Interband Contributions from the Magnetic Field on Hall Effects for Dirac Electrons in Bismuth

Yuki Fuseya,[1,*] Masao Ogata,[1] and Hidetoshi Fukuyama[2]
[1]Department of Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[2]Department of Applied Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
(Received 1 April 2008; published 9 February 2009)

The Hall conductivity σ_{xy} of Dirac electrons with a spin-orbit interaction is examined. It is shown that there is an unconventional contribution to σ_{xy} generated by the interband effects of a magnetic field, which is remarkable near the band edges and does not depend on impurity scatterings so much, suggesting the same origin as the known large diamagnetism. Correspondingly, the Hall coefficient exhibits unexpected peaks at around the band edges. Implications of the present results to bismuth alloys are discussed.

DOI: 10.1103/PhysRevLett.102.066601 PACS numbers: 72.15.Gd, 72.20.−i, 75.20.−g

Electrons in a periodic potential can be described by Bloch band theory, which is the basis of understanding the electronic properties of solids. In this theory, it is natural to expect that the effects of an external magnetic field H are described by the effective Hamiltonian $\mathcal{H}_{\rm eff} = E_n(\boldsymbol{k} + e\boldsymbol{A}/c)$ except for the Zeeman effect, where $E_n(\boldsymbol{k})$ is the nth Bloch band for $H = 0$. This simple procedure has been proven to be very useful for interpreting many phenomena. Nevertheless, this substitution, $\boldsymbol{k} \rightarrow \boldsymbol{k} + e\boldsymbol{A}/c$, or the Peierls substitution, is insufficient in principle [1,2]; electrons under a magnetic field are not confined in a single Bloch band, but undergo complex interband oscillations. These effects will be referred to as interband effects of a magnetic field, which are not contained in the Peierls substitution.

The importance of the interband effect has been recognized in the studies of the orbital susceptibility, χ. In most cases, χ obtained by the Peierls substitution, the Landau-Peierls (LP) formula [1] is used for a comparison with the experimental results. However, the LP formula fails completely in some cases, e.g., to explain the anomalous behavior of graphite or bismuth. To cope with this puzzle, Adams criticized the use of the LP formula in cases where the band gap is much smaller than the Fermi energy [3]; Bi just satisfies this condition. In such cases, the interband effect of a magnetic field may make large contributions to χ. McClure succeeded to explain the large diamagnetism of graphite [4], based on the particular band structure similar to the (2×2) Dirac electron. This work is the basis for the recent active studies of graphite-type Dirac electrons, such as graphene [5–8] and α-ET_2I_3 [9].

As for Bi, it is more complicated because of the strong spin-orbit coupling of the order of 1.5 eV. The spin-orbit interaction couples with the different Bloch bands, which causes a remarkable effect of interplay between spins and orbital motion of electrons. The effective g factor becomes much larger than that of free electrons. (g can exceed 200 for Bi.) The orbital diamagnetism and the spin paramagnetism are mixed together in an essential way by the strong spin-orbit coupling, so that they cannot be separated. By considering the strong spin-orbit couplings and the associated interband effects due to a special band structure similar to Dirac electrons (here 4×4), the anomalously large diamagnetism of Bi was clearly explained [10].

Although the orbital magnetism of Bi has been understood, the transport properties of this Bi type, i.e., the Dirac electrons with the strong spin-orbit coupling, have not been examined so far in detail contrary to the graphite type [5,6]. In this Letter, we investigate Hall effects of the Dirac electrons of the Bi type, keeping in mind that the interband effects of the magnetic field essentially affect orbital magnetism. It is to be stressed that the Dirac electrons of the Bi type belong to a different class from that of the graphite type, where the spin-orbit coupling is negligibly small. The Hamiltonian of the Bi type can be written in terms of 4×4 matrices, whereas that of the graphite type can be by 2×2 matrices. These two types have similar dispersions, but they are quite different, especially in the interband effects of a magnetic field. Actually, we find a new contribution to the Hall conductivity, σ_{xy}, due to the interband effects. Since this new contribution to σ_{xy} is remarkable near the band edges and does not depend on impurity scattering so much, we consider the possibility that this new contribution is associated with the diamagnetic current in spite of the difference between them; the diamagnetic current is equilibrium quantity, while σ_{xy} is not. It is also found that the unexpected peaks of the Hall coefficient appear at around the band edges. Implications of the present results to Bi alloys are also discussed.

The model we will study is a two-band model which consists of a pair of doubly degenerate bands where their extrema is not at the center of the Brillouin zone. Such a two-band model was introduced for Bi by Cohen and Blount with a simple one-electron Hamiltonian [11]:

$$\mathcal{H} = \frac{p^2}{2m} + V + \frac{\nabla^2 V}{8(mc)^2} + \frac{\boldsymbol{p} \cdot \boldsymbol{s} \times \boldsymbol{\nabla} V}{2(mc)^2}, \qquad (1)$$

where V is the crystal potential, $\boldsymbol{s}$ is the spin, and the last term is the spin-orbit interactions. Wolff derived an effective Hamiltonian of Eq. (1) in the form which is essentially

identical to the Dirac Hamiltonian [12,13]:

$$\mathcal{H} = \Delta\beta + iv\sum_{\mu} k_\mu \beta\alpha_\mu, = \begin{pmatrix} \Delta & 0 & ivk_z & iv(k_x - ik_y) \\ 0 & \Delta & iv(k_x + ik_y) & -ivk_z \\ -ivk_z & iv(-k_x + ik_y) & -\Delta & 0 \\ -iv(k_x + ik_y) & ivk_z & 0 & -\Delta \end{pmatrix}, \tag{2}$$

where α_i and β are the 4×4 matrices that appear in the Dirac theory. (Following Wolff we have discarded the $p^2/2m$ term since this term is usually small in Bi.) Hereafter, the origin of the energy is taken at the center of the band gap 2Δ. This "relativistic" Hamiltonian already includes spin-orbit interactions, which is very strong in Bi, and can be expressed only in terms of 4×4 matrices. This is essentially different from that of the graphite type, which has negligibly small spin-orbit interactions and then can be written in terms of 2×2 matrices [5–9,14]. For pure Bi, these two-bands are located at the L point for electrons and the T point for holes. Although both carriers are essentially described by the tilted Dirac equations [9,12], the velocity of electrons, v, are assumed to be isotropic for simplicity in order to avoid complexities, which are not essential to present studies [13].

It should be emphasized here that this Hamiltonian is not in the Bloch representation but in the Luttinger-Kohn representation [15], in which the wave function, $\psi_{n\boldsymbol{k}}$, is expressed in the form $\psi_{n\boldsymbol{k}} = u_{n\boldsymbol{k}_0}(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, $u_{n\boldsymbol{k}_0}$ being the periodic part of the Bloch function at $\boldsymbol{k}_0$, e.g., the L point for electrons or the T point for holes. The wave function under the magnetic field is correctly represented only in this representation [16]. Moreover, in this representation, we can obtain the gauge-invariant results [16,17]. Note that this representation is exact and related to the Bloch wave function by a unitary transformation.

The conductivity, σ_{xx}, and the Hall conductivity, σ_{xy}, are calculated on the basis of the Kubo formula in the same way as Ref. [16]. The calculation is straightforward but rather lengthy. The final expressions are summarized as

$$\sigma_{xx} = -\frac{e^2}{\pi^3 v}\int_{-\infty}^{\infty} d\varepsilon f'(\varepsilon - \mu)\int_0^{\infty} dX[F_1(\varepsilon, X) - F_2(\varepsilon, X)], \tag{3}$$

$$F_1(\varepsilon, X) = \frac{X^2(\varepsilon^2 + \Gamma^2 - \frac{1}{3}X^2 - \Delta^2)}{\{(\varepsilon + i\Gamma)^2 - X^2 - \Delta^2\}\{(\varepsilon - i\Gamma)^2 - X^2 - \Delta^2\}}, \tag{4}$$

$$F_2(\varepsilon, X) = \frac{X^2\{(\varepsilon + i\Gamma)^2 - \frac{1}{3}X^2 - \Delta^2\}}{2\{(\varepsilon + i\Gamma)^2 - X^2 - \Delta^2\}^2} + \text{c.c.}, \tag{5}$$

$$\sigma_{xy} = \frac{e^3 vH}{12\pi^2 c}\int_{-\infty}^{\infty} d\varepsilon[F_3(\varepsilon)f(\varepsilon - \mu) + F_4(\varepsilon)f'(\varepsilon - \mu)]\text{sgn}(\varepsilon), \tag{6}$$

$$F_3(\varepsilon) = \frac{\varepsilon + i\Gamma}{\{(\varepsilon + i\Gamma)^2 - \Delta^2\}^{3/2}} + \text{c.c.}, \tag{7}$$

$$F_4(\varepsilon) = \frac{-2\Gamma^4 - \Gamma^2\Delta^2 + (\Delta^2 - \varepsilon^2)^2 + 2i\Gamma^3\varepsilon - i\Gamma\mu(\Delta^2 - \varepsilon^2)}{2\Gamma^2\varepsilon^2\sqrt{\varepsilon^2 - \Gamma^2 - \Delta^2 + 2i\Gamma\varepsilon}} + \text{c.c.}, \tag{8}$$

where $f(\varepsilon)$ is the Fermi distribution function, and μ the chemical potential. Here we have introduced a finite damping, Γ, for electrons as in Ref. [7] to represent the effects of impurity scattering present in actual materials. (We assume Γ to be constant in order to make our argument as simple and transparent as possible, although Shon and Ando have indicated that Γ somewhat depends on energy and momentum in the case of graphene [14].)

The μ dependence of σ_{xx} and σ_{xy} at $T = 0$ are shown in Figs. 1(a) and 1(b), respectively. The normalization factors are taken to be $\sigma_{xx0} = e^2/\pi^2 v$ and $\sigma_{xy0} = e^3 v/12\pi^2 c$. Away from the band edge, $|\mu| \gg \Delta$, $\sigma_{xx} \propto \mu^2$, and $\sigma_{xy} \propto -\mu$, which are consistent with the Peierls substitution [18]. In the band-gap region, $|\mu| < \Delta$, both conductivities have small values since we have assumed a finite Γ.

The Hall coefficient defined by $R_H = \sigma_{xy}/\sigma_{xx}^2 H$ is shown in Fig. 1(c) where the normalization is taken to be $R_{H0} = \sigma_{xy0}/\sigma_{xx0}^2 H$. For $|\mu| \gg \Delta$, $R_H \propto -\mu^{-3}$ as is expected from the properties of σ_{xx} and σ_{xy} [18]. For $|\mu| \leq \Delta$, on the other hand, it is found that R_H changes its sign through $\mu = 0$, and exhibits remarkable peaks at $\mu \simeq \pm\Delta$. In the metallic region (e.g., $\mu/\Delta = 3.0$), $\sigma_{xx} \propto \Gamma^{-1}$ and $\sigma_{xy} \propto \Gamma^{-2}$. Thus, R_H does not depends on Γ as in the free-electron case. On the other hand, these relations are broken when $\mu \leq \Delta$. In the insulating region (e.g., $\mu/\Delta = 0.1$), we find that $\sigma_{xx} \propto \Gamma^2$, $\sigma_{xy} \propto \Gamma^{2.75}$, and $R_H \propto \Gamma^{-1.25}$, while at the band-edge region (e.g., $\mu/\Delta = 1.0$), $\sigma_{xx} \propto \Gamma^{0.75}$, $\sigma_{xy} \propto \Gamma^{-0.5}$, and $R_H \propto \Gamma^{-2}$; namely, R_H strongly depends on Γ. Thus the finite value of R_H in the insulating region is due to the finite Γ, which avoids the theoretical problem concerning the order of the zero-frequency and zero-temperature limits. Since the Γ dependence of R_H at the band edge is stronger than in the insulating region, clear peak structures appear in the limit of $\Gamma \to 0$ as shown in Fig. 1(c). This peak structure appears even within the intraband approximation (discussed later), and the interband contribution further increases the peak structure [the inset of Fig. 1(c):$R_H^{\text{intra}} \equiv \sigma_{xy}^{\text{intra}}/\sigma_{xx}^2$].

The sign change of R_H has been seen for the case of 2×2 Hamiltonian with $\Delta = 0$ [7]. In this case, however, the peak structures appear simultaneously with the sign change at $\mu = 0$. In contrast, our calculation for $\Delta \neq 0$ shows that the peaks appear at the band edges which are away from the sign change at $\mu = 0$. Gusynin and Sharapov have shown that a similar sign change occurs in the Hall angle,

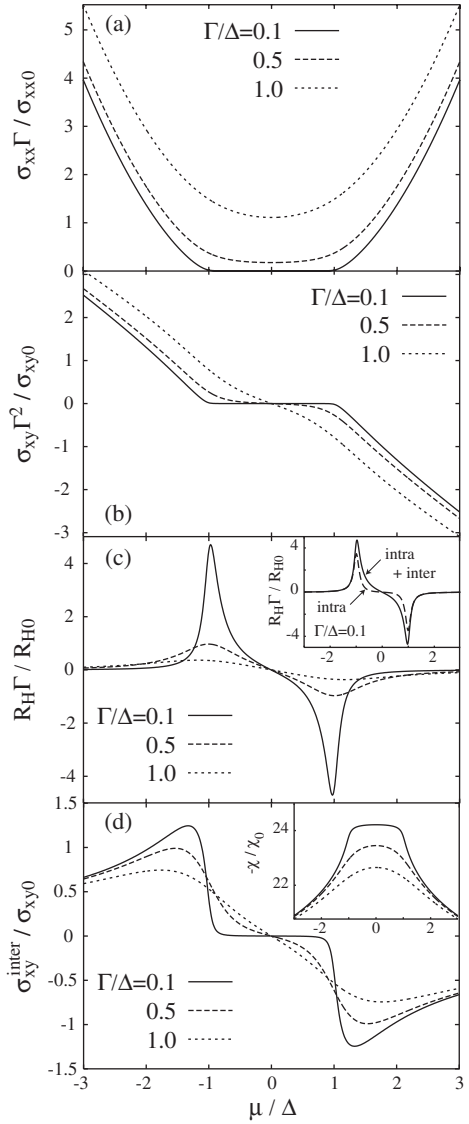

FIG. 1. The chemical-potential dependences (at $T = 0$) of (a) σ_{xx}, (b) σ_{xy}, (c) R_H, and (d) the interband contribution to σ_{xy}. The dashed line in the inset of (c) indicates $R_H^{\rm intra}$ for a particular choice of $\Gamma = 0.1$. The inset of (d) is χ vs μ, where $\chi_0 = 4e^2v/15c^2\pi^2$.

$\Theta_H = \arctan(\sigma_{xy}/\sigma_{xx})$, but there is no anomaly in Θ_H at the band edges according to their calculation [6].

Now we study the interband effects of the magnetic field on σ_{xy}. We extract the interband contribution, $\sigma_{xy}^{\rm inter}$, by subtracting the intraband contribution, $\sigma_{xy}^{\rm intra}$, from σ_{xy}, namely, $\sigma_{xy}^{\rm inter} = \sigma_{xy} - \sigma_{xy}^{\rm intra}$. Here $\sigma_{xy}^{\rm intra}$ is the Hall conductivity calculated within the intraband approximation, i.e., the Peierls substitution (cf. [16]), which is given in the present case as follows:

$$\sigma_{xy}^{\rm intra} = -\frac{e^3 v H}{6\pi^3 c} \sum_{n=\pm} \int_{-\infty}^{\infty} d\varepsilon f'(\varepsilon - \mu) \times \int_0^{\infty} dX \frac{nX^4}{[E_n(X)]^3} \frac{4\Gamma^3}{3[(\varepsilon - E_n(X))^2 + \Gamma^2]^3}, \quad (9)$$

where $E_{\pm}(X) = \pm\sqrt{X^2 + \Delta^2}$. The obtained interband contribution $\sigma_{xy}^{\rm inter}$ is shown in Fig. 1(d). The remarkable property is that $\sigma_{xy}^{\rm inter}$ takes the largest value at the band edge, and becomes smaller away from the band edge, contrary to $\sigma_{xy}^{\rm intra}$. Furthermore, $\sigma_{xy}^{\rm inter}$ does not depend on Γ so much, while $\sigma_{xy}^{\rm intra}$ does. [Note that the vertical axis of Fig. 1(b) includes a factor Γ^2.] This indicates that $\sigma_{xy}^{\rm inter}$ has a different nature from $\sigma_{xy}^{\rm intra}$.

The property of $\sigma_{xy}^{\rm inter}$ against Γ and μ is quite similar to that of the orbital susceptibility χ. The behavior of χ calculated in the gauge-invariant Kubo formula [17] is shown in the inset of Fig. 1(d). χ takes the largest value for $|\mu| \lesssim \Delta$, and becomes smaller away from the band edge. Also, χ does not depend on Γ so much. (Near the band edge and insulating region, the intraband contribution, the LP formula vanishes. As a result, almost whole χ originates from the interband contributions.) These similarities strongly suggest the correlation between $\sigma_{xy}^{\rm inter}$ and χ. The physical origin of this correlation can be understood as follows. In the insulating region, electrons in a magnetic field circulate locally and make a diamagnetic current. There are no electrons going through the crystal because of the band gap. In the band-edge region, in contrast, the electrons start to be transferred from local orbitals to the neighboring orbitals due to some scattering. These processes will generate contributions to the Hall conductivity, $\sigma_{xy}^{\rm inter}$. The diamagnetic current decreases away from the band edge as is known from the behavior of χ. Correspondingly, $|\sigma_{xy}^{\rm inter}|$ actually decreases away from the band edge. This supports the present picture. Note the difference between the present interband effect and the effect of the magnetic break down [19]. The former is the transition between different energies with an equal wave number which is of importance in the weak field. The later is quantum tunneling in which electrons hop to different wave numbers with an equal energy, which is of importance in the strong field.

Finally, let us discuss the implications of the present results to Bi. Bi and its alloys have been attracting renewed interest in the context of the spin Hall effect [20,21] and the 3D fractional quantum Hall effect [22]. In spite of these fascinating behaviors, there has been no theoretical analysis especially in the weak field limit. In order to understand these phenomena, it is indispensable to understand the motion of carriers in a magnetic field. Some measurements of R_H in Bi have already exhibited the peak structures and the rapid sign changes with respect to μ [23,24]. They are, however, not consistent with each other. This would be due to the purity of samples or the inhomogeneity of either chemical or external pressure. For further investigations, we need some guidelines. Here, we propose a clear-cut measurement, and classify the experimental situations, which have not been thoroughly clarified in spite of the intensive studies since the 1960s.

It will be rather difficult to find the peak of R_H at $\mu \simeq \pm\Delta$ when the peak is very sharp. So we propose a simul-

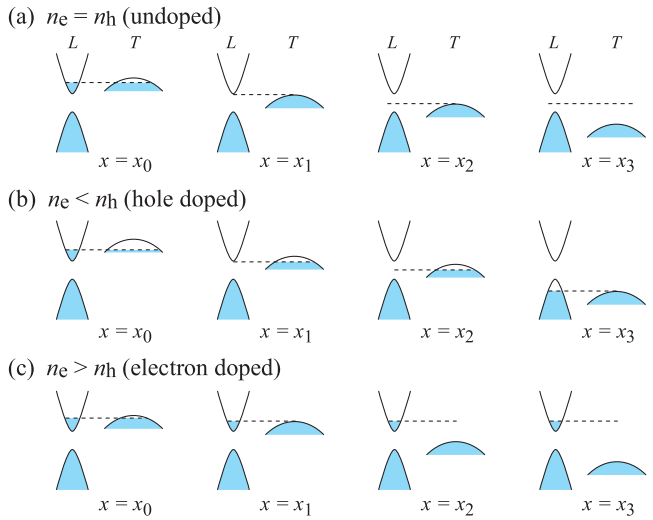

FIG. 2 (color online). Schematic band structure around the L and T points of Bi and its alloys for the (a) undoped ($n_e = n_h$), (b) hole doped ($n_e < n_h$), and (c) electron doped ($n_e > n_h$) case. The dashed lines indicate the level of the chemical potential.

taneous measurement of χ together with that of R_H to observe the band-edge property in a more transparent way. A clear kink of χ at $\mu \simeq \pm\Delta$ has been actually observed experimentally [25]. Thus, the kink in χ can be used to identify the band edge, and then we can expect the peak of R_H in the same region.

For the analysis of the experiments, it is important to distinguish following three experimental situations, which have not been recognized before even though the differences are crucial: (a) undoped ($n_e = n_h$), (b) hole doped ($n_e < n_h$), and (c) electron doped ($n_e > n_h$) Bi as illustrated in Fig. 2. Here, x denotes some controlling parameters which changes the relative position of the electron and hole band, e.g., external pressure or alloy concentration [26]. For the undoped case [Fig. 2(a)], a clear band-edge property—a peak in R_H and a kink in χ—can be seen, since n_e and n_h vanish simultaneously at $x = x_1$. This band-edge property will be clearer when H is applied perpendicular to z (trigonal axis), since the contribution of electrons is dominant [10]. In this case, the sign change in R_H will not be observed, since μ is always positive for electrons. (The conduction band at the T point is located at much higher energies from μ.) For the hole doped case [Fig. 2(b)], on the other hand, μ of electrons can be negative for $x > x_2$, so that the sign change in R_H is possible. However, the band-edge property in R_H will not be so clear due to the finite contribution from the holes at the T point, even though it will be clear in χ. For the electron doped case [Fig. 2(c)], neither the band-edge effect nor the sign change will be hardly seen. These predictions will contribute to resolve the long standing and puzzling experimental reports of R_H on Bi.

We thank A. Kobayashi for helpful discussions. The present work was partly supported by Grants-in-Aid for Scientific Research from MEXT of Japan (No. 15073210 and No. 16076203). Y. F. is supported by JSPS.

*fuseya@hosi.phys.s.u-tokyo.ac.jp

[1] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).
[2] R. Kubo and H. Fukuyama, in *Proc. of 10th Intern. Conf. on Physics of Semiconductors, Cambridge, Massachusetts, 1970* (United States Atomic Energy Commission, Springfield, Virginia, 1970).
[3] E. N. Adams, Phys. Rev. **89**, 633 (1953).
[4] J. W. McClure, Phys. Rev. **104**, 666 (1956).
[5] V. P. Gusynin and S. G. Sharapov, Phys. Rev. Lett. **95**, 146801 (2005).
[6] V. P. Gusynin and S. G. Sharapov, Phys. Rev. B **73**, 245411 (2006).
[7] H. Fukuyama, J. Phys. Soc. Jpn. **76**, 043711 (2007).
[8] M. Nakamura, Phys. Rev. B **76**, 113301 (2007).
[9] A. Kobayashi, Y. Suzumura, and H. Fukuyama, J. Phys. Soc. Jpn. **77**, 064718 (2008).
[10] H. Fukuyama and R. Kubo, J. Phys. Soc. Jpn. **27**, 604 (1969); **28**, 570 (1970).
[11] M. H. Cohen and E. I. Blount, Philos. Mag. **5**, 115 (1960).
[12] P. A. Wolff, J. Phys. Chem. Solids **25**, 1057 (1964).
[13] The general Dirac Hamiltonian and the reciprocal effective mass tensor are given as $\mathcal{H} = \Delta\beta + i\boldsymbol{k}\cdot[\sum_\mu \boldsymbol{W}(\mu)\beta\alpha_\mu]$, $\vec{\alpha} = \Delta^{-1}\sum_\mu \boldsymbol{W}(\mu)$, by Wolff [12]. Here, $\boldsymbol{W}$ corresponds to the matrix elements of the velocity operator. In the model used here, we assumed $\vec{\alpha}$ to be proportional to a unit matrix.
[14] N. H. Shon and T. Ando, J. Phys. Soc. Jpn. **67**, 2421 (1998).
[15] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[16] H. Fukuyama, H. Ebisawa, and Y. Wada, Prog. Theor. Phys. **42**, 494 (1969); H. Fukuyama, *ibid.* **42**, 1284 (1969).
[17] H. Fukuyama, Prog. Theor. Phys. **45**, 704 (1971).
[18] We can estimate the μ dependence of σ_{xx} and σ_{xy} in the case of $\mu \gg \Delta$ as follows. For $\mu \gg \Delta$, $E \sim vk$, and the density of states, $N(E) = \sum_{\mathbf{k}} \delta(E - vk) \propto E^2$. Then, $\sigma_{xx} \propto v^2 N(\mu) \propto \mu^2$, and the carrier density $n = \int_0^\mu N(E)dE \propto \mu^3$, so that $\sigma_{xy} = \sigma_{xx}^2/n \propto \mu$.
[19] M. H. Cohen and L. M. Falicov, Phys. Rev. Lett. **7**, 231 (1961).
[20] S. Murakami, Phys. Rev. Lett. **97**, 236805 (2006).
[21] D. Hsieh *et al.*, Nature (London) **452**, 970 (2008).
[22] K. Behnia, L. Balicas, and Y. Kopelevich, Science **317**, 1729 (2007).
[23] A. L. Jain, Phys. Rev. **114**, 1518 (1959).
[24] N. B. Brandt and Y. G. Ponomarev, Sov. Phys. JETP **28**, 635 (1969).
[25] L. Wehrli, Phys. Kondens. Mater. **8**, 87 (1968).
[26] We can modify the band structure by alloying Sb, which corresponds to the chemical pressure [24]. It changes the relative location of the bands at L and T point. The alloying Te (Sn, Pb) not only gives chemical pressure, but also dopes electron (hole) carriers.