Bulk Rashba Spin Splitting and Dirac Surface State in $p$-Type (Bi$_{0.9}$Sb$_{0.1}$)$_2$Se$_3$ Single Crystal

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Herein, bulk Rashba spin splitting (RSS) and associated Dirac surface state in (Bi$_{0.9}$Sb$_{0.1}$)$_2$Se$_3$, exhibiting dominant $p$-type conductivity is reported. It is argued that the synchrotron diffraction studies that origin of the bulk RSS is due to a structural transition to a non-centrosymmetric $R3m$ phase below $\approx 30$ K. The Shubnikov–de Haas–Van oscillations are observed in the magnetoresistance curves at low temperature. The extrapolation of the linear plots for both the || and $\perp$ component in the Landau level fan diagram meet at $n = 0.40(6)$ for $1/H = 0$, which is close to $n = 0.5$ is recommended for the Dirac particles. The magnetization results at low temperature exhibit substantial orbital magnetization consistent with the bulk RSS. The bulk RSS and Dirac surface states are confirmed by the first-principles density functional theory calculations. The coexistence of orbital magnetism, bulk RSS, and Dirac surface state is unique for $p$-type (Bi$_{0.9}$Sb$_{0.1}$)$_2$Se$_3$, making it an ideal candidate for spintronic applications.

1. Introduction

Recently, topological insulators (TI) exhibiting Rashba spin–orbit splitting (RSS) due to the presence of 2D electron gas states have been recognized as key materials for next-generation spintronic devices without the requirement of an external magnetic field for manipulation of spins.[1−3] The spin degeneracy in such nonmagnetic materials is lifted by the strong Rashba spin–orbit coupling (SOC) associated with the broken space inversion symmetry. Rashba effect was first reported in the bulk wurtzite crystals,[6] and subsequently, it was realized in the 2D electron gases.[7,8]

In this article, we report bulk RSS in Bi$_2$Se$_3$ with dominant $p$-type conductivity, driven by hole doping. Synchrotron diffraction studies confirm structural transition from $R3m$ to a non-centrosymmetric structure of $R3m$ around 30 K, below which significant negative thermal expansion is observed. First-principles electronic structure calculations based on DFT for the $R3m$ structure confirm bulk RSS and the presence of surface state similar to the pristine Bi$_2$Se$_3$. Transport experiment reveals Shubnikov–de Haas–Van (SdH) oscillations in the low-temperature magnetoresistance curves, where the Berry phase, as determined from the Landau-level fan diagram, confirms the gap-less Dirac surface states along and $\perp$ to [001] direction. The saturation of magnetization curves at low temperature having a significantly large value of the magnetization suggests possible orbital magnetism. The result is consistent with the bulk RSS. The unique combination of orbital magnetism, bulk RSS, and conducting Dirac surface state in $p$-type (Bi$_{0.9}$Sb$_{0.1}$)$_2$Se$_3$ systems is expected to be important for spintronic applications.

2. Experimental and Computational Details

Single crystal of (Bi$_{0.9}$Sb$_{0.1}$)$_2$Se$_3$ was grown using a modified Bridgman method.[17,18] Synchrotron diffraction study was performed on the powdered crystal with a wavelength of 0.20694 Å (60 keV) recorded at P02.1 beamline of PETRA III, Hamburg, Germany by using a Perkin Elmer XRD1621 area detector.
The low temperature (T) studies were carried out by using a cryogen-free JANIS (USA) cryostat.

The Seebeck coefficient (S) and resistivity (ρ) were measured by using a home-built setup,[17] coupled to a multifunctional probe of the PPMS system of Quantum Design (PPMS-II). The DC magnetization was measured by a SQUID VSM of Quantum Design.

First-principles electronic structure calculations within density functional theory (DFT) had been carried out using plane-wave basis and projector augmented wave (PAW)[199] potential as implemented in the Vienna Abinitio Simulation Package (VASP).[200] For exchange-correlation functional, we used Perdew–Burke–Ernzerhof (PBE)[21] generalized gradient approximation (GGA). In the self-consistent cycle, energy cut-off of 550 eV has been used with a gamma-centered 9k mesh around the Fermi level and 20 unit cell thick slab calculations necessary for the background from the Wannier functions. The maximally localized Wannier functions (MLWFs) following the formulation of Wannier90.[22] The slab calculations necessary to understand topological properties have been calculated using iterative Green’s function approach[23–26] as implemented in the WannierTools package.[26] For calculations, a 20 unit cell thick slab along the c-axis (0001) with periodic boundary conditions along a- and b-axes was used.

3. Results and Discussion

The quality of the crystal is checked using X-ray diffraction studies and transmission electron microscopy of the powdered as well as single crystal sample (Figure S1 and S2, Supporting Information). The elemental analysis of the crystal using energy-dispersive X-ray spectroscopy coupled with a scanning electron microscope and X-ray photoemission spectroscopy confirms the desired composition, as discussed in the SI (See supplementary informations). The T variations of ρxx recorded in the zero-field and magnetic field (H) applied || and ⊥ [001] direction are shown in Figure 1a,b, respectively, for different H. A minimum in ρxx(T) is observed around 30 K (Tm), the magnetoresistance (MR), defined as [ρxx(H) − ρxx(H = 0)]/ρxx(H = 0), are recorded, and depicted in Figure 1c for H || to [001] direction for selected T. A clear signature of oscillation is observed at 2 K, where maxima as well as minima in ρxx(H) are found at a regular interval of 1/H, pointing to a typical manifestation of the SdH oscillation.[27–29] The SdH oscillation is evident only at 2 K for the ⊥ component, having a much smaller amplitude and lower frequency, as shown in Figure 1d. The values of MR(%) increase with T for both the components and then, they decrease with further increasing T, showing a maximum around Tm.

Figure 1e shows the periodical oscillatory component (Δρxx) with 1/H for the || component. The Δρxx is obtained by subtracting the background from the ρxx(H) isotherms. The Fast Fourier transform (FFT) of Δρxx(H) is depicted in Figure 1f, which exhibits a peak around 210 kOe for the measurement along [001], analogous to the observed single peak for the pristine compound.[30–32]

A single peak is also observed around 2670 kOe for H ⊥ to [001] direction. The oscillation frequency provides the extremal area of cross section (A0) of the Fermi surface (FS) according to the Onsager relation, FSdH = (ℏ/2πe)A0, where A0 = kF. The difference between the || and ⊥ component in FSdH points to a highly anisotropic FS, analogous to Bi2Se3.[30,31] The values of FSdH provide the values of Fermi momentum (kF) ≈ 2.5 × 10−2 Å and 9.0 × 10−2 Å−1 for the || and ⊥ components, respectively.

Temperature dependence of the amplitude of the oscillations at 210 kOe follows the standard Lifshitz–Kosevich (L–K) expression,[34,35] as shown in Figure 1g by the continuous curve. As obtained from the fit, the value of the effective cyclotron mass (m∗) is 0.14 m, where m is the free electron mass. Thus, the

![Figure 1](image-url)

**Figure 1.** T variations of ρxx at selected H for H: a) || and b) ⊥ [001] direction. H dependence of MR (%) for H: c) || and d) ⊥ [001] direction for selected T. e) Oscillatory component (Δρxx) with 1/H and f) amplitude of FFT component with frequency (FSdH) at selected T, showing a peak, as highlighted by the vertical line. g) Oscillation amplitude with T. Inset of g): Semi-log plot of ln|η| with 1/H with η = ρxxH sinh(2e2kF T/ΔEn(H)). h) Landau level fan diagram: n with 1/H.
The Fermi velocity is obtained as \( \nu_F = \frac{\hbar k_F}{m^*} \), which provides the value of Fermi energy, \( E_F \approx \frac{1}{2} m^* \nu_F^2 \approx 17.34 \text{ meV} \). The slope of the semi-log plot of \( \ln[\rho_{xx} H \sinh(2\alpha k_F T/\Delta E_{fi}(H))] \) with \( 1/H \) provides the value of Dingle temperature, \( T_D = 11.99 \text{ K} \), as shown in the inset of Figure 1g. The life time (\( \tau \)) of the surface charge carriers is obtained to be \( 1.01 \times 10^{-11} \text{ s} \) using \( \tau = \hbar/(2\pi k_F T_D) \), which provides the mean free path, \( l = \nu_F \tau \) and mobility, \( \mu = \tau e/m^* \), as 21.14 nm and 0.80 \( \times 10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), respectively. These values are close to the values for \( \text{Bi}_2\text{Se}_3 \).[30,31] The nth maxima observed in the MR-H curves are plotted with \( 1/H \) in Figure 1h. The extrapolation of the linear plots for both the \( \parallel \) and \( \perp \) component, the representative of the Landau level fan diagram, meet at \( 1/H = 0 \) with \( n = 0.40(6) \), which is close to 0.5, recommended for the Dirac particles,[28,36,37] and consistent with the results of pristine \( \text{Bi}_2\text{Se}_3 \).[30] Our results suggest that the topologically nontrivial states are retained even for nearly 10% Sb doping in \( \text{Bi}_2\text{Se}_3 \).

The carrier concentration and mobility are investigated from the Hall measurement, which is given in Figure S3, Supporting Information. The Hall results confirm the dominant \( p \)-type conduction. The values of the Seebeck coefficient \( S \) with \( T \) are shown in Figure 2a. At room temperature, the value of \( S \) is positive, indicating a dominant \( p \)-type conduction. The \( p \)-type conductivity has also been realized by the Ca[38] and Mn[39] doping in \( \text{Bi}_2\text{Se}_3 \). The value of \( S \) decreases with decreasing \( T \) down to 2 K, displaying a shoulder at \( T_m \), as indicated by an arrow.[40] The \( H \) dependence of \( S \) is recorded at selected \( T \), shown in Figure S4, Supporting Information, where \( H \) is applied along the [001] direction. The value of \( \Delta S/S_0 \), defined as \( [S(H) - S(H = 0)]/S(H = 0) \), is plotted with \( T \) at \( H = 70 \text{ kOe} \), in the inset of Figure 2a. The value decreases with decreasing \( T \) and exhibits a minimum close to \( T_m \), below which it increases sharply. The maximum value of \( |\Delta S/S_0| \) is 55% for \( H = 70 \text{ kOe} \). The characteristic \( T \) variations of \( S \) and magneto-Seebeck response indicate the possibility of RSS below \( T_m \), as suggested in the theoretical works.[41–43] The results indicate a structural transition close to \( T_m \), Below \( T_m \), the negative thermal expansion in \( V(T) \) is observed, which is 0.07% at 5 K with respect to the value at \( T_m \). This structural transition at \( T_m \) may be correlated with the observed electrical transport and Seebeck coefficient. As shown in Figure 1a,b, a minimum is observed in the MR curves, whereas an anomaly in \( S(T) \) is highlighted by an arrow in Figure 2a close to the structural transition, at \( T_m \). We note that the structural transition at

![Figure 2](source.com)  
**Figure 2.** a) Thermal variations of \( S \). Inset of (a): \( \Delta S/S_0 \) with \( T \) at 70 kOe applied along [001] direction. b) Magnetization curves (\( M \) vs \( H \)) at selected \( T \) for \( H \) applied along [001] direction. Inset depicts the plot of \( M \) with \( T \) at 30 kOe.
low temperature was absent for the parent Bi$_2$Se$_3$ compound.\textsuperscript{[49]} Current results may indicate that 10\% Sb doping in Bi$_2$Se$_3$ leads to the structural transition.

The experimental results discussed earlier not only suggest the presence of Dirac surface state but also predict the possibility of bulk RSS. In view of this, electronic structure calculations have been carried out using the experimental lattice parameters of the low-T R$3m$ structure. In order to simulate doping, we have substituted one of the six Bi sites with an Sb atom in the unit cell. This leads to Bi$_{1-x}$Sb$_x$Se$_3$ with $x = 0.16$, which is adequate to capture the experimental doping concentration of 10\% (i.e., $x = 0.2$). Subsequently, doping breaks the inversion symmetry of the system. The nonspin-polarized band structure has been shown in Figure 4a. The directions of the k-path and the high symmetry k-points, which are used to calculate the band structure, have been shown in Figure 4h. The bulk band structure indicates that the system is an insulator with a calculated direct band gap of 0.2 eV. The orbital projected

Figure 3. a) Synchrotron diffraction pattern with the Rietveld refinement, as indicated by the continuous curve at 5 K. Thermal variations of: b) $a$, c) $c$, and d) $V$.

Figure 4. a,b) The electronic band structure of Bi$_{1-x}$Sb$_x$Se$_3$ without and with SOC respectively. The inset shows enlarged view of the conduction bands around the $\Gamma$ point. c,d) The orbital characters projected on the band structure without and with SOC, respectively. Red, blue, and magenta color indicates Se-$p$, Bi-$p$, and Sb-$p$ states. Fermi energy is set to zero in the energy axis. e,f) The spin textures of the inner and outer branch of the conduction band around the $\Gamma$ point. The color bar indicates the contribution of the out-of-plane spin component. g) Surface state spectrum along the [001] direction, here the color bar indicates the contribution of the bands. Black color indicates the bulk energy gap. h) Brillouin zone of the system.
nonspin-polarized band structure has been shown in Figure 4c to identify the orbital contribution in the low energy valence and conduction bands. The occupied Se-p states lie from $-4$ eV up to the Fermi level to form the low energy valence bands. While, the conduction bands are mainly formed with completely unoccupied Bi-p and Sb-p states.

The SOC included band structure has been shown in Figure 4b, which clearly shows that the inclusion of SOC lifts the degeneracy of the bands and splits them along some particular directions in the k-space. In particular, we have considered the low lying conduction bands around the $\Gamma$ point and shown the enlarged view of the band structures without and with SOC in the inset of Figure 4a,b, respectively. A substantial amount of splitting of the bands is found along $\Gamma$-M and $\Gamma$-K directions of the Brillouin zone, perpendicular to the (0001) direction, which indicate the existence of Rashba–Dresselhaus effect in the system. In Figure 4e,f and, we have shown the spin textures of the inner and outer branches of the spin split bands around the $\Gamma$ point. The rotating nature of the in-plane spin components around the $\Gamma$ point indicates the dominance of the Rashba effect.

The finite value of the out-of-plane spin component may be attributed due to the presence of the higher order non-linear terms.[50] The system belongs to the C$_{3v}$ point group symmetry, which can host out-of-plane spin component through the higher order Dresselhaus term, which has been proposed recently.[51] Further, from band splitting, we have estimated the linear Rashba ($\alpha$$_{2D}$) and Dresselhaus ($\alpha$$_{0}$) parameters of the system around the $\Gamma$ point.[52] Our calculated values of $\alpha$$_{2D}$ and $\alpha$$_{0}$ are 0.6 and $-0.2$ eVÅ, respectively, which reveals the predominant contribution of the Rashba effect around the $\Gamma$ point. The presence of the Rashba effect induces an in-plane k-dependent relativistic magnetic field, and is expected to manifest in the transport properties.

The fatness of the bands in the presence of SOC (see Figure 4d) shows the presence of Bi-p character in the valence band maxima whereas, Se-p character in the conduction band minima at the $\Gamma$ point. This implies an inversion between Bi-p and Se-p states in presence of SOC, suggesting the possibility of hosting topological properties. To explore the topological properties, we have calculated the surface band structure of a semi-infinite slab of Bi$_2$Sb$_2$Se$_3$, which is constructed in a rotated frame having the quintuple layers along the [0001] direction. The surface band structure is then projected into the bulk band structure and the result is shown in Figure 4g. Surface band structure show conducting states which form a Dirac cone in the bulk energy gap, which is the signature of a topological insulator. Topological systems that lack inversion symmetry are of particular interest as they can simultaneously host conducting state at the surface and Rashba effect in the bulk, enhancing their scope of application.

To conclude, the proposed RSS elegantly construes the correlation between structural, electrical, magnetic, and thermoelectric transport results. Below $T_m$, the occurrence of bulk RSS is driven by the combined effect of structural distortion to a non-centrosymmetric structure and the strong SOC. Our experimental results of bulk RSS and associated nontrivial conducting surface state in the p-type Sb doped Bi$_2$Se$_3$, are further corroborated with first-principles electronic structure calculation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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