Charge Density Wave Orders and Enhanced Superconductivity under Pressure in the Kagome Metal CsV$_3$Sb$_5$

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Superconductivity in topological kagome metals has recently received great research interests. Here, charge density wave (CDW) orders and the evolution of superconductivity under various pressures in CsV$_3$Sb$_5$ single crystal with V kagome lattice are investigated. By using high-resolution scanning tunneling microscopy/spectroscopy (STM/STS), two CDW orders in CsV$_3$Sb$_5$ are observed which correspond to 4a$_1$×1a$_2$ and 2a$_1$×2a$_2$ superlattices. By applying pressure, the superconducting transition temperature $T_c$ is significantly enhanced and reaches a maximum value of 8.2 K at around 1 GPa. Accordingly, CDW state is gradually declined as increasing the pressure, which indicates the competing interplay between CDW and superconducting state in this material. The broad superconducting transitions around 0.4–0.8 GPa can be related to the strong competition relation among two CDW states and superconductivity. These results demonstrate that CsV$_3$Sb$_5$ is a new platform for exploring the interplay between superconductivity and CDW in topological kagome metals.

1. Introduction

2D kagome lattice consisting of corner-sharing triangles has been studied deeply for a long time due to frustration-driven exotic quantum phases, such as quantum spin liquid state.\cite{1-3} Moreover, owing to the unique structure, kagome lattice can host dispersionless flat bands due to destructive interference and linearly dispersive Dirac energy bands resemble those in honeycomb lattice.\cite{4,5} When taking spin-orbit coupling and magnetization into consideration, many peculiar phenomena can be observed. For instance, large intrinsic anomalous Hall effect associated with massive Dirac/Weyl points in magnetic kagome metal Fe$_3$Sn$_2$ and Co$_5$Sn$_2$S$_2$\cite{6-9} negative magnetoresistance related to chiral anomaly and the observations of characteristic surface Fermi-arcs in Co$_5$Sn$_2$S$_2$\cite{9-11}. Furthermore, the superconductivity in flat bands system and doped spin-1/2 kagome lattice with breaking time-reversal symmetry has been predicted.\cite{12,13} However, due to the limitation of novel kagome materials, the studies of superconductivity in kagome systems are scarce.

Recently, topological kagome metal family AV$_3$Sb$_5$ (A = K, Rb, Cs) have attracted significant attention.\cite{14} They have a layered hexagonal centrosymmetric structure with space group P6/mmm (No. 191). The crystal structure of AV$_3$Sb$_5$ is composed of V$_3$Sb$_5$ slabs and A layers stacking along the c-axis (Figure 1a). In the V-Sb slab, the V atoms form 2D kagome layer with one kind of Sb1 atoms occupy the centers of hexagons, and another kind of Sb2 atoms form 2D honeycomb lattice below and above the kagome layer (Figure 1b). Different from other kagome materials, these compounds exhibit superconductivity, and the superconducting transition temperature $T_c$ is 0.93 K for KV$_3$Sb$_5$, 0.92 K for RbV$_3$Sb$_5$, and 2.5 K for CsV$_3$Sb$_5$, respectively.\cite{15-18}
and density-functional theoretical calculations indicate that results of angle-resolved photoemission spectroscopy (ARPES) and muon spin spectroscopy measurements all found no and local moments.[14,15,17,20] On the other hand, high-resolution evidence for the existence of long/short range magnetic order I

Moreover, STM study also found that the topological charge activity in Josephson junctions of K1

Figure 1. Structure, STM topographies, longitudinal resistivity, magnetic susceptibility, and dI/dV spectra of CsV3Sb5 single crystal. a) Crystal structure of CsV3Sb5 and b) the top view of Cs layer and V-Sb slabs. c,d) Constant-current STM topographies taken on the Cs- and Sb-terminated surfaces, respectively (Vc = 500 mV, Ic = 20 pA; Vs = −500 mV, Is = 20 pA). e) Temperature dependence of longitudinal resistivity ρxx (T) at zero field. The insets are enlarged view of ρxx (T) below 5 K and dρ/dT versus T curve. The position of TC,DW is marked by arrow. f) Magnetic susceptibility χ (T) as a function of temperature with ZFC and FC modes at μ0H = 1 T for H || c. Inset: temperature dependence of magnetic susceptibility 4πχ (T) with ZFC and FC modes at μ0H = 1 mT for H // ab. g,h) dI /dV spectra measured without and with 1 T magnetic field on the Cs- and Sb-terminated surfaces, respectively. The dI /dV spectra in (g,h) are measured at 0.6 K with 50 μV modulation.

There is also a proximity-induced spin-triplet superconductivity in Josephson junctions of K1

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2. Results and Discussion

The longitudinal resistivity ρxx (T) as a function of temperature at zero field is shown in Figure 1e. It shows metallic behavior at normal state and an anomaly at TC,DW = 94 K, indicating the appearance of CDW state. There is a remarkably drop in the ρxx (T) curve at low temperature (inset of Figure 1e), corresponding to the superconductivity transition in CsV3Sb5 single crystal. The onset superconductivity transition temperature TC,onset and zero resistivity temperature TC,zero is about 3.46 and 2.5 K, respectively, in good agreement with previous results.[15] As shown in Figure 1f, the magnetic susceptibility χ (T) curves with zero-field-cooling (ZFC) and field-cooling (FC) modes at μ0H = 1 T for H || c do not show any signature of magnetic order in the whole temperature range. In addition, we observe a sharp decline around 94 K in χ (T) curve, further indicating the existence of CDW state. The temperature dependence of magnetic susceptibility 4πχ (T) with ZFC and FC modes at 1 mT for H // ab is shown in the inset of Figure 1f. The determined TC for CsV3Sb5 single crystal is about 2.49 K, very close to the value derived from ρxx (T) curve.

To gain further insight into the CDW orders and superconductivity in CsV3Sb5, we performed low-temperature STM measurements on the CsV3Sb5 single crystal. As shown in Figure 1c,d, there are two typical cleaving surfaces with the Cs layer and the Sb layer, respectively. The superconducting gap can be measured on both these surfaces and can be suppressed by external magnetic field (Figure 1g,h). In the Sb-terminated surface, there are the randomly distributed Cs atoms, and we can also find large Cs-atom-free regions for imaging. Figure 2a shows the high-resolution STM topography taken on the Cs-atom-free region in the Sb-terminated surface. Around the intrinsic defects in the Sb surface, a series of concentric circles
can be observed, they are the quasiparticle-interference (QPI) patterns of the electronic states around Γ point in CsV₃Sb₅ (Figure S2, Supporting Information). The superstructures and stripe-like superlattices can also been seen in Figure 2a. Their periodicities can be indentified in the Fourier-transform (FT) image of the STM topography (Figure 2b,c). The 2a × 2a superstructure is a CDW order and it is related to the magnetization and transport anomaly at T_{CDW} ≈ 94 K.[15,25–27] This CDW order is driven by the Peierls instability characterized by the softening of a breathing phonon mode in the kagome lattice (Figure S3, Supporting Information).[28] This calculated in-plane component of CDW order (2a × 2a superstructure) is consistent with the STM results. It is noted that recent experimental studies indicate there is also a modulation along the c axis, that is, 3D CDW order with 2a × 2a × 2c superlattice.[27,29,30] In addition to 2a × 2a pattern, the STM topography also shows the stripe-like pattern which has 4a × 1a periodicity (Figure 2b,c). This stripe-like superstructure has not been experimentally observed in the cousin compound KV₃Sb₅ and other kagome systems. Its origin still needs further investigations. The dI / dV spectra taken on the defect-free region (Figure 2d) are spatially uniform. According to the band calculations (Figure 2e), the −220 meV peak in the dI / dV spectra corresponds to the van Hove singularity (VHS) of the electronic states at M point, and the dip at −300 meV is related to the Dirac point (DP) in CsV₃Sb₅.[26,31] We note that there is an energy dip located near the Fermi level which may be the CDW gap in this material.

In order to understand the relationship between superconductivity and CDW, we study the temperature dependence of electrical resistivity ρ(T) at various pressures using 7373 as pressure transmitting medium (PTM; Figure 3a). They all show metallic behavior in the whole pressure range. With applying pressure, we found that CDW temperature T_{CDW} gradually shifts to lower temperature (Figure S4, Supporting Information). Here, we only observe the change of CDW transition with 2a × 2a superlattice under pressure in transport measurement. The absence of 4a × 1a CDW transition in ρ(T) curves possibly be related to the small gaped Fermi surfaces (FSs) along Q_{4a} vector. In contrast, the T_{c,onset} increases continuously with increasing pressure and reaches a maximum value ≈ 8.0 K at 0.82 GPa (Figure 3b). Interestingly, the superconducting transition width ΔT_c at 0.41 and 0.82 GPa becomes large and reaches 2.06 and 2.43 K, respectively. In addition, we have also performed the high-pressure measurements on CsV₃Sb₅ single crystal in three independent runs using NaCl as PTM (Figure 3c; Figure S5, Supporting Information). These results show that our experiment is reproducible and reliable. Interestingly, there is a reentering superconductivity when the pressure above 15.32 GPa (Figure 3c; Figures S5 and S6, Supporting Information), the two superconducting domes are also observed in other works, such as LaFe₄As₃−xHₓ (x < 0.53) and CeCu₂Si₂ etc.[32–36]
ρ(T) as a function of temperature at various fields in different runs is presented in Figure S5, Supporting Information. It can be clearly seen that Tc is gradually suppressed by magnetic field. Deviating from the Werthamer–Helfand–Hohenberg theory based on the single-band model, the upper critical field, , has a positive curvature close to Tc (H = 0 T), as shown in Figure 3d. This is similar to the behaviors of both MoTe2[37] and 2H-NbSe2.[38] The upper critical field Hc2 (T) curves in different runs can be well fitted by the formula Hc2 (T) = Hc2(0)[1 − (T / Tc)]1/2, where Hc2(0) is the upper critical field at T = 0 K. Tc is determined at the 50% drop of normal state resistivity. The fitted Hc2 (0) is 6.4 T at 1.07 GPa, which yields a Ginzburg–Landau coherence length ξC(0) = [Φ0/2πHc2(0)] of ~7 nm. The somewhat higher Hc2 (0) indicates the high sample quality of the as-grown CsV3Sb5. The corresponding data obtained at 1.18, 4.34, and 50.71 GPa is also shown in Figure 3d. It should be noted that the Hc2 (0) in different runs is smaller than Pauli limiting field Hπ(0) (1.84 Tc = 8.1, 14.7, 13.87, and 76 T), suggesting that the Pauli paramagnetic effect could be negligible. As shown in Figure 3f, the combined phase diagram of TCDW and Tc provides a clear relation between CDW and superconductivity. The superconductivity coexists with CDW in CsV3Sb5 under ambient pressure. Below 1 GPa, Tc is very sensitive to pressure and increases remarkably by applying pressure, accompanied by a decline of TCDW. This observation suggests that there is a mutually competing interaction between CDW and superconductivity, that is, enhanced Tc is accompanied by strong suppression of CDW order under pressure. Raman spectroscopy measurements found no evidence for the structural phase transition below 10.84 GPa (Figure 3e; Figure S7, Supporting Information), demonstrating the increased Tc at low pressure range cannot arise from structural phase transition. It might be a consequence of the variation in the density of states at the Fermi level under pressure. At ambient pressure, the existence of two CDW states in CsV3Sb5 results in the gap opening over part of the FSs in the direction of the Q1a and 4a vectors. As pressure increases, both of two CDW states are gradually suppressed and the FSs could be restored, accordingly Tc increases. In addition, it should be remarked that Tc continues to increase after the absence of TCDW and its maximum value Tc(onset) reaches ~8.2 K at around 1 GPa. It could be due to the CDW state along Q4a vector direction is not destructed completely by pressure when the 2a × 2a CDW state is fully suppressed, leading to the further increase of Tc until the 4a × 1a CDW state disappeared above 1 GPa. In recent studies,[39] the disappearance of the CDW states could be related to the suppression of Sb2 atoms displacements which is crucial for the stability of CDW states, according to the results of anisotropic compression in high-pressure XRD and the unperturbed electronic structure under this pressure range. On the other hand, the values of ΔTc at 0.4–0.8 GPa become larger than those in other pressure ranges, which is also observed in recent study.[40,41] It might be attributed to the extremely strong competitive interplay among CDW states with 2a × 2a superlattices and superconductivity in CsV3Sb5. When
the pressure is above 1 GPa, $T_{\text{onset}}$ starts to decrease consecutively and reaches 2.07 K at 10.3 GPa. Finally, it disappears completely with pressure up to 13.13 GPa (Figure 3f).

3. Conclusion

In summary, we successfully grow the CsV$_3$Sb$_5$ single crystal using the self-flux method. With applying pressure, the CDW transition at $\approx$94 K under ambient pressure is suppressed gradually and the $T_c$ enhances significantly up to 8.2 K. The observation of two CDW states with $4a \times 1a$ and $2a \times 2a$ superlattices by STM experiment indicates that the broad superconducting transition could be related to the strong competitive relationship between CDW states and superconductivity. Recently theoretical calculation indicates that the nontrivial $Z_2$-type topological band structure remains the same after the CDW transition. The electron–phonon coupling in the CDW phase is too weak to rationalize the superconductivity in CsV$_3$Sb$_5$.\[28\] Thus, the resistivity anomaly/CDW, a nontrivial topological state, and possible unconventional superconductivity are all observed in CsV$_3$Sb$_5$, all contributing to the highly intertopological state, and possible unconventional superconductivity completely with pressure up to 13.13 GPa (Figure 3f).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

Q.W. and P.K. contributed equally to this work. This work was supported by the National Key R&D Program of China (Grant No. 2018YFA0704300, 2018YFE0202600, and 2016YFA0300504), the National Natural Science Foundation of China (Grant No. U1932217, 11974246, 11822412, 11774243, 11784042, 12004250, and 61771234), the National Science Foundation of Shanghai (Grant No. 19ZR1477300), the Science and Technology Commission of Shanghai Municipality (19JC143900 and 20YF1430700), the Beijing Natural Science Foundation (Grant No. 2200005) and the China Postdoctoral Science Foundation (Grant No. 2021M692132). The authors thank the support from CHEM (02161943) and Analytical Instrumentation Center (SPST-AIC10112914), SPST, ShanghaiTech University.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

kagome lattice, charge density wave, high pressure, superconductivity

Received: April 13, 2021
Revised: July 26, 2021
Published online: September 3, 2021

[1] L. Balents, Nature 2010, 464, 199.
[2] T. H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, Y. S. Lee, Nature 2012, 492, 406.
[3] Y. Zhou, K. Kanoda, T.-K. Ng, Rev. Mod. Phys. 2017, 89, 025003.
[4] Z. H. Liu, M. Li, Q. Wang, G. Wang, C. Wen, K. Jiang, X. Lu, S. Yan, Y. Huang, D. Shen, J.-X. Yin, Z. Wang, Z. P. Yin, H. C. Lei, S. C. Wang, Nat. Commun. 2020, 11, 4002.
[5] M. Kang, L. Ye, S. Fang, J.-S. You, A. Levitan, M. Han, J. I. Faco, C. Jozwiak, A. Bostwick, E. Rotenberg, M. K. Chan, R. D. McDonald, D. Graf, K. Kataneczech, E. Vescovo, D. C. Bell, E. Kaxiras, J. van den Brink, M. Richter, M. P. Chimire, J. G. Checkelsky, R. Comin, Nat. Mater. 2020, 19, 163.
