Supplemental Material: Cyclic Ferroelectric Switching and Quantized Charge Transport in $CuInP_2S_6$

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In this Supplemental Material, we provide computational details on all of our calculations, as well as discuss how we identified the midpoint structure $\overline{M}$ of the cross-gap cooperative switching path. We additionally provide an energy profile for the aforementioned switching path.

COMPUTATIONAL DETAILS

All first-principles density functional theory (DFT) calculations are performed using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) method [1, 2], and employ the generalized-gradient approximation to the exchange-correlation functional, as parametrized by Perdew-Burke-Ernzerhof [3]. van der Waals (vdW) interactions are taken into account by using the zero-damping D3 method of Grimme [4]. The energy convergence criterion for all self-consistent DFT calculations is set to 10^{-7} eV, while the force convergence criterion for atomic coordinate relaxation is set at 10^{-3} eV/Å; for plain elastic band (PEB) and nudged elastic band (NEB) calculations [5–7], the latter is set to 0.025 eV/Å. All calculations employ a kinetic energy cutoff of 400 eV for the plane waves, and all employ Γ-centered k-meshes. For electric polarization (computed using the Berry phase theory [8]) the k-mesh size is $8 \times 8 \times 15$, while for all other calculations it is $8 \times 8 \times 4$. All calculations are performed for systems at zero temperature.

MIDPOINT OF THE THROUGH-GAP COOPERATIVE SWITCHING PATH

As discussed in the main text, despite being found at the same value of $\Delta_c = 0.25$, the M^+ and M^- structures are distinct, and therefore do not link up to form a continuous switching path. To remedy this problem, we turn to the PEB and NEB methods to identify a path connecting the two structures. In all PEB and NEB calculations about to be described, the lattice vectors and internal atomic coordinates are permitted to vary so as to preserve the symmetry of the initial paths provided. The initial paths are obtained by linearly interpolating the lattice vectors and internal atomic coordinates between the two endpoint structures of the path.

Initially, we perform a PEB calculation initialized on a path with a single structure between M^+ and M^-. The structure is obtained by selecting the midpoint of the linear interpolation between M^+ and M^-, and is found in space group $C2/c$. The output of this PEB calculation is subsequently used as the only input intermediate structure in an NEB calculation with the same anchor points; we label the result of this follow-up NEB calculation as $\widetilde{M}$. $\widetilde{M}$ is then used to initialize an NEB calculation in which the initial path is composed of structures residing on the combination of linearly interpolated paths between M^+ and $\widetilde{M}$, and $\widetilde{M}$ and M^-. Although the calculation satisfies the convergence criteria, we find that resulting path is still discontinuous.

We subsequently change the anchor points of the NEB calculation, selecting the states at $\Delta_c = 0.18$ and 0.32; under appropriate applied strain these states become the ±HP states residing on the quadruple-well potential for CIPS. Using the new anchor points and selecting the structure residing on the midpoint of the linear interpolation between them, we perform the same sequence of PEB followed by NEB calculation as described above. The output is labeled $\widehat{M}$. We then generate an initial path composed of structures residing on the linearly interpolated paths between the structure at $\Delta_c = 0.18$ and $\widehat{M}$, and $\widehat{M}$ and the structure at $\Delta_c = 0.32$, respectively. In the course of the calculation, $\widehat{M}$ evolves into the structure we refer to as $\overline{M}$, found in space group $C2/c$. We find that $\overline{M}$ does not differ significantly from $\widetilde{M}$, and we thus identify the former as defining the energy barrier for cooperative cross-gap switching.

ENERGY PROFILE OF THE COOPERATIVE SWITCHING PATH

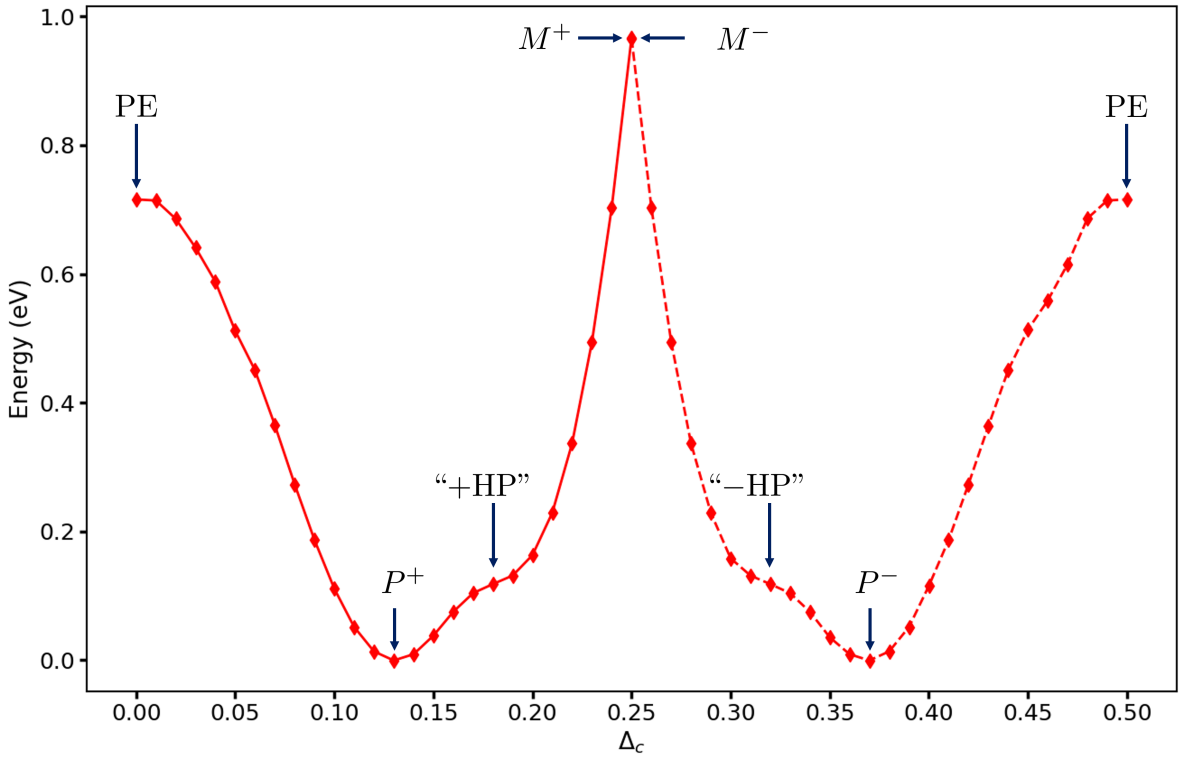

FIG. 1. The energy profile as a function of Δ_c of the combined through-layer and cross-gap cooperative switching paths. We indicate the locations of the points corresponding to the PE phase, $P^{\pm}$, and $M^{\pm}$ structures. By "±HP" we indicate the structures that under applied strain will turn into the proper ±HP states residing on the quadruple-well potential of CIPS. Although in the main text the states derived from P^- feature negative values of Δ_c, here we have used the fact that Δ_c is defined modulo 1/2 to translate the corresponding portion of the curve to lie in the range $0.25 \leq \Delta_c \leq 0.5$.

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