Multiband $k \cdot p$ theory for holes at the $T$-point in bismuth

Yuki Fuseya
Department of Engineering Science, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
E-mail: fuseya@pc.uec.ac.jp

Abstract. Effective $g$-factor for multiband system with a strong spin-orbit interaction is investigated. A simple, general, and gauge-invariant formula for the effective $g$-factor is obtained on the basis of $k \cdot p$ theory. By taking into account the symmetry for the $T$-point in Brillouin zone of bismuth, the formula of the effective $g$-factor is further simplified. The obtained results give a reasonable explanation for the longstanding puzzle about the large anisotropic $g$-factor of holes in bismuth.

1. Introduction
Bismuth has been studied from the dawn of solid state physics. Diamagnetism, Seebeck, Nernst, Shubnikov-de Haas and de Haas-van Alfen effects were all discovered in elemental solid of bismuth. The reason why such discoveries happened in succession is closely related to its specific electronic structure [1–4]. The crystal structure of bismuth, the rhombohedral structure, is obtained from two interpenetrating fcc lattices by adding two types of lattice distortions along the body diagonal direction: shift one sublattice relative to the other and stretch both sublattices. By these distortions, energy gaps open at the $L$- and $T$-point in the Brillouin zone and the lowest conduction band at the $L$-point overlaps with the highest valence band at the $T$-point, namely, the crystal becomes semimetallic (Fig. 1).

The effective Hamiltonian of bismuth has been studied mainly for the electrons at the $L$-point. A two-band model was introduced by Cohen and Blount on the basis of $k \cdot p$ theory with large spin-orbit interaction (SOI) [6], which succeeded to give an interpretation of the anomalously large $g$-factor at the $L$-point observed in bismuth. Soon later, Wolff pointed out that Cohen-Blount’s two-band model is essentially equivalent to the Dirac Hamiltonian in the relativistic quantum mechanics [7] by applying a suitable unitary transformation to the spin space [8]. Hence, the electrons at the $L$-point in bismuth can be described as the Dirac electrons in solids. Nowadays this two-band model becomes the “standard model” for bismuth since it has been succeeded in interpreting various physical properties of bismuth, such as magneto reflection [9–11], diamagnetism [12, 13], and angular dependent quantum oscillations [14–16]. The properties of the Dirac electrons in solids has attracted modern interests, such as interband effects on Hall conductivity [17–19], spin polarized electric current [20], and spin Hall effect [21, 22].

On the other hand, for holes at the $T$-point of bismuth, it has been believed that its effective Hamiltonian is given by a much simpler form than that of electrons [1, 23], since the angle resolved quantum oscillation measurements show that the $T$-point hole has a (free electron like)
Figure 1. Band structure of bismuth obtained by the tight-binding approximation [5].

parabolic dispersion with an anisotropic effective mass [24–26]. In order to explain the energy spectrum under a magnetic field, Smith, Baraff and Rowell phenomenologically introduced a spin mass tensor $m_s$ defined by $g^s = 4m^2\hbar \cdot m_s \cdot \hbar / \det m_s$, where $g^s$ is the effective $g$-factor, $m$ is the bare electron mass, and $\hbar$ is a unit vector along the magnetic field direction. Their model with the spin mass can fit well with the angle resolved quantum oscillation results [15, 16, 23]. However, there still remains some mysteries about the $g$-factor of holes in bismuth: (i) the microscopic origin of the effective $g$-factor (or spin mass) is unknown; (ii) there is no reasonable explanation for the vanishingly small effective $g$-factor for $B \perp$ trigonal axis [15]; (iii) why the ratio of the Zeeman splitting to the cyclotron energy, $M$, can greatly exceed 1 ($M = 2.12$ for $B \parallel$ trigonal axis), in spite of the fact that the two-band model predicts that $M$ is independent from the field direction and its maximum is $M = 1$ [6, 8].

In this paper, we derive a general theory of the effective $g$-factor on the basis of the multiband $\mathbf{k} \cdot \mathbf{p}$ theory. By applying the obtained formulae to the $T$-point holes in bismuth, we show that the longstanding puzzles (more than half a century) can be solved in a unified picture.

2. Multiband $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian

We start from the one electron Hamiltonian with a SOI,

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar^2}{4m^2c^2} \sigma \cdot \nabla V(\mathbf{r}) \times \mathbf{p},$$

(1)

where $V(\mathbf{r})$ is the periodic potential arising from the crystal, $\sigma$ is the Pauli spin matrix vector, and $c$ is the light velocity. By applying $\mathbf{k} \cdot \mathbf{p}$ theory, we obtain the eigenvalue equation

$$\sum_{n'} \left[ \epsilon_{nk_0} + \frac{\hbar^2 k^2}{2m} \delta_{nn'} \delta_{\sigma\sigma'} + \hbar \mathbf{k} \cdot \mathbf{v}^\sigma_{nn'} \right] c_{n'\sigma'}(\mathbf{k}) = \epsilon c_{n\sigma}(\mathbf{k}),$$

(2)
where $\epsilon_n k_0$ is the energy of $n$th Bloch band at a band extremum $k_0$, $v^\sigma_{\sigma'}$ is a matrix element of the velocity operator $v = p/m + (\hbar/4m^2c^2)\sigma \times \nabla V(r)$ between $n$th band with $\sigma$ spin and $n'$th band with $\sigma'$ spin states, $c_{n\sigma}(k)$ is an expansion coefficient for the eigenfunction, and the wave vector $k$ is measured from $k_0$. If we consider an $n$-band systems with a large SOI, Eq. (2) becomes

$$
\begin{pmatrix}
\epsilon_0 & 0 & h k \cdot v_{01}^\uparrow & h k \cdot v_{01}^\downarrow & h k \cdot v_{02}^\uparrow & h k \cdot v_{02}^\downarrow & \cdots \\
0 & \epsilon_0 & 0 & h k \cdot v_{01}^\uparrow & h k \cdot v_{01}^\downarrow & h k \cdot v_{02}^\uparrow & h k \cdot v_{02}^\downarrow & \cdots \\
h k \cdot v_{10}^\uparrow & h k \cdot v_{10}^\downarrow & \epsilon_1 & 0 & h k \cdot v_{12}^\uparrow & h k \cdot v_{12}^\downarrow & \cdots \\
h k \cdot v_{10}^\uparrow & h k \cdot v_{10}^\downarrow & \epsilon_1 & 0 & h k \cdot v_{12}^\uparrow & h k \cdot v_{12}^\downarrow & \cdots \\
h k \cdot v_{20}^\uparrow & h k \cdot v_{20}^\downarrow & h k \cdot v_{21}^\uparrow & h k \cdot v_{21}^\downarrow & \epsilon_2 & 0 & \cdots \\
h k \cdot v_{20}^\uparrow & h k \cdot v_{20}^\downarrow & h k \cdot v_{21}^\uparrow & h k \cdot v_{21}^\downarrow & \epsilon_2 & 0 & \cdots \\
& & & & & & & \ddots
\end{pmatrix}
= \begin{pmatrix}
c_0^\uparrow \\
c_0^\downarrow \\
c_1^\uparrow \\
c_1^\downarrow \\
c_2^\uparrow \\
c_2^\downarrow \\
& & & & & & & \ddots
\end{pmatrix}
\epsilon
= \begin{pmatrix}
\epsilon
\end{pmatrix},
$$
(3)

where $\uparrow$ and $\downarrow$ denote the degree of freedom of Kramers doublet. The quadratic term $\hbar^2k^2/2m$ in Eq. (2) is discarded from $\epsilon$ since its contribution is much smaller than the $h k \cdot v^\sigma_{\sigma'}$ terms. By expanding the Cohen-Blount’s notation [6], we have relations

$$
t_n = v_{bn}^\uparrow = v_{n0}^\uparrow,
$$
(4)

$$
u_n = v_{bn}^\downarrow = -v_{n0}^\downarrow,
$$
(5)

when the system is symmetric with respect to the time reversal and space inversion operation [27]. Then, we have a multiband $k \cdot p$ Hamiltonian in the form

$$
\mathcal{H} = \begin{pmatrix}
\epsilon_0 & 0 & h k \cdot t_1 & h k \cdot u_1 & h k \cdot t_2 & h k \cdot u_2 & \cdots \\
0 & \epsilon_0 & -h k \cdot u_1^* & h k \cdot t_1^* & -h k \cdot u_2^* & h k \cdot t_2^* & \cdots \\
h k \cdot u_1 & h k \cdot t_1 & \epsilon_1 & 0 & h k \cdot s_1 & h k \cdot w_1 & \cdots \\
h k \cdot u_1^* & h k \cdot t_1^* & \epsilon_1 & 0 & -h k \cdot w_1^* & h k \cdot s_1 & \cdots \\
h k \cdot u_2 & h k \cdot t_2 & h k \cdot s_1 & h k \cdot w_1 & \epsilon_2 & 0 & \cdots \\
h k \cdot u_2^* & h k \cdot t_2^* & h k \cdot s_1^* & h k \cdot w_1^* & \epsilon_2 & 0 & \cdots \\
& & & & & & & \ddots
\end{pmatrix}.
$$
(6)

If we consider the two band system $(n = 0, 1)$, Eq. (6) is equivalent to the Cohen-Blount’s two-band model.

### 3. Effective $g$-factor of multiband $k \cdot p$ Hamiltonian

In order to obtain a general formula for the $g$-factor, we need to derive an effective Hamiltonian of a particular band under a magnetic field in terms of $2 \times 2$ matrix including the spin degree of freedom. This can be systematically achieved by using the Löwdin partitioning, which is a canonical transformation[28, 29]. The canonical transformed Hamiltonian is generally expressed in a perturbative form as

$$
\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots,
$$
(7)

$$
\mathcal{H}^{(0)}_{mm'} = \mathcal{H}^{0}_{mm'},
$$
(8)

$$
\mathcal{H}^{(1)}_{mm'} = \mathcal{H}^{1}_{mm'},
$$
(9)

$$
\mathcal{H}^{(2)}_{mm'} = \frac{1}{2} \sum_{\ell} \mathcal{H}_{m\ell}^t \mathcal{H}_{m'\ell}^t \left( \frac{1}{E_m - E_{\ell}} + \frac{1}{E_{m'} - E_{\ell}} \right),
$$
(10)
where $\mathcal{H}^0$ is a Hamiltonian with known eigenvalues and $\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'$. In the present case, we get

$$\mathcal{H} = \frac{\pi \cdot \alpha \cdot \pi}{2m} + \sum_{n \neq 0} \left[ \frac{im\mu_B}{\epsilon_0 - \epsilon_n} \left( \begin{array}{c} -(t_n \times t_n^* + u_n \times u_n^*) \\ -2t_n^* \times u_n \\ t_n \times t_n^* + u_n \times u_n^* \end{array} \right) \cdot B \right],$$

up to the second order, where $\mu_B$ is the Bohr magneton, $\alpha = \sum_{n \neq 0} \alpha_n$ is the inverse mass tensor of $n = 0$ band, and

$$\alpha_{n,ij} = \frac{t_{ni}t_{nj}^* + t_{nj}t_{ni}^* + u_{ni}u_{nj}^* + u_{nj}u_{ni}^*}{E_0 - E_n}.$$

We made the replacement $\hbar k \rightarrow i\nabla + (e/c)A \equiv \pi$ in the multiband $k \cdot p$ Hamiltonian (6) and used the commutation relation $\pi \times \pi = -i(\hbar e/c)B$, where $e$ is the elementary charge, $B$ is the external magnetic field, and $A$ is the vector potential satisfying $B = \nabla \times A$. By using this commutation relation, the resultant formulae are gauge invariant.

The first term of Eq. (11) gives the cyclotron energy

$$\hbar \omega_c = \frac{\hbar eB}{m^*_c},$$

for $B \parallel i$. The second term of Eq. (11) gives the Zeeman energy

$$E_Z = \pm m\mu_B \sqrt{B \cdot G \cdot B},$$

$$G_{ij} = 4 \left( \sum_{n \neq 0} \frac{t_n \times u_n}{E_0 - E_n} \right)_i \left( \sum_{n \neq 0} \frac{t_n^* \times u_n^*}{E_0 - E_n} \right)_j
- \left( \sum_{n \neq 0} \frac{t_n \times t_n^* + u_n \times u_n^*}{E_0 - E_n} \right)_i \left( \sum_{n \neq 0} \frac{t_n \times t_n^* + u_n \times u_n^*}{E_0 - E_n} \right)_j.$$

The effective $g$-factor is defined by the Zeeman energy as $E_Z = \pm g^* \mu_B B_i/2$, so we have a general formula of the effective $g$-factor in the form

$$g^* = 2m \sqrt{G_{ii}}.$$

This is the answer to the question (i). Then the ratio of the Zeeman splitting to the orbital splitting, which characterizes the effect of crystalline SOI, for $B \parallel i$ is given by

$$M = \frac{\Delta E_Z}{\hbar \omega_c} = \sqrt{\frac{G_{ii}}{\alpha_{jj} \alpha_{kk} - \alpha_{jk}^2}},$$

where $i, j,$ and $k$ are perpendicular to each other.
When we apply Eq. (17) to the two-band model \((n = 0, 1)\), we have

\[
G_{zz} = \frac{1}{\Delta^2} \left[ 4 \left( |t_{1x}|^2 |u_{1y}|^2 + |t_{1y}|^2 |u_{1x}|^2 \right) + 2 \left( |t_{1x}|^2 |t_{1y}|^2 + |u_{1y}|^2 |u_{1x}|^2 \right) \right.
\]

\[
- \left( t^2_{1x} t^*_{1y} + t^2_{1y} t^*_{1x} + u^2_{1x} u^*_{1y} + u^2_{1y} u^*_{1x} \right)
\]

\[
- 2 \left( t_{1x} t^*_{1y} u_{1y} u^*_{1x} + t_{1y} t^*_{1x} u_{1x} u^*_{1y} - t_{1x} t^*_{1y} u_{1x} u^*_{1y} - t_{1y} t^*_{1x} u_{1x} u^*_{1y} \right) \right]
\]

\[
= \alpha_{xx} \alpha_{yy} - \alpha^2_{xy} = (\hbar \omega_c)^2,
\]

so \(M = 1\), which, of course, agrees with the result of Cohen-Blount.

\[
\alpha_{x} (6) = \langle T_{45}^- (1) | \alpha \rangle = (a_n, i a_n, 0)
\]

\[
u (6) = \langle T_{45}^- (1) | \nu \rangle = (-a_n, -i a_n, 0),
\]

\[
u (45) = \langle T_{45}^- (1) | \nu \rangle = (0, 0, b_n),
\]

where operator \(C\) reverses the spin and \(a_n, b_n\) are complex numbers \([30, 31]\). The \(x\), \(y\), and \(z\)-directions are taken along the binary, bisectrix, and trigonal axes.

**Figure 2.** Energy levels at the \(T\)-point in bismuth. The selection rules for the hole band \((T^-_{45})\) are indicated by the arrows: the solid arrows are for the transitions of \(x\) and \(y\) components and the dashed arrow is for that of \(z\) component \([30]\). Here, \(x\), \(y\), and \(z\)-directions are taken along the binary, bisectrix, and trigonal axes.

### 4. Holes at the \(T\)-point of bismuth

So far, we have derived a general theory of the effective \(g\)-factor for multiband systems with a strong SOI. The obtained formulae are applicable for various systems. In the following, we shall obtain a further simplified formula of the \(g\)-factor of the holes at the \(T\)-point in bismuth by taking into account the specific symmetry of the \(T\)-point.

The group theoretical symmetry of band at the \(T\)-point has been investigated both experimentally and theoretically \([1, 30, 31]\). The symmetry of each band are indicated in Fig. 2. The matrix elements related to the hole band \((T^-_{45})\) are finite only for

\[
t_n^{(6)} = \langle T_{45}^- (1) | \nu \rangle = (-a_n, i a_n, 0)
\]

\[
u_n^{(6)} = \langle T_{45}^- (1) | \nu \rangle = (-a_n, -i a_n, 0),
\]

\[
u_n^{(45)} = \langle T_{45}^- (1) | \nu \rangle = (0, 0, b_n),
\]

where operator \(C\) reverses the spin and \(a_n, b_n\) are complex numbers \([30, 31]\). The \(x\), \(y\), and \(z\)-directions are taken along the binary, bisectrix, and trigonal axes. By substituting Eqs. (20)–(22) into Eq. (16), only \(G_{zz}\) is finite as

\[
G_{zz} = 4 \left| \sum_{n \neq 0} \frac{2 a_n^2}{\epsilon_0 - \epsilon_n} \right|^2,
\]

5
and the other ($G_{xx} = G_{yy} = G_{xy} = G_{yz} = G_{zx}$) are zero since the effective $g$-factor is given by the outer products of $t_n$ and $u_n$. Consequently, the Zeeman splitting as a function of the field direction is given by $\Delta E_Z(\theta) = 2m\mu_B B \cos \theta \sqrt{G_{zz}}$, where $\theta$ is an angle from the trigonal axis. Therefore, $G_{zz}$ is finite for $B \parallel$ trigonal and is zero for $B \perp$ trigonal, which gives a possible solution to the mystery (ii).

The ratio of the Zeeman splitting to the cyclotron energy becomes

$$M = \sqrt{\frac{\sum_{n \neq 0} a_n^2}{\sum_{n \neq 0} a_n^2} \left( \frac{\epsilon_0 - \epsilon_n}{\epsilon_0 - \epsilon_n} \right)^2}. \quad (24)$$

This analytic result tells us how the ratio $M$ behaves. Let’s consider a simple example with three band model ($n = 0, 1, 2$). If $\epsilon_0 < \epsilon_1 < \epsilon_2$,

$$M = \frac{\epsilon_0 - \epsilon_n}{\epsilon_0 - \epsilon_n} \leq 1, \quad (25)$$

where $\tilde{a}_n = a_n / \sqrt{\epsilon_0 - \epsilon_n}$. If $\epsilon_2 < \epsilon_0 < \epsilon_1$,

$$M = \frac{\epsilon_0 - \epsilon_n}{\epsilon_0 - \epsilon_n} \geq 1. \quad (26)$$

Consequently, we can obtain a simple understanding about the ratio $M$ from these examples. When the contribution from the lower (higher) energy band is dominant, the ratio $M$ will increase (decrease). This gives a reasonable explanation to the mystery (iii). Moreover, by evaluating $M$ from the tight-binding model of Liu and Allen [5] with Eqs. (12), (16), and (17), we obtain $M = 2.08$, which agrees well with the experimental value of $M = 2.12$ [15].

5. Conclusion

In this paper, we have investigated the $g$-factor on the basis of the multiband $k \cdot p$ Hamiltonian with the strong SOI. The general formula of the effective $g$-factor was derived in the gauge invariant form by applying the Löwdin partitioning to the multiband $k \cdot p$ Hamiltonian. The effective $g$-factor of holes at the $T$-point in bismuth was obtained by considering the specific symmetries for the $T$-point. It was found that the effective $g$-factor for holes is highly anisotropic; $g^* = 0$ for the field perpendicular to the trigonal axis. Further more, it was shown that the ratio of the Zeeman splitting to the cyclotron energy becomes larger than $M = 1$, which is the maximum value of the two-band model, when the contributions from the lower energy band is taken into account. $M = 2.08$ was numerically obtained by applying the theoretical results to the tight-binding calculation. These results gives possible solutions to the longstanding problem for the holes at the $T$-point in bismuth in a unified picture.

References

[1] Dresselhaus M S 1971 J. Phys. Chem. Solids 32 3
[2] Édèl’mann V S 1976 Adv. Phys. 25 555
[3] Issi J P 1979 Aust. J. Phys. 32 585
[4] Fuseya Y, Ogata M and Fukuyama H 2015 J. Phys. Soc. Jpn. 84 012001
[5] Liu Y and Allen R E 1995 Phys. Rev. B 52 1566
[6] Cohen M H and Blount E I 1960 Phil. Mag. 5 115
[7] Dirac P A M 1928 Proc. Roy. Soc. Lond. A 117 610
[8] Wolff P A 1964 J. Phys. Chem. Solids 25 1057
[9] Maltz M and Dresselhaus M S 1970 Phys. Rev. B 2 2877
[10] Vecchi M P and Dresselhaus M S 1974 Phys. Rev. B 9 3257
[11] Vecchi M P, Pereira J R and Dresselhaus M S 1976 Phys. Rev. B 14 298
[12] Fukuyama H and Kubo R 1970 J. Phys. Soc. Jpn. 28 570
[13] Mikitik G P and Sharlai Y V 2000 Low Temp. Phys. 26 39–46
[14] Sharlai Y V and Mikitik G P 2009 Phys. Rev. B 79 081102(R)
[15] Zhu Z, Fauquè B, Fuseya Y and Behnia K 2011 Phys. Rev. B 84 115137
[16] Zhu Z, Fauquè B, Malone L, Antunes A B, Fuseya Y and Behnia K 2012 Proc. Natl. Acad. Sci. U.S.A. 109 14813
[17] Fuseya Y, Ogata M and Fukuyama H 2009 Phys. Rev. Lett. 102 066601
[18] Fukuyama H, Fuseya Y, Ogata M, Kobayashi A and Suzumura Y 2012 Physica B, 407 1943
[19] Kajita K, Nishio Y, Tajima N, Suzumura Y and Kobayashi A 2014 J. Phys. Soc. Jpn. 83 072002
[20] Fuseya Y, Ogata M and Fukuyama H 2012 J. Phys. Soc. Jpn 81 013704
[21] Fuseya Y, Ogata M and Fukuyama H 2012 J. Phys. Soc. Jpn 81 093704
[22] Fuseya Y, Ogata M and Fukuyama H 2014 J. Phys. Soc. Jpn. 83 074702
[23] Smith G E, Baraff G A and Rowell J M 1964 Phys. Rev. 135 A1118
[24] Kao Y H 1963 Phys. Rev. 129 1122
[25] Brandt N B, Dolgolenko T F and Stuposhenko N N 1964 Sov. Phys. JETP 18 908
[26] Bhargava R N 1967 Phys. Rev. 156 785
[27] Yafet Y 1963 Solid State Phys. 14 1 – 98 ISSN 0081-1947
[28] Löwdin P O 1951 J. Chem. Phys. 19(11) 1396–1401
[29] Winkler R 2003 Spin-Orbit Coupling Effects in Two-Dimensional Electron and Hole Systems (Springer-Verlag)
[30] Golin S 1968 Phys. Rev. 166(3) 643–651
[31] Bate R T, Einspruch N G and May P J 1969 Phys. Rev. 186(3) 599–608