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Quantum oscillations and optical conductivity in Rashba spin-splitting BiTeI

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We report the observation of Shubnikov-de Haas (SdH) oscillations in single crystals of the Rashba spin-splitting compound BiTeI, from both longitudinal (Rxx(B)) and Hall (Rxy(B)) magnetoresistance. Under magnetic field up to 65 T, we resolved unambiguously only one frequency \( F = 284.3 \pm 1.3 \) T, corresponding to a Fermi momentum \( k_F = 0.093 \pm 0.002 \) Å\(^{-1}\). The amplitude of oscillations is strongly suppressed by tilting magnetic field, suggesting a highly two-dimensional Fermi surface. Combining with optical spectroscopy, we show that quantum oscillations may be consistent with a bulk conduction band having a Rashba splitting momentum \( k_R = 0.046 \pm 0.0005 \) Å\(^{-1}\).

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The claim of a large Rashba spin-splitting of the bulk electronic bands in BiTeI is based on a combination of theoretical calculations and photoemission spectroscopy (ARPES). Strong spin orbit interaction, originating from the presence of Bi with its large atomic number, and the absence of a center of inversion in the crystal structure give rise to a significant Rashba term in the Hamiltonian \( H_R = \alpha_R (\hat{\epsilon}_z \times \vec{k}) \cdot \vec{S} \), where \( \alpha_R \) is the Rashba parameter characterizing the strength of the effect, \( \hat{\epsilon}_z \) is the direction along which the inversion symmetry is broken, \( \vec{k} \) represents the momentum, and \( \vec{S} \) is the spin of the electrons. The significance of the \( \alpha_R \) parameter becomes more clear if we look at the effect of the Rashba term on the energy of a free electron system, which becomes \( E_k = \hbar^2 k^2 / (2m^*) \pm |\alpha_R| k \). The result is that electron energies are split between those with spin up (+) and spin down (−) in a plane perpendicular to \( \epsilon_z \), as sketched in the upper inset of Fig. 1(a). The momentum and energy splitting both depend on the parameter \( \alpha_R \).

The Rashba effect is of particular interest for the field of spintronics, where one aims to manipulate the spin of electrons for potential applications; moreover, a large value of \( \alpha_R \) is very desirable. Values of \( \alpha_R \approx 3 \) eVÅ were found for asymmetric Bi/Ag(111) interface. Recently, Ref. [1] reported an even larger Rashba splitting, \( \alpha_R = 3.8 \) eVÅ, in the bulk electronic bands of BiTeI. Optical spectroscopy of this compound found indeed an electronic excitation spectrum consistent with the splitting of the bulk conduction and valence bands and further photoemission study suggested the 3D nature of these bands. More recent ARPES reports however, indicated the reconstruction of the band structure at the Te (or I) terminated surface and the existence of surface electronic branches, possibly with even larger Rashba spin-splitting. On the theoretical side, ab-initio calculations for BiTeX(X=Cl, Br, I) do claim the formation of a surface 2D electron system distinct from the bulk states that has a larger Rashba splitting.

Given that the fate of the surface states in BiTeI is still a debated issue and noting the particular sensitivity of photoemission experiments to the surface, we measured the in-plane longitudinal magnetoresistance \( R_{xx}(B) \) and transverse (Hall) resistance \( R_{xy}(B) \) in single crystals of BiTeI, searching for Shubnikov-de Haas oscillations as an alternative route to investigate the Fermi surface. Furthermore, we combine the results with optical reflectance data to understand better the origin of these oscillations.

Single crystals of BiTeI were grown by chemical vapor transport and Bridgman method. Two samples were initially screened and both revealed very similar quantum oscillations. Then, a complete study was performed on one sample with approximate dimensions 4×6×0.09 mm\(^3\). Gold wires were attached using silver paint and the sample resistance was measured using a commercial resistance bridge. The experiment was performed in the SCM-2 facility at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee. The facility consists of a top loading \(^3\)He cryostat, with sample in liquid and a base temperature of 0.3 K, and an 18–20 Tesla superconducting magnet. Samples were mounted on a rotating probe with an angular resolution better than 1°. Further magnetoresistance measurements up to 65 Tesla were also performed at the pulsed magnetic field facility of the NHMFL, in Los Alamos. Optical reflectance measurements were performed at the University of Florida. The data for frequencies between 30 and 5000 cm\(^{-1}\) (4–620 meV), at temperatures as low as 10 K, were obtained using a helium flow cryostat mounted on a Bruker 113v Fourier spectrometer. Higher frequency reflectance, up to \( \omega \approx 30000 \) cm\(^{-1}\) was measured at room temperature with a Zeiss microscope photometer and used to extrapolate the 10 K data for Kramers-Kronig analysis.

The main panel of Fig. 1(a) shows the high magnetic field data for \( R_{xx} \) at 0.3 K plotted against inverse field, obtained from the measurements in DC magnetic field up to 18 T. A small modulation, periodic in \( 1/B \) can be directly observed in the figure. Oscillations are also resolved in the transverse resistance \( R_{xy} \) as can be seen from the lower inset of Fig. 1(a), where \( dR_{xy}/dB(B) \) is plotted. However, as shown in the main panel of
Fig. (b), the oscillatory behavior emerges undoubtedy in the magneto-resistance data above 25 T and their amplitude increases with magnetic field up to 65 T. Fourier transform (FFT) of these data yields a single frequency of oscillations, with the value $F = 284.3 \pm 1.3$ Tesla, for the field applied normal to the sample surface. In the lower inset of Fig. (b), we compare the FFT frequencies obtained from DC and pulsed magnet filed, respectively; nearly perfect agreement can be observed.

This oscillation frequency is directly proportional to the area of the Fermi surface $S_F = 2\pi e F/h$ and furthermore to the Fermi momentum, for which we obtain $k_F = (S_F/\pi)^{1/2} = 0.093 \pm 0.002$ Å$^{-1}$. Notably, this value of $k_F$ is comparable to that from some of the outer Fermi surfaces observed in photoemission experiments; it is nearly identical to the results from Ref. [1] and [2] which assign it to a bulk conduction branch and agrees within 50% with the values from Ref. [3] but for electronic bands assigned to the surface. Moreover, it also agrees within better than 50% with the value of $k_F$ for the surface states near the bottom of the conduction band, obtained from band structure calculations.

Most importantly, this value of the Fermi momentum allows us to make an important observation about the magnitude of the Rashba splitting in BiTeI. When the chemical potential is situated above the Dirac cone, Rashba splitting of a conduction band should give rise to two Fermi surfaces, one associated with the outer and another with the inner branches, respectively, as is sketched in the upper inset of Fig. (a). Therefore, two oscillation frequencies may be observed in SdH effect. On the other hand, if the chemical potential lies below the Dirac cone, one would expect a single, double degenerate frequency, corresponding to a momentum $k_F \leq k_R$, where $k_R$ is the Rashba momentum as shown in the upper inset of Fig. (a). Most of the previously cited ARPES and theoretical studies seem to agree that in BiTeI, $k_R \approx 0.05$ Å$^{-1}$. This value is about half of that obtained in our SdH study, clearly indicating that in our sample, the Fermi momentum is not situated below, but rather at the Dirac cone or slightly above, where the momentum associated with the outer Fermi surface becomes $k_F \geq 2k_R$. To further narrow the position of the chemical potential, we searched for possible hint of a low frequency oscillation, originating from the inner branch. In the upper inset of Fig. (b) we show the sample magneto-resistance obtained, both in DC and in pulsed magnetic field, after subtracting a continuous background consisting of a linear and a quadratic term. There is indeed a hint of another modulation periodic with $1/B$, but with such a large period (low frequency), that only about half of a period can be resolved, even in a magnetic field as high as 65 T. It is also possible that the carrier density of this branch is so low that the quantum limit is reached at very low magnetic field. If we assign the peak and the dip marked with arrows in Fig. (b) to half of a period, than the frequency would be no larger than 3T, which in turn, would place the Fermi energy in our sample less than 2 meV above the Dirac cone. Therefore, given that SdH effect is a robust measurement, we believe that we can estimate within about 1% the Rashba momentum as $k_R = 0.046 \pm 0.0005$ Å$^{-1}$.

![FIG. 1. (Color online) (a) Main panel: Longitudinal resistance $R_{xx}$ vs. $1/B$ at $T = 0.3$ K for the magnetic field applied normal to sample surface. Upper inset: 1D representation of a Rashba spin-split conduction band showing the momentum ($k_R$) and the energy ($E_R$) splitting. Lower inset: The field derivative of $R_{xx}(B)$ above 8 T, showing the presence of SdH oscillations. (b) Main panel: Magneto-resistance of BiTeI measured in pulsed magnetic field applied perpendicular to sample surface at $T = 4$ K. Upper inset: Magneto-resistance obtained from two different measurements, in pulsed and DC magnetic field (multiplyed by a factor of 20 for clarity), after subtracting a linear and quadratic background. Lower inset: FFT of SdH oscillations from pulsed (dashed line) and DC magnetic field (continuous line), respectively, scaled in amplitude for clarity.](image-url)
available magnetic field. In contrast, a strictly 2D layer backed by a conducting bulk may lose orbital coherence at small angles if a tilted field drives carriers into the bulk.

![Graph](image)

**FIG. 2.** (Color online) Main panel: $R_{xx}(B)$ above 10 T for different angles between the magnetic field and the sample surface. Upper inset: $\Delta R_{xx}$ vs. the magnetic field component along the normal to sample surface and a sketch of the sample in tilted magnetic field. Lower inset: Angle dependence of the oscillation frequency (symbols) and fit to $1/\cos(\theta)$ (dashed line).

The main panel of Fig. 2 shows the high magnetic field behavior (above 10 T) of $R_{xx}$ for different angles $\theta$ between the field and the sample surface at $T = 0.3K$, as sketched in the upper right inset. It can be visually observed that the oscillations are rapidly suppressed with increasing $\theta$ and that they are absent above $\theta \approx 30^\circ$. The angular dependence of their frequency, shown in the lower inset of Fig. 2 has a $1/\cos(\theta)$ behavior, indicating a 2D character of the Fermi surface, whether it corresponds to bulk or surface electrons. In the upper inset of Fig. 2 we display $\Delta R_{xx}$, obtained after background subtraction. First, we notice again the rapid decrease of oscillation amplitude with the angle of the magnetic field. Although not shown here, we measured up to $\theta > 90^\circ$, rotating the sample both directions with respect to the magnetic field and we confirm that oscillations only exist for $|\theta| \leq 30^\circ$. Second, we see that their period scales remarkably well with the component of magnetic field perpendicular to the sample surface ($1/|B| \cdot \cos(\theta)$). These behavior of SdH oscillations with angle is similar to that obtained from surface carriers of 2D structures and of some of the topological insulators, supporting the possibility of surface charge accumulation in BiTeI. On the other hand, BiTeI is a layered compound and a two-dimensional behavior may be induced, particularly at such low temperature, by stacking faults, similar to the observations in InSe compounds. Further studies of $c$-axis transport may shed light on this issue. Nevertheless, we will show later that optical reflectance, which is dominated by bulk properties, is in good agreement with the assumption that our observed oscillations originate from the bulk. Thus, from the SdH frequency, we calculate a 3D carrier concentration as $n_{3D} = (1/3/\pi^2)(2eF/h)^{3/2}$ and obtain $n_{3D} = 2.7 \times 10^{19}$ cm$^{-3}$.

To investigate further the carrier properties, we measured the temperature and magnetic-field dependence of the quantum oscillations. Figure 3(a) shows the resistance $\Delta R_{xx}$ (after background subtraction) versus inverse field at different temperatures. Oscillations are visible up to at least 20 K, although significantly damped due to the thermal broadening of the quantized Landau levels. The effect of temperature is also evident if we look at the amplitude of the Fourier transform shown in Fig. 3(b). This quantity is expected to follow the Lifshitz-Kosevich temperature dependence, $\gamma T/\sinh(\gamma T)$, with $\gamma = 14.69 m^2/\hbar m^*B$, where $B$ is the magnetic field, $m^*$ is the effective mass, and $m_0$ the rest mass of the electron. Figure 3(c) shows that result of the fit to the above expression for the amplitude at $1/B = 0.06 T^{-1}$. We repeated the analysis for different values of $1/B$ and for the SdH oscillations from the Hall resistance, and obtained $m^* = 0.19 \pm 0.02m_0$.

At fixed temperature, the amplitude of the SdH oscillations is enhanced at increased field (decreased $1/B$) as $\Delta R_{xx} \propto \exp(-\gamma T_D) \cos(2\pi F/B + \pi)$, where $\gamma$ is defined above and $T_D$ is the Dingle temperature, $T_D = h/(2\pi k_B\tau)$, related to the lifetime $\tau$ of the electron. In Fig. 3(a) we show the fit of the data at 0.3 K, where it can be seen that both the amplitude and the phase are well reproduced by only considering one frequency. We obtain a Dingle temperature $T_D = 32 \pm 6$ K, which in turn gives a lifetime $\tau = 3.9 \pm 0.6 \times 10^{-14}$ s, and an estimated mobility $\mu = e\tau/m^* = 360 \pm 60$ cm$^2/(Vs)$.

We investigated further the electronic properties of BiTeI by optical reflectance. The main panel of Fig. 4 shows the optical reflectance spectrum $R(\omega)$ of the same sample at $T = 10$ K. The data are similar to a previous optical study, there are several features at low frequency associated with lattice vibrations, a clear sharp plasma edge at about 850 cm$^{-1}$ ($\approx 0.1$ eV) and broad structure at higher frequencies due to interband transitions. This reflectance is dominated by the bulk carriers. If we were to assume that the SdH oscillations originate from surface electrons, then they would create an impedance mismatch due to a surface impedance, which we estimated to $R_{\square} \approx 1 \Omega$. A free-standing thin film with this impedance has a reflectance of $R = (Z_0/R_{\square})^2/(2+Z_0/R_{\square})^2 \approx 0.02$, where $Z_0 = 377 \Omega$ is the vacuum impedance. However, we see in Fig. 4 that at low frequencies $R(\omega) \approx 0.96$. Also, a few Angstrom-thick layer with a surface impedance of $R_{\square} \approx 1 \Omega$ would only attenuate the incident light by about 1% in the frequency range of our measurements. Simulations show that for a conducting bulk (as we find) the addition of a monolayer-thick conducting surface layer changes the reflectance by less than 0.5%. Therefore, most of the light probes the bulk.
difficult to know precisely, particularly in our relatively
errors, as the precise thickness where the current flows is
however that the Hall measurements are more prone to
dence of SdH oscillations, but it disagrees up to a factor of
agreement with the value from the temperature depen-
ded on the free-carrier contribution to
σ(ω).

The lattice vibrations and interband transitions seen in
Kramers-Kronig-derived conductivity is very similar.)
Analysis of optical reflectance may use either
Kramers-Kroning transformation or fits to a model such
as the Drude-Lorentz model in order to estimate other
optical quantities, such as the optical conductivity σ(ω).
Here we have fit R(ω) with the Drude-Lorentz model and the result is shown in Fig. 4 as the dash-dot line.
The corresponding Drude contribution to the conductivity
σ1(ω) = σb/(1 + ω2τb2) is shown in the inset. (The
Kramers-Kronig-derived conductivity is very similar.)
The lattice vibrations and interband transitions seen in
Fig. 4 will be discussed in a separate work, here we focus
on the free-carrier contribution to σ1(ω). From the fit
we obtain the scattering rate 1/τb = 118 ± 5 cm−1 (τb ≈ 4.5 × 10−14 s), the plasma frequency ωp = 3030 cm−1
(≈ 6 × 1014 rad/s) and, hence, the bulk conductivity
σb = 1300 ± 80 Ω−1 cm−1. The scattering rate for
the bulk carriers, obtained from optical measurements
agrees well with that obtained from Dingle tempera-
ture. Furthermore, if we assume an effective mass of
≈ 0.19m0, determined above, then from plasma fre-
quency ω2p = nbε2/(m∗0e0), we calculate a bulk carrier
concentration nb ≈ 2 × 1019 cm−3. This is also in fair
agreement with the value from the temperature depen-
dence of SdH oscillations, but it disagrees up to a factor of
two with the result from Hall measurements. We believe
however that the Hall measurements are more prone to
errors, as the precise thickness where the current flows is
difficult to know precisely, particularly in our relatively
thick samples. Therefore, relying on quantum oscillations
and optical reflectance, we may conclude that the bulk carrier concentration, corresponding to the chemical
potential situated within 2 meV from the Dirac cone is nb = (2.35 ± 0.35) × 1019 cm−3.
In conclusion, we measured Shubnikov-de Haas oscilla-
FIG. 3. (Color online) (a) ΔR xx vs.1/B (with B above 10 T
and applied perpendicular to the sample surface) at tem-
peratures from 0.3 to 20 K. The dashed line is a fit of the
data at 0.3 K to the expression: exp(−γT) cos(2πF/B + π)
as explained in the text. (b) Fourier transform of the
data from panel (a). (c) Amplitude of the oscillations at
1/B = 0.06 T−1 for different temperatures, normalized to
the value at 0.3 K (symbols) and a fit (dot-dash line) to the
temperature-dependent damping term γT/sinh(γT), as ex-
plained in the text.
FIG. 4. (Color online) Main panel: R(ω) at T = 10 K (con-
tinuous red line) and a Drude-Lorentz fit (dashed dotted black
line). Inset: Real part of optical conductivity obtained from
the Lorentz-Drude fit, from which the bulk DC conductivity
and the scattering rate of the bulk carriers are obtained.

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