

LETTER

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Perfect charge compensation in WTe_2 for the extraordinary magnetoresistance: From bulk to monolayer

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Abstract – The electronic structures of the WTe_2 bulk and layers are investigated by using the first-principles calculations. The perfect electron-hole (n - p) charge compensation and high carrier mobilities are found in the WTe_2 bulk, which may result in the large and non-saturating magnetoresistance (MR) observed very recently in the experiment (ALI M. N. *et al*, *Nature*, **514** (2014) 205). The monolayer and bilayer of WTe_2 preserve the semimetallic property, with equal hole and electron carrier concentrations. Moreover, very high carrier mobilities are also found in WTe_2 monolayer, indicating that the WTe_2 monolayer would have the same extraordinary MR effect as the bulk, which could have promising applications in nanostructured magnetic devices.

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In the past few decades, transition metal dichalcogenides (TMDs) with the formula MX_2 (M = transition metal of group 4–10; X = S, Se, or Te) have received a lot of attention due to their diverse properties. Ranging from insulating to metallic, some of them exhibit behaviors of superconductivity [1] and charge density wave [2]. Most of the MX_2 systems crystallize in a layered structure, with the building blocks (X - M - X sandwich layers) stacked along the c -axis. Within the sandwich layer, the atoms are covalently bonded, while the interactions among the layers are much weaker, mainly of the van der Waals type. The recent advances in the experimental techniques have made it possible to exfoliate two-dimensional (2D) ultrathin layers from the MX_2 bulk [3,4]. The 2D MX_2 materials can largely preserve the versatile properties, but some distinctive characteristics can be introduced due to the quantum confinement effect. For example, the transition of indirect-direct band gap takes place in MoS_2 when the bulk structure is exfoliated into a monolayer [5], which opens up new potential applications in the fields of phototransistors [6], photocatalyst [7], electroluminescence [8], etc.

Very recently, extremely large magnetoresistance (MR) without saturation even at very high fields was observed in WTe_2 [9]. MR evaluates the change in electrical resistance by the application of a magnetic field. A large MR effect can have promising applications such as magnetic field sensors [10] and magnetic information storage [11]. The main origin of the extraordinary MR effect in WTe_2 is ascribed to the perfect n - p charge compensation in this material, based on the investigations by the angle-resolved photoelectron spectroscopy (ARPES) [12]. When applied in nanoelectronics, it is desirable to obtain nanostructured systems which have the performance as good as, or even better than, their bulk counterparts. Almost at the same time, a huge negative MR effect was reported in the ultrathin layers of $\text{TiTe}_{2-x}\text{I}_x$ due to the frustrated magnetic structures induced by the anionic doping [13]. The excellent MR effect of the WTe_2 bulk inspires us to explore how the WTe_2 layer will perform, which is very critical in the applications of nanoelectronics.

In this work, the electronic properties of WTe_2 layers as well as the bulk structure are investigated based on the first-principles calculations. Our results show that both the monolayer and bilayer of WTe_2 maintain the same semimetal properties as the bulk, with equal hole and electron carrier concentrations, suggesting that the

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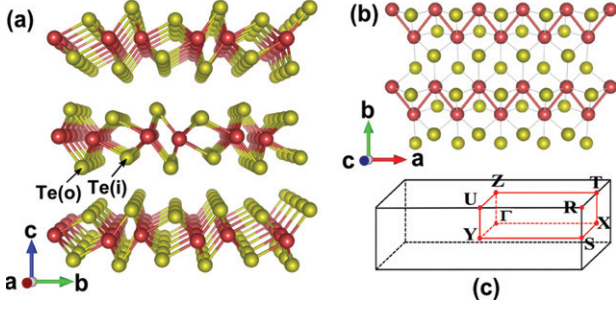


Fig. 1: (Color online) Crystal structure of the WTe_2 bulk viewed along (a) the a -axis (parallel to the W-W zigzag chains) and (b) the c -axis (perpendicular to the stacked layers); (c) the corresponding first Brillouin zone. The red and yellow balls represent W and Te atoms, respectively. Te(i) and Te(o) stand for the atoms shrunk inside and moved outside the sandwich layer, respectively.

non-saturating MR effect may also exist in the WTe_2 layers. Moreover, the high carrier mobilities found in the WTe_2 monolayer indicate that the MR effect in the monolayer would be comparable to that in the bulk system.

Our calculations were performed via a projector augmented-wave (PAW) pseudopotential approach within the density functional theory (DFT) as implemented in the ABINIT code [14–16]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [17] were used for the exchange-correlation energy. For bulk and bilayer, the van der Waals interactions were treated by the vdW-DF1 functional [18]. Spin-orbit coupling was included in the calculations of the electronic properties. The plane-wave cutoff energy was set to be 600 eV in all the calculations. For the case of monolayer and bilayer, a vacuum of 12 Å was added between the layer and its periodic image, so that they can be treated as independent entities. In the self-consistent calculations, the Brillouin zones were sampled with an $8 \times 4 \times 1$ Monkhorst-Pack k mesh. Both the lattice parameters and the atomic positions of all the structures were fully relaxed until the force acting on each atom became less than 0.5×10^{-3} eV/Å. The Fermi surface was plotted using the XCrySDen software¹ [19].

The crystal structure of the WTe_2 bulk viewed along different directions are demonstrated in figs. 1(a) and (b), respectively, with the corresponding first Brillouin zone shown in fig. 1(c). The space group of the WTe_2 bulk is $Pnm2_1$. Most of the sulfides and selenides are rhombohedral or hexagonal, and the metal atoms are trigonal prismatic or octahedral coordinated by six chalcogen atoms. However, in WTe_2 , the octahedron of tellurium atoms is slightly distorted and the metal atoms are displaced from their ideal octahedral sites, forming zigzag metal-metal chains along the a -axis [20], which is shown in fig. 1(b). The structural difference has endowed this kind of material with properties distinct from the other MX_2 system.

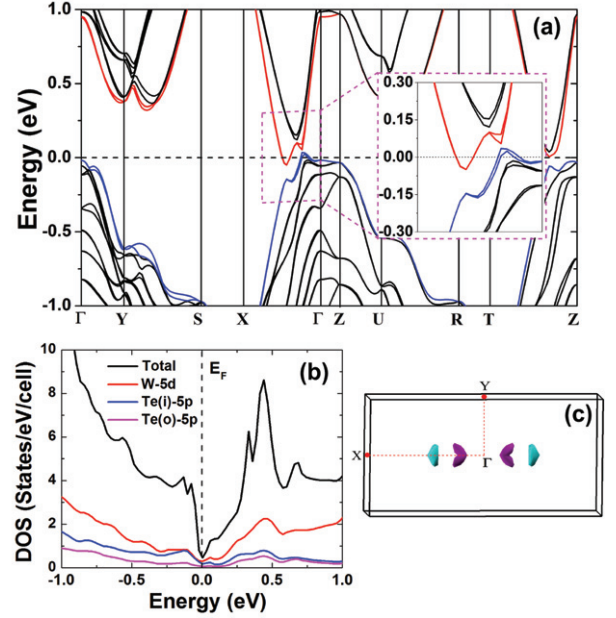


Fig. 2: (Color online) (a) Band structure, (b) total and partial density of states (DOS), and (c) Fermi surface (FS) of the WTe_2 bulk.

After full relaxation, the obtained crystal constants are $a = 3.54$ Å, $b = 6.34$ Å and $c = 14.44$ Å, which agree well with the experimental results [20]. The nearest distance between W-W atoms along the zigzag chain is 2.87 Å, only 0.14 Å larger than that in the pure metal crystal of tungsten. Because of the distorted octahedral structure, the Te atom layers become buckled (see fig. 1(a)), with Te(i) atoms shrunk a little inside the sandwich layer and Te(o) atoms moved slightly outside.

The electronic band structure and the density of states (DOS) of the WTe_2 bulk are shown in figs. 2(a) and (b), respectively, which agree well with the previous reports [9,21]. A strong anisotropic band dispersion is observed in the band structure. The bands along the Γ -Z direction (perpendicular to the sandwich layers in real space) are much flatter than those along the other directions, reflecting the quasi-two-dimensional layered structure of the WTe_2 bulk. The very small DOS at the Fermi energy (E_F) signals the semimetallic nature of the WTe_2 bulk. The corresponding W-5d and Te-5p partial DOS included in fig. 2(b) show that the DOS at the E_F ($N(E_F)$) is dominated by the W-5d state, followed by the Te(i)-5p state. The Te(o)-5p state contributes little to the $N(E_F)$. The Fermi surface of the WTe_2 bulk is demonstrated in fig. 2(c), which exhibits highly anisotropic property. Note that in the band structure, there exists a small overlap between the top of the valence band (hole pocket) and the bottom of the conduction band (electron pocket) along the X- Γ direction in the vicinity of the Fermi level. The enlarged overlap part of the band structure is shown in the inset of fig. 2(a). Hole and electron pockets with appropriately the same size are found, which agrees well with the ARPES results [12]. In experiment, it was analyzed

¹Code available from <http://www.xcrysdn.org/>.

that these two pockets may lead to the perfect carrier compensation and therefore the large MR effect in WTe₂. However, the exact values of the hole (*p*-type) and electron (*n*-type) carrier concentrations are still lacking. To obtain these values, the band-decomposed DOSs are calculated. In particular, to calculate the *p*-type carrier concentration, we calculate the DOS of the bands in blue color in fig. 2(a) and then integrate the DOS from E_F to the valence band maximum (VBM); to calculate the *n*-type carrier concentration, the DOS of the bands in red color is integrated from the E_F to the conduction band minimum (CBM). The carrier concentrations, $p = 7.7 \times 10^{19} \text{ cm}^{-3}$ and $n = 7.5 \times 10^{19} \text{ cm}^{-3}$, are obtained, coinciding perfectly with each other.

In the semiclassical two-band model,

$$\text{MR} = \frac{\sigma\sigma'(\sigma/n + \sigma'/p)^2(B/e)^2}{(\sigma + \sigma')^2 + \sigma^2\sigma'^2(1/n - 1/p)^2(B/e)^2}, \quad (1)$$

where σ and σ' are the electrical conductivities of electrons and holes without external magnetic field, respectively. n and p are the electron and hole concentrations, respectively. When $n = p$, the MR increases as B^2 without saturation. Using this two-band model, we can qualitatively interpret the experimentally observed behavior of MR as a function of the external magnetic field in WTe₂ [9].

Next, we focus on the electronic properties of WTe₂ ultrathin layers. The calculated electronic structures of the WTe₂ monolayer and bilayer are plotted in figs. 3(a) and (b), respectively. The band structures of WTe₂ layers are different from that of the bulk, which was also found in WS₂ [22]. What is different from the case of the WTe₂ bulk is that the VBM of WTe₂ layers are located at the Γ -point. From monolayer to bilayer, more valence (in blue color) and conduction (in red color) bands cross the Fermi energy, thus the overlap of valence and conduction bands becomes larger in the bilayer, which can also be seen from the Fermi surface in figs. 3(e) and (f). Combined with the calculated DOS (see figs. 3(c) and (d)), we can see that the WTe₂ monolayer and bilayer remain semimetals. The semimetallic property is very different from that reported in the WTe₂ monolayer with the artificial 2H structure [23], which is a direct-band-gap semiconductor. The $N(E_F)$ for both the monolayer and bilayer are dominated by the W-5d state, followed by the Te(i)-5p state, which is the same as in the case of the WTe₂ bulk. Interestingly, for the semimetal monolayer and bilayer, equal *n*- and *p*-type carrier concentrations are also obtained. The calculated carrier concentrations for the monolayer and bilayer are, respectively, $n = p = 1.6 \times 10^{13} \text{ cm}^{-2}$ and $n = p = 1.4 \times 10^{13} \text{ cm}^{-2}$. The perfect charge compensation indicates that the non-saturating MR as a function of the external magnetic field may also exist in the WTe₂ monolayer and bilayer.

From eq. (1), we can see that when $n = p$, MR obeys

$$\text{MR} = \sigma\sigma'(B/e)^2/n^2 = \mu_e\mu_h B^2, \quad (2)$$

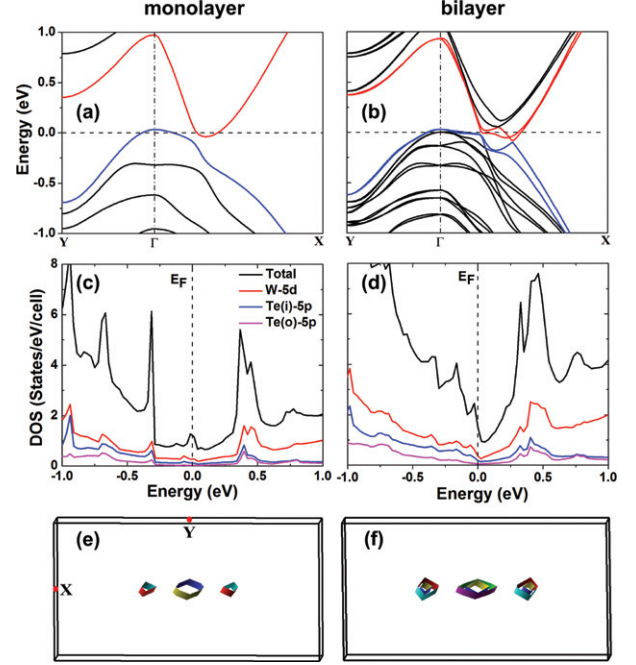


Fig. 3: (Color online) Band structure of the WTe₂ (a) monolayer and (b) bilayer; total and partial density of states (DOS) of the WTe₂ (c) monolayer and (d) bilayer; Fermi surface (FS) of the WTe₂ (e) monolayer and (f) bilayer.

where μ_e and μ_h are the carrier mobilities of electrons and holes, respectively. Therefore, in order to obtain a large MR at a specific magnetic field, high carrier mobility will be desirable. The carrier mobility can be calculated using the deformation potential (DP) model based on the effective mass approximation [24–26]. The mobilities for the bulk (μ_β^{3D}) and two-dimensional system (μ_β^{2D}) along a certain direction β are respectively expressed as

$$\mu_\beta^{3D} = \frac{2\sqrt{2}\pi e\hbar^4 C_\beta^{3D}}{3(k_B T)^{3/2} (m^*)^{5/2} E_1^2} \quad (3)$$

and

$$\mu_\beta^{2D} = \frac{2e\hbar^3 C_\beta^{2D}}{3k_B T (m^*)^2 E_1^2}. \quad (4)$$

Here C is the elastic modulus and can be defined as $C_\beta^{3D} = [\partial^2 E / \partial \delta^2] / V_0$ and $C_\beta^{2D} = [\partial^2 E / \partial \delta^2] / S_0$ for 3D and 2D systems, respectively, where E , δ , V_0 , and S_0 are, respectively, the total energy, the applied strain along the β direction, the volume, and the area of the investigated system. T is the temperature and m^* is the effective mass. The DP constant E_1 is obtained by $E_1 = dE_{\text{edge}}/d\delta$, where δ is the applied strain by a step of 0.5% and E_{edge} is the energy of the band edges (VBM for the holes and CBM for the electrons). Here we only compare the values of the WTe₂ monolayer with those of the bulk. The calculated m^* , C , E_1 , and room temperature μ are summarized in table 1. For the WTe₂ bulk, we focus on the two in-plane directions. Along the *a*-axis, the calculated effective masses of the hole and electron are $0.19 m_0$ and $0.15 m_0$ (m_0 is the mass of an electron), respectively. The very small effective

Table 1: Effective mass m^* , elastic modulus C , deformation potential constant E_1 , and room temperature carrier mobility μ of the WTe₂ bulk and monolayer.

	Direction	Carrier type	m^* (m_0)	C eV/Å ³ (eV/Å ²)	E_1 eV	$\mu(\times 10^3)$ cm ² V ⁻¹ s ⁻¹
Bulk	a -axis	hole	0.19	0.94	-7.24	11.23
		electron	0.15	0.94	-4.90	44.16
	b -axis	hole	0.52	1.12	-3.06	5.98
		electron	0.65	1.12	-2.37	5.70
Monolayer	a -axis	hole	0.89	7.72	-10.41	0.02
		electron	0.30	7.72	-4.27	1.09
	b -axis	hole	0.54	9.12	0.58	21.25
		electron	0.28	9.12	-1.42	13.13

masses result in the extremely high carrier mobilities in the WTe₂ bulk, 1.12×10^4 and 4.42×10^4 cm²V⁻¹s⁻¹ for p - and n -type carriers, respectively. Along the b -axis, however, the effective masses are much larger, $0.52 m_0$ for the hole and $0.65 m_0$ for the electron, which result in much smaller carrier mobilities, 5.98×10^3 and 5.70×10^3 cm²V⁻¹s⁻¹ for p - and n -type carriers, respectively. The carrier mobility exhibits an obvious anisotropic property. From eq. (2), we can see that the value of MR is proportional to $\mu_h \mu_e$, therefore, the very high mobilities obtained along the a -axis may be responsible for the large MR measured along this direction; while the strong anisotropic property of the carrier mobility explains why the measured MR is one-dimensional. For the WTe₂ monolayer, the effective mass m^* of the hole along the a -axis is $0.89 m_0$, larger than that along the b -axis ($0.54 m_0$), due to the relatively flatter band along the Γ -X direction. Besides, DP constants E_1 along the a -axis are much larger than those along the b -axis. Consequently, the mobilities along the b -axis are much larger than those along the a -axis. The electronic transport of the WTe₂ monolayer also exhibits a strong anisotropic property. On the other hand, for the direction of b -axis, the mobilities of both the hole and electron as well as their product ($\mu_h \mu_e$) are comparable to the bulk results, thus we can expect that the large MR effect would also exist along this direction. Our results indicate that not only the WTe₂ bulk but also the monolayer may exhibit the extraordinary MR effect.

It should be mentioned that the band structures are calculated in the limit of 0 K, which means that the perfect charge compensation can only be obtained at an extremely low temperature. On the other hand, the carrier mobility will be decreased with increasing the temperature, due to the greater scattering from the phonon. Therefore, for both the WTe₂ bulk [9] and the monolayer, the large MR effect will only be measured at low temperatures and will be strongly weakened with the increase of the temperature.

In summary, we have investigated the electronic properties of the WTe₂ bulk and layers. The perfect charge compensation as well as the large carrier mobilities are found in the WTe₂ bulk, which is ascribed to be the source of

the large and non-saturating MR observed experimentally. Moreover, the WTe₂ monolayer and bilayer preserve the semimetallic property and both of them are found to have equal hole and electron carrier concentrations. Our results indicate that the same extraordinary MR effect as in the WTe₂ bulk may also exist in the WTe₂ monolayer, which will have promising applications in nanostructured magnetic devices. Further experimental investigations are needed to confirm our computational results.

* * *

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REFERENCES

- [1] SIPOS B., KUSMARTSEVA A. F., AKRAP A., BERGER H., FORRÓ L. and TUTIŠ E., *Nat. Mater.*, **7** (2008) 960.
- [2] WILSON J. A., DI SALVO F. J. and MAHAJAN S., *Adv. Phys.*, **24** (1975) 117.
- [3] COLEMAN J. N., LOTYA M., O'NEILL A., BERGIN S. D., KING P. J., KHAN U., YOUNG K., GAUCHER A., DE S., SMITH R. J., SHVETS I. V., ARORA S. K., STANTON G., KIM H.-Y., LEE K., KIM G. T., DUESBERG G. S., HALLAM T., BOLAND J. J., WANG J. J., DONEGAN J. F., GRUNLAN J. C., MORIARTY G., SHMELIOV A., NICHOLLS R. J., PERKINS J. M., GRIEVESON E. M., THEUWISSEN K., MCCOMB D. W., NELLIST P. D. and NICOLSI V., *Science*, **331** (2011) 568.
- [4] SMITH R. J., KING P. J., LOTYA M., WIRTZ C., KHAN U., DE S., O'NEILL A., DUESBERG G. S., GRUNLAN J. C., MORIARTY G., CHEN J., WANG J.,

- MINETT A. I., NICOLosi V. and COLEMAN J. N., *Adv. Mater.*, **23** (2011) 3944.
- [5] KUC A., ZIBOUCHE N. and HEINE T., *Phys. Rev. B*, **83** (2011) 245213.
- [6] YIN Z., LI H., LI H., JIANG L., SHI Y., SUN Y., LU G., ZHANG Q., CHEN X. and ZHANG H., *ACS Nano*, **6** (2012) 74.
- [7] LI Y., LI Y.-L., ARAUJO C. M., LUO W. and AHUJA R., *Catal. Sci. Technol.*, **3** (2013) 2214.
- [8] SUNDARAM R. S., ENGEL M., LOMBARDI A., KRUPKE R., FERRARI A. C., AVOURIS PH. and STEINER M., *Nano Lett.*, **13** (2013) 1416.
- [9] ALI M. N., XIONG J., FLYNN S., TAO J., GIBSON Q. D., SCHOOP L. M., LIANG T., HALDOLAARACHCHIGE N., HIRSCHBERGER M., ONG N. P. and CAVA R. J., *Nature*, **514** (2014) 205.
- [10] DAUGHTON J., BROWN J., CHEN E., BEECH R., POHM A. and KUDE W., *IEEE Trans. Magn.*, **30** (1994) 4608.
- [11] PRINZ G. A., *Science*, **282** (1998) 1660.
- [12] PLETIKOSIĆ I., ALI M. N., FEDOROV A. V., CAVA R. J. and VALLA T., *Phys. Rev. Lett.*, **113** (2014) 216601.
- [13] GUO Y., DAI J., ZHAO J., WU C., LI D., ZHANG L., NING W., TIAN M., ZENG X. C. and XIE Y., *Phys. Rev. Lett.*, **113** (2014) 157202.
- [14] GONZE X., AMADON B., ANGLADE P.-M., BEUKEN J.-M., BOTTIN F., BOULANGER P., BRUNEVAL F., CALISTE D., CARACAS R., CÔTÉ M., DEUTSCH T., GENOVESE L., GHOSEZ PH., GIANTOMASSI M., GOEDECKER S., HAMANN D. R., HERMET P., JOLLET F., JOMARD G., LEROUX S., MANCINI M., MAZEVET S., OLIVEIRA M. J. T., ONIDA G., POUILLON Y., RANGEL T., RIGNANESE G.-M., SANGALLI D., SHALTAF R., TORRENT M., VERSTRAETE M. J., ZERAH G. and ZWANZIGER J. W., *Comput. Phys. Commun.*, **180** (2009) 2582.
- [15] GONZE X., BEUKEN J.-M., CARACAS R., DETRAUX F., FUCHS M., RIGNANESE G.-M., SINDIC L., VERSTRAETE M., ZERAH G., JOLLET F., TORRENT M., ROY A., MIKAMI M., GHOSEZ PH., RATY J.-Y. and ALLAN D. C., *Comput. Mater. Sci.*, **25** (2002) 478.
- [16] GONZE X., RIGNANESE G.-M., VERSTRAETE M., BEUKEN J.-M., POUILLON Y., CARACAS R., JOLLET F., TORRENT M., ZERAH G., MIKAMI M., GHOSEZ PH., VEITHEN M., RATY J.-Y., OLEVANO V., BRUNEVAL F., REINING L., GODBY R., ONIDA G., HAMANN D. R. and ALLAN D. C., *Z. Kristallogr.*, **220** (2005) 558.
- [17] PERDEW J. P., BURKE K. and ERNZERHOF M., *Phys. Rev. Lett.*, **77** (1996) 3865.
- [18] DION M., RYDBERG H., SCHRÖDER E., LANGRETH D. C. and LUNDQVIST B. I., *Phys. Rev. Lett.*, **92** (2004) 246401.
- [19] KOKALJ A., *Comput. Mater. Sci.*, **28** (2003) 155.
- [20] MAR A., JOBIC S. and IBERS J. A., *J. Am. Chem. Soc.*, **114** (1992) 8963.
- [21] AUGUSTIN J., EYERT V., BÖKER TH., FRENTRUP W., DWELK H., JANOWITZ C. and MANZKE R., *Phys. Rev. B*, **62** (2000) 10812.
- [22] KLEIN A., TIEFENBACHER S., EYERT V., PETTENKOFER C. and JAEGERMANN W., *Phys. Rev. B*, **64** (2001) 205416.
- [23] AMIN B., KALONI T. P. and SCHWINGENSCHLÖGL U., *RSC Adv.*, **4** (2014) 34561.
- [24] BARDEEN J. and SHOCKLEY W., *Phys. Rev.*, **80** (1950) 72.
- [25] PRICE P. J., *Ann. Phys.*, **133** (1981) 217.
- [26] XI J., LONG M., TANG L., WANG D. and SHUAI Z., *Nanoscale*, **4** (2012) 4348.