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Superconducting properties of indium-doped topological crystalline insulator SnTe

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Abstract – We report on the superconducting properties of indium-doped SnTe. SnTe has recently been explored as a topological crystalline insulator. Single crystals of Sn$_{0.5}$In$_{0.5}$Te have been synthesized by a modified Bridgman method. Resistivity measurement performed in the range 1.6–300 K shows a metallic normal state with onset of superconducting transition at $T_c=4.5$ K. Bulk superconductivity has also been confirmed by DC magnetization, AC susceptibility and rf penetration depth measurements. Zero-temperature upper critical field, lower critical field, coherence length, and penetration depth are estimated to be 1.6 T, 1 mT, 143.5 Å and 853 nm, respectively. The temperature dependence of the low-temperature penetration depth indicates $S$-wave fully gapped characteristics with BCS (Bardeen-Cooper-Schrieffer) gap $\Delta_0=1.247$ meV. Hall and Seebeck coefficient measurements confirm the dominance of hole conduction with possible phonon-drag effects around $\sim 45$ K. Resistive transition studied under applied magnetic field shows thermally activated flux flow behaviour.

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Introduction. – The discovery of superconductivity in the degenerate many-valley semiconductor SnTe traces its origin to its theoretical prediction by Cohen [1] and its subsequent experimental verification by Hein [2]. Way back in 1966, the dependence of the critical magnetic fields and Ginzburg-Landau parameter of SnTe on the carrier concentration (due to Sn vacancies) was reported. The superconducting transition temperature $T_c$ was found to increase with increasing carrier concentration from 0.034 K ($7.5 \times 10^{20}$ per cm$^3$) to 0.214 K ($20.0 \times 10^{20}$ per cm$^3$). The relevance of quasi-local impurity states achieved through In/Tl doping onto SnTe/PbTe leading to superconductivity were also studied [3]. In a revival of sort, around 2010, there were reports of remarkable increase in $T_c$ to $\sim 2$ K when SnTe was doped at the Sn site with In. Conspicuously, this was achieved for similar carrier concentration as compared to the off-stoichiometric specimen [4]. Very recently, this novel system of SnTe has been assigned to an exotic class of topological crystalline insulators and an optimal superconducting $T_c$ of 4.7 K [5] and 4.5 K [6] has been reported. Superconductors derived from topological insulators are important for studying proximity effects at the insulator-superconductor interface.

The research of 1960s identified that superconductivity appeared at a carrier concentration corresponding to a second valence band filling in SnTe: a phenomena that was quickly generalized to other IV-VI semiconductors. Hein et al. [7] confirmed that it was indeed inter-valley scattering which was important in the determination of the BCS electron-phonon coupling parameter $\lambda$. If interband or intervalley scattering is possible, then that can help overcome the Coulomb repulsion leading to superconductivity. But there have been suggestions that the manifold increase in transition temperature with In doping could possibly be not due to a mechanism associated with inter-valley scattering. Notably, indium is known to skip the +2 valence, in favour of +1 and +3 in most compounds. This tendency leads to the suggestion as to whether valence fluctuations associated with In impurities in SnTe might play a dominant role in the enhanced superconductivity [4].

In the recent past, the renewed interest in SnTe relates to its characterization as a topological crystalline insulator (TCI) [8]. A topological insulator (TI) is an unusual quantum state of matter that is protected by time-reversal symmetry and possesses a full band gap in the bulk but has

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gapless surface states. The discovery of TI prompted the search for other topological states which may be protected by other symmetries and one such candidate is the TCI in which the metallic surface states are protected by the mirror symmetry of the crystal structure. Such TCI phase in SnTe has been confirmed by Tanaka et al. by angle-resolved photoemission spectroscopy (ARPES) [9]. The characteristic metallic Dirac-cone surface band has been confirmed. Curiously, such gapless surface states have not been seen in PbTe, but the narrow-band-gap semiconductor Pb_{0.77}Sn_{0.23}Se undergoes a phase transition from the TI to the TCI phase as a function of temperature [10]. Very recently, topological crystalline superconductivity (TCS) in Sn_{1-x}In_xTe (x = 0.045) has been claimed through the existence of surface Andreev bound state by performing point-contact spectroscopy [11]. This is a hallmark of unconventional superconductivity. Thin film of the topological crystalline insulator SnTe has also been grown epitaxially on Bi_2Se_3 that has made it possible for the observation of the topological surface state in a TI [12]. The critical question that remains to be answered is whether the superconductivity in Sn_{1-x}In_xTe, derived from a TCI phase, shows any departure from BCS superconductivity. In conventional BCS theory, superconductivity is achieved through the exchange of phonons between the electrons of opposite spins. Some new aspects have been uncovered recently; for example in the Cu-doped topological insulator Bi_2Se_3 [13], the shape of Fermi surface becomes more 2D-like as the carrier concentration increase [14]. In this paper, we report on the growth and extensive characterization of single crystals of Sn_{0.5}In_{0.5}Te (with optimal T_c) and try to ascertain its basic superconducting properties and identify in what way it may be different from a normal impurity scattering driven degenerate semiconductor-superconductor. Specifically, we report on the successful synthesis of 50% In-doped SnTe (with optimal T_c) single crystals that indicate signatures of S-wave symmetry with robust type-II characteristics. We also estimate the important superconducting parameters such as the critical fields, coherence length, penetration depth and the scaling parameters for the observed thermally activated flux flow.

Experimental methods. – Single crystals of Sn_{1-x}In_xTe were prepared by a modified Bridgman method for various doping (x = 0, 0.25, 0.4 and 0.5), but in this paper, we focus on the properties of the specimen with optimal T_c (x = 0.5). Single crystals were obtained by melting stoichiometric amounts of high-purity elemental powder of Sn (99.99%), Te (99.999%) and shots of In (99.999%) at 900°C for 5 days in sealed evacuated quartz tubes. Intermittent shaking was performed for the homogeneity of melt sample. Sample was slowly cooled to 770°C over a period of 72 hours, annealed at 770°C for 48 hours followed by fast cooling to room temperature. Silvery-shiny single crystals were cleaved along the basal plane of crystal growth. X-ray Diffraction was carried out on the powdered samples by RIGAKU powder X-ray Diffractometer (Miniflex 600). Resistivity, Hall, and magnetization measurements were performed on a Cryogenic physical properties measurements system (PPMS). RF Penetration depth was measured on a separate 8T Cryogen Free Magnet in the temperature range 1.6-6K. Thermo-electric power was measured in bridge geometry across two copper blocks in conjunction with chip heaters to produce a dynamic temperature gradient.

Results and discussion. – The XRD pattern of Sn_{0.5}In_{0.5}Te presented in fig. 1 is in accordance with the reference data from JCPDF (No. 089-3974) [15] that confirm phase purity of the as-grown samples. The specimen crystallizes in rock-salt structure with space group Fm\overline{3}m. Rietveld refinement of observed XRD peaks was carried out with the help of FULLPROF software. The \chi^2 is found to be 1.76. Other parameters for Rietveld fit are found to be \(R_p = 15.4\), \(R_{wp} = 21.4\) and \(R_e = 16.2\) which indicates a good fitting to the experimental data. In the inset (a) of fig. 1, the schematic representation of the cubic crystal structure is depicted.

The calculated lattice parameter is \(a = 6.265\) Å and the cell volume is 245.65 Å³. In the inset (b), we show the surface morphology images obtained from a Zeiss EVO\( \text{\textregistered} \)40 SEM analyzer. From the SEM image it is clear that the crystals were cleaved in clear planes and we can see a clear and smooth surface in the 20μm magnification range. Inset (c) of fig. 1 shows the EDAX analysis (Bruker AXS Microanalysis) that confirms intended atomic percentage doping of indium in as-grown samples.
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Quantitative analysis shows Te, Sn and In atomic percentage as 48.46%, 25.95% and 25.59%, respectively, at a particular specimen point which is close to the average nominal concentration.

Resistivity data for Sn$_{0.5}$In$_{0.5}$Te measured by the four-probe method in the temperature range 1.6–300 K are shown in fig. 2. The compound shows robust metallic behaviour in the normal state. For defining $T_c$, we use linear extrapolation method where $T_c^{\text{offset}}$ and $T_c^{\text{onset}}$ are identified as intersection point between the slope line across transition and the extrapolated line from the normal state and the zero resistance state, respectively (schematically defined in inset (b) of fig. 2). $T_c^{\text{(Zero)}}$, on the other hand, is temperature corresponding to zero resistance state and is slightly lower than $T_c^{\text{offset}}$ (that is used to define the irreversibility field). As shown in the inset (a) of fig. 2 (in an expanded temperature scale), a superconducting transition is observed with $T_c^{\text{onset}}$ at 4.5 K and $T_c^{\text{onset}}$ at 4.3 K. The resistivity changes from 0.88 mΩ cm at 300 K to 0.67 mΩ cm just above the transition temperature. The corresponding residual resistivity ratio (RRR) is found to be 1.31. Inset (b) of fig. 2 shows the resistive transitions $\rho(T)$ in the presence of external magnetic fields applied perpendicular to the a-b plane of the sample as well as to the transport current direction. The transition width between $T_c^{\text{onset}}$ and $T_c^{\text{offset}}$ is about 0.2 K in low magnetic fields but that increases up to $\sim$0.6 K for higher fields.

Inset (c) of fig. 2 shows the upper critical field $H_{c2}$ and the irreversibility field $H_{irr}$ as estimated from the magneto-resistance data from fig. 2, inset (b). The criterion used for defining $H_{c2}$ (corresponding to complete suppression of superconductivity) and the irreversibility field $H_{irr}$ (corresponding to onset of dissipation) is schematically defined in fig. 2, inset (b). The numerical value of $\mu_0 H_{c2}(0)$ was calculated by applying the Werthamer-Helfand-Hohenberg (WHH) formula: $\mu_0 H_{c2}(0) = -0.69 \mu_0 T_c \frac{dH_{c2}/dT|_{T_c}}{\mu_0 H_{c2}(0)}$. Using the value of slope $\mu_0 dH_{c2}/dT|_{T_c} = -0.496$ T/K the value of $\mu_0 H_{c2}(0)$ is found to be 1.6 T. Balakrishnan et al. and Gu et al. report $H_{c2}(0)$ of 1.42 T and 1.49 T for 40% and 45% In doping, respectively. Similar measurements for field applied parallel to the crystal plane provided identical slope (and $\mu_0 H_{c2}(0)$) confirming the isotropic behaviour of the superconducting parameters. From the above value of $\mu_0 H_{c2}(0)$, the Ginzburg-Landau coherence length $\xi = (2.07 \times 10^{-7} / 2\pi \mu_0 H_{c2})^{1/2}$ is estimated to be $\xi(0) = (143.5 \pm 2.2)$ Å which is lower than the value 15.2 nm reported in ref. [5]. For the determination of the lower critical field $H_{c1}$, we have used the deviation from the linearity method (in Meissner state) from magnetization vs. magnetic-field measurements. The value of $\mu_0 H_{c1}$ estimated from isothermal magnetization measurements at $T = 2$ K is $\sim$1 mT (inset (b) of fig. 3). Further, $\mu_0 H_{c1}$ is related to the value of penetration depth and coherence length as follows [16]:

$$H_{c1} = \frac{\Phi_0}{4\pi \lambda^2} \left( \ln \frac{\lambda}{\xi} + 0.485 \right).$$ (1)

Using $\mu_0 H_{c1} = 1$ mT, $\xi_{GL}(0) \sim 143.5$ Å and $\Phi_0 = 2.0 \times 10^{-7}$ G cm$^2$, the zero-temperature value of penetration depth was found to be $(853 \pm 97.40)$ nm. This value is significantly higher than the value of penetration depth derived from recent $\mu$s measurement $\lambda(0)$ nm for $x = 0.45$ [17].

Figure 3 shows the variation of DC magnetization with temperature for Sn$_{0.5}$In$_{0.5}$Te under ZFC (zero field cooled) and FC (field cooled) protocols at an applied magnetic field of 0.5 mT. The $T_c$ for this sample can be observed around 4.4 K that is slightly lower than what is observed in the resistivity measurement. The isothermal $M-H$ loop at constant temperature $T = 2$ K in fields up to 2 T is shown in the inset (a) of fig. 3. The corresponding nominal critical current density $J_c$ of the sample with rectangular cross-section ($a \times b$ with $a \sim 2.76$ mm, $b \sim 2.86$ mm) perpendicular to the applied field, was calculated from the Bean critical state expression $J_c = (20 \Delta m)/(V a(1-a/3b))$, where $V$ is the sample volume, $\Delta m = m^+ - m^-$, and $m^+(m^-)$ is the moment associated with increasing (decreasing) field. The critical current density $J_c$ vs. magnetic field at $T = 2$ K was derived and it was found that the $J_c$ decreases dramatically from the zero field value $3.4 \times 10^3$ A cm$^{-2}$ to 60.5 A cm$^{-2}$ at $H = 0.5$ T. The AC

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susceptibility measured in an AC drive field with a frequency of 781 Hz is shown in inset (c) of fig. 3. A DC applied field was superimposed parallel to the AC field (∼0.5 mT) to check the AC losses in the mixed state. The real part of AC susceptibility for external DC fields of 0 T and 0.25 T.

The temperature dependence of London penetration depth gives important information about the pairing symmetry and superconducting gap [18]. We have measured the temperature dependence of the change in penetration depth using the tunnel diode oscillator technique [20], muon spin rotation and mutual coil induction. Since the length scale probed is of the order of λ, it is less sensitive to surface inhomogeneities and gives an understanding of bulk properties of the system [21]. Also this technique has been used to decipher the pairing mechanism in MgB$_2$ [22] and cuprate [23] and pnictide superconductors [24]. In fig. 4 we plot the change in penetration depth Δλ as a function of reduced temperature (T/Tc). Inset (a) of fig. 4 shows the change in penetration depth Δλ scaled with λ$_0$ (total change in penetration depth) as a function of temperature measured down to the lowest temperature 1.69 K.

A sharp change in data at T$_c$ = 4.4 K shows the onset of the diamagnetic state. The measured quantity which is the shift in the resonant frequency, ΔF ≡ f$_s$ − f$_0$ is proportional to χ(T), where χ is the total magnetic susceptibility, f$_0$ is the resonance frequency in the absence of sample, and f$_s$ is the resonance frequency in the presence of sample. The change in penetration depth is defined as

$$\Delta\lambda(T) = -(T/\lambda_0)^2 \ln 2 F(T)$$

where $\Delta\lambda$ is the shift in penetration depth normalized to the total change in penetration depth at low temperature, $\lambda_0$ is the penetration depth at zero temperature, and $F(T)$ is the temperature dependence of the change in penetration depth measured down to the lowest temperature 1.69 K.

In special cases, impurity scattering changes this temperature dependence of $\Delta\lambda$ from T to T$^2$ [23]. The $\Delta\lambda$ data of fig. 4 are very well fitted to eq. (2) up to T/T$_c$ ≤ 0.5 as shown by the red solid line. The value $\Delta\lambda$ obtained for Sn$_{0.5}$In$_{0.5}$Te is shown in inset (b). The Seebeck coefficient is positive in the whole temperature range.

Fig. 3: (Colour on-line) DC magnetization measurement under the ZFC/FC protocol is shown for an external field of 5 Oe. The data have been taken during the warming cycle. A typical $M$-$H$ curve at $T = 2$ K is shown in the inset (a). The criterion to determine $H_{c3}$ is described in the inset (b). Inset (c) shows the real part of AC susceptibility for external DC fields of 0 T and 0.25 T.

Fig. 4: (Colour on-line) The change in penetration depth is plotted as a function of reduced temperature. The red solid curve shows the fitting using the BCS eq. (2). Inset (a) shows the change in penetration depth normalized to the total change in penetration depth down to 1.69 K. The temperature dependence of the Seebeck coefficient for Sn$_{0.5}$In$_{0.5}$Te is shown in inset (b). The Seebeck coefficient is positive in the whole temperature range.
from fitting depends slightly on the temperature limit \( < 2.25 \text{ K} \) \((~T_c/2)\) chosen for the fitting of the data but nevertheless it does not affect the temperature dependence of \( \Delta \lambda \). The gap value found from fitting was \( \Delta_0 = 1.247 \text{ meV} \) with corresponding gap ratio 2\( \Delta_0/k_B T_c \) = 6.4 and \( \lambda(0) = 832 \text{ nm} \) which is very close to calculated value of 853 nm from eq. (1). The value of the gap ratio is higher than the weak-coupling BCS value of 3.53 which suggests strong coupling features in \( \text{Sn}_{0.5}\text{In}_{0.5}\text{Te} \). This is in contrast to the weak-intermediate coupling projection from specific-heat measurements on \( \text{Sn}_{0.6}\text{In}_{0.4}\text{Te} \) [5].

The penetration depth flattens at very low temperature values indicating fully developed superconducting gap in this compound. A nodeless superconducting gap has also been observed in thermal conductivity and specific-heat measurements in \( \text{Sn}_{1-x}\text{In}_{x}\text{Te} \) [28,29]. On fitting the low temperature data with power law \( T^n \) gives \( n \sim 6 \) which rules out the possibility of \( d \)-wave pairing in \( \text{Sn}_{0.5}\text{In}_{0.5}\text{Te} \).

The Seebeck coefficient \( (S) \) of single crystals of \( \text{Sn}_{0.5}\text{In}_{0.5}\text{Te} \) with respect to copper is shown in the inset (b) of fig. 4. \( S \) is positive in the whole temperature range as verified from Hall measurements as well. At the lowest measured temperature \( (12 \text{ K}) \), \( S \) has a maximum value of \( 2.24 \mu\text{V/K} \), but it curiously shows a peak structure at \( \sim 45 \text{ K} \) with varying temperature. While the origin of such sharp peak needs more detailed analysis, for the present it would suffice to report that such peaks in the temperature dependence of thermopower (TEP) is usually observed due to the phonon-drag effects [30]. The Hall coefficient \( (R_H) \) did not show any sharp variation around this temperature and the positive value of \( 0.09 \text{ cm}^3/\text{C} \) remained almost constant between 12 and 100 K (data not shown). No such peak structure was observed in the Seebeck coefficient of the parent compound SnTe either, although the magnitude of the Seebeck coefficient was expectedly higher.

Under the gamut of type-II superconductivity, the broadening of the resistive transition, \( \rho(T) < 1\% \rho_n \) (where \( \rho_n \) is the resistivity in the normal state just above the transition), in a magnetic field is interpreted in terms of a dissipation of energy caused by the motion of vortices. This interpretation is based on the fact that in the low-resistance region, the resistance is caused by the creep and flow of magnetic vortices. In the mixed state, the flux lines will be pinned due to various interactions, e.g., impurities, stress, extended defects, etc. During flux creep, flux line or flux bundles can be thermally activated over the pinning energy barrier, even if the Lorentz force exerted on the flux bundle by the current is smaller than the pinning force. The \( \rho(T) \) dependences of such thermally activated origin are described by the Arrhenius equation \( \rho = \rho_0 \exp(-U_0/k_B T) \), where, \( U_0 \) is the flux-flow activation energy. This can be obtained from the slope of the linear parts of an Arrhenius plot and \( \rho_0 \) is a field-independent pre-exponential factor. Investigations of high-\( T_c \) superconductors and artificial multilayers have showed that the activation energy exhibits different power-law dependences on a magnetic field, i.e. \( U_0(B) \sim B^{-n} \). Figure 5 shows plots of \( \ln \rho \) vs. \( 1/T \) for the calculation of activation energy \( U_0 \) at various fields from 0 to 0.9 T. The activation energy \( U_0 \) is determined from the slope of the curve in this linear region. We get straight lines over the 5 decades of the resistivity which validates the thermally activated flux flow (TAFF) defined by the Arrhenius law. The activation energy varies from \( U_0/k_B \sim 500.4 \) to 142.5 K for the magnetic field of \( \mu_0 H = 0.05 \text{ T} \) and \( \mu_0 H = 0.9 \text{ T} \), respectively. The magnetic field vs. the activation energy \( U_0 \) plot shown in the inset (a) of fig. 5 suggests the power-law dependence on magnetic field \( U_0 \), with \( n = 0.6 \) (\(<0.9\text{T}) \). A rapid decrease of the activation energy for the sample in region \( B > 0.9 \text{ T} \) was also observed and it reflected a dramatic loss of the current-carrying capabilities of the superconductor due to the weakening of the meagre flux line pinning with increasing magnetic field.

This was also confirmed from the remanent magnetization experiment results of which are summarized in the inset (b) of fig. 5. In this experiment an external field was applied and then removed followed by measurement of the remanent magnetization. We observe a sharp single peak in \( d\mu_B/d(\log \mu_0 H) \) vs. \( \log(\mu_0 H) \) at 30 mT which indicates only one dominant scale of current loops. This implies that only intragrain super current exists and intergrain pinning is negligible.

Conclusion. – In conclusion, we have successfully synthesized single crystals of \( \text{Sn}_{x}\text{In}_{1-x}\text{Te} \), and an optimal
resistive $T_c$ onset of 4.5 K is confirmed for $x = 0.5$. The calculated value of $\mu_0 H_{c2}(0)$ is found to be 1.6 T under WHH extrapolation. The corresponding Ginzburg-Landau coherence length is estimated to be (143.5 ± 2.2) Å. The zero-temperature London penetration depth is estimated to be 832 ± 97.4 nm. The low-temperature penetration depth data fit well to the S-wave pairing symmetry and no strong deviation from isotropic BCS theory is observed. In essence, no unconventional superconductivity as expected for a superconductor derived from a topological crystalline insulating phase is observed.

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