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Spin-orbit enhanced carrier lifetimes in noncentrosymmetric semiconductors

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A B S T R A C T

We show that the carrier recombination rate of noncentrosymmetric materials can be strongly modified by spin-orbit coupling. Our proposed mechanism involves the separation of conduction and valence bands into their respective spin components, which changes the transition dipole moments between them. The change in the carrier recombination can be either positive or negative in sign, or vary depending on the location of carriers in the Brillouin zone. We have performed a large scale DFT screening study to identify candidate materials that display this effect. We have selected three materials, Pb_4SeBr_6 , ReTe_3Br_5 , and $\text{CsCu}(\text{BiS}_2)_2$, which span the range of behaviors, and discuss their electronic band structure in greater detail. We find transition dipole moment enhancement factors of up to three orders of magnitude, reflecting the physical impact of spin-orbit coupling on the carrier lifetime. Therefore, further explorations of the spin-orbit coupling and lattice symmetry could prove to be useful for manipulating the photophysics of materials.

1. Introduction

Radiative recombination of carriers is a major loss mechanism in many semiconductors. Long carrier lifetimes are desirable for the collection of carriers in charge transport devices and for the observation of excited-state physics in general. In most solid-state materials, the radiative recombination rate [1–3] is of the order of 10^{-15} – $10^{-13} \text{ cm}^3\text{s}^{-1}$, and it is mostly regarded as an unavoidable loss mechanism.

In this paper, we show that the carrier recombination rate is strongly affected by the presence of spin-orbit coupling, and that it can be quenched by choosing spin-orbit materials where the spin degree of freedom can impose selection rules on the lowest-energy interband transitions. We present a mechanism by which spin-orbit coupling either enhances or reduces the carrier lifetime, by separating the energy bands into different spin components, and hence modifying the radiative recombination rate.

This mechanism was first proposed in the halide perovskites [4,5] as an explanation for the anomalously long carrier lifetimes in these materials [6–8]. The halide perovskites, which have recently emerged as efficient solar cell materials [9–12], contain large spin-orbit coupling due to the heavy Pb and I atoms and are thought to display dynamically and locally broken inversion symmetry [13–16]. This results in a Rashba-type band structure [17], which has been theoretically proposed in halide perovskites [18–20] and observed there in different types of experiments [21–23].

We show that this mechanism of spin-orbit induced carrier lifetime

enhancement is not limited to hybrid perovskites. We present materials that display this effect in their static ground-state structures. We show that, depending on material, the relative orientation of spins in the conduction and valence bands may be such that carrier recombination is suppressed, enhanced, or displays a more complex k -dependent behavior. Below, we provide examples of materials displaying each of these behaviors.

2. Description of lifetime enhancement mechanism

We first outline the mechanism behind spin-orbit induced carrier lifetime enhancement. This mechanism relies on electron and hole carriers occupying states where radiative recombination is dipole-forbidden (dark states). In this paper, we focus on the situation where the transition is dipole-forbidden in the spin sector, that is, because the electron and hole carriers have opposite (or nearly opposite) spin orientations. This situation is brought about by having a material with strong spin-orbit coupling, which causes a lifting of spin-degeneracies of bands. Electron and hole carriers in the band extrema would then be in particular spin states, with their spin directions being material-dependent quantities. For instance, the bands of Rashba-type materials [17] have a vortex-like arrangement of spins near high-symmetry points in the Brillouin zone. If the spins of electron and hole are anti-aligned (aligned), this would cause an enhancement (reduction) of carrier lifetime. In most materials, the electron and hole spins would not be perfectly aligned or anti-aligned; the degree of enhancement or reduction in carrier lifetime

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depends on their relative directions.

This effect requires a population of electron and hole carriers in dipole-forbidden states. Because of this selection rule, these carriers cannot be directly optically excited into these states, but can only arrive there by excitation into higher-energy states followed by relaxation into the dipole-forbidden states. It is necessary that these excitation and relaxation processes are not forbidden by selection rules and that they occur fairly rapidly, ensuring that a significant portion of carriers are in the dipole-forbidden states.

In Fig. 1, we provide a concrete example of how this process occurs in a typical Rashba band structure [17]. This band structure, which occurs in noncentrosymmetric materials with strong spin-orbit coupling, contains conduction and valence bands which are each spin-split away from a high-symmetry point and degenerate at that point. The conduction band minimum (CBM) and valence band maximum (VBM) are therefore located away from the high-symmetry point. Upon excitation by a photon, an electron and a hole are created in bands with the same spin orientation (thick green arrow in Fig. 1). Shortly afterward, the electron and hole each relax via phonon scattering events, which occur primarily to states of the same spin orientation. We note that there are intraband (blue arrows in Fig. 1) as well as interband (red arrow in Fig. 1) of this kind, allowing the carriers to relax to the CBM and VBM. A quasi-static distribution of carriers is thus established at the CBM and VBM. Here, their recombination is suppressed because of the opposing spin orientations of the CBM and VBM.

This mechanism bears some similarity to dark excitons, which are bound electron-hole pairs with parallel spins, and as a result have a long radiative lifetime [24]. However, there are several differences. Firstly,

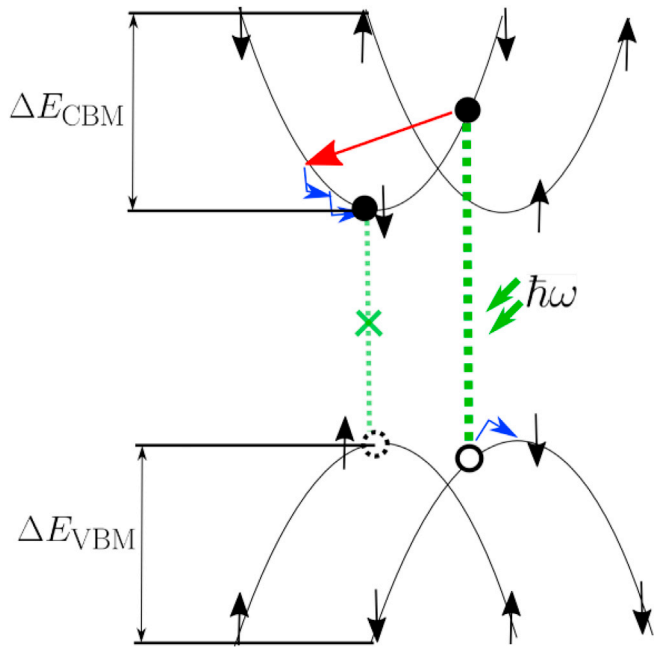


Fig. 1. Schematic showing carrier excitation and relaxation processes in a Rashba band structure. The black arrows indicate the directions of the spins. After absorption of photons (green, right), spin-aligned electrons and holes are created. The excited electrons relax to the conduction band minimum due to interband (red) and intraband (blue) phonon scattering processes, which usually do not flip the electron spin. Similarly, the holes relax to the valence band maximum without flipping their spins. After this thermalization process, radiative (vertical) recombination of electrons and holes is spin-forbidden due to opposite spin directions (crossed green line, left). The conduction band energy splitting (ΔE_{CBM}) and valence band energy splitting (ΔE_{VBM}) are shown in the figure: they are defined as the splitting of the two spin-components of the conduction and valence bands, at the band extrema. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

this mechanism pertains to free carriers instead of bound excitons, and is of greater relevance in situations where collection of current is important. Secondly, the dark exciton states are usually populated via an intersystem crossing [25], which is mediated by the spin-orbit coupling. Here, the population of dark states is achieved by phonon scattering, which is typically a faster process [26,27] than intersystem crossings. Such phonon scattering processes are available only to free carriers. In both mechanisms, the size of the energy splitting opened by spin-orbit coupling determines the ratio of majority-spin to minority-spin states at a given temperature.

To summarize, the requirements for spin-orbit enhanced carrier lifetime are a strong spin-orbit interaction to ensure a large enough spin-splitting, a breaking of inversion symmetry to correctly order the spin-split bands to ensure that the CBM and VBM states are dipole forbidden, and fast carrier relaxation.

3. Methodology

We screened the MATERIALS PROJECT database [28] for materials exhibiting a range of spin-orbit influences on carrier lifetime. We constrained our search to noncentrosymmetric materials with heavy elements ($Z > 49$) which have non-magnetic ground states. Furthermore, we have restricted our search to thermodynamically stable materials, or metastable materials with decomposition energies of less than 0.1 eV/atom. We have chosen materials with fewer than 30 atoms per unit cell, for computational efficiency. This screening resulted in 421 candidate materials, for which we performed density functional theory (DFT) calculations of the band structure and transition dipole moments (TDMs). These calculations were done with the PBE density functional [29], using norm-conserving RRKJ pseudopotentials [30], and using a planewave basis set with kinetic energy cutoff of 60 Ry. Spin-orbit coupling was included at the fully-relativistic level for all calculations.

Table 1

Selected noncentrosymmetric materials with large spin-orbit coupling, obtained from querying the MATERIALS PROJECT database. Tabulated are the direct and indirect band gaps, the spin-orbit splitting at the conduction band minimum (ΔE_{CBM}) and at the valence band maximum (ΔE_{VBM}), and the sign of the lifetime enhancement factor. “+” indicates that the ordering of spin-split valence and conduction bands results in carrier lifetime enhancement, while “−” indicates lifetime reduction, and “*” indicates that the lifetime enhancement or reduction is dependent on the direction of the k -vector from the band minima. See Fig. 1 for the definition of valence and conduction band splittings. Where available, original experimental references are given. For comparison, data for β -MAPbI₃ is given in the last row.[†] For NaBiS₂, the calculation was performed for the theoretical $T = 0$ K symmetry-broken phase, and not the inversion symmetric rocksalt phase observed in experiment.

	Direct gap (eV)	Indirect gap (eV)	ΔE_{CBM} (meV)	ΔE_{VBM} (meV)	Δr	Ref.
ReTe ₃ Br ₅	1.2157	1.1986	27.6	6.3	+	[32]
Pb ₄ SeBr ₆	1.5588	1.5006	30.8	1.7	+	[33]
CsCu(BiS ₂) ₂	0.2066	0.2056	81.2	75.5	*	[34]
NaBiS ₂	0.3454	0.3375	84.1	92.5	−	[35] [†]
Ga ₁₂ Ag ₂ Te ₁₉	0.73	0.6685	0.0	30.8	−	
KI ₃ ·H ₂ O	1.7388	1.693	22.6	8.7	+	[36]
TiNO ₂	1.9635	1.6023	132.4	9.8	−	
Cs ₂ Se	2.0306	1.7223	0.0	41.1	*	[37]
PbS (bilayer)	1.2678	1.2678	36.0	18.5	*	[38]
LaMoN ₃	1.3212	1.1059	95.0	0.0	−	
Sb ₂ Pb ₂ O ₇	1.6772	1.4991	29.5	0.0	+	[39]
Ir ₂ Te ₅	0.8637	0.7409	19.4	0.0	−	[40]
La ₃ AgGeS ₇	1.9512	1.9359	20.9	5.5	+	[41]
Hf ₂ N ₂ O	2.2349	2.0904	0.0	26.0	−	
Hg ₃ AsS ₄ Br	1.6323	1.4992	0.0	38.7	+	[42]
LaCrAgO ₆	0.7335	0.7141	0.0	41.4	−	
β -MAPbI ₃	0.641	0.641	48	44	−	[19, 43]

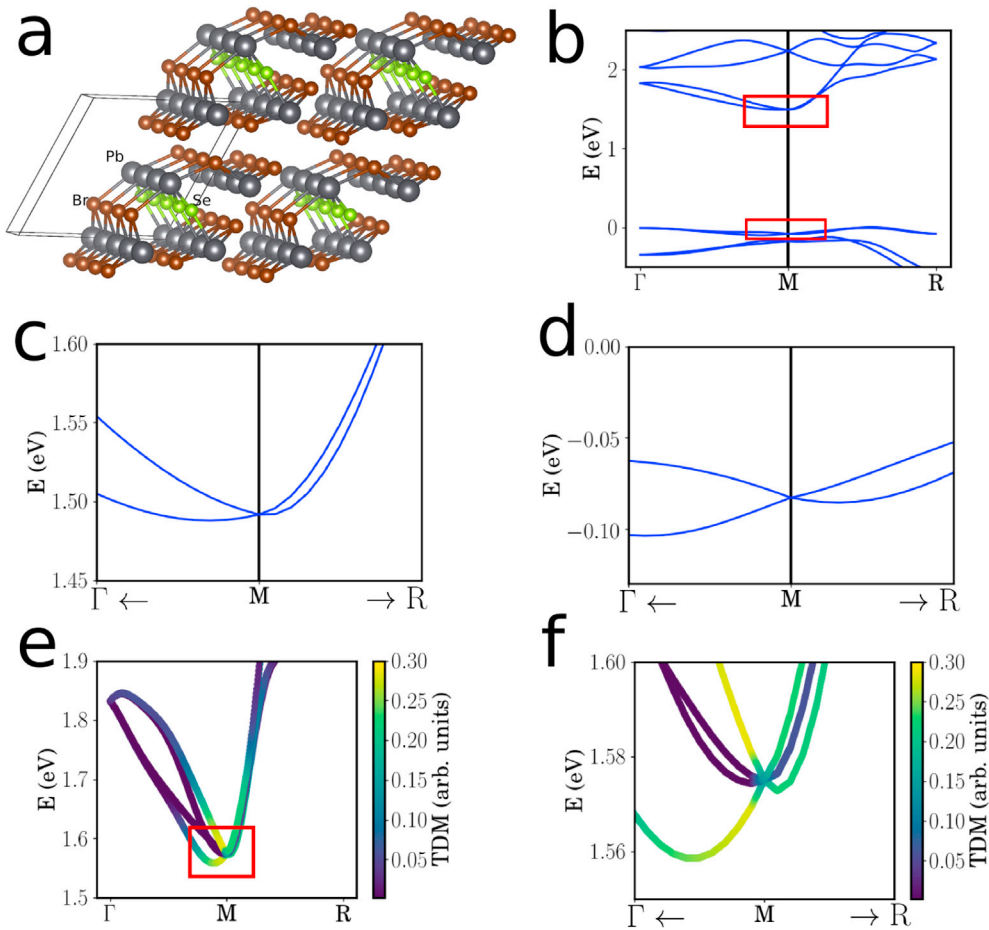


Fig. 2. a) Crystal structure of Pb_4SeBr_6 , with primitive unit cell depicted. Colored spheres represent Pb (grey), Se (light green), and Br (brown). b-d) DFT band structure of Pb_4SeBr_6 , showing conduction (c) and valence (d) bands. e-f) Transition dipole moments of the four lowest-energy transitions between valence and conduction bands, with color representing the magnitude of transition dipole moments. f) Magnified view of transition dipole moments near the band edge. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

A Monkhorst-Pack [31] $8 \times 8 \times 8$ k -point mesh was used for the self-consistent evaluation of the charge densities.

From these DFT calculations, we have selected 16 materials with large spin-orbit splittings of the valence or conduction band (Table 1). These materials have spin-orbit splittings larger than the room-temperature energy scale, and they therefore can host spin-resolved carrier

populations. We have tabulated the relative ordering of spin-split conduction (CB1, CB2) and valence (VB1, VB2) bands. This was done by considering the TDMs of the four transitions from CB1 and CB2 to VB1 and VB2. If the lowest-energy transition (VB1 \rightarrow CB1) has a lower TDM than the higher-energy transitions VB1 \rightarrow CB2 and VB2 \rightarrow CB1, carrier recombination will be suppressed. The highest-energy transition in this

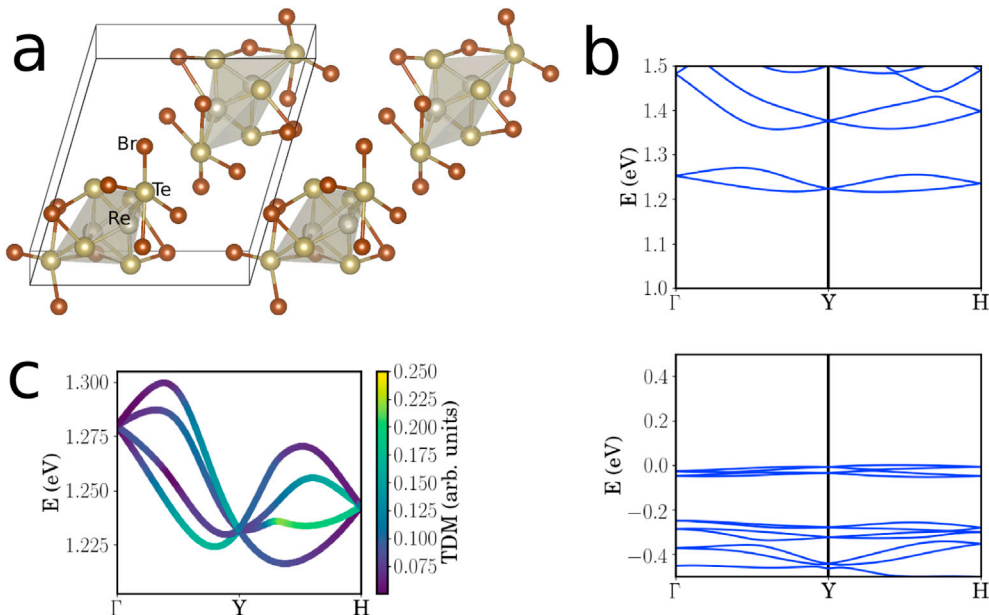


Fig. 3. a) Crystal structure of ReTe_3Br_5 , with primitive unit cell depicted. Colored spheres represent Re (silver), Te (gold), and Br (brown). b) DFT band structure of ReTe_3Br_5 , showing conduction (top) and valence (bottom) bands. c) Transition dipole moments of the four lowest-energy transitions between valence and conduction bands, with color representing the magnitude of transition dipole moments. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

manifold of states, $VB2 \rightarrow CB2$, often has a similar TDM to $VB1 \rightarrow CB1$ because they have similar relative spin orientations (See Fig. 1). However, the highest transition does not affect the carrier population strongly if the spin-orbit splitting is larger than room temperature. Among the materials in Table 1, we find examples where the ordering of bands either suppresses or enhances carrier lifetime, as well as more complex cases where the band structure contains both of these effects simultaneously, in different parts of the Brillouin zone. In the following, we will discuss representative examples of each case in more detail.

4. Materials displaying spin-orbit modified carrier lifetime

In Ref. [4], we showed that dynamic structural fluctuations play an important role in enhancing the carrier lifetime enhancement in $MAPbI_3$. In the high-symmetry structure of tetragonal phase $MAPbI_3$, the order of Rashba-split bands increases carrier recombination. However, structural fluctuations at room temperature change the ordering of bands to decrease carrier recombination instead. This is particularly important in the hybrid perovskites because of their weak bonds and dynamically fluctuating molecular components. For the materials presented below, we discuss their TDM properties in their most stable static structures, because dynamical fluctuation is not a necessary ingredient for a material to display spin-orbit-modified carrier lifetime.

Pb_4SeBr_6 [33] in its $Imm2$ structure consists of one-dimensional chains aligned along the a -axis (Fig. 2a). It has a Rashba band structure at the M point, with the largest splitting of the conduction band of

30.8 meV occurring along the Γ -M direction (Fig. 2c), and the largest splitting of the valence band of 1.7 meV occurring along the same direction. At the conduction band minimum, which is also located along Γ -M, we find that carrier recombination of the $VB1 \rightarrow CB1$ transition is enhanced relative to the $VB2 \rightarrow CB1$ and $VB1 \rightarrow CB2$ transitions (Fig. 2e). At the CBM, the TDM of the $VB1 \rightarrow CB1$ transition is 2530 times the TDM of the $VB2 \rightarrow CB1$ transition.

$ReTe_3Br_5$ [32] has the opposite ordering of bands at its band edges. The $P2_1$ phase of this material is made up of free-standing $Re_2Te_6Br_{10}$ octahedral units, with Te located at the vertices of the octahedra and the two Re located at their interior (Fig. 3a). Each apex of the Te_6 octahedron is bonded to four Br, while the remaining two Br are bonded to Te at the equatorial plane of the octahedron. The conduction band has a spin-orbit splitting of 27.6 meV (Fig. 3b), while the valence band has a splitting of 6.3 meV. Fig. 3c shows that recombination of the $VB1 \rightarrow CB1$ transition is suppressed at the band edges, which are located along the Y-H line. In this material, the ratio of the TDMs of the lowest-energy $VB1 \rightarrow CB1$ transition to the higher-energy $VB2 \rightarrow CB1$ transition is 0.426.

Besides affecting the TDMs, a secondary effect of spin-orbit coupling is to shift the locations of the VBM and CBM. In Pb_4SeBr_6 , the CBM is only shifted slightly away from the M point (Fig. 2c), whereas it is shifted to a much greater extent along the Y-R line in $ReTe_3Br_5$, where the spin-orbit splitting is so large that it is comparable to the band width. The VBM and CBM will generally be shifted to different positions, resulting in an indirect band gap. This is another factor which suppresses the recombination rate. The extent of this suppression depends on the energy scale

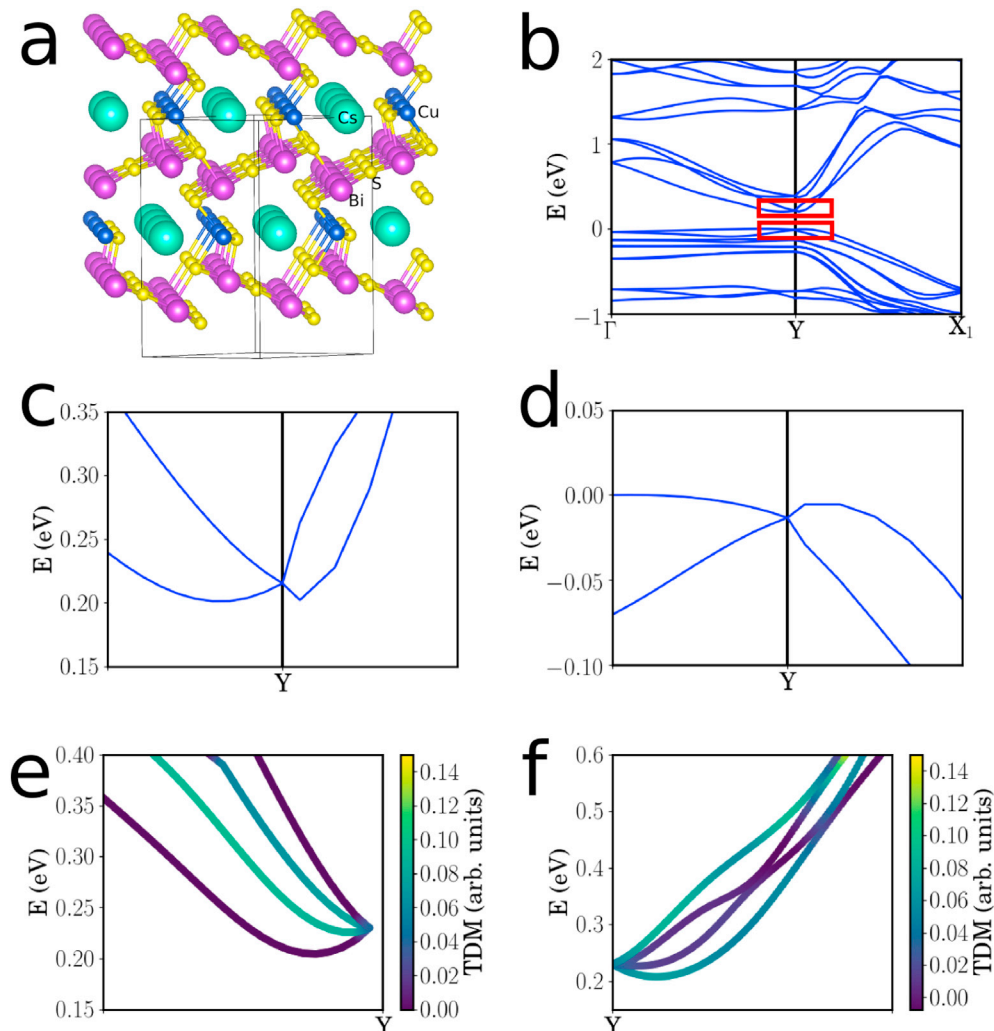


Fig. 4. a) Crystal structure of $CsCu(BiS_2)_2$, with primitive unit cell depicted. Colored spheres represent Cs (cyan), Cu (blue), Bi (magenta), and S (yellow). b-d) DFT band structure of $CsCu(BiS_2)_2$, showing conduction (c) and valence (d) bands. e-f) Transition dipole moments of the four lowest-energy transitions between valence and conduction bands, with color representing the magnitude of transition dipole moments, along the Γ -Y direction (e), and along the Y- X_1 direction (f). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

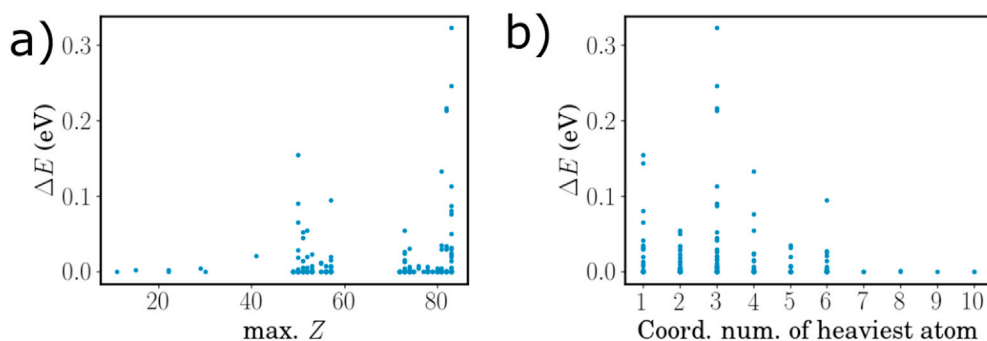


Fig. 5. a) The maximum frontier orbital spin-splitting over a material's Brillouin zone (for either conduction or valence bands) as a function of the maximum atomic number of all atoms in the materials' structure. Each point represents a single material from the set of candidate materials described in the text. b) The maximum frontier orbital spin splitting as a function of the coordination number of the heaviest atom in the structure. The spin splitting can potentially be large when the heaviest atom has low coordination, in particular, for coordination numbers 1 and 3.

over which the band gap is indirect. If the difference between the direct and indirect band gaps is not much bigger than the room temperature energy scale (such as in Pb_4SeBr_6 and ReTe_3Br_5), the indirect gap effect will be masked by the Fermi distribution of carriers. Some materials, such as Cs_2Se (Table 1), have a much greater difference between direct and indirect gaps, and will display this effect to a greater extent. We note that in these spin-orbit materials, it is rare for the difference between direct and indirect gaps to be so large that it affects absorption of visible light. They thus act effectively as direct gap semiconductors when absorbing light, and as indirect gap semiconductors for carrier recombination.

Compared to Pb_4SeBr_6 and ReTe_3Br_5 , the band structure and TDM structure of $\text{CsCu}(\text{BiS}_2)_2$ is more complex. This material, which belongs to space group $\text{Cmc}2_1$, is made up of a $\text{Cu}(\text{BiS}_2)_2$ network which has one-dimensional channels, occupied by Cs atoms (Fig. 4a) [34]. There is a direct band gap at the Y point. Both conduction and valence bands display large spin-orbit splittings, of 81.2 meV and 75.5 meV respectively. We find that carrier recombination is suppressed along the Γ -Y direction (by a factor of 0.00102), but is enhanced along the Y- X_1 direction (by a factor of 3.29). This example shows that recombination enhancement or reduction can be a function of k -vector direction. In this situation, we expect carriers to accumulate in the sections of the band edges where recombination is reduced, here, along the Γ -Y direction. This will lead to an anisotropic k -space distribution of carriers, which can be detected by time-resolved excited-state optical measurements.

Finally, we query our database of materials to find trends that are likely to result in large splittings of the conduction and valence bands (Fig. 5). As expected from strong spin-orbit interaction being essential for the Rashba effect, we find that the potential for large spin splittings increases with the atomic weight of the heaviest atom in the structure. However, even though broken inversion symmetry is required for the Rashba effect, the magnitude of the spin splittings are not strongly affected by the magnitude of the material polarization, but only the presence of polarization (see SI). This is because the spin splitting in these materials arises from inversion symmetry breaking in bulk and not the presence of an electric field. Instead, we find a stronger correlation with the bonding environment of the heavy atoms in the structure. Taking the coordination number (CN) of the heaviest atom in the structures, we find large spin splittings when CN is low, and in particular, when $\text{CN} = 1$ and $\text{CN} = 3$. Here, CN is defined as the number of atoms having a radial distance within 5% of the closest neighbor to an atom. The environment surrounding highly coordinated atoms tends to be more spherical, resulting in weaker symmetry breaking of the atomic sites. The exception is when $\text{CN} = 2$. Atoms at such sites are in a linear bonding environment, which locally does not break inversion symmetry. In contrast, sites with $\text{CN} = 1$ and $\text{CN} = 3$ must break local inversion symmetry.

5. Conclusions

In conclusion, we have shown that materials with large spin-orbit coupling and broken inversion symmetry can have their TDMs, and hence carrier recombination rates, strongly modified by spin-orbit

coupling. Our DFT calculations have shown that carrier recombination can either be enhanced, reduced, or redistributed in k -space by this mechanism. While the halide perovskites are thus far the only class of materials displaying experimental evidence for this effect, we have shown that there are potentially many more materials that would as well. This raises the possibility for the targeted use of spin-orbit materials in optoelectronics applications and for observing excited-state photophysics.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jpccs.2018.02.016>.

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