Star-of-David pattern charge density wave with additional modulation in the kagome superconductor CsV$_3$Sb$_5$ revealed by $^{51}$V-NMR and $^{121/123}$Sb-NQR

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Abstract

$AV_3Sb_5$ ($A =$ K, Rb, Cs) is a novel kagome superconductor coexisting with the charge density wave (CDW) order. Identifying the structure of the CDW order is crucial for understanding the exotic normal state and superconductivity in this system. Here, we report $^{51}$V nuclear magnetic resonance (NMR) and $^{121/123}$Sb nuclear quadrupole resonance (NQR) studies on kagome-metal CsV$_3$Sb$_5$. Below the CDW transition temperature $T_{CDW} \sim 98$ K, an abrupt change of spectra was observed, indicating that the transition is of the first order. By further analysing the spectra, we find that the CDW order is commensurate. And most remarkably, we obtain the first experimental evidence that the charge modulation of the CDW order is of star-of-David pattern and accompanied by an additional charge modulation in bulk below $T^* \sim 40$ K. Our results revealing the unconventional CDW order provide new insights into $AV_3Sb_5$.
I. INTRODUCTION

Compounds with kagome or honeycomb lattices provide a rich material base for exploring exotic physical phenomena, including topological electronic states[1], highly frustrated magnetisms[2–4], and quantum spin liquids [5–9]. They are perfect platforms to study the relation between topology, frustration and electron correlation. However, materials with geometrical frustrated lattice showing superconductivity is still very limited.

Recently, a new transition metal family $AV_3Sb_5$ ($A = K, Rb, Cs$) with perfect vanadium kagome-net was found[10]. Angle-resolved photoemission spectroscopy (ARPES), Shubnikov de Haas (SdH) oscillations and density functional theory (DFT) studies categorize $AV_3Sb_5$ into a $Z_2$ topological class with non-trivial topological bands[11, 12]. Furthermore, $AV_3Sb_5$ system was found to be superconducting with $T_c$ range from 0.9 K to 3 K[12, 13]. Above $T_c$, another phase transition exists at 80 K $\sim$ 100 K revealed by magnetic susceptibility and resistivity measurements[10, 13]. Scanning tunneling microscopy (STM), optical spectroscopy and ARPES experiments infer that the phase transition around $T = 80$ K $\sim$ 100 K is a CDW transition[14–21]. In the CDW state, hard X-ray scattering and STM measurements observe a $2a_0 \times 2a_0 \times 2c_0$ superlattice[14, 22–26]. A star-of-David distortion, which was found in the known CDW of 1T-TaS$_2$[27], was assumed in the kagome plane[14, 22, 28]. As the cleavage surface is A or Sb plane, STM measurements can not directly detect the charge modulation in the vanadium kagome plane. Based on the DFT calculations, an inverse deformation to the star-of-David structure, tri-hexagonal pattern, was suggested to be the distorted structure[19, 29, 30]. However, this has not been clarified by any microscopic probe in the kagome plane yet. Moreover, a $4a_0$ charge modulation was suggested to emerge inside the CDW state below $T \sim 60$ K[24, 28]. The additional charge modulation along c-axis was also reported by X-ray scattering studies[30], while not confirmed by other STM and X-ray scattering studies[22, 23].

The existence of the CDW order was further elaborated by experiments under pressure. Transport measurements show that applying pressure can suppress the CDW order and enhance $T_c$ by almost three times in $AV_3Sb_5$[31–34], which makes the pressure-temperature phase diagram resemble many unconventional superconductors[35, 36]. This suggests a close relationship between CDW and superconductivity. This seems to be further supported by the emergence of the pairing density wave in the superconducting state, which might be due to the influence of the CDW order[24]. In the current stage, the structure of the CDW order in $AV_3Sb_5$ is still indistinct, and
identifying it is very important for understanding the origin of the CDW order, and its relation to the superconductivity.

In this work, we have performed $^{51}\text{V-NMR}$ and $^{121}/^{123}\text{Sb-NQR}$ measurements on CsV$_3$Sb$_5$. By studying the spectra at low temperatures, we demonstrate that the CDW order is commensurate, and has the star-of-David type structural distortion. Below $T^* \sim 40$ K, a further line splitting is observed in $^{51}\text{V-NMR}$ spectra, while a line broadening was observed in $^{121}\text{Sb-NQR}$ spectra. This implies the appearance of an additional charge modulation, and further demonstrates the unconventional nature of the CDW order.

II. RESULTS AND DISCUSSIONS

A. Charge density wave order: $^{51}\text{V-NMR}$ results

In the crystal structure of CsV$_3$Sb$_5$ shown in Fig. 1(a), three V atoms consistute one triangle which is corner-shared to other V triangles, forming a perfect V-kagome lattice. In the unit cell, all V sites are equivalent. A magnetic field of $B_0 = 11.997$ T along the $c$-axis is applied for $^{51}\text{V-NMR}$ measurements. The total Hamiltonian under magnetic field is:[37]:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_Q = -\gamma \hbar I \cdot B_0 (1 + K) + e^2 q Q 2I (2I-1)[(3I_x^2 - I^2) + \frac{1}{2} \eta (I_x^2 + I_y^2)]$$  (1)

where $K$ is the Knight shift, $eq = V_{ZZ} = \frac{\partial V^2}{\partial Z^2}$ is the electric field gradient (EFG) along the principle axis and $V$ is the electric potential, $Q$ is the nuclear quadrupole moment, and $\eta = |V_{XX} - V_{YY}|/|V_{ZZ}|$ is the asymmetry parameter of EFG. The nuclear quadrupole resonance frequency $\nu_Q$ is defined as $\frac{3e^2 q Q}{2\hbar(2I-1)}$. $\gamma$ is nuclear gyromagnetic ratio, which is 11.193 MHz/T for the $^{51}\text{V}$ nucleus. Since the nuclear spin $I$ of $^{51}\text{V}$ is 7/2, there should appear seven transition lines. Indeed, the $^{51}\text{V-NMR}$ spectrum at 101.7 K (above $T_{\text{CDW}}$) shown in Fig. 1(b) consists of one central peak and six satellite peaks. With decreasing temperature down to 90.3 K, we find that all NMR lines split into two lines with area ratio around 1:1 as illustrated in the bottom of Fig. 1(b). No spectral weight is lost during the transition. We also note that the splitting of the first low frequency satellite, $\delta f_{\text{satellite}} = 0.0818$ MHz, is different from the splitting of the central peak, $\delta f_{\text{center}} = 0.0842$ MHz, indicating that both magnetic and quadrupole shifts contribute to the observed line splitting. This behavior is the same with the CDW order in YBa$_2$Cu$_3$O$_y$ and Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+y}$ [38, 39], suggesting that a charge modulation occurs at low temperatures. For the one dimensional (1D) incommensurate
CDW order, the NMR spectrum should have two peaks of equal intensities, and most importantly, a continuum between the two peaks[40]. For the 2D or 3D cases, the spectrum should only have one symmetric peak. These features for the incommensurate CDW are not observed in $^{51}$V-NMR spectra, indicating that the observed CDW order is not incommensurate. On the other hand, the
commensurate CDW results in discrete peaks\cite{41}, which is consistent with our observation, proving that the CDW order is commensurate.

To further investigate the CDW evolution, we make a contour plot of the central lines from \( T = 100 \) to \( 90 \) K as shown in Fig. 1(c). Between \( T = 98 \) K and \( 93 \) K, three lines are seen, implying the coexistence of the CDW and a charge-uniform phase. With decreasing temperature, the NMR intensity gradually shifts from the line of the charge-uniform state to the two split lines related with the CDW state. These are the typical features of the first-order transition. We fit the \(^{51}\)V-NMR spectra with Lorentz function to get the resonance frequency \( f \) of central peaks. After subtracting the second-order perturbation from the quadrupole interaction (See Supplementary Materials for additional analysis\cite{42}), we obtain the temperature dependent Knight shift \( K_c \) plotted in Fig. 1(d). The difference of the Knight shift between \( l_1 \) and \( l_2 \) is contributed from the spatial distribution of charge density in CDW phase. The \( l_1 \) and \( l_2 \) lines correspond to the V sites located at low density and high density area, respectively. \( \Delta K \) is defined as the Knight shift difference of two split central peaks, and the results are summarized in Fig. 1(e). \( \Delta K \) abruptly increases to non-zero at \( 98 \) K, again suggesting that the CDW transition is of the first order.

We further measure the temperature dependence of \(^{51}\)V-NMR spin-lattice relaxation rate divided by \( T \), \( 1/T_1 T \) as shown in Fig. 1(f). The \( 1/T_1 T \) decreases with decreasing \( T \) down to around 200 K, but starts to increase towards \( T_{CDW} \). Since Knight shift deceases with deceasing temperatures, the decease of \( 1/T_1 T \) at high temperatures might be due to the band effect as Co or Ni doped BaFe\(_2\)As\(_2\) systems\cite{43, 44}. At low temperatures, the increase of \( 1/T_1 T \) down to \( T_{CDW} \) is due to the CDW fluctuations, which is a characteristic of the CDW order. Below \( T_{CDW} \), \( 1/T_1 T \) is measured at both \( l_1 \) and \( l_2 \) lines, and both are found to decrease with decreasing temperature due to the critical slowing down of CDW fluctuations. In the end, we note that the averaged Knight shift of two split lines is smaller than the extrapolation from high temperature \( K_c \), suggesting a gap opening at partial Fermi surface in the CDW state.

**B. The structure of CDW order: \(^{121}/^{123}\)Sb-NQR results**

Next, we use \(^{121}/^{123}\)Sb-NQR to obtain more information about the structure of the CDW order. There are two types of Sb sites in CsV\(_3\)Sb\(_5\), namely, Sb1 located in the center of vanadium hexagon and Sb2 located above vanadium triangle as shown in Fig. 1(a). Sb has two type of isotopes, \(^{121}\)Sb (\( I = 5/2 \)) and \(^{123}\)Sb (\( I = 7/2 \)). For \(^{121}\)Sb nucleus, NQR spectrum should have two resonance peaks
FIG. 2: (Color online) $^{121/123}$Sb-NQR spectra and illustration of possible CDW patterns. (a) The NQR spectra of $^{121/123}$Sb at 101.5 K (above $T_{CDW}$) and 5.1 K (below $T_{CDW}$). There are five pairs of resonance peaks in spectrum above $T_{CDW}$, marked by five pairs of arrows. Each pair of resonance peaks comes from two types of Sb sites in the crystal structure, namely, Sb1 and Sb2. (b) Close-up of the spectrum between 71 MHz and 79 MHz, corresponding to $\pm 1/2 \leftrightarrow \pm 3/2$ transitions of $^{121}$Sb. Below the CDW phase transition, one resonance peak from Sb2 splits into two peaks marked as Sb2-a and Sb2-b, and the peak from Sb1 shifts to high frequency. (c) and (d) show the star-of-David and Tri-hexagonal patterns, respectively. The black dashed open circles represent V site in the pristine crystal structure. The dark yellow and shallow yellow solid circles represent two types of V sites. The olive and shallow olive solid circles represent two types of Sb1 site. The blue and shallow blue solid circles represent two types of Sb2 sites. The black dashed parallelogram represents the unit cell in the new structure.

corresponding to $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ transitions. For $^{123}$Sb nucleus, NQR spectrum should have three resonance peaks corresponding to $\pm 1/2 \leftrightarrow \pm 3/2$, $\pm 3/2 \leftrightarrow \pm 5/2$ and $\pm 5/2 \leftrightarrow \pm 7/2$ transitions. So total ten lines should be observed in $^{121/123}$Sb-NQR spectrum for CsV$_3$Sb$_5$, which is indeed seen at $T > T_{CDW}$ in the normal state (see Fig. 2(a)). Considering the atomic ratio between Sb1 and Sb2 are 1 : 4, we assign the lower and higher frequency line in each pair corresponding to Sb1 and Sb2, respectively. Figure 2(b) shows the $^{121/123}$Sb-NQR spectrum at $T <$
$T_{\text{CDW}}$. With decreasing temperature, an abrupt change of Sb-NQR spectrum was seen in the CDW state (See Supplementary Figure S4 in Supplementary Materials[42]). Unlike a simple splitting observed in $^{51}$V-NMR spectrum, three lines are observed for two Sb sites. We will show below how to assign different sites and the observed change of Sb-NQR spectrum can be attributed to the star-of-David pattern in the CDW state.

Considering the atomic ratio between Sb1 and Sb2, we can assign that the two peaks around 74 MHz are from Sb2 site and another peak is from Sb1 site. A much larger frequency shift is observed for Sb1 site comparing to Sb2 site. The resonance frequencies of all lines are related to the NQR frequency $\nu_Q$ and the asymmetry parameter $\eta$. From the $^{121/123}$Sb-NQR spectra, we can deduce $\nu_Q$ and $\eta$ as shown in Table. I (the detailed calculation is presented in Supplementary Materials[42]). As the change of structure parameter is less than 1% in the CDW state[10], the main contribution to EFG should be from the unclosed 5$p$ shell of Sb, similar to the case of O site from the CuO$_2$ plane in cuprate high-$T_c$ superconductors[45]. As the principle axis of EFG is along $c$-axis, the observation of 9% increase in $\nu_Q$ and no change in $\eta$ at Sb1 site suggest a strong band renormalization at that Sb1-$p_z$ orbital in the CDW state, which is consistent with ARPES results[21]. However, in contrast to the Sb1 site, $\nu_Q$ of the Sb2 site changes less than 1%, suggesting that the band renormalization of the Sb2-$p_z$ orbital is small. Moreover, $\eta$ increases to 0.1 in the CDW state, implying that a population disparity between Sb2-5$p_x$ and 5$p_y$ orbitals might emerge, like the change of the As-4$p$ orbitals inside the nematic state in iron-based high-$T_c$ superconductors[46, 47]. This has not been captured by ARPES measurements so far. The reason might be that the population disparity between Sb2-5$p_x$ and 5$p_y$ orbitals is small, since $\eta$ only changes slightly. Therefore, experiments with high energy resolution are needed to reveal this feature.

Along with the CDW transition, the star-of-David and tri-hexagonal types, corresponding to breathing phonon mode of the kagome lattice, are proposed to be the possible structures as illustrated in Fig. 2(c) and (d), respectively[14, 29]. The star-of-David type corresponds to the expansion of Sb1 centering V-hexagon and Sb2 centering V-triangle, and vice versa for the tri-hexagon type. Both structures form a $2a_0 \times 2a_0$ superlattice. In both structures, two types of V sites exist with atomic ratio of V1 : V2 site = 1 : 1, which explains why $^{51}$V-NMR central peak splits into two peaks with area ratio of 1 : 1. Besides this, another feature for the proposed structure is that both Sb1 and Sb2 sites should change to two types of sites, namely Sb1/Sb2-a and Sb1/Sb2-b as present in Fig. 2 (c) and (d). The atomic ratio between Sb1/Sb2-a site and Sb1/Sb2-b site should
TABLE I: Experimental results of the quadrupole frequency $\nu_Q$ and the asymmetry parameter $\eta$ of the Sb1 and Sb2 sites. The detailed calculation process of $\eta$ can be found in Supplementary Materials[42]. The unit of $\nu_Q$ is MHz. $\eta$ is a dimensionless parameter.

| $T$  | site | $\nu_Q$ ($^{121}$Sb) | $\nu_Q$ ($^{123}$Sb) | $\eta$ |
|------|------|-----------------------|-----------------------|--------|
| 101.5 K | Sb1 | 71.716 | 43.520 | 0 |
|      | Sb2 | 73.728 | 44.763 | 0 |
| 5.1 K  | Sb1-a/Sb1-b | 78.179 | 47.456 | 0 |
|      | Sb2-a | 73.039 | 44.370 | 0.0974 |
|      | Sb2-b | 73.295 | 44.505 | 0.0991 |

be 1 : 3. In our study, we find that Sb2 peak indeed splits into two peaks with area ratio around 1 : 3, which is consistent with both star-of-David and tri-hexagonal patterns. In principle, two peaks with area ratio 1 : 3 should also be observed for Sb1 site. As the six V atoms are very far from the Sb1 site, the difference between Sb1-a and Sb1-b site could be very small, making them indistinguishable in the NQR spectrum (see Fig. 2(b)).

However, we note that the $\nu_Q$ of Sb2-a is smaller than that of Sb2-b. For the star-of-David type structure, the average distance between Sb2-a and its nearest V atoms is longer than that between Sb2-b to its nearest V atoms. With the smaller distance between the V atom to the Sb atom, the influence to the local electron distribution of Sb site will be larger. This means that the EFG at Sb2-b site should be stronger than that at Sb2-a site. Therefore, the $\nu_Q$ of Sb2-b should be larger than that of Sb2-a, which is consistent with our results (see Fig. 2(b) and Table I). On the contrary, the EFG at Sb2-a site should be stronger than that at Sb2-b site for the tri-hexagonal type structure distortion, leading to the $\nu_Q$ of Sb2-a larger than that of Sb2-b. So our results provide the direct evidence for the star-of-David structural distortion in the CDW state. Our observation is in contrast to the recent reports by combining DFT calculation with ultrafast pump-probe reflectivity experiments[19], STM microscopy images[29] and quantum oscillation measurements[30], in which the tri-hexagonal type structure distortion was suggested. In these studies, the electron correlation effect is not considered in the DFT calculation. Therefore, our results suggest that the electron-electron interaction should be considered for understanding the CDW forming mechanism.
C. Additional charge modulation inside the CDW state

FIG. 3: (Color online) Evidence for the additional charge modulation inside the CDW state. (a) Central peaks of $^{51}$V-NMR spectra at various temperatures below $T = 60$ K. (b) Temperature-dependent full width of half maximum (FWHM) of all Sb sites. The FWHM of both sites start to increase below $T^* \sim 40$ K marked by the black arrow.

Inside the CDW state, we further find another charge modulation at lower temperatures. As shown in Fig. 3(a), two central peaks of the V site further split into four below $\sim 40$ K. Such further splitting is ten times smaller than the main splitting. So in a less clean sample, only a line broadening can be seen (see Supplementary Figure S7 in Supplementary Materials[42]). By comparing the central lines at different fields, we show that the further splitting is mainly contributed from the Knight shift difference (see Supplementary Figure S8 in Supplementary Materials[42]). The magnetic field is applied along the $c$-axis, which does not introduce any additional symmetry breaking force. Thus, the further splitting observed in $^{51}$V-NMR central lines is due to the emergence of a new charge modulation on top of the star-of-David pattern CDW order. This additional charge modulation is further supported by the increase of FWHM of all Sb sites below the same characteristic temperature $T^*$ as shown in Fig. 3(b). The Sb-NQR line width is much broader than the $^{51}$V-NMR linewidth, so only a line broadening is observed here. Note that the amplitude of this modulation is very small, which can explain why such additional charge modulation was not observed in some STM and X-ray scattering measurements[22, 23].

There are several charge modulation patterns that can be compatible with our NMR data, such as the $4a_0$ [24, 28], $4c_0$ [30] and checkboard patterns as shown in Fig. 4. In this work, we can not distinguish which is the right pattern. But we note that the breaking of the in-plane rotational
FIG. 4: (Color online) **Illustration of possible CDW patterns below** $T^*$. $4a_0$, $4c_0$ and checkboard charge modulations compatible with the NMR spectra under the background of star-of-David type lattice distortion are shown in (a), (b) and (c), respectively. The grey level represents the charge density.

symmetry was observed by measuring $c$-axis resistivity with the in-plane rotation of magnetic field[49]. This suggests that the $4a_0$ pattern which breaks the rotational symmetry, is more likely. The $4a_0$ pattern was also reported by STM measurements[24, 28]. As STM can only obtain the images of surfaces, this $4a_0$ pattern was suggested to be due to electron correlations related to the surface instability and electron-phonon interaction[29]. In contrast, NMR detects bulk information, so our results suggest a possible $4a_0$ pattern in bulk, forming the nematic order. Especially, we have noticed that the in-plane anisotropy of the magnetoresistance was observed in the superconducting state, suggesting the twofold feature of superconductivity[48, 49]. Therefore, intertwining between nematicity and superconductivity should be considered for further investigation of the pairing mechanism in CsV$_3$Sb$_5$.

**III. CONCLUSION**

We have performed NMR and NQR measurements on the kagome superconductor, CsV$_3$Sb$_5$. Below the CDW transition temperature $T_{CDW} = 98$ K, the abrupt changes of both $^{51}$V-NMR and
$^{121/123}$Sb-NQR spectra indicate that the CDW transition is of the first order. By analysing the spectra in the CDW state, we show that the structural distortion is of the star-of-David type, which is in contrast with DFT calculations. This implies that electron correlations should be considered for modeling this system. Below $T^* \sim 40$ K, we further find an additional splitting of $^{51}$V-NMR lines and broadening of $^{121}$Sb-NQR lines, implying the appearance of an additional charge modulation on top of the star-of-David type CDW. All these show that the CDW order in CsV$_3$Sb$_5$ is very unique which will be important in the future exploration of the relationship between CDW and superconductivity.

*Note Added: During the preparation of this manuscript, we are aware of reports of the commensurate CDW and the first-order CDW transition [50, 51] in CsV$_3$Sb$_5$, which are consistent with our results.*

**Methods**

**Samples**

Single crystal CsV$_3$Sb$_5$ was synthesized by self-flux method [10]. The typical size of the single crystal is around 3 mm×2 mm×0.1 mm. $T_c$ was determined by DC susceptibility measured by a superconducting quantum interference device with the applied field 1 Oe parallel to the $c$-axis (see Supplementary Figure S1 in Supplementary Materials[42]). $T_c$ is close to 3.5 K which is among the highest values for this compound, indicating its high quality.

**NMR and NQR measurements**

$^{51}$V-NMR experiments were performed on one single crystal sample at a fixed magnetic field along the $c$-axis. The spectra were obtained by adding Fourier transforms of the spin-echo signal recorded for regularly spaced frequency values. $^{121/123}$Sb-NQR spectra were measured on a collection of $\sim 50$ single crystals by sweeping the frequency point by point, and integrating spin-echo intensity. Given the principle axis of EFG of $^{121/123}$Sb along the $c$-axis, we arrange the CsV$_3$Sb$_5$ single crystal flakes along the $c$ direction, ensuring the radio-frequency field $H_1$ in the $ab$ plane.

**Data Availability**

The data that support the findings of this study are available from the corresponding authors upon reasonable request.
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Author contributions

J. Luo and Z. Zhao contributed equally to this work. The single crystals were grown by Z.Z., H.T.Y. and H.J.G. The NMR measurements were performed by J.L., Z.Y.Z., J.Y., A.F.F. and R.Z. R.Z. and G.-q.Z. wrote the manuscript with inputs from J.L. All authors have discussed the results and the interpretation.

Competing Interests

The authors declare no competing interests.

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