LETTER

Shubnikov-de Haas (SdH) Oscillation in Self-Flux Grown Rhombohedral Single-Crystalline Bismuth

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Abstract
The historic de Haas-van Alphen effect observed in the late 1950s in CSIR-NPL by J.S. Dhillon and D. Shoenberg in pure bismuth and zinc metal is revisited in this article through a single-crystalline phase of bismuth crystal, which is observed in terms of resistivity as predicted by Shubnikov-de Haas (SdH) oscillations. The single crystal of bismuth is grown through solid-state reaction under an optimized heat treatment whose purity and structural phase are confirmed through XRD, SEM, and EDAX. The transport properties of single crystal show the presence of SdH oscillations from a temperature range of 2 to 10 K. The occurrence of oscillations in the transverse magnetic field confirms the presence of the Fermi surface. Landau level (LL) fan diagram reveals the presence of topological surface states and the Berry’s phase confirmation from temperature-dependent SdH oscillations, concluding the presence of a noble topological phase of bismuth exhibiting SdH oscillations.

Keywords Single crystal bismuth · Berry phase · SdH oscillations · Topological bismuth · LL fan diagram · Dingle temperature

1 Introduction
Bismuth is an all-time fascinating material for condensed matter physicists. Starting from the late 1778 discovery of large anomalous diamagnetism to Seebeck effect in 1821, Nernst effect 1886, Kapitza’s law of magnetoresistance 1928, De Haas-van Alphen effect 1930, Shubnikov-de Haas effect 1930, cyclotron resonance 1955, oscillatory magnetostriction 1963, topology 2006, and anomalous quantum oscillation in longitudinal magneto-thermoelectric power in 2018 have resolved a lot of vague uncertainties of science [1–12]. The historical phenomenon of the de Haas-van Alphen effect was experimentally observed in the late 1930s by W.J. De Haas et al. [6], and it was revisited in CSIR-NPL by J.S. Dhillon and D. Shoenberg in the 1950s [9]. J.S. Dhillon et al. observed de Haas-van Alphen effect in pure bismuth and zinc metal through torque method at 4.19 K and 1.5 K between about 1.5 and 32kG [9]. In both these experiments by W.J. De Haas et al. [6] and J.S. Dhillon et al. [9], oscillations in magnetization with respect to the field were observed in bismuth. Moreover, J.S. Dhillon et al. considered various elements such as Zn, Bi, Pb, Ag, Au, and Cu for their study and only Bi and Zn were found to have oscillations in their magnetization analysis [9]. Furthermore, at that time, J.S. Dhillon et al. concluded that these oscillations were dependent on temperature, and related to its temperature dependence of steady susceptibility [9]. In 1962, Shubnikov-de Haas came up with the idea of finding oscillations in resistivity, same as being observed in magnetization as a function of the magnetic field [7]. This time, Shubnikov-de Haas observed oscillations in the transverse magnetoresistance of bismuth metal and predicted the Fermi surface of bismuth in three- and four-carrier models [7]. Furthermore, these oscillations were studied in various Sn-, Pb-, and Sb-doped Bi along with nanoribbons, nanowires, electron deposited Bi thin films, single crystals, and tin ionized Bi [9, 13–30].

Later, in 2005, the term topology changed the scenario of condensed matter physics as Charles Kane and Eugene Mele theoretically predicted the existence of topological insulators (TI) [31–34]. TI has a unique property of insulating at the bulk, while the surface shows the exotic state which...
is conducting. The electronic wave function of the charge carriers is dependent on the geometry as it changes from bulk to surface [35–37]. The surface states (SS) make the system relentless to nonmagnetic doping as the SS are protected by time-reversal symmetry (TRS). Such a trifling character provides numerous novel applications as the topological states are robust to nonmagnetic perturbation and show dissipation-less spin current transport. These applications include spintronic, thermoelectric, magnetic memory storage, magneto-electric devices, next-generation batteries, THz generators, transistors, photodetectors, and sensor applications [38–40]. Among these TIs, bismuth is found to have high-order intrinsic topology [5, 8, 31, 34, 36, 41, 42]. Thus, the bismuth metal has been fascinating for condensed matter physicists from the late 1950s to till date. This article revisited the SdH oscillation in the pure bismuth single crystal. The amplitude of SdH oscillations is found to be dependent on temperature, which is modelled to show its topological phases, while the temperature and field dependence of SdH oscillations reveal the information about 2D charge carriers. The short article on low-temperature magnetotransport of rhombohedral Bi crystal beautifully clubs together the topology and the Shubnikov-de Haas quantum oscillations.

2 Experimental Details

High purity (99.999%) bismuth (Bi) powder was taken to grow Bi single crystal using the self-flux method via solid-state reaction route [43]. Figure 1 shows the detailed heat treatment, and the inset image shows the obtained silvery shiny Bi crystal of size ≈ 1 cm × 0.5 cm (see for more details ref. [43]). For characterization, i.e., structural and transport properties, thin flakes were mechanically cleaved from an obtained single crystal. The table top Rigaku Miniflex II (X-ray diffractometer with radiation Cu-Kα (λ = 1.5406 Å)) was used to record diffraction spectra at room temperature, while the powder XRD pattern was Rietveld refined using FullProf software, and its crystal structure was extracted through VESTA software. The scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDAX) was performed to study its morphology and elemental composition. The vibration modes were recorded by a Renishaw Raman spectrometer equipped with a 514-nm laser. The transport measurements were performed using the quantum design physical property measurement system (PPMS) up to 14 T and down to 2 K.

3 Results and Discussion

To investigate the phase purity of synthesized Bi crystal, the mechanically cleaved flakes were crushed into powder, and X-ray diffraction (XRD) spectra of the powder were recorded at room temperature. Figure 2a depicts the Rietveld refinement of powder XRD spectra in a 2θ range from 20 to 80°. The fitting of all diffraction peaks confirms that the grown crystal is in a single phase. The synthesized crystal belongs to a rhombohedral crystal structure with \( R3m \) (166) space group having refined lattice parameters \( a = b = 4.546(1) \text{Å} \) and \( c = 11.859(6) \text{Å} \). Furthermore, to investigate the growth direction of grown crystal, XRD spectra were recorded on mechanically cleaved flake, which reveals that Bi crystal-lized along (00\( l \)) diffraction plane with \( l = 3n \) \((n = 1, 2, 3, \ldots)\) as shown in Fig. 2b. An additional peak at 2θ = 48.82° is also observed, which may be due to the misalignment of the crystal, as mentioned in our previous article [43]. We did several runs of flake XRD with different orientations and found that intensity of seemingly misaligned peak (202) changes, but is present. Besides misalignment of the crystal flakes, various polytypes of rhombohedral Bi could also be the reason behind the presence of the said peak [44]. The Rietveld refined parameters were used to draw Bi unit cells using VESTA software, as shown in the inset of Fig. 2b.

The vibrational modes of single-crystalline flake were recorded at room temperature, and Fig. 3 shows the observed Raman modes of studied bismuth crystal. Two peaks were observed at 69.84 and 96.91 cm\(^{-1}\), which corresponds to \( E_g \) and \( A_{1g} \) vibrational modes respectively. The observed peaks are in good agreement with previous reports [45–47]. The surface morphology of as-grown crystal was studied by performing SEM on cleaved Bi flake and is shown in the inset of Fig. 3. The layered growth along one direction and absence of any grain boundaries reveals the crystalline nature of synthesized Bi, which is in accordance with XRD spectra in Fig. 2a. Another inset represents the EDAX, which shows the absence of any impurity element in as-grown Bi crystal.
The transport properties are investigated using Quantum design PPMS. Figure 4a represents the temperature dependence of longitudinal resistivity in zero magnetic fields applied perpendicular to the sample. The four-probe arrangement is used to measure resistivity of sample and the applied field is perpendicular to sample surface, as illustrated in lower inset schematic of Fig. 4a. It is observed that with decreasing temperature from 300 to 2 K, the resistivity is monotonically decreased from 1.35 to 0.21 mΩ-cm, which signifies the metallic nature of the grown crystal. The residual resistivity ratio \(\text{RRR} = \rho(300 \text{ K})/\rho(2 \text{ K})\) is found to be 6.43, which corresponds to high crystalline nature, and this value is in accordance with previous reports on TI single crystals [48, 49]. The left inset of Fig. 4a represents the electrical resistivity behaviour as a function of transverse magnetic field, ranging from 0 to 14 T at different temperatures, varying from 2 to 100 K.

To investigate the magnetotransport, the magnetoresistance (MR) has been determined using the formula \(\text{MR\%} = (\rho(\text{H}) - \rho(0))/\rho(\text{H}) \times 100\%\) where \(\rho(\text{H})\) and \(\rho(0)\) are resistivity at applied and zero magnetic fields respectively. Figure 4b shows the transverse MR\% of Bi crystal in a magnetic field up to 14 T at different temperatures. The plotted MR\% is calculated by averaging the measured MR data in both positive and negative field directions. It is observed that MR varies linearly with the magnetic field at all measured temperatures and is non-saturating up to 14 T. For temperature 2 K, the value of MR\% is \(\approx 1700\%\) at the highest measured magnetic field 14 T which further decreased to \(\approx 1000\%\) as the temperature is increased to 100 K.

In MR measurements, the signature of Shubnikov-de Haas (SdH) oscillations has been observed at low temperatures. To further explore the observed SdH effect in Bi crystal, the resistance versus applied magnetic field measurements have been performed by varying the temperature between 2 and 10 K. For clarity and better understanding, a derivative of resistance with respect to the applied field at different temperatures is shown in Fig. 5a. The oscillatory behaviour of \(dR/dH\) displays the periodic variation of maxima or minima against the inverse magnetic field, which is due to the presence of the SdH effect. Also, the dependence of maxima/minima positions on transverse magnetic fields suggests that SdH oscillations do possibly originate from 2D surface states [50]. The occurrence of oscillations in the transverse magnetic field confirms the presence of the Fermi surface, and its cross-section area depends on the frequency of these oscillations. The fast Fourier transform (FFT) of
dR/dH vs. 1/H has been performed at respective temperatures to investigate these oscillations, as shown in the inset of Fig. 5a. The occurrence of a single frequency peak at ≈ 18.92 T indicates the existence of a single pocket near the Fermi surface. According to Onsager relation, the SdH oscillation frequency (F) is proportional to the cross-section area ($A_F$) of the Fermi surface by relation $F = (\hbar/2\pi e)A_F$. Here, $\hbar$ and $e$ are Plank’s constant divided by 2π and electronic charge respectively, the calculated cross-sectional area of Fermi surface corresponding to frequency 18.92 T which comes out to be $180.59 \times 10^{15}$ m$^{-2}$. Assuming a circular cross-section of the Fermi surface, the Fermi wave vector ($k_F$) is described as $k_F = (A_F/\pi)^{1/2}$. The obtained value of the Fermi wave vector corresponding to $A_F$ is found to be 0.024 Å$^{-1}$, which is consistent with the literature [50]. Also, the 2D surface carrier density ($n_{2D}$) can be calculated from the Fermi wave vector by using relation $n_{2D} = k_F^2/4\pi$; the obtained value of $n_{2D}$ is found to be $4.57 \times 10^{11}$ cm$^{-2}$ which is comparable and in accordance with previous reports on topological insulators [20, 51, 52].

In order to investigate the topological nature of electrons, the occurrence of Berry’s phase has been extracted from quantum oscillations data through the Landau level (LL) fan diagram. In the LL fan diagram, the Landau index ($n$) is plotted as a function of the inverse magnetic field, as shown in the main panel of Fig. 5b. Here, the integral LL index has been assigned to the minima of quantum oscillations in the dR/dH vs. 1/H plot for the entire field range at 2 K, and the

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**Fig. 4** a Variation of electrical resistivity as a function of temperature from 300 to 2 K; upper inset represents the dependence of resistivity on magnetic field up to 14 T at different temperatures, and lower inset shows the schematic of four-probe resistivity measurement. b Magnetoresistance of Bi crystal at different temperatures

**Fig. 5** a Behaviour of dR/dH of Bi crystal as a function of magnetic field at different temperatures; inset shows the temperature dependence of FFT spectrum of oscillations. b Landau level fan diagram; upper left inset shows oscillation amplitude as a function of temperature fitted with L-K formula and lower right inset is Dingle plot for Bi crystal
4 Conclusion

Quantum SdH oscillations are seen at low \( T \) (below 10 K) and higher fields (up to 14 T) in transverse magnetic field for studied rhombohedral Bi single crystal. The LL fan diagram shows a finite intercept of \(-0.501\), which corresponds to \( \pi \) Berry’s phase and concludes the topological nature of SdH oscillations arising from surface states. Along with the topological confirmation, various other parameters are also calculated, which includes effective mass \( m^* \) of \( 0.23 m_e \), Fermi velocity of \( 7.6 \times 10^5 \) m/s, Fermi level of 757.9 meV, scattering time of charge carriers of \( 4.2 \times 10^{-13} \) s, the carrier mobility of 3289.9 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and mean free path of 326.2 nm, respectively. This study investigates the intrinsic topological nature of bismuth using transport property analysis and predicts the application of bismuth in spintronics and quantum computing field.

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Declarations

Conflict of Interest

The authors declare no competing interests.

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