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Orbital-dependent Rashba coupling in bulk BiTeCl and BiTeI

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Abstract. By all-electron *ab initio* calculations, the layered polar semiconductor BiTeCl is shown to host giant bulk Rashba spin splitting, similar to the recently reported compound BiTeI. In both materials, the standard Rashba–Bychkov model is no longer applicable, because of huge band extrema shifts even in the absence of spin–orbit coupling and a strong momentum dependence of the Rashba coupling constant (α_R). By assuming α_R to be orbital dependent, a phenomenological extension of the Rashba–Bychkov model is proposed which explains the splitting behavior of states with small in-plane momentum.

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1. Introduction

In spintronics both the spin degree of freedom of the electron and its charge are exploited in device applications. Purely electrical control of spins, including generation, rotation and resonant manipulation, is one of the central problems of the growing field of semiconductor spintronics [1–8]. It is enabled by the interaction between the spin and the motion of electrons (spin–orbit coupling (SOC)) and promoted by the relativistic enhancement in solids [6]. In particular, momentum-dependent spin splitting in non-magnetic materials becomes possible by SOC even in the absence of an external magnetic field, given that space inversion symmetry is broken. While bulk inversion asymmetry (BIA) always leads to spin splitting of the Dresselhaus type [9], Rashba spin splitting usually exists in systems with structural inversion asymmetry (SIA) [10]. SIA can be caused by symmetry breaking at crystal surfaces [11–17], in semiconductor heterostructures [18–23] and in semiconductor monolayers [24]. For applications, one key parameter is the size of the SOC-induced spin splitting, which can be enhanced (as compared to traditional quantum-well structures [18, 19]) in materials that contain heavy elements.

Recently, giant bulk Rashba spin splitting was discovered in the layered polar semiconductor BiTeI [25–27]. The size of the splitting is one of the largest ever known, indicating the great potential of BiTeI for spintronic applications. Furthermore, although the Rashba splitting is identified for the surface state, it is of bulk origin due to the intrinsic BIA in polar crystals. The influence of the SIA caused by symmetry breaking at the surface is small [25]. The bulk nature of the Rashba splitting is exciting since all the spin-polarized carriers of the bulk are involved and, hence, anomalous magnetotransport and optical effects are possible in such materials [28–30]. Previous studies on the bulk Rashba spin splitting in BiTeI have employed the standard Rashba–Bychkov (RB) model to characterize the spin splitting behavior. In this paper, we will first use all-electron *ab initio* calculations to identify BiTeCl as another material hosting giant bulk Rashba spin splitting. We will then demonstrate that the standard RB model for the two-dimensional electron gas (2DEG) is not applicable for the bulk Rashba splittings in BiTeCl and BiTeI. Accordingly, an extended model will be proposed by assuming an orbital-dependent Rashba coupling constant (α_R) and it will be employed to explain the splitting behavior in both materials.

BiTeCl, like BiTeI, is a layered polar semiconductor with intrinsic BIA [31]. The crystal structure consists of slabs in which Bi is octahedrally coordinated by six Te/Cl atoms, see figure 1(a). Successive Te–Bi–Cl sandwiches with semi-ionic bonds are separated by a van der Waals gap, giving rise to a quasi-2D nature. In contrast to BiTeI, see figure 1(b), the BiTeCl unit cell comprises two Te–Bi–Cl slabs with space group $P6_3mc$ (no. 186). Bi, Te and Cl occupy 2b [(2/3, 1/3, z_{Bi})], 2b [(2/3, 1/3, z_{Te})] and 2a [(0, 0, z_{Cl})] Wyckoff sites, respectively, where z denotes the fractional coordinates of the atoms.

2. Methodology

Full-potential linearized augmented plane wave calculations are performed employing the WIEN2k package [32]. We use the experimental lattice constants $a = 4.2426 \text{ \AA}$ and $c = 12.397 \text{ \AA}$ for BiTeCl [31], whereas z_{Bi} , z_{Te} and z_{Cl} are determined by atomic force minimization as 0, 0.6422 and 0.8646, respectively. These values give rise to almost exactly the same bond lengths and angles as obtained by experiments [31]. A threshold energy of -9.0 Ry for separating the valence states from the core states is used. Moreover, we set $R_{\text{mt}} = 2.5 \text{ Bohr}$

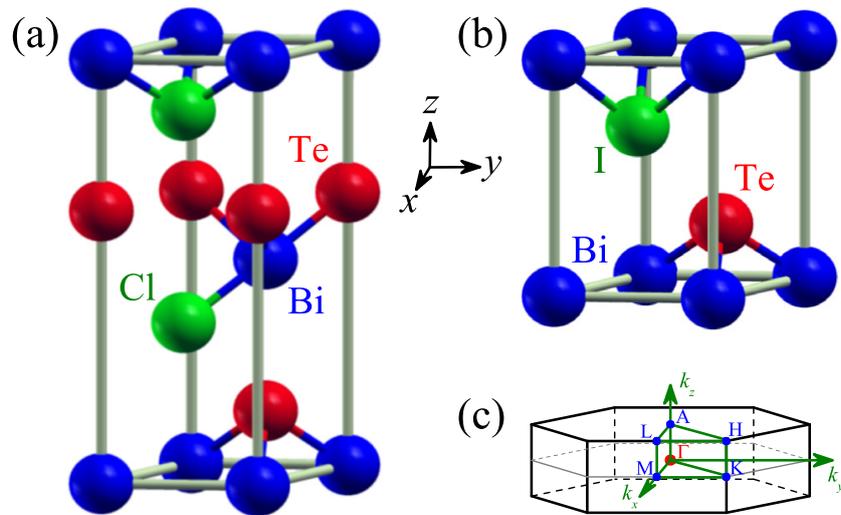


Figure 1. (a), (b) Unit cells of the layered polar compounds BiTeCl and BiTeI. (c) The first Brillouin zone.

for all atoms, $R_{mt}K_{\max} = 10$ and $\ell_{\max} = 10$. The same \vec{k} -mesh ($20 \times 20 \times 10$) and exchange-correlation functional [33] are used in all calculations. SOC is included using a second variational method with scalar relativistic orbitals as the basis, where states up to 10 Ry above the Fermi energy (E_F) are taken into account in the basis expansion. Analogous calculations are performed for BiTeI, using the crystal structure proposed in [26].

3. Results and discussion

The electronic band structure of BiTeCl in the absence of SOC is shown in figure 2(a). A semiconducting nature is identified, with both the conduction band minimum (CBM) and the valence band maximum (VBM) located near the Γ -point. While the Bi 6p dominated CBs remain unoccupied, the occupied VBs show mainly a Cl 3p and Te 5p character, indicating charge transfer from Bi to Te/Cl and an ionic nature of the Bi–Te/Cl bonds. In addition, the much higher electronegativity of Cl as compared to Te leads to a strong energetic separation between the Bi 6p and Cl 3p bands. Consequently, the Te 5p bands appear closer to E_F than the Cl 3p bands. Further analysis shows that the CBM and VBM mainly trace back to the Bi 6p_z and Te 5p_z orbitals, respectively. The Te 5p_z states lie higher in energy than the Te 5p_{xy} states near the Γ -point, which is similar to BiTeI and can be attributed to the negative crystal field splitting [26].

Without SOC all bands are at least twofold spin degenerate. In the presence of SOC, the BIA in BiTeCl causes the twofold spin degeneracy to be lifted throughout the Brillouin zone except for some special \vec{k} -points with high symmetry, see figure 2(b). Importantly, the lowest CB and the highest VB, which are dispersing from the Γ -point toward the zone boundaries in the $k_z = 0$ plane, are spin split, and both the CBM and VBM are not located at the Γ -point, see figure 2(d). That is, both the electrons (near the CBM) and the holes (near the VBM) in bulk BiTeCl show a Rashba spin splitting. In the standard RB model for a 2DEG [34], the size of the Rashba splitting is characterized by three parameters: the momentum offset k_0 , the Rashba energy E_R and the Rashba coupling constant α_R . When k_0 and E_R are determined according to figure 2(d), α_R can be readily evaluated via the relationship $\alpha_R = 2E_R/k_0$. The

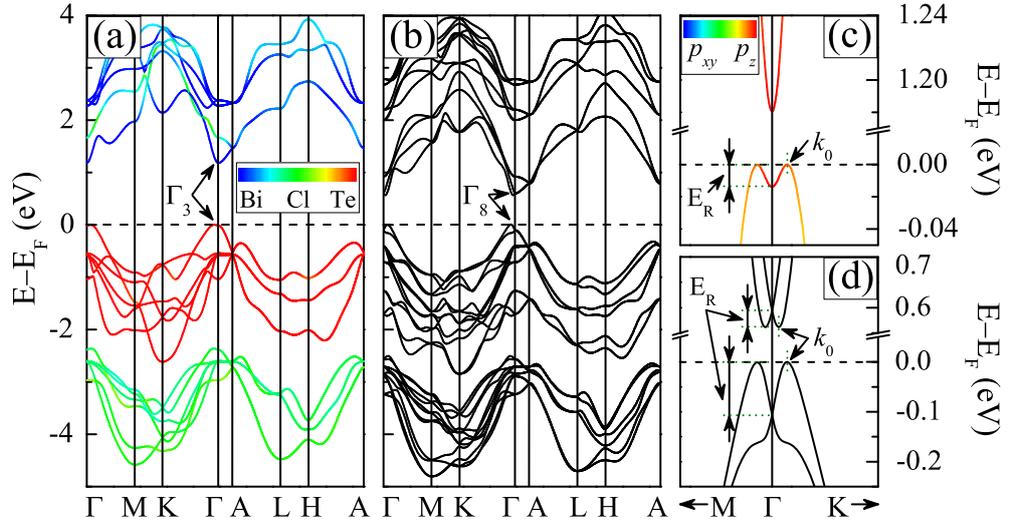


Figure 2. (a) Electronic band structure of BiTeCl in the absence of SOC. The contributions to the electronic states from different elements are indicated by different colors. (b) Electronic band structure of BiTeCl in the presence of SOC. In (a) and (b), the band symmetries around the Fermi level at the Γ -point are given. (c) Zoom of (a). The orbital character is color-coded. (d) Zoom of (b).

Table 1. The momentum offset k_0 (\AA^{-1}), Rashba energy E_R (eV) and Rashba coupling constant α_R (eV \AA) in the standard RB model for the giant bulk Rashba spin splittings (electrons at the CBM and holes at the VBM) in BiTeCl and BiTeI. The contributions of non-SOC effects are given in parentheses, see text for details.

	CBM			VBM		
	k_0	E_R	α_R	k_0	E_R	α_R
BiTeCl	0.030	0.030	2.00	0.070	0.106	3.03
				(0.070)	(0.014)	(0.40)
BiTeI	0.053	0.108	4.07	0.072	0.157	4.36
				(0.060)	(0.014)	(0.47)
BiTeI ^a	0.052	0.1	3.85	–	–	–

^a Experimental results from [25].

results obtained for BiTeCl, as listed in table 1, are much larger than the typical values for the Rashba splitting in conventional semiconductor quantum wells [18, 19]. They are comparable with systems (including BiTeI, see table 1) with enhanced Rashba splitting [11–16, 20–25].

The giant bulk Rashba spin splitting in BiTeCl is similar to that in BiTeI, except for the fact that the former is observed at the Brillouin zone center, while the latter appears at the zone boundary (A -point, $k_{\parallel} \approx 0$ and $k_z = \pi/c$) [25, 26]. However, we argue that there is no essential difference between the two cases. We recalculate the electronic band structure of BiTeI using a $1 \times 1 \times 2$ superstructure, which resembles the unit cell of BiTeCl, see above. The Rashba splitting is found to appear near the Γ -point in the $k_z = 0$ plane, similar to BiTeCl. This is because the doubled z -axis in the superstructure causes the $k_z = \pi/c$ plane to be folded back and

fall on the $k_z = 0$ plane. Noting further the similar crystal structures and chemical compositions, the Rashba splittings in BiTeCl and BiTeI should have essentially the same physical origin. Indeed, all the necessary conditions of the Rashba splitting in BiTeI (including a strong SOC in a BIA system, a narrow band gap and an identical symmetry of the top VB and bottom CB [26]) are also satisfied in BiTeCl, see figure 2.

Although the three parameters from the standard RB model can be employed to characterize the Rashba spin splittings in BiTeCl and BiTeI, a strong deviation from this simple model is revealed by further inspection of the electronic band structures. According to the standard RB model, band extrema shifted away from Γ/A by SOC should be shifted back by turning off the SOC in the calculations. This phenomenon applies to the splitting near the CBM in both BiTeCl (figure 2(c)) and BiTeI (not shown). For the splitting near the VBM, however, k_0 remains finite in the absence of SOC in both materials, in contradiction to the standard RB model. See figure 2(c) for BiTeCl as an example. The non-SOC contributions to the Rashba splitting can also be characterized in terms of k_0 , E_R and α_R , which are obtained from figure 2(c) and the relationship $\alpha_R = 2E_R/k_0$ of the standard RB model. The values given in table 1 are significant, indicating failure of the standard RB model in explaining the Rashba splittings in both the materials. We emphasize that the non-SOC effects explain, at least partially, the large difference between the α_R values for electrons and holes, see table 1, which should be the same according to [26].

The deficiency of the standard RB model to describe BiTeCl and BiTeI is also reflected by the \vec{k} -dependence of α_R . By taking the derivative of the spin splitting $\Delta E(k_{\parallel})$ with respect to k_{\parallel} , we obtain the k_{\parallel} -dependence of α_R for both the electrons near the CBM and the holes near the VBM. The results are shown in figures 3 and 4 for BiTeCl and BiTeI, respectively. In both materials, α_R shows a strong \vec{k} -dependence. This contradicts the standard RB model, where a constant α_R is assumed [34]. Therefore, a more sophisticated model is required. Noting that the standard RB effect and the bulk Rashba spin splitting have the same physical origin, namely a lifting of the electron spin degeneracy due to the SOC and the absence of inversion symmetry, we propose in the following phenomenologically an extended model to explain the bulk Rashba spin splittings in BiTeCl and BiTeI.

In the standard RB model, the parabolic band dispersion of a 2DEG causes the SOC-induced splitting to depend linearly on $|\vec{k}|$, i.e. $\Delta E(k) = 2\alpha_R|\vec{k}|$ [34]. Moreover, α_R is \vec{k} independent, and is determined only by the SIA-related potential gradient normal to the plane in which the electrons move [34, 35]. The situation is changed in bulk materials, where the potential gradient, which is required for an SOC-induced spin splitting, is provided by the BIA-induced potential asymmetry [35]. Due to different spatial extensions, electrons with different orbital characters should experience different potential gradients. Accordingly, the SOC strength is expected to vary with the orbital character of a specific electronic band. This expectation is confirmed by examining the orbital characters of the bands near the CBM and VBM of both BiTeCl and BiTeI. Taking the band near the VBM in BiTeCl as an example, α_R decreases in response to the increase/decrease of the p_{xy}/p_z character, see the bottom panel of figure 3 as well as figure 2(c).

The competition between the p_{xy} and p_z characters in determining the SOC strength suggests strongly an orbital-dependent α_R in BiTeCl and BiTeI. Assuming the same strength of SOC for a specific orbital, the SOC strength for a given eigenstate can be considered as a linear combination of the orbital SOC strengths. To be quantitative, α_R is rewritten in an orbital-dependent form as $\alpha_R = \alpha_{R,p_{xy}}c_{p_{xy}} + \alpha_{R,p_z}c_{p_z}$ ($c_{p_{xy}} + c_{p_z} = 1$), where $\alpha_{R,p_{xy}}/\alpha_{R,p_z}$ is the

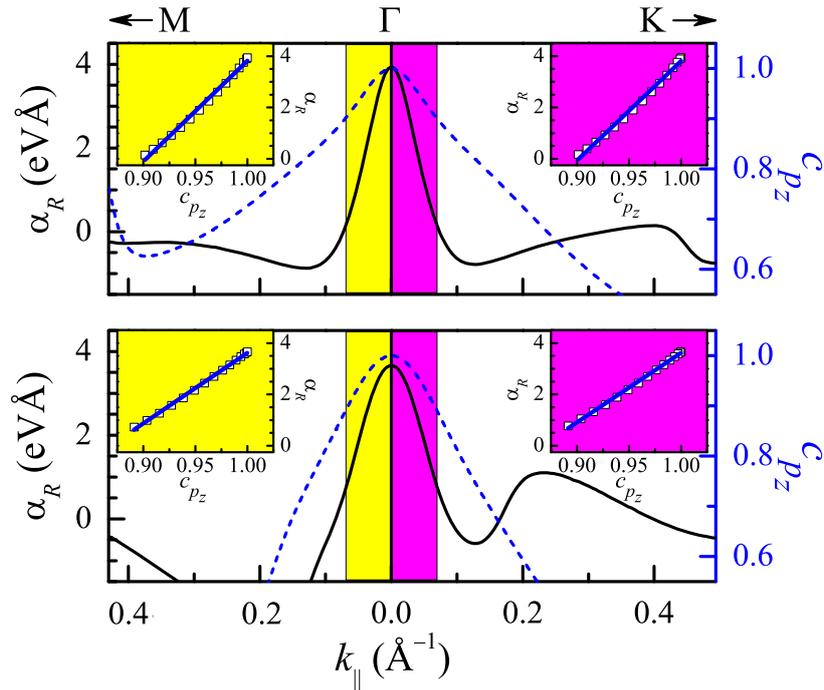


Figure 3. BiTeCl: \vec{k} dependence of the Rashba coupling constant (α_R , solid lines) for electrons near the CBM (top) and holes near the VBM (bottom) and corresponding p_z character of the electronic states (c_{p_z} , dashed lines). The insets show α_R as a function of c_{p_z} (open squares) for states near the Γ -point (shaded areas) as well as a linear fit (solid lines). Results along Γ -M and Γ -K are shown on the left and right sides, respectively.

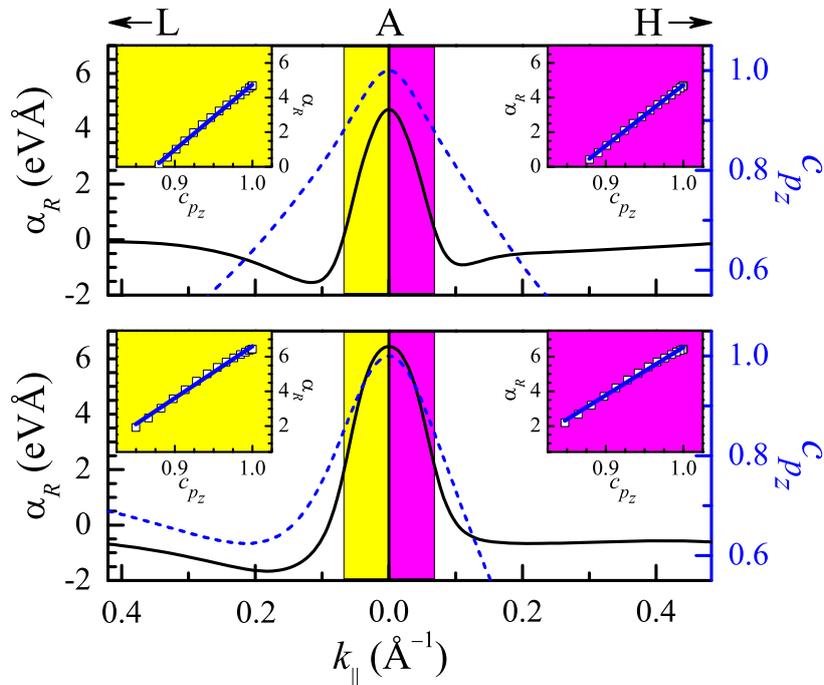


Figure 4. BiTeI: presentation analogous to figure 3, but for the spin splitting near the A-point.

Table 2. The calculated p_{xy} and p_z components of the Rashba coupling constant (eVÅ) for electrons near the CBM and holes near the VBM in BiTeCl and BiTeI, applying the extended RB model.

	BiTeCl				BiTeI			
	CBM		VBM		CBM		VBM	
	$\Gamma-M$	$\Gamma-K$	$\Gamma-M$	$\Gamma-K$	$A-L$	$A-H$	$A-L$	$A-H$
$\alpha_{R,p_{xy}}$	-35.3	-35.0	-23.9	-23.4	-32.9	-30.4	-23.3	-21.3
α_{R,p_z}	3.80	3.85	3.60	3.65	4.75	4.75	6.60	6.65

p_{xy}/p_z component of α_R and $c_{p_{xy}}/c_{p_z}$ is the weight of the p_{xy}/p_z character of a given electronic state. Only p characters are considered, because they dominate the electronic states at the CBM and VBM. Two different components, $\alpha_{R,p_{xy}}$ and α_{R,p_z} , are assumed, since SOC-induced spin splittings are caused mainly by potential asymmetry along the z -direction [25]. We stress that the orbital-dependent α_R in our extended RB model is in line with its original definition in the standard RB model. Provided that all components of α_R are the same ($\alpha_R = \alpha_{R,p_{xy}} = \alpha_{R,p_z}$), the extended RB model degenerates to the standard RB model. In the following, we use the extended model to explain the bulk Rashba spin splittings in BiTeCl and BiTeI.

For BiTeCl and BiTeI α_R is shown in the insets of figures 3 and 4 as a function of c_{p_z} , for states near both CBM and VBM along $\Gamma-M/A-L$ and $\Gamma-K/A-H$. When k_{\parallel} is large, a strong deviation from a linear dependence is observed (not shown). This can be understood as the result of a deviation from the 2DEG approximation, the band crossings and/or considerable interband couplings at \vec{k} -points far away from Γ/A . For $k_{\parallel} \lesssim 0.07 \text{ \AA}^{-1}$, however, α_R shows an almost linear dependence on c_{p_z} , see the insets in figures 3 and 4, indicating the validity of the extended RB model near Γ/A . Using a linear fit of these data, $\alpha_{R,p_{xy}}$ and α_{R,p_z} can be readily obtained from the slope and intercepts. The results for BiTeCl and BiTeI are presented in table 2. The values along $\Gamma-M$ are almost the same as along $\Gamma-K$, reflecting an in-plane isotropy of α_R . This indicates that the in-plane potential asymmetry has very little effect on α_R . Indeed, the predominance of the out-of-plane potential asymmetry for the Rashba splitting has been confirmed experimentally by angular resolved photoemission spectroscopy for BiTeI [25]. Moreover, $\alpha_{R,p_{xy}}$ and α_{R,p_z} have opposite sign, confirming the competition between the p_{xy} and p_z orbital characters. Rather different values of $\alpha_{R,p_{xy}}$ and α_{R,p_z} can be ascribed to the different spatial extensions of the p_{xy} and p_z orbitals due to which they experience different potential gradients. Angular resolved photoemission spectroscopy reveals a predominant in-plane nature of the spin orientation of the Rashba spin-split bands, which is in line with the predominant out-of-plane nature of the potential asymmetry.

4. Conclusion

In conclusion, the giant bulk Rashba spin splitting recently observed in BiTeI has also been identified for electrons near the CBM and for holes near the VBM in BiTeCl, by all-electron *ab initio* calculations. As in the case of BiTeI, the Rashba splitting in BiTeCl is ascribed to a combination of the BIA and the strong coupling between the top valence band and the bottom conduction band. For both materials, the standard RB model is not appropriate. Firstly, in the absence of SOC the band extrema remain at \vec{k} -points with finite k_{\parallel} for holes near the VBM. Secondly, the Rashba coupling constant shows a remarkable \vec{k} -dependence. We have proposed

a phenomenological extension of the standard RB model by assuming the Rashba coupling constant to be orbital-dependent and have shown that this model succeeds in explaining the spin splitting for states with small k_{\parallel} in both BiTeCl and BiTeI.

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