The Influence of the Rashba Effect

Heavy atoms and inversion symmetry breaking may promote Rashba effects in halide perovskites. Sam Stranks and Paulina Plochocka propose experiments to assess the existence of these effects and their implications on the photophysics of perovskites.

In semiconductors, electrons and holes are typically described in an effective mass approximation with spin-degenerate parabolic dispersion around extrema points of the valence and conduction bands. The presence of heavy atoms in the crystal leads to spin orbit coupling (SOC) which, combined with a breaking of the inversion symmetry, gives rise to Rashba-type effects[1]. As a consequence, the spin degeneracy in *k*-space is lifted and the valence band maxima (VBM) and/or conduction band minima (CBM) are shifted away from the symmetry points in the Brillouin zone.

It has been proposed that metal halide perovskites possess both necessary properties for Rashba-type effects[2]. These systems, such as the archetypical methylammonium lead iodide ($MAPbI_3$), exhibit a very strong SOC due to the presence of heavy ions in the crystal structure such as lead or iodide. In contrast to many semiconductors, the SOC in these halide perovskites is stronger in the conduction than in the valence band[3]. There are various means in which the symmetry has been proposed to be broken in the three-dimensional centro-symmetric perovskite crystal structures, including octahedral tilting of the inorganic lead-halide cage and dynamic rotation of the organic cation on the time scale of a few picoseconds[4]. The latter breaks the symmetry on a very local scale but preserves global centro-symmetry, which is consistent with measurements of phonon dispersions that reveal fluctuating symmetry-broken domains on a scale of ~1-3 nm in size[5].

The Rashba-type effects lead to the intriguing possibility of the fundamental bandgap being indirect in these halide perovskite systems[2, 3] (Fig. 1a). The indirect band is only slightly shifted in *k*-space (k_0) and is predicted to be at slightly lower energy (ΔE~50 meV)[3] than the direct band. This could have an enormous impact on the dynamics of charge carriers: light absorption may proceed through direct transitions, but recombination of cooled carriers may be slowed by the band extrema shift in *k*-space leading to a forbidden indirect transition[2].

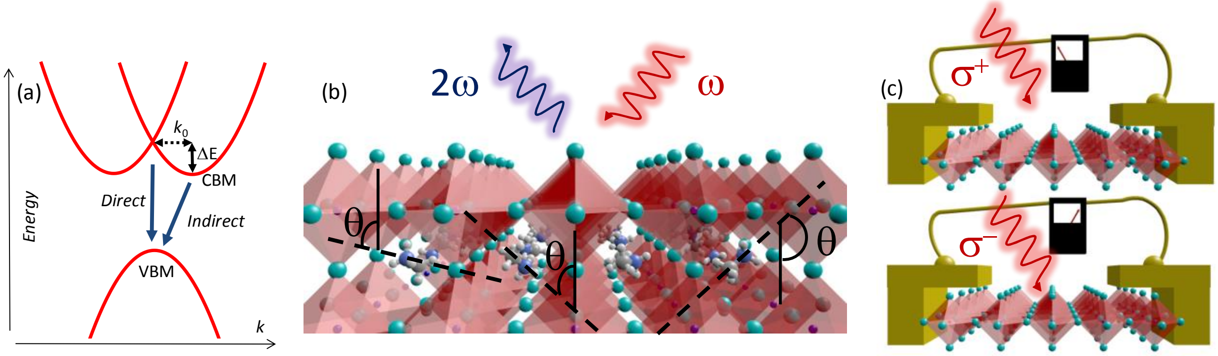

Figure 1. Rashba effects in halide perovskites and selected experiments to observe them. **a,** Schematic band diagram of the bands slightly shifted in *k*-space by k_0. An indirect band gap with an energy ΔE~50 meV below the direct gap is introduced[3, 6, 7]. **b,** Schematic of the SHG effect in $MAPbI_3$ where the crystal inversion symmetry is broken due to the dynamic rotation of the cations. Red octahedra with light-blue spheres represent the inorganic lead-halide cage, and the blue and grey spheres represent the organic cations. The random orientation of the cations in each unit cell is marked by their different angles θ. The incident light of frequency ω (red wavy arrow) interacts with the sample and generates light of frequency 2ω (blue wavy arrow). **c,** Schematic of circular photogalvanic measurements with polarised incident light (wavy arrows, with either σ^+ or σ^- polarization). Electrodes are shown in yellow.

There are still only a few reports providing experimental indications for these theoretical predictions. Time-resolved photoconductivity measurements have been recently used to show that excitation below the direct gap into an indirect band leads to the photo-generation of mobile carriers, which exhibit slower recombination than those carriers generated by excitation into the direct band[6]. These results are supported by very recent observations of a circular photogalvanic effect: electric current is generated in a thin halide perovskite film excited with circularly-polarized light below the optical bandgap. Moreover, left-handed and right-handed excitation induces photocurrents of opposite directions, providing direct evidence for phototransport in spin-split bands (Fig. 1c)[8]. In another experiment, hydrostatic pressure was applied to perovskite samples to decrease the Rashba effect and shift the system to a more direct bandgap, observing a rapid increase in the recombination rate and an activation energy for recombination of $\Delta E \sim 60$ meV[7]. Polarization- and angle-resolved photoemission spectroscopy (ARPES) has been employed to extract the dispersion of the highest energy VB in a $MAPbBr_3$ single crystal, revealing spin splitting[9]. We note that this photoemission technique is surface-sensitive and therefore may exaggerate Rashba-type effects by selectively probing surface sites at which symmetry is more likely to be broken than the bulk.

The few experimental reports published to date have not yet settled the debate over the presence of the Rashba effect; hence, we now consider which experiments are potential "smoking guns" to validate or falsify the theoretical predictions of the Rashba-type splitting in halide perovskites. In bulk crystals, second harmonic generation (SHG) with electric dipole symmetry response is a nonlinear optical process in which the photon with frequency ω is upconverted to a photon with doubled frequency (2ω) only in materials with broken inversion symmetry (Fig. 1b). Hence, this optical technique can be used to probe the crystal symmetry. Furthermore, it could be performed with micrometer spatial resolution to determine whether local grain-to-grain heterogeneity, surfaces or grain boundaries lead to local inversion symmetry breaking. Another elegant way to probe Rashba-type couplings is to exploit the simple spin-charge conversion and introduction of an unbalanced spin population (for instance through circularly polarized light), motivating further experiments along the lines of circular photogalvanic (Fig. 1c), spin galvanic effect and magneto-gyrotropic measurements[10].

Rashba-type effects may also be accessed through measurements on the exciton fine structure. In semiconductors, the exchange interaction splits the dark and bright excitonic states, with the dark state being the lowest one. The bright states can be further split by lowering the symmetry of the crystal. Recently it has been proposed that the Rashba effect impacts the order of the states in colloidal $CsPbBr_3$ nanocrystals — making a bright triplet the ground state — and strongly enhances the exchange splitting of the bright states[11]. It should be noted that quantum confinement and surface effects may significantly contribute to symmetry breaking in these nanocrystal systems. Hence, low-temperature measurements of the exciton fine structure in larger three-dimensional perovskites crystals will be required to isolate the exchange spitting originating purely from the Rashba effect.

Still, an important question remains: if there is indeed a Rashba effect, what role will it play in the operation of perovskite optoelectronic devices and solar cells? Charge carrier recombination is influenced not only by the direct or indirect nature of the band gap, but also by a number of other factors including carrier trapping[12] and possible polaronic screening effects[13]. The relative contributions still need to be decoupled, but it is likely that traps are the main factor affecting recombination in most perovskite solar cells to date[12]. As the material quality further improves and the number of traps is reduced, the Rashba effect may play a more significant role: the indirect band gap may even cause an unwanted ~50 mV voltage loss in the device performance. Nevertheless, it is likely that the net symmetry breaking in highly crystalline bulk films — those used in planar heterojunction solar cells — will be negligible, thus reducing the contributions of the Rashba effect on recombination. Indeed, in typical three-dimensional solar cell materials, recombination rates appear to be primarily direct and radiative, at least at high charge densities[14]. Another important question is whether we can exploit the effect in novel device applications. The Rashba parameter $\alpha = 2\Delta E/k_0$ in halide perovskites estimated from ARPES measurements and predicted theoretically is of the order a few eV·Å, which is comparable with the highest values reported for bulk crystals, rendering them promising for spintronics[10]. It has also been proposed[15] that the strength of the Rashba splitting can be controlled via an external electric field in the direction perpendicular to the plane. Such an approach may find application in spin field-effect transistors to generate, control and detect the spin current and prepare spin states. As demonstrated in the recent study on colloidal perovskite nanocrystals[11], Rashba effects may be more prominent if three-dimensional centro-symmetric structures are replaced by nanocrystals or by two- or quasi-two-dimensional analogues in solar cells or light emitting devices[16]. Thus, tactical materials engineering may allow controlled exploitation of Rashba physics to tailor the behavior of perovskite-based devices.

Studies of Rashba-type effects in perovskites are still in their early stages, and further understanding of the phenomena and impact on charge carrier recombination and transport will allow us to fully remove or maximally exploit the effect, as desired.

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