Anisotropic upper critical field, Seebeck and Nernst coefficient of Nb$_{0.20}$Bi$_2$Se$_3$ superconductor

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Abstract
We present the magneto-transport and the thermoelectric (Seebeck and Nernst coefficient) studies of the Nb-doped Bi$_2$Se$_3$ superconductor. The angle-dependent magnetoresistance study highlights the anisotropy of upper critical field ($H_{c2}$) for in-plane and out-of-plane magnetic field orientation with the anisotropy parameter $\Gamma \sim 1.3$. The estimated value of the carrier concentration ($\sim$10$^{19}$ cm$^{-3}$) for Nb$_{0.20}$Bi$_2$Se$_3$ is one order larger than for Bi$_2$Se$_3$. Doping of Nb shows a significant decrease in the Seebeck coefficient value and the estimated Fermi temperature of the three-dimensional Fermi surface at the centre of Brillouin zone in the zero-temperature limit enhances by $\sim$4 times in comparison to pristine Bi$_2$Se$_3$. We have observed a large value ($\sim$2.3 $\mu$V K$^{-1}$ T$^{-1}$) of Nernst coefficient for Bi$_2$Se$_3$ at room temperature, which decreases with Nb doping ($\sim$0.5 $\mu$V K$^{-1}$ T$^{-1}$).

Keywords: superconductivity, electronic transport, thermoelectric coefficient

Some figures may appear in colour only in the online journal

1. Introduction

Three-dimensional topological insulators (TIs) are one of the most active research fields in condensed matter physics. TIs are characterized by their non-trivial gapless surface states, where electrons have spin-momentum locking with time-reversal symmetry [1]. Doped Bi$_2$Se$_3$ such as (Cu/Sr/Nb),Bi$_2$Se$_3$ have been identified as a promising TI material for the realization of topological superconductivity [2]. These topological superconductors (TSCs) are characterized by bulk superconducting gap with gapless conducting surface states [2]. Unlike the TIs, where the surface states consist of Dirac fermions, the surface states in TSCs consist of Majorana fermions, which are their own antiparticles [3]. The experiments have revealed the unique features of zero-bias conductance peak and the Majorana zero modes in the TSCs [4, 5]. Moreover, angle resolved photoelectron spectroscopy measurements in TSCs showed the existence of non-trivial surface states in normal states [6, 7].

Recent experiments reveal that carrier-doped Bi$_2$Se$_3$ is a nematic TSC, with two-component $E_u$ order parameter that belongs to crystal point group $D_{3d}$, which spontaneously break three-fold rotational symmetry, leading to a nematic order [8–10]. Nematic superconductivity has been observed in Cu, Sr, and Nb doped Bi$_2$Se$_3$ superconductors [11] below superconducting transition temperature ($T_c$) in the angle dependent measurements of spin susceptibility, heat capacity, magnetoresistance (MR), and magnetic torque [11–16]. The study of temperature dependence of London penetration depth indicate the presence of symmetry-protected point nodes consistent with $E_u$ odd-parity pairing [17]. Further, the penetration depth study on the proton irradiated sample showed odd frequency pairing for superconductivity where
order parameter has symmetry protected nodes [18]. These results suggest the realization of topological superconductivity in the nonmagnetic disordered system [18]. Further, Wu et al discussed the power-law temperature dependence of the penetration depth in a TSC with a fully gapped bulk [19]. Asaba et al investigated the nematicity in hysteresis through torque magnetometry in Nb$_2$Bi$_2$Se$_3$ and also showed nodeless superconducting gap, which is consistent with odd parity $p$-wave pairing [15]. The quantum oscillation results on Nb-doped Bi$_2$Se$_3$ have shown the multi orbit nature of the electronic state which is in contrast to one bulk Fermi pocket in Bi$_2$Se$_3$, Cu$_3$Bi$_2$Se$_3$ and Sr$_2$Bi$_2$Se$_3$ [20]. In a recent study Cho et al has shown the presence of superconducting-fluctuation-induced nematic order above $T_c$ [21]. Therefore, superconductivity in Nb$_2$Bi$_2$Se$_3$ compound offers rich physics from the point of view of nematicity in different quantities as well as electronic transport discussed via quantum oscillations. Recent studies have revealed that superconducting behaviour in Nb$_2$Bi$_2$Se$_3$ results from the (BiSe)$_3$-1NbSe$_2$ misfit phase, that is present as impurity phase for low composition and as a main phase for higher composition ($x > 0.50$) with the BiSe$_3$ phase [22–24]. The Seebeck and Nernst effect in Nb$_{0.20}$Bi$_2$Se$_3$ TSC has remain unexplored. Nernst effect provides an insight to understand the electronic properties of exotic topological materials. Nernst signal gives information on small anomalous contributions, such as extrinsic contribution from magnetic impurity scattering and intrinsic contribution from Berry curvature. The magnitude of Nernst signal depends upon the quasiparticle mobilities and corresponding Fermi energies. In this article, we present detailed angle-dependent magneto-transport and thermoelectric studies on the good quality single crystalline Nb$_{0.20}$Bi$_2$Se$_3$ superconductor. The structural studies of the compound showing the single crystal x-ray diffraction (XRD) pattern, Rietveld refinement pattern on powered sample, and Raman spectroscopy are shown in the supplemental material (figures S1 and S2 (available online at stacks.iop.org/SUST/35/075015/mmedia)). Our powder XRD pattern matches with the literature and suggests the presence of impurity phase [22–24]. We have discussed the anisotropic upper critical field ($H_{c2}$) for in-plane ($ab$-plane) and out-of-plane ($c$-axis) through angle-dependent magneto-transport study in the superconducting state. Our studies rule out the presence of spontaneous magnetization and the Hall signal in superconducting phase, which has been linked to the chiral superconductivity in the compound. Furthermore, the thermoelectric properties of Nb$_{0.20}$Bi$_2$Se$_3$ are discussed through temperature-dependent Seebeck and Nernst coefficient data in the zero-temperature limit within the single-band picture for Fermi liquid metals, which are compared with the results on pristine Bi$_2$Se$_3$.

2. Experimental details

2.1. Sample synthesis

Single crystals of Nb$_{0.20}$Bi$_2$Se$_3$ were synthesised using melt growth technique. High purity elements Bi granular (>99.99%), Se pellets (>99.999%) and Nb wire (1 mm dia, 99.8%) were accurately weighed according to the stoichiometric amount, vacuum sealed and subjected to three-step heat treatments for homogeneity of the compounds. In first step, Bi$_2$Se$_3$ was prepared at 850 °C for 48 h, slowly cooled to 550 °C and annealed for 72 h, after that it was furnace off cooled to room temperature. In second step, prepared Bi$_2$Se$_3$ was ground using mortar and pestle and taken in form of pellets, with Nb wire which is subjected to heat treatment at 850 °C for 96 h, slowly cooled to 620 °C for 24 h and furnace off cooled to room temperature. In third step, the ingots obtained in previous step were reground, pelletized, and placed to similar heat treatment as in step 2. The single crystals were obtained from ingots by easily cleaving along the basal plane.

2.2. Measurements

Phase purity and crystal structure were studied through x-ray diffraction pattern using a rotating anode Rigaku Smartlab diffractometer in Bragg Brentano geometry (Cu–K$_\alpha$, $\lambda = 1.5418$ Å) on powered as well as thin flake sample. Room temperature Raman measurements were performed using a Horiba LabRAM HR Evolution Raman spectrometer with solid state laser (532 nm). Angular magneto-transport measurements were carried out on a horizontal rotator in PPMS (DynaCool, Quantum Design Inc.) in temperature range 1.8–300 K and magnetic fields up to 8 T. The standard four-probe method was used for resistivity and Hall effect measurements. The magnetisation measurements were performed using a SQUID magnetometer (MPMS-3, Quantum Design Inc.). Thermal transport (Seebeck and Nernst coefficient) measurements were performed on a homebuilt setup integrated with PPMS using multifunctional probe assembly [25].

3. Results and discussion

3.1. Magneto-transport studies

The longitudinal resistivity $\rho_{xx}(T)$ of Nb$_{0.20}$Bi$_2$Se$_3$ shown in figure 1(a) follows metallic behaviour down to 3.5 K, below which it shows superconductivity in agreement with the literature [20, 22]. Inset shows the temperature-dependent magnetization (M) in both zero-field cooled and field cooled measured at $H = 10$ Oe. The magnetization values (emu gm$^{-1}$) at 1.8 K are similar with the value in literature corresponding to the Nb composition of $x = 0.20$ [22]. The magnetisation measurements were performed in a configuration when $H // ab$ plane to minimize the effect of demagnetization factor. The low temperature $\rho_{xx}(T)$ measured at different fields is presented in figure 1(b) for $H // c$-axis of the crystal. With increasing magnetic fields, $T_c$ shifts to lower temperature and gradually suppressed to zero. Further, magnetic field dependence of resistivity $\rho_{xx}(H)$ at different temperatures below $T_c$ is shown for different orientation of the sample, $H // c$-axis
and $H // ab$-plane (in-plane) in figures 1(c) and (d), respectively. It is to note that the superconducting transition gets more broaden for $H // ab$-plane in comparison to $H // c$-axis, with the transition width $\Delta H = H$ (onset of SC transition) $\sim H$ (offset of SC transition) of 0.63 and 0.28 for $H // ab$-plane and $H // c$-axis, respectively, which reflect the anisotropy in the upper critical field values. Figure 2(a) shows the $M$–$H$ loop with $H // ab$-plane at 1.8 K revealing the type-II superconducting behaviour without any magnetic Nb contribution, in agreement with the hysteresis loop as discussed previously [26, 27]. $M$–$H$ at different temperatures below $T_c$ is discussed in figure S3 (supplementary materials). Figure 2(b) shows the schematic for the angle-magnetic field dependent resistivity measurements, where $\theta = 0^\circ$ corresponds to the geometry when $H // c$-axis and $\theta = 90^\circ$ when $H // ab$-plane, and current is always perpendicular to the field direction. We have extracted the upper critical field ($H_{c2}$) from the above resistivity curves (figures 1(b)–(d)) as shown in figure 2(c). The $H_{c2}$ values at different temperatures were obtained from the fields at which the resistivity of the sample has reached to 50% of the normal state resistivity values at different temperatures. The $H_{c2}$ vs $T$ data as shown in figure 2(c), were fitted using generalised Ginzburg–Landau equation given by $H_{c2}(T) = H_{c2}(0)(1 - T^2)/(1 + T^2)$ where $T = T/T_c$ is the reduced temperature, $H_{c2}(0)$ is the zero-temperature upper critical field and $T_c$ is 3.2 K. The fitting gives zero-temperature extrapolated upper critical field values as $H_{c2}^{ab}(0) = 0.7$ T and $H_{c2}^{c}(0) = 0.55$ T. Applying the Werthamer–Helfand–Hohenberg formula, which describes the behaviour of upper critical field ($H_{c2}$) in conventional type-II Bardeen–Cooper–Schrieffer (BCS) superconductors, we extracted $H_{c2}^{orb}(0)$ using [28] $\mu_0H_{c2}^{orb}(0) = -0.693\left(\frac{4\mu_0\xi}{\pi H_{c2}^{orb}(0)}\right)T_c$, where the slope $|dH_{c2}(T)/dT|$ can be obtained from the linear fitting of the curves in graph. The value of zero-temperature orbital limited upper critical field, $\mu_0H_{c2}^{orb}(0)$, along the $c$-axis and parallel to $ab$-plane, were calculated to be 0.43 T and 0.56 T, respectively. Using $H^P(0) = \Delta/\sqrt{2\mu_0}$ and $\Delta = 1.76k_BT_c$ we evaluate the Pauli limiting field $H^P(0) = 6.1$ T for $H // c$-axis. The Maki parameter, $\alpha = \sqrt{2\mu_0H_{c2}^{orb}(0)/H^P(0)}$, calculated as $\alpha = 0.098(13)$ and $H_{c2}(0) = 0.42$ T (0.55 T) for $H // c$-axis ($ab$-plane) [28, 29]. Since $\alpha$ is less than one hence the Flude–Ferrell–Larkin–Ovchinnikov state is not favourable [30].

The superconducting coherence length can be extracted from the following expressions: $H_{c2}^{c} = \frac{\Phi_0}{\pi\xi_{ab}^2}$, $H_{c2}^{ab} = \frac{\Phi_0}{\pi\xi_c^2}$; where $\Phi_0 = 2.07 \times 10^{-7}$ Oe cm$^2$ is the magnetic quantum flux, and $\xi_{ab}$ and $\xi_c$ are the superconducting coherence length in the $ab$ plane and along the $c$-axis, respectively. The superconducting coherence lengths $\xi_{ab}(0)$ and $\xi_c(0)$ at 0 K, were estimated to be $\sim 25$ nm and $\sim 19$ nm, respectively. The effective upper critical field for anisotropic superconductor varies between two orientations depending upon the superconducting...
the extracted $\theta$ range is when magnetic field is parallel to $c$-axis ($H \parallel c$), and $\theta = 90^\circ$ is when magnetic field is parallel to $ab$-plane ($H \parallel ab$). (c) $H$–$T$ phase diagram (obtained from figures (1(b))–(d)) along with the extrapolated generalised Ginzburg–Landau upper critical field fit. (d) Polar plot showing $\rho_{xx}$ ($T$, $\theta$) at $H = 0.3$ T below $H_c2$ measured between $T = 1.8$ K and $3.8$ K. (e) The $\rho_{xx}(H)$ measured at $T = 1.8$ K at different angles, showing the anisotropy in $\rho_{xx}(H)$. (f) Polar diagram showing anisotropy of $H_{c2}$ at $T = 1.8$ K obtained from figure (c), red curve shows the anisotropic Ginzburg–Landau fit (equation (1)).

Figure 2. (a) $M(H)$ at 1.8 K showing superconducting hysteresis loop. (b) Schematic of angular-magneto-transport measurement geometry: angle ($\theta = 0^\circ$) is when magnetic field is parallel to $c$-axis ($H \parallel c$), and $\theta = 90^\circ$ is when magnetic field is parallel to $ab$-plane ($H \parallel ab$). (c) $H$–$T$ phase diagram (obtained from figures (1(b))–(d)) along with the extrapolated generalised Ginzburg–Landau upper critical field fit. (d) Polar plot showing $\rho_{xx}$ ($T$, $\theta$) at $H = 0.3$ T below $H_c2$ measured between $T = 1.8$ K and $3.8$ K. (e) The $\rho_{xx}(H)$ measured at $T = 1.8$ K at different angles, showing the anisotropy in $\rho_{xx}(H)$. (f) Polar diagram showing anisotropy of $H_{c2}$ at $T = 1.8$ K obtained from figure (c), red curve shows the anisotropic Ginzburg–Landau fit (equation (1)).

anisotropic ratio, $\Gamma = H_{c2}^{ab}/H_{c2}^{c}$ is $\sim 1.3$. Similar values have been discussed for Cu, Nb, Sr doped Bi$_2$Se$_3$ [17, 31, 32]. The anisotropy in $H_{c2}$ is attributed to the layered crystal structure, which has been ascribed to the dimensional crossover in the literature [33, 34]. The carrier density calculated using the one-band Drude model from the Hall data at 5 K, and assuming a spherical Fermi surface where $k_F = (3\pi^2n)^{1/3}$, mean free path, $l$ can be estimated from the relation $l = \hbar k_F/\rho_0 n e^2$. With $n = 3.33 \times 10^{19}$ cm$^{-3}$ and $\rho_0 = 2.29 \times 10^{-3}$ $\Omega$ cm ($T = 5$ K), we calculate $k_F = 8.47 \times 10^8$ cm$^{-1}$ and $l = 4.5$ nm, which is less than the coherence length. Comparing the mean free path, $l$ and coherence length, $\xi_{ab}$, $\xi_c$, we find that for our sample, $l < \xi_{ab}$, $\xi_c$ which is not in the clean limit.

Figure 2(d) shows the polar plot for the angular dependence of resistivity measured in fixed applied magnetic field $H = 0.3$ T (below the $H_{c2}$ value) in the superconducting regime at different temperatures ($T = 1.8$, 1.9, 2.0, 2.2, 2.4, 2.6) and normal state ($T = 3.8$ K). The angular dependence of resistivity reflects the two-fold anisotropy in superconducting state. We see that normal state magneto-resistivity ($T = 3.8$ K) does not show any variation for different angles. Furthermore, we measured $\rho_{xx}(H)$ at $\theta = 0$, 15, 30, 45, 60, 75, and 90° with respect to $c$-axis of sample at $\pm 1$ T field in superconducting state at $T = 1.8$ K (see figure 2(e)). It is to mention here that the current is always kept perpendicular to the magnetic field directions. We find that the $H_{c2}$ value increases as magnetic field gets parallel to $ab$-plane of sample ($\theta = 90^\circ$). The extracted $H_{c2}$ values are plotted with different angles in polar plot in figure 2(f). The graph clearly depicts the two-fold anisotropy of $H_{c2}$ in superconducting state. This can be understood according to anisotropic Ginzburg–Landau theory, effective mass anisotropy leads to the anisotropy of the upper critical field [35]. The upper critical field at an angle $\theta$ is given by

$$H_{c2}^{ab}(\theta) = \frac{H_{c2}^{c}(0)}{\sqrt{\cos^2(\theta) + \Gamma^{-2}\sin^2(\theta)}}$$

such that $\theta = 0$ is the angle between applied magnetic field and $c$-axis of the sample, and $\theta = \pi/2$ is when field is parallel to the plane of layers, i.e. along the $ab$-plane. Anisotropic parameter $\Gamma = \sqrt{m^*_c/m^*_a}$, defines anisotropy between the effective masses of the quasiparticles along the $c$-axis and the $ab$ plane. This is derived from the upper critical field anisotropy, $\Gamma = H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ [33, 35]. We fit the data (figure 2(f)) with the formula (equation (1)) that describes the two-fold anisotropy of layered superconductors, with $\Gamma = 1.3$, and $H_{c2}(0) = 0.26$ T. Therefore, effect of crystal anisotropy for in-plane and out-of-plane is evident in two-fold anisotropy of both resistivity and upper critical field data in superconducting state. Previous reports on Nb$_2$Bi$_2$Se$_3$ have discussed the two-fold anisotropy for in-plane measurements, when magnetic field is rotated in $ab$-plane (basal), resulting in nematic superconductivity [26]. Recent studies reveal that the presence of two-fold anisotropy in $ab$-plane due to presence of BiSe cubic phase, which exists with Misfit phase (BiSe)$_{1.1}$NbSe$_2$ for higher composition of x ($x > 0.50$) [22–24]. While we cannot exclude this for in-plane and out-of-plane measurements,
it is difficult to comment on the exact role of misfit phase for the in-plane and out-of-plane anisotropy in superconducting state.

Further, we performed MR measurements at various temperatures in normal state (above 4 K), in magnetic fields $\pm 8$ T as illustrated in figure 3(a). The percentage change in MR is defined as $MR\% = \frac{\rho(H) - \rho(H=0)}{\rho(H=0)} \times 100\%$. The Nb$_{0.3}$Bi$_3$Se$_3$ is found to exhibit $H^2$ dependence at low fields and non-saturating linear behaviour at high fields, similar to the parent compound Bi$_3$Se$_3$ with a maximum value of $\sim 35\%$ at $T = 4$ K which is comparable to that of Bi$_2$Se$_3$ [36]. As observed from the plots (shown as fit in black) that quadratic field dependence of MR increases with increase in temperature. The quadratic dependence of MR is attributed to the deflection of charge carriers due to the Lorentz force under the applied magnetic fields, which gets saturated at high fields, followed by linear MR (LMR). LMR is usually observed in topological materials, explained using classical Parish Littlewood model [37] and quantum model by Abrikosov [38]. The LMR at low temperatures seems to originate from the linear energy dispersion, as observed for the gapless topological surface states observed in (Bi, Sb)$_2$(Se, Te)$_3$, Dirac and Weyl semimetals and other topological materials [39–41].

The Hall resistivity ($\rho_{xy}$) measured in low temperature (1.8–3.4 K) and low fields ($\pm 0.5$ T), is presented in figure 3(b). The observed $\rho_{xy}(H)$ behaviour is a typical of a BCS superconductor which gives zero Hall coefficient hence, no carrier charges in SC state. It is reported that Nb doped Bi$_3$Se$_3$ spontaneously breaks time reversal-symmetry due to finite magnetisation and observation of finite Hall resistivity in zero-field below $T_c$ [42, 43]. Our Hall effect studies are in sharp contrast with above studies, since the Hall effect is zero in superconducting state which is true for a superconductor. This is also supported by M–H isotherm measured at $T = 1.8$ K plot as depicted in figure 2(a), which does not show the presence of any additional magnetic contribution in superconducting state. Additionally, our M–H isotherm does not reveal any sign of saturation at high fields, which has been earlier reported for finite magnetic moments from paramagnetic contribution in superconducting state [42]. Therefore, our Hall resistivity, together with M–H results implies that Nb atoms does not contribute towards magnetism in superconducting state, which are contrary to the claims of the time-reversal symmetry breaking in superconducting states. Nevertheless, superconductivity in this compound has been explored using muon-spin resonance experiments in zero-field, which does not show any evidence of magnetic fields in SC state [44]. Thus, the expected TRS breaking in this compound has not been observed experimentally.

The $\rho_{xy}(H)$ measured at $T = 5–300$ K and $H = 0–8$ T is presented in figure 3(c). The Hall resistivity data has been antisymmetrized using the formula $\rho_{xy}(H) = (\rho_{xy}(+H) - \rho_{xy}(-H))/2$, to remove any offset voltage due to contact misalignment. The $\rho_{xy}(H)$ is linear in the complete field range with negative slope implying electrons as dominant charge carriers in this system. The carrier density ($n$) and Hall mobility ($\mu$) are calculated based upon the one-band Drude model and the temperature dependence is shown in figure 3(d). The carrier density and mobility lie within the range (1–3.5) $\times 10^{19}$ cm$^{-3}$ and (80–125) cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The carrier density

![Figure 3](image-url)
Figure 4. (a), (b) Temperature dependence of Seebeck coefficient, \( S_{xx} \) and \( S_{xx}/T \) in zero-field, respectively, and (c), (d) temperature dependence of Nernst coefficient, \( \nu \) and \( \nu/T \) at field 8 T, respectively. Inset in figure (c) shows the schematic for Seebeck and Nernst effect measurement. Inset in figure (d) shows the low-temperature region of \( \nu/T \).

is one order larger compared to the parent \( \text{Bi}_2\text{Se}_3 \) [36], but comparable to that reported in literature for doped \( \text{Bi}_2\text{Se}_3 \) [32, 45, 46].

3.2. Thermoelectric studies

Temperature dependence of Seebeck coefficient \( (S_{xx} = E_x/|\nabla T_x|) \) and Nernst coefficient \( (\nu = S_{xy}/E_y = E_y/|\nabla T_y|) \) are presented in figure 4 for undoped \( \text{Bi}_2\text{Se}_3 \) and \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) single crystal. Inset shows the schematic for the Seebeck and Nernst effect measurement, where thermal gradient was applied along the \( ab \)-plane and the magnetic field was oriented along the \( c \)-axis. The negative value of \( S_{xx} \) shows \( n \)-type conduction for both compounds with the room temperature values of \( S_{xx} \approx -140 \mu \text{V K}^{-1} \) and \( -38 \mu \text{V K}^{-1} \) for \( \text{Bi}_2\text{Se}_3 \) and \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) respectively. A clear superconducting transition for \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) could not be observed as \( S(T) \) value becomes very close to zero in low-temperature limit \( (S \approx -0.04 \mu \text{V K}^{-1} \text{ at } T = 4 \text{ K}) \). Generally, \( S_{xx} \) in metals is a sum of diffusion term \( (S_{\text{diff}}) \) and the phonon-drag term \( (S_{\text{drag}}) \). Within the Fermi liquid picture and in the absence of phonon drag, \( S_{xx}(T) \) shows linear temperature dependence given by the Mott expression [47],

\[
S_{xx}/T = \pm \frac{\pi^2 k_B^2 T}{2 e} N(\varepsilon_F) = \pm \frac{\pi^2 k_B^2}{3 e} \frac{N(\varepsilon_F)}{n}
\]

where \( k_B \) is Boltzmann’s constant, \( e \) is electron charge, \( n \) is the carrier density, and \( T_F \) is the Fermi temperature. The density of states \( N(\varepsilon_F) \) is related to the Fermi energy as \( N(\varepsilon_F) = 3n/2k_B T_F \). Figure 4(b) presents the temperature dependence of \( S_{xx}/T \) for both the compounds. The slope of \( S_{xx}/T \) vs. \( T \) curve is inversely proportional to \( T_F \).

The zero-temperature extrapolated value of \( S_{xx}/T \) for \( \text{Bi}_2\text{Se}_3 \) and \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) are \( -0.83 \mu \text{V K}^{-2} \) and \( -0.17 \mu \text{V K}^{-2} \), that corresponds to \( T_F \) values of 516 K and 2536 K, respectively. The data is consistent with the large number of \( n \)-type charge carriers observed for \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) \( (10^{20} \text{ cm}^{-3}) \) than parent \( \text{Bi}_2\text{Se}_3 \) \( (10^{18} \text{ cm}^{-3}) \). The obtained \( T_F \) values for \( \text{Nb}_{0.20}\text{Bi}_2\text{Se}_3 \) are similar to those for other TSCs such as \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) [48] and \( \text{Sr}_2\text{Bi}_2\text{Se}_3 \) [32].

The value of Sommerfeld coefficient \( (\gamma) \) and Debye temperature \( (\Theta_D) \) were estimated from low temperature heat capacity data (see figure S4 in supplementary materials). The Sommerfeld coefficient \( \gamma \) is given by \( \gamma = \frac{k_B}{\Theta_D} \frac{\pi^2}{3} \frac{k_B^2}{e} N(\varepsilon_F) \) [47]. We find that \( S_{xx}/T \) and \( \gamma \) values decrease upon Nb doping in \( \text{Bi}_2\text{Se}_3 \), reflecting a change in Fermi surface. With a simple Debye model to the phonon contribution, Debye temperature \( (\Theta_D) \) was calculated using \( \Theta_D = \left( \frac{12 \pi^4}{5 \Theta} n R \right)^{1/3} \), where \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) is the ideal gas constant and \( n \) is number of atoms for \( \text{Bi}_2\text{Se}_3 \). The density of states at the Fermi energy is calculated as \( N(\varepsilon_F) = \frac{3}{8} \frac{k_B^2}{e} \). We find that the density of states decreases with Nb doping. Considering the BCS theory of superconductivity, the electron-phonon
coupling strength ($\lambda_{ph}$) can be approximated from the McMillan formula [49]:

$$\lambda_{ph} = \frac{\mu^2}{1.04 + \mu^2 \ln \left( \frac{\nu}{\nu_c} \right)},$$

where $\mu^*$ is the coulomb coupling parameter empirically valued as 0.13. The $\lambda_{ph}$ was estimated to be 0.7, suggesting intermediate coupling strength (BCS weak coupling case: $\lambda_{ph} \ll 1$; strong-coupling case: $\lambda_{ph} > 1$). Using $S_{av}/T$ and $\gamma$, we derived dimensionless parameter $q$, given by $q = \frac{S_{av}}{\gamma N_A}$, where $N_A$ is the Avogadro number [47]. The parameter $q$ defines a correlation between Seebeck coefficient ($S$) and electronic specific heat ($\gamma$) of the system. The obtained $q$ values are shown in Table 1.

Earlier, large value of $q$ (∼107) has been observed for ‘Kondo insulator’ (CeNiSn) due to the extremely low carrier density [47]. Here, carrier density for Bi$_2$Se$_3$ is in range 10$^{18}$ cm$^{-3}$, $q$ value (∼34) and for Nb$_{0.20}$Bi$_2$Se$_3$, $q$ value (∼22.4). Thus, we find that $S_{av}/T$ and $\gamma$ values decrease upon Nb doping in Bi$_2$Se$_3$, which reflects a change in Fermi surface. Additionally, the ratio of $T_c$ to $T_F$ can be used to get information about the electronic correlation strength in superconductors [50]. The ratio $T_c/T_F \sim 0.0013$ implies a weakly correlated superconductor [51]. Assuming single band transport and a spherical Fermi surface, we have calculated the Fermi wave vector ($k_F$), effective mass ($m^*$) and Fermi velocity ($v_F$), using $k_B T_F = \hbar k_F^2/2m^*$ and $h k_F = m^* v_F$, which are shown in Table 1. We find that the values of $k_F$, $m^*$, $v_F$ are comparable with those obtained from quantum oscillations analysis inNb-doped Bi$_2$Se$_3$ [20, 24].

Figure 4(c) presents the Nernst coefficient measured in presence of magnetic field $H = 8$ T for both undoped Bi$_2$Se$_3$ and Nb$_{0.20}$Bi$_2$Se$_3$. We have observed a large Nernst coefficient ($\nu / T_F \sim 2.3 \mu V K^{-1} T^{-1}$) at room temperature for pristine Bi$_2$Se$_3$, which decreases upon Nb doping (∼0.5 $\mu V K^{-1} T^{-1}$). The large value of Nernst coefficient is usually discussed in literature due to the presence of Dirac dispersion bands at the Fermi level, multiple bands, and fluctuation forms of spin-density-wave (SDW) in iron-pnictide superconducting compounds [52]. Since, Bi$_2$Se$_3$ and its derivatives have Dirac cone at the Fermi surface, large value of Nernst coefficient is consistent with the linear dispersion relation of the bands crossing the Fermi level. The Nernst coefficient in parent Bi$_2$Se$_3$ and Nb$_{0.20}$Bi$_2$Se$_3$ is positive above $T = 170$ K, with a sign change at 170 K, and reaches a minimum (valley) at ∼38 K, then finally goes close to zero. Similar kind of sign change in Nernst coefficient has been reported in earlier in iron pnictide compounds [53] due to the SDW fluctuations, Fe-based superconductors [54] described to the Fermi surface reconstruction and recently in Fe$_3$Sn$_2$ [55], that has been attributed to the anomalous Nernst effect. The anomalous contribution to Nernst effect arise from an intrinsic mechanism link with the Berry curvature. Additionally, the Hall resistivity versus magnetic field data is linear with negative slope and can be fitted with the single band model implying the electron as dominant charge carriers in Bi$_2$Se$_3$ and Nb$_{0.20}$Bi$_2$Se$_3$. It is to note that Nernst coefficient can be of any sign, without any direct relation to carrier type. Within the Boltzmann theory, in a single band picture, following expression links the Nernst coefficient ($\nu$) with the Fermi temperature ($T_F$) [56], $\nu = \frac{2}{3} \frac{\hbar^2}{T \pi^2 m^*},$ where $k_B$ is Boltzmann’s constant, $e$ is electron charge and $\mu$ is mobility. This formula positively correlates the Nernst effect with the carrier mobility. Thus, undoped Bi$_2$Se$_3$ has more Nernst signal value with the high carrier mobility (∼3844 cm$^2 V^{-1} s^{-1}$ at 5 K) than the Nb$_{0.20}$Bi$_2$Se$_3$ which has low carrier mobility (∼82 cm$^2 V^{-1} s^{-1}$ at 5 K). The $\nu / T$ for undoped Bi$_2$Se$_3$ and Nb$_{0.20}$Bi$_2$Se$_3$ in zero-temperature limit is −0.01 $\mu V K^{-2} T^{-1}$ and −0.0023 $\mu V K^{-2} T^{-1}$, respectively, which is consistent with the mobility values. Obtained value of the low temperature Nernst signal for Bi$_2$Se$_3$ is in the same range as reported by Fauqué et al [57] although it depends upon the carrier density. Table 1 summarizes the parameters obtained from the $S/T$ zero-temperature limit, $S_{av}/T$ and $\nu / T$ values are obtained at lowest temperature (2 K).

**Table 1.** Parameters obtained from the value of $S/T$ in zero temperature limit, electron mobility, Fermi temperature, and other parameters within the single band picture of Fermi liquid.

| Sample     | Bi$_2$Se$_3$ | Nb$_{0.20}$Bi$_2$Se$_3$ |
|------------|--------------|--------------------------|
| $S^*/T$ ($\mu V K^{-2}$) | −0.73 | 0.0098 |
| $\nu^*/T$ ($\mu V K^{-2} T^{-1}$) | 0.022 | 0.014 |
| $T_F$ (K) | 516 | 2530 |
| $\mu$ (cm$^2 V^{-1} s^{-1}$) | 3844 | 82 |
| $\Theta_0$ (K) | 150 | 144 |
| $\gamma$ (mJ mol$^{-1}$ K$^{-2}$) | 2.35 | 0.72 |
| $N(eV/F)$ (states eV$^{-1}$ per f.u.) | 0.99 | 0.31 |
| $\nu = \frac{2}{3} \frac{\hbar^2}{\pi^2 m^*}$ | 34 | 22.4 |
| $T_c/T_F$ | — | 0.0014 |
| $k_B (10^8 cm^{-1})$ | 3.6 | 8.5 |
| $m^*$ | 0.11 $m_e$ | 0.13 $m_e$ |
| $v_F (10^7 cm s^{-1})$ | 3.78 | 7.79 |
| $l$ (nm) | 89.9 | 4.5 |

4. Conclusion

We have investigated the magneto-transport and thermoelectric studies for Nb$_{0.20}$Bi$_2$Se$_3$ single crystals. Our results show the anisotropic superconductivity for in-plane (basal) and out-of-plane in angular dependence of resistivity and upper critical field in SC state, which are explained through the anisotropic effective mass Ginzburg–Landau theory. The Hall effect measurements strongly suggest the absence of spontaneous magnetization in superconducting state, which is also supported via the $M$–$H$ plot, thus contradicting the claims of chiral superconducting phase in Nb$_{0.20}$Bi$_2$Se$_3$. The results presenting thermoelectric response on Nb$_{0.20}$Bi$_2$Se$_3$ are compared with pristine Bi$_2$Se$_3$, showing enhancement in Fermi temperature (∼4 times), with decrease in Seebeck value. The large Nernst coefficient at room temperature is ascribed due to the linear band dispersion relation in both Bi$_2$Se$_3$ and Nb$_{0.2}$Bi$_2$Se$_3$.

**Data availability statement**

All data that support the findings of this study are included in the article and the associated supplementary file.
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