Tuning the charge density wave quantum critical point and the appearance of superconductivity in TiSe_2

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The transition metal dichalcogenide TiSe_2 is an ideal correlated system for studying the interplay between superconductivity (SC) and a charge density wave (CDW) because both symmetry-breaking phases can be easily controlled by either Cu intercalation or physical pressure. SC appears in proximity to a CDW quantum critical point (QCP) induced by both Cu intercalation and applied pressure, raising the possibility of CDW-driven SC. Here, we report tuning the CDW QCP by simultaneously controlling Cu intercalation and external pressure and the appearance of a SC dome centered on the tunable QCP. When subjected to pressure, CDW ordering of Cu-intercalated $\text{Cu}_{0.025}\text{TiSe}_2$ is completely suppressed at 2.3 GPa, where the residual resistivity and the resistivity-temperature exponent decrease sharply, indicating the presence of the CDW QCP. The upper critical field of $\text{Cu}_{0.025}\text{TiSe}_2$ is 3.51 kOe, 16 times larger than that of pristine TiSe_2 , and its temperature dependence is linear, indicating that SC of TiSe_2 is switched from the two-dimensional- to anisotropic three-dimensional-like by Cu intercalation. These discoveries show that the simultaneous application of Cu intercalation and pressure move the CDW QCP and that the highest SC transition temperature is pinned to the QCP, suggesting that the SC in TiSe_2 is strongly correlated with CDW quantum criticality.

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I. INTRODUCTION

A charge density wave (CDW) is a quantum state in which electrons at the Fermi energy organize themselves into a collective mode with a gap in the single-particle excitation spectrum [1]. Because the Fermi surface of low-dimensional materials is particularly susceptible to an instability induced by charge and atomic lattice modulation associated with a CDW, these materials are prone to host a CDW. Observation of CDW order in proximity to the superconducting (SC) phase of high- T_c cuprates and other low-dimensional systems raises the fundamental question of whether the two symmetry-breaking phases compete, coexist, or cooperate [2–6]. Most

studies have focused on tuning the fermiology by applying a single nonthermal control parameter, establishing that static CDW and SC orders compete for parts of the Fermi surface. The interplay between SC in low-dimensional correlated systems and quantum fluctuations associated with the CDW quantum critical point (QCP), however, is still being debated.

The two-dimensional (2D) transition metal dichalcogenide (TMD) TiSe_2 , in which Se-Ti-Se layers are separated by a van der Waals gap [7], has been extensively studied to probe the interplay between SC and CDW via various external parameters such as doping [8–11], intercalation [12–17], pressure [18–21], and layer thickness [22–25]. The maximal SC transition temperature ($T_{c,\text{max}}$) emerges at a point where the CDW transition temperature is suppressed to zero by external pressure and/or Cu intercalation [12,18]. An x-ray scattering study of TiSe_2 under high pressure reveals, however, that the CDW state in TiSe_2 is separated into a commensurate CDW (CCDW) and an incommensurate CDW (ICDW) under pressure. The CCDW state disappears at the optimal pressure, showing $T_{c,\text{max}}$ (~ 3.0 GPa) and indicating that the CCDW and SC orders of TiSe_2 are closely related [13,14,16,17,26,27]. In contrast, the ICDW state is not suppressed even at a pressure of 5.1 GPa, suggesting that the SC and ICDW orders proceed to develop separately [10,19].

The effects of external pressure and Cu intercalation in TiSe_2 are similar in that both suppress the CDW order and induce SC. By contrast, the change in other physical properties

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depends on the control parameter [13,18]. For example, the sign of the Hall coefficient (R_H) is positive for pristine TiSe_2 , whereas it is negative for Cu_xTiSe_2 because a small amount of Cu intercalation ($x = 0.015$) changes the major charge carrier type from hole to electron [13]. The upper critical field (H_{c2}) for pressure-induced SC of TiSe_2 is 0.23 kOe ($T_c = 0.7$ K at 3.5 GPa), whereas that for the Cu-intercalated $\text{Cu}_{0.07}\text{TiSe}_2$ is 12.6 kOe ($T_c = 3.9$ K at ambient pressure), an enhancement in H_{c2} of 55 times [17,18]. Maschek *et al.* [26] considered two different pairing mechanisms in the Cu intercalation (x)-pressure-temperature (x - P - T) phase diagram of TiSe_2 : enhanced electron-phonon coupling provided by phonon-mode softening as the CDW QCP is approached with Cu-intercalation at atmospheric pressure and by pressure-enhanced hybridization of a hybrid phonon-exciton mode that softens in proximity to the pressure-induced CDW QCP in pure TiSe_2 . Therefore, simultaneously controlling both pressure and Cu intercalation is crucial to deepening our understanding of the origin of SC in the CDW TiSe_2 system and exploring the possibility of CDW-driven SC.

Here, we report electrical resistivity measurements on Cu-intercalated TiSe_2 ($x = 0.025$) under pressures as high as 3.1 GPa. Like the pressure effects on pristine TiSe_2 , the SC state of $\text{Cu}_{0.025}\text{TiSe}_2$ is induced by the application of pressure, while the CDW transition temperature (T_{CDW}) is suppressed. Our comprehensive x - P - T phase diagram shows that the CDW state is suppressed at a critical pressure where T_c reaches its maximum. The upper critical field (H_{c2}) of $\text{Cu}_{0.025}\text{TiSe}_2$ at 3.1 GPa is 3.51 kOe, and its temperature dependence is quasilinear, which is significantly different from that of pristine TiSe_2 under pressure (3.5 GPa) [18,19], but is similar to Cu-intercalated $\text{Cu}_{0.07}\text{TiSe}_2$ at ambient pressure [12,17]. These results imply that Cu intercalation between the Se-Ti-Se layers separated by a van der Waals gap in Cu_xTiSe_2 induces a dimensional crossover from 2D- to three-dimensional (3D)-like SC properties in TiSe_2 . Our results that the maximal T_c is pinned to the CDW QCP without regarding Cu intercalation, external pressure, or simultaneous application of both control parameters reflect that there is a strong correlation between CDW QCP and the SC of TiSe_2 .

II. EXPERIMENT

Cu-intercalated TiSe_2 single crystals, Cu_xTiSe_2 with $x = 0.025$, were synthesized by the vapor transport method [12,28]. The crystal structure and chemical composition ratio of the fabricated Cu_xTiSe_2 single crystals were determined using a powder x-ray diffractometer (Rigaku miniflex-600) and energy-dispersive x-ray spectrometer (EDX), respectively. EDX scans for the overall area of the sample showed $x = 0.025 \pm 0.003$ on average, while x ranges from 0.027 to 0.021 at some specific sites such as craters. Both a - and c -axis lattice parameters obtained from powder x-ray diffraction (PXRD) measurements are also consistent with previous results [12], indicating that crystals of $\text{Cu}_{0.025}\text{TiSe}_2$ are reproducible and homogeneously synthesized. The standard four-point contact technique was used to measure the electrical resistivity (ρ) of the Cu_xTiSe_2 samples that were prepared in bar shapes, and we had screened many crystals to select the best quality sample for the pressure experiment. Quasihydrostatic pressure

FIG. 1. (a) Schematic phase diagram of Cu_xTiSe_2 as a function of the degree of Cu intercalation [12]. The concentration $x = 0.025$ is marked with an arrow, and open symbols represent current experiments. (b) Crystal structure of Cu_xTiSe_2 . The Ti atom is located at the center of an octahedral structure formed by six Se atoms. These structures form Se-Ti-Se layers (the Ti and Se atoms are blue and green, respectively). The Cu atoms (orange) are intercalated in the van der Waals gap between the Se-Ti-Se layers. (c) Powder x-ray diffraction pattern (PXRD) of the $x = 0.025$ sample is plotted as a function of the angle and compared with the calculated pattern obtained via Rietveld refinement.

environments were achieved using a silicone fluid and a glycerol-water mixture (60/40) as a pressure transmitting medium for pressures up to 2.5 and 3.5 GPa in a cylindrical clamp-type and an indenter-type cell, respectively [29,30]. The pressure inside the cell was determined by measuring the suppression of the SC transition temperature of Sn and Pb [31], and they showed a sharp SC transition at all pressures, reflecting that the pressure was applied smoothly. A custom-built helium-pumping cryostat was used for resistivity measurements from 1.4 to 300 K. The SC properties down to 0.3 K were studied by applying an external magnetic field using the Oxford Heliox VL system.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature vs Cu intercalation (T - x) phase diagram, with the location of $x = 0.025$ marked by the arrow. Energy-dispersive x-ray spectroscopy (EDS) measurements were used to determine the actual ratio of intercalated Cu atoms in TiSe_2 crystals. Figure 1(c) shows the θ - 2θ scans of the PXRD patterns of Cu_xTiSe_2 with $x = 0.025$. The a - and c -axis lattice parameters that were calculated using FULLPROF software are 6.017 and 3.54 Å, which are consistent with those in a previous study [12]. Both a and c increase smoothly with the Cu content, indicating that Cu atoms are successfully intercalated in the van der Waals gap, separating the Se-Ti-Se layers with ionic bonding [12], as illustrated in Fig. 1(b).

Figure 2(a) shows the temperature dependence of the electrical resistivity (ρ) of $\text{Cu}_{0.025}\text{TiSe}_2$ under pressure. Values of ρ at room temperature $\rho(300$ K) are reduced by the

FIG. 2. Electrical resistivity of $\text{Cu}_{0.025}\text{TiSe}_2$. The electrical resistivity (ρ) and its first derivative ($d\rho/dT$) are plotted for pressures of 0.3, 0.9, 1.7, 2.5, and 3.1 GPa in (a) and (b), respectively. The arrows in (b) mark the minimum $d\rho/dT$, which are assigned as T_{CDW} . (c) Magnified view of ρ near T_c plotted for 1.7, 2.5, and 3.1 GPa, where the down arrows mark the onset of the superconducting phase transition. (d) Analysis of the low-temperature resistivity by using the power-law form of $\rho(T) = \rho_0 + AT^n$, where the best result of the least squares fitting is plotted as a black curve. $\rho(T)$ is rigidly shifted for clarity with an offset (ρ_{offset}) against values at ambient pressure (1 bar), where it is 48, 230, 245, and 250 for 0.9, 1.7, 2.5, and 3.1 GPa, respectively. (e) Overlay of the residual resistivity (ρ_0) and the temperature exponent n in the T vs P phase diagram. A sharp reduction of ρ_0 and n is observed in the vicinity of P_c , where T_c is maximum.

application of external pressure because of the increased overlap between adjacent orbitals. This large reduction of $\rho(300\text{ K})$ under pressure has been widely observed in TMDs, which consist of stacked layers with a van der Waals gap [32,33]. Figure 2(b) displays the first derivative of the resistivity ($d\rho/dT$) as a function of the temperature, where a dip feature corresponds to T_{CDW} , as indicated by the arrows. Because any features associated with an ICDW in TiSe_2 are difficult to observe by electrical resistivity measurements [19], we assume that the dip in $d\rho/dT$ arises from the CCDW phase transition. When subjected to pressure, the T_{CDW} of $\text{Cu}_{0.025}\text{TiSe}_2$ decreases and disappears at the critical pressure (P_c) near 2.3 GPa, where T_c is the maximum ($T_{c,\text{max}}$).

Figure 2(c) shows a magnified view of the electrical resistivity of $\text{Cu}_{0.025}\text{TiSe}_2$ near the SC phase transition, at which the onset of T_c is $\sim 1.4\text{ K}$ at 1.7 GPa. We note that the SC phase transition occurs in broader temperature ranges at 1.7 and 2.5 GPa compared with 3.1 GPa. Similar broadening in

the SC phase transition is also observed in materials in close proximity to a QCP, where SC coexists with other ordered states such as CDW and antiferromagnetic (AFM) phases [12,32,34]. To make a better understanding, however, we need further analysis via such spectroscopic studies as muon spin spectroscopy (μSR) or nuclear magnetic resonance (NMR) measurements. The temperature dependence of the resistivity in the normal state ($T > T_c$) is plotted with an offset for clarity in Fig. 2(d) and was analyzed using the power-law form of $\rho(T) = \rho_0 + AT^n$. As shown in Fig. 2(e), the residual resistivity ρ_0 decreases with increasing pressure for $P < P_c$, whereas it is almost saturated above P_c , indicating that the rapid decrease in ρ_0 is closely related to the destruction of the CDW gap. The resistivity temperature exponent n , which is displayed by the square symbols on the right ordinate of Fig. 2(e), is > 2 , which is expected from Landau-Fermi liquids in normal metals. An anomalously large exponent n was also observed in pristine TiSe_2 under pressure, which was ascribed

FIG. 3. Temperature-dependent upper critical field (H_{c2}) of $\text{Cu}_{0.025}\text{TiSe}_2$. Electrical resistivity for the magnetic field applied within ($H \parallel ab$) and perpendicular to the plane ($H \parallel c$) plotted as a function of temperature in (a) and (b), respectively. (c) Temperature dependences of the upper critical field plotted for $H \parallel ab$ (circles) and $H \parallel c$ (squares), obtained from the onset of the superconductivity (SC) transition temperature $T_{c,\text{onset}}$. (d) The anisotropy ratio of the upper critical field ($\Gamma = H_{c2}^{ab}/H_{c2}^c$). Notice that Γ is almost independent of temperature. (e) Upper critical field divided by T_c . The data for $x = 0$ and 0.07 are from Refs. [17,18], respectively. (f) Reduced upper critical field (h) plotted as a function of the reduced temperature (t) and fitted with the linear and square root forms of $h = \alpha_i(1 - t)$ and $h = (1 - t)^{1/2}$, respectively, where the best results are sequentially plotted using solid and dotted lines.

to a phonon-assisted interband scattering mechanism [18]. With increasing pressure, n increases slightly from 3.5 to 3.6 at 0.9 GPa, is sharply reduced to a minimum ($n \approx 2.85$) near 2.3 GPa ($= P_c$), and gradually increases with further application of pressure. We note that a similar pressure dependence of n was observed for pristine TiSe_2 and was explained in terms of the quantum fluctuations associated with the CCDW QCP [18].

The low-temperature resistivities of $\text{Cu}_{0.025}\text{TiSe}_2$ at 3.1 GPa are represented for magnetic fields applied parallel ($H \parallel ab$) and perpendicular ($H \parallel c$) to the ab plane in Figs. 3(a) and 3(b), respectively. As shown in Fig. 3(c), the

upper critical field H_{c2} obtained with the criterion of the onset of SC transition ($= T_{c,\text{onset}}$) increases linearly with decreasing temperature for both field orientations and extrapolates to 1.93 and 3.51 kOe at zero-temperature limit for $H_{c2}^c(0)$ and $H_{c2}^{ab}(0)$, respectively. Although T_c of the Cu-intercalated material increases twice as fast as that of pristine TiSe_2 , its $H_{c2}^{ab}(0)$ is one order of magnitude larger than that ($= 0.22$ kOe) of pristine TiSe_2 . The Ginzburg–Landau coherence lengths can be estimated as $\xi_{ab}(0) = 414 \text{ \AA}$ [$H_{c2}^c(0) = \phi_0/2\pi\xi_{ab}^2(0)$] and $\xi_c = 226 \text{ \AA}$ [$H_{c2}^{ab}(0) = \phi_0/2\pi\xi_{ab}(0)\xi_c(0)$], where $\phi_0 (= 2.07 \times 10^{-15} \text{ Tm}^2)$ is the quantized magnetic flux [35]. Figure 3(d) shows that the H_{c2} anisotropy ($\Gamma = H_{c2}^{ab}/H_{c2}^c$) of the compound with $x = 0.025$ is ~ 1.6 and is almost independent of the temperature, which is like the Γ (~ 1.7) of $\text{Cu}_{0.07}\text{TiSe}_2$ at ambient pressure [17].

Figure 3(e) shows $H_{c2}^{ab}(T)$ divided by T_c , $H_{c2}^{ab}(0)/T_c$, for pristine and Cu-intercalated TiSe_2 on a semilogarithmic scale. The upper critical field ratio of the Cu-intercalated TiSe_2 was 0.28, 2.21, and 3.42 kOe/K for the pristine, $x = 0.025$, and $x = 0.070$ materials, respectively. Figure 3(f) displays the reduced upper critical field $h = H_{c2}^{ab}(T)/H_{c2}^{ab}(0)$ of the pristine (circles), $\text{Cu}_{0.025}\text{TiSe}_2$ (diamonds), and $\text{Cu}_{0.07}\text{TiSe}_2$ (triangles) as a function of the reduced temperature $t = T/T_{c,\text{onset}}$. Here, $h(t)$ of pristine TiSe_2 is well expressed by the 2D behavior, that is, $h(t) = (1 - t)^{1/2}$. In contrast, $h(t)$ of both Cu-intercalated TiSe_2 shows a t -linear behavior, indicating a crossover from 2D- to 3D-like SC behavior via Cu intercalation [36]. Similar effects have also been reported in the dependence of the c -axis resistivity (ρ_c) on Cu-intercalation level [13,37]. With increasing Cu intercalation, ρ_c rapidly decreases from 40 $\Omega \text{ cm}$ at $x = 0$ to 17 $\Omega \text{ cm}$ at $x = 0.015$, indicating that only a small amount of Cu intercalation has a significant effect on interlayer coupling and, thereby, the dimensional crossover in SC properties.

Figure 4(a) compares the temperature-pressure phase diagram of pristine TiSe_2 (open symbols) and Cu-intercalated $\text{Cu}_{0.025}\text{TiSe}_2$ (solid symbols) systems. In both compounds, T_{CDW} is gradually suppressed under pressure and extrapolates to zero temperature at 3.0 and 2.3 GPa for the pristine and $x = 0.025$ compounds, respectively. Commensurate with the change in T_{CDW} , the pressure-induced SC dome of $\text{Cu}_{0.025}\text{TiSe}_2$ shifts to the lower pressure side and shows a maximum at the projected CDW QCP of 2.3 GPa, indicating the strong correlation between the CDW and SC orders in the TiSe_2 system. Because the minimum of the first derivative of the resistivity of TiSe_2 corresponds to the CCDW transition temperature determined from the high-pressure x-ray scattering experiment [18,19], the CDW QCP in $\text{Cu}_{0.025}\text{TiSe}_2$ could be related to the suppression of the CCDW, supporting that CCDW is related to the SC order, whereas the ICDW behaves entirely independently. We note that these results are inconsistent with SC produced by the hybridization of exciton and phonon modes: the CDW QCP and T_c maximal pressure was predicted to be different in the model [26], while our results show that they occur at the same point. To make a clearer understanding of SC mechanism, more experimental as well as theoretical work on SC gap is required at various intercalation levels.

Figure 4(b) shows an x - P - T phase diagram for CDW Cu_xTiSe_2 superconductors [12,14,17,18]. In the x - T plane

FIG. 4. (a) Temperature vs pressure phase diagram of Cu_xTiSe_2 . The solid and open symbols represent T_{CDW} (squares) and T_c (circles) for the $x = 0.025$ and 0 compounds [18,19], respectively. The dotted line for $x = 0.025$ is an extrapolated phase boundary that ends at 2.3 GPa, the projected charge density wave (CDW) quantum critical point (QCP). (b) Cu intercalation–pressure–temperature (x - P - T) phase diagram representing three datasets: (i) at ambient pressure, T_{CDW} and T_c in the x - T plane, (ii) at $x = 0$, T_{CDW} and T_c in the P - T plane, and (iii) at $x = 0.025$, T_{CDW} and T_c in the P - T plane. The results from previous studies [12,14,17–19] are plotted together with those from this paper. The superconductivity (SC) transition temperature (T_c) is multiplied by 20 for visibility.

at ambient pressure, the CDW ordering temperature is suppressed with Cu intercalation and is projected to 0 K at $x_c = 0.07$, where the SC transition temperature reaches a maximum. The coincidence of the projected CDW QCP and maximum T_c suggests the possibility of CDW-driven SC in TiSe_2 . Like Cu intercalation, the application of external pressure to pristine TiSe_2 , as displayed in the P - T plane at $x = 0$, reveals that the CDW order is completely suppressed at the critical pressure P_c , where the induced SC transition temperature is maximal. Although the separate application of

Cu intercalation and external pressure reveals a close connection between the CDW QCP and SC, it has been argued to be coincidental in the sense that each tuning parameter may produce an SC phase of which the mechanism is different [26]. By contrast, the $\text{Cu}_{0.025}\text{TiSe}_2$ was adjusted using both control parameters simultaneously and succeeded in moving the CDW QCP from 3.0 to 2.3 GPa. Together with the moved QCP, the SC dome is shifted to lower pressure, and the T_c maximum is pinned to the shifted QCP, evidencing that critical fluctuations associated with the CCDW QCP produce the necessary attractive interaction to form SC electron pairs.

In conclusion, we report that the CDW QCP of TiSe_2 can be adjusted via the simultaneous application of Cu intercalation and physical pressure. The CDW transition temperature of Cu-intercalated Cu_xTiSe_2 ($x = 0.025$) decreases with increasing pressure and is terminated near 2.3 GPa, the optimal pressure (P_c) at which T_c is the maximum. The upper critical field of the Cu-intercalated compound is 3.51 kOe, 16 times larger than that of the pristine compound, and its temperature dependence changes from a square root form for the pristine compound to a linear one for $x = 0.025$, indicating a crossover from 2D- to 3D-like SC behavior via Cu intercalation. Control of SC dome via the tunable CDW QCP in Cu_xTiSe_2 is like the f -electron-based AFM superconductor CeRhIn_5 , where the SC dome is pinned to the moved AFM QCP via Sn doping [38]. In addition, our finding that the SC dome of TiSe_2 is shifted along with CDW QCP suggests the possibility of a class of strongly correlated SC systems where SC and CDW are intertwined.

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