Giant Rashba Splitting in CH$_3$NH$_3$PbBr$_3$ Organic-Inorganic Perovskite

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As they combine decent mobilities with extremely long carrier lifetimes, organic-inorganic perovskites have opened a whole new field in optoelectronics. Measurements of their underlying electronic structure, however, are still lacking. Using angle-resolved photoelectron spectroscopy, we measure the valence band dispersion of single-crystal CH$_3$NH$_3$PbBr$_3$. The dispersion of the highest energy band is extracted applying a modified leading edge method, which accounts for the particular density of states of organic-inorganic perovskites. The surface Brillouin zone is consistent with bulk-terminated surfaces both in the low-temperature orthorhombic and the high-temperature cubic phase. In the low-temperature phase, we find a ring-shaped valence band maximum with a radius of 0.043 Å$^{-1}$, centered around a 0.16 eV deep local minimum in the dispersion of the valence band at the high-symmetry point. Intense circular dichroism is observed. This dispersion is the result of strong spin-orbit coupling. Spin-orbit coupling is also present in the room-temperature phase. The coupling strength is one of the largest reported so far.

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Organic-inorganic perovskite compounds (OIPCs) have potential applications in optoelectronics ranging from high-efficiency thin film solar cells to photodetectors and scintillators, and from optical refrigeration to low-threshold nanolasers. Yet, fundamental questions remain open concerning the electronic structure underlying their favorable photo-transport properties. Relativistic effects, i.e. spin-orbit coupling (SOC) and resulting spin splitting, are expected because of the constituting heavy elements. Spin splitting could be strong enough to contribute to the long carrier lifetimes in OIPCs, and to allow for OIPC-based spintronic devices. Spin splitting found in calculations is extremely sensitive to the orientation of the organic cation and to distortions of the inorganic cage, with calculated Rashba parameters of energetically similar structures ranging from 0.1 eV Å$^{-1}$ to almost 10 eV Å$^{-1}$. As direct measurements of the electronic structure are lacking, the actual extend of Rashba splitting in OIPCs remains unknown. Yet, intense circular dichroism in pump-probe spectroscopy and spin dependence of charge dissociation and recombination at room temperature in CH$_3$NH$_3$PbI$_3$ hint to the possibility to create spin polarization in OIPCs.

We report measurements of the electronic structure of single-crystal CH$_3$NH$_3$PbBr$_3$ using angle-resolved photoelectron spectroscopy (ARPES). CH$_3$NH$_3$PbBr$_3$ grows large cubic single crystals, as shown in figure (a) suitable for cleaving in ultrahigh vacuum and for ARPES experiments. Applying a leading edge method that takes into account the density of states (DOS) of the OIPC, we extract the dispersion of the highest-energy valence band (VB). We find a spin-splitting of the band, quantified by the Rashba parameter $\alpha$. The effect of Rashba splitting on band dispersion is illustrated in figure. Rashba splitting arises when orbitals with SOC are subject to symmetry-breaking electric fields. It causes a splitting of a doubly spin-degenerate band into two bands shifted with respect to each other in k-space by $k_0$. At the central high-symmetry point, a minimum arises of depth $E_0$. For CH$_3$NH$_3$PbBr$_3$ we find Rashba parameters $\alpha = 2E_0/k_0$ of 7±1 eV Å and 11±4 eV Å in the orthorhombic and the cubic phase, respectively. These values are amongst the highest ones reported. Our findings point out the critical role of local inversion-symmetry breaking fields in OIPCs, and of the resulting spin splitting. We hope our study will stimulate further investigations of spin structure in OIPCs to elucidate the role of spin splitting and possible spin polarization in existing and future applications.

Crystal were synthesized according to the modified procedure in reference. For details of sample preparation see figure S1 of the Supplemental Material. Resulting CH$_3$NH$_3$PbBr$_3$ single crystals with sizes of ≈ 0.5 cm are shown in figure (c). They exhibit a cubic shape, exposing (001)-oriented facets. Clean surfaces were prepared by cleaving crystals in vacuum (base pressure $10^{-6}$ Pa) parallel to the exposed (001) face. This results in a single, optically flat terrace with an area of several mm$^2$. Samples were then transferred...
FIG. 1: Influence of spin-orbit coupling (SOC) and the resulting Rashba effect on VB dispersion. (a, b) Without SOC, a doubly spin-degenerate band with a single maximum is expected. (d, e) In the presence of SOC and inversion-symmetry breaking fields, it splits up into two spin-split bands. The strength of SOC is quantified by the Rashba parameter $\alpha$. Arrows in (e) depict the orientation of the in-plane component of the spin. (c) shows the samples under investigation.

FIG. 2: ARPES data from single crystal CH$_3$NH$_3$PbBr$_3$ in the (a, c, e) low-temperature temperature orthorhombic and the (b, d, f) room-temperature cubic phase. (a, b) Normal emission ARPES spectra. (c, d) Close-up of the VBM region of ARPES spectra recorded at the centers $\Gamma$ and the corners $\bar{M}_o$ and $\bar{M}_o$ of the orthorhombic and the cubic surface Brillouin zone, respectively. Bulk-terminated surface Brillouin zones for both phases are illustrated in the insets. The position of the VBM is determined by parabolic fits to the data (solid lines). Spectra from the Brillouin zone boundary are offset by 0.07 for reasons of clarity. (e, f) Position of the highest-energy VB as a function of parallel momentum.

to ultrahigh vacuum (base pressure $2 \times 10^{-8}$ Pa) within 1 min. We monitor possible loss of methylamine using thermal desorption spectroscopy. No desorption of the organic compound was detectable below 320 K, see figure S2 (a) [27]. ARPES spectra were recorded using unpolarized light with a photon energy of 21.2 eV (He I). Satellite lines were subtracted. The fourth harmonic of a femtosecond Ti:Sa oscillator ($h\nu = 6.2$ eV) was used for laser-ARPES. Spectra were recorded with an ellipsoidal display-type analyzer [28]. It collects two-dimensional angular photoelectron distribution patterns from an acceptance cone covering $-35^\circ$ to $45^\circ$ both along and perpendicular to the plane of light incidence without the need to move sample or analyzer. During cooling, we perform in situ using photoluminescence spectroscopy reproducing the phase transitions reported in literature [28], see figure S2 (b) [27].

Figure 2 (a) shows a normal emission photoelectron spectrum of CH$_3$NH$_3$PbBr$_3$ in the low-temperature orthorhombic phase. The VBs extend roughly from $-6$ eV to $-1$ eV, with a width of 5 eV matching the one reported from calculations [18, 30]. The doping level exhibits sample-to-sample variations from intrinsic, as shown in figure 2 (a), to p-type with the VB maximum (VBM) close to the Fermi level, as in figure 2 (a). Doping acts as a rigid shift of the spectra, and otherwise does not affect the results reported here. The room-temperature normal emission spectrum of CH$_3$NH$_3$PbBr$_3$ is shown in Figure 2 (b). Substructures appear less pronounced than at low temperature. The widths of the spectra are similar.

As known from calculations [18, 30], the highest-energy VB has a significantly smaller effective mass than deeper-lying bands, and contributes little to the DOS. The DOS is approximately parabolic on a scale of several hundred meV around the band edges [12, 20, 32, 33], in contrast to the typical square-root behavior of three-dimensional semiconductors with parabolic bands. Accounting for this particular DOS, we use a modified leading-edge method to determine the position of the
The VB edge is approximated by a parabolic fit to the ARPES spectra, reflecting the DOS found in calculations. The procedure is illustrated in Figure 2 (c) and (d) for CH$_3$NH$_3$PbBr$_3$ in the low-temperature and room-temperature phase. The fitting curve is set to zero above the vertex, giving the position of the topmost VB. At the VBM, photoemission intensity drops to zero. We find no indication of in-gap surface electronic states. The low trap density allows a detailed analysis of the VB edge, which was not possible in a previous study on CH$_3$NH$_3$PbI$_3$ thin films [34] with surface traps all the way up to the Fermi level.

The insets in figure 2 (c) and (d) show the surface Brillouin zones expected for bulk-terminated (001) surfaces in both phases. Here $a = 6$ Å [35, 36] is the cubic lattice constant. The low-temperature Brillouin zone is approximated by a square, since domains of different orientation can form upon cooling the crystal, which are not resolved by our experiment (spatial resolution: 3 mm). The given surface Brillouin zone reflects domains with out-of-plane alignment of the orthorhombic $b$ axis.

The position of the VB edge for various parallel momenta is shown in figure 2 (e) and (f) for both phases under investigation. The number of k-points was reduced for reasons of clarity. At low temperature, band maxima are located at normal emission, i.e. at $(0, 0)$, and at around $(±0.5, ±0.5)$ Å$^{-1}$. Their periodicity is consistent with the bulk-terminated surface Brillouin zone shown in figure 2 (c) and a reciprocal lattice constant of $\sqrt{2} \cdot \frac{b}{a} = 0.7$ Å$^{-1}$. No indications of surface reconstructions are found. Also, we do not observe band maxima at the $ar{M}$$_a$ points, which would be the signature of domains with in-plane orientation of the $b$ orthorhombic axis. The observed out-of-plane alignment of the $b$ axis at the surface is consistent with scanning tunneling microscopy [37]. In the room-temperature phase, figure 2 (f), only the band maxima at the boundaries of the Brillouin zone remain, whereas its center forms a minimum. This is consistent with the bulk terminated surface of the cubic crystal as shown in the inset of figure 2 (d), without indications of surface reconstructions.

Figures 3 (a) and (b) show close-ups of the band maxima. Data for equivalent maxima were averaged for better statistics. Figures 3 (c) and (d) show the photoemission intensity after averaging along the azimuthal direction in the vicinity of individual high-symmetry points. Black symbols depict their average.

To test this interpretation, we performed laser-ARPES using circularly polarized light. Circular dichroism is a necessary consequence of spin-orbit coupling. Because of the low photon energy of the laser ($h\nu = 6.2$ eV), the technique is limited to the VBM at normal emission of the low-temperature phase. Since ARPES signal from the VB overlaps with secondary electrons at low kinetic energies, an exponential background was introduced in the fitting procedure in addition to the parabolic VB DOS. Figures 4 (a, b) show the resulting dispersion. Data analysis is restricted to $|k_0| < 0.08$ Å$^{-1}$ because of the low photon energy. Again, a ring-shaped maximum with $k_0 = 0.043 ± 0.005$ Å$^{-1}$ and $E_0 = 0.16 ± 0.02$ eV is found. The dispersion matches the one from the conventional ARPES experiment in figure 3 (c). Notably, the information depth in laser-ARPES is a factor 15 larger because...
of reduced photon energy \( E_0 \) and emission angle. A circular dichroism map is given in figure 4(c). It shows the difference \( \sigma^+ - \sigma^- \) in photoemission intensity from the VB in experiments with right- and left-handed circularly polarized light. The amplitude of the circular dichroism signal \( |k_i| \) is 0.2 ± 0.05.

The most simple model accounting for SOC is the Rashba Hamiltonian \( \frac{\alpha}{k} \). Its solutions \( E^\pm = \hbar^2 k^2 / 2m^* \pm \alpha |k| \) are two parabolas offset in k-space. The parameters are the effective mass \( m^* \) of the bands and the Rashba parameter \( \alpha \). The measured VB dispersion of CH$_3$NH$_3$PbBr$_3$ deviates from a parabola, but is closer to a hyperbola or even a cone, consistent with the parabolic DOS \( 12, 20, 32, 33 \). The resolution of our experiment is insufficient to reliably extract effective masses at the maximum of the bands. The parameter \( \alpha = 2E_0/k_0 \) however, can be determined consistently. We find \( \alpha_o = 7 \pm 1 \text{ eV Å} \) and \( \alpha_c = 11 \pm 4 \text{ eV Å} \) for the orthorhombic and the cubic phase. These range at the lower and upper half of (c), respectively. Circular dichroism signal, showing the difference in the intensity distribution of photoelectrons after excitation with right- and left-handed circularly polarized light.

FIG. 4: (a) Dispersion of the central band maximum of the low-temperature orthorhombic phase from laser-ARPES \( (h \nu = 6.2 \text{ eV}) \). (b) VB dispersion (black filled symbols, left axis) and circular dichroism signal (blue and red squares, right axis) after azimuthal averaging. Azimuthal averaging of the circular dichroism signal was performed separately for \( k_y < 0 \) and \( k_y > 0 \), or the lower and upper half of (c), respectively. (c) Circular dichroism signal, showing the difference in the intensity distribution of photoelectrons after excitation with right- and left-handed circularly polarized light.
thus forming a crucial ingredient to phototransport in the material. Enhancement of carrier lifetimes by one to two orders of magnitude were predicted for CH$_3$NH$_3$PbI$_3$ and a static Rashba splitting in the conduction band of $E_0 = 0.1 \ldots 0.2 \text{ eV}$. The VB Rashba splitting is mediated by the SOC of the Pb $6p$ orbital for both CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, but is sensitive to details of the crystal structure. In most OIPCs, the Rashba splitting is stronger in the conduction band than in the VB. Calculations also report a complex spin structure involving both Rashba and Dresselhaus spin splittings. We hope our results will stimulate further studies on the effect of spin splitting and polarization on the electronic properties of this multifaceted system.

In summary, we report measurements of the electronic structure of single crystal CH$_3$NH$_3$PbI$_3$ in the orthorhombic and the cubic phase. Using a modified leading edge method, which accounts for the DOS of the OIPC, we extract the dispersion of the highest-energy VB. Surface Brillouin zones are consistent with bulk terminated surfaces. In the low-temperature phase, the orthorhombic $b$ axis shows preferential out-of-plane alignment at the surface. No indication of surface electronic states within an energy range of 1 eV above the VB maximum is found. Most importantly, we find a splitting of the VBM in k-space by $k_0 = 0.043 \text{ Å}^{-1}$, giving rise to a minimum around 0.16 eV deep at the high symmetry points. Together with the observed circular dichroism, the dispersion indicates a Rashba splitting that is amongst the strongest reported.

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