monolayer, respectively). The calculated cohesive energies of penta-PdN₂ and penta-PtN₂ are 4.37 and 5.01 eV per atom, respectively. Using the same calculation methods, we also calculate the cohesive energies of pyrite PdN2 and PtN2, which have the buckled pentagonal structures and have been synthesized experimentally.40-42 The calculated results are 4.24 and 4.87 eV per atom for pyrite PdN₂ and PtN₂, from which one finds that penta- MN_2 are energetically more stable than pyrite MN_2 . In order to evaluate the dynamic stability, we also calculate the phonon dispersion of penta-MN₂, with results shown in Fig. 2(a and b). For both of penta-PdN₂ and penta-PtN₂, there are no imaginary modes in the entire Brillouin zone, demonstrating that the penta-MN₂ monolayers are dynamically stable.



Fig. 2 (a and b) Phonon band structures of penta-PdN₂ and penta-PdN₂, respectively. (c) Variation of the total potential energy of penta-PdN₂ with simulation time during AIMD simulation at 700 K and (d) that of penta-PtN₂ at 2000 K. The insets are the top and side views of the geometrical structures at the end of simulation.

We then perform ab initio molecular dynamics (AIMD) simulations to study the thermal stability of penta-MN₂. The $3 \times 3 \times 1$ supercells are constructed to reduce the constraint of periodic boundary conditions. For penta-PdN₂, the simulations are carried out at a temperature of 700 K, for 6 picoseconds (ps) with a time step of 1 femtosecond (fs). The variations of the total potential energies for the $3 \times 3 \times 1$ penta-PdN₂ supercells with respect to simulation time are plotted in Fig. 2(c). We can see that the average values of the total potential energy remain nearly constants during the entire simulations, confirming that penta-MN₂ are thermally stable at 700 K. However, when we increase the temperature to 900 K, the structure is found to be seriously disrupted. It suggests that penta-PdN₂ has a melting point between 700 and 900 K. Much more interesting is that, using the same method, penta-PtN2 can withstand temperatures as high as 2000 K (see Fig. 2(d)), and it has a melting point between 2000 and 2500 K. Like the case of other metal nitrides such as IrN₂ and OsN₂,⁴³ penta-PtN₂ exhibits potential as a highly refractory material.

It is necessary to estimate the effect of lattice distortion on structural stability as well. Therefore, we calculate the linear elastic constants to investigate the mechanical stability of penta-MN₂ under small lattice distortion. The elastic constants are obtained by applying the finite distortion method⁴⁴ and the results are summarized in Table 1. Here we use the standard

Table 1 Elastic constants C and in-plane Young's modulus E in the unit of N m⁻¹ and Poisson's ratio ν of penta-MN₂

Structure	C ₁₁	C_{22}	C_{12}	C_{66}	Ε	ν
Penta-PdN ₂	129.2	129.2	16.9	28.9	127	0.13
Penta-PtN ₂	227.7	227.7	40.2	42.2	220	0.18

Voigt notation⁴⁵ and the elastic constants C_{11} , C_{22} , C_{12} , and C_{66} are components of the elastic modulus tensor, corresponding to the second partial derivative of strain energy with respect to strain (all other components are strictly zero for 2D structures). According to Born–Huang criteria,⁴⁶ for a mechanically stable 2D sheet, its elastic constants need to satisfy $C_{11}C_{22} - C_{12}^2 > 0$, $C_{66} > 0$. From the results in Table 1, the elastic constants of penta-PdN₂ and penta-PtN₂ both meet the criteria, confirming that the penta-MN₂ monolayers are mechanically stable.

3.3 Mechanical properties

With the formula $E = (C_{11}^2 - C_{12}^2)/C_{11}$, we obtain the in-plane Young's moduli of penta-MN₂, which are shown in Table 1 as well. The Young's modulus of penta-PtN₂ is 220 N m⁻¹, close to 271 N m⁻¹ of the *h*-BN monolayer⁴⁵ and 263.8 N m⁻¹ of pentagraphene,⁸ indicating the good in-plane stiffness of penta-PtN₂. Although the Young's modulus of penta-PdN₂ (127 N m⁻¹) is smaller than that of penta-PtN₂, it is larger than those of the MoS_2 monolayer (120 N m⁻¹), germanene (42 N m⁻¹) and silicene (61 N m⁻¹).^{47,48} The high in-plane stiffness implies the strong bonding in penta-MN₂, which is beneficial to the structure stability. In addition, we also calculate the Poisson's ratio of penta-MN₂ by $\nu = C_{12}/C_{11}$, and present the results in Table 1. Besides, the ideal strength is also a very important mechanical property of a nanomaterial. Thus, we apply various biaxial tensile strains to the monolayers and calculate the corresponding stress to study the ideal strength of penta-MN₂. The calculated results are plotted in Fig. 3(a and b), which show that the strain at the maximum stress is 17.5% for penta-PdN₂ and 15.0% for penta-PtN2. The high in-plane Young's modulus and high ideal strength indicate that the penta-MN₂ monolayers exhibit excellent mechanical properties.

3.4 Electronic properties

To study the charge distribution of penta- MN_2 , we calculate the deformation charge density which is defined as the total charge density with the contribution of isolated M and N atoms being subtracted. The slices on the (001) plane are shown in Fig. 4(a and b), where the blue and red regions represent the depletion and accumulation of charge, respectively. It is obvious that the electrons transfer from M to N atoms in penta- MN_2 since M is less electronegative as compared with N. Furthermore, the



Fig. 3 Stress-strain relationship of (a) penta-PdN₂ and (b) penta-PtN₂ under biaxial tensile strain. The black arrows denote the strain at the maximum stress.



Fig. 4 In-plane deformation charge density slices of (a) penta-PdN₂ and (b) penta-PtN₂, where the blue and red regions represent depletion and accumulation of charge, respectively. The units of colour bar both are e Å⁻³. (c and d) are ELF slices of penta-PdN₂ and penta-PtN₂ with slices crossing the structure plane.

Bader charge analysis^{49–51} shows that each Pd (Pt) atom transfers 0.66 (0.76) e to each N₂ dimer, consistent with the results of deformation charge density.

In addition, to get the bonding feature of penta- MN_2 , we also perform the electron localization function (ELF) analysis, which is widely used to analyze the spatial distribution of electrons. ELF is defined as:

$$ELF = \frac{1}{1 + (D/D_h)^2}$$
 (2)

$$D = \frac{1}{2} \sum_{i} |\nabla \Phi_{i}|^{2} - \frac{1}{8} \frac{|\nabla \rho|^{2}}{\rho}$$
(3)

$$D_{\rm h} = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} \tag{4}$$

where Φ_i is the Kohn–Sham orbital and ρ is the local density. The value of ELF is renormalized to be in the range of 0.0 to 1.0, where 0.0 represents a very low charge density, while 0.5 and 1.0 represent delocalized and localized electrons, respectively. Fig. 4(c and d) show that the electrons are localized on the N–N bonds, suggesting the strong covalent bonding in the N₂ dimer. In contrast, the electrons on the N–M bonds are localized around N atoms while the electron density is very low near M atoms, showing a feature of ionic bonding.⁵² These results coincide with the structural characteristics of penta-MN₂, which are composed of a N₂ dimer and a transition metal ionic center.

We then calculate the electronic band structures of penta- MN_2 to explore the electronic properties. The PBE results for penta-PdN₂ and penta-PtN₂ are plotted in Fig. 5 and 6, respectively. It is clear that there is no gap between the valence and conduction bands of penta-PdN₂, demonstrating its metallic character. However, the band structures of penta-PtN₂ show



Fig. 5 Electronic band structures and orbital-weighted electronic band structures of penta-PdN₂. The color bar indicates the weight of atomic orbital contribution to the band structures. The inset is the detail of band structures near the Fermi level at M point.

that it is a direct bandgap semiconductor with a small band gap of 75 meV. The valance band maximum (VBM) and conduction band minimum (CBM) are both located at the M point of the first Brillouin zone.

To better understand the electronic properties of penta- MN_{2} , their orbital hybridization forms are studied. The atomic orbital contributions to the band structures of penta-PdN₂ and penta-PtN₂ are shown in Fig. 5 and 6. The ground state electronic configuration of an isolated N₂ dimer is $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4$. Our results show that for both of penta-PdN₂ and penta-PtN₂, the occupied electronic bands near the Fermi level are mainly contributed by d orbitals of M atoms, because these orbitals have higher energy and transfer electrons to N-N dimers, and they coordinate with unoccupied orbitals of N-N. Meanwhile, the electronic bands in the energy range of -5 to -3 eV for penta-PdN₂ and -4 to -2 eV for penta-PtN₂ are contributed by d orbitals of M atoms with slight contributions from the p orbitals of N atoms, suggesting that d orbitals of M atoms can hybridize with the π_{2p} of N–N dimers. Also, the deeper occupied bands in the energy range from -8 to -6 eV are mostly contributed by N-N dimers because their energies are much lower than that of the M-d states.

3.5 Carrier mobility

Besides the mechanical and electronic properties, the carrier mobility is also a significant factor to determine the performance of a semiconductor. By using the acoustic-phononlimited scattering model, we calculate the carrier mobility of



Fig. 6 Electronic band structures of and orbital-weighted electronic band structures of penta-PtN₂. The color bar indicates the weight of atomic orbital contribution to the band structures. The inset is the detail of band structures near the Fermi level at M point.

Table 2 Effective mass (m^*), deformational potential constant (E_1), 2D elastic modulus (C_{2D}) and carrier mobility (μ) for electrons and holes of penta-PtN₂

Carrier	type	m^*/m_0	E_1 (eV)	C_{2D} (J m ⁻²)	$\mu (10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$
PtN ₂	e h	0.118 0.198	$\begin{array}{c} 1.401 \\ 1.391 \end{array}$	227.7 227.7	219 132

penta-PtN₂. Due to the tetragonal symmetry of penta-PtN₂, the carrier mobility along *x* and *y* directions is isotropic. All the calculated results containing effective mass, deformational potential constants, 2D elastic modulus and carrier mobility are summarized in Table 2. We can see that the effective mass of electron and hole are 0.118 m_0 and 0.198 m_0 for penta-PtN₂. According to equation (a), the light effective mass and high 2D elastic modulus lead to ultrahigh carrier mobilities ($\mu_e = 219 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 132 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) which are higher than that of phosphorene (1–26 × 10³ cm² V⁻¹ s⁻¹). and even are close to that of graphene ($\sim 200 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The ultrahigh carrier mobility allows penta-PtN₂ to be of potential application in electronic devices.

4. Conclusions

In summary, by using the CALYPSO code, we obtain the 2D ground-state structures of MN_2 (M = Pd, Pt), which are composed entirely of pentagons. DFT calculations confirm their dynamical, thermal and mechanical stabilities. Moreover, compared with

the experimentally synthesized pyrite MN₂, the penta-MN₂ monolayers show several distinct characteristics: (1) penta-MN₂ monolayers are more stable than the pyrite structures in energy; (2) penta-MN₂ show high melting point. Particularly, penta-PtN₂ can withstand the temperature over 2000 K before it breaks down; (3) penta-MN₂ possess high in-plane Young's modulus and high ideal strength; (4) penta-PtN₂ has ultrahigh carrier mobility, with the values of $\mu_e = 219 \times 10^3$ cm² V⁻¹ s⁻¹, $\mu_h = 132 \times 10^3$ cm² V⁻¹ s⁻¹, which are higher than those of phosphorene and comparable with graphene. These excellent properties of penta-MN₂ imply their potential applications in high refractory materials and nanoscale electronic devices. The present study would deepen our understandings on the diversity of geometries and properties of 2D metal nitrides.

Conflicts of interest

There are no conflicts to declare.

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References

- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
- 2 C. Zhi, Y. Bando, C. Tang, H. Kuwahara and D. Golberg, *Adv. Mater.*, 2009, **21**, 2889–2893.
- 3 H. Liu, Y. Du, Y. Deng and P. D. Ye, *Chem. Soc. Rev.*, 2015, 44, 2732–2743.
- 4 M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi and M. W. Barsoum, *ACS Nano*, 2012, **6**, 1322–1331.
- 5 K. F. Mak, C. Lee, J. Hone, J. Shan and T. F. Heinz, *Phys. Rev. Lett.*, 2010, **105**, 136805.
- 6 S. Cahangirov, M. Topsakal, E. Akturk, H. Sahin and S. Ciraci, *Phys. Rev. Lett.*, 2009, **102**, 236804.
- 7 C. L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *Appl. Phys. Express*, 2012, 5, 045802.
- 8 S. H. Zhang, J. Zhou, Q. Wang, X. S. Chen, Y. Kawazoe and P. Jena, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 2372–2377.
- 9 P. Urbankowski, B. Anasori, T. Makaryan, D. Er, S. Kota, P. L. Walsh, M. Zhao, V. B. Shenoy, M. W. Barsoum and Y. Gogotsi, *Nanoscale*, 2016, 8, 11385–11391.
- M. Khazaei, M. Arai, T. Sasaki, C.-Y. Chung, N. S. Venkataramanan, M. Estili, Y. Sakka and Y. Kawazoe, *Adv. Funct. Mater.*, 2013, 23, 2185–2192.

- 11 I. R. Shein and A. L. Ivanovskii, *Comput. Mater. Sci.*, 2012, 65, 104–114.
- 12 Y. Xie and P. R. C. Kent, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 235411.
- 13 G. Gao, G. Ding, J. Li, K. Yao, M. Wu and M. Qian, *Nanoscale*, 2016, **8**, 8986–8994.
- M. Khazaei, A. Ranjbar, M. Ghorbani-Asl, M. Arai, T. Sasaki,
 Y. Liang and S. Yunoki, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2016, **93**, 205125.
- 15 X. Zhang, Z. Zhang, X. Zhao, D. Wu, X. Zhang and Z. Zhou, J. Mater. Chem. A, 2017, 5, 2870–2875.
- 16 G. M. Veith, A. R. Lupini, L. Baggetto, J. F. Browning, J. K. Keum, A. Villa, L. Prati, A. B. Papandrew, G. A. Goenaga, D. R. Mullins, S. E. Bullock and N. J. Dudney, *Chem. Mater.*, 2013, 25, 4936–4945.
- 17 C. Zhang, J. Liu, H. Shen, X.-Z. Li and Q. Sun, *Chem. Mater.*, 2017, **29**, 8588–8593.
- 18 S. Gong, C. Zhang, S. Wang and Q. Wang, J. Phys. Chem. C, 2017, 121, 10258–10264.
- 19 J. Li, X. Fan, Y. Wei, H. Liu, S. Li, P. Zhao and G. Chen, *Sci. Rep.*, 2016, 6, 33060.
- 20 C. Zhang and Q. Sun, J. Phys. Chem. Lett., 2016, 7, 2664–2670.
- 21 F. Wu, C. Huang, H. Wu, C. Lee, K. Deng, E. Kan and P. Jena, *Nano Lett.*, 2015, **15**, 8277–8281.
- 22 J. I. Cerda, J. Slawinska, G. Le Lay, A. C. Marele, J. M. Gomez-Rodriguez and M. E. Davila, *Nat. Commun.*, 2016, 7, 13076.
- 23 J. Chen, G. Schusteritsch, C. J. Pickard, C. G. Salzmann and A. Michaelides, *Phys. Rev. Lett.*, 2016, **116**, 025501.
- 24 X. Li, Y. Dai, M. Li, W. Wei and B. Huang, *J. Mater. Chem. A*, 2015, **3**, 24055–24063.
- 25 A. Lopez Bezanilla and P. B. Littlewood, J. Phys. Chem. C, 2015, **119**, 19469–19474.
- 26 A. D. Oyedele, S. Yang, L. Liang, A. A. Puretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A. W. Ghosh, Z. Liu, C. M. Rouleau, B. G. Sumpter, M. F. Chisholm, W. Zhou, P. D. Rack, D. B. Geohegan and K. Xiao, *J. Am. Chem. Soc.*, 2017, 139, 14090–14097.
- 27 Y. Wang, Y. Li and Z. Chen, J. Mater. Chem. C, 2015, 3, 9603–9608.
- 28 M. Yagmurcukardes, H. Sahin, J. Kang, E. Torun, F. M. Peeters and R. T. Senger, J. Appl. Phys., 2015, 118, 104303.
- 29 S. Zhang, J. Zhou, Q. Wang and P. Jena, *J. Phys. Chem. C*, 2016, **120**, 3993–3998.
- 30 Y. Wang, J. Lv, L. Zhu and Y. Ma, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 82, 094116.
- 31 Y. Wang, M. Miao, J. Lv, L. Zhu, K. Yin, H. Liu and Y. Ma, J. Chem. Phys., 2012, 137, 224108.

- 32 G. Kresse and J. Furthmuller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 11169–11186.
- 33 G. Kresse and D. Joubert, Phys. Rev. B: Condens. Matter Mater. Phys., 1999, 59, 1758–1775.
- 34 P. E. Blochl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, 50, 17953–17979.
- 35 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 36 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, 13, 5188–5192.
- 37 A. Togo and I. Tanaka, Scr. Mater., 2015, 108, 1-5.
- 38 J. Bardeen and W. Shockley, Phys. Rev., 1950, 80, 72-80.
- 39 E. Ressouche, V. Simonet, B. Canals, M. Gospodinov and V. Skumryev, *Phys. Rev. Lett.*, 2009, **103**, 267204.
- 40 J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira and A. J. Nelson, *Science*, 2006, 311, 1275–1278.
- 41 J. C. Crowhurst, A. F. Goncharov, B. Sadigh, J. M. Zaug, D. Aberg, Y. Meng and V. B. Prakapenka, *J. Mater. Res.*, 2008, 23, 1–5.
- 42 D. Aberg, B. Sadigh, J. Crowhurst and A. F. Goncharov, *Phys. Rev. Lett.*, 2008, **100**, 095501.
- 43 A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.*, 2006, **96**, 155501.
- 44 Y. Le Page and P. Saxe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 104104.
- 45 R. C. Andrew, R. E. Mapasha, A. M. Ukpong and N. Chetty, Phys. Rev. B: Condens. Matter Mater. Phys., 2012, 85, 125428.
- 46 J. Wang, S. Yip, S. R. Phillpot and D. Wolf, *Phys. Rev. Lett.*, 1993, **71**, 4182–4185.
- 47 R. John and B. Merlin, *Cryst. Struct. Theory Appl.*, 2016, 5, 43–55.
- 48 Q. Peng and S. De, Phys. Chem. Chem. Phys., 2013, 15, 19427-19437.
- 49 G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.*, 2006, 36, 354–360.
- 50 E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, J. Comput. Chem., 2007, 28, 899–908.
- 51 W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.
- 52 A. Savin, R. Nesper, S. Wengert and T. F. Fässler, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1808–1832.
- 53 J.-H. Chen, C. Jang, S. Xiao, M. Ishigami and M. S. Fuhrer, *Nat. Nanotechnol.*, 2008, **3**, 206.
- 54 R. Fei and L. Yang, Nano Lett., 2014, 14, 2884-2889.
- 55 J. Qiao, X. Kong, Z. X. Hu, F. Yang and W. Ji, *Nat. Commun.*, 2014, 5, 4475.