

The impact of anisotropy and anharmonicity on the magneto-optical properties of bulk 3D and 2D lead halide perovskites

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The renaissance of interest in halide perovskites, triggered by their unprecedented performance in optoelectronic applications, elicited worldwide efforts to uncover various intriguing physical properties, with a particular interest in spin-orbit effects. The current work presents magneto-optical experimental evidence for anisotropic electron-hole interactions in the 3D orthorhombic MAPbBr₃ and the 2D (PEA)₂PbI₄ bulk single crystals. The evidence was seen in the magneto-photoluminescence spectra while monitoring several different crystallographic directions. The observations exposed a highly non-linear response to a magnetic field and asymmetry to the influence of the sign of the magnetic field. A theoretical model implementing anisotropy in the electron-hole interaction, Rashba effect, Landé *g*-factors, and a lesser contribution from an Overhauser effect corroborated the experimental results.

A continuation of the work involved the investigation of the anharmonic ground-state of the (PEA)₂PbI₄ compound, using complementary information from low-temperature x-ray diffraction (XRD) to the photoluminescence spectroscopy, which was also supported by density functional theory (DFT) calculations. The study extrapolated four crystallographic configurations from the low-temperature XRD. These configurations imply that the ground state has an intrinsic disorder stemming from two coexisting chiral sub-lattices, each with a bi-oriented organic spacer molecule. We further show evidence that these chiral structures form unevenly populated ground states, portraying uneven anharmonicity, where surface effects may tune the state population. Our results uncover a disordered state that may be associated with a dynamic Rashba effect. The current efforts include using a unique pump-probe experiment to follow a dynamic Rashba effect. Also, preliminary magneto-photoluminescence of (F-PEA)₂PbI₄ uncovered two opposing chiral structures alone through the entire temperature range under investigation. This result was already corroborated by XRD measurements, confirming the locking of the F-PEA degree of freedom. Further study is ongoing regarding the relation between anharmonicity, the Rashba effect, and the dependence on structure and composition.

*Equal contribution