Light- and Temperature-Modulated Magneto-Transport in Organic–Inorganic Lead Halide Perovskites

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ABSTRACT: The optoelectronic properties and charge carrier dynamics in hybrid organic—inorganic perovskites under steady-state illumination are the key elements for understanding their high efficiency. We present temperature-dependent Hall and photoconductivity measurements down to a temperature of 4.2 K on single crystals of MAPbI3 and MAPbBr3 in magnetic fields up to 30 T and observed different transport regimes. For temperatures down to 25 K, charge transport is dominated by acoustic phonon scattering as inferred from the temperature dependence of both zero and high-field resistance. Below 25 K, transport is determined by thermally activated hopping of charge carriers reflected in a diverging zero-field resistance and a strong decrease in the carrier’s mobility and concentration. Our findings demonstrate the importance of performing experiments at low temperature to unravel the fundamental charge carrier dynamics and stimulate the need for a comprehensive theoretical model for perovskite-based devices.

High energy conversion efficiency in combination with a low-cost production makes hybrid organic–inorganic perovskites ideal for photovoltaic applications.1–3 The superior device performance of this class of materials is associated with a high absorption coefficient,4 low exciton binding energies,5–8 and extended carrier lifetimes and diffusion lengths of photogenerated charge carriers. Recently it has been shown in MAPbI3 (MA = CH3NH3+) that this extended carrier lifetime originates from a slow, thermally activated recombination process due to the mixed direct—indirect character of the band structure.9 The intrinsic photophysical parameters such as carrier mobility, charge diffusion, and recombination dynamics have been investigated indirectly by fast spectroscopic techniques.10–13 However, these techniques probe carrier dynamics at short time scales after absorption of the incident photons in contrast to perovskite-based optoelectronic devices operating under steady-state illumination. Therefore, it is crucial to perform transport measurements under steady illumination to determine the fundamental photophysical properties and to identify the intrinsic scattering mechanisms on impurities, defects, and phonons at low temperatures when the thermal energy becomes negligible to unravel the superior device performance of these materials. To date, steady-state photoluminescence experiments have established that the Fröhlich interaction between longitudinal optical phonons and charge carriers is the dominant contribution at room temperature.14 However, there is no clear picture describing which mechanisms are dominant at different temperatures, in particular to distinguish the charge carrier interaction with optical and acoustic phonons. Moreover, organic–inorganic lead halide perovskites undergo structural phase transitions with decreasing temperature, potentially altering the charge carrier properties due to the coupling between structural fluctuations and electronic properties. MAPbI3 exhibits two phases below room temperature: a tetragonal phase (I4/mcm) from 293 to 160 K followed by an orthorhombic (Pnma) phase below 160 K.15 MAPbBr3 is in the cubic phase (Pm3m) down to 237 K and then exhibits two tetragonal phases between 155 and 150 K (I4/mcm and P4/mmm) followed by an orthorhombic phase (Pna21) below 144 K.15

In this Letter, we present a temperature-dependent Hall and magneto-resistance study under steady-state illumination in bulk single crystals of MAPbBr3 and MAPbI3. This method allows us to directly access the photogenerated charge carrier concentration and mobility. From the temperature-dependent

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study of the zero and high-field resistance, we unambiguously identify distinct transport regimes. In the orthorhombic phase, between 100 and 25 K where a maximum in the charge carrier mobility is found, transport is governed solely by scattering with acoustic phonons evident from the temperature dependence of the carrier mobility (\(\mu_s \propto T^{-3/2}\)). Below 25 K, we observe an exponential increase in the resistance accompanied by a strong decrease in the charge carrier concentration which is attributed to thermally activated hopping of charge carriers.

We first present the sample characterization for both MAPbBr3 and MAPbI3 single crystals at 300 K in Figure 1. These single crystals have been used to make devices on which four or six electrodes have been evaporated (see inset to Figure 1b). The magnetic field \(B\) is applied perpendicular to the device configuration used for measurements. (a) Hall resistance \(R_{xy}\) as a function of the magnetic field \(B\) (inset: \(I-V\) characteristics; the ohmic regime is indicated by the blue line; \(V_{TFL} = 0.45 \text{ V}\) for MAPbBr3 in the dark. (b) \(R_{xx}\) and \(R_{xy}\) as a function of \(B\) under steady-state illumination for MAPbBr3 (inset: schematic representation of the device configuration used for measurements). (c) \(R_{xy}\) as a function of \(B\) (inset: \(I-V\) characteristics; ohmic regime see blue line; \(V_{TFL} = 6.2 \text{ V}\) for MAPbI3 in the dark. (d) \(R_{xx}\) and \(R_{xy}\) as a function of \(B\) under steady-state illumination for MAPbI3. The extracted transport parameters \(n, n_s, and \mu_s\) are indicated in each plot.

The transport properties of the devices alter under steady state illumination (2 mW, \(\lambda = 373 \text{ nm}\)). In all photoconductivity measurements, the incident photon energy (\(E_g = 3.3 \text{ eV}\)) is larger than the band gap \(E_g\) (\(E_g = 2.2 \text{ eV MAPbBr_3, E}_g = 1.5 \text{ eV MAPbI_3}\)), therefore generating electron–hole pairs via photon absorption. Using the continuity equation for photocurrent dynamics in the steady-state case, see the Supporting Information, electron–hole recombination (bimolecular decay) is identified as the dominant mechanism at the photoexcitation power used in our experiment in agreement with other measurements in bulk single crystals and in thin perovskite films.

In Figure 1b,d, the transverse resistance \(R_{xx}\) and \(R_{xy}\) are plotted as a function of \(B\) at \(T = 300 \text{ K}\). \(R_{xy}\) shows a linear increase in \(B\), and from its slope, a sheet carrier concentration of \(n_s = 4.3 \times 10^{12} \text{ cm}^{-2}\) for MAPbBr3 and \(n_s = 9.3 \times 10^{11} \text{ cm}^{-2}\) for MAPbI3 is extracted, in agreement with the values reported in the literature. (10,11,18–22)

The observed linearity in \(R_{xy}\) even up to 30 T in the dark and under illumination indicates that charge transport is dominated by one type of charge carrier. From the extracted
sheet carrier concentrations and the zero-field resistivity $\rho_{zz}$, taking into account the device geometry (see Experimental Methods), we find a carrier mobility of $\mu_s = 6.3 \text{ cm}^2/(\text{V s})$ for MAPbBr$_3$ and $\mu_s = 68 \text{ cm}^2/(\text{V s})$ for MAPbI$_3$ under steady-state illumination. This mobility is in the order of magnitude as reported in ref 20 and by roughly 2 orders of magnitude smaller than the electron mobility in conventional inorganic semiconductors such as Si or GaAs and thereby is not a hindrance in terms of their power conversion efficiency. The transverse resistance $R_{xx}$ as a function of the magnetic field is shown in Figure 1b,d for both materials up to 30 T under illumination. We observe a slight increase in $R_{xx}$ for MAPbBr$_3$ due to classical
orbital effects, whereas the $R_{xx}$ does not change significantly for MAPbI$_3$.

We now focus on transport experiments for $T < 100$ K under steady-state illumination. Figure 2 depicts typical curves for $R_{xx}$ at $B = 0$ as a function of temperature $T$ in MAPbBr$_3$ (Figure 2a) and MAPbI$_3$ (Figure 2b). Both materials exhibit qualitatively similar temperature dependence which can be divided in two regimes. With decreasing temperature below 100 K, $R_{xx}$ decreases ($dR/dT > 0$) until a saturation is reached around 35 K resembling a purely metallic behavior that can be attributed to electron–phonon scattering. For MAPbBr$_3$, this decrease is linear as a function of $T$ from 100 to 40 K as indicated by the dashed blue line. We find the highest sheet conductivity of $\sigma_s = 1.8 \times 10^{-4}$ $1/\Omega$ at $T = 35$ K for MAPbBr$_3$ and $\sigma_s = 5.8 \times 10^{-5}$ $1/\Omega$ at $T = 32$ K for MAPbI$_3$ (see inset i in Figure 2).

Regime I, $T < 20$ K, is characterized by an exponential increase in $R$ ($dR/dT > 0$) for both devices in which $R_{xx}$ increases by roughly 2 orders of magnitude compared to regime II. Hence, this regime is dominated by thermally activated hopping of electrons that are bound in traps resulting from impurities and defects that can be associated with an average energy $\Delta$. Thermal activation in the order of $\Delta$ leads to a charge carrier conductivity which is proportional to $\exp(-\Delta/k_B T)$, where $k_B$ is the Boltzmann constant. In Figure 2a,b, inset ii, we extract $\Delta = 2.7$ meV for MAPbBr$_3$ and MAPbI$_3$ indicated by the dashed line.

We then explore the transport parameters in the orthorhombic phase between 4.2 and 100 K. In Figure 3a,b, the Hall resistance $R_{xy}$ for MAPbBr$_3$ at different temperatures in the dark and under steady-state illumination is illustrated. Data for MAPbI$_3$ are shown in the Supporting Information in Figure S3. Without illumination, the Hall resistance is linear in $B$, and from the low-field $R_{xy}$, we extract $n$, which is plotted as a function of temperature in the inset of Figure 3a. We find that the carrier concentration strongly decreases with decreasing temperature from 30 K ($n = 5.2 \times 10^{15}$ cm$^{-3}$) to 4.2 K ($n = 1.2 \times 10^{14}$ cm$^{-3}$). The linear Hall resistance $R_{xy}$ under illumination as a function of $B$ is presented in Figure 3b for $T = 5.1, 16,$ and 50 K. In Figure 3c, we plot $n_s$, extracted from the slope of $R_{xy}$, and the carrier mobility $\mu_s$, obtained from the temperature dependence of the zero-field resistivity, as a function of temperature. $n_s$ increases by an order of magnitude from 4.2 to 50 K and then saturates around $n_s = 1.2 \times 10^{15}$ cm$^{-2}$ for $T > 50$ K. At the same time, $\mu_s$ first increases ($\mu_s \sim T^{3/2}$, indicated by the straight red line) with increasing temperature.
and has its maximum at 16 K ($\mu_s = 20 \text{ cm}^2/(\text{V s})$). We note that a $T^{3/2}$ dependence of the carrier mobility is reminiscent of charged impurity scattering in semiconductors. For $T > 25$ K, $\mu_s$ decreases with increasing temperature ($\mu_s \propto T^{-3/2}$, straight line) which is the regime where charge carrier scattering is dominated by acoustic phonons.

Next, we focus on the emergence of a large magnetoresistance (MR) in organic–inorganic lead halide perovskites in the orthorhombic regime, which is an independent probe to determine the underlying scattering mechanisms of charge carriers. The MR is defined as $MR = [R_{xx}(B) - R_{xx}(0)]/R_{xx}(0) = \Delta R_{xx}/R_{xx}(0)$, where $R_{xx} = \Delta R_{xx}$ is the resistance in the presence of a magnetic field $B$.

In nonmagnetic materials as hybrid perovskites, the transverse MR is proportional to $B^2$ for $B \to \infty$, see for example ref 27. Figure 4 illustrates the observation of a large MR in MAPbBr$_3$. Data for MAPbI$_3$ are shown in the Supporting Information in Figure S4. In Figure 4a,b, we show the MR at different temperatures up to 30 T without and under steady-state illumination. The MR at 30 T reaches 400% in dark and 300% under illumination. Moreover, the MR in the presence of steady-state illumination exhibits the $B^2$-dependence, see Figure 4c,d at 5.1 and 100 K (red line) reflecting the classical MR behavior in the case of open orbits.27,28

The MR is strongly suppressed with increasing temperature as illustrated in Figure 4a. At 30 T and 30 K, the MR is 12% in the dark and 120% under illumination. With increasing temperature, the MR under illumination is also gradually suppressed (10% at 100 K). Interestingly, at low temperature (4.2 K), we find that the MR is first decreasing for $B < 1.5 \text{ T}$ and then turns into a strongly positive and quadratic MR. As the temperature increases, this negative low-field MR becomes weaker and the onset of quadratic MR shifts to higher magnetic field values (see inset to Figure 4a). This negative MR at low $B$ is also present under illumination and remains more pronounced at higher temperature compared to the MR in dark (see inset to Figure 4b). In contrast, the crossover from a negative MR to a positive MR under illumination gradually shifts toward lower magnetic fields with increasing temperature. This low-field negative MR occurs solely in regime I and is attributed to a field-enhanced conductivity in the thermally activated hopping transport regime due to an increase in the effective mean free path of the carriers in the presence of a small magnetic field.

Measuring resistivity at different temperatures and plotting MR as a function of magnetic field normalized by the zero-field resistances results in a temperature-independent curve referred to as Kohler plot, in which all MR curves that are governed by the same scattering mechanisms merge. Figure 4e illustrates such a Kohler plot for the MR for the data presented in Figure 4b as a function of $B^2$ normalized by $R_{xx}(0)^2$. As inferred from the temperature dependence of the zero-field resistivity (Figure 2) for $T > 30$ K, we clearly see that all isotherms of magnetoresistance are dominated by one scattering mechanism which has been identified as scattering of acoustic phonons in Figure 3e. Next, we plot the square root of the inverse MR, $(R_{xx}(0)/\Delta R_{xx})^{1/2}$, which is proportional to the scattering rate $1/\tau$, as a function of the temperature at 30 T (see inset to Figure 4e). For $T > 30$ K, the linear increase in $(R_{xx}(0)/\Delta R_{xx})^{1/2}$ with increasing $T$ also suggests that electron–phonon scattering is the dominant scattering mechanism in this regime.27

Using magneto-transport under steady-state illumination, we have determined the temperature-dependent photophysical properties and identified the electron–acoustic phonon scattering as the dominant scattering in single crystals of MAPbBr$_3$ and MAPbI$_3$. Our work paves the way towards exploring more advanced groups of perovskites or complex devices such as thin-film field-effect transistors ultimately leading to the development of the next-generation devices.

### EXPERIMENTAL METHODS

**Device Synthesis and Characterization.** The bulk single crystals with flat facets up to $4 \times 4 \text{ mm}^2$ and a thickness of 1 mm were grown using the inverse temperature crystallization (ITC) method as reported in the literature.26 As-grown crystals with a regular shape have been chosen for the experiments, and a small amount of Au has been evaporated (in vacuum) on the sample edges, either in a four-terminal, eight-terminal, or Hall-bar configuration. The sample preparation has been carried out under ambient conditions. Au wires with a diameter of 25 $\mu$m have been attached by means of Ag conductive paste to the device which we mounted on a chip carrier. The contact resistances (two-terminal resistances) were above 40 M$\Omega$ in the dark and hundreds of kilo-ohms under monochromatic illumination. Prior to the transport experiments, we measured $I$–$V$ curves of the contacts pairs (see insets to Figures 1a,c).

**Magneto-Transport Experiments.** A special probe that is equipped with an optical fiber, a calibrated Cernox thermometer, and a strain gauge heater has been employed. For the transport experiments, the sample in the chip carrier has been mounted under ambient conditions in the probe that has been put in a vacuum tube equipped with an additional inner vacuum chamber (IVC) to perform transport experiments between 4.2 and 300 K. In the vacuum tube, the sample was either kept in the dark or has been illuminated with monochromatic light. The vacuum tube and the IVC has been evacuated at room temperature ($<10^{-3}$ mbar). After pumping, a small amount of $^4$He contact gas has been added to the vacuum tube to ensure a thermal equilibrium for the temperature-dependent measurements from 300 to 4.2 K (these were the conditions throughout the entire experiments). The vacuum tube has then been put in a cryostat for the experiments at low temperatures and high magnetic fields. The temperature was controlled and stabilized using a standard Lakeshore temperature controller. The DC measurements have been performed using a Keithley 6221 current source, and the DC voltage has been recorded by standard (nano)voltmeters (Keithley 2000 or 2184). For the AC measurements, the same current source at frequencies around 13 Hz and Stanford 830 Lock-in amplifiers with suitable preamplifiers were employed. The applied excitation current was in the range between 10 nA and 1 $\mu$A (always in the ohmic regime). A solid-state laser (373 nm) was utilized for the photoconductivity measurements. Each power has been measured using a standard power meter prior to device exposure. For the light intensity (illumination source intensity) used in our experiments, a saturation of the photocconductivity has been observed within a few seconds to roughly 10 s. Once the photocconductivity was constant, we performed the resistance and Hall measurements as a function of magnetic field or temperature.

For the experiments in a magnetic field, either a 15 T superconducting magnet or a 33 T Bitter magnet with a 32 mm room-temperature bore was used. The magnetic field was oriented always perpendicular to the current along the c-axis. We measure the transverse resistance $R_{xx}$ (transverse magneto-
resistance) and Hall resistance $R_{xy}$ in the direction perpendicular to the magnetic field $B$ (i.e., both the applied current and the electric field are in the plane perpendicular to the magnetic field $B$).

The resistivity $\rho$ of the devices (van der Pauw geometry) was extracted from the measured resistance $R_{xx}$ using the method as described in ref 29. In a device with four contacts, both Hall configurations have been measured. For all resistance or resistivity curves presented, $R_{xx} / (R_{xy})$ has been measured for both positive and negative magnetic fields, and the data have been symmetrized (antisymmetrized). In the Supporting Information, we have employed a six-terminal MAPbI$_3$ device in Hall-bar geometry.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00941.

Estimation of the effective bulk carrier concentration ($n_b$) of the crystals under steady-state illumination, carrier lifetime ($\tau$), and diffusion length ($L_d$); additional transport data on a bulk single crystal of MAPbI$_3$; and optical characterization measurements at room temperature (PDF)

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**Notes**

The authors declare no competing financial interest.

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(23) The Supporting Information includes a discussion on photoconduction dynamics, the device characterization under steady-state illumination, measurements on a MAPbI$_3$ device, and optical characterization.


