Chiral electronic excitations in the quasi-two-dimensional Rashba system BiTeI

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The optical transitions between spin-polarized bands of the quasi-two-dimensional Rashba system BiTeI are investigated using polarization-resolved resonant Raman spectroscopy. We detect chiral excitations between states with opposite helicity and compare spectra to calculations within a three-band model. Using the resonant Raman excitation profile, we deduce the Rashba parameters and band gaps of the higher conduction bands near the Fermi level, and compare the parameters to values obtained by ab initio density functional theory.

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The chirality of a physical state or an excitation is a configurational property of an object that cannot be superimposed on its mirror image, thereby imparting a handedness [1–3]. In solids, the wave functions of chiral excitations are antisymmetric under mirror reflection. Examples include excitons in cuprates [4–6], electron-hole excitations in graphene [7], collective spin modes in Dirac materials [8], collective modes in the hidden order phase of exotic heavy fermion systems [9], to name a few. The reciprocity breaking chiral excitations could result in three-spin excitations with a volume $S_i \cdot S_j \times S_k$ [10], chiral spin modes [8], circular charge current [11], chiral excitons [4,12], or excitations of higher-order multipoles [9,13] which break mirror symmetries.

Systems with strong spin-orbit coupling give rise to electronic bands with a helical spin texture, where the spin and momentum of the electron are intrinsically coupled. For systems where inversion symmetry is broken, the Rashba interaction [14] induces linear momentum-dependent splitting of the spin-degenerate electronic bands [15–20]. The resulting subbands are spin polarized with opposite helicity. The set of direct transitions between occupied and unoccupied Rashba-split bands of opposite helicity forms the excitation spectra of the electronic continuum of chiral symmetry, the “Rashba continuum.” We have chosen to investigate the quasi-two-dimensional (2D) Rashba system BiTeI using resonant electronic Raman scattering to gain deeper insight into the nature of the chiral Rashba continuum.

BiTeI is a polar, noncentrosymmetric semiconductor (space group $P\overline{3}m1$, point group $C_{3v}$) regarded as the archetypical quasi-2D Rashba system [21–23]. It is a van der Waals-bonded layered structure, composed of a series of triangular network layers of I, Bi, and Te atoms stacked along its polar axis [24,25] [see Fig. 1(b)]. Because of its layered structure, the bulk electronic bands are weakly dispersive along $k_z$ [26]. However, the band gaps and in-plane electronic dispersions within the $M$-$\Gamma$-K ($k_z = 0$) and L-A-H ($k_z = \pi/c$) planes of the Brillouin zone (BZ) significantly differ from one another [see Fig. 1(c)]. The principal conduction band (CB0), the highest valence band (VB0), and the next-lowest conduction band (CB1) all exhibit large Rashba splitting near the $\Gamma$ point and A point of the BZ [21,27] [see Fig. 1(d)]. Despite being classified as a semiconductor, BiTeI is naturally doped due to nonstoichiometry [25]; the chemical potential crosses CB0 and the charge carriers are electrons. Thus, BiTeI contains multiple Rashba continua due to the CB0 $\rightarrow$ CB0 and VB0 $\rightarrow$ CB0 transitions.

BiTeI belongs to a materials class with a single polar axis of rotation $z$ and a Rashba-like dispersion of the electronic bands

$$E_\sigma(k) = \frac{k^2}{2m^*} + \eta \sigma_R k,$$  

where $m^*$ is the effective mass of the electron (assuming an isotropic, in-plane dispersion) and $k$ is the quasimomentum of the electrons within the normal plane of the polar axis $xy$, $\eta$ denotes the helicity of the subband, and the factor $\sigma_R = 2E_R/k_R$ is the “Rashba parameter” that describes the magnitude of the $k$-dependent energy splitting [see Fig. 1(a)]. $\eta = \pm 1$ specifies whether the spin of the electron is parallel ($\eta = 1$) or antiparallel ($\eta = -1$) to $k \times \hat{z}$. The strength of $\sigma_R$ depends on the interaction of the total angular momentum of the electron with the electrical potential gradients close to heavy atomic nuclei within the lattice [18–20].

In this Letter, we use polarization-resolved resonant electronic Raman spectroscopy to study the continua of chiral excitations arising from transitions between helical electronic states in BiTeI. By scanning the energy of the incident photons, we selectively enhance distinct continua excitations at
The measured spectral intensities were corrected for the spectral response of the optical setup as well as the optical power absorption of the material medium.

The scattering polarization geometries, defined by the incident and collected light polarizations, are labeled as $e_i e_f$, where $e_i (e_f)$ refers to the polarization of the incident (collected) light, respectively. The energies of the incident and collected photons are denoted as $\omega_i$ and $\omega_f$, respectively. The two optically distinct spatial directions that result from the layered structure lie either in the $xy$ plane or along the $z$-axis direction. The incident and collected photons were polarized in the $xy$ plane and propagated along $z$. The secondary emission spectra contain both the photoluminescence (PL) and the Raman excitations. All of the measurements were performed in four scattering polarization geometries: XX, YX, RR, and RL. For linearly polarized light, the direction of the incident photon polarization is denoted as $X$, and the direction orthogonal to $X$ in the $xy$ plane is denoted as $Y$. R and L denote right and left circularly polarized light, respectively, such that $R(L) = X \pm i Y$.

In Table I, the Raman selection rules for BiTeI are listed for all four used scattering polarization geometries [30]. The Raman-active excitations for the material with the $C_{3v}$ point group can be classified by the $A_1$, $A_2$, and $E$ irreducible representations. $A_2$ excitations are chiral because they are antisymmetric with respect to the three vertical mirror reflections of the $C_{3v}$ point group and are the focus of this Letter. The resonant Raman scattering process can uniquely probe electronic excitations with an antisymmetric Raman tensor [11,13,31,32].

In Fig. 2, we plot the results of secondary emission measurements performed for the four scattering polarization geometries. PL features correspond to radiative electronic transitions at the $A$ point between CB1/CB2 and CB0, and their emission energy is independent of the excitation energy $\omega_i$. The energies of the Raman-related features emitted at the scattering energy $\omega_i$ are fixed at the Raman shift $\omega_R = \omega_f - \omega_i$ for any $\omega_i$. To aid the reader’s eye, the measured secondary emission cross section is plotted against $\omega_i$ for different $\omega_f$ in the panels on the left-hand side of Fig. 2, and plotted against the Raman shift on the right-hand side.

| Scattering polarization geometry | Irreducible representations |
|---------------------------------|-----------------------------|
| XX or YY                        | $A_1 + E$                   |
| YX or XY                        | $A_2 + E$                   |
| RR or LL                        | $A_1 + A_2$                 |
| RL or RL                        | $2E$                        |

For the Raman experiments, we used a $Kr^+$ laser with photon energies ranging between 1.55 and 2.65 eV in the quasibackscattering geometry. All spectra were acquired with 150 grooves/mm diffraction gratings (spectral resolution of $\sim 3$ meV) in a triple-stage spectrometer setup with a charge coupled device (CCD) detector. Single crystals of BiTeI were cleaved in a nitrogen-rich environment and then transferred into a continuous He-flow optical cryostat where all spectra were taken at 15 K.

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| RL or RL                        | $2E$                        |
The measured secondary emission spectra were acquired with XX transitions (violet) indicated by the shaded regions in (g)–(l).

Energy (a)–(f) and Raman shift (g)–(l) for CHIRAL ELECTRONIC EXCITATIONS IN THE … PHYSICAL REVIEW B 105, L161105 (2022)

The relevant spectral features are shaded in Fig. 2, with PL features in Table II. The CB2 → CB0 transition occurs at the A point, where CB2 is the next-lowest conduction band.

The Δ2 spectral intensity undergoes a resonant enhancement near ω_i = 2.57 eV. To account for this resonance, we note that the VB1 → CB2 energy gap, where VB1 is the next-highest valence band, is overestimated by DFT. The DFT-calculated VB1 → CB2 energy gap is 1.3 eV, however, the angle-resolved photoemission spectroscopy (ARPES) measurement places the VB1 → CB0 gap at about ~1.0 eV [26]. The gap measured by emission Δ2 is 1.65 eV compared to its calculated value at 2.0 eV (see Table II). Therefore, the true VB1 → CB2 energy gap is about ~2.65 eV, and the resonance near ω_i = 2.57 eV is due to the VB1 → CB2 transition at the A point. In addition, the Δ2 feature appears partially polarized under resonance, favoring light emission in YX and RL over XX and RR polarizations. The transition selection rules for the states near the A point cannot account for its polarized nature. This implies that VB1 and CB2 bands are spin polarized away from the A point.

We now turn to the Raman excitations with A2symmetry [see Figs. 2(g)–2(l)]. The A2 Raman excitations can be deduced from the scattering polarization geometries by noting that A2 excitations are present with equal intensity in XY and RR but are absent in XX and RL scattering polarizations (see Table I). The A2 Raman excitation features are plotted in Fig. 3 and are labeled as either A2^CB0 or A2^VB0. All of the A2 Raman excitations at frequencies ω_R shift with increasing incident photon energy ω_i. The A2^CB0 and A2^VB0 electron-hole excitations fall within the limits of the Rashba continua excited under resonant conditions involving both CB1 and CB2 bands as the intermediate states (see Table III).

Since the wave functions of the A2 excitations are antisymmetric with respect to the exchange of the x and y axes, there are two (left- and right-handed) enantiomeric isomers of the A2 excitation. However, the charge density distributions corresponding to these excitations are identical under the mirror reflections of C_3v. Thus, the two isomers are indistinguishable from one another in RR or LL scattering spectra.

To verify the assignment of the A2 signal to the continua of electronic transitions between Rashba split bands, we calculated the high-energy Raman scattering spectra throughout the BZ. The general expression for the differential light scattering cross section per unit scattered frequency per unit solid angle is \(d^2\sigma/d\omega_d\Omega \propto \frac{\gamma}{R} \) [34], where \(R\) is the transition rate given by Fermi’s golden rule,

\[
R \propto \int d^3k \frac{\omega_i}{\omega_f} |H_{f,i}|^2 \delta(\bar{\epsilon}_{f,k} - \bar{\epsilon}_{i,k} - \omega_R),
\]

where \(\bar{\epsilon}_{i,k} = \epsilon_i(k) + i\gamma\) are the energy eigenvalues for the initial (i), intermediate (m), and final (f) states, and \(\gamma\) is the

![FIG. 2. Secondary emission spectra plotted against absolute energy (a)–(f) and Raman shift (g)–(l) for ω between 1.83 and 2.65 eV. The measured secondary emission spectra were acquired with XX (red), YX (black), RR (blue), and RL (green) scattering polarization configurations. The PL features originating from the CB1 → CB0 and CB2 → CB0 transitions at the A point are indicated by the shaded in regions of (a)–(f). The A2-symmetry Raman features due to CB0 → CB0 transitions near the A point (red) and VB0 → CB0 transitions (violet) are indicated by the shaded in regions in (g)–(l). The scales of I(ω_i) for each panel are chosen for the best readability.](image-url)
determine the lowest \( E_F \) by relating it to the carrier concentration determined from Hall effect measurements [37].

In Fig. 3, we display model calculations overlaid with \( A_2 \) Raman data for a set of incoming excitation photon energies \( \omega_i \) between 1.55 and 2.65 eV. The calculation captures the slightly asymmetric character of the otherwise Lorentzian-like line shape, which is due to the resonant denominator \( (\epsilon_{m,k} - \epsilon_{i,k} - \omega_i)^2 + \gamma^2 \). More importantly, the calculation of the \( A_2^{\text{VB0}} \) continuum captures the large shift of the Raman peak signal with increasing \( \omega_i \), which is due to the joint density of states of transitions between CB0 subbands. The \( A_2^{\text{VB0}} \) continuum has a single resonance at the principal band gap between VB0 and CB0, which occurs around \( k_{xy} = \frac{\pi}{\Gamma} \). Although the \( A_2^{\text{VB0}} \) continuum can, in principle, begin at \( \omega_R = 0.3 \) eV, Pauli blocking due to occupied CB0 states pushes the lower limit of the continuum to higher energies, depending on the carrier concentration of the sample. The strong \( A_2^{\text{VB0}} \) features for \( \omega_i = 2.60 \) and 2.65 eV excitations are due to transitions that occur near the \( k_c = \pi / c \) plane of the BZ. Thus, the calculation provides good confirmation that the observed spectral features correspond to Raman-active intersubband transitions between Rashba-split bands.

Finally, we compare DFT calculations of CB1 and CB2 to the dispersion acquired through the Raman scattering calculation (see Table IV). Near the \( \Gamma \) point, the CB1 and CB2 dispersions are close to their values calculated by DFT. In the proximity of the \( A \) point, the CB1 Rashba dispersion parameters, including \( \Delta_1 \), \( \alpha_R \), and \( m^*_{CB1} \), are also close to the values calculated by DFT. However, the CB2 parabolic dispersion parameters differ from the DFT calculated ones; \( \Delta_2 \) and \( m^*_{CB2} \) are 80\% and 41\% of their respective values calculated by DFT. The disparity between deduced CB2 parameters and the dispersion given by DFT is surprising considering that the CB1 and CB0 parameters are well described by DFT. This is further evidence that some aspect of the CB2 band is not accounted for in the DFT calculation.

In conclusion, we probed the continua of electronic transitions between Rashba-split helical bands in the quasi-2D Rashba system BiTeI. The continua belong to the antisymmetric \( A_2 \) irreducible representation of the \( C_{3v} \) point group, thus the excitations are chiral. The quasi-2D nature of the electronic structure allows for the selective excitation of chiral electronic continua originating from different areas of the BZ, which is only possible by exploiting the resonant Raman scattering effect.

### Table IV. Higher conduction-band parameters of BiTeI near the \( A \) point of the BZ using the three-band model calculation, and corresponding parameters given by DFT. The in-plane effective mass \( m^* \) is represented as a fraction of the rest mass of the electron \( m_e \).

| Parameter | CB1 | CB2 |
|-----------|-----|-----|
| \( \alpha_R \) (meas.) | 1.35 eV Å | \( \sim 0 \) \( m_e \) |
| \( \alpha_R \) (DFT) | 1.15 eV Å | 0 |
| \( m^* \) (meas.) | 0.15m_e | 0.14m_e |
| \( m^* \) (DFT) | 0.20m_e | 0.34m_e |

*If the CB2 band is Rashba spin-split, then its value of \( \alpha_R \) is below the analysis uncertainty.*
By comparing spectroscopic data to calculations within a three-band model, the CB1 band was confirmed to have a Rashba dispersion with parameters similar to those given by DFT: $\Delta_1 = 1.48$ eV, $\alpha_R = 1.35$ eV Å, and $m^* = 0.15m_e$. The CB2 parabolic dispersion differs significantly from DFT calculations: $(\Delta_2, m^*) = (1.65 \text{ eV}, 0.14m_e)$ vs $(2.05 \text{ eV}, 0.34m_e)$ as calculated by DFT. Under resonance, the CB2 $\rightarrow$ CB0 transition appears partially polarized, suggesting that CB2 is also spin polarized away from the A point.

More generally, the presented approach of studying BiTeI may enable control of chiral electronic excitations in systems with a strong Rashba-like dispersion and offers critical insight into novel chirality-based phenomena in quasi-2D Rashba systems.

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