ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

Electric field manipulation of multiple nonequivalent Dirac cones in the electronic structures of hexagonal CrB_4 sheet

Jinkun Wang(王锦坤), Yajiao Ke(柯亚娇), Qingxing Xie(谢晴兴), Yanli Li(李艳丽), Jiafu Wang(王嘉赋)

Citation: Chin. Phys. B . 2018, 27(9): 097304. **doi:** 10.1088/1674-1056/27/9/097304

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Modulating the properties of monolayer C_2N: A promising metal-free photocatalyst for water splitting

Song Yu(俞松), Yong-Chao Rao(饶勇超), Xiang-Mei Duan(段香梅)

Chin. Phys. B . 2017, 26(8): 087301. **doi:** 10.1088/1674-1056/26/8/087301

Effect of PECVD SiN_x/SiO_yN_x-Si interface property on surface passivation of silicon wafer

Xiao-Jie Jia(贾晓洁), Chun-Lan Zhou(周春兰), Jun-Jie Zhu(朱俊杰), Su Zhou(周肃), Wen-Jing Wang(王文静)

Chin. Phys. B . 2016, 25(12): 127301. **doi:** 10.1088/1674-1056/25/12/127301

Study on influences of TiN capping layer on time-dependent dielectric breakdown characteristic of ultra-thin EOT high-*k* metal gate NMOSFET with kMC TDDB simulations

Hao Xu(徐昊), Hong Yang(杨红), Wei-Chun Luo(罗维春), Ye-Feng Xu(徐烨峰), Yan-Rong Wang(王艳蓉), Bo Tang(唐波), Wen-Wu Wang(王文武), Lu-Wei Qi(祁路伟), Jun-Feng Li(李俊峰), Jiang Yan(闫江), Hui-Long Zhu(朱慧珑), Chao Zhao(赵超), Da-Peng Chen(陈大鹏), Tian-Chun Ye(叶甜春)

Chin. Phys. B . 2016, 25(8): 087305. **doi:** 10.1088/1674-1056/25/8/087305

Electronic and magnetic properties at rough alloyed interfaces of Fe/Co on Au substrates: An augmented space study

Priyadarshini Parida, Biplab Ganguli

Chin. Phys. B . 2016, 25(5): 057302. **doi:** 10.1088/1674-1056/25/5/057302

Modulating doping and interface magnetism ofepitaxial graphene on SiC(0001)

Pan Zhou(周攀) and Da-Wei He(何大伟)

Chin. Phys. B . 2016, 25(1): 017302. **doi:** 10.1088/1674-1056/25/1/017302

Electric field manipulation of multiple nonequivalent Dirac cones in the electronic structures of hexagonal CrB_4 sheet*

Jinkun Wang(王锦坤)[1], Yajiao Ke(柯亚娇)[1,†], Qingxing Xie(谢晴兴)[1], Yanli Li(李艳丽)[1], and Jiafu Wang(王嘉赋)[1,2,‡]

[1] *Department of Physics and Institute of Applied Condensed Matter Physics, School of Science, Wuhan University of Technology, Wuhan* 430070, *China*

[2] *Hubei Engineering Research Center of RF-Microwave Technology and Application, Wuhan University of Technology, Wuhan* 430070, *China*

(Received 20 July 2018; revised manuscript received 20 August 2018; published online 28 August 2018)

Two-dimensional materials with Dirac cones have significant applications in photoelectric technology. The origin and manipulation of multiple Dirac cones need to be better understood. By first-principle calculations, we study the influence of external fields on the electronic structure of the hexagonal CrB_4 sheet with double nonequivalent Dirac cones. Our results show that the two cones are not sensitive to tensile strain and out-of-plane electric field, but present obviously different behaviors under the in-plane external electric field (along the B–B direction), i.e., one cone holds while the other vanishes with a gap opening. More interestingly, a new nonequivalent cone emerges under a proper in-plane electric field. We also discuss the origin of the cones in CrB_4 sheet. Our study provides a new method on how to obtain Dirac cones by the external field manipulation, which may motivate potential applications in nanoelectronics.

Keywords: borophene, multiple Dirac cones, electric field manipulation, first-principle calculation

PACS: 73.22.–f, 71.20.Ps **DOI:** 10.1088/1674-1056/27/9/097304

1. Introduction

Atomically thick two-dimensional (2D) materials have increasingly attracted great interest since the successful preparation of graphene.[1–3] Group IV, V, and VI elements-based 2D structures also have some similar and even novel properties to graphene.[4–8] In the past few years, boron has attracted enormous attention since the orthorhombic monolayer borophene has been synthesized.[9] Researchers are widely exploring, both theoretically[10–12] and experimentally,[13–16] in constructing borophene with the honeycomb structure like graphene. Due to the problem that one boron atom has only three valence electrons distributed in four available orbitals, it is necessary to introduce some transition metal atoms with extra electrons to form a stable hexagonal lattice.[17,18] Just like most 2D materials, this structure with monolayer boron honeycombs possesses single equivalent Dirac cone in the first Brillouin zone. To date, as far as we know, electric structures with multiple nonequivalent Dirac cones have been found only in stable boron bilayers with sandwiched group VI–B elements (molybdenum,[19] chromium,[20] or wolfram[21]).

The fascinating features and potential applications of 2D materials with Dirac cones have led to further explorations on manipulating the electronic, magnetic, and transport properties of these Dirac materials by applying external fields.[22,23] The electric field, usually applied in the out-of-plane direction, may open band gaps at the Dirac points and cause other effects.[24–26] Tensile strain can also adjust the behaviors of the Dirac materials by shifting the Dirac cone to a higher energy,[27,28] tuning the Fermion velocity,[29] or opening an observable band gap.[30,31] Remarkably, in large in-plane tensile strains ($> 10\%$), a Dirac cone-like crossing at the Γ point in the band structure emerges in arsenene[32] and graphdiyne.[33] Seeing that the various effects of in-plane tensile strains result essentially from adjusting the position of the atoms on lattice, while in-plane electric fields may also do the same thing,[34] we wonder whether the sandwiched borophene with two nonequivalent Dirac cones has diverse effects under the in-plane electric field, such as the gap opening at Dirac points or the emergence of a new cone.

In this paper, using first-principle calculation method, we study the influence of in-plane electric field, with tensile strain as a comparison, on the crystal and electronic structures of the CrB_4 sheet with two nonequivalent Dirac cones. Our results show that the band structure of this 2D CrB_4 is not sensitive to tensile strains, but presents some novel properties when the external electronic fields are applied along some specific directions. We are interested in finding out the essence of this phenomenon, which can help us deeply understand the origin of massless quasi-particles and inspire us in manipulating Dirac states artificially.

*Project supported by the National Natural Sciences Foundation of China (Grant Nos. 11704294 and 11504281), the Natural Science Foundation of Hubei Province, China (Grant No. 2016CFB586), and the Fundamental Research Funds for the Central Universities, China (Grant Nos. 2017IVA078, 2018IVB017, 2017IB013, 2018IB009, and 2018IB011).

†Corresponding author. E-mail: keyajiao@whut.edu.cn

‡Corresponding author. E-mail: jasper@whut.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd

2. Computational method

The calculations were based on the density functional theory (DFT), and the geometry relaxations and electronic properties were carried out with the Castep package.[35] The exchange–correlation energy was described by the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.[36,37] A vacuum layer about 36.9 Å was used to decouple the interactions of the neighboring slabs. A Monkhorst-Pack $13 \times 13 \times 1$ k-point mesh for hexagonal cells and a $9 \times 9 \times 1$ k-point mesh for orthorhombic ones were taken for geometry optimization with a 500 eV plane-wave cutoff energy until all forces were smaller than 0.005 eV/Å and the energy converged within 2.5×10^{-6} eV. As for the calculations of the electronic properties, the k-points and the cutoff energy were consistent with that for geometry optimization. In order to study the external electric field effect, we set a series of electric fields along the out-of-plane direction and the in-plane direction, respectively, and allowed atoms to freely relax in space without symmetry constrains. The normal electric field is applied along the Z-axis, which is (001) direction. Since the directions of the B–B bond and the Cr–Cr bond are respectively equal to the directions of the X-axis and the Y-axis in Cartesian coordinate, the in-plane electric field was applied along the (100) direction and (010) direction, respectively.

3. Results and discussion

When no external field is applied, the CrB_4 crystal with double boron honeycomb layers, as shown in Figs. 1(a) and 1(b), is forming a stable planar configuration of *P6mmm* space group with the lattice constant $a = 2.89$ Å after total energy optimization. To verify the kinetic stability of the CrB_4 sheet, we also performed binding energy, phonon spectrum, and molecular dynamics calculations (see detailed proof in Supplementary material, part 1). Both the positive frequencies corresponding to no imaginary frequency modes and the linear dispersion around the Γ point in the phonon dispersion indicate the dynamical stability of the crystal. From the band structure of CrB_4 in Fig. 1(c), one may find two discrete cones near Fermi surface. Their coordinates, in the first Brillouin zone (BZ), are

$$\boldsymbol{K} = (-1/3, 2/3, 0), \quad \boldsymbol{J} = (-x_J/3, 2x_J/3, 0)$$
$$(x_J = 0.52543).$$

To further analyze the characteristics of the two nonequivalent cones, we draw the energy contour maps in the first BZ for both the valence (Fig. 1(d)) and the conduction bands (Fig. 1(e)). On the energy contour maps, different colors represent different energies, and each contour line has the same energy; the point K is at the vertex of the hexagonal first BZ, and the other point J is located between Γ and K. From the two energy contour maps, one can find that, in the areas around the two conical points K and J, each energy contour line forms a concentric circle, confirming that both cones are isotropic Dirac cones.

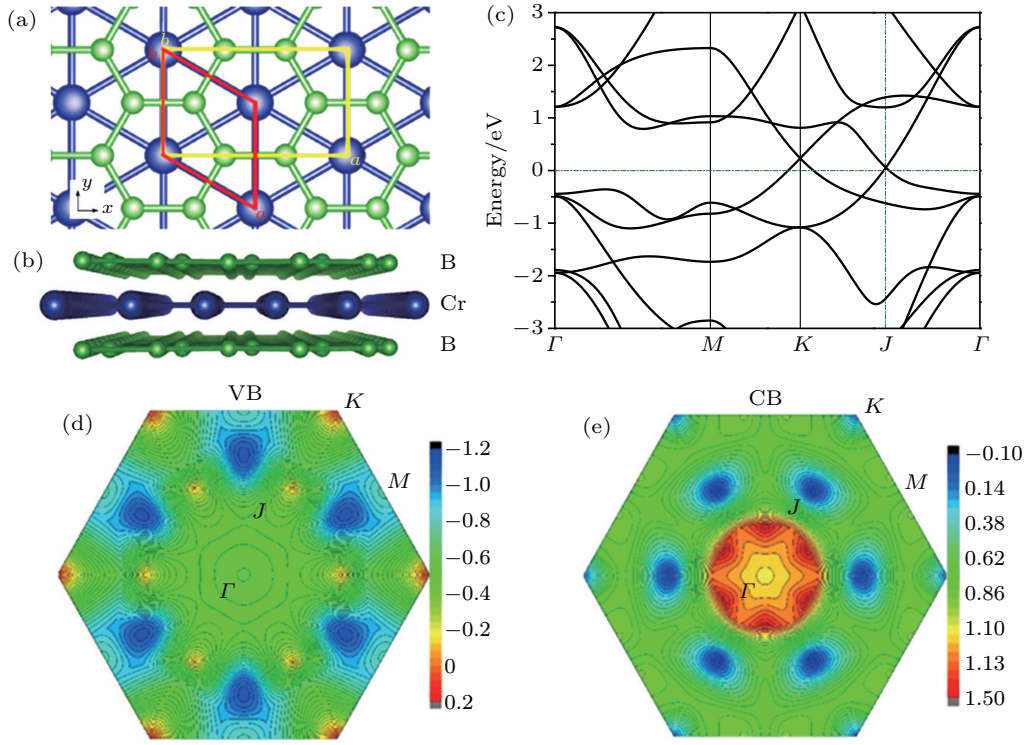


Fig. 1. (color online) The crystal and band structures of CrB_4. (a) The top and (b) side views of CrB_4. (c) The band structure, and the energy contour maps of both (d) the valence bands (VB) and (e) the conduction bands (CB) of CrB_4 in the first Brillouin zone.

When electric fields are applied to the CrB_4 sheet, if the direction of the fields is out-of-plane, there is no observable change of the band structure (not shown here); meanwhile, if the direction of the electric fields is in-plane, the electronic structure shows rich phenomena.

The band structures of CrB_4 under different in-plane electric fields along the Cr–Cr bond direction are shown in Fig. 2. The calculation paths are along the edge of the first BZ. Since the system has lost *P6mmm* symmetry and the lattice constants have changed after applying the in-plane electric fields, the points "*M*" and "*K*" here are just the midpoint of the edge and the vertex of the first BZ, respectively. The point "*J*" here still denotes the point on the Γ–"*K*" line with a distance $|\Gamma''J''| = x_J|\Gamma''K''|$ ($x_J = 0.52543$) as before. From Fig. 2, one can find that as the electric field increases, non-zero band gaps open at both of the two cones around *K* and *J*, and the band structure gradually loses the characteristic of the Dirac cone.

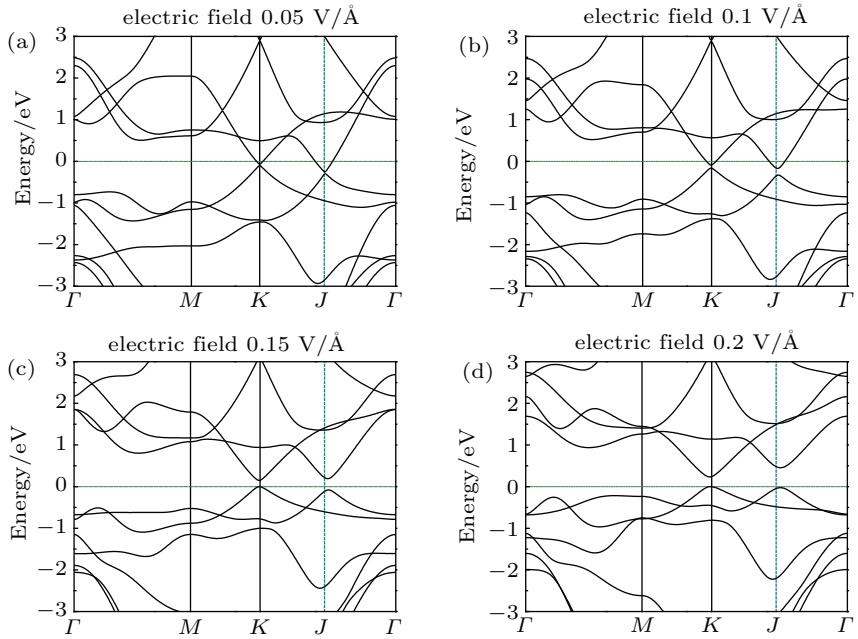


Fig. 2. (color online) The band structures of CrB_4 crystal under external electric fields in the direction of Cr–Cr bonds.

In the case that the electric fields are along the B–B bond direction, the band structures (shown in Fig. 3) undergo interesting variation, which has greatly aroused our research enthusiasm. In Fig. 3, the naming rules for the three points *M*, *K*, and *J* are the same as that for Fig. 2. According to the results in Fig. 3, in the electric field up to 0.25 V/Å, the Dirac cone located at *K* point always holds, but the other cone located at *J* vanishes with a gap opening, losing the characteristic of the Dirac cone. Interestingly, under an electric field 0.25 V/Å, a new cross-like structure near the Fermion surface occurs between *J* and Γ. By verification calculations (not shown here), we confirm that this cross-like structure is a new cone with a tiny gap.

The lattice parameter *a* and the length of B–B bonds in the CrB_4 sheet are both stretched by nearly 2% under 0.25 V/Å electric field along the direction of B–B bonds. Noticing that in-plane uniaxial tensile strains could also stretch the crystal and result in the emergence of Dirac cones in other systems,[32,33] we wonder whether the behaviors of the two Dirac cones in CrB_4 are homologous to the results of tensile strains; so we tried to apply in-plane tensile stains as a verification method. Generally, an orthorhombic cell is easier to apply strains in two normal directions than a hexagonal cell.[38,39] Thus, we chose the orthorhombic cell (see the yellow frame in Fig. 1(a)) rather than the hexagonal cell (red frame in Fig. 1(a)) for the CrB_4 sheet, and then calculated its electronic structures. Nevertheless, this change of the unit cell selection brought an unexpected phenomenon, i.e., the two discrete Dirac cones become almost overlapping. Hence, we have developed a general method to map the corresponding points in the reciprocal space in the two cases of the cell selection (see detailed proof in Supplementary material, part 2) so as to distinguish the two conical points and then discuss the behaviors of the two Dirac cones under tensile strains. According to our calculation results, when we choose the orthorhombic cell, the two conical points located between Γ and *X* points in first BZ are now

$$\bar{K} = (0, 1/3, 0),\ J' = (0, 2x_J/3, 0) \quad (x_J = 0.52543).$$

These two points are equivalent to the original *K* and *J* points in the case of the hexagonal cell, respectively (see detailed proof in Supplementary material, part 3).

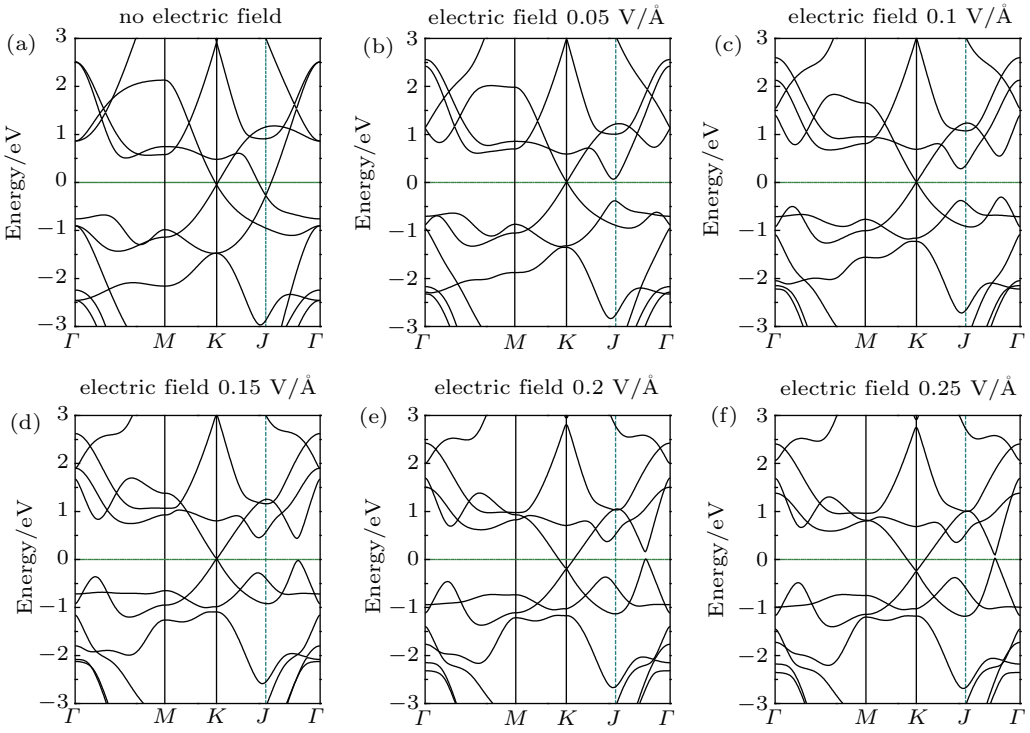


Fig. 3. (color online) The band structures of CrB_4 crystal under external electric fields in the direction of B–B bonds.

Seeing that, in the case of orthorhombic cell, the directions of X-axis and Y-axis are just along the directions of B–B bonds and Cr–Cr bonds, respectively, we apply uniaxial tensile strains for above 2% and 4% in both X-axis and Y-axis directions. The uniaxial stain is defined as $\varepsilon = \Delta a/a_0$, where a_0 is the lattice parameter of the unstrained cell and $\Delta a + a_0$ is that of the strained cell. According to the calculation results, as shown in Fig. 4, when strains are applied along both the X-axis and the Y-axis, the band structures present no observable change with only the positions of the two Dirac cones of the latter moving upwards, which is not the same as the band structure when the electric fields are applied. Although the two Dirac cones have some response to the in-plane strains, the most conspicuous phenomenon, i.e., the vanishing and creation of Dirac cones near the Fermion surface, does not occur.

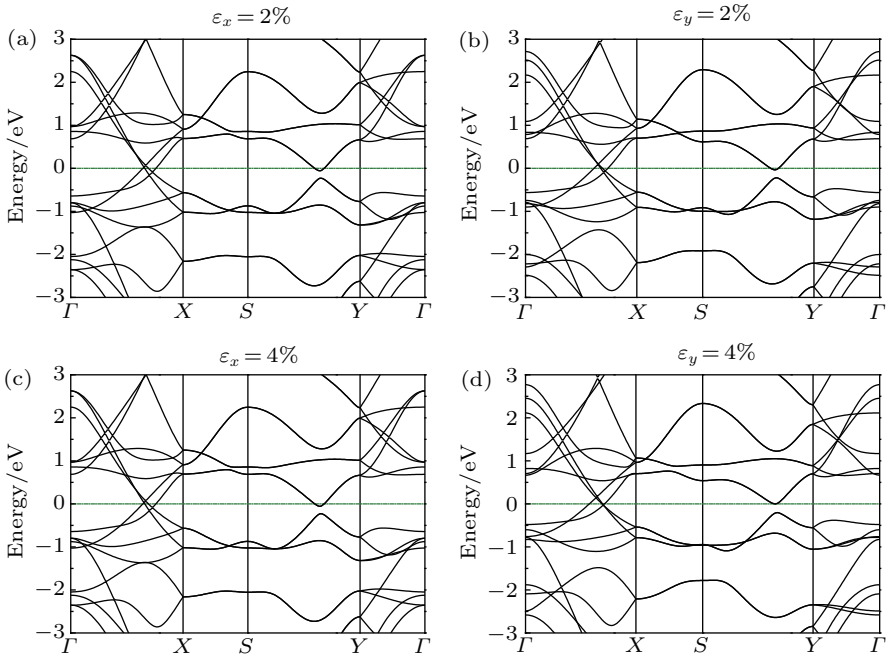


Fig. 4. (color online) Band structures of CrB_4 with respect to the uniaxial strains.

In our CrB_4 crystal, the boron atoms are electronegative while the chromium atoms are electropositive. When the in-plane electric fields are applied, besides the crystal stretching and expansion, the chromium atoms and boron atoms shift to opposite directions. A reasonable hypothesis to explain the band structure variation phenomenon of CrB_4 in electric fields is that the chromium atoms no longer stay at the center of the boron hexagon, and thus lead a remarkable change in the electronic structure; this indicates that the behaviors of the band structure under electric field are not homologous to the results of tensile strains. To quantitatively describe the relative shift of atoms, we define an offset parameter, $\delta = 1 - x/r$, as shown in the inset of Fig. 5. As the boron and chromium atoms shift, the offset parameter varies. We summarized the energy gap between Γ and J and the corresponding δ under different in-plane electric fields applied in the B–B bond direction, as shown in Fig. 5(a). From Fig. 5(a), one can find that as the strength of the applied electric fields increases, both of the energy gap and $-\delta$ decrease to their minima at the same electric field, which is about 0.24 V/Å. According to the band structure in the case of this electric field, as shown in Fig. 5(b), one can see that an almost closed cone appears near the Fermion surface between J and Γ, and that the band energy in the area around the new cone is almost in linear dispersion. In addition, if we remove the electric field but keep the crystal structure with the same atomic positions as that in the case of 0.24 V/Å electric field, one can find that the new cone still exists (shown in Supplementary material, part 4). All of these strong evidences indicate that the origin of the new cone under the in-plane electric field along the B–B bonds results mainly from the change of the interaction between the boron and chromium atoms.

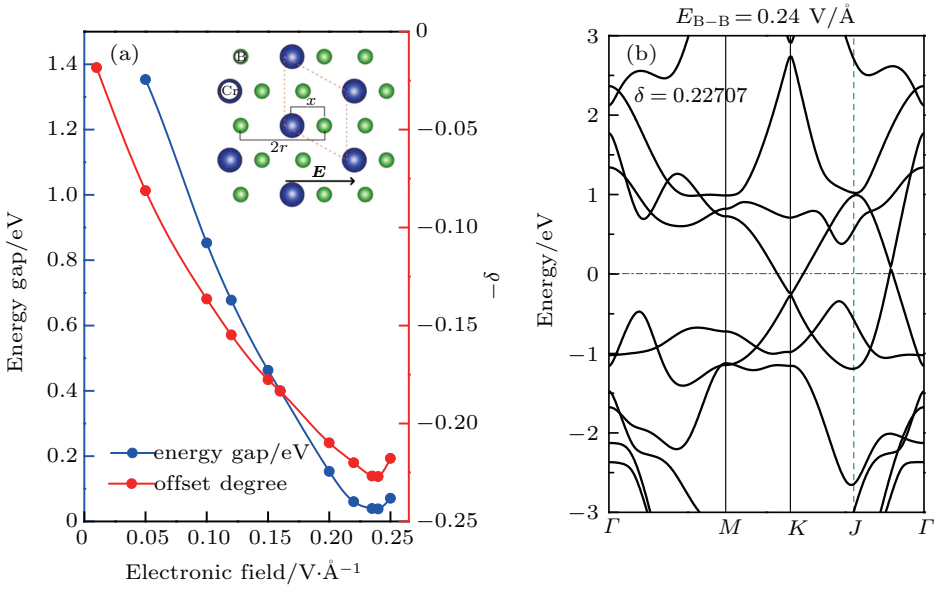


Fig. 5. (color online) The offset degree δ and energy gap under the in-plane electric field. (a) The offset degree δ with its definition shown in the inset, and the energy gap between Γ and J as a function of the electric field. (b) The band structure of CrB_4 crystal under 0.24 V/Å electric field in the direction of B–B bonds.

In Ref. [40], a model based on the tight bonding approximate (TBA) shows that the double Dirac cones in triangular-lattice metamaterials are originated from the hopping energies between different atoms. As we know, the electric fields can change the distance between atoms and then lead to a change of the hopping energy. Our work shows that a proper in-plane electric field can cause the disappearance and occurrence of Dirac cones, which might be hard to be explained by this simple model. We believe that the dominant factors for the phenomena of both the vanishing and emergence of Dirac cones in one system may be buried in some specific combinations of the hopping energies between boron and chromium atoms. Detailed theoretical model will be published elsewhere.

4. Conclusion

In summary, we have performed a study on the electronic structures of the hexagonal CrB_4 sheet with multiple nonequivalent Dirac cones under external electric fields and tensile strains. Our results show that the in-plane electric field can obviously change the band structure of the CrB_4 system, while the out-of-plane electric fields bring no obvious influence on it. When the in-plane electric fields are along the Cr–Cr bonds, the two Dirac cones vanish with gap opening. When the electric fields are along the B–B bonds, the cone located at the K point holds while the other cone located at J vanishes. More fascinating is that under a proper electric field along the B–B bonds, a new Dirac cone with tunable gap occurs between J and Γ. When the in-plane tensile strains are applied, the two original Dirac cones always hold and no new cone emerges,

which means that the behaviors of the band structure under different in-plane electric fields are not homologous to the results of in-plane tensile strains. Finally, by analyzing the indirect correlation between the electrically dependent band gap of the new cone and the atomic relative offset, we find that the reason of the occurrence and disappearance of a Dirac cone is the change of the interatomic interaction, which is caused by the relative shift between the boron and chromium atoms.

From this work we realize that (i) in addition to the out-plane electric field often studied in the literature, the in-plane electric field may also have an observable effect on the band structure of 2D materials with multiple Dirac cones, and the effect depends on the direction of the field; (ii) the in-plane electric field not only lead to the vanishing of Dirac cones (by opening band gaps), but can also cause the emergence of new Dirac cones under a proper direction and intensity of the field. Hereby we would propose a new method to manipulate 2D Dirac materials, especially to create new Dirac cones, by applying an in-plane electric field, and we expect our study could stir new inspiration in artificially manipulating Dirac states in 2D systems.

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666
[2] Song X F, Hu J L and Zeng H B 2013 *J. Mater. Chem. C* **1** 2952
[3] Zawadzki W 2017 *J. Phys.-Condes. Matter* **29** 373004
[4] Liu H, Neal A T, Zhu Z, Luo Z, Xu X F, Tomanek D and Ye P D 2014 *ACS Nano* **8** 4033
[5] Zhao J J, Liu H S, Yu Z M, Quhe R G, Zhou S, Wang Y Y, Liu C C, Zhong H X, Han N N, Lu J, Yao Y G and Wu K H 2016 *Prog. Mater. Sci.* **83** 24
[6] Yuan J H, Yu N N, Xue K H and Miao X S 2017 *Appl. Surf. Sci.* **409** 85
[7] Yuan J H, Xie Q X, Yu N N and Wang J F 2017 *Appl. Surf. Sci.* **394** 625
[8] Wu Z B, Zhang Y Y, Li G, Du S X and Gao H J 2018 *Chin. Phys. B* **27** 077302
[9] Mannix A J, Zhou X F, Kiraly B, Wood J D, Alducin D, Myers B D, Liu X L, Fisher B L, Santiago U, Guest J R, Yacaman M J, Ponce A, Oganov A R, Hersam M C and Guisinger N P 2015 *Science* **350** 1513
[10] Wu X, Dai J, Zhao Y, Zhuo Z, Yang J and Zeng X C 2012 *ACS Nano* **6** 7443
[11] Penev E S, Bhowmick S, Sadrzadeh A and Yakobson B I 2012 *Nano Lett.* **12** 2441
[12] Ma F, Jiao Y, Gao G, Gu Y, Bilic A, Chen Z and Du A 2016 *Nano Lett.* **16** 3022
[13] Corso M, Auwarter W, Muntwiler M, Tamai A, Greber T and Osterwalder J 2004 *Science* **303** 217
[14] Piazza Z A, Hu H S, Li W L, Zhao Y F, Li J and Wang L S 2014 *Nat. Commun.* **5** 3113
[15] Xu J Q, Chang Y Y, Gan L, Ma Y and Zhai T Y 2015 *Adv. Sci.* **2** 1500023
[16] Li D F, Chen Y, He J, Tang Q Q, Zhong C Y and Ding G Q 2018 *Chin. Phys. B* **27** 036303
[17] Zhang L Z, Wang Z F, Du S X, Gao H J and Liu F 2014 *Phys. Rev. B* **90** 161402(R)
[18] Zhang H, Li Y, Hou J, Du A and Chen Z 2016 *Nano Lett.* **16** 6124
[19] Xie S Y, Li X B, Tian W Q, Chen N K, Zhang X L, Wang Y L, Zhang S B and Sun H B 2014 *Phys. Rev. B* **90** 035447
[20] Xu C, Li Q, Liu C M, Duan M Y and Wang H K 2016 *Int. J. Mod. Phys. B* **30** 1650098
[21] Zhang C M, Jiao Y L, Ma F X, Bottle S, Zhao M W, Chen Z F and Du A J 2017 *Phys. Chem. Chem. Phys.* **19** 5449
[22] Polini M, Guinea F, Lewenstein M, Manoharan H C and Pellegrini V 2013 *Nat. Nanotechnol.* **8** 625
[23] Naumis G G, Barraza-Lopez S, Oliva-Leyva M and Terrones H 2017 *Rep. Prog. Phys.* **80** 096501
[24] Zhan D, Yan J X, Lai L F, Ni Z H, Liu L and Shen Z X 2012 *Adv. Mater.* **24** 4055
[25] Rowlands D A and Zhang Y Z 2014 *Chin. Phys. B* **23** 037101
[26] Xiong W, Xia C, Du J, Wang T, Peng Y, Wei Z and Li J 2017 *Nanotechnology* **28** 195702
[27] Kaloni T P, Cheng Y C and Schwingenschlogl U 2013 *J. Appl. Phys.* **113** 104305
[28] Wang Y L and Ding Y 2013 *Solid State Commun.* **155** 6
[29] Wei L, Zhang X M, Liu X B, Zhou H C, Yang B and Zhao M W 2017 *RSC Adv.* **7** 52065
[30] Zhong X L, Yap Y K, Pandey R and Karna S P 2011 *Phys. Rev. B* **83** 193403
[31] Mu Y W, Ding F and Lu H G 2015 *RSC Adv.* **5** 11392
[32] Zhang H, Ma Y and Chen Z 2015 *Nanoscale* **7** 19152
[33] Cui H J, Sheng X L, Yan Q B, Zheng Q R and Su G 2013 *Phys. Chem. Chem. Phys.* **15** 8179
[34] Kim J, Jhi S H and Wu R 2016 *Nano Lett.* **16** 6656
[35] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[36] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
[37] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
[38] Elahi M, Khaliji K, Tabatabaei S M, Pourfath M and Asgari R 1953 *Phys. Rev. B* **91** 8
[39] Gong P L, Deng B, Huang L F, Hu L, Wang W C, Liu D Y, Shi X Q, Zeng Z and Zou L J 2017 *J. Phys. Chem. C* **121** 20931
[40] Sakoda K 2012 *Opt. Express* **20** 9925