Spin splitting in band structures of BiTeX (X=Cl, Br, I) monolayers

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Spin splitting in band structures of BiTeX (X=Cl, Br, I) monolayers

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Abstract. In systems with breaking of inversion symmetry a perpendicular electric field arises that interacts with the conduction electrons. It may give rise to electron state splitting even without influence of external magnetic field due to the spin-orbital interaction (SOI). Such a removal of the spin degeneracy is called the Rashba effect. Nanostructure with the Rashba effect can be part of a spin transistor. Spin degeneracy can be realized in a channel from a material of this type without additive of magnetic ions. Lack of additive increases the charge carrier mobility and reliability of the device. *Ab initio* simulations of BiTeX (X=Cl, Br, I) monolayers have been carried out using VASP wherein implemented DFT method. The study of this structures is of interest because such sort of structures can be used their as spin-orbitronics materials. The crystal parameters of BiTeCl, BiTeBr, BiTeI have been determined by the ionic relaxation and static calculations. It is necessary to note that splitting of energy bands occurs in case of SOI included. The values of the Rashba coefficient a_R (in the range from 6.25 to 10.00 eV·Å) have high magnitudes for spintronics materials. Band structure of monolayers structures have ideal Rashba electron gas, i.e. there no other energy states near to Fermi level except Rashba states.

1. Introduction

In the last decade, spintronics has become a priority direction for micro- and nanoelectronics element base development. Appropriate choice of materials and structures based on these materials is one of the main scientific issues faced by the researchers.

Consequently, particular interest arises in relation to materials, which exhibit the Rashba effect [1]. This effect appears in systems with inversion symmetry breaking. It may give rise to electron state splitting even without influence of external magnetic field due to the spin-orbital interaction (SOI).

In the presence inversion symmetry breaking in structure the spin-degenerate parabolic band splits into two spin-polarized bands. This formulation yields new extreme at a momentum offset (k_0) and energy splitting (E_R) that are related to each other via $\alpha_R = 2 \cdot E_R / k_0$ (figure 1). The two Rashba split branches have opposite spins, which can influence the photoexcitation's optical and magnetic properties, a situation that may benefit spintronics because it enhances the spin-to-charge conversion efficiency.

Rashba effect is central physical phenomenon of spin-orbitronics. The operation of transistors can be realized on the basic principles of the effect described above. The spin-transistor construction, proposed by Datta and Das [2], is very similar to the conventional field-effect transistor, where the

SOI in channel is tuned by gate voltage, which is the Rashba effect [3–5]. Furthermore, a typical spin transistor still has not been implemented experimentally.

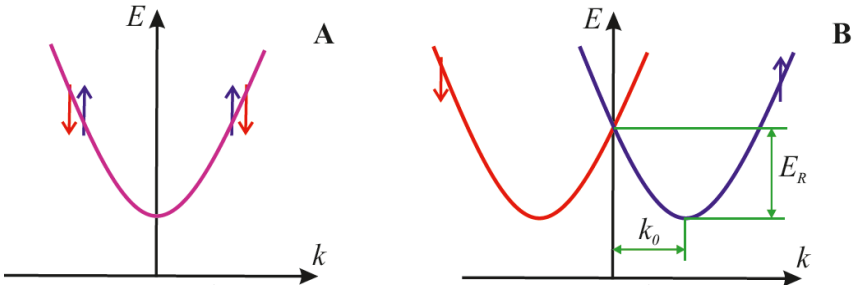

Figure 1. Wave function (a) without and (b) with Rashba spin splitting.

Until now, spin-transistor samples that have been manufactured in laboratory conditions and are based on the Rashba effect have a number of disadvantages, which are primarily associated with low efficiency of used materials.

It is known that the inversion symmetry breaking condition is observed in materials with wurtzite, zins-blende and 2D structures, and in structures, that are grown along crystallographic directions, that ensure the quantum well formation [6–10]. That is one of the possible reasons for the emergence of the Rashba effect.

Unique properties arise in materials with the transition to a two-dimensional structure. A special role is played by relativistic effects. In particular, spin-orbit interactions become important. BiTeX (X=Cl, Br, I) monolayer has a hexagonal crystal structure with breaking the inversion symmetry. Also heavy metals in the chemical compounds provide a large value of α_R. Therefore, the study of such structures is of interest from the point of view of the spin-orbitronics materials.

Right choosing of materials and structures based on this materials is one of the main scientific problem for investigators. Important conditions, which should be satisfied for devices based on these materials, are high Rashba parameter value; ideal Rashba electron gas; compatibility with advanced technological processes of micro- and nanoelectronic device manufacturing.

2. Computational details

Our calculations were performed based on the density functional theory (DFT). The projector-augmented wave (PAW) [11] potentials and Perdew–Burke–Ernzerhof (PBE) [12] functional have been used. A cutoff energy of 500 eV and 11×11×1 k-points grids determined by a fine grid of gamma-centered method [13] in the Brillouin zone have been used. The valence electron configurations for Bi, Te, Cl, Br and I were $[Xe]4f^{14}5d^{10}6s^26p^3$, $[Kr]4d^{10}5s^25p^4$, $[Ne]3s^23p^5$, $[Ar]3d^{10}4s^24p^5$ and $[Kr]4d^{10}5s^25p^5$, respectively. A vacuum layer of 20 Å along *z* direction was constructed to eliminate the interaction with spurious replica images. The atomic structures were relaxed until the forces on all unconstrained atoms were smaller than 0.01 eV/Å. The DFT-D3 method of Grimme demonstrated demonstrated the smallest difference between the calculated and experimental magnitude of lattice constants and have been used for further calculation. All of calculations have been carried out using VASP (Vienna Ab-initio Simulation Package) [14, 15] wherein implemented methods described above. Structural figures and charge density drawings were produced by VESTA package [16].

3. Crystal structure

The crystal structures of BiTeX (X=Cl, Br, I) have three atoms in unit cell and a layered structure along crystallographic *c* axis (figure 2). Within unit cell a Bi atom is located between one Te atom and one X atom thus forming a monolayer with three kinds of atoms. This monolayres weakly coupled each other via the van der Waals interactions in bulk structure. The distance between atoms in

monolayer is less than interlayer distances within bulk structure along c crystallographic direction. Such nature of the bonds provides the possibility of forming a monolayer consisting of three kind of atoms.

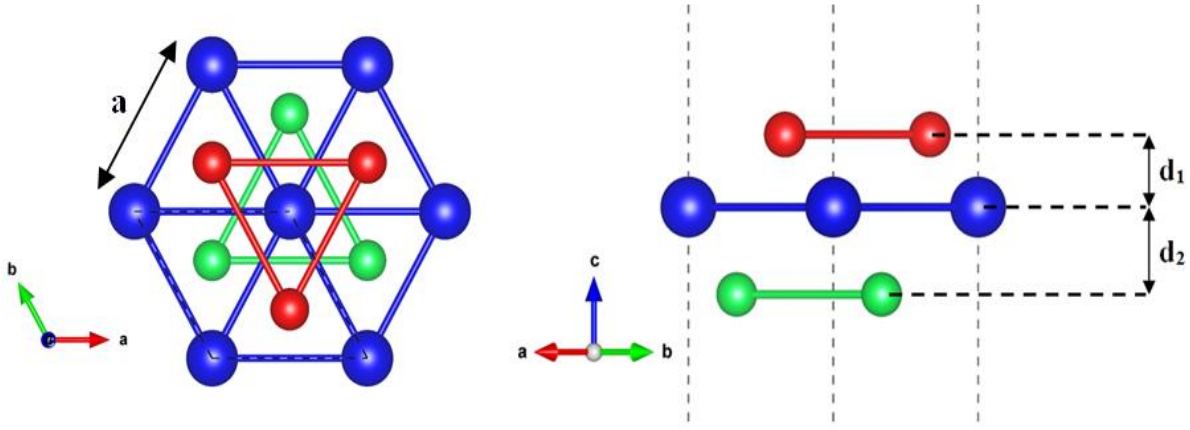

Figure 2. Unit cell of BiTeX (X=Cl, Br, I) monolayer.

Ground states of BiTeX (X=Cl, Br, I) monolayers have been calculated via *ab initio* simulation. The distances of Bi–Te (d_1) and Bi–X (d_2), as well as the calculated lattice constant *a* of the hexagonal unit cell are collected in table 1.

Table 1. Structure parameters of monolayer BiTeX (X=Cl, Br, I).

Structure	Lattice constant *a*, Å	d_1, Å	d_2, Å	Exp. lattice constant *a*, Å
BiTeCl	4.26	1.79	1.62	4.241[17]
BiTeBr	4.28	1.76	1.84	4.266[18]
BiTeI	4.35	1.73	2.08	4.339[19]

The obtained values of the lattice constant are in good agreement with the data from the experimental works [17–19].

BiTeX (X=Cl, Br, I) monolayers have a hexagonal crystal structure and is built up of alternating layers of Te, Bi, and X atoms stacked along the hexagonal axis what breaks the inversion symmetry. The broken inversion symmetry leads to the charge in the crystal is expected to distribute unevenly along the Te–Bi–X layers, giving rise to intrinsic internal potential gradient. Thus BiTeX monolayers have electrical gradient along the normal direction to the monolayer plane.

4. Band structures with spin splitting

Calculations of the band structures for BiTeX (X=Cl, Br, I) monolayers are performed taking into account the spin-orbit interaction (SOI). The electronic band structures of the BiTeI monolayer is depicted in figure 3. Conduction band minimum is locates at the near Γ point. Band structure has an indirect character and has gap of 0.74 eV. Band structures of the BiTeI monolayer consist of six conduction and twelve valence bands. The Fermi level is in the middle of the band gap. Conduction bands mostly compose Bi-6p electronic states. Twelve valence bands form valence bands of which the six bottom ones are the tellurium levels, and the six top ones are iodine levels.

The band structures have significant changes in the case of SOI included. The splitting of the energy bands occurs, i.e spin degeneracy disappears. We note that splitting is significant because the

structures under study consist of heavy metals. Strongly band splitting are effect from broken inversion symmetry. Because of conduction band minimum locates near the Γ point, thus forming a significant Rashba spin splitting.

The character of band structures of BiTeCl and BiTeBr is similar to character of band structure BiTeI. The band gaps of BiTeCl and BiTeBr are 0.94 and 0.89 eV, respectively (figure 4).

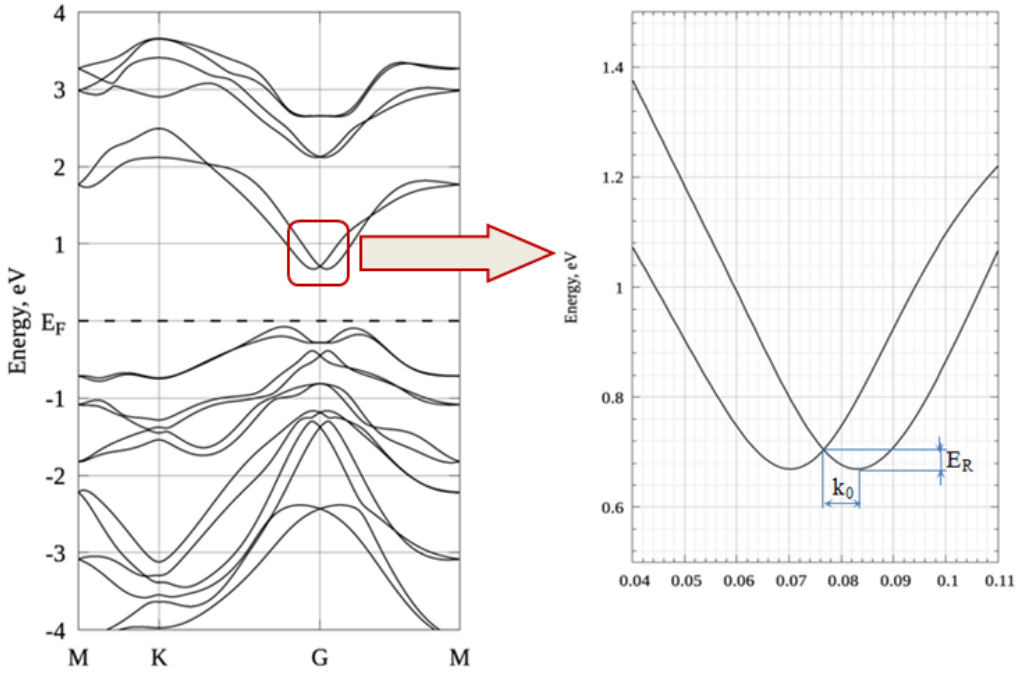

Figure 3. Band structure of BiTeI monolayer with SOI.

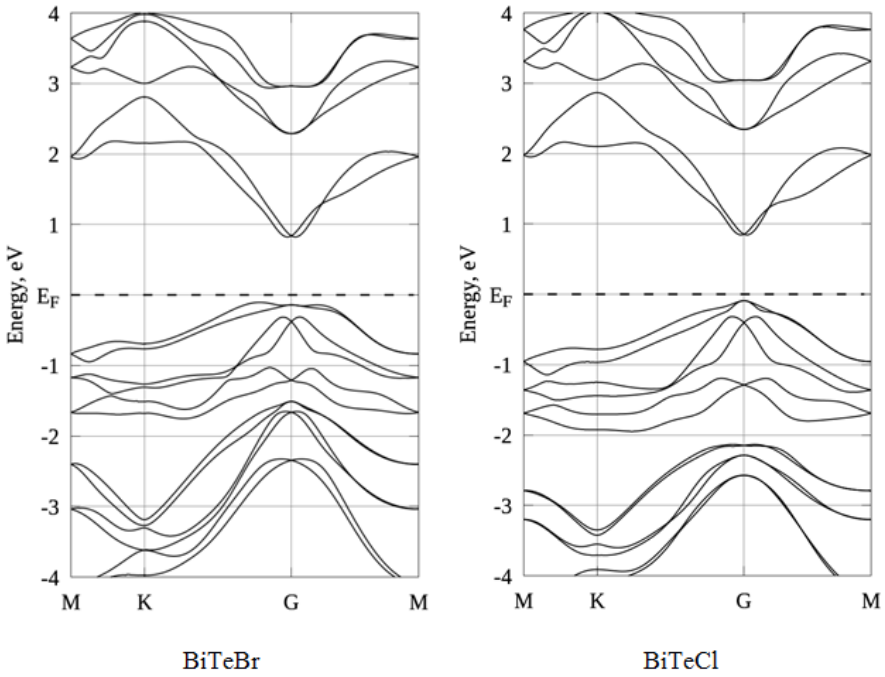

Figure 4. Band structure of BiTeBr and BiTeCl monolayers with SOI.

Parameters of the Rashba spin splitting including the momentum offset k_0, the Rashba energy E_R and the coupling constant α_R (Rashba parameter) have been calculated (table 2) as

$$E_{\mathrm{R}} = \frac{\hbar^2 k_0^2}{2m^*}, \quad (1)$$

$$k_0 = \frac{\mathrm{m}^* \alpha_{\mathrm{R}}}{\hbar^2}. \quad (2)$$

The characteristic of spin splitting of the conduction band in the BiTeCl monolayer k_0 and E_R are evaluated to be 0.0032 Å^{-1} and 0.01 eV, respectively. Based on k_0 and E_R, the Rashba parameter α_R can be estimated as 6.25 eV·Å (table 2). For the BiTeBr and BiTeI monolayers the evaluated values of k_0, E_R and α_R are 0.048 Å^{-1}, 0.017 meV, 7.08 eV·Å, and 0.068 Å^{-1}, 0.034 meV, 10.0 eV·Å respectively.

Table 2. Parameters of the Rashba spin splitting.

Structure	Calculated			Referencies [20]		
	E_{R}, eV	k_0, Å^{-1}	α_{R}, eV·Å	E_{R}, eV	k_0, Å^{-1}	α_{R}, eV·Å
BiTeCl	0.010	0.032	6.250	–	–	–
BiTeBr	0.017	0.048	7.080	0.018	0.027	1.310
BiTeI	0.034	0.068	10.000	0.040	0.043	1.860

The values obtained for the Rashba coefficient are in the range from 6.25 to 10.00 eV·Å. Our results are in good agreement with previous theoretical calculations. In standard materials of micro- and nanoelectronics, the value of α_R is of the order of 0.1 eV·Å, which is insufficient for effective application in spintronics.

5. Conclusion

In the present work, the BiTeX (X=Cl, Br, I) compounds were studied by first-principles simulation using density functional theory. The crystal structures of BiTeCl, BiTeBr, BiTeI have been established from the ionic relaxation and static calculations. The band structures of BiTeCl, BiTeBr, BiTeI monolayers have been observed via first principles simulation with spin-orbit interaction included and we note that ones have significant changes in this case. The splitting of the energy bands occurs, i.e spin degeneracy disappears. The values of the Rashba coefficient a_{R} (in the range from 6.25 to 10.00 eV $\cdot$ Å) have high magnitudes for spintronics materials. Band structures of the investigated compounds have ideal Rashba electron gas, i.e. there no other energy states near to Fermi level except Rashba states. Thus, the BiTeCl, BiTeBr, BiTeI monolayers can theoretically be considered as the spin-orbitronics material for manufacturing gate-controlled devices, such as FETs.

Acknowledgments

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