Charge order landscape and competition with superconductivity in kagome metals

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In the kagome metals AV₃Sb₅ (A = K, Rb, Cs), three-dimensional charge order is the primary instability that sets the stage for other collective orders to emerge, including unidirectional stripe order, orbital flux order, electronic nematicity and superconductivity. Here, we use high-resolution angle-resolved photoemission spectroscopy to determine the microscopic structure of three-dimensional charge order in AV₃Sb₅ and its interplay with superconductivity. Our approach is based on identifying an unusual splitting of kagome bands induced by three-dimensional charge order, which provides a sensitive way to refine the spatial charge patterns in neighbouring kagome planes. We found a marked dependence of the three-dimensional charge order structure on composition and doping. The observed difference between CsV₃Sb₅ and the other compounds potentially underpins the double-dome superconductivity in CsV₃(Sb,Sn)₅ and the suppression of Tc in KV₃Sb₅ and RbV₃Sb₅. Our results provide fresh insights into the rich phase diagram of AV₃Sb₅.
Especially at the vHS filling fractions \( n = 3/12 \) and \( 5/12 \) (Fig. 1a), the Fermi surface of the kagome lattice is perfectly nested by three symmetry-equivalent nesting vectors \( \mathbf{Q}_1, \mathbf{Q}_2 \), and \( \mathbf{Q}_3 \). The electronic structure of the AV\(_3\)Sb\(_5\) series follows this script, with multiple kagome-derived vHSs –2–26. Accordingly, as displayed in Fig. 1b, a density functional theory (DFT) calculation of phonon frequency reveals six unstable modes exactly at the \( \mathbf{Q}_1, \mathbf{Q}_2 \), and \( \mathbf{Q}_3 \) in-plane wave vectors—three at M (that is, at the out-of-plane momentum \( k_z = 0 \)) and the other three at L (\( k_z = \pi \))—indicating that the pristine kagome structure is unstable towards the \( 2 \times 2 \) charge distortion27–29. Combined with the experimental identification of three \( Q \)-vectors of M and L phonons, various microscopic 3D-CO structures can be realized in the AV\(_3\)Sb\(_5\) series (Fig. 1h–m): Star-of-David or SoD (–M,–M,–M); tri-hexagonal or TrH (M,M,M); alternating SoD and TrH (L,L,L); staggered SoD (–M,–L,–L); staggered TrH (M,L,L); and staggered alternating SoD and TrH (M,M,L). Going beyond these simple \( 3Q \) superpositions, the free energy analysis indicates that the trilinear coupling of M and L phonon modes plays a central role in defining the exact 3D-CO structures and the leading instabilities (Supplementary Discussion 1 for details)28. For example, due to the coupling term \( \bar{Q} \), the LLL phase is invariably accompanied by MMM or inverse MMM distortions and becomes the LLL + MMM phase. The MML phase similarly acquires additional M and L phonon distortions from the \( \mathbf{Q}_2 \) and \( \mathbf{Q}_3 \) terms and, most importantly, does not appear as a leading instability of the free energy28. In the following, we will consider the five structures—MMM, inverse MMM, MLL, inverse MLL and LLL + MMM—as candidate 3D-CO structures, which are identified as the leading instabilities of the AV\(_3\)Sb\(_5\) system in the literature28.
We emphasize here that identifying the exact structure and symmetry of 3D-CO is of paramount importance for understanding the electronic symmetry breaking transitions and phase diagram of AV₃Sb₅. This is because CO formation has the highest energy scale in the AV₃Sb₅ series \( (T_{\text{CO}} = 78 – 102 \ \text{K}) \) and thus defines the background symmetry under which other electronic phases emerge (stripe order, nematicity, flux phase and superconductivity). For example, if CO crystalizes in the inverse MLL, MLL or MML phases (Fig. 1k–m), experimental band dispersion of CsV₃Sb₅ measured above \( T_{\text{CO}} \), at 120 K \( (c) \) and below \( T_{\text{CO}} \), at 6 K \( (d) \). The in-plane momentum \( k_z \) is defined to follow the F-K-M-K high-symmetry directions of the surface Brillouin zone. Solid arrows in \( c \) and \( d \) mark the original bands, while the dashed arrows in \( d \) indicate the replica bands. 

Electronic reconstruction from the out-of-plane component of 3D-CO. Schematics of the out-of-plane folding of the Brillouin zone \( (e) \). Panels \( f, h \) and \( j, g, i \) and \( k \) represent the dispersions measured above \( (f) \), at the first Brillouin zone with photon energy 86 eV, at the second Brillouin zone with photon energy 86 eV and at the first Brillouin zone with photon energy 113 eV, respectively. Solid arrows in \( g, i \) and \( k \) indicate the doubling or splitting of the kagome bands in the 3D-CO state. Supplementary Fig. 2 shows the visualization of splitting at other photon energies.
We start with a brief description of the overall electronic structure of AV₃Sb₅, as displayed in Fig. 2a, the DFT band calculation for CsV₃Sb₅ reveals four bands near $E_F$; an electron pocket at the Brillouin zone centre $\Gamma$ (G band), a $d_{xy}/d_{xz}$ orbital kagome band with Dirac point at approximately $-0.27$ eV and vHS near $E_F$ (K1 band), a $d_{xy}/d_{xz}$ orbital kagome band with Dirac point at approximately $-1.3$ eV and vHS near $E_F$ (K2 band) and an additional $d_{xy}/d_{xz}$ orbital kagome band with opposite parity from the K2 band (K’2 band). All band dispersions have been closely reproduced in previous ARPES studies 36–38. Meanwhile, in the experimental geometry used in the present study, only the G, K1 and K2 bands are visible in the ARPES spectra (Fig. 2c), for example due to the destructive interference of photoelectrons from the K1 and K2 bands in the 3D-CO state. For the inverse MLL and MLL (along the in-plane momentum direction. Yellow arrows in Fig. 3 highlight the splitting of the K1 and K2 bands in the 3D-CO state. For the inverse MLL and MLL (d and e), the calculation is averaged over three $C_2$-symmetric CO domains to account for the macroscopic beam spot size. Corresponding domain-resolved dispersions are presented in Extended Data Fig. 4. For the inverse MLL (a) and MLL (b) structures with the $2 \times 2 \times 1$ periodicity, we artificially folded the Brillouin zone along $k_z$ for a proper comparison with other structures. Insets show the zoomed-in view of the lower K1 Dirac band (DB), whose splitting sensitively depends on the microscopic structure of 3D-CO (yellow arrows). Colour bars are from 0 (black) to 1 (white) (arbitrary units).

Fig. 3 | Theoretical calculation of electronic reconstruction in AV₃Sb₅ and its dependence on the microscopic structure of 3D CO. a–e. Calculated dispersion of CsV₃Sb₅ at $k_z = 0$ in the inverse MLL, MMM, LLL + MMM, inverse MLL and MLL phases, respectively. For simplicity, the dispersion is unfolded along the in-plane momentum direction. Yellow arrows in highlight the splitting of the K1 and K2 bands in the 3D-CO state. For the inverse MLL and MLL (d and e), the calculation is averaged over three $C_2$-symmetric CO domains to account for the macroscopic beam spot size. Corresponding domain-resolved dispersions are presented in Extended Data Fig. 4. For the inverse MLL (a) and MLL (b) structures with the $2 \times 2 \times 1$ periodicity, we artificially folded the Brillouin zone along $k_z$ for a proper comparison with other structures. Insets show the zoomed-in view of the lower K1 Dirac band (DB), whose splitting sensitively depends on the microscopic structure of 3D-CO (yellow arrows). Colour bars are from 0 (black) to 1 (white) (arbitrary units).

3D-CO modulation patterns across adjacent kagome planes, which allows us to constrain the 3D-CO structure and symmetry in the AV₃Sb₅ series. Using this approach, we determine that the band splitting of CsV₃Sb₅ is most consistent with the staggered SoD and TrH structure (LLL + MMM phase), while those in KV₃Sb₅, RbV₃Sb₅, and Sn-doped CsV₃Sb₅ are markedly different from CsV₃Sb₅ and can be assigned to the staggered TrH structure (MLL phase). The tunability of the 3D-CO CsV₃Sb₅ allows us to constrain the 3D-CO structure and symmetry in the AV₃Sb₅ series. Using this approach, we determine that the band splitting of CsV₃Sb₅ at $k_z = 0$ in the inverse MMM, MMM, LLL + MMM, inverse MLL and MLL phases, respectively. For simplicity, the dispersion is unfolded along the in-plane momentum direction. Yellow arrows in highlight the splitting of the K1 and K2 bands in the 3D-CO state. For the inverse MLL and MLL (d and e), the calculation is averaged over three $C_2$-symmetric CO domains to account for the macroscopic beam spot size. Corresponding domain-resolved dispersions are presented in Extended Data Fig. 4. For the inverse MLL (a) and MLL (b) structures with the $2 \times 2 \times 1$ periodicity, we artificially folded the Brillouin zone along $k_z$ for a proper comparison with other structures. Insets show the zoomed-in view of the lower K1 Dirac band (DB), whose splitting sensitively depends on the microscopic structure of 3D-CO (yellow arrows). Colour bars are from 0 (black) to 1 (white) (arbitrary units).

As summarized in Fig. 2, we observed two distinct electronic reconstructions induced by 3D-CO in CsV₃Sb₅. First, as shown in Fig. 2b–d, we detected clear shadow bands below $T_{\text{CO}}$ (dashed arrows in Fig. 2d), which are the replica of the original bands (solid arrows in Fig. 2c,d) folded along the in-plane momentum direction. This is a direct consequence of the new periodicity arising from the in-plane component of CO, which folds the pristine Brillouin zone to the smaller $2 \times 2 \times 2 CO$ Brillouin zone (schematics in Fig. 2b). Such shadow bands and in-plane folding effects have been observed in other CO systems, such as transition metal dichalcogenides 40 and rare-earth trichalcogenides 41. At the same time, as shown in Fig. 2e–k, a detailed inspection below $T_{\text{CO}}$ additionally reveals an unusual doubling or splitting of the kagome bands along the energy axis. Such splitting could be visualized only after careful optimization of the spectral quality 42. At the simplest level, one can understand the band doubling as a consequence of the out-of-plane component of the 3D-CO, which folds the Brillouin zone along the $k_z$ direction and superimposes the $k_z = 0–\pi/2$ bands onto the $k_z = \pi–\pi/2$ bands (schematics in Fig. 2e). In the case of CsV₃Sb₅, we find three regions in the band structure where the doubling becomes most prominent: near the vHS of the K1 band (Fig. 2g,k), at the lower Dirac band of the K1 band (Fig. 2g,l) and at the K2 band near $E_F$ (Fig. 2k).
We also refer to Fig. 4f–h and Extended Data Fig. 3 for the corresponding energy distribution and momentum distribution curves, highlighting the band splitting in the 3D-CO state.

The key idea of this study comes from the realization that the doubled-band dispersion in the 3D-CO state is actually more than the simple superposition of $k_z = 0 \rightarrow \pi/2$ and $k_z = \pi \rightarrow \pi/2$ bands of the pristine structure. In the 3D-CO state, the adjacent kagome layers in AV$_3$Sb$_5$ become distinct upon realizing different CO patterns on each layer (Fig. 1j–m). The altered hopping pathways between the two charge-ordered kagome planes further reconstruct the doubled-band dispersion. This mechanism depends on the detailed ionic displacement patterns in adjacent kagome planes, making the band splitting strongly dependent on the 3D-CO structure. This provides a unique and highly constrained approach to resolve the microscopic structure of 3D-CO in the AV$_3$Sb$_5$ series.

To illustrate this idea further, we simulated the reconstruction of CsV$_3$Sb$_5$ bands in possible 3D-CO structures using DFT. Figure 3a–e shows the electronic structure of CsV$_3$Sb$_5$ at $k_z = 0$ in the 3D-CO state.

Fig. 4 | Electronic reconstructions in KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and Sn-doped CsV$_3$Sb$_5$ in the 3D-CO state. a–e, ARPES spectra of KV$_3$Sb$_5$ (a and d), RbV$_3$Sb$_5$ (b and e) and Sn-doped CsV$_3$Sb$_5$ (c) measured at 6 K. The spectra in a–e are collected with 93 eV, 92 eV, 88 eV, 85 eV and 84 eV photons, respectively. Green, red and purple arrows indicate the splitting of the K$_1$ vHS and K$_2$ band. Yellow arrows highlight the absence of splitting on the lower Dirac band of K$_1$. f, Energy distribution curves measured near the Fermi momentum ($k_F$) of the K$_1$ vHS. g, Momentum distribution curves of the K$_2$ band measured at the Fermi energy ($E_F$). h, Momentum distribution curves of the lower K$_1$ Dirac band measured at $-0.4$ eV. The arrows in f–h highlight the presence or absence of the 3D-CO-induced splitting. a.u., arbitrary units. i–k, Comparison between the DFT band structures of the inverse MLL, MLL and LLL + MMM phases. Double-headed arrows indicate the CO gaps at the M point induced by the SoD and TrH distortions. l–o, Comparison between the ARPES spectra of KV$_3$Sb$_5$, RbV$_3$Sb$_5$, Sn-doped CsV$_3$Sb$_5$ and CsV$_3$Sb$_5$ taken with vertically polarized light. The dashed line and filled circles are guides to the eye, emphasizing that the CO gaps in KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and Sn-doped CsV$_3$Sb$_5$ correspond to the TrH distortion of the MLL phase. Colour bars are from 0 to 1 (a.u.).
Discussion 2). We thus conclude that the observed band splitting supports the LLL + MMM structure or alternating SoD and TrH phase (Fig. 1) as the microscopic 3D-CO structure in CsV$_3$Sb$_5$. Intriguingly, the investigation of KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and Sn-doped CsV$_3$Sb$_5$ in (K,Rb)V$_3$Sb$_5$ (K$_{0.02}$V$_{0.98}$Sb$_5$) revealed an electronic reconstruction markedly different from the CsV$_3$Sb$_5$ case. Figure 4 displays ARPES spectra of KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and Sn-doped CsV$_3$Sb$_5$ measured at 6 K in the CO state. Similar to the case of CsV$_3$Sb$_5$, the doubling or splitting of the K1 vHS (Fig. 4a–c) and K2 bands (Fig. 4d,e) is clearly observed across the whole family. The corresponding energy distribution curves of the K1 vHS (Fig. 4f) and momentum distribution curves of the K2 band (Fig. 4g) also unambiguously demonstrate the presence of band doubling. We note that in Fig. 4f, the clear trend of increasing magnitude of splitting with decreasing size of the alkali metal is apparent, and it may reflect the enhanced degree of k$_z$ dispersion from Cs to K [refs. 1,27]. We thus conclude that the 3D-CO is a universal phenomenon in the AV$_3$Sb$_5$ series. However, we observe that the behaviour of the lower K1 Dirac band in KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and Sn-doped CsV$_3$Sb$_5$ is very different from that of the CsV$_3$Sb$_5$ case. As highlighted with yellow arrows in Fig. 4a–e, the lower Dirac dispersion of the K1 band does not undergo a splitting in the 3D-CO state, in contrast to the observations in CsV$_3$Sb$_5$ (Fig. 2g,i).

The inverse MMM, MMM, LLL + MMM, inverse MLL and MLL phases, respectively (Supplementary Table 1 for the exact structures used in the calculation). In accordance with the experimental results, the doubling of the K1 and K2 kagome bands is closely reproduced in the 3D-CO phases (yellow arrows in Fig. 3c, for example). Crucially, the details of band splitting become noticeably different in each 3D-CO phase. In particular, the lower K1 Dirac band barely splits in the inverse MMM, MMM, inverse MLL and MLL phases (Fig. 3a,b,d,e), while an apparent doubling is observed in the LLL + MMM structure (Fig. 3c). The doubling of the lower K1 Dirac band in the latter closely reproduces the ARPES spectra in Fig. 2g,i and is a direct consequence of the coexistence of two CO gaps arising from the alternating SoD and TrH layers in the 3D-CO structure (more information is below and in Supplementary Discussion 2). We thus conclude that the observed band splitting supports the LLL + MMM structure or alternating SoD and TrH phase (Fig. 1) as the microscopic 3D-CO structure in CsV$_3$Sb$_5$.
The absence of the splitting for the lower K Dirac band can be further confirmed from the momentum distribution curves in Fig. 4h. Compared to the calculations in Fig. 3, this behaviour rules out the LLL + MMM structures (Fig. 3c,f) but is consistent with the inverse MMM, MMM, inverse MLL and MLL structures (Fig. 3a,b,d,e). In case of the inverse MMM and MMM structures, however, the charge distortions are identical in neighboring kagome planes (2 × 2 × 1 structure); therefore, they cannot induce the out-of-plane band doubling observed on the K1 and K2 band. This leaves the inverse MLL or MLL phases, intrinsically breaking C₃ rotational symmetry, as possible ionic displacement motifs in KV₃Sb₅, RbV₃Sb₅, and Sn-doped CsV₃Sb₅.

One can further distinguish the inverse MLL (staggered SoD) and MLL (staggered TrH) phases by recognizing the difference in the charge order gaps induced by the in-plane SoD and TrH distortions. As shown in the DFT band structures of Fig. 4i,j, the TrH distortion of the MLL phase produces a much larger gap at the M point, Δ₁₁ = 0.22 eV, compared to the SoD distortion, Δ₁₀ = 0.13 eV. In the case of the LLL + MMM structure with alternating SoD and TrH kagome planes, the SoD and TrH gaps simultaneously manifest in the spectrum (Fig. 4k), resulting in the splitting of the lower K Dirac band observed in CsV₃Sb₅. For the detailed inspection of the CO gap near the M point, we acquired additional ARPES maps with vertical light polarization (Fig. 4l–o). A close comparison of the ARPES spectra of KV₃Sb₅, RbV₃Sb₅, and Sn-doped CsV₃Sb₅, (Fig. 4l–n) with that of CsV₃Sb₅ (Fig. 4o) clearly suggests that the CO gap of the former compounds corresponds to the larger gap, that is, to a TrH distortion. We thus conclude that the 3D-CO in KV₃Sb₅, RbV₃Sb₅, and Sn-doped CsV₃Sb₅ manifests in the MLL phase, in contrast with the LLL + MMM structure in pristine CsV₃Sb₅. This implies that despite the charge ordering tendency of the kagome lattice being universal in the AV₃Sb₅ family, the microscopic details of 3D-CO are strongly dependent on the chemical composition and doping, adding to the rich physics that can be realized in the AV₃Sb₅ series.

The observation of the evolution and tunability of the 3D-CO structure within the AV₃Sb₅ family offers important insights into the exotic electronic phenomena realized in AV₃Sb₅ species and their dependence on chemical composition (Supplementary Discussion 3). In the following, we discuss the empirical correlation between the 3D-CO structure and the superconducting phenomenology of the AV₃Sb₅ family, providing a new framework to understand the double-dome superconductivity in CsV₃Sb₅ and the suppression of Tc in KV₃Sb₅ and RbV₃Sb₅.

One of the most intriguing aspects of the CsV₃Sb₅ phase diagram is the emergence of a double superconducting dome, which signals a non-trivial interplay between CO and superconductivity. The double superconducting dome was first discovered in the pressure–temperature phase diagram of CsV₃Sb₅ (refs. 14,15) and subsequently observed as a function of Sn substitution in CSv₃Sb₅–Snₓ (refs. 18,19). The remarkable tunability of the 3D-CO state across otherwise similar compounds suggests that the AV₃Sb₅ series is a candidate host for a rich phase diagram of emergent electronic phases, enabling new opportunities for fundamental studies at the nexus of strong correlation phenomena and topology.

Online content
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Methods
Sample synthesis and ARPES
High-quality single crystals of pristine and Sn-doped AV₃Sb₅ were synthesized via a flux method as described in refs. 1, 2, 4, 5. ARPES experiments were performed at Beamline 7.0.2 (MAESTRO) of the Advanced Light Source, equipped with an R4000 hemispherical electron analyser (Scienta Omicron). The samples were cleaved inside an ultra-high vacuum chamber with a base pressure better than ~4 × 10⁻¹¹ Torr. We kept the following experimental geometry throughout the measurement except as otherwise specified: horizontal analyser slit, linear horizontal light polarization and Γ–K–M direction of the sample aligned to the scattering plane. For each sample, the photon energy was scanned from 60 eV to 200 eV, covering more than three complete 3D Brillouin zones. The kₓ plane is determined based on the nearly free-electron final state approximation. For the high-resolution data in Figs. 2 and 4, we selected the photon energies for each sample that best visualize the band splitting around kₓ = 0. The energy and momentum resolutions were better than 20 meV and 0.01 Å⁻¹.

DFT calculations
DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) 51, 52, 53 with the generalized gradient approximation Perdew–Burke–Ernzerhof exchange–correlation functional 54 and the pseudo potential formalism based on the projector augmented-wave method 55. The phonon frequency spectrum was derived from the Hessian matrix (which encodes the second derivatives of the atomic position coordinates) computed with the density functional perturbation theory method, using a 4 × 4 × 2 supercell unit 56. We further simulated various 2 × 2 × 2 CO states from combinations of the unstable M and L phonon modes. The CO structures were relaxed with a 350 eV energy cut-off for the plane-wave basis and a 4 × 4 × 2 grid sampling in the momentum space Brillouin zone. Supplementary Table 1 shows the detailed characterization of the 3D-CO structures after relaxation. To elucidate the electronic properties of these COs, we performed electronic band structure unfolding and projections based on the Wannier models derived from DFT ground states, using Wannier 90 code.

Data availability
Data associated with this paper are available on the Harvard Dataverse at https://doi.org/10.7910/DVN/KJRGXU.

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Author contributions
M.K., J.-H.P. and R.C. conceived the project; M.K. and J.Y. performed the ARPES experiments and analysed the resulting data with help from S.H.R., J.K., C.J., A.B. and E.R.; S.F. performed the theoretical calculations with help from E.K. and J.C.; and B.R.O., Y.M.O. and S.D.W. synthesized and characterized the crystals. M.K. and R.C. wrote the manuscript with input from all coauthors.

Competing interests
The authors declare no competing interests.

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Extended Data Fig. 1 | Fermi surface and overall electronic structure of pristine and Sn-doped AV₃Sb₅ (A=K, Rb, Cs). a–d, Fermi surfaces of KV₃Sb₅, RbV₃Sb₅, CsV₃Sb₅ and Sn-doped CsV₃Sb₅, respectively. e–h, Wide energy-momentum range ARPES spectra of KV₃Sb₅, RbV₃Sb₅, CsV₃Sb₅ and Sn-doped CsV₃Sb₅, respectively. All data are acquired at the base temperature 6 K, that is in the charge ordered state.
Extended Data Fig. 2 | $k_z$ dispersion of (K,Rb,Cs)V$_3$Sb$_5$. a-c, $k_y$-$k_z$ map of KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ respectively, acquired at 0.5 eV binding energy. d-f, Corresponding $k_z$-$E$ map acquired at $k_y=0$. The pronounced $k_z$ dispersion of the G band is clearly visible in panels d-f from which we determined the inner potential for each sample, 5.4, 4.3, and 7.3 eV, respectively.
Extended Data Fig. 3 | Momentum- and energy-distribution-curves highlighting the band splitting in 3D-CO phase. a–c, Momentum-distribution-curves (MDCs) across the lower K1 Dirac band above (140 K, panel b) and below (6 K, panel c) the 3D-CO transition. The dashed line in panel a marks the region where the MDCs are extracted. The doubling of the lower K1 Dirac band is observed only in the case of CsV3Sb5. d–f, Energy-distribution-curves (EDCs) across the K1 vHs above (140 K, panel e) and below (6 K, panel f) the 3D-CO transition. The dashed line in panel d marks the region where the EDCs are extracted. The doubling of the K1 vHs is universally observed at the low temperature as marked with the arrows in panel f.
Extended Data Fig. 4 | Domain-resolved electronic structures of CsV₃Sb₅ in \( C_2 \) symmetric 3D-CO phases. a–c, Domain-resolved dispersion of CsV₃Sb₅ in the inverse MLL 3D-CO phase. The location of three different \( \mathbf{k} \)-paths with respect to the \( C_2 \) rotation axis is schematically displayed above each panel. d–f, Same with a–c but in the MLL phase. Corresponding domain-averaged electronic structures are shown in Fig. 3d, e.