Superconductivity Below 2.5K in Nb_{0.25}Bi_{2}Se_{3} Topological Insulator Single Crystal

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Abstract
We report crystal growth and below 2.5K superconductivity of Nb_{0.25}Bi_{2}Se_{3}. These crystals are grown by self-flux method. The X-ray diffraction (XRD) pattern of a grown crystal flake shows (00l) plane (c-orientation) growth. The Rietveld refinement of crushed crystal powder XRD (PXRD) pattern confirms the phase purity of the studied sample having R-3m space group of rhombohedral crystalline structure. The Raman spectrum of the studied Nb_{0.25}Bi_{2}Se_{3} crystal distinctly shows three well-defined vibrational modes in terms of A^{1}_{1g}, E^{g}_{2}, and A^{2}_{1g} at around 72, 129, and 173 cm^{-1}, which are slightly shifted in comparison with pure Bi_{2}Se_{3}. Magnetization studies in terms of field cooled (FC) and zero field cooled (ZFC) magnetic susceptibility measurements show the diamagnetic transition (T_{c onset}) of the compound at around 2.5K and near saturation of the same below around 2.1K. The isothermal magnetization (MH) being taken at 2K revealed the lower critical field ($H_{c1}$) of around 50 Oe and the upper critical field ($H_{c2}$) of 900 Oe. It is clear that the studied Nb_{0.25}Bi_{2}Se_{3} is a bulk superconductor. The superconducting critical parameters thus calculated, viz the coherence length, upper and lower critical fields, and superconducting transition temperature for a grown Nb_{0.25}Bi_{2}Se_{3} single crystal are reported here.

Keywords Doped topological insulators · Crystal growth · Structural details · Superconductivity

1 Introduction

Topological insulators (TIs) with extraordinary quantum properties in terms of their highly conducting surface and bulk insulating transport properties deep within due to time reversal symmetry (TRS) protected surface/edge states had attracted the attention of condensed matter physics community at large [1–3]. Besides several other quantum properties, more recently, superconductivity could be induced in TIs by application of hydrostatic pressure [4], superconducting proximity effect, and by doping or intercalation of suitable elements like Cu [5, 6], Sr [7, 8], Nb [9, 10], Tl [11], and Pd [12]. Understanding of the surface conductivity of TIs had yet been to some extent clear in terms of Dirac point driven electronic structure. The superconductivity of TIs further complicates the situation in terms of the copper pairs being formed by the edge/surface states driven carriers. Superconducting TIs do further host some novel properties besides the known usual superconductivity phenomenon, viz zero-biased conduction peak [13], quantized thermal hall conductivity [14], anomalous Josephson effect [15], odd frequency Cooper pairs [16], and Majorana fermions [17]. It is clear that the superconducting TIs are very much a suitable choice for fundamental research related to quantum phenomenon [4–12].

Keeping in view that Bi_{2}Se_{3} is one of the most studied topological insulators, in current short letter, we report the crystal growth and characterization of Nb_{0.25}Bi_{2}Se_{3} superconductor. Although scant reports exist on superconducting TIs [4–17], yet, it is important to reproduce the new observations in different laboratories. This is the main purpose of the short letter concluding that superconductivity exists in Nb_{0.25}Bi_{2}Se_{3} below 2.5K with lower and upper...
critical fields at 2K of around 50 Oe and 900 Oe, respectively. This is in conformity with earlier results [9, 10].

2 Experimental

\( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) single crystal was grown by self-flux method in simple automated furnace via solid state reaction route, as reported by some of us recently [18]. The schematic heat treatment of \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) single crystal is shown in left side inset of Fig. 1. One of the important issues is to not only very slow cooling (1 °C/h) from 950 °C melt to 600 °C but also quench in ice after annealing for 24 h at 600 °C. This is necessary to avoid the segregation of Nb as an impurity in the matrix. Details can be followed from ref. 18. XRD on mechanically cleaved crystal flake and powder form had been carried out using Rigaku made Mini Flex II X-ray diffractometer having Cu K\( \alpha \) radiation of 1.5418 Å wavelength. Raman spectra of a grown \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) single crystal are recorded at room temperature using the Renishaw Raman spectrometer. Magnetization studies are done on PPMS (physical property measurement system) from Quantum Design (QD).

3 Results and Discussion

Figure 1 depicts the Rietveld refinement of gently crushed powder XRD pattern of the \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \). The studied grown crystal is crystallized in rhombohedral structure having R-3m space group [19]. All the observed diffraction lines are indexed on the XRD pattern. Hardly any un-reacted peak is seen within X-ray limit. The fitted parameter (\( \chi^2 \)) value is found to be ~7.43, which is reasonably good as far as Rietveld PXRD is concerned. Atom positions obtained from Rietveld refinement of PXRD data are Bi [0, 0, 0.4018(6)] and Se [0, 0, 0.2086(5)] and lattice parameters of the grown \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) single crystal are \( a = b = 4.1458(3) \) Å and \( c = 28.5759(2) \) Å of \( \alpha = \beta = 90^\circ \) and \( \gamma = 120^\circ \). The VESTA software drawn representative unit cell of the studied \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) single crystal can be seen in ref. 18. The studied crystal morphology as seen from scanning electron microscope (SEM) was seen to be laminar type and the stoichiometric formula being calculated from EDAX analysis is close to the nominal compositional value, for details see ref. 18.

Figure 2 shows the Raman spectrum for both reported [20] pure Bi\(_2\)Se\(_3\) and the studied \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) crystal, one over the other. Clearly alike Bi\(_2\)Se\(_3\), the studied \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) crystal also shows the characteristic vibrational modes for these systems, i.e., \( A_{1g}, E_g, \) and \( A_{2g} \). These modes are seen at 70.66, 130.20, and 174.547 \( \text{cm}^{-1} \) for pure Bi\(_2\)Se\(_3\) and at 70.29, 129.99, and 172.23 \( \text{cm}^{-1} \) for \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \), respectively. The Raman shift peaks are observed to move to lower frequency side in spectra, while the intensity of the peaks found to be decreasing for \( A_{1g} \) and \( A_{2g} \) and increasing for \( E_g \) mode. The observed lower Raman shift values for the studied \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) crystal may be due to intercalation of Nb atoms residing in van der Waals gap between two quintuple layers weakening the bonding forces [19–21].

Figure 3 depicts the magnetization versus temperature response of the studied \( \text{Nb}_{0.25} \text{Bi}_2 \text{Se}_3 \) crystal under field cooled (FC) and zero field cooled (ZFC) conditions under an applied field of 20 Oe. A clear diamagnetic transition appears in both...
Fig. 3  FC and ZFC magnetization (MT) of the Nb_{0.25}Bi_{2}Se_{3} single crystal from 1.5 to 5.5K at 20 Oe applied field, the inset shows the isothermal magnetization (MH) of the same at 2, 2.2, and 2.4K

FC and ZFC plots with a critical temperature near 2.5K, confirming the onset of superconductivity in the studied Nb_{0.25}Bi_{2}Se_{3} crystal. The diamagnetic signal observed at 2.5K saturates at around 2.1K, thus indicating the superconducting transition width to be around 0.4K. Lower inset in Fig. 3 shows isothermal magnetization (MH) curve for the studied Nb_{0.25}Bi_{2}Se_{3} crystal at 2, 2.2, and 2.4K, i.e., below the critical temperature. The wide open MH plots confirm the observation of bulk superconductivity right up to 2.4K. The lower critical field $H_{c1}$ is found to be 50 Oe and upper critical field $H_{c2}$ being 900 Oe at 2K. The same are 8.25 Oe and 400 Oe at 2.2K and 7.10 Oe and 200 Oe at 2.4K. The $H_{c1}$ is defined as the deviation of linear diamagnetic plot towards mixed state and is marked with a straight line in the inset of Fig. 3. The $H_{c2}$ is roughly known to coincide with the irreversibility field of a type-II superconductor MH plot. This is marked on corresponding plot in the inset of Fig. 3. It is clear from the Fig. 3 inset that the studied Nb_{0.25}Bi_{2}Se_{3} crystal is a type-II superconductor. Critical field for the studied Nb_{0.25}Bi_{2}Se_{3} crystal, as calculated from the formula $H_{c2} = (H_{c1} \times H_{c2})^{1/2}$, is found to be 212.13 Oe at 2K upper critical field at 0K, i.e., $H_{c2}(0)$ is measured by using the GL equation given below, where $t$ represent reduced temperature $T/T_{c}$.

$$H_{c2}(T) = H_{c2}(0) \times \left[\frac{(1-t^{2})}{(1+t^{2})}\right]$$

$H_{c2}(0)$ is found to be 4.1 × 10^{3} Oe, i.e., around 0.4T at 2K. Ginzburg-Landau parameter kappa ($\kappa$) is determined by using the formula $H_{c2}(0) = k \times 2^{1/2} \times H_{c2}$ and is found to be 13.66 which is far greater than $1/2^{1/2}$, hence confirming the type-II superconductivity of the studied Nb_{0.25}Bi_{2}Se_{3} crystal. Coherence length of the Nb_{0.25}Bi_{2}Se_{3} crystal is determined by using the formula $H_{c2}(0) = \frac{\phi_{0}}{2 \kappa 2(0)^{2}}$, where $\phi_{0}$ is flux quanta. The value of flux quanta is 2.0678 × 10^{-15} Wb. Thus calculated coherence length $\xi(0)$ of studied Nb_{0.25}Bi_{2}Se_{3} crystal is found to be 2.83 Å. Further, penetration depth $\lambda(0)$ is determined by kappa parameter using the formula $\kappa = \lambda(0)/\xi(0)$ which is found to be 38.65 Å at 2K. The fundamental superconducting parameters of the studied Nb_{0.25}Bi_{2}Se_{3} crystal at 2K are given in Table 1.

**Table 1** Structural and basic superconducting parameters for the studied Nb_{0.25}Bi_{2}Se_{3} single crystal

| Physical Property (Nb_{0.25}Bi_{2}Se_{3}) | Corresponding values |
|----------------------------------------|----------------------|
| Crystal structure                      | Rhombohedral; R-3m space group, |
|                                        | $\alpha = 90^\circ$ and $\gamma = 120^\circ$ |
| Lattice parameters                     | $a = b = 4.1458(3)$ Å and $c = 8.5759(2)$ Å |
| Superconducting critical temperature and fields | $T_{c}^{onset} = 2.5K$, $\Delta T_{c} = 0.4K$ |
|                                        | $H_{c1} = 50$ Oe, $H_{c2} = 900$ Oe, $H_{c2}(0) = 212.13$ Oe, $H_{c2}(0) = 4100$ Oe |
| Coherence length                       | $\xi(0) = 2.83$ Å |
| Penetration depth                      | $\lambda(0) = 38.65$ Å |
| Ginzburg-Landau parameter kappa ($\kappa$) | $\kappa = 13.66$ |
| Raman mode positions                   | $A_{1g} = 70.29$ cm^{-1} |
|                                        | $E_{g} = 129.99$ cm^{-1} |
|                                        | $A_{2g} = 172.23$ cm^{-1} |

4 Conclusion

In summary, in this the short letter, we studied low temperature magnetic properties of the Nb_{0.25}Bi_{2}Se_{3} single crystal which confirms that the sample is superconducting. Various superconductivity critical parameters, viz critical field, kappa parameter, coherence length, and penetration depth, are calculated. The studied Nb_{0.25}Bi_{2}Se_{3} single crystal is a type-II superconductor. The phase purity of the grown crystal is confirmed by PXRD. The Raman shift in vibration modes due to Nb intercalation is also seen and briefly discussed.

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