

Supplementary Material for

**Spectroscopic Evidence for a Three-Dimensional Charge Density
Wave in Kagome Superconductor CsV_3Sb_5**

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1. Calculated band structure of CsV_3Sb_5 along high-symmetry directions and their orbital nature

Figure S1 shows the calculated band structure of CsV_3Sb_5 along high-symmetry directions (Γ -K-M- Γ -A-H-L-A) and their orbital nature which corresponding the calculated band structure in Fig. 1g. It can be clearly observed that the electronic-like band around the Brillouin zone (BZ) center is dominated by the p_z orbital of Sb atoms.

2. Calculated band structure of CsV_3Sb_5 along high-symmetry directions when considering the $2\times 2\times 2$ lattice reconstruction

Figure S2a-S2d show the crystal structure of CsV_3Sb_5 when considering the $2\times 2\times 2$ lattice reconstruction due to the CDW caused by the alternate stacking of star of David (SoD)- and tri-hexagonal (TrH)-like distortions along c axis (Fig. S2a), the alternate stacking of SoD- and TrH-like distortions with in-plane π phase shift along c axis (Fig. S2b), the alternate stacking of the TrH-like distortions and its in-plane π phase shift along c axis (Fig. S2c) and the alternate stacking of the SoD-like distortions and its in-plane π phase shift along c axis (Fig. S2d). In this case, due to the lattice constant expands to $2\times 2\times 2$ times as pristine, the corresponding Brillouin zone (BZ) should shrinks to $0.5\times 0.5\times 0.5$ times as before which will result in the reconstruction of the electronic structure in the new BZ. Fig. S2e-S2h show the unfolded calculated bands of CsV_3Sb_5 along high-symmetry directions (Γ' -K'-M'- Γ' -A'-H'-L'-A') when considering the $2\times 2\times 2$ lattice reconstruction that corresponding to Fig. S2a-S2d.

3. Detailed Fermi surface mapping of CsV_3Sb_5

Figure S3 shows the Fermi surface map of CsV_3Sb_5 measured at 150 K (20 K) in the sample cleaved at high temperature (HTC, 150 K) with the photon energy of 57 eV (Fig. S3a for 150 K, Fig. S3e for 20 K), 62 eV (Fig. S3b for 150 K, Fig. S3f for 20 K) and 120 eV (Fig. S3c for 150 K, Fig. S3g for 20 K) and measured at 120 K (20 K) in the sample cleaved at low temperature (LTC, 20 K) with the photon energy of 95 eV (Fig. S3d for 120 K, Fig. S3h for 20 K). Comparing the data above (150 K and 120 K) and below (20 K) the CDW transition temperature (94 K), no obvious in-plane Fermi surface folding caused by a CDW was observed.

4. Distinguish the surface states of CsV_3Sb_5

Figure S4 shows the calculated band structure of CsV_3Sb_5 along the Γ -K-M- Γ directions for a ten-unit-cell-thick slab, which can help us distinguish the surface states from bulk states in CsV_3Sb_5 . The bands marked by arrows in Fig. S4a are the surface states. Based on the analysis of Fig. S1, the orbital nature of the surface states can be determined as the p_z orbital of Sb atoms. Further analysis showed that the surface states marked in Fig. S4a are contributed by Sb1 atoms (the Sb atom in the V-Sb plane, blue lines in Fig. S4b). When the sample surface is terminated by Cs atoms, the surface states can be clearly observed (Fig. S4b). However, the surface states vanish in the sample where the surface is terminated by Sb atoms as shown in Fig. S4c.

5. Detailed photon energy dependent ARPES spectral intensity map of CsV_3Sb_5 at 20 K.

Figure S5 shows the detailed photon energy dependent ARPES spectral intensity map of CsV_3Sb_5 measured at 20 K in the sample cleaved at low temperature (20 K) at the binding energy of 0 eV (Fig. S5a), 0.1 eV (Fig. S5b), 0.2 eV (Fig. S5c), 0.3 eV (Fig. S5d), 0.4 eV (Fig. S5e) and 0.5 eV (Fig. S5f) with the photon energy range from 25 eV to 110 eV. It can be clearly observed that there are some periodic structures along the k_z direction.

6. Photon energy dependent spectra for photoemission intensity at the BZ center of CsV_3Sb_5 .

Figure S6 shows the photon energy dependent spectra for photoemission intensity at the BZ center of CsV_3Sb_5 measured at 20 K which correspond to the measurements in Fig. 4e-4g in the main manuscript.

7. Distinguish the CDW configurations that result in a $2\times 2\times 2$ lattice reconstruction in CsV_3Sb_5 .

Fig. S7a-S7d shows the calculated band structure of CsV_3Sb_5 along the M-K- Γ -K-M direction when considering the $2\times 2\times 2$ lattice reconstruction due to the CDW caused by the alternate stacking of SoD- and TrH-like distortions (Fig. S7a) (TrH-like distortions with in-plane π phase shift, Fig. S7b) along the c axis, the alternate stacking of the TrH-like (Fig. S7c) (SoD-like, Fig. S7d) distortions and its in-plane π phase shift. Fig. S7e and

Fig. S7g show the band structure along M-K- Γ -K-M direction measure at 20 K (Fig. S7e) and 120 K (Fig. S7g) with the photon energy of 70 eV. In order to observe band features more clearly, we do the EDC second derivative image for Fig. S7e and Fig. S7g which are shown in Fig. S7f and Fig. S7h. It can be clearly observed that there are two bands (δ_1 band and δ_2 band) around the M point at 20 K but only one band (δ band) around the M point at 120 K. It can be inferred that the emergent δ_1 band at 20 K is the band folding due to the CDW. In addition, it can be found that only the CDW configurations with the alternate stacking of SoD- and TrH-like distortions (or TrH-like distortions with in-plane π phase shift) along the c axis can induce two bands (δ_1 band and δ_2 band) around the M point which is in agreement with our experimental data. Therefore, it can be inferred that the 3-dimensional CDW configuration of CsV_3Sb_5 along the c direction is likely the alternate stacking of SoD- and TrH-like distortions (or TrH-like distortions with in-plane π phase shift).

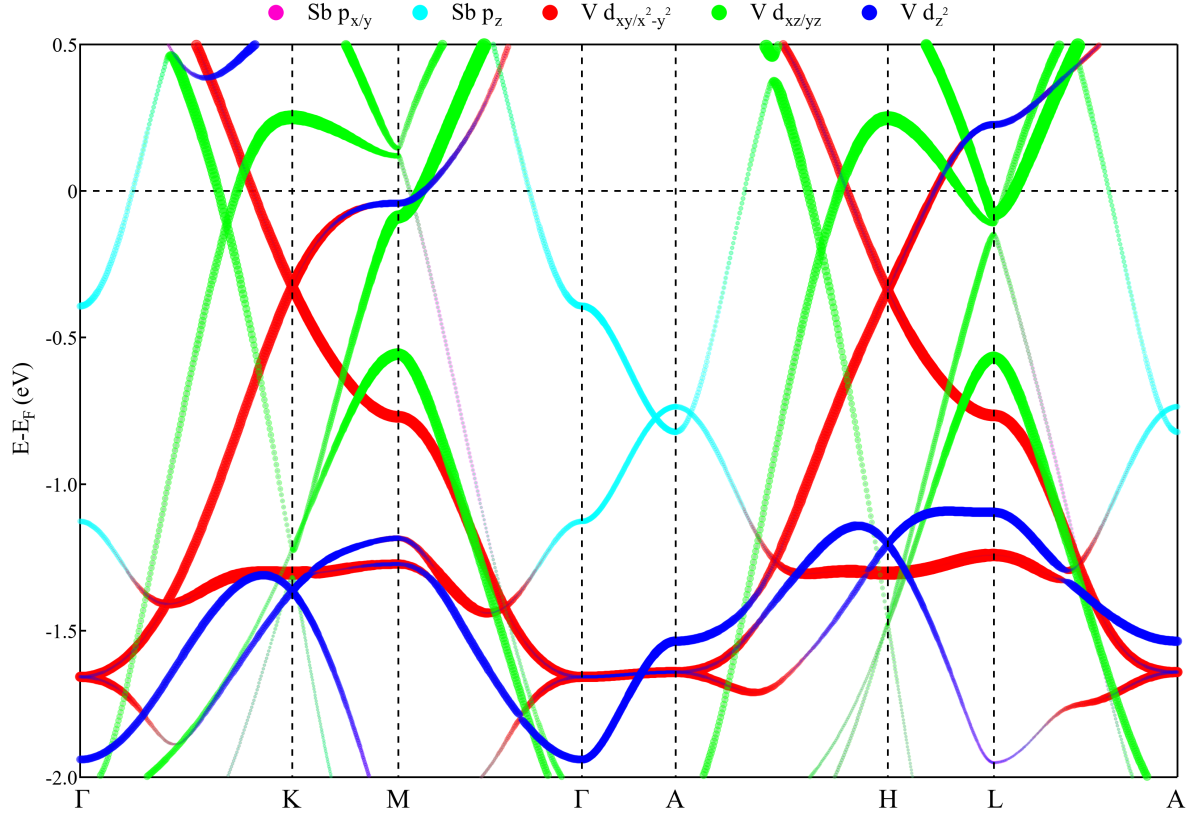


FIG. S1. **Calculated band structure of CsV_3Sb_5 along high-symmetry directions and their orbital nature.** Calculated band structure of CsV_3Sb_5 along high-symmetry directions across the Brillouin zone without considering the CDW. The orbital nature of bands are marked by different colors that pink is the $p_{x/y}$ orbital of Sb atoms, cyan is the p_z orbital of Sb atoms, red is the d_{xy/x^2-y^2} orbital of V atoms, green is the $d_{xz/yz}$ orbital of V atoms and blue is the d_{z^2} orbital of V atoms.

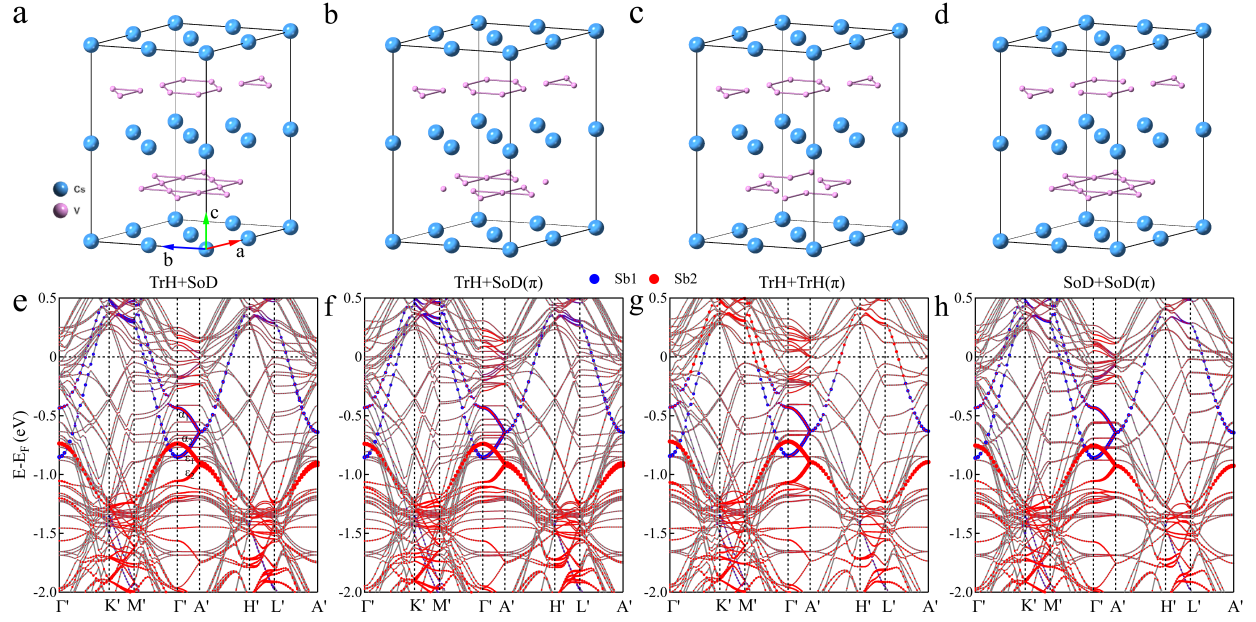


FIG. S2. **Single crystal structure and calculated band structure of CsV_3Sb_5 along high-symmetry directions when considering the $2 \times 2 \times 2$ lattice reconstruction.** (a-d) One unit cell of CsV_3Sb_5 when considering the $2 \times 2 \times 2$ lattice reconstruction due to the CDW caused by the alternate stacking of SoD- and TrH-like distortions along c axis (a), the alternate stacking of SoD- and TrH-like distortions with in-plane π phase shift along c axis (b), the alternate stacking of the TrH-like distortions and its in-plane π phase shift along c axis (c) and the alternate stacking of the SoD-like distortions and its in-plane π phase shift along c axis (d). (e-h) The unfolded calculated bands of CsV_3Sb_5 along high-symmetry directions ($\Gamma' - K' - M' - \Gamma' - A' - H' - L' - A'$) when considering the $2 \times 2 \times 2$ lattice reconstruction that corresponding to (a-d). Γ' , K' , M' , A' , H' , L' are the high-symmetry points of the folded BZ due to the $2 \times 2 \times 2$ lattice reconstruction which corresponding to Γ , K , M , A , H , L in the unfolded BZ.

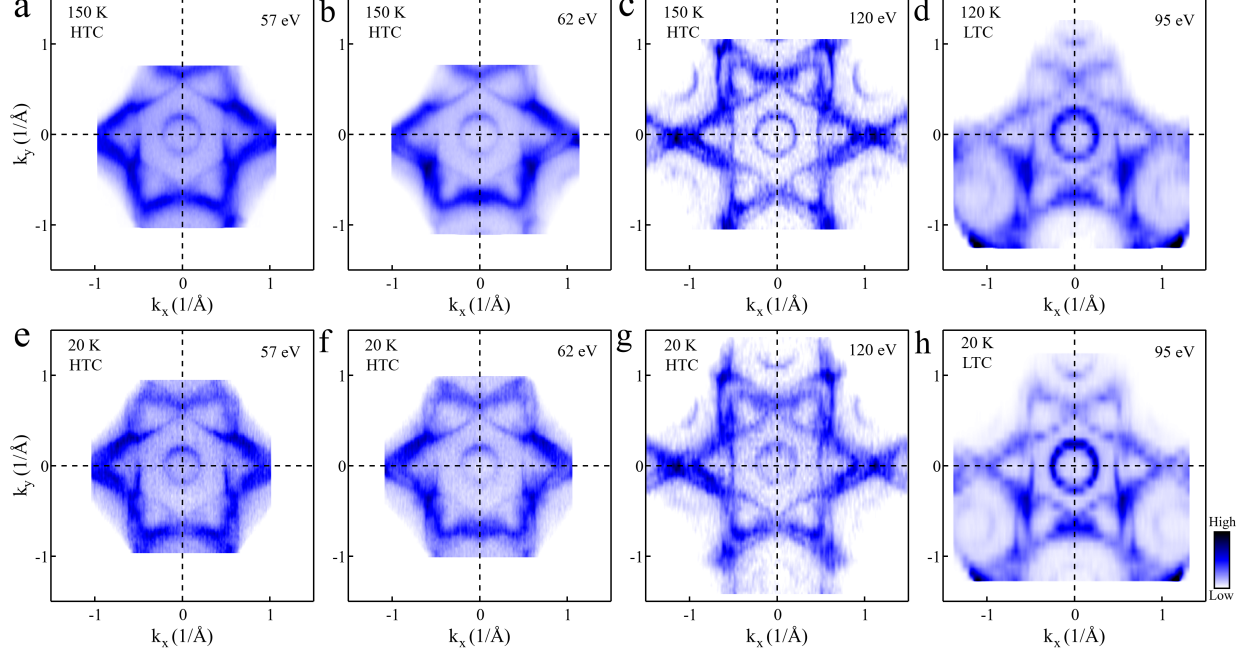


FIG. S3. **Fermi surface mapping of CsV_3Sb_5 .** (a-c) Fermi surface mapping of CsV_3Sb_5 measured at 150 K in the sample of high temperature cleavage (HTC) with the photon energy of 57 eV (a), 62 eV (b) and 120 eV (c). (d) Fermi surface mapping of CsV_3Sb_5 measured at 120 K in the sample of low temperature cleavage (LTC) with the photon energy of 95 eV. (e-g) Fermi surface mapping of CsV_3Sb_5 measured at 20 K in the sample of high temperature cleavage (HTC) with the photon energy of 57 eV (e), 62 eV (f) and 120 eV (g). (h) Fermi surface mapping of CsV_3Sb_5 measured at 20 K in the sample of low temperature cleavage (LTC) with the photon energy of 95 eV.

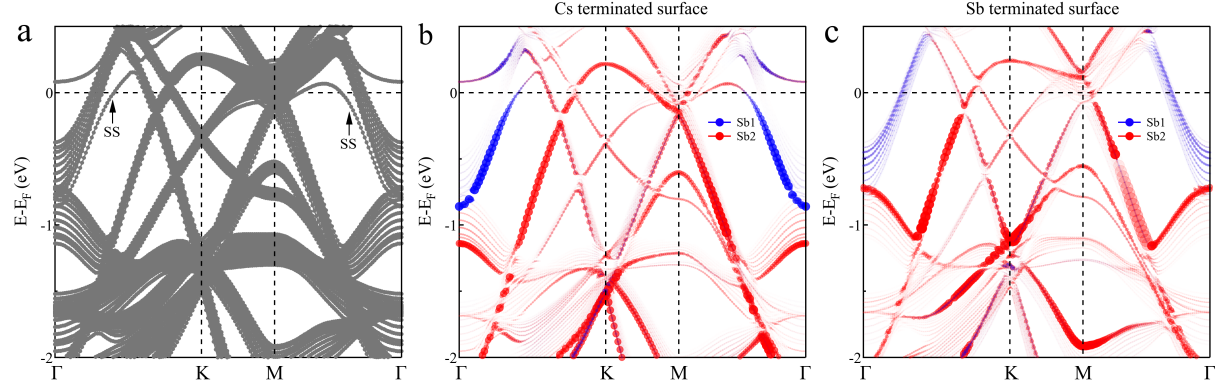


FIG. S4. **The calculated band structures of CsV_3Sb_5 along Γ -K-M- Γ directions for a ten-unit-cell-thick slab.** (a) The original data. The bands marked by arrows are the surface state (SS). (b-c) The calculated band structures which show the orbitals contributed by Sb atoms in the sample with terminated surface covered by Cs atoms (b) and Sb atoms (c). The thickness of the lines represent the proportion of the orbital. The blue lines are the orbital from Sb1 atoms, and the red lines are the orbital from Sb2 atoms.

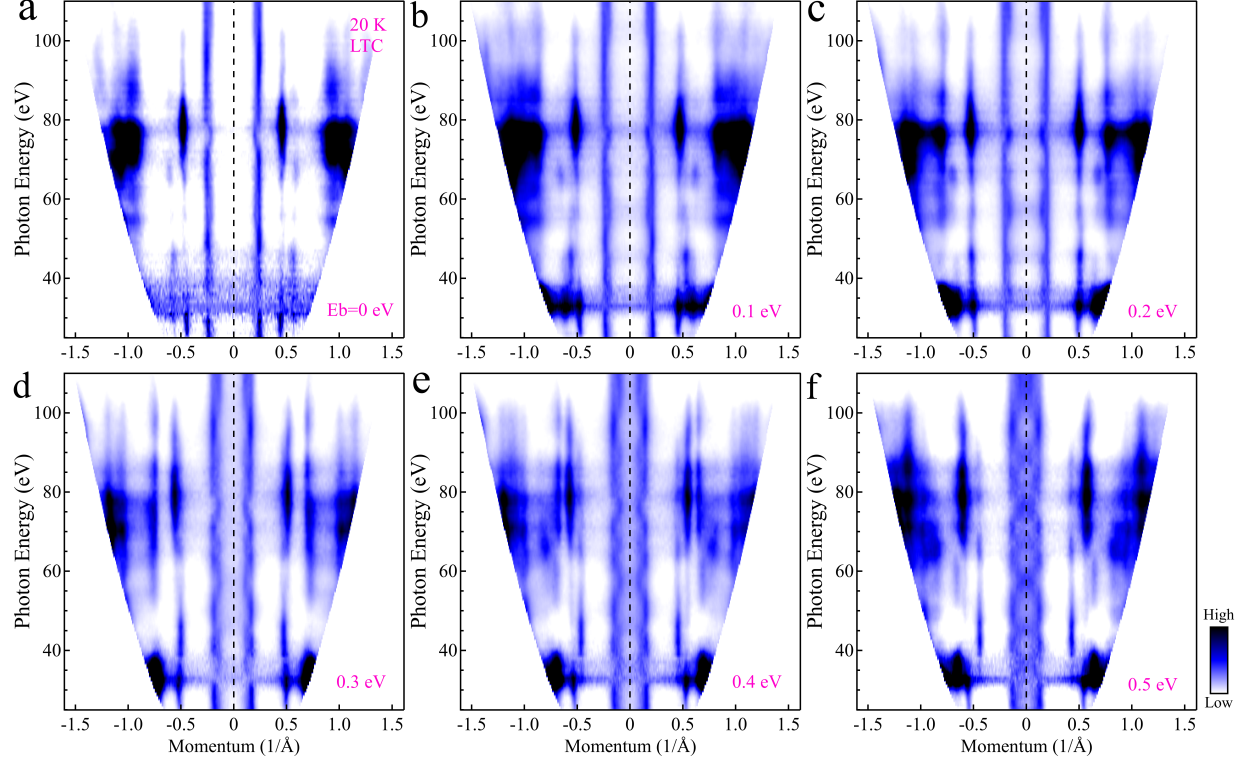


FIG. S5. **Photon energy dependent ARPES spectral intensity map of CsV_3Sb_5 .** (a-f) Photon energy dependent ARPES spectral intensity map of CsV_3Sb_5 measured at 20 K in the sample of the low temperature cleavage (LTC) at the binding energy of 0 eV (a), 0.1 eV (b), 0.2 eV (c), 0.3 eV (d), 0.4 eV (e) and 0.5 eV (f).

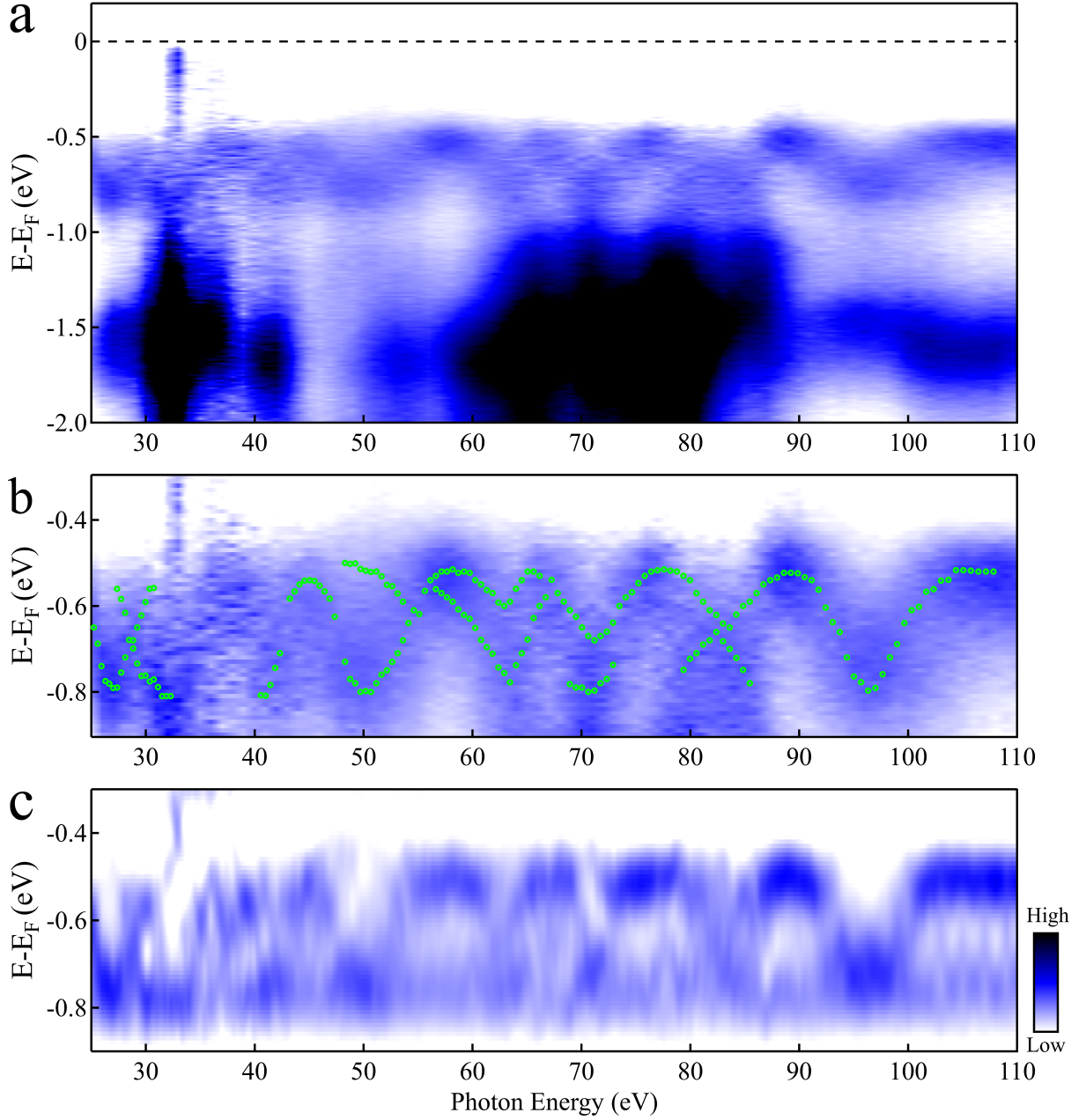


FIG. S6. **Photon energy dependent spectra for photoemission intensity at the BZ center of CsV₃Sb₅.** (a) Photon energy dependent spectra for photoemission intensity at the BZ center. The intensity are normalized in the range of -0.8 eV to -0.5 eV. (b) The zoom in of (a). The green open circles mark the peak position of main subbands which extracted from Fig. 4f. (c) The corresponding energy distribution curve (EDC) second derivative image of (b), but it is normalized around -0.8 eV.

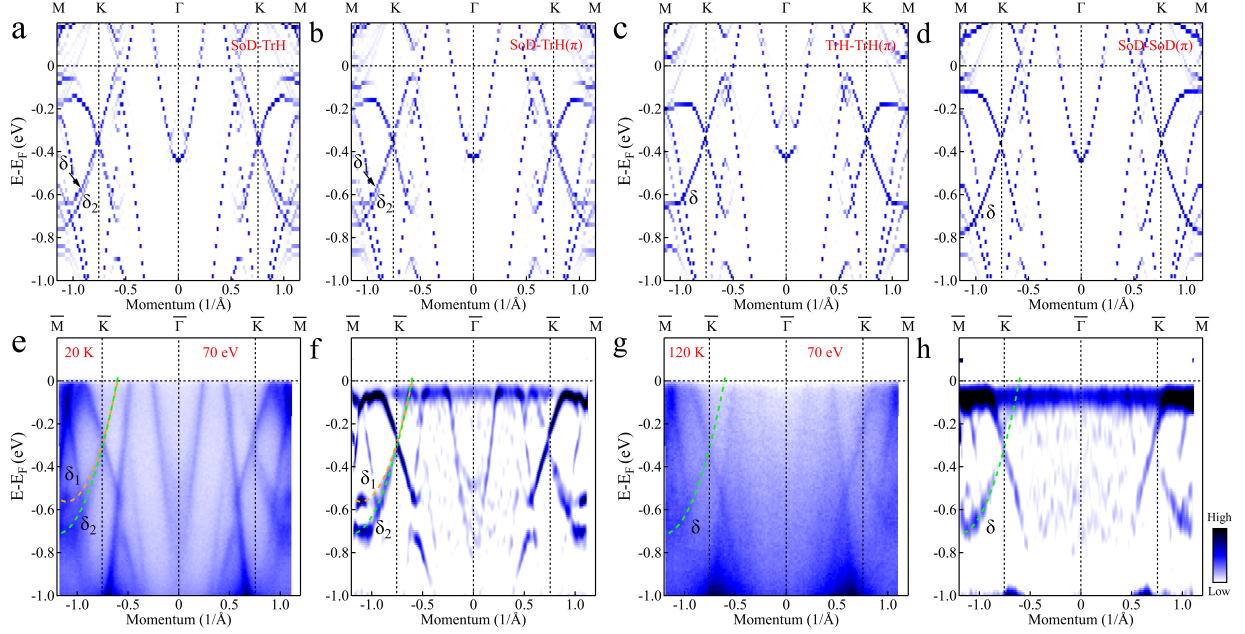


FIG. S7. **Distinguish the CDW configurations that result in a $2 \times 2 \times 2$ lattice reconstruction in CsV_3Sb_5 .** (a-d) Calculated band structure of CsV_3Sb_5 along M-K- Γ -K-M direction when considering the $2 \times 2 \times 2$ lattice reconstruction due to the CDW with the alternate stacking of SoD- and TrH-like distortions along c axis (a), the alternate stacking of SoD- and TrH-like distortions with in-plane π phase shift along c axis (b), the alternate stacking of the TrH-like distortions and its in-plane π phase shift (c) and the alternate stacking of the SoD-like distortions and its in-plane π phase shift (d). (e) and (g) Band structure along M-K- Γ -K-M direction measured at 20 K (e) and 120 K (g) with the photon energy of 70 eV. (f) and (h) The corresponding EDC second derivative image of (e) and (g).