Orbital-Hybridization-Driven Charge Density Wave Transition in CsV₃Sb₅ Kagome Superconductor

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1. Introduction

Spontaneous symmetry breaking is a quintessential concept in condensed matter physics. Landau's theory of phase transition emphasizes the importance of symmetry and links phase transitions to symmetry-breaking phenomena such as superconductivity,[1,2] superfluidity and Bose–Einstein condensation,[3,4] long-range charge density wave (CDW) [5,6] and magnetic transition.[7] Symmetry-breaking phenomena are often found in quantum systems where the complex interplay of charge, spin, lattice, and orbital degrees of freedom takes place.[8,9] Among other macroscopic quantum phenomena, the periodic distortion of the long-range CDW is well-recognized for the role it plays at the atomistic level. Yet the mechanism that underlies its competitive or complementary relationship with unconventional superconductivity [10,11] remains unresolved. Recent reports of exotic chiral orders in the layered kagome Dirac metals, AV₃Sb₅ (A = K, Rb, Cs),[12] are tantalizingly appealing to the research community.
community. With their unique lattice geometry, kagome Dirac metals host a diverse range of exotic properties and topologically nontrivial states, exhibiting giant anomalous Hall conductivity,\[^{13}\] magneto-quantum oscillations,\[^{16}\] topological charge order,\[^{12,13}\] and superconductivity.\[^{16,17}\] Although there are reports of normal-state CDW of the topological chiral charge order \[^{12}\] and diverse superconducting gaps structures in kagome materials,\[^{18}\] the roles of fundamental properties such as Fermi surface nesting,\[^{19}\] electron–phonon coupling,\[^{20}\] and orbital hybridization play in these symmetry-breaking phenomena remain largely unclear. Notably, this interest is further catalyzed by the effects of hybridization between different constituent atomic orbitals and their close association with various quantum phase-transition processes.\[^{21–25}\]

Here we report the direct participation of the V3d—Sb5p orbital hybridization in mediating the CDW transition dynamics in CsV3Sb5. The combination of temperature-dependent X-ray absorption spectroscopy and first-principles studies in this comprehensive study further reveals the inverse Star of David (ISD) as the preferred structure in the CDW phase. Contrary to the conventional view where long-range order is mediated solely by the vanadium atoms,\[^{20,26,27}\] this study unambiguously highlights the pivotal role that the constituent antimony orbitals play on the formation of van Hove singularity structures and the stability of the CDW states in AV3Sb5 systems, through their extensive interaction and the complementary effects between the V- and Sb-atoms on the electronic structures (Figure 1a).\[^{28–30}\] Our study additionally gains importance in light of the recent report where Sb–oxygen covalency contributes to the emergence of superconductivity in antimonates.\[^{31}\] Reciprocal space mappings (RSMs) along the (004)\[^{H}\] and (105)\[^{H}\] orientations (Figure 2b,c, respectively) further confirmed the good crystalline property of the single-crystal sample via the weakly diffusing features B and C from the main peak A.

The presence of the CDW states in the CsV3Sb5 sample is confirmed through the magnetic susceptibility, \(\chi(T)\), where it exhibits a sharp decline at \(\approx 94\) K for \(\mu_0H = 1\) T and \(H_{//ab}\) (Figure 2d).\[^{13,16}\] Temperature-dependent magnetic susceptibility \(4\pi\chi(T)\) under zero-field-cooling (ZFC) and field-cooling (FC) modes at 1 mT for \(H_{//ab}\) (Figure 2e) also confirms the superconducting state in this sample at \(T_C = 2.6\) K.\[^{16}\]

2. Results and Discussion

2.1. Validation of Sample Quality

Layered CsV3Sb5 single crystals were synthesized via a self-flux growth method.\[^{16}\] This class of AV3Sb5 materials exists in both the conventional 1 × 1 hexagonal crystal structure\[^{13}\] and the \(\sqrt{3} \times \sqrt{3} R30^\circ\) reconstruction.\[^{12}\] Figure 1b displays the Scanning tunneling microscopy (STM) topographic image of the Cs-terminated surface which indicates the typical single-unit-cell terrace of \(\approx 9.4\) Å (Figure 1c).\[^{13,33}\] The two unique cleaved Cs surface morphologies along the red dotted lines (Figure 1d) are plotted in Figure 1e where they correspond to the 1 × 1 hexagonal and \(\sqrt{3} \times \sqrt{3} R30^\circ\) structures, respectively.

The very high crystallinity and quality of the CsV3Sb5 sample is further confirmed via high-resolution X-ray diffraction (HR-XRD), in its diffraction pattern and its regular hexagonal structure (Figure 2a).\[^{34}\] Reciprocal space mappings (RSMs) along the (004)\[^{H}\] and (105)\[^{H}\] orientations (Figure 2b,c, respectively) further confirmed the good crystalline property of the single-crystal sample via the weakly diffusing features B and C from the main peak A.

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2.2. Temperature-Dependent X-ray Absorption Spectroscopy Characterization

To investigate the evolving electronic structures and orbital-coupling properties of CsV3Sb5 in temperature ranges near \(T_{CDW}\), the temperature-dependent X-ray absorption spectroscopy (XAS) is conducted to examine how the V3d orbital evolves in this temperature range. The characteristic peaks registered by the XAS measurements correspond to the unoccupied band above the Fermi surface, which is strongly sensitive to lattice symmetry, crystal field splitting, and orbital hybridization.\[^{35,36}\] Figure 3a displays the temperature-dependent V L-edge XAS spectra of the CsV3Sb5 sample over a wide temperature range around \(T_{CDW}\). In the XAS spectra, where should C* (\(\approx 518.2\) eV) and D* (\(\approx 519.2\) and \(\approx 525.6\) eV, respectively) are observed. Feature A* is attributed to the slight hybridization between atomic orbitals while C* and D* are the L2,3-edges representing the V2p1/2/p3/2 \(\rightarrow 3d\) electronic transitions.\[^{37}\] all displaying very weak temperature variation that falls within the experimental error range between 40 and 300 K. While feature C* registers a slight temperature variation, there is no clear temperature-dependent trend that is noticeable. Conversely, we noticed a prominent shoulder B* (denoted by black solid arrow) before the L1-edge displaying very strong and clear temperature-dependent unlike the other aforementioned features in the XAS spectra. To better distinguish the temperature-dependent intensity of the respective features, an intensity differential map, \(\Delta I = \mu(T) - \mu(T_{CDW} = 94\) K), is plotted for the entire temperature range between 40 and 300 K (Figure 3b) with the XAS spectrum at \(T_{CDW} = 94\) K taken as reference. The intensity differential, \(\Delta I\), displays very strong temperature-dependent fluctuation at \(\approx 518.2\) eV where feature B* is located, while remaining largely unchanged in the other spectral regions, especially where the V3d absorption edges are located. These are indications that the V3d orbital does not mediate or participate in the formation of the CDW states alone. Instead,
the strong temperature-dependence of shoulder $B^*$ particularly near $T_{CDW}$ provides strong suggestion to investigate in detail the interaction and hybridization of the V3d orbital with their neighboring electronic bands. Notably, the roles of orbital hybridization in mediating the CDW phase transition are not merely restricted to kagome systems. Instead, the stability and formation of CDW states have also been reported to be mediated by such hybridization effects in multiple systems including 2D transition-metal dichalcogenides and unconventional superconductors, where they instigate the energy band reconstruction that enables the gap opening. This in turn facilitates the formation of the CDW states. Hence, the combination of our study and previous reports attests to the complementary effects of the V- and Sb-atoms in the form of V3d–Sb5p orbital hybridization in dictating the electronic structures and CDW states in AV3Sb5 systems. As we will show later by a combination of temperature-dependent analysis of feature $B^*$ and a series of first-principles studies, it can be deduced that V3d–Sb5p orbital

Figure 1. Structural transition dynamics at $T_{CDW}$ and morphology of the CsV3Sb5 single crystal samples. a) Schematic depiction of the changes in V 3d–Sb5p orbital hybridization strength during the structural transition of CsV3Sb5 from the pristine to the ISD structure at $T_{CDW}$. b) Topographic image (setpoint: $V = -0.1$ V, $I = 30$ pA) of the Cs-terminated terrace to the bottom Sb surface. c) Line profile along the red dashed line in (b). Inset represents the side view of the atomic structure in CsV3Sb5. d) High-resolution STM image of the two main types of cleaved Cs surface morphologies: $\sqrt{3} \times \sqrt{3} R30^\circ$ and $1 \times 1$ (setpoint: $V = 0.1$ V, $I = 50$ pA). e) Line profile along the red dashed line in (d) shows the measured lattice period of $\approx 9.3$ Å belonging to the $\sqrt{3} \times \sqrt{3} R30^\circ$ configuration and the period $\approx 5.4$ Å of the conventional $1 \times 1$ hexagonal structure. Inset shows the atom arrangement of the respective surface structures—$\sqrt{3} \times \sqrt{3} R30^\circ$ and $1 \times 1$. 
hybridization is directly involved in the formation of the CDW states.

Detailed temperature-dependent analysis of feature $B^*$ in the XAS spectra is performed. Figure 3c displays the trend with decreasing temperature from 300 K, where the peak intensity first decreases with decreasing temperature and eventually sharply minimizes at $T_{\text{CDW}} = 94$ K. Below 94 K, the intensity of $B^*$ rises again. A detailed analysis of the intensity evolution of feature $B^*$ is given by segmenting the temperature range into four main temperature regions: Region I ($\approx 140–300$ K), Region II just above $T_{\text{CDW}}$ ($\approx 94–140$ K), Region III just below $T_{\text{CDW}}$ ($\approx 70–94$ K), and Region IV at lowest temperatures ($\approx 30–70$ K).

At high-temperature Region I, the kagome structure is dominated by strong thermal vibrations where effects such as the inter-orbital hybridization and electron–electron correlations are overshadowed by phonon interactions. Unique thermal behavior in the form of lattice vibrations has been reported to take place in kagome materials in this temperature region, which significantly overshadow the orbital hybridization effects.$^{[30,41,42]}$ Conversely, thermal effects and phonon interactions are suppressed at low-temperature (in temperature Region IV below $\approx 70$ K). In this temperature region, the intensity of feature $B^*$ rises continuously to approximately back to its original intensity as temperature decreases to 40 K. The effects observed in temperature Region IV can be attributed to the strong electron–electron correlations associated with another nematic symmetry-breaking order$^{[5,19]}$ dominating in this low-temperature range, which screens the effects of orbital hybridization.

Nevertheless, as we consider temperature Regions II and III that is located close to the CDW transition temperature ($T_{\text{CDW}} = 94$ K), with the temperature decreasing and as it...
approaches $T_{CDW}$ in temperature Region II, feature $B^*$ registers an abrupt intensity drop (approximately gradient: –0.065) and minimizes at $T_{CDW} = 94$ K. Below 94 K in temperature Region III, the intensity of feature $B^*$ then exhibits a rapid upturn with a gradient of $\approx 0.050$ (see inset of Figure 3c). The unique temperature trends in regions II and III near $T_{CDW}$ provide important suggestions for electronic orbital behaviors in mediating the CDW transition.

2.3. Density of States Analysis

To provide further insights into the orbital behaviors between the pristine and CDW states and to better track the transient properties taking place at $T_{CDW}$, detailed first-principles calculations have been conducted. While the kagome lattice is known to be in its conventional pristine structure above $T_{CDW}$, CDW transition is accompanied by a 3D $2 \times 2 \times 2$ lattice reconstruction associated with the movement of the constituent V atoms.\[12,19\] Previous studies have shown that the “Star of David” (SOD) and ISD structures are possible resulting structures below $T_{CDW}$, as they exhibit enhanced structural stability compared to their high-temperature pristine counterpart.\[19\]

Nevertheless, there is no consensus on a preferred structure or if they co-exist in the CDW state.\[26,43\]

Figure 3d presents the contributions from the respective atomic orbitals to the density of states (DOS) of the CsV$_3$Sb$_5$ kagome lattice in its high-temperature pristine state. As expected, the V3d orbital has dominant contribution to the DOS near the Fermi level. Moreover, the Sb5p orbital also plays a pivotal role as evidenced by a much larger contribution to the DOS than the other constituent orbitals. The significant DOS contributions by the V3d and Sb5p orbitals also apply to the low-temperature ISD and SOD structures (see Figure S3, Supporting Information). The domination of the two main electronic states, V3d and Sb5p orbitals, near the Fermi level are therefore clear indications that there is a presence of strong V3d—Sb5p orbital hybridization taking place.

To further confirm the central role that V3d–Sb5p hybridization plays during the CDW transition, the PDOS of the V3d and Sb5p orbitals (Figure 4a,b, respectively) are compared in the pristine, SOD and ISD states. While the PDOS in the pristine and SOD states are almost identical, we note the significant difference in the ISD structure, especially near feature $\sigma$. The variation of the PDOS and the changes in energy positions of feature $\sigma$ in both the V3d and Sb5p orbitals have a direct effect on the hybridization strength. While feature $\sigma$ of both orbitals shifts to higher energies, its intensity in the V3d orbital remains unchanged, and that of Sb5p is enhanced (Figure 4b).

In terms of feature $\alpha$, while the V3d orbital does not show any

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**Figure 3.** Temperature-dependent XAS characterization, density of states (DOS) and partial density of states (PDOS) analyses for different lattice structures of CsV$_3$Sb$_5$. a) Temperature-dependent V L$_{2,3}$-edge XAS spectra, and b) differential XAS spectral intensity ($\Delta \mu = \mu(T) - \mu(T = 94 \text{ K})$) derived from the XAS spectra. c) Temperature-dependent intensity of feature $B^*$ in four separate temperature regions between 300 and 40 K. Inset: Intensity variation of feature $B^*$ in temperature regions II and III located near $T_{CDW}$. d) DOS of pristine state CsV$_3$Sb$_5$ near the Fermi level with PDOS contributions from the atomic orbital constituents of V3d, Sb5p and other orbitals (see Supporting Information for DOS of SOD and ISD structures).
changes in PDOS between different structures (Figure 4a), the PDOS component of the Sb5p orbital in the 0.8–1.2 eV energy range (Figure 4b) displays a very slight but noticeable difference between the pristine and ISD structures. Whereas the α feature of the SOD structure is practically identical to its pristine counterpart. While these differences may be minor, the variation in the PDOS component of the Sb5p orbital may play a role in modifying the V3d–Sb5p hybridization between different structural phases. Meanwhile, the larger contribution by the Sb5p orbital in terms of the σ feature in the PDOS strengthens the V3d–Sb5p hybridization in the ISD structure.

Note that the PDOS of the V3d orbital (Figure 4a) near the Fermi level yields identical features that are experimentally derived from the V L-edge XAS spectrum near 519 eV (Figure 3a). Features α and σ of the V3d orbital PDOS (Figure 4a) are responsible for V L-edge features C* and B*, respectively (Figure 3a). The energy separation of ~0.8 eV between features σ and α in the PDOS calculation is also consistent with the separation between features B* and C* in the V L-edge spectra. It is safe to conclude that the temperature-dependent behavior of feature B* is attributed to the change in feature σ of the PDOS during the CDW transition. Since feature σ of both the V3d and Sb5p orbitals changed under ISD lattice distortion but remains virtually unchanged in the SOD state, the temperature-dependent behavior in the XAS spectra, therefore, indicates pristine-to-ISD lattice at T_{CDW}.

To further investigate how the V3d–Sb5p hybridization evolves during the CDW transition, PDOS of both the V3d and Sb5p orbitals during the intermediate steps of the pristine-to-ISD transition.
Sb5p orbitals are calculated separately as functions of lattice distortion between the pristine (initial) and ISD (final) states (see Supporting Information for the simulation of the pristine-to-SOD transition process). Since the lattice distortion process can be regarded as the straight motion of V-atoms due to space group and symmetric properties,[19] the fractional distortion can therefore be defined as \( \gamma = \frac{d}{d_0} \), where \( d \) represents the V-atom displacement while \( d_0 \) denotes the complete displacement of the V-atom when the final ISD structure is obtained. Figure 4c,d displays the PDOS of V3d and Sb5p orbitals, respectively, at the intermediate states of the pristine-to-ISD transition, depicting how \( \sigma \) evolves due to its association with the temperature-dependent feature \( B^s \) in the XAS spectra. While the intensity of \( \sigma \) changes non-trivially with \( \gamma \) of both the V3d and Sb5p orbitals gradually shifts to a higher energy with increasing \( \gamma \) distortion.

2.4. Tracking the Pristine-to-ISD Structural Transition Process

To better track the evolution of feature \( \sigma \) as a function of \( \gamma \), Figure 4e,f plots its relative intensity and position, respectively, in its intermediate states. For lattice distortion \( \gamma \gtrsim 0.6 \), the intensity of \( \sigma \) belonging to the V3d orbital is suppressed with increasing \( \gamma \) (Figure 4e). Meanwhile, the intensity of \( \sigma \) belonging to the Sb5p orbital remains nearly unchanged. This gives rise to a weaker V3d–Sb5p orbital hybridization strength due to the suppression in the DOS contribution by the V3d orbital. This explains the significant drop in the intensity of feature \( B^s \) of the XAS spectrum as \( T \) approaches \( T_{CDW} \) in temperature Region II (Figure 3c). With the progressing lattice distortion at \( \gamma > 0.6 \), the intensity of \( \sigma \) for both the V3d and Sb5p orbitals are enhanced along with a significant drop in terms of their energy difference (Figure 4f). This leads to an enhancement in the V3d–Sb5p orbital hybridization, which in turn brings about a significant increase in the intensity of feature \( B^s \), as reflected in the XAS spectrum in temperature Region III (Figure 3c). We can therefore attribute the temperature-dependent behavior of feature \( B^s \) in the XAS spectrum to the changes in the V3d–Sb5p orbital hybridization during the CDW transition process, during which the pristine-to-ISD transition can be regarded as a continuous lattice deformation process. As discussed in Figure S7 (Supporting Information), pristine-to-SOD transition is ruled out during the CDW transition.

3. Conclusion

Our work points to the critical role that hybridization between the V and Sb orbitals plays in mediating the formation of the CDW states in the CsV3Sb5 kagome unconventional superconductor. Demonstrated direct participation of the Sb atomic orbitals in the CDW transition process opens new discussions on the long-held view that the long-range charge order is mediated solely by vanadium atomic orbitals. This finding is also relevant to general understanding of the critical roles that Sb orbitals play in electronic phase transitions in different materials, bearing in mind the recent report of their direct involvement in the interplay between superconductivity and CDW orders in antimonates. Apart from providing convincing evidence of the pristine-to-ISD structural transition at \( T_{CDW} \), our study also provides further insights into the lattice distortion during the intermediate stages of this CDW transition process where the structural transformation is shown to behave in a manner that resembles thermal molecular motion. Ultimately, our study delivers a significant breakthrough toward the fundamental understanding and control of the correlated phases emerging from the kagome lattice. Not only does it renew previous discussions on the roles that constituent atomic orbitals play in the CDW and superconductive properties in kagome materials,[44] it also provides new exploratory insights toward orbital origins of other novel topological and unconventional orders.

4. Experimental Section

Sample Synthesis: CsV3Sb5 single crystals were grown by spontaneous nucleation in a self-flux method. First, a mixture of high-purity Cs ingots, V and Sb powders (with a molar ratio of 10:3:28, and a total mass of \( 3 \) g) was loaded in an alumina crucible. The alumina crucible was jacketed in a Ta tube. Thereafter, the Ta tube was welded through Argon arc melting and then sealed in an evacuated quartz ampoule. Subsequently, the quartz ampoule was loaded into a muffle furnace, heated up to 1193 K, and maintained at this temperature for 24 h. The furnace was then gradually cooled to 773 K at a rate of 2 K h\(^{-1}\). The obtained crystals were wrapped by flux which could then be washed off by alcohol. Shiny millimeter-size plate-like crystals were then harvested. The crystals were stable in air for several weeks.

Scanning Tunneling Microscopy Measurements: The samples were exfoliated in situ at room temperature (300 K) in a preparation chamber, high-resolution STM measurements were then performed at 77 K at ultrahigh vacuum condition (\( \approx 10^{-10} \) mbar) in an Omicron UHV system interfaced to a Nanonis controller. Electrochemically etched tungsten tips were used as the grounded probe while the sample holder has a voltage bias applied to it.

High-resolution X-ray Diffraction and Reciprocal Space Mapping Measurements: High-resolution X-ray diffraction (HR-XRD) experiments were performed at the X-ray Demonstration and Development (XDD) beamline at the Singapore Synchrotron Light Source (SSLS).

Magnetization Measurements: Temperature dependence of magnetic susceptibility was measured on Quantum Design Magnetic Property Measurement System (MPMS3).

X-ray Absorption Spectroscopy: Temperature-dependent X-ray absorption spectroscopy (XAS) measurements were performed on freshly cleaved CsV3Sb5 single crystal samples at the Soft X-ray–ultraviolet (SUV) beamline at the Singapore Synchrotron Light Source, in a vacuum chamber with a base pressure of \( \approx 10^{-9} \) mbar via the total electron yield (TEY) mode.[45,46] The incident X-ray was projected at a normal incident angle onto the sample surfaces. The XAS measurements were in a descending temperature sequence (i.e., 300 \( \rightarrow 200 \rightarrow 100 \rightarrow 98 \rightarrow 96 \rightarrow 94 \rightarrow 92 \rightarrow 90 \rightarrow 40 \) K). \( \approx 20 \) min of waiting time was given at each temperature point before the start of each measurement.

First-Principles Calculations: First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) code,[47,48] implementing density functional theory (DFT). For the electron exchange-correlation functional, the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE) was used.[49] The energy cutoff of the plane-wave basis was set to 400 eV and the zero damping DFT-D3 van der Waals correction was employed throughout the calculations.[50] In the pristine phase, the atomic positions and lattice vectors were fully optimized using the conjugate gradient (CG) scheme until the maximum force on each atom was below 0.01 eV Å, with an energy precision of \( 10^{-5} \) eV. The Brillouin zone (BZ) was sampled using a \( 19 \times 19 \times 11 \) \textGamma-centered Monkhorst–Pack grid.
the 2 × 2 × 1 phase, the energy precision was set to 10⁻⁷ eV and a k-mesh of 9 × 9 × 11 (19 × 19 × 11) was used in stationary (density of state, DOS) calculations.[3]\\n
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
S.H., C.S.T., L.L., and Y.L. contributed equally to this work. X.Y. conceived the project. L.Y. synthesized the samples with help from C.G. S.H. and C.S.T. performed the XRD and XAS experiments and analyzed the data with help from P.Y., C.D., and X.Y. J.G. performed the STM experiments and analyzed the data. L.L., L.Z., M.V.M., and V.Y. contributed to the theoretical interpretations. S.H. and C.S.T. wrote the manuscript, with input from all the authors.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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