Non-uniform vestigial charge-4e phase in the Kagome superconductor CsV$_3$Sb$_5$

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Pair density wave state and its vestigial charge-4e and 6e superconducting phases have been reported in the Kagome superconductor CsV$_3$Sb$_5$. By treating the charge density waves that are ordered at high temperatures as static backgrounds, we notice that all pair density waves have the same wavevector in the folded 2D Brillouin zone. This wavevector is at a high symmetry point and preserves time-reversal symmetry. The PDW state is thus neither ‘FF’-like nor ‘LO’-like. With this non-degenerate pair density wave, we illustrate the resulting necessity for the vestigial charge-4e phase to be non-uniform. We will also highlight the importance of disorder in stabilizing vestigial phases in a commensurate system.

I. INTRODUCTION

Recently discovered Kagome superconductor CsV$_3$Sb$_5$ (CVS) is a fascinating material for experimental and theoretical research on its exotic charge and superconducting orderings. Multiple commensurate charge density waves have been discovered with the exploration of the time-reversal symmetry. Deep in the superconducting phase, commensurate pair density waves were found in CVS. Recently, vestigial charge-4e and 6e superconducting phases were reported from the Little-Parks oscillation.

In this work, we take an in-depth analysis of vestigial phases. Since charge orderings appear at a much higher temperature than the superconductivity, we treat them as a static background. In the resulting folded Brillouin zone, all PDWs have the same in-plane wavevector. Their out-of-plane wavevectors are unknown but are not crucial for the Little-Parks oscillation on CVS flakes. All PDWs are then the same and are described by a single order parameter $\Delta_Q$. $Q$ is at a high symmetry point: $Q = -Q$, and PDW preserves time-reversal symmetry. This PDW is thus neither ‘FF’-like nor ‘LO’-like.

For vestigial phases, the conventional uniform charge-4e superconducting state $\Delta^{4e} = \Delta_Q \Delta_{-Q}$ requires the two-fold degenerate PDW (i.e. ‘LO’-like state $\Delta_{\pm Q}$). For CVS with a non-degenerate PDW, such a phase does not exist. We will explicitly illustrate this point and propose a non-uniform charge-4e phase, as a composite order between PDW and uniform superconductivity: $\Delta^{4e} = \Delta_0 \Delta_Q$. We will discuss the properties of this phase, as well as ways to detect it. We will also highlight the importance of disorder in stabilizing vestigial superconducting phases in a general commensurate system.

In Sec II, we will focus on the folded Brillouin zone and discuss the properties of the non-degenerate PDW state in CVS. We will illustrate a problem of the sequence of phase transitions that prohibits the conventional uniform charge-4e phase. We will introduce our proposed non-uniform charge-4e phase and discuss its properties. In Sec III, we will discuss the necessity for disorder in stabilizing the vestigial charge-4e and 6e superconducting phases, for a general commensurate system. We will obtain a phase diagram for CVS as a function of disorder and temperature. In Sec IV, we will discuss the connection between our proposed charge-4e phase with the existing experimental results. We will also discuss the possible ways to detect this phase.

II. ANALYSIS

We now briefly review the experimental results on the CDW and vestigial phases in CVS. The first CDW was observed at 94K with 2$a_0$ periodicity in the XY-plane. Its wavevectors, shown as blue dots in Fig.1, preserve the 6-fold rotational symmetry. The second CDW is ordered at 50K with 4$a_0$ periodicity in the XY-plane. It is unidirectional, and its wavevectors are shown as red dots. The CDW ordering temperatures are much higher than the superconducting $T_c \approx 2.8K$.

![Fig. 1: The Bragg peaks from the Kagome lattice structure](image)

Deep in the superconducting phase at 300mK, four additional CDW peaks (black circles at $\pm Q_1, \pm Q_2$) are observed in STM. $\pm Q_3$ is a higher harmonics of the 4$a_0$-CDW.

![Fig. 1: The Bragg peaks from the Kagome lattice structure](image)
same wave vectors are observed in the spatial variation of the superconducting gap magnitude. The peak at \( \pm Q_3 \) is a higher harmonics of the unidirectional CDW, which exists even above the superconducting phase.

The out-of-plane wave vectors remain unclear. For the 2\( a_0 \)-CDW, different out-of-plane periodivities (either two or four lattice spacings) have been reported. The out-of-plane wave vectors for the unidirectional CDW and PDW are unknown. Another important feature is the contradicting results on whether time-reversal symmetry is broken at the 2\( a_0 \)-CDW transition, which is not relevant for this work.

Since the 2\( a_0 \) and 4\( a_0 \)-CDWs are ordered at much higher temperatures than the superconductivity, we should treat them as static backgrounds when analyzing the superconducting phases. That means we need to fold the Brillouin zone according to these CDWs. For the Little-Parks oscillation performed on CVS flakes, out-of-plane wave vectors are not important, and we will neglect them in the following discussions. Discussion on the possible effect of the out-of-plane wave vectors in a 3D crystal can be found in the appendix.

![FIG. 2: Unfolded Brillouin (black line), folded Brillouin zone due to 2\( a_0 \)-CDW (blue line), and folded Brillouin zone due to both 2\( a_0 \) and 4\( a_0 \)-CDW (red line). In the last folded Brillouin zone, PDW (black circle) is located at the corner.](image)

The folded Brillouin is shown in Fig.2. The original BZ is a hexagon, denoted in the solid black line. Let us first fold it according to the 2\( a_0 \) CDW (blue dot). The resulting BZ (blue line) remains to be a hexagon, while its length reduces to half of the original BZ. PDWs (black circles) are now folded onto the edge of the resulting BZ. PDWs at \( \pm Q_1 \) are thus the same, while Q\(_1\) and Q\(_2\) remains different.

Now we further fold the BZ according to the unidirectional 4\( a_0 \)-CDW (red dots). The final BZ (red line) becomes a rectangle, reflecting the rotational symmetry breaking. All four PDWs (originally \( \pm Q_{1,2} \)) are now located at the corner of the BZ, so they are the same. The peak at \( \pm Q_3 \) (dashed red circle in Fig.1), as a higher harmonics of the unidirectional CDW, is now folded to the origin.

In sum, there is a single non-degenerate PDW with a center of mass momenta Q, that satisfies Q = \(- Q\). This is different from the well-studied ‘LO’-like state, where PDW is two-fold degenerate and has opposite center-of-mass momenta. The PDW state in CVS is also different from the ‘FF’-like state since its momentum Q preserves time-reversal symmetry.

![FIG. 3: (Top) Conventional phase diagram hosting vestigial charge-4e phase with degenerate PDW \( \Delta_{\pm Q} \). The blue line is the superconducting transition while the red line is the CDW transition. The remaining symmetry in each phase is included. Depending on the commensurability of the CDW, CDW transition breaks U(1) (incommensurate) or \( Z_m \) (commensurate) symmetry. (Middle) Phase diagram hosting a uniform charge-4e phase with non-degenerate PDW, which is unlikely to achieve. (Bottom) Our proposed phase diagram hosting the non-uniform charge-4e phase \( \Delta_{4e} \) = \( \Delta_0 \Delta_{-Q} \). The complete phase diagram with the charge-6e phase can be found in a later analysis.](image)

The vestigial charge-4e and charge-6e superconducting phases were observed in the Little-Parks oscillation. Let us first analyze the charge-4e phase. In the conventional interpretation, the charge-4e phase is uniform, where \( \Delta_{4e}^i = \Delta_Q \Delta_{-Q} \) is ordered and \( \Delta_{\pm Q} \) is disordered. This understanding requires the two-fold degenerate PDW \( \Delta_Q \) and \( \Delta_{-Q} \). The phase diagram is shown in the top panel of Fig.3 where the blue line is the superconducting transition and the red line is the CDW transition. The remaining symmetry in each phase is included. The superconducting transition is a U(1) symmetry breaking. If the CDW \( \rho_{2Q} = \Delta_Q \Delta_{-Q}^* \) is incommensurate, then its peaks in real space are not pinned.
by the underlying lattice. In this case, CDW transition is another U(1) symmetry breaking. If the CDW is commensurate, then its peaks in real space are pinned by the lattice. In this case, CDW transition is a $\mathbb{Z}_m$ symmetry breaking, if its periodicity is $m$ times the lattice spacing. To host the charge-4e phase, the superconducting transition needs to have a higher $T_c$ than the CDW transition. For incommensurate CDW, this requirement can be satisfied in a clean system, as long as the superconductivity has a larger stiffness. For commensurate CDW, in a clean system, discrete symmetry breaking generically happens at a higher $T_c$ than continuous symmetry breaking. CDW disorder is then needed to suppress the CDW $T_c$, for the charge-4e phase to survive.

In CVS, the above construction becomes exotic, because the PDW $\Delta_Q$ is non-degenerate. One can always define a similar charge-4e phase, where $\Delta_Q^2$ is ordered but $\Delta_Q$ is disordered. But this phase cannot be stabilized. In this phase, U(1) symmetry breaks into a $\mathbb{Z}_2$ symmetry. The phase diagram is shown in the middle panel of Fig.3. To host this charge-4e phase, the continuous U(1) symmetry breaking needs to happen at a higher temperature than the discrete $\mathbb{Z}_2$ symmetry breaking, for the same order parameter. This is unlikely to happen for a clean system. For a disordered spin system, a similar phase diagram is possible, if (temperature-dependent) random-field Ising disorder pins the spin along a particular axis. However, this type of disorder is not allowed for superconductivity due to gauge symmetry.

Now we would like to propose an alternative charge-4e order parameter to handle the issue in the sequence of phase transitions. We will use two independent charge-2e order parameters, with different center-of-mass momenta. In CVS, we can only use the PDW $\Delta_Q$ (with phase $\theta_A$) and the uniform superconductivity $\Delta_0$ (with phase $\theta_B$). Our proposed charge-4e order is thus $\Delta_Q^{4e} = \Delta_0 \Delta_Q$. The resulting phase diagram (bottom panel in Fig.3) is similar to the conventional understanding of degenerate PDW. The superconducting transition is a U(1) symmetry breaking, where $\theta_A + \theta_B$ is ordered. The CDW transition is a $\mathbb{Z}_2$ symmetry breaking, where $\theta_A - \theta_B$ is ordered. Here the periodicity of the CDW is two lattice spacing (with the consideration of the static 2$a_0$ and 4$a_0$ CDW), because of $Q + Q = 0$. To host the charge-4e phase, the continuous U(1) symmetry breaking needs to have a higher $T_c$ than the discrete $\mathbb{Z}_2$ symmetry breaking. This is difficult to achieve for a clean system. However, CDW disorder can suppress the CDW $T_c$ while not suppressing the superconducting $T_c$, allowing the charge-4e phase to survive.

The proposed charge-4e phase breaks translational symmetry, so it is a ‘quadruple density wave’. Whether or not the charge carriers have non-zero momenta is not relevant for the Little-Parks experiments. Just like the PDW state in this system, this charge-4e phase is also neither ‘FF’ nor ‘LO’-like. Its magnitude is a constant in real space, and it preserves time-reversal symmetry.

We now turn to the charge-6e superconducting phase. In the folded Brillouin zone, the order parameter is either $\Delta^{6e}_Q = \Delta_Q \Delta_Q \Delta_Q$ or $\Delta^{6e}_Q = \Delta_Q \Delta_0 \Delta_0$. The former state preserves translational symmetry. The latter state breaks the translation symmetry so it is more exotic. We believe that the former state is the relevant one. It is the same as the conventional constructions in[9]. In the unfolded Brillouin zone, it can be rewritten as $\Delta^{6e}_Q = \Delta_Q \Delta_Q \Delta_Q$, where $Q_i$ are related by three-fold rotation. This conventional construction does not have the same problem as in the charge-4e case, because more than one charge-2e order parameter is used. In this charge-6e phase, $2\theta_A + \theta_B$ is ordered, and the remaining symmetry is $\mathbb{Z}_2$. CVS only has two independent charge-2e order parameters with different center-of-mass momenta. It satisfies the minimal requirement for vestigial superconducting phases. This leads to the following general properties. Suppose the charge-4e and charge-6e phases coexisted, this would allow us to solve for $\theta_A$ and $\theta_B$. So the coexisting phase is exactly the charge-2e superconducting phase at low temperatures. In this phase, PDW is ordered. To induce this non-uniform state, either $\Delta^{4e}$ or $\Delta^{6e}$ have to be non-uniform. In CVS, it is the charge-4e order that carries the non-zero momentum. For completeness, we list all induced orders in CVS from the coexistence of charge-4e and charge-6e orders:

$$
\rho_Q = \Delta_0^{6e,\ast} \Delta_0^{6e,\ast} \Delta_Q^{4e} \Delta_Q^{4e} + c.c.
$$
$$
\Delta_0 = \Delta_0^{6e,\ast} \Delta_Q^{4e} \Delta_Q^{4e} + c.c.
$$
$$
\Delta_Q = \Delta_Q^{6e} \Delta_Q^{4e} + c.c.
$$

\begin{align*}
\text{Charge-2e} & \quad \text{Charge-4e} & \quad \text{Charge-6e} & \quad \text{Normal} \\
(\Delta_Q) & \neq 0 & (\Delta_Q) & = 0 \\
(\Delta_0) & \neq 0 & (\Delta_0 \Delta_Q) & \neq 0 \\
0 & \mathbb{Z}_2 & \mathbb{Z}_2 & \mathbb{Z}_2 \times U(1)
\end{align*}

FIG. 4: The sketched phase diagram as a function of temperature, at a fixed disorder strength. The Blue solid line is the continuous superconducting transition. The red solid line is the continuous CDW transition. The double solid line is a first-order phase transition. The remaining symmetry in each phase is included.

The relevant phase diagram following the Little-Parks experiment in[9] is shown in Fig.4. Single solid lines denote the continuous phase transitions, while double solid lines denote the first-order phase transitions. The remaining symmetry in each phase is included. Here, in the normal state, the 2$a_0$ and 4$a_0$-CDWs are already ordered.

We will now go through phase transitions. The superconducting transition from the normal phase to the charge-6e phase breaks U(1) symmetry, and $\Delta^{6e}_Q = \Delta_Q \Delta_Q \Delta_0 \Delta_0$ is ordered. The CDW transition from the charge-4e to the charge-2e phases breaks the $\mathbb{Z}_2$ symmetry, where the commensurate CDW $\rho_Q = \Delta_0 \Delta_Q$ is
ordered. For the phase transition between the charge-6e and charge-4e phases, we believe that a direct first-order phase transition is the most possible scenario. An alternative scenario is an intermediate coexisting phase. Since the coexisting phase is exactly the charge-2e phase at low temperatures, it is unlikely to reappear at a higher temperature.

In this section, we already highlighted the importance of CDW disorder in stabilizing the vestigial superconducting phases in a general commensurate system. The complete phase diagram with disorder strength can be found in the next section.

III. DISORDER EFFECT

In this section, we will focus on the effect of CDW disorder. The sketched total phase diagram under temperature and disorder strength is shown in Fig. 5. The red solid line marks the CDW $T_c$ while the blue solid line marks the superconducting $T_c$. At zero disorder, discrete symmetry breaking generically has a higher $T_c$ than continuous symmetry breaking, so the vestigial phase is the CDW phase. As disorder increases, CDW is suppressed and the competing superconductivity is effectively enhanced. For sufficiently strong disorder, the superconducting $T_c$ can be higher than the CDW $T_c$. This leads to the vestigial superconducting phase. In this phase diagram, we assumed that the system is 3D. For 2D systems, commensurate CDW does not develop long-range ordering under disorder. In that case, the CDW transition line turns into a cross-over line, describing CDW short-range ordering.

The crossing between the two phase transitions could be a tetracritical point (which is used in this phase diagram). Instead, multiple bicritical points are also possible for the crossing. The nature of the crossing depends on microscopic and does not affect the following discussions on the vestigial superconducting phases.

We now focus on the phase transition between the charge-4e and charge-6e phases. As mentioned in the previous section, the coexisting charge-4e and charge-6e phase is exactly the charge-2e phase at low temperatures, where the charge density wave $\rho_Q$ is ordered. CDW disorder thus suppresses the coexisting phase. This feature will not appear if both charge-4e and charge-6e phases are uniform. Here we present the minimal Landau Ginzburg Wilson theory to describe the effect of CDW disorder. The free energy density is:

$$f(r) = \frac{u_{4e}}{2}|\Delta_{4e}^c|^2 + \frac{k_{4e}}{2}|\nabla\Delta_{4e}^c|^2$$

$$+ \frac{u_{6e}}{2}|\Delta_{6e}^c|^2 + \frac{k_{6e}}{2}|\nabla\Delta_{6e}^c|^2 + \text{higher order terms}$$

$$+ [h(r) + c.c.] + U(|\rho|^2 - \rho^2)$$

$$\rho \equiv (\Delta_{4e}^c)^2(\Delta_{6e}^c)^2$$

, where the CDW $\rho$ is explicitly induced by the coexistence of the charge-4e and 6e superconductivity. As a commensurate CDW, the underlining lattice structure imposes a pinning potential $U > 0$, making $\rho$ a $\mathbb{Z}_2$ Ising field. The random-field CDW disorder $h(r)$ is assumed to be local: $h(r) = 0$, $h(r)h(r') = h^2\delta(r - r')$. $\langle \cdots \rangle$ denotes the configurational average.

Fig. 5: The sketched phase diagram as a function of temperature and CDW disorder strength. Single solid lines are continuous phase transitions, and double solid lines are first-order phase transitions. The remaining symmetry in each phase is included. In the normal phase, 2$a_0$ and 4$a_0$-CDWs are well-ordered.

Let us assume that the charge-4e and 6e superconductivity could coexist in a clean system. Suppose the charge-4e superconductivity is stronger, then $\Delta_{6e}$ is locked to be an Ising field relative to $\Delta_{4e}$ by the lattice pinning potential. The CDW disorder effectively becomes a random-field disorder coupled to $\Delta_{6e}$ (or more precisely, to $(\Delta_{6e})^2$). Sufficiently strong CDW disorder will then suppress the $\Delta_{6e}$ order, therefore, suppressing the coexisting phase. This will lead to a first-order phase transition between the charge-4e and 6e phases at strong disorder, denoted as the double solid lines.

The first-order phase transition cannot go beyond the vestigial superconducting phase. So it has to end at either the red line or the blue line, resulting in a bicritical point (black dot). Since the critical point is located at a relatively weak disorder, it is likely to be at the red line, where the charge-4e and charge-6e phases can then coexist. A bicritical point at the blue line is not forbidden, but it would require the disorder to favor one of the vestigial superconducting phases over another.

Experimentally, both the charge-4e and charge-6e phases are observed. The corresponding CDW disorder strength is marked by the dashed arrow, which can then recover the previous phase diagram in Fig. 4.

IV. DISCUSSION

We now turn to experimental signatures of the non-uniform charge-4e phase. In the Little-Parks
experiment\cite{1} the charge-4e phase is found to be less robust than the charge-6e phase, in terms of the amplitude of resistivity oscillation. This is exotic since the charge-4e phase is located at a lower temperature. In our proposal, the charge-4e phase is non-uniform while the charge-6e phase is uniform, which naturally provides a possible explanation for the above feature.

It would be important to have a more direct probe on the quadruple density wave $\Delta_Q$. Since it is neither 'LO'-like nor 'FF'-like, it does not have those well-known features, making it difficult to distinguish from a uniform charge-4e phase. For example, the quadruple density wave phase does not host any CDW (like $\rho_Q$), and it does not have the superconducting diode effect. The phase-sensitive measurement will thus be crucial to verify it, and we propose the following measurements based on the proximity effect. When putting the quadruple density wave next to a uniform charge-2e superconductor, it will induce a PDW order $\Delta_Q = \Delta_Q^{(2)}e^{i\pi}$, as well as a CDW order $\rho_Q = \Delta_Q^{(4)}e^{i\pi}$. These can be captured in STM. An indirect probe for the quadruple density wave is to examine the low-temperature charge-2e phase. Since the charge-4e order is non-zero in the charge-2e phase, the PDW and the uniform charge-2e order can mutually induce each other through the term $\Delta_Q^{(2)}\Delta_Q^{(4)}$ in GLW theory. Consequently, the PDW and uniform charge-2e order must always coexist. Checking the lack of split transitions in the charge-2e phase will then indirectly verify the quadruple density wave $\Delta_Q$.

Since the three-fold rotational symmetry has been broken at high temperatures, it becomes irrelevant in the above discussion of vestigial phases. However, it is worth distinguishing the lack of split transitions from a similar one in systems under six-fold rotational symmetry. If $Q_{1,2,3}$ are related by three-fold rotation, then the following PDWs can induce a uniform charge-2e order: $\Delta_0 = \Delta_Q, \Delta_{Q_2}, \Delta_{Q_3}$. However, the reverse is not true, and a purely uniform charge-2e phase is allowed. If the uniform charge-2e component is dominant (like in CVS\cite{2}, such a phase is expected to appear, leading to a split transition.

Our analysis is for the Little-Parks oscillation on CVS flakes, where out-of-plane momenta play little role. For a 3D crystal, whether or not PDW is degenerate remains unknown, since the out-of-plane wavevectors of PDW are not reported. Some preliminary analysis for 3D crystal can be found in the appendix, where we listed the requirements for PDW to be non-degenerate.

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**Appendix A: Explicit check on the in-plane wavevectors**

In this section, we will explicitly check the in-plane wavevectors of the PDW. For PDW at $Q_1$ and $-Q_1$, the difference in their wavevectors is equal to three times the $2a_0$ CDW wavevectors, shown as the blue arrows. For PDW at $Q_1$ and $-Q_2$, the difference in their wavevectors is equal to three times the $4a_0$ CDW wavevectors, shown as the red arrows.

To have the non-uniform charge-4e phase, the opposite momenta $\pm Q_1$ needs to be folded into the same point. This does not rely on the existence of the $4a_0$ CDW.

**Appendix B: The effect of the out-of-plane wave-vectors**

In the main text, we focused on the Little-Parks oscillation on CVS flakes, where out-of-plane wave vectors are not important. In this section, we are going to study the effect of the out-of-plane wave vectors on a 3D crystal.

As the out-of-plane wave vectors are included, PDW could become degenerate. Since we do not know any
FIG. 6: How to match the in-plane wave-vectors. The red arrow denotes the 4$a_0$-CDW, while the blue arrow denotes the 2$a_0$-CDW.

information about the out-of-plane wave vectors for the PDW, there is very little we can check. Here, we are going to study the simplest scenario, where PDWs have zero out-of-plane wave vectors, and the out-of-plane wave vector of the 4$a_0$-CDW is also assumed to be zero. Then the mismatch on the out-of-plane wave vectors can only come from the 2$a_0$-CDW.

Now suppose PDW $Q_1$ and $Q_2$ have a mismatch in the out-of-plane direction: $Q_1 - Q_2 = \sum_a P_a + \delta_z$. Here $\sum_a P_a$ is a linear combination of the 2$a_0$ and 4$a_0$-CDWs that matches in-plane momenta. $\delta_z$ is the mismatch in the third dimension.

If the out-of-plane periodicity of the 2$a_0$-CDW is two times lattice spacing, then this mismatch can only be $\delta_z = \pi$. It is easy to remove the mismatch, by adding another three 2$a_0$-CDWs: $P_1 + P_2 + P_3$ to the above linear combination. Here $P_{1,2,3}$ are related by the three-fold rotation. Adding $P_1 + P_2 + P_3$ does not change the in-plane wave-vectors, but it changes the out-of-plane wave-vector by $\pi$. We then get $Q_1 - Q_2 = \sum_a P_a + (P_1 + P_2 + P_3)$, i.e. $Q_1$ and $Q_2$ are still the same point in the folded Brillouin zone. And the PDW is still non-degenerate.

If the out-of-plane periodicity of the 2$a_0$-CDW is four times lattice spacing, then this mismatch can be $\delta_z = \pi/2$, $\pi$, or $3\pi/2$. In this case, adding $P_1 + P_2 + P_3$ changes out-of-plane wave-vector by $3\pi/2$. By repeatedly adding $P_1 + P_2 + P_3$, all three possible mismatches can be removed.

If $\pm Q_i$ start with different out-of-plane wave vectors, then they could be folded together under certain conditions: (1) the difference is $\pi$ and the 2$a_0$-CDW has out-of-plane periodicity equal to two lattice spacing. (2) the difference is $\pi/2$, $\pi$ or $3\pi/2$ if the 2$a_0$-CDW has out-of-plane periodicity equal to four lattice spacing. This is the requirement for the charge-4e phase to be non-uniform.