Microscopic nature of the charge-density wave in kagome superconductor RbV$_3$Sb$_5$

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The recently discovered vanadium-based kagome metals AV$_3$Sb$_5$ (A = K, Rb, Cs) offer the possibility to study the interplay between competing electronic orderings, such as charge density order and superconductivity. We focus on the former and provide a comprehensive set of $^{51}$V, $^{87}$Rb, and $^{121}$Sb magnetic resonance measurements on an RbV$_3$Sb$_5$ single crystal. Elucidating the symmetries and properties of the CDW phase is essential to understanding the unconventional electronic orderings occurring in this material. We establish the structure of the $2 \times 2 \times 2$ superlattice that describes the system below the charge density wave transition by combining both experimental and computational methods, with a methodology that can be readily applied to the remaining compounds of the same family. Our results give compelling evidence that the CDW structure occurring below 103 K for RbV$_3$Sb$_5$ is the so-called Inverse Start of David pattern $\pi$-shifted along the c axis (also known as staggered tri-hexagonal).

Over the last years, kagome materials have attracted widespread interest in the field of condensed matter due to the possibility of studying the ground and excited states that emerge from the interplay between a frustrated geometry of the crystalline structure and a nontrivial band topology [1–13]. In this context, the vanadium-based kagome materials AV$_3$Sb$_5$ (A = Rb, Cs, K) [14–17] are of particular interest owing to the recent discovery of a superconducting ground state below $T_c \sim 0.9 - 2.5$ K. In addition to the low temperature superconducting transition, these systems undergo a Charge Density Wave (CDW) transition at a temperature $T_{CDW} \sim 80 - 104$ K [15, 16, 18, 19]. ARPES combined with DFT suggests that the specific order of the CDW is cation-dependent [20]. Scanning tunneling microscopy (STM) and Muon spin spectroscopy ($\mu$SR) observed a chiral charge order that breaks time-reversal symmetry [19, 21–23], which leads to the anomalous Hall effect even in the absence of magnetism of electronic origin [17, 24]. The CDW order plays a central role in the definition of the superconducting gap structure [25] and has therefore been a matter of great attention.

In this work, we focus on RbV$_3$Sb$_5$ and unambiguously identify the ground state structure below the CDW transition. At room temperature, RbV$_3$Sb$_5$ has a layered structure (henceforth Pristine) structure with hexagonal symmetry (space group P6/mmm, No. 191), as shown in Fig. 1a. It consists of Rb layers and V-Sb slabs alternated along the c axis, and it is isostructural to KV$_3$Sb$_5$ and CsV$_3$Sb$_5$ [15]. The most important feature of this material is the two-dimensional (2D) kagome layer formed by the V atoms (Fig. 1b), whose 3$d$ orbitals give rise to a number of peculiar features in the electronic band structure extensively described in literature [18, 26]. One of the key features is the occupation of van Hove singularities close to the Fermi energy, and the Sb $p$-orbitals have also been suggested to play a crucial role in completing the description of the three Van Hove singularity structures [27].

For $T > T_{CDW}$, the high-temperature phase contains two inequivalent Sb sites: Sb1 sites are co-planar with V, while Sb2 sites are located off-plane below and above the V layer. Sb1 sits in the center of V hexagons while Sb2 prospectively falls in the center of V triangles, forming graphene-like hexagon layers.

In the CDW state, below $T_{CDW} = 103$ K, the lattice undergoes a structural transition. First-principles calculations initially proposed two possible distortions for the arrangement of the kagome planes. One is the Star-of-David (SD) distortion (Fig. 1b) of V atoms, which resembles the well-known motif of the CDW state found in transition-metal dichalcogenides [28, 29]. The other is an inverse deformation of the SD pattern (ISD, Fig. 1c). This results in a periodic arrangement of V atoms in triangles and hexagons which is also called Tri-Hexagonal (TrH) structure.

Regarding the stacking along the c axis, different arrangements have been proposed: i) repetition of SD or ISD (Fig. 1b and c), ii) alternation of ISD and SD, iii) a $\pi$-shift translation between adjacent planes (SD-$\pi$ and ISD-$\pi$, Fig. 1d and e). The overall distortion must therefore be described in, at least, a $2 \times 2 \times 2$ supercell. Higher order modulations have been observed in the Cs variant only, but they manifest in a competing state nearly degenerate with a $2 \times 2 \times 2$ phase.

Table I summarizes the currently proposed CDW structures, as they are identified by different techniques for each compound of the family, showing that the attribution is still highly controversial and possibly material dependent. Actually, the identification of the precise CDW configuration and symmetries is crucial to give the proper basis for theoretical modeling of the exotic orders predicted for this family compound [30].

In this work, we resolve this controversy for RbV$_3$Sb$_5$ by combining $^{51}$V/$^{87}$Rb NMR and $^{121}$Sb NQR measurements with Density Functional Theory (DFT) calculations unambiguously identifying the crystalline structure of the CDW phase.

To this aim, $^{51}$V/$^{87}$Rb nuclear magnetic resonance (NMR) spectra have been collected on a single crystal of RbV$_3$Sb$_5$
FIG. 1: (Color online) The crystalline structure of RbV₃Sb₅, above and below $T_{\text{CDW}}$. a) The pristine phase adopted above $T_{\text{CDW}}$, with the V atoms (in red) forming a 2D kagome lattice. The Sb atoms are divided into two sets: Sb1 (in blue) and Sb2 (in dark green). The Rb atoms are labeled in magenta. b), c), d), e) The four possible structures proposed below $T_{\text{CDW}}$: Star-of-David (SD), Inverse Star-of-David (ISD) or tri-hexagonal, (staggered) Star-of-David and Inverse Star-of-David with \( \pi \)-shift (SD-\( \pi \) and ISD-\( \pi \), respectively). Here, the Sb atoms in the top figures are not displayed for clarity purposes.

TABLE I: Charge-density wave structures ($T < T_{\text{CDW}}$) for AV₃Sb₅ ($A = \text{Cs, K, Rb}$) from the literature.

| Phase | Atom Set | Occupation |
|-------|----------|------------|
| ISD-\( \pi \) | CsV₃Sb₅ | N [18, 31], X [32, 33] | A + D [20, 34], A [36] |
| ISD-\( \pi \) | KV₃Sb₅ | S [35], D [34] | X [32], D [20, 34] |
| SD-\( \pi \) | Sb1 | N [18], X [32, 33] | S [35] |
| SD+ISD | Sb1 | X [37], A + D [20, 38] | A + D [38] |
| SD-\( \pi \) | Sb2 | N [39] | / |
| ISD-\( \pi \) | Sb2 | A [41, 42] | A [43] |

Legend: N = NMR, X = XRD, S = STM, A = ARPES, D = DFT.

TABLE II: Atomic occupations for $^{51}\text{V}$, $^{121}\text{Sb}$ and $^{87}\text{Rb}$ atoms in RbV₃Sb₅ above and below CDW transition.

| Phase | Atom Set | Multiplicity |
|-------|----------|--------------|
| Pristine | Rb | 1 |
| | V | 3 |
| | Sb1 | 1 |
| | Sb2 | 4 |
| 2x2x2 CDW (ISD or SD, no \( \pi \)-shift) | Rb1/Rb2 | 6/2 |
| | V1/V2 | 12/12 |
| | Sb1-a/Sb1-b | 2/6 |
| | Sb2-a/Sb2-b | 8/24 |
| 2x2x2 CDW (ISD or SD, with \( \pi \)-shift) | Rb1/Rb2 | 4/4 |
| | V1/V2 | 12/12 |
| | Sb1-a/Sb1-b/Sb1-b* | 2/2/4 |
| | Sb2-a/Sb2-b/Sb2-b* | 8/8/16 |
$^{121}\text{Sb}$ (with nuclear spin $I = 5/2$) NQR measurements are the most sensitive to distinguish between the SD and ISD structures, as already shown for the case of Cs$\text{V}_3\text{Sb}_3$ [31, 40]. Due to the different and lower symmetry of their position, Sb2 and Sb1 nuclei are distinguished into Sb2-a/Sb2-b and Sb1-a/Sb1-b when the SD or the ISD structures are considered, and further separated into Sb2-a/Sb2-b/Sb2-b” and Sb1-a/Sb1-b’/Sb1-b” non-equivalent sites when a $\pi$-shift is introduced, as shown in Fig. 1.

Table III summarizes the $A_0/A_l$ ratio obtained from the area of the NQR peaks and the relative site occupation in the ISD-$\pi$ phase. The values are in very good agreement, within the experimental uncertainty. As a result, we can attribute the bump at around 145 MHz to the combined signal from Sb1-b’ and Sb1-b” sites of the $\pi$-shifted ISD structure, as shown in center of Fig. 2.

Incidentally, we note that the two peaks at the lowest and highest frequencies have been previously assigned to the Sb1-b’ and Sb2-a sites by earlier NQR studies [39, 40]. However, this conclusion is inconsistent with the expected ratio between the area of the two peaks.

To further justify the site assignment, we also collect the $3/2 \rightarrow 1/2$ NQR transition and we estimate the asymmetry parameter $\eta$ of the EFG tensor from the following ratio, valid if $\eta \leq 0.1$ [44, 46, 47]

$$\frac{v_Q^{121}(5/2 \rightarrow 3/2)}{v_Q^{121}(3/2 \rightarrow 1/2)} \approx 2(1 - \frac{35}{27}\eta^2).$$

The experimental values of $\eta$ for Sb sites are compared with the DFT prediction for the ISD-$\pi$ structure in Table IV. Taken together, the above results allow us to unambiguously conclude that the kagome planes undergo an ISD distortion in the CDW phase, according to the crystalline structure (center) and experimental NQR area (right column).

![Image](image_url)
TABLE IV: Comparison between experimental and predicted values for the asymmetry parameter $\eta$.

| Site   | DFT (ISD-$\pi$) | Exp. ($T \approx 77.3$ K) |
|--------|-----------------|--------------------------|
| Sb1-a  | 0               | 0.001 ± 0.005            |
| Sb1-b' | 0.056           | 0.034 ± 0.005            |
| Sb1-b" | 0.058           | 0.034 ± 0.005            |
| Sb2-a  | 0               | 0.001 ± 0.006            |
| Sb2-b' | 0.117           | 0.074 ± 0.006            |
| Sb2-b" | 0.116           | 0.076 ± 0.006            |

[FIG. 3: Temperature dependence of the $^{87}$Rb NMR spectra above and below $T_{CDW} = 103$ K, with $H_0 = 7.95$ T // c axis.

The splitting of all the transition peaks for the $I = 3/2$ is due to the consequence of different electric field gradients and local susceptibilities at the two sites, as detailed in the SM [44]. This behavior is in agreement with the behavior of the $^{51}$V NMR in CsV$_3$Sb$_5$ [18, 31].

As already done for $^{121}$Sb NQR measurements, we consider the relative area between the two NMR peaks of a doublet, which is proportional to the ratio between the multiplicity of the corresponding inequivalent atomic sites. The stacked ISD layer with a $\pi$-shift [31] yields to a 1:1 multiplicity ratio between Rb1 and Rb2 sites. On the other hand, the structures with alternating SD and ISD layers [37] proposed for CsV$_3$Sb5 or stacked of ISD layers without $\pi$-shift yield to a 3:1 ratio [48]. Fig. 3 clearly shows that the ratio between Rb1 and Rb2 peak intensities is nearly equal to 1:1, either for the central or satellite doublets. This result excludes the alternate SD and ISD configuration and is compatible with the stacking made by ISD layers only, $\pi$-shifted from one layer to the other.

Finally, $^{51}$V NMR results are in agreement with the reports already published for $A = Cs$ [18, 31, 40] despite the difference in the spacing layer. Moreover, since the V1:V2 occupation ratio is predicted to be 1:1 for both the SD and ISD structures, this probe is of little interest for our purpose of identifying the CDW configuration of the kagome plane. These results are reported in the SM [44]. In conclusion, we measured the zero-field $^{121}$Sb spectrum and the applied field NMR spectra of $^{51}$V and $^{87}$Rb. The analysis of the NMR/NQR spectra of V, Sb, and Rb nuclei, supported by DFT simulations, allows to unambiguously identify the structure stabilized below the CDW transition occurring at $T_{CDW} = 103$ K. The analysis of the multiplicity of the nonequivalent sites for each species allows identifying the candidate low-temperature structure: a 2×2×2 superlattices formed by alternating Inverse Star-of-David layers, $\pi$-shifted from one to the other.

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