Anharmonic stabilization of ferrielectricity in CuInP$_2$Se$_6$

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(Dated: November 23, 2021)

Using first-principles calculations and group-theory based models, we study the stabilization of ferrielectricity (FiE) in CuInP$_2$Se$_6$. We find that the FiE ground state is stabilized by a large anharmonic coupling between the polar mode and a fully symmetric Raman-active mode. Our results open possibilities for controlling the single-step switching barrier for polarization by tuning the Raman-active mode. We discuss the implications of our findings in the context of designing next-generation optoelectronic devices that can overcome the voltage-time dilemma.

INTRODUCTION

Recently, ferroelectricity in layered van der Waals materials has attracted a lot of attention because of its applications in high-density nonvolatile memory devices [1, 2]. However, very few layered materials demonstrate switchable out-of-plane polarization [3–8]. Of those, the transition metal thiophosphates which includes CuInP$_2$Se$_6$ (CIPSe) are a promising family of materials that host out-of-plane ferrielectricity (FiE) with large values of polarization [4, 9, 10]. The FiE phases in this family is characterized by a negative piezoelectric response [11, 12] and a negative electrostriction [13], along with large dielectric tunability [14]. This led to device applications such as ferroelectric (FE) tunnel junctions [15] and FE field-effect transistors [16, 17].

CIPSe was reported to undergo a broad phase transition (200 K to 240 K) from the paraelectric (PE) phase (space group $P31c$) to the FiE phase (space group $P31c$) via an incommensurate phase where there is coexistence of FiE and antiferroelectric order [18, 19]. Similar to other materials in this family [20], the phase transition is expected to have a large order-disorder character in addition to a displacive character [21]. A coupled double-well model with an on-site potential and inter-oscillator coupling can reconcile with both the order-disorder character and the displacive character in these materials [20, 22]. However, the on-site potential itself should be sufficient to understand energy landscape of the low-temperature FiE phase that has come under much attention recently.

The prior works in the literature focused on obtaining the on-site potential using a Landau expansion about the polar off-centering of only the Cu atoms [10]. While the distortions of the Cu sites relative to the PE phase are large (1.2 Å) [23] it would be surprising for such a large distortion to stabilize the FiE phase without the participation of the other atoms. In fact, the origin of the polarization require at least the In atoms in addition to the Cu atoms [23]. As such, a better model for the on-site potential in terms of all the relevant atomic distortions is needed to understand the stabilization of the FiE phase.

In this paper, we address these questions and discuss the different structural distortions leading to the stabilization of the FiE phase. By choosing an ordered PE parent structure we discuss the structural distortions in the FiE phase using density functional theory (DFT) calculations and group-theoretical methods. We find that the polar displacements of the Cu and In atoms create most of the polarization in the FiE phase. Surprisingly, this polar distortion alone does not lead to a gain in the energy, and even the full polar mode leads to a very shallow double-well potential (2 meV/f.u.). We report that a strong anharmonic coupling between the polar mode and a fully symmetric Raman-active mode is necessary to stabilize the polar phase. While such a coupling is symmetry allowed even in conventional FE, we find that its magnitude is surprisingly large in CIPSe. By analysing the various contributions to the total energy we discuss the microscopic origin of this large coupling. We demonstrate that strain can be an effective knob to both enhance and suppress the FiE phase. Finally, we discuss the possible implications of this large non-linear coupling in device applications.

METHODS

We computed the first-principles total energies using Vienna ab initio simulation package (VASP) [24], with the PBE functional including van der Waals correction as implemented by Grimme (DFT-D2) [25]. We used projector augmented wave pseudopotentials with valence configurations Cu (3d$^{10}$4s$^1$), In (5s$^2$5p$^1$), P (3s$^2$3p$^3$) and Se (4s$^2$4p$^4$). Structural relaxation was done with a force convergence tolerance of 0.1 meV/Å using a conjugate-gradient algorithm. The convergence criterion for the electronic self-consistent calculations was set to $10^{-8}$ eV. A regular $8 \times 8 \times 4$ Γ-centered k-point grid was used to sample the Brillouin zone with a plane-wave cutoff energy of 600 eV. The soft-modes were computed using the density-functional-perturbation theory. Polarization was calculated using the Berry-phase approach [26]. While reporting the polarization and the distortion amplitudes...
TABLE I. The computed structural parameters for the PE phase of CIPS\v{e} with space group $P\overline{3}1c$ are compared to the corresponding experimental values [28]. $a$ and $c$ are the lattice constants. The Wyckoff positions of the symmetry inequivalent atoms are also listed with the corresponding experimental values shown in brackets.

| Atom | Wyckoff site | $x$ | $y$ | $z$ |
|------|--------------|-----|-----|-----|
| Cu   | 2d           | 0.667 (0.667) | 0.333 (0.333) | 0.25 (0.25) |
| In   | 2a           | 0 (0) | 0 (0) | 0.25 (0.25) |
| P    | 4f           | 0.333 (0.333) | 0.667 (0.667) | 0.164 (0.166) |
| Se   | 12i          | 0.349 (0.331) | 0.340 (0.340) | 0.120 (0.120) |

The relaxed crystal structure of the FiE phase with space group $P\overline{3}1c$ is shown in Fig. 1(c)-(d). The computed lattice parameters and Wyckoff positions compare well with the corresponding experimental values (see Table II) [11]. The Cu and In atoms exhibit an anti-parallel out-of-plane distortion relative to each other. Further, the P and Se Wyckoff sites are split into two sites each, corresponding to the top and bottom sub-layers within each monolayer. We label the top (bottom) trigonal Se-plane within each CIPSe layer as $Se_t$ ($Se_b$).

TABLE II. The computed structural parameters for the FiE phase of CIPS\v{e} with space group $P\overline{3}1c$ are compared to the corresponding experimental values [28]. $a$ and $c$ are the lattice constants. The Wyckoff positions of the symmetry inequivalent atoms are also listed with the corresponding experimental values shown in brackets.

| Atom | Wyckoff site | $x$ | $y$ | $z$ |
|------|--------------|-----|-----|-----|
| Cu   | 2b           | 0.667 (0.667) | 0.333 (0.333) | 0.154 (0.147) |
| In   | 2a           | 0 (0) | (0) | 0.255 (0.259) |
| P    | 2b           | 0.333 (0.333) | 0.667 (0.667) | 0.327 (0.326) |
| P    | 2b           | 0.333 (0.333) | 0.667 (0.667) | 0.157 (0.158) |
| Se   | 6c           | 0.310 (0.301) | 0.325 (0.323) | 0.105 (0.110) |
| Se   | 6c           | 0.358 (0.355) | 0.008 (0.005) | 0.371 (0.371) |

the center of mass of the P atoms is used as the origin. This choice does not affect our results. The presented values of the Kohn-Sham eigenvalues, the Ewald energy, and the Hartree energy were from the values reported in the VASP output. We used the ISOTROPY software suite to aid with the group-theoretic analysis [27].

RESULTS AND DISCUSSION

Crystal structure

We chose the bulk ordered high-symmetry structure of CIPS\v{e} with space group $P\overline{3}1c$ (see Fig. 1 (a)-(b)) as the reference PE structure for studying the FiE phase [29]. Apart from serving as a zero-point reference for polarization this phase also allows us to study the one-step barrier for the switching of polarization. The computed lattice parameters and the occupied Wyckoff positions agree well with the average experimental parameters in the $P\overline{3}1c$ phase (see Table I) [28]. The crystal structure is similar to the transition metal trichalcogenides with a trigonal lattice [30, 31]. However, two different atoms (Cu and In) occupy the metal site. This naturally creates an inversion-asymmetry within each layer. The Cu and In ions have a nominal charge of +1 and +3, respectively, resulting in an outer-shell electronic configuration of $d^{10}$ for both the atoms. They both are octahedrally coordinated by six Se atoms. The layers are stacked such that the P$_2$Se$_6$ ligand sits on top of the Cu atom from the other layer, thereby, recovering inversion symmetry. This interlayer inversion center is labeled (‘×’) in Fig. 1.

The PE phase is unstable with both zone-center and zone-boundary instabilities. As we are interested in understanding the FiE phase which is reported to have the same cell size as the PE phase [11], we only consider the zone-center instability here. We verified that the relaxed structures from the other instabilities have higher energy than the FiE phase.

The polar mode that transforms as the $\Gamma^-_2$ irreducible representation (irrep) of $P\overline{3}1c$ is the primary order parameter for the transition from the PE phase to the FiE phase. There are six symmetry-adapted modes that transform as the $\Gamma^-_2$ irrep. Four of them are labeled $\Gamma^-_2[A_3]$, and involve the displacement of one of the four atom types along the out-of-plane direction. Fig. 1 (c) shows the $\Gamma^-_2[A_3]$ mode for the Cu atom. In addition, there are two symmetry adapted modes (SAMs) comprising of the in-plane distortions of the Se octahedron. The first mode labeled $\Gamma^-_2[A_1]$ is a breathing mode corresponding to the expansion (compression) of the trigonal $Se_t$- ($Se_b$-) plane along (away from) the direction of the Cu displacement (see Fig. 1 (f)). This results in an in-phase rotation of the trigonal Se-planes about the P$_2$ bond. The second mode labeled $\Gamma^-_2[A_2]$ is a breathing mode about the P$_2$ bond (see Fig. 1 (g)), resulting in an in-phase rotation about the Cu atoms. The polar mode is made up of a combination of these six SAMs.

In addition, the polar mode induces a Raman-active mode which preserves the full symmetry of the parent space group (labeled $\Gamma^+_1$). This mode in turn is made up of a combination of four SAMs that involve the displacement of only the P and Se atoms. Two of these SAMs are labeled $\Gamma^+_1[A_3]$ and correspond to the out-of-plane expansion of the individual P and Se layers. Fig. 1 (h)
shows this $\Gamma_1^+ [A_3]$ mode for the Se atoms. The other two modes involve the in-plane distortion of the trigonal Se-planes, and are labeled $\Gamma_1^+ [A_1]$ and $\Gamma_1^+ [A_2]$. The $\Gamma_1^+ [A_1]$ mode corresponds to the expansion of both the top and bottom trigonal Se-planes about the Cu atoms (see Fig. 1 (j)), whereas the $\Gamma_1^+ [A_2]$ mode involve the out-of-phase rotation of the top and bottom trigonal Se-planes about the Cu atoms (see Fig. 1 (j)).

**The origin of polarization**

Table III shows the amplitude of the corresponding SAMs in the FiE phase. Notably, the largest distortion involves the out-of-plane motion of the Cu atoms towards the Se$_t$ trigonal face (labeled $\Gamma_1^- [A_3]$: Cu), and has an amplitude of 1.15 Å. Such a large distortion is atypical even for FEs. It is reasonable to assume that this will lead to large anharmonicity in the phonon modes, as we demonstrate later.

Table IV lists the atom-projected polarization with respect to the PE phase. The contributions from both $\Gamma_1^+$ and $\Gamma_2^-$ displaceable modes are included. The polar distortions of the Cu and In atoms carry a polarization of 6.17 $\mu$C/cm$^2$ and -2.70 $\mu$C/cm$^2$, respectively. As the Born-effective charge for In (2.24) is larger than that of

![Figure 1](image-url)

**FIG. 1.** The crystal structure and the atomic distortions in the paraelectric (PE) and ferrielectric (FiE) phases of CuInP$_2$Se$_6$ (CIPSe). (a) The top-view and (b) the side-view of the PE phase ($P31c$) with one of the inversion center labeled (‘x’). (c) The top-view and (d) the side-view of the FiE phase ($P31c$). The Se-Se bonds are shown only as visual aid for the modes involving the Se atoms. The FiE phase can be decomposed into six polar symmetry adapted modes (SAMs) and four fully symmetric SAMs that transform as the $\Gamma_2^-$ and $\Gamma_1^+$ irreducible representation (irrep) of $P31c$, respectively. The arrows represent the local distortions. All the arrows have the same amplitude. (e) The displacement of the Cu atom towards the top trigonal Se sub-layers (Γ$^{+}_2$[A$_3$]). (f) The expansion (contraction) of the trigonal Se$_t$ (Se$_b$) planes (Γ$^{+}_2$[A$_1$]), and (g) the in-phase rotation of the Se$_t$ and Se$_b$-planes about the Cu atoms (Γ$^{+}_2$[A$_2$]). (h) The out-of-plane expansion of the Se sub-layers (Γ$^{+}_2$[A$_3$]), (j) an in-plane expansion of the trigonal Se-planes (Γ$^{+}_3$[A$_1$]), and (j) the out-of-phase rotation of the Se$_t$-planes and the Se$_b$-planes (Γ$^{+}_1$[A$_2$]) about the Cu atoms $^*$. The additional three out-of-plane polar modes ($\Gamma_2^-[A_3]$) involving only one of the In, P or Se atoms, and the out-of-plane breathing modes involving only the P atoms ($\Gamma_1^+[A_3]$: P) are not shown for the sake of clarify.

| SAM in $P31c$ | Amplitude (Å) |
|---------------|---------------|
| $\Gamma_1^+ [A_3]$: P | -0.01 |
| $\Gamma_1^+ [A_1]$: Se | 0.03 |
| $\Gamma_1^+ [A_1]$: Se | 0.08 |
| $\Gamma_1^+ [A_2]$: Se | 0.03 |
| $\Gamma_2^+ [A_3]$: Cu | 1.15 |
| $\Gamma_2^+ [A_3]$: In | -0.18 |
| $\Gamma_2^+ [A_3]$: Se | 0.05 |
| $\Gamma_2^+ [A_1]$: Se | 0.13 |
| $\Gamma_2^+ [A_2]$: Se | 0.00 |
TABLE IV. The contribution to polarization from the distortions of the various atoms with respect to the PE phase. The contributions from both $\Gamma_1^+$ and $\Gamma_2^-$ displace modes are included.

| Atom         | Polarization ($\mu$C/cm$^2$) |
|--------------|-------------------------------|
| Cu           | 6.17                          |
| In           | -2.71                         |
| Se           | -0.96                         |
| CuIn         | 3.29                          |
| CuSe         | 5.60                          |
| InSe         | -3.82                         |
| CuInSe (FiE-phase) | 2.58                     |

FIG. 2. The decomposition of the total polarization as a function of the fractional amplitude of the fully symmetric mode ($Q_{\Gamma_1^+}$) and the polar mode ($Q_{\Gamma_2^-}$). The polar mode creates most of the polarization.

FIG. 3. The energy as a function of the atom-projected polar mode ($Q_{\Gamma_2^-}$). The energy as a function of the full polar mode that is unstable (black), and the component of the mode involving the displacement of only the Cu atoms (blue), the In atoms (orange), and both Cu and In atoms (red). The energy gain from only the polar modes is small.

Energy profile of the polar mode

While the Cu and In atoms lead to most of the polarization in the FiE phase, from Fig. 3 we find that neither the individual distortion of the Cu atoms (blue lines) or In atoms (orange line), nor the collective ferrielectric distortion of both the atoms (red lines) creates a double-well potential with respect to the PE phase [33]. This highlights the inadequacy of models based on a Landau expansion of only the Cu polar off-centering to explain the FiE phase [10]. The energy profile for the full polarization in the PE phase (black curve in Fig. 3) shows a shallow double-well potential (2 meV). Here, while we present the total energy as a function of the polar mode along the relaxed PE-FiE direction we verified that similar results are obtained if we choose instead the polar soft-mode eigenvectors from the force-constant matrix (see Fig. S1 in supplementary) [34]. This highlights the importance of the collective distortion of all atoms that transforms as the $\Gamma_2^-$ irrep of $P31c$ rather than just the displacement of Cu (or In) atom as discussed in prior research [10, 18, 19], as the primary order parameter for understanding the symmetry lowering phase transition in CIPSe.

Interestingly, both the well-depth and amplitude of the Cu (0.90), a relatively small displacement of In atoms (0.18 Å) can carry a large dipole moment. This results in the reported FiE phase with partial cancellation of polarization between the two sites, and a net polarization along the direction of the Cu displacement. The fully-relaxed FiE phase has a total polarization of 2.58 $\mu$C/cm$^2$, which compares well with prior first-principles predictions [10]. Even though the polarization is smaller than what is typically observed in conventional FEs, it is larger than other reported ferrielectrics such as ammonium sulphate (0.62 $\mu$C/cm$^2$) [32].
polar mode at the minimum are much smaller than that of the fully-relaxed FiE phase. The fully-relaxed FiE phase has an energy gain of 98 meV/f.u. with respect to the PE phase. This is in sharp contrast to other proper FEs where the dominant polar distortion on its own accounts for a large portion of the energy gain in the polar phase characterized by a deep double-well potential [35]. This large energy difference in CIPSe immediately suggests that to understand the microscopic mechanism that stabilizes the polar phase requires not only the polar mode but also the nonpolar modes.

**Total energy surface**

To explain the above mentioned discrepancy we compute the energy surface (see Fig. 4 (a)) by varying fractional amplitudes of the fully symmetric mode \((Q_{1+}^1)\) and the polar mode \((Q_{1+}^2)\). We find that the total energy goes up with \((Q_{1+}^2)\). This is expected as the initial configuration is completely relaxed. We also recover the shallow double-well as we condense \((Q_{1-}^2)\) mode. The lowest energy structures corresponding to the fractional coordinates of \((1, ±1)\) have 61 meV/f.u. lower in energy than the PE phase. While further stabilization (37 meV/f.u.) of the FiE phase is provided by a full structural relaxation, Fig. 4 (a) shows that the dominant factor leading to the stabilization of the FiE phase is the strong anharmonic coupling between the polar mode and the fully symmetric mode. Such anharmonicity has also been reported in other members of the thiophosphate family [36].

To quantify this anharmonic coupling, we fit the energy surface about the PE phase. The total energy \((E)\) can be written as,

\[
E = E_0 + b_{02}Q_{1+}^2 + b_{04}Q_{1+}^4 + b_{06}Q_{1+}^6 \\
+ b_{08}Q_{1+}^8 + c_{12}Q_{1+}^2 Q_{1-}^2 + c_{14}Q_{1+}^4 Q_{1-}^4 \\
+ a_{20}Q_{1+}^6 + \cdots
\]

(1)

where \(E_0\) is the energy of the PE phase that is set to zero, \(a_{ij}\) and \(b_{ij}\) are the real-valued coefficients of the expansion about \(Q_{1+}^2\) and \(Q_{1-}^2\), respectively. The free energy expansion considered in Eqn. 1 is only for the on-site interactions. Additional intersite coupling coming from the zone-boundary modes needed to considered to discuss order-disorder transition [20]. As \(Q\)'s are in fractional units, the coefficients in the fit have units of energy allowing us to compare the contribution from each term. \(c_{ij}\)'s are the real-valued coefficients corresponding to the anharmonic coupling between the two modes. Anharmonicity due to coupling between multiple modes has attracted a lot of attention in the context of non-proper FEs [37–41] and anti-ferroelectrics [42, 43]. However, in the case of proper FEs even though such a coupling between the polar mode and the fully symmetric mode is allowed by symmetry they are considered to be small and are typically ignored [44]. They have also been completed ignored in prior works on CIPSe [10]. We will show that such an anharmonic coupling is crucial to the stabilization of the polar phase, and is key to controlling the polarization in CIPSe.

Table V shows the coefficients obtained from fitting the energy surface in Fig. 4 (a). For the total energy to be bounded the coefficients of the largest-order polynomial for each mode should be positive. As the 6th-order coefficient of the polar mode \((b_{06})\) was negative we included up to the 8th-order term. The asymptotic standard error in the fit was less than 8.2%, with most coefficients within 4.5%. The fit can be further improved by adding additional terms (see Tab. S1 in supplementary) [34]. As the overall conclusions are independent of these additional terms, we omit them in the discussion of the minimal model.

We find \(b_{02}\) to be negative and \(b_{04}\) to be positive as expected of a characteristic double-well potential due to a polar-instability [45]. However, from Table V it is clear that the anharmonic coupling is anomalously large with \(c_{12}\) about 8 times larger than the harmonic term \(b_{02}\). For perspective, this is comparable to the improper FE coupling between the polar mode and the zone-boundary mode in YMnO₃ [38]. The effective quadratic coefficient \((B_{02}^{ef})\) including the anharmonic terms from Eqn. 1 is,

\[
B_{02}^{ef} = (b_{02} + c_{12}Q_{1+}^2). \quad (2)
\]

The strong anharmonic coupling renormalizes \(B_{02}^{ef}\) to become more negative. Similar renormalization of the optimal polarization and the Curie-Weiss temperature in conventional oxide FEs was discussed due to electrostriction [45]. But an anomalously large contribution of the fully symmetric mode leading to this renormalization as we find in CIPSe, is new and surprising.

**The microscopic mechanism of the coupling**

Prior works discussed the possibility that a filled \(d^{10}\) outer-shell electronic configuration is second-order Jahn-Teller active, leading to the off-centering of both the Cu and In atoms in this class of materials [9, 46–48]. So to elucidate the physical origin of the large nonlinear coupling between the polar mode and the fully symmetric mode, we analyzed the various contributions to the total energy. Specifically, we focus on the Kohn-Sham eigenvalues and the Ewald energy - i.e., the electrostatic ion-
Our analysis gives a clear microscopic mechanism of the unusual coupling between the polar mode and the fully symmetric mode that leads to the stabilization of the FiE phase. We find that this anharmonic stabilization persists even in the monolayer limit (see Fig. S5 in supplementary) [34].

**Strain-control of FiE**

We also explored the effect of other distortions that transform as the $\Gamma^+_1$ irrep of the space group $P\overline{3}1c$. Previous works on oxides showed that polar-distortions naturally couple to strain [35, 49]. So, we discuss the case of an in-plane bi-axial strain ($\epsilon_{x^2+y^2}$), which uniformly expands the 2D-area for positive values. The effect of this strain is similar to that of the displace $\Gamma^+_1$ mode.
stead of directly tuning the displacive $\Gamma$ axial strain can be easily controlled experimentally in-relaxing the lattice constants in the FiE phase. As bi- and largely accounts for the additional 37 meV gain from electrical switching of the polar state can be achieved should be faster than applying a mechanical strain. 

The application of such an optical field probes allowing for the optical control of the switching fully symmetric mode is Raman active, in addition to me-symmetric mode, instead of the polar mode. Since the up-state to the down-state is determined primarily over possibilities to both enhance and suppress the energy barrier corresponding to a single-step switching of polarization from the polarization.

When the barrier energy is reduced sufficiently, a faster electrical switching of the polar state can be achieved within the transition state theory, assuming a one-step switching process. On removal of the two fields the higher barrier around the FiE phase, for example in the un-strained case, can be recovered. This will lead to a long-lifetime of the polar phase, which can be even enhanced for instance by engineering a tensile strain as shown in Fig. 5. This understanding can provide a first step to addressing the voltage-time dilemma.

We note that this approach for overcoming the voltage-time dilemma is not unique to CIPSe. Other materials where the origin of the order parameter that defines the memory state is different from the factors that stabilizes it has the potential to overcome this inherent bottleneck. Improper FE, pseudoproper FE, hybrid improper FE and triggered phases are all potential candidates for this as the polarization itself is not the primary order param-eter. We note that a strain-induced suppression of the barrier was recently reported in hybrid improper FE.

Finally, we comment on the nature of the FiE phase. Within a displacive picture CIPSe is a proper FiE as the polar mode fully determines the FiE phase. However, unlike conventional proper FE where the energy lowering term is $P^2$, the driving term that stabilizes the polar phase is dominated by the anharmonic coupling between the polar mode and the fully symmetric Raman active mode. This coupling has been largely overlooked in prior studies of CIPSe. It also distinguishes CIPSe from other proper FE where the polar phase is driven by a change in hybridization, or through steric effects, or through a hyper-FE mechanics, or an entangled FE.

While our discussion is centered around a on-site model for the total energy, our results should also be important in a multi-step switching process. Future works need to include the effect of zone-boundary instabilities also to understand the order-disorder nature of the phase tran-sition and the intermediate incommensurate phase re-reported at the phase boundary. Similarly, the impact of our findings in the context of the unconventional electromechanical response found in the domain walls in this family of materials, and in the actual path of polarization switching under an applied field also needs to be explored.

In summary, we discuss the origin of polarization and the structural-stabilization of ferrielectricity in CIPSe. The distortions of the Cu and In atoms create most of the polarization in FiE CIPSe. On the other hand, the in-plane fully symmetric distortions of the Se atoms stabilizes the FiE phase via an anharmonic coupling to the po-

Figure 5 shows the total energy profile for the FiE phase relative to the PE phase for various value of $\epsilon_{x^2+y^2}$. For the unstrained case (red solid line) we recover the FiE phase as the low-energy state. We find that for a compre-sive strain of 1 % (green line) the FiE phase, although a local minimum, has higher energy (4 meV/f.u.) than the PE phase with a small energy barrier (12 meV/f.u.) between the states. For intermediate values of compres-sive strain where the FiE remains the ground state but where the energy barrier is comparable to the quantum fluctuations a quantum PE state could be stabilized by strain where quantum fluctuations suppress the ordering of dipole moments. Incidentally, a quantum paraelectric phase was proposed in this family of materials driven by chemical substitution.

For a compressive strain of 2 % (magenta line) the po-
lar instability is fully suppressed and the PE phase be-
comes the lowest energy structure. On the other hand, for a tensile strain (1 % shown in black lines and 2 % shown in blue line) the well-depth around the FiE phase becomes deeper. Note that the FiE phase has a $\epsilon_{x^2+y^2}$ strain of ~ 1% relative to the PE phase (see Tab. I), and largely accounts for the additional 37 meV gain from relaxing the lattice constants in the FiE phase. As bi-axial strain can be easily controlled experimen-tally instead of directly tuning the displacive $\Gamma_1^+$ mode, mechanical strain can be an effective tool to both suppress and enhance the FiE phase, providing a way to tune the energy barrier corresponding to a single-step switching of the polarization.

CONCLUSION AND OUTLOOK

Our analysis suggests that the barrier that needs to be overcome in a single-step switching of polarization from the up-state to the down-state is determined primarily by a large nonlinear coupling between the polar mode and the fully symmetric Raman-active mode. This opens up possibilities to both enhance and suppress the energy barrier for polarization switching by modifying the fully symmetric mode, instead of the polar mode. Since the fully symmetric mode is Raman active, in addition to me-chanical strain, it should also couple to ultra-fast optical probes allowing for the optical control of the switching barrier. The application of such an optical field should be faster than applying a mechanical strain.

When the barrier energy is reduced sufficiently, a faster electrical switching of the polar state can be achieved
a nominal strain.

ACKNOWLEDGEMENT

This research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility and used resources of the Compute and Data Environment for Science (CADES) at ORNL. Computations also used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231. We thank Petro Maksymovych for discussions.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the submission of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

AUTHOR CONTRIBUTIONS

P.G. and N.S. designed the project. N.S. performed all the calculations and analysis. N.S. also produced the first draft of the manuscript which was rewritten subsequently by all authors. P.G. oversaw the entire project.

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While one might conclude from Fig. 3 that the energy-surface for In displacement (orange) is flatter compared to the Cu displacement (blue), this is not the case. The energy reported is with respect to the fractional shift of the atoms. From Table III, we can see that the amplitude of the shift of the Cu atoms is more than six times that of the In atoms.
SUPPLEMENTAL MATERIAL

Unstable soft-mode eigenvectors from force-constant matrix

Fig. 6 compares the total energy as a function of the polar soft-mode eigenvectors from the force-constant matrix (violet) in the PE phase (space group P$3\bar{1}$c) and as a function of the polar mode along the relaxed PE-FiE direction. The obtained trends are similar, especially for smaller distortions. The well-depth in the former case is 4 meV/Cu. This is similar to the 2 meV/Cu we find in the latter case. The rest of the energy gain to 98 meV/Cu in the relaxed structure is unaccounted for if we consider only the polar modes. This highlights the anharmonic nature of CIPSe and emphasizes the need for the presented Landau model including anharmonicity.

Origin of the anti-parallel distortion of atoms at the Cu and In sites

The anti-parallel distortion between the Cu and In atoms can be understood by studying their local bonding network. Fig. 7 shows the top-view of the structural distortions within a single layer in the FiE phase relative to the PE phase. Each In atom (see In atom highlighted by a broken black circle in Fig. 7) is surrounded by three Cu atoms (labeled 1-3). In the FiE phase, all the three Cu atoms are displaced in the same direction, for instance, along the out-of-plane direction. The Se$_b$ trigonal face expands while the Se$_t$ trigonal face contracts. However, the six Se atoms that are octahedrally coordinated with the In atom, are edge shared with the Se atoms around the three labeled Cu atoms. As the Cu displacement causes an expansion (contraction) of the top (bottom) Se layer around the Cu atoms, this in turn, results in a contraction (expansion) of the top (bottom) Se layer around the In atoms. If the atom at the In site has a tendency to off-center this naturally leads to an anti-polar distortion between the Cu atoms and the atom at the In sites.

Improved fit for the total energy

The fit to the energy surface can be improved by using additional coupling terms ($c_{22}$, $c_{24}$) in the total energy expansion about the PE phase. This new total energy ($E$) can be written as,

$$
E = E_0 + b_{02}Q_{12}^2 + b_{04}Q_{12}^4 + b_{06}Q_{12}^6 + b_{08}Q_{12}^8 + c_{12}Q_{12}^2Q_{12}^2 + c_{22}Q_{12}^2Q_{12}^2 + c_{24}Q_{12}^2Q_{12}^2 + a_{20}Q_{12}^4 + a_{22}Q_{12}^4 + a_{24}Q_{12}^4 + a_{26}Q_{12}^4 + a_{28}Q_{12}^4 + a_{30}Q_{12}^4 + a_{32}Q_{12}^4 + a_{34}Q_{12}^4 + a_{36}Q_{12}^4 + a_{38}Q_{12}^4 + a_{40}Q_{12}^4 + a_{42}Q_{12}^4 + a_{44}Q_{12}^4 + a_{46}Q_{12}^4 + a_{48}Q_{12}^4 + a_{50}Q_{12}^4 + a_{52}Q_{12}^4 + a_{54}Q_{12}^4 + a_{56}Q_{12}^4 + a_{58}Q_{12}^4 + a_{60}Q_{12}^4 + a_{62}Q_{12}^4 + a_{64}Q_{12}^4 + a_{66}Q_{12}^4 + a_{68}Q_{12}^4 + a_{70}Q_{12}^4 + a_{72}Q_{12}^4 + a_{74}Q_{12}^4 + a_{76}Q_{12}^4 + a_{78}Q_{12}^4 + a_{80}Q_{12}^4 + a_{82}Q_{12}^4 + a_{84}Q_{12}^4 + a_{86}Q_{12}^4 + a_{88}Q_{12}^4 + a_{90}Q_{12}^4 + a_{92}Q_{12}^4 + a_{94}Q_{12}^4 + a_{96}Q_{12}^4 + a_{98}Q_{12}^4 + a_{100}Q_{12}^4 .
$$

While a term that is linear in the fully symmetric mode ($Q_{12}^+$) is symmetry allowed, we do not include this as the PE phase is fully relaxed. The fitted coefficients are shown in Table VI. While these additional terms improve the fit to the total energy, we note that our conclusions in the main text are qualitatively unaffected.

FIG. 6. The energy as a function of the mode amplitude ($Q_{12}^-$) of the polar soft-mode eigenvectors from the force-constant matrix (violet crosses), and of the polar mode along the relaxed PE-FiE direction.

FIG. 7. The top-view of the structural distortions within a single layer in the FiE phase relative to the PE phase. The three Cu atoms around the central In atom (in broken black circle) are labeled 1-3. Distortions into (out of) the plane are denoted by ‘×’ (broken circles). At each atomic site only the dominant symmetry adapted distortion is shown for clarity.

TABLE VI. The value of the coefficients (in meV) in Equ. 3 from fitting the energy surface shown in Fig. 3 (a) in the main text.

| Coefficient | Value   |
|-------------|---------|
| $b_{02}$    | -47.1   |
| $b_{04}$    | 245.7   |
| $b_{06}$    | -116.0  |
| $b_{08}$    | 17.3    |
| $c_{22}$    | 93.0    |
| $c_{24}$    | -27.8   |
| $a_{20}$    | 102.6   |
FIG. 8. The decomposition of the total energy surface in (a) the contribution from the ion-ion electrostatic (Ewald) interaction (eV/Cu atom), and (b) the Hartree energy, as a function of the fractional amplitude of the fully symmetric mode \(Q_{\Gamma_1}\) and the polar mode \(Q_{\Gamma_2}\). All the reported energies are relative to the fully-relaxed PE phase \((P\bar{3}1c)\).

Remarks on the total energy decomposition

It is important to point out that the discussion in the main text decomposing the total energy into its contributions from the Kohn-Sham electronic energy and the Ewald energy fails to explain all the features we find in the total energy surface. This highlighting the importance of the other contributions to the total energy including the Hartree term - the electron-electron interaction energy. Fig 8 shows that Hartree term typically competes with the Ewald energy, leading to partial cancellation between the two contributions. However, the energy gain from the Hartree term on condensation of the polar mode (0.51 eV/Cu) is not enough to overcome the energy penalty from the Ewald term (14.1 eV/Cu).

Other contributions to the total energy need to be taken into account to explain all the features in the total energy surface. But we note that, the presented energy-decomposition provides a simple model to understand the microscopic origin of the coupling between the polar mode and the fully symmetric mode.

Atom-projected bandstructure

Fig. 9 shows the atom-projected bandstructure of (a) the PE and (b) FiE phase along the high-symmetry directions in the two-dimensional Brillouin zone. The FiE phase has a larger band gap compared to the PE phase. Further, the structural distortions in the FiE phase relative to the PE phase leads to a change in the atom-projected contributions to the band edges. This is most evident in the valance band maximum (VBM). In the PE phase the VBM has contributions from both the Cu (red) and Se (cyan) atoms. In the FiE phase the contribution to the VBM from the Cu atom is smaller while the contribution from the Se atoms dominates the bands. This suggests a charge transfer between the Cu and Se atoms from the PE phase to the FiE phase.

Anharmonic stabilization in the monolayer limit

To check the validity of our mechanism of stabilization of polarization, we performed similar calculations for three different cases. We considered a monolayer including dipole correction (see Fig. 10 (a)), as well as two cases where one of the layers in the bulk unit cell is constrained to be PE (see Fig. 10 (b)), and the other is FiE (see Fig. 10 (c)). For simplicity we calculated the total energy using the same distortions for the polar mode and the fully symmetric mode as in the bulk fully-relaxed case. We observed a strong stabilization of the polar phase due to the anharmonic coupling between the polar mode and the fully symmetric mode in all the cases.

Zone-center and zone-boundary instabilities in the PE phase

The fully-relaxed structures resulting from the zone-center and zone-boundary modes are tabulated in Table VII. The distortions are labeled by the irreps of \(P\bar{3}1c\), and the corresponding order parameter direction leading to the unique space group is also listed. The total energy for each structure is listed relative to the FiE ground state (space group \(P31c\)). The corresponding space groups the structures form are also listed. The relatively small energy difference between the different structures is consistent with a strong order-disorder character to the phase transition.
FIG. 10. The energy surface as a function of the fractional amplitude of the fully symmetric mode \( Q_{\Gamma_1} \) and the polar mode \( Q_{\Gamma_2} \). (a) Monolayer, (b) bulk with one layer fixed to PE phase, (c) bulk with one layer fixed to FiE-phase. All the reported energies are relative to the fully-relaxed PE phase \( P\overline{3}1c \).

TABLE VII. The energy of different isotropy subgroups of PE phase. The structures are labeled by the irreps of \( P\overline{3}1c \) and the distinct order parameter directions under which the phonon modes transform are listed. The energies (meV/f.u.) obtained for the fully relaxed structures with respect to the FiE ground state (space group \( P\overline{3}1c \)) are listed. The positive real numbers \( a, b, c \) and \( d \) represents the irrep directions.

| Irrep | Order parameter direction | Space group | Energy (meV/f.u.) |
|-------|---------------------------|-------------|------------------|
| Undistorted parent | \( \Gamma_2 \) | \( (a) \) | \( P\overline{3}1c \) | 98 |
| \( \Gamma_2 \) | \( (a) \) | \( P\overline{3}1c \) | 0 |
| \( M_2 \) | \( (a; 0, 0) \) | \( P2_1/c \) | 12 |
| \( M_2^+ \) | \( (a; 0, 0) \) | \( P2_1/c \) | 8 |
| \( K_3 \) | \( (a, a, b, -b) \) | \( P1 \) | 24 |
| \( K_3 \) | \( (0, 0, b, -b) \) | \( C2/c \) | 53 |
| \( K_3 \) | \( (a, -a, b, -b) \) | \( Cc \) | 9 |
| \( K_3 \) | \( (a, b, c, d) \) | \( P1 \) | 16 |