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► **To cite this version:**

Charles Paillard, Laurent Bellaïche. Light: A new handle to control the structure of cesium lead iodide. *Physical Review B*, 2023, 107 (5), pp.054107. 10.1103/PhysRevB.107.054107 . hal-03993958

HAL Id: hal-03993958

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Submitted on 17 Feb 2023

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Light, a new handle to control the structure of cesium lead iodide

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(Dated: January 10, 2023)

CsPbI₃ is of high interest for photovoltaic applications owing to its low bandgap, provided it could be stabilized in its γ perovskite phase. Instead, it energetically prefers to adopt a so-called yellow, δ phase, with much larger bandgap and reduced photovoltaic properties. Here, using an original constrained Density Functional Theory method, we mimic the effect of thermalized photo-excited carriers, and show that larger concentrations in photo-excited carriers (i.e. larger optical pump fluences) effectively reduce the energy difference between the δ non-perovskite ground state and the γ perovskite phase. Even further, the stability of the phases could be potentially reversed and therefore the γ phase stabilized under strong illumination. We also report large photostriction, i.e., large photo-induced strain for all phases in this material, making CsPbI₃ suitable for other applications such as photo-driven relays and photoactuators.

I. INTRODUCTION

Halide perovskites represent a new hope to achieve efficient and affordable solar power conversion. They have quickly grown to achieve more than 25% power conversion efficiency [1]. Their domain of application extends far beyond the mere solar cell, as their good photo- or electroluminescent properties [2, 3] make them prime candidates for laser or light-emitting diode applications [4, 5]. However, many of those halide perovskites suffer from severe stability issues with respect to humidity or temperature, in particular when they are made of a hybrid of organic - inorganic cations [6]. As a result, the fully inorganic lead halide perovskites, CsPbX₃ (X=I, Br, Cl) have been considered most promising owing to their larger stability. [7]. Among those, CsPbBr₃ significantly starts absorbing at wavelengths below 550 nm (green), while CsPbCl₃ absorbs in the near UV spectral domain. [2] As a result, those two compounds are not particularly promising to convert efficiently the solar spectrum into useful energy.

On the other hand, the perovskite phase of CsPbI₃ absorbs wavelengths as high as 700 nm [2]. Unfortunately, lead cesium iodide is only metastable in a perovskite phase; the more stable δ -phase has much worse optical absorption properties [8]. The instability of the perovskite phase has recently been elucidated to stem from rattling of the Cs ion in its coordination cage, based on X-ray diffraction measurements on single crystals from 100 K to 295 K [9]. The perovskite phase can nonetheless be stabilized by substituting some I⁻ with Br⁻ at the expense of degraded absorption properties [2], or metastabilized through cooling from the high-temperature phase [10]. Yet, temperature or pressure are slow, cumbersome and energy-inefficient

control parameters. Methods allowing to easily and efficiently control the appearance of the perovskite phase in CsPbI₃ are thus highly desirable.

In the present work, we study the relative stability of the main four phases of CsPbI₃: the δ -phase, which is the non-perovskite ground state; the γ -phase which is the low-energy orthorhombic perovskite phase; the β -phase is an intermediate tetragonal perovskite structure, while the α -phase is the cubic prototypical and high-temperature perovskite. All four phases are depicted in the Supplementary Information.

Density Functional Theory (DFT) calculations are employed in an original scheme which constrains excited electrons (resp. holes) in the conduction (resp. valence) bands during the self-consistent cycle to mimic thermalized photo-excited carriers. Our results indicate that above bandgap light may help tune the relative stability of the γ and δ phases. Even further, knowing that the γ phase is dynamically stable in dark conditions [11], our results may provide a pathway to trigger a transition to the perovskite phase without having to realize heavy and slow thermal cycles [10]. Furthermore, a large photo-induced strain is also calculated in all phases and in particular in the *stable* δ -phase, which is of high importance to use CsPbI₃ in photostrictive devices [12].

II. METHODS

In order to study the possibility of triggering a phase transition towards a perovskite phase in CsPbI₃, we used the constrained-DFT scheme developed in Ref. [13] as implemented in Abinit [14–18], with a plane wave cut-off of 40 Ha. The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional revised for solids (named PBESol) was employed. All calculations reported here include spin-orbit coupling (SOC). Plane Augmented Wave (PAW) pseudopotentials were regenerated for PBESol using the PBE pseudopotential parameters used

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78 in the Jollet-Torrent-Holzwarth (v1.1) table [19, 20] and
 79 the AtomPAW software [21]. The discretization of the
 80 Brillouin zone was performed using a Γ -centered mesh
 81 having 7×10^{-3} Bohr $^{-1}$ sampling density along each recip-
 82 rocal lattice vector direction. Self-consistent field cycles
 83 were considered converged when the difference in forces
 84 between two iterations was smaller than 10^{-8} Ha.Bohr $^{-1}$;
 85 structural relaxation was performed until the maxi-
 86 mum calculated force laid below 5×10^{-7} Ha.Bohr $^{-1}$.
 87 Fermi-Dirac distributions with a smearing temperature of
 88 0.004 Ha characterize the occupation of electronic states.
 89 The lattice constants obtained in the electronic ground
 90 state are in good agreement with lattice constants mea-
 91 sured experimentally or calculated using the Local Den-
 92 sity Approximation (LDA) [22, 23] (see Supplementary
 93 Information [24]). The reciprocal space paths used for
 94 the band structures in Figure 1 are detailed in Ref. [25]
 95 In order to simulate photo-excitation, we constrained a
 96 finite number n_{ph} of electrons (resp. holes) to lie in the
 97 conduction (resp. valence) bands with a Fermi-Dirac dis-
 98 tribution characterized by two separate quasi-Fermi lev-
 99 els for photo-excited electrons and holes.

100 III. PHOTO-INDUCED PHASE TRANSITIONS

101 A. Structural and electronic properties in dark

102 We start by describing the electronic and energetic
 103 properties of CsPbI $_3$ in "dark" conditions ($n_{ph} = 0$). The
 104 band structures of the δ and γ phases are depicted in Fig-
 105 ures 1a,d. The γ phase (Figure 1a) has a direct bandgap
 106 of 0.63 eV located at the Γ point. The electronic bandgap
 107 of the δ phase is indirect and 1.79 eV large. The top of
 108 the valence band is located on the YT segment, while
 109 the bottom of the conduction band is close to X. The
 110 direct bandgap, depicted with black empty circles, is lo-
 111 cated near X in reciprocal space, and is 1.80 eV large.
 112 In Table I, we summarize the values of bandgaps for the
 113 γ and δ phases, and compare with experimental and the-
 114 oretical works. The predicted bandgaps calculated with
 115 SOC underestimate both experimental and theoretical
 116 values obtained without SOC, as consistent with the lit-
 117 erature [26, 27, 32].

118 The energy of the four phases without photoexcitation
 119 is depicted in Figure 2 (see points at $n_{ph} = 0$). The
 120 lowest-energy structure is the δ -phase, which lies below
 121 the γ -phase by roughly 80 meV/f.u. This qualitatively
 122 differs from Ref. [22], but agrees well with experimental
 123 observations of the δ -phase being the most stable state.
 124 The difference with Ref. [22] might be due to a different
 125 exchange-correlation functional used. We note, further-
 126 more, that the relative energies of the phases δ , γ , β and
 127 α agree well with the observed phase transitions upon
 128 cooling. [8, 10, 23, 33, 34]

	δ -phase		γ -phase
	$E_{g,indirect}$	$E_{g,direct}$	$E_{g,direct}$
This work, PBEsol, SOC	1.79	1.80	0.63
This work, PBEsol, no SOC	2.37	2.48	1.59
Ref. [28], PBE	-	-	1.78
Ref. [29], PBE	-	2.56	-
Ref. [30], PBE	-	2.6	1.75
Ref. [31], Exp	-	-	1.68
Ref. [9], Exp	-	2.58	1.63

TABLE I. Summary of electronic bandgaps, in eV, of different phases in CsPbI $_3$.

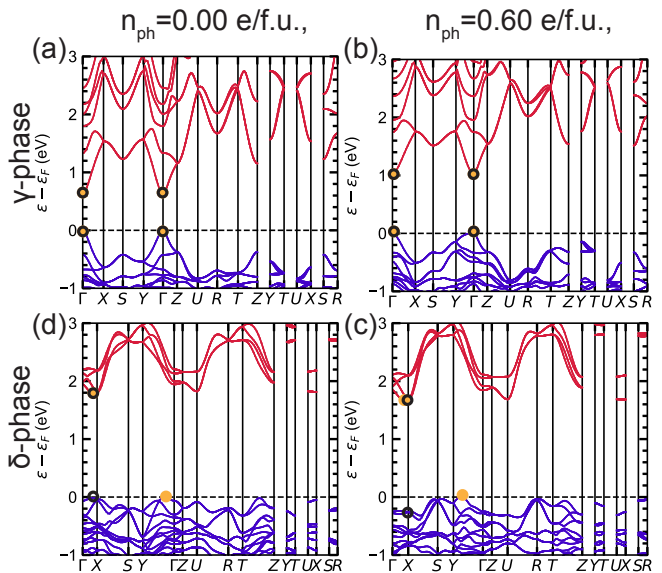


FIG. 1. Band structures obtained in the γ (a-b) and δ (c-d) phases for $n_{ph} = 0.00$ e/f.u. (electronic ground state; a and c) and $n_{ph} = 0.6$ e/f.u. (b and d) respectively; orange plain circles indicate the location of the electronic bandgap, and black empty circles depict the direct bandgap.

129 B. Energetics of phases under photoexcitation

130 Upon increasing the relative concentration of photo-
 131 excited carriers n_{ph} , the energy difference between the δ
 132 phase and γ phase (teal circles in Figure 2) significantly
 133 decreases, and even changes sign at 0.3 e/f.u. This indi-
 134 cates that (i) for concentrations lower than 0.3 e/f.u.,
 135 the transition temperature between the δ and γ phases
 136 will potentially decrease when illuminating the sample
 137 with above-bandgap light and large fluence; and (ii) a
 138 potential phase transition from the yellow δ phase to the
 139 perovskite γ phase could occur under sufficiently intense
 140 illumination with above bandgap energy photons. For a
 141 thin film, such concentration is reachable with high in-
 142 tensity lasers. Prior experiments on MAPbI $_3$ [35] and
 143 a simple model (see Appendix A) indicate that laser
 144 pulses of 25 mJ.cm $^{-2}$ fluence and 3 eV photon energy

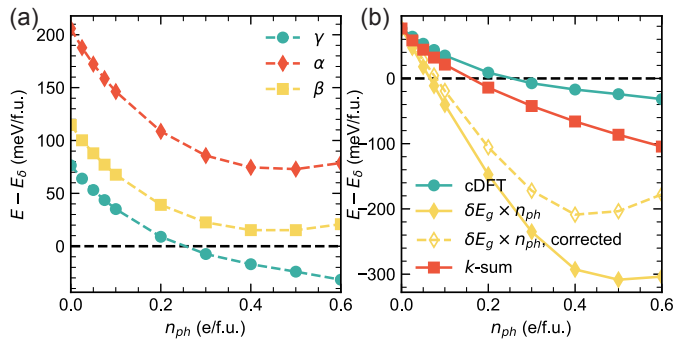


FIG. 2. (a) Energy of the α , β , γ phases relative to the δ phase as a function of the concentration of photo-excited carriers; (b) Comparison between the constrained-DFT calculations (teal circles), the toy model given in Eq. 1 (yellow diamonds), the toy model corrected using the experimental bandgaps (yellow dashed diamonds), and numerical integration (red squares) of the population of the "dark" band structures electronic states (see Appendix A for details.)

may achieve these large concentration of photo-excited carriers. None of the other known phases of CsPbI_3 seem to become more stable in the range of concentrations in photo-excited carriers explored here.

We now attempt to elucidate the origin of this potential photo-induced phase transition. In other perovskites, mostly oxides and ferroelectrics, previous works showed that photo-excited carriers had a strong impact on phonon instabilities. [13, 36] In particular, in cubic lead titanate and barium titanate, it had been found that phonon instabilities related to the development of electrical polarization were suppressed under illumination [13]. Here, the phonon spectrum of the cubic α phase (see Supplementary Information) shows that photo-excited carriers hardly modify the unstable phonon branches. This is consistent with the fact that no other perovskite-phase becomes more stable than the γ phase in Figure 2. There does not seem to be any other perovskite phase that could develop under illumination besides the γ phase, which is itself dynamically stable [11].

C. Toy model

As a result, the case could be made that the proposed phase transition origin lies in the difference of electronic bandgaps of the δ and γ phases. In a two-level system (e.g. limiting ourselves to the bottom of the valence band and top of the conduction band), a simple toy model can be designed to further prove this point. Akin to the extension of Landau's theory to the description of degenerate semiconductors [37] or to explain photostriction in ferroelectric oxides [38], one may simply say that the difference of energy between the two phases is:

$$E_\gamma(n_{ph}) - E_\delta(n_{ph}) = \Delta E_0 + \delta E_g(n_{ph}) \cdot n_{ph} \quad (1)$$

In the above equation, ΔE_0 is the energy difference between the δ and γ phase in "dark" conditions (roughly 80 meV/f.u.); $\delta E_g(n_{ph}) = E_{g,\gamma}(n_{ph}) - E_{g,\delta}(n_{ph})$ denotes the difference of bandgaps between the γ and δ phases, and n_{ph} represents the concentration of photo-excited carriers. We plot that quantity in Figure 2b as filled yellow diamond, for both unclamped and clamped calculations. It can be seen that qualitatively the result of the *ab-initio* calculations and those obtained from Equation 1 are similar. This supports the scenario of an electronically controlled energy difference between the two phases. Quantitative discrepancies between the model in Equation 1 and DFT results stem from the fact that the photo-excited carriers are distributed across more than one level and one k -point owing to the finite smearing temperature. One should, in fact, integrate over the (partially) occupied conduction (and valence) states in order to obtain a better match. The integration over the ground state band structure is depicted in red squares in Fig 2b and detailed in Appendix B. The agreement is quantitatively better, and the remaining difference with constrained-DFT calculations is likely to stem from some band reconfiguration under illumination.

Note that, because our calculations underestimate the bandgap of CsPbI_3 , the critical concentration of photo-excited carriers is likely underestimated. We used our toy model (see Equation 1) with experimental values of the bandgaps of the γ and δ phases. The corrected curve, in dashed yellow diamonds in Figure 2b, slightly increases the critical n_{ph} of the transition. Interestingly, we also performed some calculations without SOC (see Supplementary Information [24]). In such case, the bandgaps of both the δ and γ phases match the experimental ones well. The transition is then observed at a larger concentration of photo-excited carriers (≈ 0.6 e/f.u.), as expected from the electronic nature of the photo-induced phase transition. The true critical concentration would be better determined using more accurate and costly exchange-correlation functionals.

Given the electronic nature of the proposed phase transition, one might wonder whether the formation of excitons could hinder the present phenomenon. Indeed, we have so far treated the photo-excited electrons and holes using a one-body Hamiltonian provided by the Kohn-Sham implementation of DFT. We note, however, that the exciton binding energy in CsPbI_3 reported in magneto-optical experiments is fairly small, of the order of 15 meV [39]; likewise, calculations report values in the range 1.5-44 meV [40, 41]. In other words, and in particular at non-cryogenic temperatures, excitons will mostly dissociate into photo-excited free carriers. Note also that we need demanding numerical criteria to obtain well converged results, which is incompatible with the use of larger supercells. Consequently, the tendency of hybrid perovskites to disorder and to adopt medium range correlations [42, 43], and how these latter react to illumination, are not explored in this work. At last, we focused on phases which were previously experimentally

234 reported. It is possible, although no evidence points in
 235 that direction, that other unknown phases could be ac-
 236 cessed in CsPbI₃ under illumination. The use of genetic
 237 algorithms coupled to the constrained-DFT method used
 238 in this work could reveal such phases.

239 IV. PHOTOSTRICTION

240 We also looked at the photostrictive response of
 241 CsPbI₃. It is given in Table II, in which estimates use the
 242 value of the photo-induced strain at $n_{ph} = 0.025$ e/f.u. in
 243 Figure 3. We chose such value because it is small enough
 244 to be in a linear regime for most phases in CsPbI₃. Con-
 245 sequently, we plot, in Figure 3, the photo-induced strain
 246 for all four phases of CsPbI₃ considered in this work.
 247 a , b and c refer to the lattice constants of the princi-
 248 pal axes sorted by increasing length. In the case of the
 249 α cubic phase for which $a = b = c$, we report only a ,
 250 while for the β tetragonal phase, $a = b \neq c$, and we
 251 report only a and c . Interestingly, and as also summa-
 252 rized in Table II, the δ -phase exhibits the largest pho-
 253 tostrictive response. Compared to calculations of bulk
 254 oxides such as BiFeO₃ [44], PbTiO₃ [38] or the brown-
 255 millerite SrCoO_{2.5} [45], CsPbI₃ exhibits superior pho-
 256 tostrictive properties in all of its phases. Note that in
 257 Table II, the photostriction of rhombohedral BiFeO₃ re-
 258 ports that of the pseudocubic cell parameter, calculated
 259 using the Δ SCF method in Table 1 of Ref. [44]; similarly
 260 for rhombohedral BaTiO₃ [38]. Note also that we report
 261 in Table II, photo-induced strains from Δ SCF calcula-
 262 tions [38, 44, 46] corresponding to indirect transitions to
 263 match as closely as possible the results that would be
 264 obtained using the constrained-DFT method employed
 265 here.

266 We must also stress that at large concentrations in
 267 photo-excited carriers ($n_{ph} > 0.1$ e/f.u.), the photo-
 268 induced response can become highly non-linear, espe-
 269 cially in the β and α phases. While large photo-induced
 270 strain is observed across all phases in the large n_{ph}
 271 regime, Figure 3 and Table II show that the δ phase
 272 possesses the largest photomechanical sensitivity under
 273 low illumination conditions.

274 A recent study has attributed the large photostriction
 275 in *cubic* cesium lead halide perovskite to the strong an-
 276 tibonding nature of the bottom of the conduction band.
 277 [47] Our results indicate that the strong photo-induced
 278 strain permeates through all phases of CsPbI₃, at least in
 279 the large n_{ph} regime. The large photo-induced strain in
 280 CsPbI₃, and in general in hybrid perovskites [48], may
 281 find applications in improving the photovoltaic power
 282 conversion efficiency [49]. Interestingly, to achieve pho-
 283 tostriction comparable to the 0.125% expansion reported
 284 in MAPbI₃ films [48], one could use 413 nm wavelength
 285 laser pulses of 8.5 mJ.cm⁻².

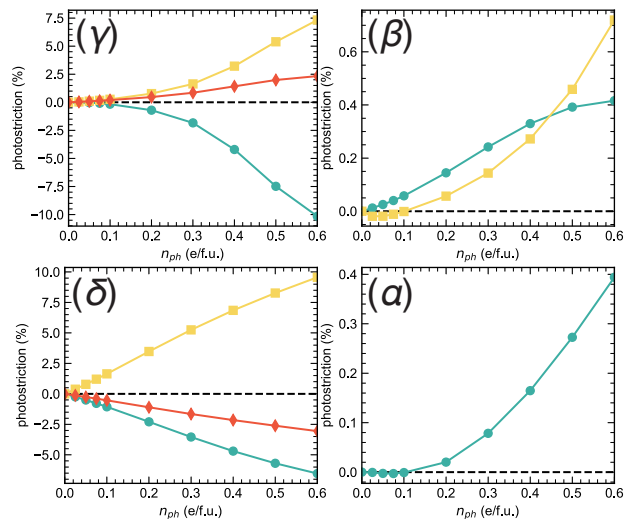


FIG. 3. Photo-induced strain in lead cesium iodide, along the principal crystallographic axes of each phase (γ), (β), (δ) and (α). Dashed open symbols in the δ and γ phases show calculations with SOC.

Material	Phase	$\delta a/a$	$\delta b/b$	$\delta c/c$
% / (e/f.u.)]				
CsPbI ₃	α	-0.02	-	-
	β	0.5	-	-0.8
	γ	0.2	1.4	1.5
	δ ,	-9.9	15.3	-5.1
BiFeO ₃ (perovskite [44])	$R3c$	-1.5	-	-
BaTiO ₃ (perovskite [38])	$R3m$	-0.2	-	-
PbTiO ₃ (perovskite [38])	$P4mm$	-1.0	-	-3.1
SrCoO _{2.5} (brownmillerite [45])	$Ima2$	-	-	+0.4
SnS (2D ferroelectric [46])		-56.9	14.2-28.4	-

TABLE II. Estimates of the linear photo-induced strain in lead cesium iodide calculated using the constrained-DFT method (no SOC/SOC values reported). Other reported compounds were calculated using the Δ SCF (Self-Consistent Field) method.

V. CONCLUSION

287 The constrained-DFT approach employed in the
 288 present study unveils that thermalized photo-excited car-
 289 riers can reduce, and even invert, the relative energy dif-
 290 ference between the δ phase and the γ perovskite phase
 291 of CsPbI₃. This allows to envision new ways to transform
 292 into or better stabilize the γ -phase, which is highly im-
 293 portant for photovoltaic applications. In particular, the
 294 present work proposes that visible light could trigger a
 295 photo-induced phase transition towards the γ perovskite
 296 phase, which is of high interest for photovoltaic appli-
 297 cations. Once the photo-transition is achieved and the
 298 light removed, it is likely that the γ -phase will remain
 299 kinetically stable since it has already been proven to be

300 metastable under dark conditions using thermal quench-
 301 ing [10, 50]. It is unclear at present whether CsPbI₃
 302 could sustain the proposed intensity to reach the phase
 303 transition. Working near the yellow to black phase tran-
 304 sition temperature should lower the critical value of light
 305 intensity necessary to reach the transition. Conversely,
 306 one could expect that using visible illumination (for in-
 307 stance with lasers) will lower the transition temperature,
 308 leading to more efficient and ecological manufacturing of
 309 CsPbI₃-based devices. In addition, our calculations re-
 310 veal that CsPbI₃ is an efficient photostrictive material,
 311 especially in the δ phase, which was previously thought
 312 to be a detrimental phase with respect to photovoltaic
 313 applications. This work may thus pave the way for other
 314 and easier applications of CsPbI₃ in photo-actuators.

315 ACKNOWLEDGMENTS

316 C. P. acknowledges an international mobility funding
 317 opportunity from a public grant overseen by the ANR as
 318 part of the “Investissements d’Avenir” program (ANR-
 319 10-LABX-0035, LabexNanoSaclay), the Arkansas High
 320 Performance Computing Center on which calculations
 321 were performed, and a computing grant from GENCI
 322 (project AD010913519). L. B. thanks ARO Grant No.
 323 W911NF-21-1-0113.

324 Appendix A: Photo-induced carrier estimate

325 We estimate the photo-excited carrier concentration.
 326 Considering the power balance sketched in Figure 4, the
 327 total absorbed energy from a laser of fluence I_0 imping-
 328 ing on a sample of cross-section S , thickness d , having
 329 absorption and reflection coefficient α and R is

$$E_{tot} = (1 - R)I_0(1 - e^{-\alpha d})S \quad (\text{A1})$$

330 As a result, the total number of photons absorbed is

$$N_{photons} = \frac{E_{tot}}{\hbar\omega} = \frac{(1 - R)I_0(1 - e^{-\alpha d})S}{\hbar\omega}, \quad (\text{A2})$$

331 with $\hbar\omega$ the average photon energy within the incident
 332 beam. Assuming that each absorbed photon yields an
 333 electron - hole pair, we would thus have a photo-excited
 334 carrier density, expressed in e/f.u. of

$$n_{ph} = \frac{N_{photons}}{Sd} \times \frac{V_\delta}{4}, \quad (\text{A3})$$

335 where V_δ is the volume of the δ phase unit cell. The
 336 factor 1/4 comes from the fact that there are 4 formula
 337 units in the δ phase unit cell.

338 Assuming, for the sake of simplicity, that photons in
 339 the laser beam carry an energy $\hbar\omega = 3$ eV (413 nm), we
 340 take for the δ phase a value of $\alpha \approx 2 \times 10^5$ cm⁻¹ [8]. We

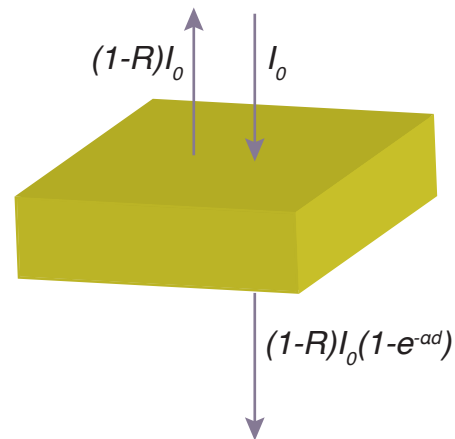


FIG. 4. Sketch of what happens to a ray of light of intensity I_0 impinging on a material.

341 take a reflection coefficient $R = 0.15$, similar to what can
 342 be found in CsPbBr₃ thin films, a parent compound [51].
 343 This allows us to obtain a crude estimate of the value
 344 of n_{ph} depending on the pump fluence, which we plot
 345 in Figure 5. Note that in Figure 5, we assumed a sam-
 346 ple uniformly illuminated of thickness 323 nm, area size
 347 $S = 0.0625$ cm², which is submitted to a laser pulse car-
 348 rying an energy up to 4 mJ. The geometrical parameters
 349 involved were taken from photostriction experiments car-
 350 ried out on thin films of MAPbI₃ [35]. One observes that
 351 reasonable pulse energy can lead to the desired concen-
 352 tration of photo-excited carriers in thin films.

353 Note that in the previous simple derivations, we as-
 354 sumed that every electron-hole pair relaxes into thermal-
 355 ized carriers in their respective bands (valence bands for
 356 holes; conduction bands for electrons). We also assume
 357 that the recombination time of excited carriers is large
 358 enough compared to the pulse duration. Typical relax-
 359 ation times in CsPbI₃ are of the order of a few nanosec-
 360 onds [52, 53] (depending on the sample quality). Picosec-
 361 ond laser pulses could therefore be suitable this model.
 362 A more complex model would solve a balance equation or
 363 the real time Bethe-Salpeter equation to obtain a more
 364 accurate relation between the pump fluence and the av-
 365 erage number of photoexcited carriers.

366 Appendix B: Numerical integration and toy model

367 One can understand the physical mechanisms at play
 368 using a simple toy model. It is detailed in Eq. 1. This
 369 amounts to consider completely flat conduction and val-
 370 lence bands, *i.e.* a two level system. To further re-
 371 fine our model, we performed a numerical integration
 372 of the ground state band structures. In other words,
 373 we consider a model (denoted as “ k -sum in the main
 374 manuscript) of the form:

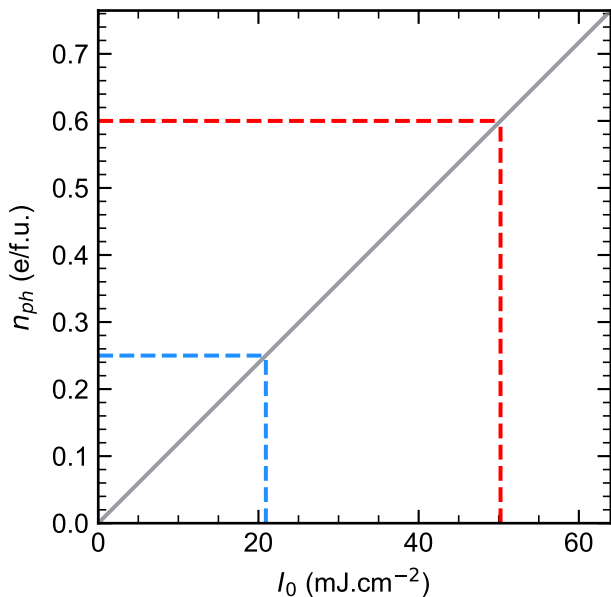


FIG. 5. Estimated photo-induced carrier concentration induced by a 3 eV laser pulse. Dotted blue and red line correspond to the concentration necessary to achieve the $\delta \rightarrow \gamma$ transition with and without SOC, according to Figure 2 of the main manuscript.

$$E_{\gamma}(n_{ph}) - E_{\delta}(n_{ph}) = \Delta E_0 + [(E_c^{\gamma}(n_{ph}) - E_v^{\gamma}(n_{ph})) - (E_c^{\delta}(n_{ph}) - E_v^{\delta}(n_{ph}))]. \quad (\text{B1})$$

$E_{\gamma/\delta}^c(n_{ph})$ represents the electronic energy change due to the electrons in the conduction band, and can be expressed as:

$$E_c^{\gamma/\delta}(n_{ph}) = \sum_k \sum_c w_k f(\varepsilon_{k,c}^{\gamma/\delta}, \mu_e, T) \varepsilon_{k,c}^{\gamma/\delta}, \quad (\text{B2})$$

where c represent the conduction band index, k the k -point in the irreducible discretized Brillouin zone, w_k its weight, μ_e the electronic quasi-Fermi level, T the smearing temperature, and $\varepsilon_{k,c}^{\gamma/\delta}$ is the eigenvalue of k -point k with band index c , taken in the γ/δ phase calculated with $n_{ph} = 0$ e/f.u. $f(\varepsilon_{k,c}^{\gamma/\delta}, \mu_e, T)$ represents the Fermi-Dirac population of this state with energy $\varepsilon_{k,c}^{\gamma/\delta}$.

Similarly, $E_{\gamma/\delta}^v(n_{ph})$ is the energy change caused by the presence of holes in the valence bands.

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