Letter

Crystalline spin–orbit interaction and the Zeeman splitting in Pb$_{1-x}$Sn$_x$Te

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Abstract

The ratio of the Zeeman splitting to the cyclotron energy ($M = \Delta E_z/h\omega_c$), which characterizes the relative strength of the spin–orbit interaction in crystals, is examined for the narrow gap IV–VI semiconductors PbTe, SnTe, and their alloy Pb$_{1-x}$Sn$_x$Te on the basis of the multiband $k \cdot p$ theory. The inverse mass $\alpha$, the $g$-factor $g$, and $M$ are calculated numerically by employing the relativistic empirical tight-binding band calculation. On the other hand, a simple but exact formula of $M$ is obtained for the six-band model based on the group theoretical analysis. It is shown that $M < 1$ for PbTe and $M > 1$ for SnTe, which are interpreted in terms of the relevance of the interband couplings due to the crystalline spin–orbit interaction. It is clarified both analytically and numerically that $M$ is not a quantized value but a continuous one, and $M = 1$ is obtained just at the band inversion point, where the transition from trivial to nontrivial topological crystalline insulator occurs. By using this property, one can detect the transition point only with the bulk measurements. It is also proposed that $M$ is useful to evaluate quantitatively a degree of the Dirac electrons in solids.

Keywords: spin–orbit interaction, Zeeman splitting, $k \cdot p$ theory, topological crystalline insulator, narrow gap IV–VI semiconductor, Pb$_{1-x}$Sn$_x$Te

(Some figures may appear in colour only in the online journal)
It was newly clarified that the ratio $M$ with the relativistic empirical tight-binding calculation [16] for PbTe, the top valence band of even parity ($\tau^1$ in Bi) has been a puzzle for more than half a century [6–10]. Actually, the anisotropic and large $M$ in Bi has been a puzzle for more than half a century [6–10]. Very recently, this longstanding puzzle was eventually solved based on the multiband $k \cdot p$ theory [15]. It was newly clarified that the ratio $M$ contains the information of the interband effects due to the crystalline SOI. The formula of the ratio $M$ given there is so general that it is applicable for various systems where the SOI plays an important role. Therefore, we can henceforth obtain new and rich informations of the crystalline SOI by measuring the ratio $M$ in various systems.

As another strongly spin–orbit coupled systems, the family of narrow-gap IV–VI semiconductors with rock-salt structure, such as PbTe, SnTe, GeTe, PbSe and SnSe, is of prime importance well recognized in the field of thermoelectronics [17] but newly interested in spin–orbit physics. Their alloy Pb$_{1-x}$Sn$_x$Te is the first known band inverted materials [16, 18, 19] (figure 1). The band inversion occurs since the ways of band modification due to SOI are different between PbTe and SnTe. Interestingly, the system turns from trivial to nontrivial topological crystalline insulator at this band inversion [20, 21]. Such a band inversion can affect the ratio $M$ through the interband effect of SOI, which has never been recognized in other strongly spin–orbit coupled systems.

Figure 1. Band structures of (a) PbTe and (b) SnTe obtained by the relativistic empirical tight-binding calculation [16]. (c) Positions of the energy band at the $L$-point as a function of Sn content ($x$) in Pb$_{1-x}$Sn$_x$Te calculated by the virtual crystal approximation.

In this paper, we report for the first time the intimate properties of the ratio $M$ in the band inverted system of Pb$_{1-x}$Sn$_x$Te based on the multiband $k \cdot p$ theory with the relativistic empirical tight-binding band calculation. We show how the ratio $M$ changes by the band inversion. The obtained results establish the validity of the universal understandings obtained in [15]. As a by-product, it reveals that $M$ is useful not only to obtain the information of the crystalline SOI effect, but also to detect the band inversion point only by the bulk measurement of quantum oscillations. Furthermore, $M$ can be also used to evaluate quantitatively the ‘Diracness’ of the materials.

The multiband $k \cdot p$ theory yields general formulas for the inverse mass tensor $\alpha$ and the $g$-factor $g$ in the forms [15]:

$$
\alpha_{ij} = \frac{\delta_{ij}}{m} + \sum_{n=0}^{\infty} \frac{t_{n}u_{ij}^{n} + u_{ij}u_{n}^{*} + c.c.}{E_n - E_0},
$$

(1)

$$
g_i = 2m\sqrt{G_{ii}},
$$

(2)

$$
G_{ii} = 4 \left( \sum_{n=0}^{\infty} \frac{t_n \times u_n}{E_n - E_0} \right)_i^2 \left( \sum_{n=0}^{\infty} \frac{t_n \times u_n^{*} + u_n \times u_n^{*}}{E_n - E_0} \right)_i^2,
$$

(3)

where $i$ and $j$ denote the directions, $E_0$ is the target band, and $E_n$ is the energy of the $n$th nearest energy band from $E_0$, $t_n$ ($u_n$) is the interband matrix element of the velocity operator between the 0th and $n$th band for the same (opposite) spins as $t_n = \langle \psi_0 | v | \psi_n \rangle$ ($u_n = \langle \psi_0 | v | \psi_n^{*} \rangle$). Equations (1)–(3) are general formulas to be valid for various materials. For the rocksalt structure of Pb$_{1-x}$Sn$_x$Te, we take the longitudinal axis (c) parallel to (1 1 1)-direction and the transverse axis ($x$ and $y$) perpendicular to it. The ratios are then given by

$$
M_\parallel = \frac{G_{xx}}{\sqrt{\alpha_{xx}}}, \quad M_\perp = \frac{G_{zz}}{\sqrt{\alpha_{zz}}},
$$

(4)

where $M_\parallel$ and $M_\perp$ are for the magnetic field along the longitudinal and transverse directions, respectively.

For two-band Hamiltonian only with $E_0$ and $E_1$, which is equivalent to the Dirac Hamiltonian, equations (1)–(3) yield $M_\parallel = M_\perp = 1$, the common result of the two-band model [3, 5, 14]. If we further take into account the contributions from the other band (i.e, more than three bands), it was shown that the interband contributions from the higher (lower) energy bands decrease (increase) the ratio $M$ from unity for finite region in $x$, where the band modification due to SOI keeps unity for finite region in $x$, where the band inversion point is shown in figure 1(c). For SnTe, on the other hand, the top valence band has odd parity ($\tau^1$), which couples with even parity bands ($L^s_6$, $L^s_{43}$). Then, the contribution from the lower energy bands become relevant resulting in $M$ larger than unity. It is naively expected that $M$ keeps unity for finite region in $x$, where the two-band approximation is valid, but no one has examined both theoretically and experimentally.

First, we see the properties of $M$ calculated by the numerical band calculations. Here we adopt the relativistic empirical tight-binding model by Lent et al [16], $s$-, $p$-, and $d$-orbitals
are taken as the basis, i.e. 18 band model. (The number of the eigenenergy is 36 including the spin.) The band structures for PbTe and SnTe so obtained are shown in figures 1(a) and (b). In order to obtain the band structure of Pb$_1$-Sn$_x$Te alloy, we employ the virtual crystal approximation, which demonstrates correctly the band inversion between conduction and valence bands [16]. The energy levels at the L point are shown in figure 1(c) as a function of the alloy composition $x$. The band inversion occurs at $x = 0.381$, which quantitatively agrees with the experimental values for PbTe: $\alpha_L = 3.40, \alpha_e = 39.3, g_L = 65.7, \text{and } g_e = 19.1$ with the band gap $\Delta = 0.182$ eV are in good agreement with the experimental values for PbTe: $\alpha_L = 42.2, g_L = 65.3, g_e = 13.4, \text{and } \Delta = 0.191$ eV [22].

There are four significant features of $M$: (i) $M_{\perp \perp} < 1$ for PbTe and $M_{\parallel \parallel} > 1$ for SnTe; (ii) $M_{\perp \perp} = 1$ just at the band inversion point; (iii) $M$ is very isotropic for PbTe side while it is anisotropic for SnTe side; and (iv) $M$ diverges in the SnTe side. The property (i) is consistent with the expectation above, whereas properties (ii)–(iv) are the results that are firstly revealed by the present calculation. These properties can be clearly interpreted based on the group theoretical analysis in the following.

For PbTe, the matrix elements with the $L_6^+\top$ top valence band are given as [23]

$$t_{61} = \langle L_6^+(L_4)|\psi\rangle(L_6^-(L_3)) = (a,ia,0),$$

$$u_{63} = \langle L_6^+(L_3)|\psi\rangle(L_6^-(L_1)) = (0,0,b),$$

$$t_{45} = \langle L_6^+(L_2)|\psi\rangle(L_6^-(L_0)) = (c,−ic,0) = u_{45},$$

$$t_{62} = \langle L_6^+(L_0)|\psi\rangle(L_6^-(L_2)) = (0,0,d),$$

$$u_{62} = \langle L_6^+(L_2)|\psi\rangle(L_6^-(L_0)) = (e,ie,0),$$

where $a \sim e$ are complex numbers, $C$ is the product of space inversion and time-reversal operators. $L_{1,2,3}^{\pm}$ denote the band symmetries without the SOI. A straightforward calculation yields

$$\alpha_{xx} = \alpha_{yy} = 2\left(\frac{|a|^2}{\Delta_1} + \frac{2|c|^2}{\Delta_2} + \frac{|e|^2}{\Delta_3}\right),$$

$$\alpha_{zz} = 2\left(\frac{|b|^2}{\Delta_2} + \frac{|d|^2}{\Delta_3}\right),$$

$$G_{xx} = G_{yy} = 4\left(\frac{|ab|^2}{\Delta_1^2} + \frac{|de|^2}{\Delta_2^3} + \frac{abcd^*e^* + ab'c'de}{\Delta_1\Delta_3}\right),$$

$$G_{zz} = 4\left(\frac{|d|^2}{\Delta_2} - \frac{2|e|^2}{\Delta_2} + \frac{|e|^2}{\Delta_3}\right),$$

Figure 2. Sn content dependences of (a) the inverse mass, (b) the $g$-factor, and (c) the ratio of the Zeeman splitting to the cyclotron energy for the longitudinal (||) and the perpendicular (\perp) direction of the magnetic field.

where $\Delta_0 = E_0 - E_a$ and $\Delta_1 < \Delta_2 < \Delta_3 < 0$ for PbTe. Here, although we take into account whole six bands originating from the $p$-orbitals, only the contributions from the four bands ($E_{0.3}$) are finite.

From equations (5)–(8), we obtain exact formulas of $M_{\parallel \perp}$ as

$$M_{\parallel} = \frac{1 - \lambda|X|^2 + \lambda'|Y|^2}{1 + \lambda|X|^2 + \lambda'|Y|^2}, \quad \lambda = \Delta_2/\Delta_3.$$

where $X = \sqrt{2}c/a, \ Y = e/a, \ Z = d'/b', \ \lambda = \Delta_2/\Delta_3$ and $\lambda' = \Delta_2/\Delta_3$. (Note that these forms reproduce $M_{\parallel} = M_{\perp} = 1$ if we take into account the contributions only from $E_0$ and $E_1$.)

(i) For PbTe, $\lambda$ and $\lambda'$ are positive small values. Then, it can be shown from equations (9) and (10) that both $M_{\parallel}$ and
M⊥ are less than unity due to the contributions from the higher energy bands. For SnTe, the analytic forms for α⊥, g⊥, and M are the same as equations (5)–(10) except for the different values of α ∼ e. However, in the SnTe case, Δ1 < 0 < Δ2 < Δ3 and so λ, λ′ < 0 due to the band inversion. Consequently, both M⊥ and M⊥ become greater than unity. These results verify the general understandings of M [15] in a clearer manner.

(ii) Furthermore, equations (9) and (10) give an exact proof of another important property of M—both M⊥ and M⊥ are ‘non-quantized’ values and cross unity just at the band inversion point (λ = λ′ = 0). This is rather surprising since it is naively believed so far that M = 1 (or the nontrivial Berry’s phase [24–26]) is something quantized value and so it should hold for a finite range where the band gap is small and the two-band approximation is valid. However, equations (9) and (10) prove that M is a continuous value and not quantized for the actual materials, where there are always small but finite contributions from the other bands. M = 1 is true only when the band gap Δ1 = 0.

(iii) Figure 3 shows the Sn content dependences of α∥/α⊥, g∥/g⊥, and M⊥/M⊥, which represent their anisotropy. It is clearly seen from figure 3 that M in the PbTe side is very isotropic, while it is highly anisotropic in the SnTe side. These properties can be also explained based on equations (9) and (10). For small λ- and λ′-terms, the anisotropy of M can be written in the form

$$\frac{M_\perp}{M_\parallel} \simeq 1 - \frac{3}{2} \lambda |\mathbf{X}|^2 + \frac{1}{2} \lambda' |\mathbf{Y} + \mathbf{Z}|^2.$$  

Hence, the contributions from E1 can compensate with that from E2, so that M of PbTe should be considerably isotropic, though the surprisingly isotropic M of the present result will be due to an accidentally perfect compensation. Actually, if we calculate M from other tight-binding model by Lach-hab et al [27], we obtained $M_\parallel/M_\perp = 0.909$; still isotropic, but not so perfectly. (Note that the expansion of equation (11) is valid for PbTe side, but invalid for SnTe side, where $M_\perp$ diverges.)

(iv) Equations (9) and (10) also prove that M⊥ can diverge at some point of λ, λ′ < 0, i.e. in the SnTe side and never diverge in the PbTe side. There are two possibilities: (1) both M∥ and M⊥ diverge due to $1 + \lambda|\mathbf{X}|^2 + \lambda'|\mathbf{Y}|^2 \to 0$; (2) only M⊥ diverges due to $1 + \lambda'|\mathbf{Z}|^2 \to 0$. In the present calculation, only M⊥ diverges at $x = 0.938$, which means $1 + \lambda'|\mathbf{Z}|^2$ becomes zero (i.e. $\alpha_{\parallel} \to 0$). By analyzing the properties of both M∥ and M⊥, we can obtain the detailed informations of the interband matrix elements due to the crystalline SOI.

One of the most useful and practical aspects of the ratio M is to be able to compare different materials through the common index M. It is worth noting that, for the holes at T point in Bi, $M \sim 2$ for one direction of the magnetic field, and $M = 0$ for the perpendicular direction [6–10, 15]. These properties are very different from the isotropic $M \sim 1$ in PbTe, although the T point of rhombohedral Bi has the equivalent symmetries to the L point of rocksalt PbTe [23]. This difference can be interpreted as the difference of the order of the band: the hole band of Bi has the $T_{45}$ symmetry, which is equivalent to $L_{45}$, whereas that of PbTe has the $L_{6}$ symmetry. Only this difference causes the significant difference in the property of M. In other words, M is very sensitive to the symmetry of the band and the interband matrix elements that is crucial for the crystalline SOI.

The initial purpose of the present work was to study the ratio M for the specific model of Pb1−xSnTe alloys and enrich the understanding of the general properties of M. The present results, however, give rise to byproducts. First, by using the property (ii), we can detect the exact point of the band inversion through the ‘bulk’ measurement of M, such as the quantum oscillation measurements. This means the bulk detection of the transition from the trivial to the non-trivial topological crystalline insulator [20, 21]. This approach will be a complement to the optical spectroscopy measurements.

Second, we can quantitatively evaluate the ‘Diracness’ in terms of M. Nowadays various type of materials have been recognized as the Dirac electron systems, whose effective Hamiltonian is given by the Dirac Hamiltonian, e.g. Bi [5, 14], PbTe, Ca3PbO [28] etc. Naively, when the band dispersion of the candidate material looks like Dirac dispersion, one may call it the Dirac electron system. But the judgment of this kind is too sensual. If one uses M as the indicator of the Dirac electrons, one can make a quantitative comparison of the Diracness between different materials. For example, $M = 1.00$–1.02 for electron carrier in Bi with the field along the bisectrix axis [10], while $M = 0.834$ for PbTe.

In summary, we studied the ratio of the Zeeman splitting to the cyclotron energy, $M = \Delta E_2/h\omega_c$ for Pb1−xSnTe based on the multiband $k \cdot p$ theory. By employing the tight-binding band calculation, we calculated α, g, and M numerically. Based on the group theoretical analysis, we obtained the simple but exact formulas of M, (9) and (10), which deepen the understandings of M. These formulas prove that M is not quantized but is a continuous value. This non-quantized nature of M is an important point and would have wide applications. We certified that $M < 1$ for PbTe and $M > 1$ for SnTe. It is rather
surprising that the band 2 eV far from the Fermi energy gives a sizable contribution to $M$; a strong indication of the large interband coupling due to the crystalline SOI. We found that $M$ crosses unity just at the band inversion point. By using this property, we can detect the transition to the topological crystalline insulator only from the bulk measurement of quantum oscillation. We can obtain detailed informations of the interband matrix elements due to the crystalline SOI by analyzing both $M_{\parallel}$ and $M_{\perp}$. Also, $M$ can be used as a good indicator that can quantitatively evaluate how the electron in crystal is close to the Dirac electrons. Our approach is not restricted to the emblematic case of Pb$_{1-x}$Sn$_x$Te. It opens new directions for other strongly spin–orbit coupled systems.

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