Observations of two-dimensional quantum oscillations and ambipolar transport in the topological insulator Bi$_2$Se$_3$ achieved by Cd doping

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We present a defect-engineering strategy to optimize the transport properties of the topological insulator Bi$_2$Se$_3$ to show a high bulk resistivity and clear quantum oscillations. Starting with a $p$-type Bi$_2$Se$_3$ obtained by combining Cd doping and a Se-rich crystal-growth condition, we were able to observe a $p$-to-$n$-type conversion upon gradually increasing the Se vacancies by post-annealing. With the optimal annealing condition where a high level of compensation is achieved, the resistivity exceeds 0.5 $\Omega\text{cm}$ at 1.8 K and we observed two-dimensional Shubnikov-de Haas oscillations composed of multiple frequencies in magnetic fields below 14 T.

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I. INTRODUCTION

The three-dimensional (3D) topological insulator (TI) realizes a novel quantum state of matter where a non-trivial $Z_2$ topology of the wavefunction of the bulk valence band leads to the emergence of a “topological” surface state consisting of helically spin-polarized Dirac fermions. The peculiar spin texture of the surface state holds promise for novel spintronics and fault-tolerant topological quantum computing, so there is a rush of research to address this surface state. However, most of the known TI materials are poorly insulating in the bulk, making it difficult to probe the surface state by transport experiments. For example, Bi$_2$Se$_3$ is considered to be a promising TI material because it has a relatively large ($\sim 0.3$ eV) bulk band gap and a nearly perfect Dirac cone as its topological surface state, however, no matter whether it is in the form of bulk crystal, nanoribbon, or epitaxial thin film, Bi$_2$Se$_3$ always accompanies a lot of Se vacancies (usually $\sim 10^{19}$ cm$^{-3}$) that act as electron donors, and as a result, the residual bulk carriers hinder the transport studies of the surface state of this material.

To achieve a bulk-insulating state in Bi$_2$Se$_3$, doping holes to compensate for the residual electrons is a viable strategy. While this was done through low-level substitution of Ca$^{2+}$ for Bi$^{3+}$, the resulting disorder was so strong that no Shubnikov-de Haas (SdH) oscillation from the surface state was observed in Bi$_{2-x}$Ca$_x$Se$_3$. A different strategy was to partially substitute Sb for Bi, which apparently reduces the Se vacancies; indeed, with a relatively large ($\sim 12\%$) Sb substitution, surface SdH oscillations were successfully observed in $n$-type Bi$_{2-x}$Sb$_x$Se$_3$, but a very high magnetic field ($\sim 60$ T) was required for the observation. It is to be noted that with the Sb doping one can never cross the band gap to reach the $p$-type regime, and hence the tuning of the chemical potential to the Dirac point is impossible. This is a pity, because Bi$_2$Se$_3$ is attractive for its isolation of the Dirac point from the bulk bands. Therefore, it is desirable to find a suitable $p$-type dopant to access the Dirac point while keeping the mobility to be sufficiently high for the surface state to be studied by the SdH oscillations.

In this paper, we show that tactful defect engineering in Bi$_2$Se$_3$ employing Cd doping in combination with Se-vacancy tuning provides a useful means to control the chemical potential across the band gap. In the literature, whereas Cd in Bi$_2$Se$_3$ was shown to behave as an acceptor, Cd-doped Bi$_2$Se$_3$ crystals always remained $n$-type due to the low solubility of Cd atoms in Bi$_2$Se$_3$; however, it has been elucidated that increasing the Se content in the Bi-Se melt for the crystal growth can suppress the formation of Se vacancies and greatly reduce the residual bulk carrier density to the level of $\sim 10^{17}$ cm$^{-3}$. Therefore, even though the solubility of Cd is low, one could achieve a $p$-type behavior by combining Cd doping and a Se-rich growth condition. Actually, we obtained a $p$-type sample with this strategy and, furthermore, starting from the $p$-type sample, we could gradually increase the Se vacancies by careful post-annealing and achieve a high level of compensation, at which the sample becomes optimally bulk-insulating and presents two-dimensional (2D) SdH oscillations below 14 T.

II. EXPERIMENTAL DETAILS

The single crystals of Cd-doped Bi$_2$Se$_3$ were grown by using elemental shots of Bi (99.9999%), Cd (99.99%) and Se (99.999%) as starting materials. To maximize the Cd content in the crystal, excess Cd and a mixture of Bi and Se with a ratio of Bi:Se = 32:68 were melted in a sealed evacuated quartz tube at 750 $^\circ$C for 48 h with intermittent shaking to ensure a homogeneity, followed by cooling slowly to 550 $^\circ$C and then annealing at the same temperature for one week. The resulting crystals are easily cleaved along the basal plane, revealing a silvery mirror-like surface. The X-ray diffraction measurements confirmed the crystal to be single phase with the proper Bi$_2$Se$_3$ structure. The actual Cd content was determined by the inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) to be 0.0020(2). The as-grown crystals were examined by X-ray Laue analy-
sis and cut into single-domain, thin bar-shaped samples with typical dimensions of $3 \times 1 \times 0.2 \text{ mm}^3$.

For each annealing experiment, samples weighing about 4.2 mg were sealed in evacuated quartz tubes and annealed at a given temperature for one week, followed by quenching into cold water. All the samples used in this work were taken from the same part of the same batch, and the variation of the Cd content was confirmed to be negligible by the ICP-AES analysis. To avoid possible surface contamination, the surface layer of the annealed crystals were removed using adhesive tapes before transport measurements.

It worth mentioning that in our annealing experiments, we took precautions to minimize the uncertainty in the annealing temperature. For each annealing run, we placed the quartz tube at the same position of the same furnace so that the temperature gradients in the furnace as well as the thermocouple calibration errors do not affect the annealing result. Also, the environment temperature was kept constant during this experiment to minimize the temperature fluctuations between different annealing runs. As a result, the annealing temperature $T_{\text{anneal}}$ was very reproducible and its variation between different runs with nominally the same $T_{\text{anneal}}$ was within $\pm 1{ }^\circ\text{C}$.

The in-plane resistivity $\rho_{xx}$ and the Hall coefficient $R_H$ were measured in a Quantum Design Physical Properties Measurement System (PPMS-9) down to 1.8 K, for which the electrical contacts were prepared by using room-temperature-cured silver paste. In addition, one of the high-resistivity samples was brought to a 14-T magnet for detailed SdH-oscillation measurements using an ac six-probe method, in which four lock-in amplifiers were employed to measure both the primary and the second-harmonic signals in the longitudinal and transverse channels at a frequency of 19 Hz. The SdH-oscillation data were taken by sweeping the magnetic fields between $\pm 14$ T with the rate of 0.3 T/min, during which the temperature was stabilized to within $\pm 5$ mK.

III. RESULTS AND DISCUSSIONS

A. $p$-type Bi$_{2-x}$Cd$_x$Se$_3$

The temperature dependence of the in-plane resistivity $\rho_{xx}$ of a Bi$_{1.998}$Cd$_{0.002}$Se$_3$ crystal grown in the Se-rich condition is shown in Fig. 1(a), together with the data for a pristine Bi$_2$Se$_3$ sample grown with the same Bi/Se ratio. The pristine Bi$_2$Se$_3$ crystal shows an essentially metallic behavior with a weak resistivity upturn below $\sim 30$ K, which is typical for low-carrier-density Bi$_2$Se$_3$. Indeed, the Hall coefficient $R_H$ in this sample at 1.8 K corresponds to the bulk electron density $n_e \sim 7 \times 10^{17} \text{ cm}^{-3}$, which is very small for Bi$_2$Se$_3$. On the other hand, in Bi$_{1.998}$Cd$_{0.002}$Se$_3$ the resistivity upturn is absent and the $\rho_{xx}$ value is lower, suggesting a higher carrier density. In fact, as shown in Fig. 1(b), $R_H$ in the Bi$_{1.998}$Cd$_{0.002}$Se$_3$ crystal is positive and its value at 1.8 K corresponds to the hole density $n_h \sim 9 \times 10^{18} \text{ cm}^{-3}$, implying that the Cd doping has created $\sim 9.7 \times 10^{18} \text{ cm}^{-3}$ of holes ($\sim 0.8$ hole per Cd atom) that outnumber the electrons coming from Se vacancies. The reason for the smaller number of doped holes compared to the Cd concentration is most likely that a small portion of Cd atoms occupy the interstitial site and act as donors. In Fig. 1(b), $R_H$ is only weakly dependent on temperature and the Hall resistivity $\rho_{yx}$ is perfectly linear in $B$ (as shown in the inset), reflecting the metallic nature of the as-grown Bi$_{1.998}$Cd$_{0.002}$Se$_3$ sample which is due to a single type of carriers (i.e., the bulk holes). The Hall mobility $\mu_H$ ($=R_H/\rho_{xx}$), also shown in Fig. 1(b), increases with decreasing temperature, reaching $\sim 1600 \text{ cm}^2/\text{Vs}$ at 1.8 K.

B. $p$-to-$n$-type conversion by post annealing

Annealing the as-grown Bi$_{1.998}$Cd$_{0.002}$Se$_3$ crystals in evacuated quartz tubes has a drastic effect on its transport properties. Figure 2(a) shows how the tempera-
The temperature dependence of $\rho_{xx}$ changes upon annealing in a narrow temperature window between 573 and 590 °C. One can see that $\rho_{xx}(T)$ evolves nonmonotonically with the annealing temperature, $T_{\text{anneal}}$; namely, $\rho_{xx}$ initially increases with $T_{\text{anneal}}$ until $T_{\text{anneal}}$ exceeds 577 °C, after which $\rho_{xx}$ decreases as $T_{\text{anneal}}$ is further increased. Notably, $\rho_{xx}$ of the sample annealed at 577 °C show a high value of 0.5 Ωcm at 1.8 K, which is three orders of magnitude larger than that of the as-grown sample. Figure 2(b) shows the typical temperature dependences of low-field $R_H$ data (defined as $R_H = \rho_{xx}/B$ for $B \approx 0$) for different $T_{\text{anneal}}$, which indicates that more and more electron carriers are introduced as $T_{\text{anneal}}$ is increased, and the sign change from $p$-type to $n$-type occurs around $T_{\text{anneal}} = 577$ °C.

Since the drastic change in the transport properties occurs in a very narrow temperature window (573 – 580 °C), one may wonder about the reproducibility of the result. As a matter of fact, the observed change was quite reproducible, as demonstrated in Figs. 3 and 4. Figures 3(a)-3(d) show the $\rho_{xx}(T)$ data for at least two samples annealed at the same temperature, where one can see that the behavior for each $T_{\text{anneal}}$ is essentially reproducible. Figures 4(a)-4(d) show the corresponding $R_H(T)$ data for the same sets of samples; here, except for the case of $T_{\text{anneal}} = 577$ °C [Fig. 4(c)], we observed reasonable reproducibility [Figs. 4(a), 4(b), and 4(d)]. For $T_{\text{anneal}} = 577$ °C, two of the three samples (A and B) showed a sign change in $R_H$ from negative to positive upon lowering temperature from 300 K, whereas the $R_H$ of sample C remained negative in the whole temperature range. Actually, this variation in the behavior of $R_H$ indicates that the $T_{\text{anneal}} = 577$ °C samples are at the verge of the $p$-to-$n$-type conversion.

Figures 4(e)-4(h) show the $\rho_{yx}(B)$ curves measured in sample “A” of each $T_{\text{anneal}}$. One can clearly see that the curve in Fig. 4(g) for $T_{\text{anneal}} = 577$ °C is nonlinear, indicating that there are at least two bands contributing to the transport. In topological-insulator samples with a large bulk resistivity, this kind of nonlinear $\rho_{yx}(B)$ curves are indications of the surface channels making noticeable contributions. Therefore, the consistently high resistivity [Fig. 3(c)] together with the complex behaviors of the Hall signal are likely to be a signature of a high level of compensation achieved in the samples annealed at 577 °C; in other words, in those samples the acceptors and donors are nearly equal in number and their delicate balance can easily change the sign of $R_H$. It is to be emphasized that our data demonstrate that this high level of compensation is reproducibly achieved with $T_{\text{anneal}} = 577$ °C. In samples annealed at other temperatures, the $\rho_{yx}(B)$ behavior is almost linear [Figs. 4(e), 4(f), and 4(h)], suggesting that the contribution of the surface to the transport properties is minor. In passing, the collection of $\rho_{xx}(T)$ and $R_H(T)$ data shown in Fig. 2 for varying $T_{\text{anneal}}$ are for sample “A” of each $T_{\text{anneal}}$ shown in Figs. 3 and 4.

### C. Defect chemistry

The above observation that a drastic change in the transport properties of Bi$_{1.998}$Cd$_{0.002}$Se$_3$ occurs in a very narrow temperature window might seem surprising. However, this behavior can be readily understood by examining the defect chemistry associated with the
annealing. In the present system, there are mainly two
different types of charged defects, the aliovalent substi-
tutional defect Cd\textsubscript{B1} and the vacancy defect V\textsubscript{Se}\textsuperscript{**} the
former acts as an acceptor and the latter as a donor.
Therefore, the effective charge-carrier density is deter-
mined by their competition and can be expressed as
\(n_{\text{eff}} = [\text{Cd}\textsubscript{B1}] - 2[\text{V}\textsubscript{Se}\textsuperscript{**}]\), where positive (negative) \(n_{\text{eff}}\)
denotes the hole (electron) density. In an as-grown sample, the
Cd\textsubscript{B1} defects are dominant and \(n_{\text{eff}}\) is positive; accord-
ingly, the chemical potential lies in the valence band.
When annealed in evacuated quartz tubes, a portion of
selenium goes into the gas phase Se\textsubscript{2} in equilibrium with the solid phase,\textsuperscript{23} resulting in the formation of more V\textsubscript{Se}\textsuperscript{**} defects while leaving Cd\textsubscript{B1} unaffected (because the \(T_{\text{anneal}}\) employed in the present study is much lower than the
melting temperature of 710 °C). The equilibrated vapor
pressure of Se\textsubscript{2} increases with increasing \(T_{\text{anneal}}\), creating
more V\textsubscript{Se}\textsuperscript{**} and eventually changing \(n_{\text{eff}}\) from positive to
negative.

To be more quantitative, one may assume that the in-
crease in the Se-vacancy concentration upon annealing,
\(\Delta[V\textsubscript{Se}\textsuperscript{**}]\), is directly reflected in the increase in the number of Se\textsubscript{2} molecules in the quartz tube, which determines the
Se\textsubscript{2} vapor pressure \(P_{\text{Se}_2}\) in constant volume, one expects a linear relation between \(\Delta[V\textsubscript{Se}\textsuperscript{**}]\) and \(P_{\text{Se}_2}\) if the Se\textsubscript{2} va-
por behaves as an ideal gas. According to Ref. \textsuperscript{23}, the
equilibrated Se\textsubscript{2} vapor pressure \(P_{\text{Se}_2}\) of Bi\textsubscript{2}Se\textsubscript{3} is related to the absolute temperature \(T\) via

\[
\log P_{\text{Se}_2}[\text{atm}] = A - B/T[\text{K}],
\]

where \(A = 7.81\pm0.50\) and \(B = 10870\pm640\) for the tem-
perature range of 527 to 627 °C. From this \(T\) dependence
of \(P_{\text{Se}_2}\), one can infer that \(\Delta[V\textsubscript{Se}\textsuperscript{**}]\) is very sensitive to the
change in \(T_{\text{anneal}}\). For example, changing \(T_{\text{anneal}}\) by just 1
°C near 577 °C results in a variation of \(\sim3.5\%\) in \(\Delta[V\textsubscript{Se}\textsuperscript{**}]\); therefore, the expected change in \(\Delta[V\textsubscript{Se}\textsuperscript{**}]\) upon changing
\(T_{\text{anneal}}\) from 575 to 580 °C is as much as \(\sim18\%\). It is thus
expected that a sign change in \(n_{\text{eff}}\) occurs abruptly in
the vicinity of \(T_{\text{anneal}} \approx 577 °C\) where \(n_{\text{eff}} \approx 0\) (namely,
\([\text{Cd}\textsubscript{B1}] \approx [V\textsubscript{Se}\textsuperscript{**}]\)), and results in a drastic change in the
transport properties as we observed.

D. Surface quantum oscillations

From the above results, it is clear that the highest level
of compensation is achieved in samples annealed at 577
°C. We therefore measured the sample C of \(T_{\text{anneal}} = 577
°C\) in a 14-T magnet using a rotation sample holder to
investigate its SdH oscillations in detail. Before the high-
field measurements, to protect the surface state from ag-
ing, the top surface of the sample was covered with Al\textsubscript{2}O\textsubscript{3}
in the following way: first, the crystal was cleaved on
both surfaces with adhesive tapes to reveal fresh sur-
faces, and then transferred into the sputtering chamber;
second, the top surface was cleaned by bias-sputtering
with Ar ions for 13 minutes and then, without breaking the vacuum, a 540-
nm-thick Al\textsubscript{2}O\textsubscript{3} film was deposited by the rf magnetron
sputtering. After this process, gold wires were bonded to
the side faces by spot welding. Probably because of the
sample heating during the spot welding, the \(R_{\text{xx}}\) value of this sample became even larger than that shown in Fig.
3(c). Also, the sign of \(R_{\text{H}}\) at low temperature changed
to negative after the process, showing the Hall response
similar to that of the sample A. The \(R_{\text{H}}(T)\) behavior of
In our measurements using an ac lock-in technique, we simultaneously recorded the primary and the second-harmonic signals during the magnetic-field sweeps. Figure 5(c) shows the magnetic-field (∆ρxx) dependences of the primary signal (ρxx) and the second-harmonic signal (Δρxx) measured at 1.4 K in magnetic fields along the C3 axis. One can see that the second-harmonic signal (Δρxx) shows pronounced oscillations, while in the primary signal (ρxx), the oscillations are hardly visible. To understand the nature of the oscillations, we show in Fig. 5(d) the plots of Δρxx and d²ρxx/dB² (second derivative of the primary signal) vs the inverse magnetic field 1/B; a comparison between the two curves indicates that they present essentially the same peak/dip positions. While this sample C after the Al₂O₃-coverage process is shown in Fig. 5(a), and its ρyy(B) curve at 1.4 K is shown in Fig. 5(b).

In our measurements using an ac lock-in technique, we simultaneously recorded the primary and the second-harmonic signals during the magnetic-field sweeps. Figure 5(c) shows the magnetic-field (∆ρxx) dependences of the primary signal (ρxx) and the second-harmonic signal (Δρxx) measured at 1.4 K in magnetic fields along the C3 axis. One can see that the second-harmonic signal (Δρxx) shows pronounced oscillations, while in the primary signal (ρxx), the oscillations are hardly visible. To understand the nature of the oscillations, we show in Fig. 5(d) the plots of Δρxx and d²ρxx/dB² (second derivative of the primary signal) vs the inverse magnetic field 1/B; a comparison between the two curves indicates that they present essentially the same peak/dip positions. While the waveforms are quite complicated, the Fourier transform (FT) spectrum of Δρxx(B⁻¹) shown in Fig. 5(e) presents three well-defined peaks at F₁ = 11 T, F₂ = 27 T, and F₃ = 33 T, indicating that the observed oscillations are SdH oscillations with multiple frequencies.

Note that the second-harmonic in ac measurements is a distortion of the input sine wave, and its occurrence is an indication of a nonlinear response. In the present case, the SdH oscillations are apparently giving rise to a peculiar non-ohmicity. This makes the second-harmonic signal to be useful for observing the SdH oscillations with a high sensitivity, although the detailed mechanism is not clear at the moment.

Figure 6(a) shows how the SdH oscillations observed in Δρxx change when the magnetic field is rotated, by plotting Δρxx versus 1/(B cos θ) where θ is the angle between B and the C3 axis. One can see that the oscillatory features are essentially dependent on the perpendicular component of the magnetic field. Also, as shown in Fig. 6(b), the angular dependences of all three frequencies in the FT spectra are consistent with 1/cos θ. These results strongly suggest that the present SdH oscillations signify 2D Fermi surface(s). We note that the SdH oscillations in this sample disappeared after keeping the sample in ambient atmosphere for a week, which suggests that the SdH oscillations were coming from the surface. (This observation also suggests that the Al₂O₃ coverage, while useful for slowing the aging of the surface of Bi₂Se₃, does not provide a perfect protection). Furthermore, one can estimate the bulk mobility of this sample to be ∼40 cm²/Vs from the values of ρxx and R₄H, and such a mobility is too low to give rise to SdH oscillations of the bulk carriers below 14 T. All told, one can reasonably conclude that the observed SdH oscillations are of the surface origin.
From the SdH-oscillation data, the Fermi wave vector \( k_F \) can be calculated via the Onsager relation 
\[ F = \frac{\hbar}{2\pi e} \pi k_F^2, \]
yielding \( k_F = 0.018, 0.029, \) and \( 0.032 \) Å\(^{-1}\) for \( F_1, F_2, \) and \( F_3, \) respectively. These are of the same order as the value \( k_F = 0.031 \) Å\(^{-1}\) reported for the topological surface state in \( n \)-type Bi\(_{2-x}\)Sb\(_x\)Se\(_3\). However, because of the multi-component nature of the oscillations that leads to complicated waveforms, it is difficult to reliably extract the cyclotron mass \( m_\text{c} \) nor the Dingle temperature for each component using the Lifshitz-Kosevich theory. This makes it impossible to identify the origins of the three oscillation frequencies, but possible reasons for the multiple components in the present case include: (i) harmonics of a fundamental frequency are observed, (ii) chemical potentials of the top and bottom surfaces are not identical and give two frequencies associated with the topological surface states, (iii) a trivial 2D electron gas created by the band bending at the surface presents additional SdH oscillations. Note that, in the case of the present sample used for the detailed SdH measurements, the top surface was covered by Al\(_2\)O\(_3\) and the bottom surface was covered by the GE varnish, so the conditions of the two surfaces were very different. To resolve the origins of those multiple frequencies, an experiment involving the gate control of the surface chemical potential to trace the energy dispersion of each branch (as was done for exfoliated Bi\(_2\)Se\(_3\)) would be desirable.

### E. Nonlinear \( \rho_{yx}(B) \) behavior

Although we could not extract the surface mobility from the SdH oscillations in the present case, we can still estimate the relevant parameters of the surface and the bulk transport channels by analyzing the nonlinear \( \rho_{yx}(B) \) behavior [Fig. 5(b)] with the simple two-band model described in Ref. 18. The solid line in Fig. 5(b) is the result of the two-band-model fitting, from which we obtained the bulk electron density \( n_b = 7 \times 10^{17} \) cm\(^{-3}\), the bulk mobility \( \mu_b = 17 \) cm\(^2\)/Vs, the surface electron density \( n_s = 1.8 \times 10^{12} \) cm\(^{-2}\), and the surface mobility \( \mu_s = 1.2 \times 10^3 \) cm\(^2\)/Vs. The observed frequencies of the SdH oscillations, 11, 27, and 33 T correspond to the surface carrier densities of \( 2.5 \times 10^{11}, 6.7 \times 10^{11}, \) and \( 8.1 \times 10^{11} \) cm\(^{-2}\) in spin-filtered surface states, respectively, and it is interesting that the sum of these numbers, \( 1.7 \times 10^{12} \) cm\(^{-2}\), appears to be consistent with the \( n_b \) value obtained from the two-band analysis. Also, it is assuring that the surface mobility \( \mu_s \) obtained from the two-band analysis, \( \sim 1200 \) cm\(^2\)/Vs, is reasonably large and is consistent with our observation of the SdH oscillations in moderate magnetic fields.

In passing, the \( \rho_{yx}(B) \) data of the sample A shown in Fig. 4(g) can also be fitted with the two-band model. The result of the fitting, shown by the solid line in Fig. 4(g), yields the bulk electron density \( n_b = 1.3 \times 10^{18} \) cm\(^{-3}\), the bulk mobility \( \mu_b = 15 \) cm\(^2\)/Vs, the surface electron density \( n_s = 2.0 \times 10^{11} \) cm\(^{-2}\), and the surface mobility \( \mu_s = 1.0 \times 10^4 \) cm\(^2\)/Vs for this sample.

### IV. CONCLUSION

In conclusion, we demonstrate that with tactful defect engineering one can optimize the transport properties of the topological insulator Bi\(_2\)Se\(_3\) to show a high bulk resistivity and clear quantum oscillations. Specifically, by employing a Se-rich crystal-growth condition we achieved the \( p \)-type state in Bi\(_2\)Se\(_3\) by Cd-doping for the first time; we then employed careful post annealing to tune the Se vacancies and achieved a high level of compensation, where the acceptors and donors nearly cancel each other and the sample presents a high \( \rho_{xx} \) value exceeding 0.5 \( \Omega \)cm at 1.8 K and shows 2D SdH oscillations consisting of multiple components below 14 T.

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