Two-dimensional wide-band-gap II–V semiconductors with a dilated graphene-like structure

Xue-Jing Zhang¹,² and Bang-Gui Liu¹,²

¹ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
² School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, People’s Republic of China

E-mail: bgliu@iphy.ac.cn

Received 15 July 2016, revised 13 September 2016
Accepted for publication 22 September 2016
Published 28 October 2016

Abstract
Since the advent of graphene, two-dimensional (2D) materials have become very attractive and there is growing interest in exploring new 2D materials beyond graphene. Here, through density-functional theory (DFT) calculations, we predict 2D wide-band-gap II–V semiconductor materials of M₃X₂ (M = Zn, Cd and X = N, P, As) with a dilated graphene-like honeycomb structure. In this structure the group-V X atoms form two X-atomic planes symmetrically astride the centering group-IIB M atomic plane. Our DFT calculation shows that 2D Zn₃N₂, Zn₃P₂ and Zn₃As₂ have direct band gaps of 2.87, 3.81 and 3.55 eV, respectively, and 2D Cd₃N₂, Cd₃P₂ and Cd₃As₂ exhibit indirect band gaps of 2.74, 3.51 and 3.29 eV, respectively. Each of the six 2D materials is shown to have effective carrier (either hole or electron) masses down to 0.03–0.05 m₀. The structural stability and feasibility of experimental realization of these 2D materials has been shown in terms of DFT phonon spectra and total energy comparison with related existing bulk materials. On the experimental side, there already are many similar two-coordinate structures of Zn and other transition metals in various organic materials. Therefore, these 2D semiconductors can enrich the family of 2D electronic materials and may have promising potential for achieving novel transistors and optoelectronic devices.

Keywords: two-dimensional semiconductor, wide band gap, first-principles calculation

1. Introduction
Since graphene was created, two-dimensional (2D) materials have been attracting a lot of attention due to their unique and important properties and promising applications in novel devices [1–9]. Graphene can host massless Dirac Fermions weakly sensitive to backscattering and travelling at very high speed over very wide distances at room temperature [6]. While it has superior performance, its zero-gap behavior is an obstacle to switching current on and off in field-effect transistors (FETs), being inconsistent with modern semiconductor technology [3, 4, 8, 9]. As for other 2D compounds, hexagonal boron nitride (h-BN) has a wide gap of 5.5 eV [10] and monolayer MoS₂, black phosphorene and monolayer As have band gaps of 1.9, 1.45 and 2.49 eV [11–13], respectively. Monolayer MoS₂ FETs have been demonstrated with a carrier mobility of 200 cm² V⁻¹ s⁻¹ at room temperature, current on/off ratios of 1 × 10⁸ and ultralow standby power dissipation [14]. Black phosphorene, arranged in a honeycomb puckered lattice, presents a high electron mobility of 1000 cm² V⁻¹ s⁻¹ and high in-plane anisotropy [12, 15]. These 2D materials can be applied in nanoelectronic devices. However, 2D semiconductors with band gaps between 2.5 and 5.5 eV should be also useful for future applications.
Here, we predict six 2D II–V wide-band-gap semiconductors M$_i$X$_2$ (M = Zn, Cd and X = N, P, As) through systematic density-functional theory (DFT) calculations. The dilated graphene-like honeycomb structures of these 2D materials are formed according to normal valence rules that each group-IIB M atom is surrounded by two group-V X atoms and each X is surrounded by three M atoms. Their structural stability and feasibility of experimental realization has been investigated in terms of DFT structural optimization, phonon spectra and total energy comparison with related existing 3D materials. On the experimental side, similar two-coordinate structures of metallic atoms have been observed in various organic materials [16, 17]. Our DFT study shows that these 2D semiconductors have wide band gaps ranging from 2.74 to 3.81 eV and most of their effective carrier masses are from 0.03$m_0$ to 0.05$m_0$. They may be potential materials for achieving novel transistors with high on/off ratios and optoelectronic devices working under violet or UV light. More detailed results will be presented in the following.

2. Computational details

Our first-principles calculations are performed with the projector-augmented wave method as implemented in the Vienna *ab-initio* simulation package (VASP) [18, 19]. The valence-electron configuration of group-IIB M and group-V X are $d^{10} \, s^2$ and $s^2 \, p^5$, respectively. We use a slab model to simulate the 2D materials by adding a 15 Å thick vacuum layer to ensure decoupling between different tri-layers (consisting of one M layer and two X layers) in the calculational model. A Γ-centered $9 \times 9 \times 1$ k-grid is employed and the plane wave energy cutoff is set to 500 eV. Furthermore, the convergence criterion for the total energy is chosen to be $10^{-5}$ eV. The cell geometry and the ionic positions are both optimized until the Hellmann–Feynman forces on each atom become less than 0.01 eV Å$^{-1}$. For structure optimization, we use the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) [20] for the exchange-correlation potential. The electronic structures (DOSs and bands) are calculated by both PBE and hybrid functional HSE06 with HFSCREEN = 0.2. [21] We take IMIX = 1 for the mixing parameter of the HSE06 functional. The latter is used to improve the theoretical description of the electronic structures, especially the semiconductor gaps.

Phonon spectra are calculated based on Phonopy [22, 23]. The size of a perfect supercell structure is $2 \times 2 \times 1$ with 8 X atoms and 12 M atoms (X = N, P and As; M = Zn and Cd). The force constants in real space are calculated by running VASP with IBRION = 8 and NSW = 1 in terms of density-functional perturbation theory (DFPT). No additional correction is made. The energy cutoff and k-grid are the same as those used in calculating electronic structures. The coordinates of the high-symmetry k-points are M (0.5, 0, 0), G (0, 0, 0), and K (0.333, 0.333, 0).

### Table 1. Calculated 2D lattice constant $a$, buckling parameter $d$, and M–X bond length $b_{MX}$ of the 2D II–V materials of M$_i$X$_2$ (M = Zn, Cd and X = N, P, As).

| System   | $a$ (Å) | $d$ (Å) | $b_{MX}$ (Å) | $\Delta E$ (eV) |
|----------|----------|----------|---------------|-----------------|
| Zn$_3$N$_2$ | 6.157    | 0.427    | 1.828         | 0.207           |
| Zn$_3$P$_2$ | 6.418    | 1.291    | 2.258         | 0.259, 0.075    |
| Zn$_3$As$_2$ | 6.484    | 1.453    | 2.370         | 0.211, 0.054    |
| Cd$_3$N$_2$ | 6.745    | 0.628    | 2.063         | 0.207           |
| Cd$_3$P$_2$ | 7.121    | 1.344    | 2.456         | 0.219, 0.029    |
| Cd$_3$As$_2$ | 7.185    | 1.505    | 2.563         | 0.185, 0.032    |

3. Results and discussion

3.1. Structures and stability

To construct reasonable 2D structures for M$_i$X$_2$ (M = Zn, Cd and X = N, P, As), the valences of group-IIB M and group-V X must be taken into account. First, we can assume that M and X are in the same plane and form a 2D dilated-honeycomb structure (space group P6/mmm), in which each M has two X neighbors and each X has three M ones. This structure has the same rotational symmetry as graphene, but the C atom at the hexagonal vertex is replaced by X atom and there is an M atom at the middle of each dilated hexagonal edge of the honeycomb unit. There are six M and six X atoms in the hexagon of the honeycomb unit. Unfortunately, this structure is unstable against a buckling of X atoms from the plane. The buckling, keeping the three-fold rotational symmetry, makes two X planes remain symmetrically astride the M plane and it can be parameterized with the distance $d$ between the M plane and both of the two X planes. This buckling makes the space group reduce to P3m1, but lowers the total energy by 0.042, 1.027, 1.419, 0.215, 1.076 and 1.476 eV per formula unit for the Zn$_3$N$_2$, Zn$_3$P$_2$, Zn$_3$As$_2$, Cd$_3$N$_2$, Cd$_3$P$_2$ and Cd$_3$As$_2$, respectively. With the optimized $d$ value and the 2D crystal lattice constant $a$, we can calculate the M–X bond length $b_{MX}$. We summarize the values of $a$, $d$ and $b_{MX}$ values in table 1, and present the 2D crystal structure in figures 1(a)–(c). It is clear that this 2D structure can be seen as a dilated, buckled honeycomb structure like graphene. To better demonstrate the effect of the buckling, we present the total energy of the 2D Cd$_3$As$_2$ as a function of $d$ in figure 1(d) because this case has the largest buckling. Furthermore, we have calculated the phonon spectra in all six cases. The phonon spectra of 2D Cd$_3$N$_2$ as a representative are presented in figure 1(e). The lowest three bands are phonon dispersion curves of two in-plane and one out-of-plane acoustic modes, and the other 12 describe the optical modes. The phonon spectra of the other five materials are similar. Because there is none of the six cases have a soft phonon mode, there is no kinetic instability for any of the six 2D M$_i$X$_2$ (M = Zn, Cd and X = N, P, As) materials [24].
To analyze the energy stability of the 2D M₃X₂ (M = Zn, Cd and X = N, P, As) and their feasibility of being experimentally synthesized we need to compare their total energies with those of corresponding 3D bulk materials that have already been experimentally realized, in addition to checking the phonon spectra. These 3D bulk materials assume different crystal structures with space groups: Ia\̅3 (for Zn₃N₂ and Cd₃N₂) [25–27], P4\̅/nmc (for Zn₃P₂, Cd₃P₂, Zn₃As₂ and Cd₃As₂) [28–33] and P4\̅32 (for Zn₃P₂, Cd₃P₂, Zn₃As₂ and Cd₃As₂) [34]. We have calculated the energy differences per atom, ΔE, between the 2D M₃X₂ (M = Zn, Cd and X = N, P, As) and the corresponding 3D crystal materials, and present the calculated results in table 1. As for both Zn₃N₂ and Cd₃N₂, the ΔE value is an energy difference per atom of 0.21 eV. For both Cd₃P₂ and Cd₃As₂, the energy difference per atom is 0.03 eV, which is the smallest value obtained. The largest value for the energy difference per atom is 0.26 in the case of Zn₃P₂. Therefore, these small energy differences, ranging from 0.03 eV to 0.26 eV, with the phonon spectra free of any soft mode, imply that these 2D materials could be realized experimentally.

3.2. Electronic structures

We present in figure 2 the electronic band structures of 2D M₃X₂ (M = Zn, Cd and X = N, P, As) calculated with PBE. It is clear that Zn₃N₂ is a direct-band-gap semiconductor with a band gap of 1.83 eV at the Γ point of the Brillouin zone, while Zn₃P₂ and Zn₃As₂ are direct-band-gap semiconductors with band gaps of 3.00 and 2.84 eV at the M point. However, the 2D Cd₃X₂ (X = N, P, As) are indirect-band-gap semiconductors with band gaps of 1.83, 2.80 and 2.61 eV, with their valence band maxima (VBM) at the M point and their conduction band minima (CBM) at the Γ point. The total DOS of the 2D M₃X₂ (M = Zn, Cd and X = N, P, As) are presented in figure 3. The energy distribution of the total DOS varies with anion X (X = N, P, As). The band gap of the Zn₃X₂ (X = N, P, or As) is slightly larger than that of the corresponding Cd₃X₂, respectively.

Figure 4 shows the partial DOSs of N and Zn in 2D Zn₃N₂, those of N and Cd in 2D Cd₃N₂, and those of As and Cd in 2D Cd₃As₂. It can be seen that the VBM of these M₃X₂...
For 2D Zn$_3$N$_2$, the N p states dominate between $-1.7 \text{ eV}$ and 0 eV and the p$_x$ and p$_y$ states hybridize with Zn d and s states in the window from $-3.42 \text{ eV}$ to $-1.38 \text{ eV}$. The N p dominant bands in Cd$_3$N$_2$ are narrower than those in Zn$_3$N$_2$. Near the VBM (from $-0.25 \text{ eV}$ to 0 eV) of 2D Cd$_3$N$_2$, there is a strong peak of the p$_z$ state with small admixtures of p$_x$ and p$_y$ states. The N p$_x$ and p$_y$ states hybrid with Cd s and d, as demonstrated in the energy window from $-2.7 \text{ eV}$ to $-1.6 \text{ eV}$. In 2D Cd$_3$As$_2$, As p states dominate between $-0.8$ and 0 eV and hybridize with Cd s states (Cd d states are too small to need to be shown here) between $-2.3$ and $-1.7 \text{ eV}$. Our calculations also show that the partial DOSs of 2D Zn$_3$P$_2$, Cd$_3$P$_2$ and Zn$_3$As$_2$ are similar to those of 2D Cd$_3$As$_2$.

### 3.3. Improved electronic properties

It is well known that the GGA usually underestimates semiconductor gaps. We use the HSE06 functional \cite{21} to achieve a better description of band gaps in 2D semiconductors. The electronic band structures of the six 2D M$_3$X$_2$ (M = Zn, Cd and X = N, P, As) calculated with HSE06 are presented in figure 5. Clearly, the HSE06 functional leads to wider band gaps of 2.87, 3.81, 3.55, 2.74, 3.51 and 3.29 eV than those obtained with PBE for 2D Zn$_3$N$_2$, Zn$_3$P$_2$, Zn$_3$As$_2$, Cd$_3$N$_2$, Cd$_3$P$_2$, and Cd$_3$As$_2$, respectively. These band gaps are wider than those of successfully fabricated MoS$_2$ and the recently theoretically studied As monolayer \cite{13, 35}. For monolayer MoS$_2$ and black phosphorene, experimental gaps (1.9 and 1.45 eV) \cite{11, 12} are substantially larger than the GGA values (1.6 and 0.91 eV), but a smaller than the HSE results (2.05 and 1.51 eV) \cite{37–39}, respectively. Therefore, we believe that for these six 2D M$_3$X$_2$ materials, the real gaps should also be a little smaller than the corresponding HSE results.
Using the HSE06 hybrid functional, we have also calculated effective carrier masses \( m^* \) of the 2D \( M_3X_2 \) (\( M = \text{Zn, Cd} \) and \( X = \text{N, P, As} \)) at the VBM and CBM. The calculated results are summarized in Table 2. For 2D Zn\(_3\)N\(_2\), the calculated effective carrier masses \( m^*_K \) and \( m^*_M \) are 0.24\( m_0 \) and 0.26\( m_0 \) (\( m_0 \) is the mass of a free electron), which are close to those of arsenene (\( m^*_K = 0.23m_0 \), \( m^*_M = 0.29m_0 \)) and antimonene (\( m^*_K = 0.20m_0 \), \( m^*_M = 0.24m_0 \)) [13] and smaller than those of monolayer Mo\(_2\)S\(_2\) (\( m^* = 0.48m_0 \)) [36]. For 2D Cd\(_3\)N\(_2\), the calculated hole effective mass \( m^*_{M} \) is 0.37\( m_0 \). However, for 2D Zn\(_3\)P\(_2\), Zn\(_3\)As\(_2\), Cd\(_3\)P\(_2\) and Cd\(_3\)As\(_2\), the hole effective masses \( m^*_{M} \) are 0.04\( m_0 \), 0.03\( m_0 \), 0.03\( m_0 \) and 0.03\( m_0 \), respectively, and these may be able to cause high carrier mobilities. For Zn\(_3\)N\(_2\) and Cd\(_3\)N\(_2\), the calculated electron effective masses, 0.03\( m_0 \), are much smaller than the hole effective masses, but for 2D Zn\(_3\)P\(_2\) and Zn\(_3\)As\(_2\), the electron effective mass, 0.17\( m_0 \), and 0.10\( m_0 \), are substantially larger than the hole effective mass values. As for 2D Cd\(_3\)P\(_2\) and Cd\(_3\)As\(_2\), the calculated electron effective masses, 0.05\( m_0 \) and 0.04\( m_0 \), are only slightly larger than the hole effective masses.

### 3.4. Further discussion

The cation (Zn or Cd) has a nominal valence of 2\(^+\) and the anion (N, P, or As) a nominal valence of 3\(^-\). Actually, the bond is not purely ionic—part of it is covalent: this can be shown by the non-zero weight of the filled Zn (or Cd) s state in figure 4. Consequently, the valence bands in figure 3 originate mainly from the p states of the anion and the conduction bands mainly from the s states of the cation. It can be seen by comparing figures 3 and 4 that the partial DOSs (projected in the atomic muffin tins) of the conduction bands are substantially smaller than those of the valence bands, and therefore the wave functions of the conduction bands are mainly in the interstitial region, being more extended in the real space. The incomplete transfer of the cation s electrons in 2D II–V semiconductors is partly because the cation has only two coordinates and partly because the bond includes some covalence as it does in usual II–VI semiconductors.

At this stage, however, one may ask the question: Can the 2D II–V semiconductors including two-coordinate cations (Zn or Cd) be experimentally realized? On the theoretical side, we have shown through DFT calculated phonon spectra

---

**Figure 5.** The band structures (\( E_F = 0 \) eV) calculated with the HSE06 functional [21] of the six 2D materials \( M_3X_2 \) (\( M = \text{Zn, Cd} \) and \( X = \text{N, P, As} \)) with the semiconductor gaps being indicated by the arrows.

**Table 2.** Semiconductor gaps (eV) and effective carrier mass values of the six 2D \( M_3X_2 \) (\( M = \text{Zn, Cd} \) and \( X = \text{N, P, As} \)) calculated with HSE06 [21]. The band gap values in parentheses are calculated with PBE.

| System     | Gap   | Hole mass | Electron mass |
|------------|-------|-----------|---------------|
| Zn\(_3\)N\(_2\) | 2.87 (1.83) | 0.24\( m_0 \) (\( \Gamma K \)), 0.26\( m_0 \) (\( \Gamma M \)) | 0.03\( m_0 \) |
| Zn\(_3\)P\(_2\) | 3.81 (3.00) | 0.04\( m_0 \) (\( M\Gamma \)) | 0.03\( m_0 \) (M\( \Gamma \)) |
| Zn\(_3\)As\(_2\) | 3.55 (2.84) | 0.04\( m_0 \) (\( M\Gamma \)) | 0.10\( m_0 \) (M\( \Gamma \)) |
| Cd\(_3\)N\(_2\) | 2.74 (1.83) | 0.37\( m_0 \) (\( M\Gamma \)) | 0.03\( m_0 \) |
| Cd\(_3\)P\(_2\) | 3.51 (2.80) | 0.03\( m_0 \) (M\( \Gamma \)) | 0.05\( m_0 \) |
| Cd\(_3\)As\(_2\) | 3.29 (2.61) | 0.03\( m_0 \) (M\( \Gamma \)) | 0.04\( m_0 \) |
and total energy comparison with existing 3D materials that these 2D II–V semiconductor materials are structurally stable and should be experimentally realizable, although the cation has only two coordinates. On the experimental side, it has been already shown that one Zn (and other transition metal) atom can indeed have two coordinates in various organic materials including Zn (and other transition metals) [16, 17]. Therefore, the answer is certain.

The semiconductor gaps in these 2D semiconductors are between that of h-BN and those of MoS2, black phosphorene and monolayer As [10–13]. The effective hole masses of 2D Zn3N2 and Cd3N2 are slightly less than those of 2D MoS2, antimonene and arsenene, but most of the effective carrier (either hole or electron) masses range from 0.03m0 to 0.05m0. [13, 17] Their 2D dilated honeycomb structure makes them structurally compatible with most of the promising 2D materials. Therefore, they can be used to form hybrid structures with other 2D materials in order to design novel electronic, spintronic, optoelectronic and other devices [3–9].

4. Conclusion

In summary, we have predicted six 2D wide-band-gap II–V semiconductor materials M3X2 (M = Zn, Cd and X = N, P, As) with a dilated, buckled graphene-like honeycomb structure. The structural stability and feasibility of experimental realization of these 2D materials has been shown through DFT phonon spectra and total energy comparison with related existing 3D materials. Since many similar two-coordinate structures of Zn and other metallic atoms have been observed in various organic materials [16, 17], these 2D materials should be experimentally realizable. Our DFT study has shown that Zn3N2, Zn3P2 and Zn3As2 are direct-band-gap semiconductors with band gaps of 2.87, 3.81 and 3.55 eV, but Cd3N2, Cd3P2, and Cd3As2 are indirect-band-gap semiconductors with band gaps of 2.74, 3.51 and 3.29 eV, respectively. The dilated, buckled honeycomb structure enriches the family of 2D materials. Our further DFT calculations show that the effective hole masses of 2D Zn3N2 and Cd3N2 are slightly less than that of the well-known 2D MoS2, and each of the six 2D materials has effective carrier (either hole or electron) masses down to 0.03m0 to 0.05m0, having the potential to achieve high carrier mobility. Therefore, these 2D II–V semiconductors may have promising applications in future electronic and optoelectronic devices.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (grant nos 11174359 and 11574366), by the Department of Science and Technology of China (grant no. 2016YFA0300701) and by the Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDB07000000).

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[2] Das Sarma S, Adam S, Hwang E H and Rossi E 2011 Rev. Mod. Phys. 83 407
[3] Khazaee M, Arau M, Sasaki T, Chung C-Y, Venkataramanan N S, Estili M, Sakkia Y and Kawazoe Y 2013 Adv. Funct. Mater. 23 2185
[4] Kaul A B 2014 J. Mater. Res. 29 348
[5] Ferrari A C, Bonaccorso F and Falco V 2015 Nanoscale 7 4598
[6] Roche S et al 2015 2D Mater. 2 030202
[7] Meunier V, Souza Filho A G, Barros E B and Dresselhaus M S 2016 Rev. Mod. Phys. 88 025005
[8] Bhimanapati G R et al 2015 ACS Nano 9 11509
[9] Grazianetti C, Cinquanta E and Mollie A 2016 2D Mater. 3 012001
[10] Blase X, Rubio A, Louie S G and Cohen M L 1994 Europhys. Lett. 28 335
[11] Mak K F, Changgu L, Hone J, Shan J and Heinz T F 2010 Phys. Rev. Lett. 105 136805
[12] Liu H, Neal A T, Zha Z, Luo X, Xun T, Tomanek D and Ye P D 2014 ACS Nano 8 4033
[13] Zhang S L, Zhang Y, Li Y F, Chen Z F and Zeng H B 2015 Angew. Chem. 127 3155
[14] Radislavjevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Nat. Nanotechnol 6 147
[15] Xia F, Wang H and Jia Y 2014 Nat. Commun. 5 4458
[16] Nguyen T, Panda A, Olmstead M M, Richards A F, Stender M, Brynda M and Power P P 2005 J. Am. Chem. Soc. 127 8545
[17] Hixx J, Underhill E J, Kefalidis C E, Maron L and Jones C 2015 Angew. Chem. Int. Ed. 54 10000
[18] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[19] Ploehl P E 1994 Phys. Rev. B 50 17953
[20] Peredew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[21] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207
[22] Togo A, Oba F and Tanaka I 2008 Phys. Rev. B 78 134106
[23] Baroni S, De Girolami S, Dao Corso A and Giannozzi P 2013 Rev. Mod. Phys. 75 515
[24] Li Y F, Liao Y L and Chen Z F 2014 Phys. Rev. B 59 1758
[25] Partin D E, Williams D J and Keefe M O 1997 J. Solid State Chem 132 56
[26] Futsuhara M, Yoshioka K and Takai O 1998 Thin Solid Films 322 274
[27] Karau F and Schnick W 2007 Z. Anorg. Allg. Chem. 633 223
[28] Zanin I E, Aleinikova K B, Afanasiev M M and Antipin M Y 2004 J. Struct. Chem. 45 844
[29] Zanin I E, Aleinikova K B, Afanasiev M M and Antipin M Y 2006 J. Struct. Chem. 47 78
[30] Rao D R and Nayak A 1992 J. Mater. Sci. 27 4389
[31] Lin-Chung P J 1971 Phys. Stat. Sol. B 47 33
[32] Shevchenko V Y, Marenklin S F and Pononarev V F 1977 Inorg. Mater. 13 1527
[33] Pietrassko A and Lukaszewicz K 1969 Acta Crystallogr. 25 988
[34] Passerini L 1928 Gazz. Chim. Ital. 58 655
[35] Lee Y H et al 2012 Adv. Mater. 24 2320
[36] Perryers H and Van de Walle C G 2004 Phys. Rev. Lett. 93 8888
[37] Ellis J K, Lucero M J and Scuseria G E 2011 Appl. Phys. Lett. 98 261908
[38] Ramasubramaniam A 2012 Phys. Rev. B 86 115409
[39] Qiao J S, Kong X H, Hu Z X, Yang F and Ji W 2014 Nat. Commun. 5 4475