Structural and Magnetotransport Studies of Iron-Intercalated Bi$_2$Se$_3$ Single Crystals

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A detailed investigation on the structural and magnetotransport properties of iron-intercalated Bi$_2$Se$_3$ single crystals is presented. The X-ray diffraction and Raman studies confirm the intercalation of Fe in the van der Waals gaps between the layers. The electrical resistivity of the compounds decreases upon intercalation, and Hall resistivity shows the enhancement of the charge carriers upon intercalation. The magnetoresistance (MR) shows the non-saturating linear behavior at higher magnetic field and low temperature. Intercalation of Fe increases the onset of the linear MR behavior, indicating the reduction in quantum effects. The Kohler scaling used on the MR data indicates single scattering process for all these compounds in the measured temperature range of 3–300 K.

1. Introduction

Topological insulators are the quantum materials with the insulating bulk and conducting surface states.$^{[1-2]}$ The peculiar property that distinguished these from trivial insulators is that the bulk bandgap is inverted due to strong spin–orbit coupling, and the gapless surface states are protected topologically by time reversal symmetry (TRS).$^{[3]}$ The 3D topological insulators have surface states with odd number of Dirac cones in which spin and momentum are locked in a chiral structure.$^{[3]}$ The spin–momentum locking prohibits the backscattering of electrons, because it requires spin flip.$^{[4]}$ Bismuth selenide (Bi$_2$Se$_3$) is one of the most studied compounds among the topological insulators family.$^{[5]}$ Bi$_2$Se$_3$ has a large bulk bandgap (300 meV) and simple surface states possessing single Dirac cone.$^{[6]}$ Topological surface states with a single Dirac cone have been observed through angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM), confirming the theoretical prediction by Kane and Mele.$^{[6-9]}$ Besides these techniques, surface states in topological insulators have been extensively studied using the quantum transport behavior also. Some of the signatures of 2D surface states discussed in the literature are Shubnikov-de Haas (SdH) oscillations, weak antilocalization (WAL), non-saturation linear magnetoresistance (LMR), and universal conductance fluctuation (UCF).$^{[10-13]}$ The quantum transport is mainly dominated by the bulk transport in such systems, as the Fermi level is usually found to be in its bulk conduction band due to selenium vacancies. These vacancies are believed to give rise to electron doping that makes the crystals to grow in an n-type material. To make the Fermi level shift inside the bandgap, Ca, Mg, and Cd are used to turn it into p-type Bi$_2$Se$_3$.$^{[14-16]}$

In recent years, intercalated Bi$_2$Se$_3$ has got rekindled attention among the researchers due to observation of unconventional superconductivity with intercalation of Cu, Sr, or Nb in Bi$_2$Se$_3$.$^{[17-19]}$ Furthermore, the doping by magnetic element in the van der Waals (vdW) gaps finds interest in engineering the band properties of the material. One ARPES study on the magnetically doped Bi$_2$Se$_3$ showed the opening of an energy gap at Dirac point, resulting from the TRS breaking by magnetic doping.$^{[20]}$ There are several experimental reports on the magnetically doped topological insulators that results in bulk magnetism: Bi$_2$–$_x$M$_x$Se$_3$ (M = Mn, Fe, Cr, and V)$^{[21-27]}$ Despite the enough information on bulk magnetism on Fe-doped Bi$_2$Se$_3$, only few have discussed magnetotransport in such systems.$^{[28,29]}$ Earlier reports on Fe-doped Bi$_2$Se$_3$ have studied the bulk ferromagnetism in conformity with the anomalous Hall effect, metal–insulator transition with suppression of magnetoresistance (MR) values at high Fe content.$^{[30,31]}$ However, the magnetotransport properties in Fe-intercalated Bi$_2$Se$_3$ systems remain largely unexplored.

In this work, Fe-intercalated Bi$_2$Se$_3$ has been comprehensively studied by means of X-ray diffraction (XRD), Raman spectroscopy, and low-temperature magnetotransport. It is confirmed that the lattice structure does not disrupt/change with intercalation up to highest concentration (x = 0.15). The resistivity and Hall measurements data, respectively, discussed the metallicity throughout the temperature range of 3–300 K, and the increase in carrier concentration with the Fe content in Bi$_2$Se$_3$ leads to the fact that Fe atoms preferably occupy the interstitial positions in the vdW gaps. The effect of magnetic doping on LMR phenomenon up to 10 T magnetic field has been discussed. Moreover, it is observed that single scattering rate is followed across the Fermi surface in these systems, as Kohler’s scaling is obeyed.

2. Results and Discussion

The orientation and crystallinity of single crystals are shown in Figure 1a–c, which clearly reveals (0 0 L) as the most preferred
The peaks are labeled with (0 0 3n) Miller indices. The Rietveld refinement for the powder XRD patterns was performed using Fullprof suite, as shown in Figure 1d–f. The Bi$_2$Se$_3$ crystallizes into the rhombohedral structure with the space group (R$\bar{3}$m). It contains five atoms in the primitive unit cell. This rhombohedral structure is formed by the stacking of quintuple layers (QLs) along the c-axis perpendicular to the ab plane. Each unit cell of Bi$_2$Se$_3$ is comprised of three QLs, each in the sequence Se(1)-Bi-Se(2)-Bi-Se(1), linked by the vdW forces. The chemical nature of both Se atoms is different; Se(2) is more ionic compared with Se(1), which is bonded to Se(1) in next QL via weak vdW bonds. The XRD pattern for Bi$_2$Se$_3$ and Fe$_{0.10}$Bi$_2$Se$_3$ confirms the phase purity; however, Fe$_{0.15}$Bi$_2$Se$_3$ shows minor secondary peak, which can be identified to 1% of the secondary monoclinic phase (C2/m) corresponding to FeBi$_2$Se$_4$. Crystallographic parameters obtained from the refinement are presented in Table 1. The lattice parameters $a$ and $c$ increase considerably with Fe content. This supports the possibility that Fe intercalates in the vdW gaps between the QLs. The ionic radii of Fe$^{2+}$ (0.92 Å) and Fe$^{3+}$ (0.78 Å) are much smaller than the Bi$^{3+}$ (1.17 Å) and Se$^{2-}$ (1.98 Å), if Fe is substituted at ionic (either Bi or Se) site, the lattice constants $a$ and $c$ should be reduced; however, there was no reduction in lattice constants.

Furthermore, there is no pronounced change in the axial ratio ($c/a$) with the doping of Fe atoms.

Raman spectra shown in Figure 2 provide information about the lattice vibrational modes. Four intrinsic active phonon modes, $E'_{g}$, $A_{1g}$, $E_{g}$, and $A_{2g}$, at 37.2, 66.6, 131.5, and 174.5 cm$^{-1}$, respectively, have been observed in accordance with the previous studies. The $E_{g}$ and $A_{1g}$ modes correspond to atomic vibrations along the plane and perpendicular to the layers, respectively. In general, the bulk phonon modes ($E_{g}$ and $A_{1g}$) are expected to shift to lower frequencies upon intercalation and toward higher frequencies upon substitution. As shown in Figure 2b, three modes are shifted to lower frequency. The redshift implies that Fe atoms occupy the sites between QLs...
and weakens the interaction between layers, which results in the decrease in phonon mode energy. The high quality of the crystal can be observed clearly, as the low-frequency $E_g$ mode has been observed in this work, which is absent in most of the reports.\textsuperscript{[38,40]} Table 2 shows the shift in peak positions for the different observed modes. As $E_g$ mode is weak, the frequency shift for this mode is not shown. Thus, the shift of peaks to lower wavenumber supports that Fe atoms are intercalated in the Bi$_2$Se$_3$ lattice.

The temperature-dependent longitudinal resistivity $\rho(T)$ of the compounds measured in the range of 2–300 K is shown in Figure 3a. The compounds show the metallic behavior throughout the temperature range, as indicated by $d\rho/dT > 0$, which points toward the presence of Se vacancies. The electrical resistivity value of Fe-intercalated Bi$_2$Se$_3$ is lower than the pristine Bi$_2$Se$_3$. The samples have residual resistivity value (RRR) ($\rho(300 \text{ K})/\rho(2 \text{ K})$) in the range of 2.2–4.7, the lowest one for the parent compound. The temperature dependence of resistivity can be fitted to a simplified model developed for bulk crystals with $\rho_{xx} = \rho_0 + \alpha \exp(-\Theta/T) + \beta T^2$, where $\rho_0$ is the residual resistivity arising from impurity scattering.\textsuperscript{[41]} The exponential and quadratic terms arise as a result of electron–phonon scattering and electron–electron scattering, respectively. The fitting parameter $\Theta$ corresponds to Debye phonon frequency, $\Theta = k_B\Theta/T$. A comparison of fitting parameters for different compounds is tabulated in Table 3. In addition, no upturn was found down to lowest temperature, as has been reported earlier in Fe-substituted Bi$_2$Se$_3$.\textsuperscript{[31,42]} The electrical resistivity for undoped and doped samples shows metallic behavior, which agrees well with the carrier density obtained from Hall measurements. This kind of behavior is commonly observed in crystals with high carrier concentration ($>10^{17} \text{ cm}^{-3}$) where bulk band conductivity dominates.

Figure 4 shows the magnetic field dependence of Hall resistivity at different temperatures. Hall resistivity was found to be linear in the magnetic field. The Hall resistivity has been anti-symmetrized using the relation, $\rho_{xy}^{\text{Hall}} = (\rho_{xy}(+H) - \rho_{xy}(-H))/2$, to eliminate the offset voltage due to misalignment.\textsuperscript{[43]} The slope of the Hall coefficient, $R_H = \rho_{xy}/\rho_{xx}$, remains negative throughout the temperature range, which confirms electron-dominated charge transport. The Hall carrier density is calculated using relation, $R_H = 1/ne$. The value of carrier density increases by one order of magnitude with Fe intercalation, as shown in Figure 4d–f. The order of carrier density variation from $10^{10}$ to $10^{17} \text{ cm}^{-3}$ for Bi$_2$Se$_3$ is in well agreement with reports.\textsuperscript{[43]} It is important to mention here that the order of carrier density for Bi$_2$Se$_3$ decides the metallic behavior of electrical resistivity, because for crystals with carrier density less than $10^{17} \text{ cm}^{-3}$, it turns to insulating behavior at low temperatures.\textsuperscript{[43,44]} The low-temperature mobilities of the compounds were found to be in the range of $\mu_0 \approx 10^2$–$10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, highest for the pure compound. As Bi$_2$Se$_3$ has lower RRR value but one order of higher magnitude of mobility as compared with Fe-intercalated compounds, the variation in the electrical resistivity of the compounds is more influenced by the carrier concentration than the internal defect or scattering. There is difference of one order of magnitude in carrier concentration between pristine and Fe-intercalated Bi$_2$Se$_3$, and the carrier concentrations show very small variation with temperature. Figure 4 shows the plot for carrier mobility($\mu$) and concentration $n = 1/R_{H,\mu}$ obtained from the zero-field longitudinal resistivity $\rho_{xx}(T)$ and the measured transverse resistivity $\rho_{xy}(B)$, respectively. Temperature dependence of carrier density is negligible below 30 K, and almost saturates, coinciding with low-temperature resistivity behavior, suggesting a common origin. The obtained carrier concentration is in the range of $(0.21 - 0.24) \times 10^{19} \text{ cm}^{-3}$ for Bi$_2$Se$_3$, $(3.27 - 3.48) \times 10^{19} \text{ cm}^{-3}$ for Fe$_{0.10}$Bi$_2$Se$_3$. 

![Figure 2](image-url)

**Figure 2.** a) Raman spectra of Fe$_x$Bi$_2$Se$_3$ ($x = 0, 0.10,$ and $0.15$) single crystals. b) Shift in peaks for mode $A_{ig}^1$. c) Schematics of all four Raman active modes.

**Table 2.** Characteristic peak positions of different modes in Raman spectra of the Fe$_x$Bi$_2$Se$_3$ ($x = 0, 0.10,$ and $0.15$). 

| Fe$_x$Bi$_2$Se$_3$ | $A_{ig}^1$ [cm$^{-1}$] | $E_g^2$ [cm$^{-1}$] | $A_{ig}^2$ [cm$^{-1}$] |
|-----------------|----------------|----------------|----------------|
| $x = 0$         | 72.03          | 131.75         | 174.50         |
| $x = 0.10$      | 71.72          | 131.49         | 173.31         |
| $x = 0.15$      | 71.52          | 130.93         | 173.33         |
and T. The weak temperature variation of Gru eH d) The Bloch model relates the a) Temperature-dependent longitudinal resistivity of Fe

$$ρ_{xx} = \frac{1}{e^2 / m} \rho_{xx}^0$$

with an increase in carrier concentration with doping. The quadratic behavior saturates at high fields (shown as solid black lines). As observed from the plots, the MR increases on increasing Fe concentration, although the qualitative behavior remains the same. This agrees with an increase in carrier concentration with doping. The quadratic field dependence of MR is understood using semiclassical model that attributed to the deflection of conduction electrons by the Lorentz force under the applied magnetic fields. This quadratic behavior saturates at high fields, followed by the LMR. The LMR may be described based on the classical model by Parish and Littlewood, which explains the linearity due to the disorder induce mobility fluctuations in an inhomogeneous sample.

As these samples are single crystalline in nature, we do not see any correlation of mobility fluctuations to explain the LMR with the classical model. A plausible explanation for the observed LMR in these systems could be the quantum origin, although no SdH oscillations are observed up to 10 T. This LMR is often explained using the quantum model of Abrikosov. In this model, LMR is explained in the quantum limit when magnetic fields are so large, such that Landau level is provided $n \ll \left( eH / \hbar c \right)^{1/2}$ and $T \ll eH / m^*$, where $N$ and $n$ are the density of scattering centers and electrons respectively, and $H$ is the applied magnetic field. This model relates the LMR to the linear energy dispersion relation of the gapless topological surface states. Abrikosov proposed that in the quantum limit when magnetic fields are so large, such that Landau level is well formed, the carrier concentration should be small enough,
so that electrons occupy only the lowest Landau level. This implies that this model is applicable in the extreme quantum limit. Moreover, it is interesting to note that not all the systems with LMR have observed the SdH oscillations.\textsuperscript{48,49} The observed

Figure 4. a–c) The Hall resistivity and d–f) the variation of carrier concentration \( n \) (left axis) and mobility \( \mu \) (right axis) with temperature for Fe\(_{x}\)Bi\(_2\)Se\(_3\) (\( x = 0, 0.10, \) and 0.15), respectively.

Figure 5. MR as a function of magnetic field at different temperatures for a) Bi\(_2\)Se\(_3\), b) Fe\(_{0.10}\)Bi\(_2\)Se\(_3\), and c) Fe\(_{0.15}\)Bi\(_2\)Se\(_3\). The black dashed lines show the quadratic field dependence at various temperatures up to different fields. Solid black lines show the linear fit to the high field data. d–f) Kohler plot of all the measured MR.
carrier density is of the order $10^{19}$ cm$^{-3}$ and indicates that these systems are far away from the quantum limit, such that electrons could hardly occupy the lowest Landau level (observed up to 10 T magnetic fields). However, the presence of LMR at higher field points the importance of surface states as well. Theoretically, as per Abrikosov’s model, conduction from gapless surface states gives rise to LMR. It is quite possible that these quantum effects are gaining sufficiently strength at higher magnetic fields and reflected in our data. Furthermore, the WAL effect has been observed in such systems.$^{[50]}$ It is observed predominantly in lower dimensional systems, where bulk carrier density is low implying less contribution from bulk. Figure 6 shows the temperature variation for the magnetic field ($B^*$) for the onset of LMR. Our results show that $B^*$ increases as the temperature increases, and with the increase in Fe concentration also. As there is an increase in carrier concentration on Fe doping, $B^*$ has larger value compared with the pristine Bi$_2$Se$_3$.

To further study the type of scattering process in our system, MR data are analyzed using Kohler’s scaling of data at different temperatures. The change in isothermal resistivity, $\Delta \rho (H)/\rho (H = 0)$, in an applied field ($H$) depends upon the quantity $\omega_c \tau$, which is the product of $\omega_c \propto H$ and $\tau(T) \propto 1/\rho(T)$, resulting in $\Delta \omega (H)/\rho(H = 0) = f (H/\rho(H = 0))$, where $\omega_c$ is the cyclotron frequency, at which magnetic field causes the charge carriers to sweep across the Fermi surface, and $\tau$ is the relaxation time.$^{[51]}$ Figure 5 shows the Kohler plots for all the measured MRs. Kohler’s rule is satisfied if there is a single scattering rate ($\tau$) at all point on the Fermi surface. All MR curves at different temperatures collapse onto a single curve, suggesting single scattering rate in these systems. Although the intercalation of Fe gives rise to increase in the carrier concentration of Bi$_2$Se$_3$, the magnetotransport processes remain largely unchanged.

3. Conclusion

In summary, structural and magnetotransport properties of Fe$_x$Bi$_2$Se$_3$ ($x = 0, 0.10$, and $0.15$) single crystals synthesized using a melt-grown technique have been reported. The XRD studies confirmed the rhombohedral crystal structure of Fe$_x$Bi$_2$Se$_3$. Rietveld refinement shows the lattice expansion, which suggests that Fe atoms are intercalated between vdW gaps. The phonon properties of the single crystals investigated through Raman spectroscopy confirm intercalation of Fe atoms at vdW gaps. By analyzing the resistivity and MR measurements, it can be found that Fe content tends to increase metallicity in Bi$_2$Se$_3$, and MR value also increases. Thus, these studies show that bulk conductance is dominant over the surface conductance. High $n$-type carrier concentrations, $10^{18}$–$10^{19}$ cm$^{-3}$, were obtained from Hall coefficient measurements.

4. Experimental Section

Single crystals of Fe$_x$Bi$_2$Se$_3$ ($x = 0, 0.10$, and $0.15$) were synthesized in the three-step process using the melt-growth method. The first step was to prepare Bi$_2$Se$_3$ for all the required compositions. High purity selenium (≥99.999%) and bismuth (≥99.99%) in the form of pellets/granules were weighed according to their nominal compositions and sealed in evacuated ($\leq 10^{-3}$ mbar) quartz tubes. An excess amount (≥3%) of Se has been used to compensate for the Se vacancies. The compounds were heated at 850 °C for 48 h, followed by cooling to 550 °C at the rate of 3 °C h$^{-1}$, where they were kept for 72 h. Next, the compounds were furnace off cooled to room temperature. Second, the grown Bi$_2$Se$_3$ and iron (≥99.98%) were melted at 850 °C for 120 h, slow cooled (3 °C h$^{-1}$) to 550 °C, and left for 24 h and then furnace off cooled to room temperature. To ensure homogeneity, samples were re-grinded, sealed, and kept for third heat treatment, where they were kept at 850 °C for 24 h and slow cooled (3 °C h$^{-1}$) to 300 °C, and then furnace off cooled to room temperature. The obtained crystals exhibited metallic appearance and were cleaved easily.

Phase purity and crystal structure analysis were carried out by powder XRD using a Rigaku Smart lab diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) at room temperature. Raman analysis was carried out using Horiba HR-Evolution spectrometer using $532$ nm solid state laser. The linear four probe technique was used to study the resistivity measurements in the temperature range of 3–300 K and a field range of 0–10 T in a Quantum Design built Physical Properties Measurement System (PPMS). The MR and the Hall-effect measurements were carried out at different temperatures in the PPMS.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bismuth selenide, intercalation, Kohler’s rule, linear magnetoresistance, topological insulators

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