Monolayer Kagome Metals $A\text{V}_3\text{Sb}_5$

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Recently, layered kagome metals $A\text{V}_3\text{Sb}_5$ ($A = \text{K, Rb, and Cs}$) have emerged as a fertile platform for exploring frustrated geometry, correlations, and topology. Here we demonstrate that $A\text{V}_3\text{Sb}_5$ can crystallize in a mono-layered form, revealing a range of properties that render the system unique by using first-principles and mean-field calculations. Most importantly, the two-dimensional monolayer preserves intrinsically different symmetries from the three-dimensional layered bulk, enforced by stoichiometry. Enrichment of the van Hove singularities, a logarithmic divergence of electronic density of states, consequently appears, leading to a variety of competing instabilities such as doublets of charge density waves and $s$- and $d$-wave superconductivity. We show that the competition between orders can be fine-tuned in the monolayer via electron-filling of the van Hove singularities. Thus, our results suggest the monolayer kagome metal $A\text{V}_3\text{Sb}_5$ as a promising platform for designer metallic quantum phases.

The kagome lattice refers to a two-dimensional (2D) planar crystal composed of corner-sharing triangles. Unique electronic structures emerge owing to the geometrical frustration of the lattice, featuring a flat band, a pair of Dirac points, and saddle-point van Hove singularities (VHSs). A prominent example of candidate kagome metals is the recently discovered vanadium-based kagome metals $A\text{V}_3\text{Sb}_5$ ($A = \text{K, Rb, and Cs}$) [1, 2]. A cascade of correlated electronic states have been observed in $A\text{V}_3\text{Sb}_5$, associated with charge density waves (CDWs) [2–17] and superconductivity [2, 14–23]. These phases are reported to be accompanied by concomitant unexpected properties such as giant anomalous Hall effects [24, 25] without long-ranged magnetic ordering [26], potential Majorana zero modes [14], and edge supercurrent [18]. The VHSs in conjugation with the Coulomb interaction is suggested as an impetus of the unconventional properties [27, 28].

Although many outstanding materials have been found to comprise a kagome lattice in a layered form [29–31], the kagome lattice in genuine two dimensions is rare in nature. This scarcity leads to prior explorations of the kagome materials based on the assumption that a three-dimensional (3D) layered system can be regarded as decoupled kagome layers. Similarly, in the case of the vanadium-
based kagome metals, current experiments are mainly focused on the 3D layered structures [1–5, 11–16, 18, 19, 21–26], while their theoretical analysis largely relies on an effective kagome model in two dimensions [6–9, 20]. The dimensionality has been tacitly assumed as an irrelevant parameter, but this assumption has been generically refuted in layered systems [32, 33]. A few research groups have made pioneering efforts to tackle this issue by successfully exfoliating thin films of AV$_3$Sb$_5$ [34–36]. However, the importance of dimensionality in this family of kagome metals has remained elusive to date.

In this work, we theoretically demonstrate that the AV$_3$Sb$_5$ monolayer is different from the 3D layered bulk by performing density-functional theory (DFT) and mean-field theory (MFT) calculations. At the crux of our results is the absence of dimensional crossover between the monolayer and the layered bulk. We argue that the symmetry-lowering is inevitable in the monolayer, enforced by the stoichiometry of AV$_3$Sb$_5$. The reduced symmetries give rise to significant changes in the formation of VHSs. Notably, unconventional VHSs appear, referred to as type-II VHSs. As a consequence, enhanced electronic instabilities are observed, leading to the emergence of competing orders such as CDW doublets, time-reversal breaking CDWs, $s$- and $d$-wave superconductivity. Our calculations predict that the AV$_3$Sb$_5$ monolayer can be thermodynamically stable. In connection with future experiments, we calculate the anomalous Hall conductivity that can probe the correlated orders. Possible experimental schemes are discussed to tune the electron-filling based on mechanical and chemical treatment.

RESULTS

Crystal structure and Symmetry

We begin by elucidating the similarities and differences between the crystal structures of the bulk and monolayer AV$_3$Sb$_5$ ($A$ = K, Rb, Cs). As delineated in Figs. 1a and b, both systems comprise multiple sub-layers. Most importantly, a 2D kagome sub-layer is formed from V atoms, coexisting with Sb sub-layers. While these are similar in both systems, differences arise from the alkali atoms $A$. In the monolayer (bulk) system, alkali metals energetically favor to form rectangular (triangular) sub-layers shown in Fig. 1b(a) (see Supplementary Note 1 for the detailed analysis of the energetics using first-principles calculations). The different formation of alkali atoms is traceable to the stoichiometry of AV$_3$Sb$_5$. The kagome layer of the monolayer takes all the electrons donated from the alkali atoms, while those in the bulk system are shared between
FIG. 1. Symmetry lowering and rearrangement of the van Hove singularity (VHS) in monolayer \( AV_3Sb_5 \). a, b Atomic structures of the bulk and monolayer \( AV_3Sb_5 \) (\( A = K, \text{Rb}, \text{Cs} \)). The monolayer structure preserves \( \sqrt{3} \times 1 \) translational and \( D_{2h} \) point group symmetries. The layered bulk preserves \( 1 \times 1 \) translational and \( D_{6h} \) point group symmetries. Black solid lines indicate the primitive unit cells and blue dashed lines indicate the \( y \)-axis. In b, dashed open circles indicate vacant alkali sites. c Schematic illustration of the VHS points in momentum space rearranged by symmetry lowering. The type-I (type-II) VHS points are marked by blue (red) circles. In the middle and right panels, the reduced (pristine) BZ of the \( \sqrt{3} \times 1 \) (\( 1 \times 1 \)) unit cell is indicated by solid (dashed) line. The bottom panels delineate the energy level of the VHS points.

the adjacent two sub-layers. Therefore, to preserve the stoichiometry, the number of neighboring alkali atoms is halved by doubling the unit cell, such that they form rectangular sub-layers.

The rectangular sub-layer with the doubled unit cell breaks translational and rotational symmetries of bulk \( AV_3Sb_5 \). The translational symmetry \( T_{1 \times 1} \) is reduced to \( T_{\sqrt{3} \times 1} \), and correspondingly, a three-fold rotational symmetry \( C_{3z} \) is lifted. This reduces the \( D_{6h} \) symmetry of the bulk to \( D_{2h} \) in the monolayer. We stress that the lowered symmetry of the monolayer \( AV_3Sb_5 \) is the fundamental symmetry, which can be stable even at room temperature protected by energy barriers from the stoichiometry enforcement, while the same symmetry is only reachable at low temperature from a cascade of phase transitions in bulk \( AV_3Sb_5 \) [4, 15]. Thus, a dimensional crossover is unlikely to occur from the bulk to the monolayer \( AV_3Sb_5 \), and unique properties arise as a result.
Rearrangement of VHSs

Most importantly, the lowered symmetry of the monolayer AV$_3$Sb$_5$ leads to rearrangement of the VHS in energy-momentum space. The mechanism of the rearrangement is illustrated in Fig. 1c, in which we trace the $k$-points that host the VHS. Hereafter, we refer to these momenta as the VHS points. The pristine BZ with the $T_{1 \times 1}$ translational symmetry initially hosts three inequivalent VHS points at $M_i$ ($i = 1, 2, 3$), as in the case of the bulk AV$_3$Sb$_5$ (left panel in Fig. 1c). Upon the zone folding by lowering $T_{1 \times 1}$ to $T_{\sqrt{3} \times 1}$, the $M_1$ VHS point is folded to $\Gamma$ and the $M_1$ and $M_2$ VHS points are merged to the $M$ point of the reduced BZ (middle panel in Fig. 1c). The symmetry-lowering further hybridizes the two states at $M$ ($M_2$ and $M_3$), such that it annihilates the VHS at $M$ and creates four new VHS points off $M$, marked as $P_i$ ($i = 1, 2, 3, 4$) in the right panel of Fig. 1c.

The rearrangement of VHS points is observed in our first-principles calculations. Figures 2a and b show exemplary DFT bands of KV$_3$Sb$_5$ with archetypal kagome bands distilled by our tight-binding theory (see Methods for the details of the TB model). In Fig. 2b, the divergence of the density of states (DOS) is clearly observed at $E = -6 (+9)$ meV. A close inspection reveals that the diverging DOS at $E = -6$ meV arises from off high-symmetry momenta at $P_i = M + (\pm 0.054, \pm 0.021)$ Å$^{-1}$ (Fig. 2d), while the divergence at $E = 9$ meV arises from the exact high-symmetry $\Gamma$ point (Fig. 2c). In this respect, the VHS points at $E = 9$ meV ($E = -6$ meV) belong to the type-I (type-II) class, where the type-I (II) refers to a class of VHSs that originates from (off) time-reversal invariant momenta [37–39]. Our calculations further reveal that the type-II VHSs generically occur in the kagome metals regardless of $A = K$, Rb, and Cs (see Supplementary Note 2 for the DFT results of the RbV$_3$Sb$_5$ and CsV$_3$Sb$_5$ monolayers).

The emergence of the type-II VHS is one of the key features of the monolayer AV$_3$Sb$_5$. Few remarks are as follows. First, the type-II VHS points $P_i$ ($i = 1, 2, 3, 4$) (Fig. 2d) consist of a mixed contribution from both the B and C sublattices (Supplementary Fig. 3), referred to as a mixed-type flavor [12, 20, 40]. This is in contrast to the type-I VHS point at $\Gamma$ (Fig. 2c), which is purely contributed from the A sublattice, referred to as a pure-type flavor. Second, the increased number of VHS points quantitatively changes the characteristic of the diverging DOS at $-6$ meV. Namely, the peak at $-6$ meV is significantly enhanced than that of the type-I VHS at 9 meV (Fig. 2b), contributed from the quartet VHS points at $P_i$ ($i = 1, 2, 3, 4$). Such quantitative changes are of immediate impact on the electronic properties, such as instabilities driven by the type-II VHS, as we will show below.
FIG. 2. VHSs in the monolayer AV₃Sb₅. a DFT and TB band structures of the KV₃Sb₅ monolayer. The DFT (TB) bands are colored by black (red). The kagome bands are reproduced by using our TB model (see Methods for the details of the TB model). A solid rectangle (dashed hexagon) in the inset depicts the reduced (pristine) BZ of the $\sqrt{3} \times 1 \ (1 \times 1)$ unit cell. b (Left panel) Magnified view of the blue box in a. (Right panel) Density of states (DOS) of KV₃Sb₅. The type-I and type-II VHSs are indicated by blue and red arrows, respectively. c, d Energy contours of the kagome bands calculated from the TB bands. Solid (dashed) white lines show the reduced (pristine) BZ. The contour curves in c and d correspond to $E = 9$ and $-6$ meV, respectively. The saddle points reside at the crossing points of the contour curves in c and d. The magnified view of the red box in d illustrates the position of type-II VHS points off $M$, marked by $P_i \ (i = 1, 2, 3, 4)$. 

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Competing orders

The rearranged VHSs manifest their properties in competing orders of correlated electronic states. In monolayer \( \text{AV}_3\text{Sb}_5 \), we employ the standard mean-field theory with the constructed TB model and uncover phase diagrams with CDWs and superconductivity (SC). The onsite and nearest-neighbor Coulomb interactions are introduced,

\[
H_{\text{int}} = U \sum_{R} \sum_{\alpha} n_{R,\alpha \uparrow} n_{R,\alpha \downarrow} + V \sum_{R} \sum_{\langle \alpha, \beta \rangle} \sum_{\sigma, \sigma'} n_{R,\alpha,\sigma} n_{R,\beta,\sigma'},
\]

where \( U \) (\( V \)) describes the on-site (nearest-neighbor) density-density type interaction and \( R, \alpha, \) and \( \sigma \) represent the lattice site, sublattice, and spin, respectively. We consider two classes of order parameters, CDWs and SC, which can significantly reduce the energy by gapping out the Fermi surface with diverging DOSs. CDWs and SC are of particular interest as they have been observed in the bulk \( \text{AV}_3\text{Sb}_5 \) in a variety of forms, including star of David (SD), inverse star of David (ISD), time-reversal symmetry breaking (TRSB) CDWs [6, 7, 10, 17].

Remarkably, any CDW order parameter in the monolayer \( \text{AV}_3\text{Sb}_5 \) forms a doublet, as illustrated in Fig. 3c. The doublet formation of CDWs is one of the key characteristics of the monolayer \( \text{AV}_3\text{Sb}_5 \), originating from the reduced symmetry. The lowered \( T_{\sqrt{3}\times 1} \)-translational symmetry of \( \text{AV}_3\text{Sb}_5 \) monolayer plays a crucial role to double the CDW channels of the higher \( T_{1\times 1} \)-symmetry, and the number of multiplets is solely determined by their quotient group, \( T_{1\times 1}/T_{\sqrt{3}\times 1} = \mathbb{Z}_2 \). For example, the two SD-CDW phases, dubbed SD-1 and SD-2, are the \( \mathbb{Z}_2 \) members, distinguished by the alkali chains hosted on and off the center of SD, respectively, as illustrated in Fig. 3c.

The corresponding phenomenological Landau theory of the doublet CDWs becomes exotic. Introducing a bosonic real two-component spinor, \( \Psi_{\text{SD}}^T \equiv (\psi_{\text{SD}-1}, \psi_{\text{SD}-2}) \) with order parameters of SD-1 (\( \psi_{\text{SD}-1} \)) and SD-2 (\( \psi_{\text{SD}-2} \)), the Landau functional for the SD-CDW phases is given by

\[
\mathcal{F}_L(\Psi_{\text{SD}}) = r_{\text{SD}}(\Psi_{\text{SD}}^\dagger \Psi_{\text{SD}}) + s_{\text{SD}}(\Psi_{\text{SD}}^\dagger \hat{\rho}_z \Psi_{\text{SD}}) + \cdots,
\]

with phenomenological constants \( r_{\text{SD}} \) and \( s_{\text{SD}} \). Here, the Pauli matrix \( \hat{\rho}_z \) describes the spinor space and higher order terms are omitted for simplicity. The \( s_{\text{SD}} \)-term describes a free-energy difference between SD-1 and SD-2, which is nonzero when the \( T_{1\times 1} \)-translational symmetry is broken. Depending on \( s_{\text{SD}} \), the system energetically favors one of the doublet CDWs, enriching phase diagrams of the monolayer \( \text{AV}_3\text{Sb}_5 \).

Our mean-field analysis indeed finds enriched phase diagrams of the \( \text{AV}_3\text{Sb}_5 \) monolayer. We consider six configurations of CDWs (see Fig. 3c) and nine spin-singlet channels of SCs (see Ta-
FIG. 3. Phase diagrams and corresponding electronic orders in the AV₃Sb₅ monolayer. a, b Phase diagrams at the chemical potentials a \( \mu_1 = -6 \) meV and b \( \mu_2 = 35 \) meV in \( U-V \) space, where \( U \) and \( V \) are the onsite and the nearest neighbor density-density type interactions. Different CDW and SC orders are indicated by different colors. X denotes a phase unidentified within our mean-field scheme. c Schematic illustration of six distinct CDW configurations. (A-B) Inverse star of David (ISD)-1,2, (C-D) star of David (SD)-1,2, (E-F) time-reversal symmetry breaking (TRSB)-1,2. In (A-D), solid and dashed blue lines indicate distinct bonding strengths. In (E,F), red arrows on the bonds indicate the direction of current bond orders. The yellow and green oriented circles represent magnetic fluxes threading the hexagons and triangles in opposite directions, respectively. The corresponding CDW and SC order parameters are detailed in Tables I and II.
ble II). In Figs. 3a, b, we illustrate representative mean-field phase diagrams of KV$_3$Sb$_5$ in $U$-$V$ space obtained at two different chemical potentials $\mu_1 = -6$ meV and $\mu_2 = 35$ meV, where the zero chemical potential is set to the neutral filling. In what follows, we point out key observations made from the phase diagrams.

First, five distinct CDW orders can be accessible by fine-tuning the chemical potential $\mu$. For example, in the vicinity of type-II VHS at $\mu_1 = -6$ meV (Fig. 3a), SD-2 and ISD-2 dominantly occur with sizable regions of ISD-1 in the energy ranges of $-0.6 \text{ eV} < U < 0.4 \text{ eV}$ and $-20 \text{ meV} < V < 40 \text{ meV}$. Similarly, a TRSB-2 CDW phase is uncovered under the condition $\mu \geq 30$ meV (Fig. 3b) in a wide range of $U$ and $V$ values. Moreover, the SD-1 phase appears near the type-I VHS at $\mu_3 = 9$ meV (see Supplementary Note 6). A small variation of chemical potential $-6 \text{ meV} < \mu < 40 \text{ meV}$ can tune the types and flavors of the VHSs, which should enable an on-demand onset of a variety of CDW phases, ranging from ISD-1/2, SD-1/2, to TRSB-2.

Second, competition between CDWs and SC is generically observed. A conventional $s$-wave SC phase is observed near $\mu_1 = -6$ meV, which competes with ISD-1/2 and SD-2 at negative $U$ and positive $V$ as shown in Figs. 3a, b. Similarly, an unconventional $d$-wave SC phase is observed near $\mu_2 = 35$ meV. This competes with ISD-1 at positive $U$ and negative $V$ interactions as shown in Fig. 3b. Regarding the $d$-wave SC, the corresponding chemical potential is quite higher than the energy of the type-II VHS $\mu_1$, closer to the edge of the high energy band. Thus, we conclude that the dominant CDW and SC phases cannot be solely explained as a results of VHS. Instead, the interplay between the VHS, filling, and interaction should be crucial for complete understanding of the competing mechanism.

The final important observation from our mean-field study is nontrivial topology of the correlated CDW gaps. Notably, a non-zero Chern number $C$ is induced in the energy spectra when gapped by the two time-reversal symmetry broken CDW phases TRSB-1 and TRSB-2. For example, the lowest unoccupied and highest occupied energy spectra of TRSB-1 (TRSB-2) host the Chern number $C = 2$ and $C = 1$ ($C = 3$ and $C = -2$), respectively. As shown in Fig. 4a, the different Chern numbers between the two phases arise due to the concurrent sign-change of the Berry curvature at high-symmetry momenta $M_1$, $K_1$, and $K_2$. These topological CDW gaps with distinct Chern numbers motivate us to calculate the anomalous Hall conductivity $\sigma_{xy}$ shown in Fig. 4b. A sign change of $\sigma_{xy}$ is found as a function of chemical potential near the Fermi energy $E = 0$. We believe this nontrivial behavior featured in $\sigma_{xy}$ can be readily observed in the Hall current measurements, leading to the experimental discovery of the TRSB-CDW phases.
FIG. 4. **Topological charge density waves and engineering of chemical potential.** a TB band structures of the TRSB-1 and TRSB-2 CDW phases. The Berry curvature $\Omega_z(k)$ are overlaid at the corresponding $k$-points in the bands. The Chern numbers $C$ induced in the bands are shown in green color. b Anomalous Hall conductivity $\sigma_{xy}$ as a function of energy $E$ for the TRSB-1 and TRSB-2 CDW phases. c DFT calculations of the chemical potential $\mu$ as a function of an uniform biaxial strain in $AV_3Sb_5$ for $A = K$, Rb, and Cs. d DFT calculations of the chemical potential $\mu$ as a function of doping concentration $x$ for $A_{1+x}V_3Sb_5$. The detailed DFT band structures under the biaxial strain and alkali doping are provided in Supplementary Note 7.

**DISCUSSION AND CONCLUSION**

We have so far investigated unique features of the $AV_3Sb_5$ monolayer. Our system is unlike the bulk, hosted in distinct symmetry class. The contrast is even more evident in the phase diagrams that we calculated with the bulk $D_{6h}$ and the monolayer $D_{2h}$ symmetries, respectively (see Supplementary Fig. 7 for the $D_{6h}$ phase diagrams). The lowered $D_{2h}$ symmetry in the monolayer features a tendency to foster the CDW orders. This is in line with the previous experiments, in which a CDW order is observed to suppress SC as the thickness of the $AV_3Sb_5$ film decreases [34, 35].

The exotic orders should be accessible in monolayer $AV_3Sb_5$ in a controlled fashion. Our
mean-field diagrams (Figs. 3a and b) show that the occurrence of a specific electronic order is highly contingent upon the correct filling of electrons, which can be fine-tuned via mechanical and chemical means. For example, by applying a uniform biaxial strain in a range of ±2% variations, μ can be tuned from 50 meV to -100 meV (Fig. 4c). Moreover, the light doping of alkali atoms A (see Fig. 4d) or substituting Sb with Sn [41] can be a fine knob to adjust the chemical potential. Owing to the 2D geometry of the AV$_3$Sb$_5$ monolayer, we believe that there exist more opportunities (such as ionic gating) to tailor the competing orders hosted therein.

Finally, we argue that the AV$_3$Sb$_5$ monolayer should be possible to synthesize. The cohesive energy of the monolayer is calculated as 3.8 eV/atom for all three alkali atoms. This value is comparable to the bulk value of ∼3.9 eV/atom. Similarly, the exfoliation energies of the monolayer are calculated as 42, 45, and 45 meV/Å$^2$ for A = K, Rb, and Cs, respectively. These values are amount to existing two-dimensional materials, such as graphene (∼ 21 meV/Å$^2$) [42], hBN (∼ 28 meV/Å$^2$) [42], and Ca$_2$N (∼ 68 meV/Å$^2$) [43]. In addition, our DFT phonon bands of the ISD-1 phase are clean of imaginary frequencies (see Supplementary Note 8), implying dynamical stability of the monolayer structure. Encouragingly, the recent experiments have successfully exfoliated thin layers of AV$_3$Sb$_5$ up to five layers using the taping methods [35]. Current developments of the chemical solution reaction method could be an appropriate technique to weaken the interlayer interaction of the bulk system and separate the monolayer [44].

**METHODS**

**Tight-binding model.** - We construct a TB model for the monolayer with $D_{2h}$ symmetry in the $\sqrt{3} \times 1$ unit cell. Introducing the six-component spinor, $\Psi^T_k = (A^T_k, B^T_k, C^T_k)$ with $\alpha^T_k = (\alpha_{1,k}, \alpha_{2,k})$, the Hamiltonian becomes $H_0 = \sum_k \Psi^\dagger_k \mathcal{H}_0(k) \Psi_k$. The indices for sublattice $\alpha \in \{A, B, C\}$ and site $i \in \{1, 2\}$ are used. The Bloch Hamiltonian $\mathcal{H}_0(k)$ is given by

$$
\mathcal{H}_0(k) = -t \left[ (c_1 \lambda_1 - s_1 \lambda_4 + c_2 \lambda_2 - s_2 \lambda_5 + 2c_3 \lambda_3) \otimes I_2 + (c_1 \lambda_1 + s_1 \lambda_4 + c_2 \lambda_2 + s_2 \lambda_5) \otimes \sigma_x \right] - t_2 \left[ (c_4 \lambda_1 - s_4 \lambda_4 + c_5 \lambda_2 - s_5 \lambda_5) \otimes I_2 + (c_4 \lambda_1 + s_4 \lambda_4 + c_5 \lambda_2 + s_5 \lambda_5 + 2c_6 \lambda_3) \otimes \sigma_x \right] (3)
+ \epsilon I_6 + \frac{\delta \epsilon}{6} \left[ (2 \lambda_0 + 3 \lambda_7 + \sqrt{3} \lambda_8) \otimes \sigma_z \right] - 2 \delta t s_3 \left[ \lambda_6 \otimes \sigma_z \right],
$$

where $(c_i, s_i) \equiv (\cos k \cdot R_i, \sin k \cdot R_i)$ with $R_1 = \frac{1}{2}(\sqrt{3}, 1)$, $R_2 = \frac{1}{2}(\sqrt{3}, -1)$, $R_3 = (0, 1)$, $R_4 = R_2 - R_3$, $R_5 = R_1 + R_3$, and $R_6 = R_1 + R_2$. Here, $t$, $t_2$, $\epsilon$, $\sigma_i$ and $\lambda_i$ are nearest-neighbor hopping, next nearest-neighbor hopping, onsite energy, $2 \times 2$ Pauli matrices and $3 \times 3$ Gell-Mann matrices, respectively. The sublattice information and the definition of the Gell-Mann matrices are provided
in Supplementary Fig. 3a and Supplementary Note 4, respectively. The last two terms give rise to onsite energy difference $2\delta \epsilon$ between two A sublattices and staggered hopping $\pm \delta t$ between the B and C sublattices, respectively. These two terms lead to the symmetry-lowering from $T_{1 \times 1} D_{6h}$ to $T_{\sqrt{3} \times 1} D_{2h}$. With parameters $(\epsilon, t, t_2, \delta \epsilon, \delta t) = (0.01, 0.42, 0.03, -0.033, 0.01)$, our TB model well reproduces the DFT bands as well as the irreducible representations of the VHS bands at $\Gamma$ and $M$ ($A_g$) for KV$_3$Sb$_5$ (see Figs. 2a, b). For Rb and Cs, we also find good agreement between the TB and DFT (see Supplementary Note 2). The TB band structures of the TRSB-1/2 phases in Fig. 4a are obtained by using parameters $(\epsilon, t, t_2, \delta \epsilon, \delta t, \Phi) = (0.035, 0.42, 0.03, -0.033, 0.01, 0.07)$ where $\Phi$ is a CDW magnitude of the TRSB-1/2 phases (see Supplementary Note 5 for detailed order parameters of the TRSB-1/2 phases).

**Mean-field theory.** - We perform the conventional zero temperature mean-field method to investigate the interaction effects. Six distinct CDW configurations and nine spin-singlet SC orders are chosen to uncover CDW and SC instabilities in our analysis (see Fig. 3c and Table I, II). We introduce the CDW and SC order parameters $(\Phi, \Delta)$ that break translational and U(1) symmetry. In the $2 \times 2$ unit cell, the mean-field Hamiltonian is written as,

$$\delta H_{MF}[\Phi] = \Phi \sum_{k, \sigma} \tilde{\Psi}_k \begin{pmatrix} 0 & O_1(k) & O_2(k) \\ O_1(k)^\dagger & 0 & O_3(k) \\ O_2(k)^\dagger & O_3(k)^\dagger & 0 \end{pmatrix} \tilde{\Psi}_k,$$

and

$$\delta H_{MF}[\Delta] = \Delta \left[ \sum_k \tilde{\Psi}_k^\dagger \hat{\Gamma}(k) \tilde{\Psi}_k + C.C. \right],$$

with the twelve-component spinor, $\hat{\Psi}_k^T = (\tilde{A}_{k}^T, \tilde{B}_{k}^T, \tilde{C}_{k}^T)$ and $\hat{\alpha}_k^T = (\alpha_{1,k}, \alpha_{2,k}, \alpha_{3,k}, \alpha_{4,k})$. The indices $i \in \{1, 2, 3, 4\}$ and $\sigma \in \{\uparrow, \downarrow\}$ denote the orbital sites and spins, respectively. We note that the order parameter $\phi \in (\Phi, \Delta)$ is set as a real value. The specific forms of $4 \times 4$ bond matrices $O_a(k)$ and $12 \times 12$ pairing gap functions $\hat{\Gamma}(k)$ are tabulated in Table I, II. After constructing the ground state of the mean-field Hamiltonian $|G, \phi \rangle$ and evaluating the ground state energy $E[\phi] \equiv \langle G; \phi | H_0 + H_{\text{int}} | G; \phi \rangle$, we obtain the phase diagrams presented in Fig. 3 (see Supplementary Notes 4 and 5 for details). 161 grids of the ground energy with $\phi_i \in [-0.08, 0.08]$ are utilized and their numerical integration at given $\phi_i$ are carried out with $80 \times 80 \mathbf{k}$-points.

**First-principles calculations.** - We perform density-functional theory (DFT) calculations using the Vienna ab initio simulation package (VASP) [45, 46] with the projector-augmented wave
Time-reversal symmetry & Bond matrix $O_a(k)$ & Label & Subgroup \\Preserved & $(O_1, O_2, O_3)$ & ISD-1 ($\Phi < 0$) or SD-1 ($\Phi > 0$) & $D_{2h}$ \\
& $(-O_1, O_2, -O_3)$ & ISD-2 ($\Phi < 0$) or SD-2 ($\Phi > 0$) & \\
Broken & $i(O_1, -O_2, O_3)$ & TRSB-1 ($\Phi \neq 0$) & $C_{2h}$ \\
& $-i(O_1, O_2, O_3)$ & TRSB-2 ($\Phi \neq 0$) & \\

| TABLE I. CDW orders in the mean-field analysis. | Both time-reversal symmetric and asymmetric types of CDWs are considered. Translational symmetry-lowering of monolayer $AV_3Sb_5$ diversifies the order parameters, leading to a doublet of CDWs (CDW-1/2). When time-reversal symmetry is preserved, $\Phi < 0$ ($\Phi > 0$) results in the ISD (SD) CDWs. Without time-reversal symmetry, the TRSBs with opposite signs of $\Phi$ are equally classified. Here, the 4 × 4 bond matrices are introduced with $O_1(k) = (-\phi_1 I_2 + \phi_1^* \sigma_x) \otimes \sigma_z$, $O_2(k) = \sigma_z \otimes (-\phi_2 I_2 + \phi_2^* \sigma_x)$, $O_3(k) = \phi_3 \sigma_y \otimes \sigma_y + \phi_3^* \sigma_z \otimes \sigma_z$ and $\phi_i \equiv \exp(\mathbf{k} \cdot \mathbf{R}_i)$. |

Berry curvature and anomalous Hall conductivity. - The berry curvature $\Omega_n(k)$ associated with the $n$-th energy band of the TB Hamiltonian $H(k)$ is given by

$$
\Omega_n(k) = -2 \sum_{m \neq n} \frac{\text{Im} \langle u_{nk} | \partial_x H(k) | u_{mk} \rangle \langle u_{mk} | \partial_y H(k) | u_{nk} \rangle}{|E_n(k) - E_m(k)|^2}.
$$

Here, $E_n(k)$ and $|u_{nk}\rangle$ are $n$th eigenvalue and eigenstate of $H(k)$ and the derivative in the momentum space $\partial_i \equiv \frac{\partial}{\partial k_i}$ is adopted. The anomalous Hall conductivity is calculated as a function of energy $E$ by integrating the $n$-band Berry curvatures for $E_n < E$ over the BZ

$$
\sigma_{xy}(E) = \frac{e^2}{2\pi \hbar} \int d^2k \sum_{E_n < E} \Omega_n(k).
$$

The numerical integration is performed by using $500 \times 500 k$-points.

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Pairing in 1 × 1 unit cell | Pairing in 2 × 2 unit cell $\hat{\Gamma}_R(\mathbf{k})$ | Label | Basis function
--- | --- | --- | ---
$A_g$ | $\frac{1}{\sqrt{3}} \lambda_0, \frac{1}{\sqrt{2}} \left[ \frac{\sqrt{3}}{2} \lambda_7 + \frac{1}{2} \lambda_8 \right], \frac{1}{\sqrt{2}} [c_1 \lambda_1 + c_2 \lambda_2], c_3 \lambda_3$ | $\frac{1}{\sqrt{3}} L_0^0, \frac{1}{\sqrt{2}} \left[ \frac{\sqrt{3}}{2} L_0^0 + \frac{1}{2} L_8^0 \right], \frac{1}{\sqrt{2}} \left[ c_1 L_1^+ + c_2 L_2^+ - (s_1 L_4^- + s_2 L_5^-) \right], \left[ c_3 L_3^+ - s_3 L_6^- \right]$ | $\Gamma^{(1)}_{A_g}, \Gamma^{(2)}_{A_g}, \Gamma^{(3)}_{A_g}$ | $x^2, y^2, z^2$
$B_{1g}$ | $\frac{1}{\sqrt{2}} \left[ -\frac{1}{2} \lambda_7 + \frac{\sqrt{3}}{2} \lambda_8 \right], \frac{1}{\sqrt{2}} [c_1 \lambda_1 - c_2 \lambda_2]$ | $\frac{1}{\sqrt{2}} \left[ -\frac{1}{2} L_7^0 + \frac{\sqrt{3}}{2} L_8^0 \right], \frac{1}{\sqrt{2}} \left[ c_1 L_1^+ - c_2 L_2^+ - (s_1 L_4^- - s_2 L_5^-) \right]$ | $\Gamma^{(1)}_{B_{1g}}, \Gamma^{(2)}_{B_{1g}}$ | $xy$
$B_{2u}$ | $\frac{1}{\sqrt{3}} [s_1 \lambda_4 - s_2 \lambda_5], s_3 \lambda_6$ | $\frac{1}{\sqrt{2}} \left[ s_1 L_1^+ - s_2 L_5^+ - (c_1 L_1^- - c_2 L_2^-) \right]$ | $\Gamma^{(1)}_{B_{2u}}, \Gamma^{(2)}_{B_{2u}}$ | $y$
$B_{3u}$ | $\frac{1}{\sqrt{2}} [s_1 \lambda_4 + s_2 \lambda_5], s_3 \lambda_6$ | $\frac{1}{\sqrt{2}} \left[ s_1 L_1^+ + s_2 L_5^+ + (c_1 L_1^- + c_2 L_2^-) \right], \left[ s_3 L_6^+ - c_3 L_3^- \right]$ | $\Gamma^{(1)}_{B_{3u}}, \Gamma^{(2)}_{B_{3u}}$ | $x$

TABLE II. **SC orders in the mean-field analysis.** Spin-singlet superconducting pairings are classified by irreducible representations (R) of the point group $D_{3h}$. The condensation of $\hat{\Gamma}_R$ channels can lower the interaction energy, which preserves the $T_{1\times1}$-translational symmetry. The momentum dependence of pairing gap functions is abbreviated by $(c_i, s_i) \equiv (\cos \mathbf{k} \cdot \mathbf{R}_i, \sin \mathbf{k} \cdot \mathbf{R}_i)$. To express pairing functions in both 1 × 1 and 2 × 2 unit cells, the 3 × 3 Gell Mann matrices $\lambda_a$ and the 12 × 12 matrices $L_{a,0}^\pm$ are introduced with 4 × 4 matrices $M_{a,0}^\pm$ (see Supplementary Note 4). The fifth column shows the lowest-order basis functions for the corresponding irreducible representation.

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