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Unusual superconductivity in the topological nodal-line semimetal candidate $Sn_xNbSe_{2-\delta}$

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Unusual superconductivity in the topological nodal-line semimetal candidate $Sn_xNbSe_{2-\delta}$

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Abstract. We report the superconductivity of the topological nodal-line semimetal candidate $Sn_xNbSe_{2-\delta}$ with a noncentrosymmetric crystal structure. The superconducting transition temperature T_c of $Sn_xNbSe_{2-\delta}$ drastically varies with the Sn concentration x and the Se deficiency δ, and reaches 12 K, relatively higher than those of known topological superconductors. The upper critical field of this compound shows unusual temperature dependence, inconsistent with the WHH theory for conventional type-II superconductors. In a low-T_c sample, the zero-temperature limit of the upper critical field parallel to the ab plane exceeds the Pauli paramagnetic limit estimated from the simple BCS weak coupling model by a factor of ~ 2, suggestive of unusual superconductivity stabilized in $Sn_xNbSe_{2-\delta}$. Together with the robust superconductivity against disorder, these observations indicate that $Sn_xNbSe_{2-\delta}$ is a promising candidate to explore topological superconductivity.

1. Introduction

Topological superconductivity has attracted great interest because of the potential of Majorana fermions for technological application [1]. Promising candidates for topological superconductors are noncentrosymmetric superconductors with strong spin-orbit coupling. The lack of centrosymmetry can induce an odd-parity pairing state, which is a prerequisite of topological superconductivity [2]. Among such noncentrosymmetric systems, the topological nodal-line semimetal $PbTaSe_2$ shows superconductivity at 3.8 K [3], and its superconducting gap exhibits nematic behavior [4], similar to metal-intercalated Bi_2Se_3 [5]. In addition, a member of the $PbTaSe_2$ family, $SnNbSe_2$, is theoretically predicted to be a topological nodal-line semimetal and a superconductor [6]. The calculated superconducting transition temperature of this compound is 7 K, relatively higher than most of the known topological superconductor candidates. The higher T_c can be beneficial to probe Majorana bound states with the energy spacing Δ^2/E_F, where Δ the superconducting gap and E_F is the Fermi energy [7], allowing us to investigate topological superconductivity.

We here report unusual superconductivity of $Sn_xNbSe_{2-\delta}$ with the same noncentrosymmetric structure as stoichiometric $SnNbSe_2$. The superconducting transition temperatures are strongly dependent on Sn concentration x and Se deficiency δ, both of which are closely correlated to carrier doping. The observed upper critical fields of $Sn_xNbSe_{2-\delta}$ cannot be described by the Werthamer–Helfand–Hohenberg (WHH) theory for conventional type-II superconductors [8, 9]. Moreover, the zero-temperature value of the upper critical field of $Sn_{0.16}NbSe_{1.76}$ is beyond the BCS Pauli paramagnetic limit. The observed anomalous upper critical fields, along with the robust superconductivity against disorder, are suggestive of a possible unconventional superconducting pairing state realized in $Sn_xNbSe_{2-\delta}$.

2. Experimental methods

Single crystals of $Sn_xNbSe_{2-\delta}$ were grown by using a self-flux method [10]. The typical size of the resulting crystals is about $1 \times 1 \times 0.3$ mm^3. We observed a single crystal x-ray diffraction pattern consistent with the noncentrosymmetric crystal structure of $SnNbSe_2$ with the space group $P\bar{6}m2$ (the upper inset of fig.1). We determined the atomic ratio of the crystals with x-ray fluorescence spectroscopy.

3. Results and discussion

$Sn_xNbSe_{2-\delta}$ undergoes a superconducting transition at low temperatures [10]. Figure 1 shows the typical temperature dependence of resistivity of $Sn_xNbSe_{2-\delta}$. Overall temperature dependence of the resistivity is metallic. Because of the high normal-state resistivity right above T_c, the typical residual resistivity ratio $RRR = \rho(300\ \text{K})/\rho(T_c)$ is ~ 3 and 30-50 times as small as that of $PbTaSe_2$ [11], indicating the presence of abundant disorder. The lower inset of Fig. 1 depicts the low-temperature resistivity of $Sn_xNbSe_{2-\delta}$. The superconducting transition temperatures T_c determined by the midpoints of resistive transitions vary up to 12 K, depending on Sn concentration x and Se deficiency δ, while no discernible correlation between T_c and $\rho(T_c)$ is observed. Surprisingly, despite the low RRR due to disorder, the observed highest T_c of 12 K is beyond the theoretical prediction of 7 K, as well as T_c of most known topological superconductors.

Figure 2(a) shows the Hall resistivity of $Sn_xNbSe_{2-\delta}$ as a function of magnetic fields at $T =$ 15 K. The Hall resistivity exhibits linear-in-H behavior, and its sign is positive, suggesting that a large cylindrical hole band around the Γ point [6] predominantly contributes to the charge

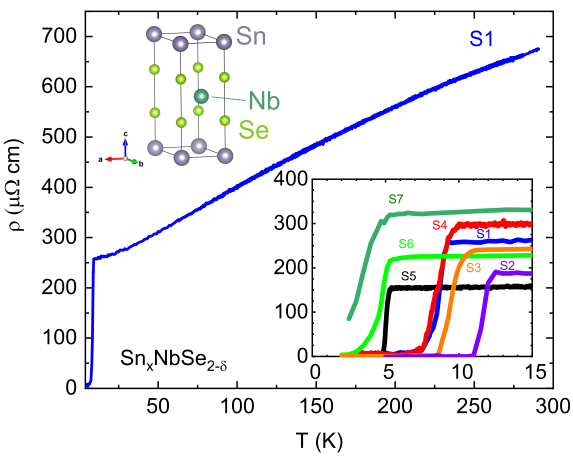

Figure 1. Main panel: Tempearture dependence of resistivity of the sample S1 ($Sn_{0.15}NbSe_{1.69}$). Upper inset: Crystal structure of $Sn_xNbSe_{2-\delta}$. Lower inset: Low-temperature resistivity of the samples S1, S2 ($Sn_{0.13}NbSe_{1.62}$), S3 ($Sn_{0.15}NbSe_{1.65}$), S4 ($Sn_{0.14}NbSe_{1.71}$), S5 ($Sn_{0.13}NbSe_{1.70}$), S6 ($Sn_{0.16}NbSe_{1.76}$), and S7 ($Sn_{0.19}NbSe_{1.73}$).

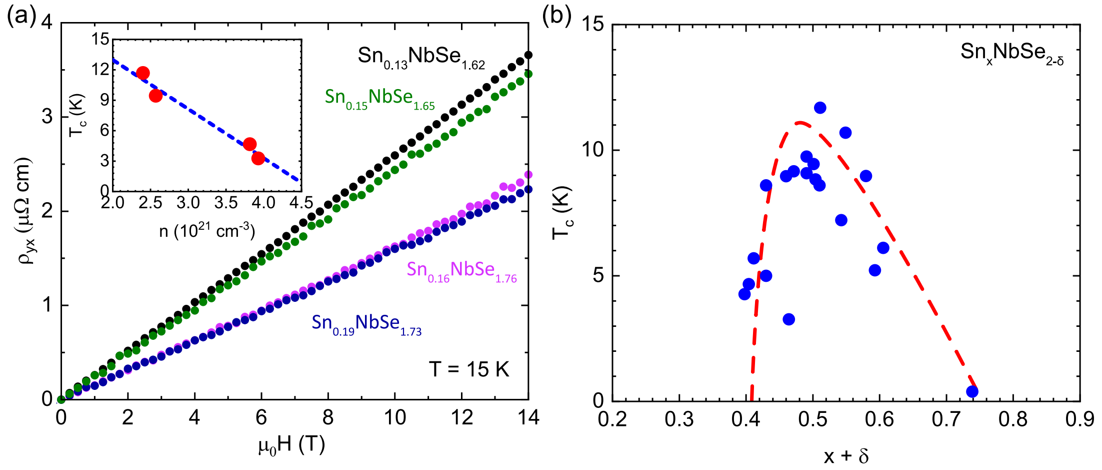

Figure 2. (a) Main panel: Hall resistivity of $Sn_xNbSe_{2-\delta}$ as a function of magnetic field at $T =$ 15 K. Inset: T_c versus the carrier concentration n obtained from the Hall coefficient $R_H = 1/ne$. A blue dashed line is a linear fit to the data. (b) Superconducting transition temperature T_c of $Sn_xNbSe_{2-\delta}$ as a function of the sum of Sn concentration x and Se deficiency δ. A red dashed line is a guide to the eye.

transport. The Hall coefficient R_H, extracted from the slope of the Hall resistivity, gives carrier densities $n \sim 10^{21}$ cm^{-3}, close to, but rather smaller than n of $PbTaSe_2$ [12]. As shown in the inset of fig.2(a), T_c linearly decreases with n in this carrier density range, suggesting that the carrier density is a key parameter to determine T_c in $Sn_xNbSe_{2-\delta}$.

In fact, T_c appears to be fine-tuned by carrier doping. Assuming that the oxidation states of Sn and Se are 2+ and 2−, respectively, the sum of the Sn concentration x and the Se deficiency δ is proportional to the number of electrons provided by intercalated Sn^{2+} and deficient Se^{2-} ions. We plot the superconducting transition temperature as a function of $x+\delta$ in Fig.2(b). We observe a superconducting dome upon varying $x+\delta$. The carrier density region in the inset of Fig.2(a) falls within the narrow range of $x+\delta = 0.40 - 0.51$ in Fig.2(b).

Figure 3 shows temperature dependence of H_{c2} of $Sn_{0.13}NbSe_{1.70}$ (T_c = 5.0 K) and $Sn_{0.14}NbSe_{1.71}$ (T_c = 8.6 K) in the in-plane magnetic field directions, $H \parallel ab$, and the out-of-plane direction, $H \parallel c$. We determined H_{c2} by the midpoints of resistive transitions, applying the electrical current I in the ab plane. We find a distinct difference in the anisotropy of H_{c2}, $\Gamma = H_{c2}^{ab}/H_{c2}^{c}$, between these samples; $\Gamma = 3.0$ in $Sn_{0.13}NbSe_{1.70}$, while $\Gamma = 1.1$ in $Sn_{0.14}NbSe_{1.71}$. Regardless of the magnetic field directions, the temperature dependence of H_{c2} of both samples increases linearly with decreasing temperatures, different from those of conventional type-II superconductors. The upper critical fields of conventional superconductors are described by the WHH theory. Its zero-temperature value $H_{c2}(0)$ is given by $H_{c2}(0) = -\alpha T_c dH_{c2}/dT \mid_{T=T_c}$, where α is 0.69 for the dirty limit and 0.73 for the clean limit [8, 9]. However, we obtained $\alpha \sim 1$ for both samples, suggesting unusual upper critical fields of $Sn_xNbSe_{2-\delta}$. Notably, the in-plane $H_{c2}(0)$ of $Sn_{0.13}NbSe_{1.70}$ is about 16 T, surpassing the simple BCS Pauli paramagnetic limit, $\mu_0 H_p = 1.84 k_B T_c = 9.3$ T, by a factor of ~ 2, suggestive of a possible odd-parity component in the pairing state allowed by the noncentrosymmetric structure. On the other hand, the out-of-plane $H_{c2}(0)$ is lower than $\mu_0 H_p$. In $Sn_{0.14}NbSe_{1.71}$, the measured zero-temperature values in both magnetic field directions are smaller than the estimated Pauli paramagnetic limit $\mu_0 H_p =$ 15.6 T, enhanced by the high T_c of 8.6 K.

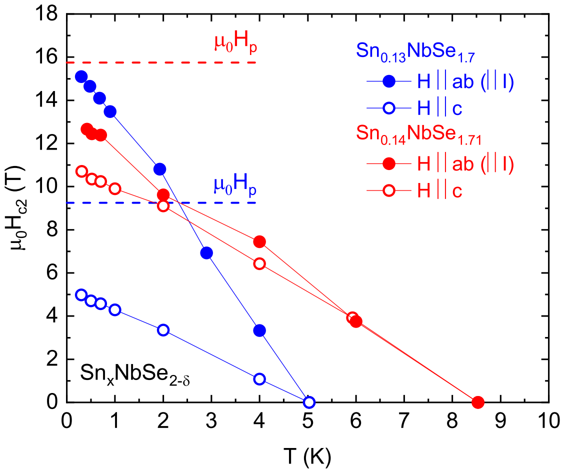

Figure 3. Temperature dependence of upper critical fields of $Sn_xNbSe_{2-\delta}$ for $H \parallel ab$ ($\parallel I$) and $H \parallel c$. A blue dashed line indicates the Pauli paramagnetic limit $\mu_0 H_p = 9.3$ T for $Sn_{0.16}NbSe_{1.76}$ and a red dashed line indicates $\mu_0 H_p = 15.6$ T for $Sn_{0.13}NbSe_{1.70}$.

4. Summary

We have investigated the resistivity, Hall effect, and upper critical fields of $Sn_xNbSe_{2-\delta}$. The superconducting transition temperatures can be fine-tuned up to 12 K by Sn concentration and Se deficiency, correlated with carrier densities. The zero-temperature value of upper critical field $\mu_0 H_{c2}(0)$ of the lower T_c sample ($Sn_{0.13}NbSe_{1.70}$) is beyond the Pauli paramagnetic limit, indicating an unusual pairing state realized in this systems. These findings suggest that $Sn_xNbSe_{2-\delta}$ can be a promising platform for exploring the relationship between superconductivity and topological properties.

Acknowledgments

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