Competing superconductivity and charge-density wave in Kagome metal CsV₃Sb₅: evidence from their evolutions with sample thickness

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(Dated: February 16, 2022)

Recently, superconductivity and topological charge-density wave (CDW) were discovered in the Kagome metals AV₃Sb₅ (A = Cs, Rb, and K), which have an ideal Kagome lattice of vanadium. Here we report resistance measurements on thin flakes of CsV₃Sb₅ to investigate the evolution of superconductivity and CDW with sample thickness. The CDW transition temperature $T_{CDW}$ decreases from 94 K in bulk to a minimum of 82 K at thickness of 60 nm, then increases to 120 K as the thickness is further reduced to 4.8 nm (about five monolayers). Since the CDW order in CsV₃Sb₅ is quite three-dimensional (3D) in the bulk sample, the non-monotonic evolution of $T_{CDW}$ with reducing sample thickness can be explained by a 3D to 2D crossover around 60 nm. Strikingly, the superconducting transition temperature $T_c$ shows an exactly opposite evolution, increasing from 3.64 K in the bulk to a maximum of 4.28 K at thickness of 60 nm, then decreasing to 0.76 K at 4.8 nm. Such exactly opposite evolutions provide strong evidence for competing superconductivity and CDW, which helps us to understand these exotic phases in AV₃Sb₅ Kagome metals.

The recently discovered V-based Kagome metals, AV₃Sb₅ (A = Cs, Rb, and K), have stimulated great interest in the field of condensed matter physics [1–4]. These compounds, consisting ideal Kagome lattice of vanadium coordinated by antimony, show superconductivity with superconducting transition temperatures ($T_c$) of 2.5, 0.92, and 0.93 K for A = Cs, Rb, and K, respectively [2–4]. Besides superconductivity, CDW transitions are revealed in the normal states at $T_{CDW}$ 78–104 K for AV₃Sb₅ by X-ray Diffraction (XRD) and scanning tunnelling microscopy (STM) measurements [2–5]. The angle-resolved photoemission spectroscopy (ARPES) experiments point out a topological surface state with multiple Dirac nodal points close to the Fermi level, suggesting that AV₃Sb₅ can be categorized as topological Kagome metals [11–13].

Furthermore, the STM study revealed a topological charge order in KV₃Sb₅ with chiral anisotropy [5], which may cause the giant anomalous Hall effect and a possibility of unconventional superconductivity [5–6]. Indeed, nodal superconductivity and a pressure-induced double dome superconductivity were found by the ultralow-temperature thermal conductivity and high-pressure resistance measurements in CsV₃Sb₅ [7]. Unconventional strong-coupling superconductivity in these V-based superconductors was also suggested by Josephson STM [8]. Although the penetration depth and nuclear magnetic resonance (NMR) measurements claimed s-wave superconductivity [9] [10], the subsequent ultralow-temperature STM demonstrated both nodal and nodalless gaps for CsV₃Sb₅ with multiple Fermi surfaces [11–12]. The exact locations of the gap nodes still need to be identified. In this context, the Kagome metal AV₃Sb₅ provides a great platform to study the interplay of superconductivity, CDW, and topological band structure.

Previously, the superconducting dome under low pressure has already indicated the competition between superconductivity and CDW in AV₃Sb₅ [7,13–16]. In this Letter, we investigate the evolution of superconductivity and CDW with sample thickness in the mechanically exfoliated CsV₃Sb₅ thin flakes by electrical transport measurement. Two non-monotonic evolutions are revealed, and the one for CDW can be explained by a 3D to 2D crossover around 60 nm. It is striking that the two evolutions are exactly opposite for superconductivity and CDW, demonstrating the competition between them in CsV₃Sb₅.

Single crystals of CsV₃Sb₅ were grown by the self-flux method [8,17]. Thin flakes of CsV₃Sb₅ were prepared by an Al₂O₃-assisted exfoliation method [17]. Al₂O₃ thin film with thickness ranging from 60 to 100 nm was deposited by thermally evaporating Al under an oxygen pressure of 10⁻² Pa on the freshly prepared surface of the bulk CsV₃Sb₅ single crystal. Then the Al₂O₃ film was picked up with a thermal release tape, along with pieces of CsV₃Sb₅ thin flakes separated from the bulk. The Al₂O₃/CsV₃Sb₅ stack was subsequently released onto a piece of polydimethylsiloxane (PDMS) upon heating, with the CsV₃Sb₅ side in contact with the PDMS surface. Next the PDMS was stenciled onto a substrate and was peeled away, leaving the Al₂O₃ film covered with CsV₃Sb₅ thin flakes on the substrate. Figure 1(b) displays an optical image of CsV₃Sb₅ thin flake on Al₂O₃ film supported on a 300 nm SiO₂/Si substrate. Then
The layers consisting ideal Kagome lattice of vanadium coordinated by antimony are separated by the alkali-metal atoms of Cs. The lattice parameters are \( a = b = 5.4949(3) \) Å and \( c = 9.3085(5) \) Å \[1\]. (b) Optical image of a thin CsV\(_3\)Sb\(_5\) flake device. Cr/Au contacts were deposited on the sample through the stencil mask for four-probe measurements. The scale bar is 40 µm. (c) Schematic structure of CsV\(_3\)Sb\(_5\) device and measurement set-up. (d) Atomic force microscopy image of the area marked by the square in (b). The scale bar is 1 µm. (e) Cross-sectional profile of the thin flake along the white line in (d). The step is about 4.8 nm in height which corresponds to five CsV\(_3\)Sb\(_5\) monolayers.

The electrodes were fabricated on the CsV\(_3\)Sb\(_5\) thin flake with direct metal deposition through stencil masks. All the devices were fabricated in an argon atmosphere with O\(_2\) and H\(_2\)O content kept below 0.5 parts per million to avoid sample degradation.

The thickness of the CsV\(_3\)Sb\(_5\) thin flakes was determined by Atomic Force Microscopy (AFM) (Park NX10). The resistance measurements of the thin flakes were performed in a physical properties measurement system (PPMS, Quantum Design) and a \(^3\)He refrigerator. All the loading processes out of the glove box were done within one minute to prevent sample from degradation.

As plotted in Fig. 1(a), CsV\(_3\)Sb\(_5\) consists an ideal Kagome lattice of vanadium coordinated by antimony, with the alkali-metal atoms of Cs intercalated between each layer. The lattice parameters are \( a = b = 5.4949(3) \) Å and \( c = 9.3085(5) \) Å \[1\]. The single crystal can be easily exfoliated to tens of nanometers by using conventional Scotch tape and PDMS films, however such method is difficult to obtain even thinner flakes of CsV\(_3\)Sb\(_5\) sample. With the help of Al\(_2\)O\(_3\), high-quality CsV\(_3\)Sb\(_5\) single crystal can be exfoliated to a few nanometers so that our study can go down to several monolayers. A typical optical image of a CsV\(_3\)Sb\(_5\) thin flake device is shown in Fig. 1(b). Transparent Al\(_2\)O\(_3\) on SiO\(_2\)/Si substrate manifests green because of diffraction. The yellow part on the Al\(_2\)O\(_3\) is the sample area. A standard four-probe method is used in the resistance measurement. The schematic device structure is plotted in Fig. 1(c). The thickness of the sample was determined by AFM in the selected area marked by red box in Fig. 1(b), along the white line which crosses the edge of the sample in AFM image shown in Fig. 1(d). The AFM measurement gives the thickness of this flake is about 4.8 nm (Fig. 1(e)), corresponding to five monolayers.

Temperature dependence of the resistance for CsV\(_3\)Sb\(_5\) thin flakes with various thickness, from bulk single crystal to 4.8 nm. The data are normalized by the values at 290 and 140 K for (a) and (b), respectively. The curves are vertically shifted for clarity. The arrows mark the CDW transition temperature \( T_{CDW} \). For the bulk single crystal, \( T_{CDW} \approx 94 \) K is consistent with previous report \[3\].
Fermi surface topology from 3D to 2D around 60 nm [18]. For bulk CsV$_3$Sb$_5$, $2 \times 2 \times 2$ superstructure [19] and $2 \times 2 \times 4$ [12] superstructure were reported, by means of X-ray diffraction, suggesting 3D CDW. Therefore, the non-monotonic evolution of $T_{CDW}$ with sample thickness in CsV$_3$Sb$_5$ may be also due to a crossover from 3D to 2D around 60 nm. Note that 60 nm is actually quite thick, far from the 2D limit.

Figure 3(a) plots the low-temperature resistance below 5 K, to show the superconducting transitions. The superconducting transition temperature $T_c$ is defined as the 10% drop of the normal-state resistance. It is found that the $T_c$ first increases from 3.64 K in bulk to a maximum of 4.28 K in the 60 nm sample, then decreases to 0.76 K in the 4.8 nm sample. To confirm that the resistance drop in the 60 nm sample is an enhanced superconducting transition, various magnetic fields are applied, as seen in Fig. 3(b). The resistance drop is suppressed with increasing magnetic field, confirming that it is a superconducting transition. The temperature dependence of upper critical field $\mu_0 H_{c2}$ is plotted in the insets of Fig. 3(b). The data can be well fitted by the Ginzburg-Landau (GL) formula $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)(1-(T/T_c)^2)/(1+(T/T_c)^2)$, giving $\mu_0 H_{c2}(0) \approx 1.78$ T. This value is much higher than that of bulk single crystal [7]. It is worthy to note that the superconducting transition become sharper with the decreasing of the sample thickness.

Based on above resistance measurements of CsV$_3$Sb$_5$ thin flakes, the evolutions of $T_{CDW}$ and $T_c$ are plotted in Fig. 4. One can see that $T_c$ shows an exactly opposite evolution, compared with that of $T_{CDW}$. Such exactly opposite evolutions provide strong evidence for competing superconductivity and CDW in CsV$_3$Sb$_5$.

In summary, we investigate the dimensionality effect on superconductivity and CDW of the new Kagome metal CsV$_3$Sb$_5$ by electrical transport measurements. The opposite non-monotonic evolutions of superconductivity and CDW with the sample thickness give strong evidence for competing superconductivity and CDW. The non-monotonic evolution of $T_{CDW}$ with reducing sample thickness can be explained by a 3D to 2D crossover around 60 nm. More theoretical calculations and experimental works are needed to clarify the underlying physics of this kind of competition.

This work was supported by the Natural Science Foundation of China (Grant No. 12034004), the Ministry of Science and Technology of China (Grant No.: 2016YFA0300503), and the Shanghai Municipal Science and Technology Major Project (Grant No. 2019SHZDZX01). Y. F. Guo was supported by the
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