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Orbital hybridization-driven charge density wave transition in CsV₃Sb₅ kagome superconductor

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Abstract: Owing to its inherent non-trivial geometry, the unique structural motif of the recently discovered Kagome topological superconductor AV₃Sb₅ (A = K, Rb, Cs) is an ideal host of diverse topologically non-trivial phenomena, including giant anomalous Hall conductivity, topological charge order, charge density wave (CDW), and unconventional superconductivity. Despite possessing a normal-state CDW order in the form of topological chiral charge order and diverse superconducting gaps structures, it remains unclear how fundamental atomic-level properties and many-body effects including Fermi surface nesting, electron-phonon coupling, and orbital hybridization contribute to these symmetry-breaking phenomena. Here, we report the direct participation of the V3d— Sb5p orbital hybridization in mediating the CDW phase transition in CsV₃Sb₅. The combination of temperature-dependent X-ray absorption and first-principles studies clearly indicate the Inverse Star of David structure as the preferred reconstruction in the low-temperature CDW phase. Our results highlight the critical role that Sb orbitals plays and establish orbital hybridization as the direct mediator of the CDW states and structural transition dynamics in Kagome unconventional superconductors. This is a significant step towards the fundamental understanding and control of the emerging correlated phases from the Kagome lattice through the orbital interactions and provide promising approaches to novel regimes in unconventional orders and topology.

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], superfluidity and Bose-Einstein condensation^[2], long-range charge-density wave (CDW)^[3] and magnetic transition^[4]. Symmetry-breaking phenomena are often found in quantum systems where the complex interplay of charge, spin, lattice, and orbital degrees of freedom takes place^[5]. 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^[6] remains unresolved. Recent reports of exotic chiral orders in the layered Kagome Dirac metals, AV₃Sb₅ $(A = K, Rb \text{ or } Cs)^{[7]}$, are tantalizingly appealing to the research 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^[8], magnetoquantum oscillations^[9], topological charge order^[7, 10], and superconductivity^[11]. Although there are reports of normal-state CDW of the topological chiral charge order ^[7] and diverse superconducting gaps structures in Kagome materials^[12], the roles of fundamental properties such as Fermi surface nesting^[13], electron-phonon coupling^[14], 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 [Nature physics 12(9), 867-873 (2016); Physical review letters 117(14), 147401 (2016); Advanced Materials 32(34), 2000153 (2020); Advanced functional materials 27(17), 1606717 (2017)].

Here we report the direct participation of the V3*d*—Sb5*p* 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 reveal the Inverse Star of David (ISD) as the preferred structure in the CDW phase. Contrary to conventional view where long-range charge order is mediated solely by the vanadium atoms^[14-15], 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 the extensive interaction and the complementary effects between the V- and Sb-atoms on the electronic structures (**Figure 1**a) ^[16] [Physical Review B 104, 205129 (2021); SciPost Physics 12, 049 (2022); Physical Review B 105(23), 35145 (2022)]. It is also immediately relevant in light of the recent report where Sb–oxygen covalency contributes to the emergence of superconductivity in antimonates^[17]. Unraveling the mechanism that governs the CDW states in CsV₃Sb₅ Kagome systems provides essential hints to identify the key ingredients of Kagome unconventional superconductors and further serves as a platform to uncover the interplay between the symmetry-breaking orders^[13, 18] and other unconventional

orders and topologies.

2. Results and Discussion

2.1. Validation of Sample Quality

Layered CsV₃Sb₅ single crystals were synthesized via a self-flux growth method^[11a]. This class of AV₃Sb₅ materials exists in both the conventional 1×1 hexagonal crystal structure^[8], and the $\sqrt{3} \times \sqrt{3}R30^{\circ}$ reconstructed structure^[18]. Figure 1b displays the Scanning tunneling microscopy (STM) topographic image of the Cs-terminated surface which indicates the typical single-unitcell terrace of ~ 9.4 Å (Figure 1c)^[8, 19]. The two unique cleaved Cs surface morphologies along the red dotted lines (Figure 1d) are plotted in Figure 1e where they corresponding to the 1×1 hexagonal and $\sqrt{3} \times \sqrt{3}R30^{\circ}$ structures, respectively.

The crystallinity and quality of the CsV_3Sb_5 sample is further confirmed to be of very high quality via high-resolution X-ray Diffraction (HR-XRD) in its diffraction pattern and its regular hexagonal structure (**Figure 2**a)^[20]. Reciprocal space mappings (RSMs) along the (004)_{HL} and $(\bar{1}05)_{HL}$ orientations (Figure 2b and 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 ~94 K for $\mu_0 H=1$ T and H//ab (Figure 2d)^[8, 11a]. 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 superconductive state in this sample at $T_C \sim 2.6$ K^[11a].

2.2. Temperature-dependent X-ray Absorption Spectroscopy Characterization

To investigate the evolving electronic structures and orbital-coupling properties of CsV₃Sb₅ in temperature regions near T_{CDW} , temperature-dependent X-ray absorption spectroscopy (XAS) is conducted to examine how the V3*d* orbitals evolve in this temperature region. 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 [Coordination Chemistry Reviews 249(1-2), 31-63 (2005); Journal of Physics: Condensed Matter 4(16), 4189 (1992)]. **Figure 3**a displays the temperature-dependent V L-edge XAS spectra of the CsV₃Sb₅ sample over a wide temperature range between T_{CDW} . In the XAS spectra, where shoulders A^* (~517.0 eV), B^* (~518.2 eV) and the characteristic peaks C^* and D^* (~519.2 and ~525.6 eV, respectively) are observed. Feature A^* is attributed to the slight hybridization between atomic orbitals while C^* and D^* are the L_{2,3}-edges representing the V2 $p_{3/2}/p_{1/2} \rightarrow 3d$ electronic transitions^[21], all displaying very weak temperature variation that falls within the experimental error range between 40 and 300 K. While feature C* registers

marginally greater 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 L₃-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, $\Delta \mu = \mu(T) - \mu(T_{CDW} = 94 \text{ K})$, 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, $\Delta \mu$, displays very strong temperature-dependent fluctuation at \sim 518.2 eV where feature B^* is located, while remaining largely unchanged in the other spectral regions, especially where the V- $L_{2,3}$ absorption edges are located. These are indications that the V3d orbitals do 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 orbitals with their neighbouring electronic bands^[22]. Notably, the roles of orbital hybridization in mediating in 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 two-dimensional transition metal chalcogenides[Physical review letters 122, 076404 (2019)] and unconventional superconductors[Nature Communications 13, 6197 (2022)] where they facilitate 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 attest to the complementary effects of the V- and Sb-atoms in the form of V3d-Sb5d orbital hybridization in dictating the electronic structures and CDW states in AV₃Sb₅ systems^[16]. As we will show later by a combination of temperature-dependent analysis of feature B^* and a series of firstprinciples study, it can be deduced that V3d—Sb5p orbital 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 300K, where the peak intensity first decreases with decreasing temperature and eventually sharply minimizes at T_{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 (~140-300 K), Region II just above T_{CDW} (~94-140K), Region III just below T_{CDW} (~70—94 K), and Region IV at lowest temperatures (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 behaviour in the form of lattice vibration take place have been reported to take place in CsV₃Sb₅ in this temperature region which significantly overshadow the orbital hybridization effects [Phys. Rev. B 104, 144418 (2021); Applied Physics Letters 119(8), 082401 (2021); SciPost Physics 12, 049 (2022)].

Conversely, thermal effects and phonon interactions are suppressed at low temperature (in temperature Region IV), where the intensity of B* rises continuously with temperature decreasing to 40 K. This is due to strong electron-electron correlations associated with another nematic symmetry-breaking order^[3a, 13] dominating in this low-temperature range, which screens the effects of orbital hybridization.

As temperature approaches T_{CDW} in Region II, feature B^* registers an abrupt intensity drop (approximately gradient: -0.065) and minimizes at T_{CDW} =94 K. Below 94 K, the intensity then exhibits a rapid upturn in temperature Region III with a gradient of ~0.050 (see inset of Figure 3c). The unique temperature trends in regions II and III near T_{CDW} provide important suggestions of electronic orbital behaviours in mediating the CDW transition.

2.3. Density of States Investigation

To provide further insights to 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 has been conducted. While the Kagome lattice is known to be in its conventional pristine structure above T_{CDW} , CDW transition is accompanied by a three-dimensional 2×2×2 lattice reconstruction associated with the movement of the constituent V atoms^[7, 13]. Previous studies have shown that the 'Star of David'(SOD) and 'Inverse Star of David' (ISD) structures are possible resulting structures below T_{CDW} . This is because they possess greater structural stability than their high-temperature pristine counterpart^[13]. Nevertheless, there is no consensus on a preferred structure or if they co-exist in the CDW state^[15a, 23].

Figure 3d presents the contributions from the respective atomic orbitals to the density of states (DOS) of the CsV₃Sb₅ Kagome lattice in its high-temperature pristine state. As expected, the V3*d*-orbital has dominant contribution to the DOS near the Fermi level. Moreover, the Sb5*p*-orbital also plays a pivotal role as evident by a much larger contribution to the DOS than the other constituent orbitals. The significant DOS contributions by the V3*d* and Sb5*p* orbitals also apply to the low-temperature ISD and SOD structures (see Supplemental Material Figure S3). The domination of the two main electronic states, V3*d* and Sb5*p* orbitals, near the Fermi level are therefore clear indications that there is a presence of strong V3*d*—Sb5*p* 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 4**a and b, respectively) are compared in the pristine, SOD and ISD states. While the PDOS in the pristine and SOD states are almost identical, note the significant difference in the ISD structure especially near feature σ . The variation of the PDOS and the changes in energy positions of feature σ in both the V3d and Sb5p orbitals have a direct effect on the hybridization strength. While feature σ 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 α , while the V3*d* orbital does not show any changes in PDOS between different structures (Figure 4a), the PDOS component of the Sb5*p*-orbital in the 0.8—1.2 eV energy (Figure 4b) displays a very slight but noticeable difference between the pristine and ISD. Whereas the α feature of the SOD structure is almost identical with its pristine counterpart. While these differences may be minor, the variation of in the PDOS component of the Sb5*p*-orbital likewise play its part in modifying the V3*d*-Sb5*p* hybridization between different structural phases. Meanwhile, the larger contribution by the Sb5*p*-orbital in terms of the σ feature in the PDOS strengthens the V3*d*—Sb5*p* hybridization in the ISD structure.

Note that the PDOS of the V3*d*-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 V3*d*-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 V3*d* and Sb5*p*-orbitals changed under ISD lattice distortion but remains virtually unchanged in the SOD state, the temperature-dependent behaviour in the XAS spectra therefore indicates pristine-to-ISD lattice at T_{CDW} .

To further investigate how the V3*d*—Sb5*p* hybridization evolves during the CDW transition, PDOS of both the V3*d* and Sb5*p* orbital are calculated separately as functions of lattice distortion between the pristine (initial) and ISD (final) states (see Supplemental Material 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^[13], the fractional distortion can therefore be defined as $\gamma = d/d_0$, 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 and d display the PDOS of V3*d* and Sb5*p* orbitals, respectively, at the intermediate stages of the pristine-to-ISD transition, depicting how σ evolves due to its association with the temperature-dependent feature *B** in the XAS spectra. While the intensity of σ changes non-trivially with γ , σ of both the V3*d* and Sb5*p*-orbitals gradually shifts to a higher energy with increasing γ distortion.

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

To better track the evolution of feature σ as a function of γ , Figure 4e and f plot its relative intensity and position, respectively, in its intermediate states. For lattice distortion $\gamma \approx 0.6$, the intensity of σ belonging to the V3*d* orbital is suppressed with increasing γ (Figure 4e). Meanwhile, the intensity of σ belonging to the Sb5*p*-orbital remains nearly unchanged. This gives rise to a weaker V3*d*—Sb5*p* orbital hybridization strength due to the suppression in the DOS contribution by the V3*d*-orbital. This explains the significant drop in the intensity of feature B^* of the XAS spectrum as *T* approaches T_{CDW} in temperature Region II (Figure 3c). With the progressing lattice distortion at γ >0.6, the intensity of σ for both the V3*d* and Sb5*p*-orbitals are enhanced along with a significant drop in terms of their energy difference (Figure 4f). This leads to an enhancement in the V3*d*—Sb5*p* orbital hybridization, which in turn brings about a significant increase in the intensity of feature B^* as reflected in the XAS spectrum in temperature Region III (Figure 3c). We can therefore attribute the temperature-dependent behavior of feature B^* in the XAS spectrum to the changes in the V3*d*—Sb5*p* 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 of the Supplemental Material, 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 to the pristine-to-ISD structural transition at T_{CDW} , our study also provides further insights to 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 towards 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, but it also provides new exploratory insights towards orbital origins of other novel topological and unconventional orders.

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Conflict of interest

The authors declare no conflict of interest.

Author Contributions:

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 analysed the data with help from P.Y., C.D. and X.Y. J.G. performed the STM experiments and analysed the data. L.L. performed the DFT calculations. L.L, L.Z., M.Z. and M.V.M. contributed the theoretical interpretations. S.H. and C.S.T. wrote the manuscript, with input from all the authors. S.H., C.S.T., L.L. and Y.L contributed equally to this work.

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Figures



Figure 1. Structural transition dynamics at T_{CDW} and morphology of the CsV₃Sb₅ single crystal samples. a) Schematic depiction of the changes in V3*d*-Sb5*p* orbital hybridization strength during the structural transition of CsV₃Sb₅ from pristine to Inverse Star of David (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 1×1 (setpoint: V = 0.1 V, I = 50 pA). e) Line profile along the red dashed line in (d) shows the measured lattice period of ~9.3 Å belonging to the $\sqrt{3} \times \sqrt{3}R30^{\circ}$ configuration and ~5.4 Å of the conventional 1×1 hexagonal structure. Inset exhibits the atom arrangement of the respective surface structures $-\sqrt{3} \times \sqrt{3}R30^{\circ}$ and 1×1 .



Figure 2. Structural and magnetic susceptibility properties of CsV₃Sb₅. a) High-resolution Xray Diffraction (HR-XRD) pattern. Insets: the optical image of the sample and the unit structure of CsV₃Sb₅. b) Reciprocal space mapping (RSM) in the (004)_{HL} and c) ($\overline{1}05$)_{HL} reciprocal space region of the sample. d) Magnetic susceptibility $\chi(T)$ at $\mu_0 H = 1$ T for H//ab. Inset: Enlarged $\chi(T)$ curve of the shaded temperature region indicating T_{CDW} transition. e) Magnetic susceptibility, $4\pi\chi(T)$, with ZFC and FC modes at $\mu_0 H = 1$ mT for H//ab, results indicate the onset of superconductive transition at $T_c \sim 2.6$ K.



Figure 3. Temperature-dependent XAS characterization, Density of States (DOS) and Partial Density of States (PDOS) analyses for different lattice structures of CsV₃Sb₅. 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 K and 40 K. Inset: Intensity variation of feature *B** in temperature regions II and III located near *T*_{CDW}. d) DOS of pristine state CsV₃Sb₅ near the Fermi level with PDOS contributions from the atomic orbital constituents of V3*d*, Sb5*p* and other orbitals (see Supplemental Material for DOS of SOD and ISD structures).



Figure 4. Partial Density of States (PDOS) of the respective constituent orbitals for different lattice structures of CsV₃Sb₅. a) PDOS of the V3*d*-orbital. Inset: Schematic of the SOD lattice. b) PDOS of the Sb5*p*-orbital. Inset: Schematic of the ISD lattice. c) Changes in the PDOS of the constituent V3*d*, and d) Sb5*p* orbitals, as functions of ISD lattice distortion, γ , during the intermediate steps of the pristine-to-ISD transition. Changing PDOS profile of feature σ with increasing γ has been tracked and indicated by yellow arrows. Insets: Zoomed-out PDOS of the V3*d* and Sb5*p* orbitals, respectively. e) Changes in the relative intensity, and f) position of feature σ for the PDOS of both V3*d* and Sb5*p* orbitals during the intermediate steps of the pristine-to-ISD transition.