



Polaronic Charge Carrier–Lattice Interactions in Lead Halide Perovskites

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Almost ten years after the renaissance of the popular perovskite-type semiconductors based on lead salts with the general formula AMX_3 (A=organic or inorganic cation; M=divalent metal; X=halide), many facets of photophysics continue to puzzle researchers. In this Minireview, light is shed on the low mobilities of charge carriers in lead halide perovskites with special focus on the lattice properties at non-zero temperature. The polar and soft lattice leads to pronounced electron-phonon coupling, limiting carrier mobility and retarding recombination. We propose that the proper picture of excited

charge carriers at temperature ranges that are relevant for device operations is that of a polaron, with Fröhlich coupling constants between $1 < \alpha < 3$. Under the aspect of light-emitting diode application, $APbX_3$ perovskite show moderate second order (bimolecular) recombination rates and high third-order (Auger) rate constants. It has become apparent that this is a direct consequence of the anisotropic polar A-site cation in organic–inorganic hybrid perovskites and might be alleviated by replacing the organic moiety with an isotropic cation.

1. Introduction

The generation, diffusion and recombination of charge carriers has been one of the most intensively studied subjects in $APbX_3$ perovskites due to their popularity as active layer in solar cells which, arguably, catapulted $APbX_3$ onto the main stage of research past 2009. Research into the optical and electronic properties dates back to several important works in the early 1990s, where self-organizing multi-quantum well (MQW) structures of inorganic MX_6 and organic capping layers were a topic of high interest and intensively studied by the groups of Ishihara,^[1–4] Muljarov,^[5] and Papavassiliou.^[6–9]

Perovskite research was later extended to the field of electroluminescence,^[10,11] with several important studies on the chemistry and optoelectronic properties throughout 1990–2000.^[12–18] Despite several favorable properties, such as solution and physical vapor deposition,^[19] and simple synthesis of MQW by self-assembly, the material did not attract major attention at this point (prior to 2009, Google scholar lists about

10000 papers in total using the keywords “lead halide perovskite”).

In 2009, it was reported that perovskites were excellent absorbers for solar cells,^[20] leading to significant improvement in power-conversion efficiency (PCE) with the introduction of a solid-state (thin film) architecture in 2012.^[21] The record PCE currently stands at 22.1%.^[22,23] In 2014, Tan and co-workers demonstrated that the same material could also be utilized in light-emitting diodes (LEDs). Our group later demonstrated that a high external quantum efficiency (EQE) could be realized from the same material and essentially the same device structure in LEDs.^[24,25] It appears that metal halide perovskites (MHPs) are, indeed, a material class that comes close to the theoretical reciprocity relationship equating the quantum efficiency in solar cells and LEDs.^[26]

Several observations have led to the expectation that MHPs might soon replace GaAs, the prohibitively high costs of which have limited its application in the PV market but which dominates the LED emitter market. This was based on apparent similarities to the direct band-gap nature of MHPs,^[27–32] their long minority carrier lifetimes (up to microseconds),^[33–36] and their associated diffusion lengths of several micrometers to millimeters.^[37,38] At the same time, it has become evident that room-temperature mobility in MHPs is moderate at best (ca. $10\text{--}100\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) when compared to most inorganic semiconductors. Hodes and co-workers reported that there is an apparent mismatch between the long carrier lifetime (τ_e), high diffusion coefficient (D), and limited mobility (μ), violating the Einstein relation: $D = \mu k_B(Tq)^{-1}$, where k_B , T , and q are the Boltzmann constant, temperature, and elementary charge, respectively.^[39,40]

Herein, we review recent studies that have indicated strong interactions between charge carriers and the lattice resulting

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in a polaron picture of carriers at non-zero temperatures. In the interest of brevity, we focus on bulk-type (single crystal and polycrystalline films) MHP properties, as have been reported for the majority of studies related to device applications.

2. Charge-Carrier Generation and Recombination Kinetics

To evaluate MHPs for optoelectronic applications, the generation and recombination of charges are of paramount importance. The physical processes following charge-carrier generation are illustrated in Figure 1. Recombination kinetics in semiconductors are often fitted by a recombination model that includes first (k_1), second (k_2), and third-order (k_3) recombination [Eq. (1)]. In the context of the materials considered herein, these are ascribed to defect-mediated (Shockley–Read–Hall (SRH), monomolecular), free-carrier radiative (bimolecular), and three-body (Auger) recombination, respectively. Recombination coefficients are obtained by assuming that the time-dependent charge density $n(t)$ is proportional to the optical density $OD(t)$ from transient absorption spectroscopy (TAS),^[41] and optical

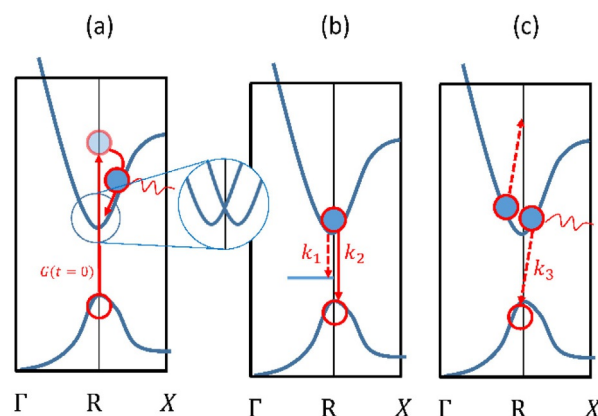


Figure 1. Generation and recombination of carriers: a) Generation of charge carriers by optical excitation at zero time. Carriers that are excited above band-gap energy thermalize by phonon emission. The inset shows the situation of the CBM in the case of Rashba splitting. b) Recombination of equilibrated carriers by either defect-mediated monomolecular recombination (k_1) or bimolecular, radiative recombination (k_2). c) Three-body Auger recombination by either direct Auger process or phonon-assisted Auger recombination (k_3). Solid arrows correspond to radiative transitions, dashed lines to non-radiative transitions, and wiggly lines to phonons.

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Table 1. Charge-carrier recombination coefficients for SRH, bimolecular and Auger recombination (k_1 , k_2 , k_3) at room temperature. The common industrialized semiconductors are shown for reference.

Material	Pump [eV]	k_1 [μs^{-1}]	k_2 [$\text{cm}^3 \text{s}^{-1}$]	k_3 [$\text{cm}^6 \text{s}^{-1}$]	Ref.
GaAs	–	–	7.2×10^{-10}	1×10^{-30}	[78]
CdTe	–	–	4.3×10^{-9}	–	[79]
Si	–	–	1.1×10^{-14}	1.4×10^{-30}	[80]
MAPbI ₃	2.1	72	1.5×10^{-10}	3.4×10^{-28}	[41]
MAPbBr ₃	2.5	27	4.9×10^{-10}	13.5×10^{-28}	[41]
MAPbI ₃	1.8	13	1.7×10^{-10}	N.A.	[81]
FAPbI ₃	1.63	152	2.97×10^{-10}	7.31×10^{-28}	[52]
FAPbI ₃	3.0	–	1.1×10^{-10}	0.022×10^{-28}	[82]
MAPbI ₃	3.0	13	3×10^{-10}	2×10^{-28}	[47]

pump terahertz probe (OPTP) experiments.^[42–47] Table 1 is a collection of literature values for the most prominent members of the organic–inorganic metal halide hybrid perovskites (OIHPs) and all-inorganic metal halide perovskite (AIP) materials.

$$\frac{\partial n(t)}{\partial t} = -k_3 n^3 - k_2 n^2 - k_1 n \quad (1)$$

Assuming that the bimolecular recombination (coefficient k_2) is the dominant radiative recombination mechanism, the photoluminescence quantum yield (PLQY) is then given by Equation (2):

$$\text{PLQY} = \frac{k_2 n}{k_1 + k_2 n + k_3 n^2} \quad (2)$$

Interpretation of photoluminescence (PL) lifetime data in terms of a sum of n -exponentials model [$I_{\text{PL}}(t) = \sum_{i=1}^n A_i \exp(-t/\tau_i)$], although it has frequently been reported,^[48] is not as straightforward as a recombination rate model and should be considered with care.

2.1. Charge-carrier generation

It is generally accepted that excited charges do not exist as a bound electron–hole state in MHPs, with the exception of a transient exciton, which causes excitonic features in absorption measurements.^[49–51] OPTP experiments on solution-grown single crystals of MAPbI₃ give the dissociation timescale of excitons < 1 ps,^[44,52] attributed to fast screening by the dielectric background. A polaron model (Fröhlich polaron) is ideally suited to describe the equilibrium state, as will be discussed in the following.

2.2. First-order recombination

The long first-order lifetimes $\tau_1 = k_1^{-1} \approx 0.1$ – $1 \mu\text{s}$ are indicative of the absence of deep defect states, which have high formation energies in MHPs.^[53–55] In MHP bulk systems, lower first-order recombination rates and conversely long minority carrier lifetimes obtained from time-resolved PL ($\tau_{\text{avg}} \approx k_1^{-1}$) are indicators of a low defect concentration and desirable in both LEDs

and solar cells. Temperature-dependent measurements on MAPbI₃ thin films have shown that k_1 increases by approximately one order of magnitude with increasing temperature from 4 to 340 K, which supports the assumption that this recombination channel is related to defects, which become ionized at elevated temperature.^[46] Special care has to be taken to avoid degradation of the material during measurement. In particular, it has been shown that even moderate excitation density can lead to a local redistribution of halide ions, greatly affecting the minority carrier lifetime.^[56] Furthermore, halide vacancy defects are known to diffuse with low energy barriers, which poses a significant challenge in biased junctions.^[57,58]

2.3. Second-order recombination processes

It has been noted that second-order recombination is much lower than predicted by Langevin theory, with deviations up to 4 orders of magnitude reported.^[59] This is not surprising, given the vastly different nature of transport in (organic) semiconductors with hopping-type (typically $\mu < 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$),^[39] compared to band-type transport in MHPs ($\mu > 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).^[60] It was very recently reported that the calculated second-order recombination rates might underestimate the intrinsic values in thick films given the strong re-absorption in MHPs which have a small Stokes shift.^[61,62] Several phenomena have been reported that limit bimolecular recombination in MHPs:

1) A possibility is a detuning ($k_{\text{CBM}} - k_{\text{VBM}} \neq 0$) of conduction-band minimum (CBM) and valence-band maximum (VBM) with respect to the reciprocal lattice vector k by spin–orbit coupling (Rashba splitting; Figure 2a,b). This has been theoretically predicted by first-principles calculations but to date no direct measurement has, to our knowledge, provided evidence of this effect.^[63] The Rashba split has been shown to be sensitive to the relative orientation of the anisotropic organic cation in OIHPs.^[64] A similar distortion of the band structure could in principle also originate from, or be amplified by, large ionic displacements arising from the soft Pb–X lattice,^[65,66] and the related electronic disorder.^[63]

2) Slow carrier recombination has also been related to slow cooling of carriers by phonon emission, termed hot phonon bottleneck (Figure 3).^[67] This seems very plausible, due to the known strong coupling between electrons and the Pb–X longitudinal optical (LO) phonons,^[68,69] and low thermal conductivity of OIHPs.^[70] The anisotropy of the A-site cation further seems to play an important role, greatly slowing down the relaxation of the carriers after pump in OIHPs, but not in AIPs.^[71,72] Lattice effects of course do not exclude Rashba splitting. In fact, considering simultaneous Rashba splitting and scattering from acoustic and optical phonons has led to a consistent description of the temperature-dependent charge mobility (Figure 2c,d).^[73] The second-order recombination rate constant has been reported to decrease with increasing temperature in MAPbI₃, as expected from slower cooling as the lattice temperature increases but because of two consecutive phase transi-

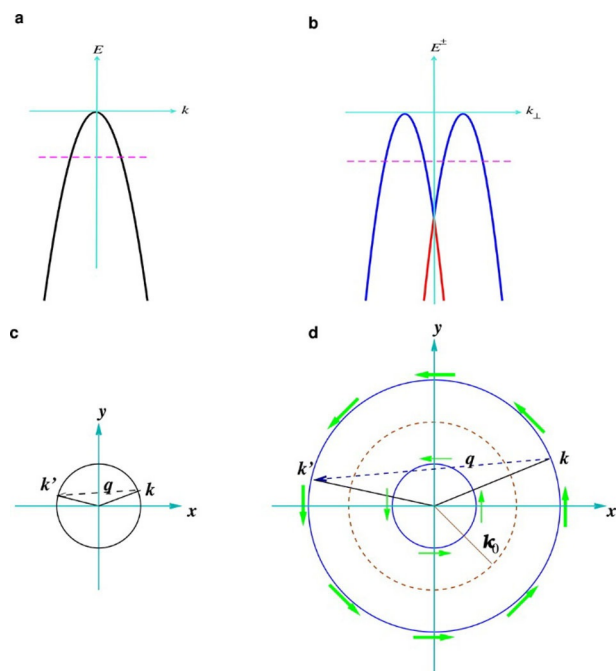


Figure 2. a, b) Schematic dispersion diagrams of the valence-band maximum without and with Rashba splitting. c, d) The corresponding (acoustic) phonon-scattering wave-vector q for both aforementioned cases. Clearly, the scattering momentum is greatly enhanced in the case of Rashba band splitting. Reproduced from Ref. [73] with permission of the American Chemical Society.

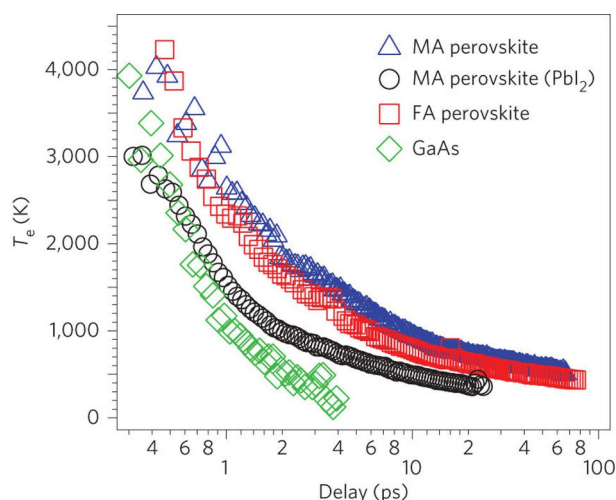


Figure 3. Experimental evidence of slow carrier cooling in OIHPs compared to efficient carrier cooling in GaAs. The electron excess temperature T_e is shown as a function of the delay time after pump (3.1 eV, $6 \times 10^{18} \text{ cm}^{-3}$). Reproduced from Ref. [67] with permission from Nature Publishing Group.

tions, the trends above 160 K (orthorhombic to tetragonal) and 310 K (tetragonal to cubic) is not entirely clear.^[46]

2.4. Third-order recombination coefficient

The high third-order recombination coefficient is most likely not a limiting factor in solar cells due to the rather moderate carrier densities, but must be considered when operating an

LED or attempting to achieve electrically pumped lasing. Three-body (Auger) recombination occurs either directly by ejection of a third charge carrier or indirectly by emission of a phonon (phonon-assisted Auger recombination).

As charge carrier mobility has been predicted to be limited by acoustic phonon scattering with large deformation potentials in MAPbI₃ whereas the thermal broadening of photoluminescence is well-matched with a LO phonon model (Fröhlich model),^[69,74] Generally, the temperature-dependence should give clarity about the mechanism involved as $\hbar\omega_{AC} < k_B T \ll \hbar\omega_{LO}$,^[75] where the indices AC and LO indicate acoustic and optical phonons, respectively, but in lead halide perovskite the optical phonons are situated somewhere around 20–30 meV,^[76] which is not significantly higher than $k_B T$ at room temperature (ca. 25 meV). Measured Auger recombination rates seem to follow an inverse temperature law, $T^{-\alpha}$ similar to charge-carrier mobility, but the limited data currently makes it hard to determine the exponent.^[46] Hopefully, OPTP experiments performed on single crystals will give further insight as polycrystalline films with the usually high defect density make it hard to distinguish scattering mechanism.^[44,77]

To summarize, OIHPs and AIPs have low first-order recombination, indicative of intrinsic low defect concentration in these materials. OIHPs show moderate bimolecular recombination, which has been linked to the anisotropic A-site and is absent in AIPs. Auger recombination in OIHPs and AIPs is high, which has to be carefully considered in high-density application such as LED or lasing. Recombination rate constants are summarized in Table 1.

Comparing OIHPs to the prototypical direct and indirect band-gap semiconductors GaAs and Si, which are widely employed for LED and solar cell applications, it is evident that bimolecular recombination in OIHP occurs at a rate almost comparable to GaAs but Auger recombination rates are approximately two orders of magnitude higher. This is less of a problem at the low excitation densities typical for solar-cell applications ($n \approx 10^{15} \text{ cm}^{-3}$)^[83] but a significant loss mechanism at high injection densities, which are typical for LEDs ($n \approx 10^{19} \text{ cm}^{-3}$),^[84] as shown in Figure 4.

3. Electron–Phonon Coupling

The low elastic constants in lead-halide perovskite (bulk modulus $< 20 \text{ GPa}$)^[85] and conversely the low LO phonon frequencies ($< 25 \text{ meV}$ or Debye temperature $\Theta_D \approx 300 \text{ K}$)^[86] of the inorganic Pb–X sublattice indicate that the lattice is essentially “hot” at room temperature. The coupling between lattice and charge carriers has been demonstrated by experiment,^[68,69] and is well-supported by first-principles calculations.^[71,73,87] The discrepancy between long diffusion lengths extracted from photoluminescence measurements and low to moderate measured carrier mobility can be rationalized by the increase in effective mass created by the phonon cloud of the carrier when forming a polaron. With regards to the size of the polaron, previous studies have indicated a rather large polaron radius ($r_p > 20 \text{ Å}$) and coupling constants that are compatible with Fröhlich polaron theory ($\alpha \approx 2$).^[51,88–90] Since calculated polaron radii are

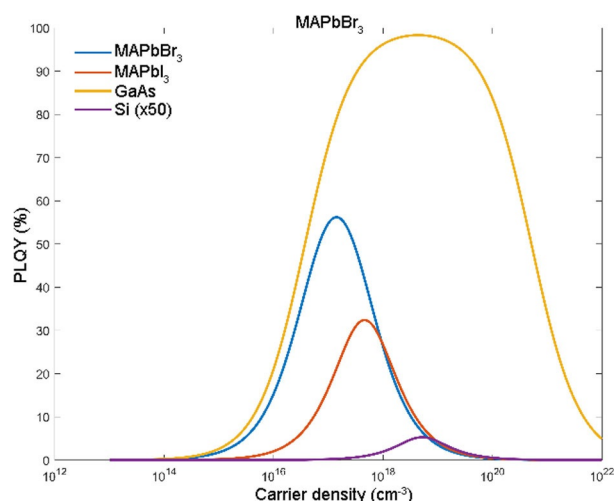


Figure 4. The theoretical photoluminescence quantum yield (PLQY) derived by using Equation (2) as a function of the carrier density using recombination rate coefficients, as given in Table 1 and the references therein. Because of high third-order recombination rates, the peak PLQY of OIHPs is located at charge densities usually associated with solar-cell operation (ca. 10^{15} cm^{-3}). The PLQY of silicon is magnified 50 times.

large with respect to the unit cell, carriers will retain band-type transport with increased effective mass. Estimations of the upper limit of room-temperature values of the mobility have given $\mu = 50\text{--}200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for MHPs, which agrees well with most measurements.^[87] Self-localization of polarons (leading to a spatially localized, small polaron) has been predicted to be supported by hybrid materials, owing to the increased disorder of an anisotropic A-site, and should therefore be absent in AIPs.^[91]

Fröhlich polaron theory^[92–94] gives the self-energy of an electron (hole) in the phonon field as $E_0 = -\alpha\hbar\omega_{\text{LO}}$, where the dimensionless coupling constant α can be calculated by using Equation (3):

$$\alpha = \frac{e^2}{\hbar c} \sqrt{\frac{m_b c^2}{2\hbar\omega_{\text{LO}}}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \quad (3)$$

where e , $\hbar$, and c are natural constants with the usual meaning, m_b is the effective carrier mass in absence of any lattice effects, ω_{LO} is the frequency of the LO phonon mode, and the last term describes an effective screening that arises from the difference of dielectric constants in the optical (ϵ_∞) and infrared (static, ϵ_0) frequency range. For values of $\alpha \leq 2$, the coupling is usually considered weak and the polaron radius and effective mass (with respect to the effective band mass m_b) are approximated by Equations (4) and (5):^[95]

$$r_p = \sqrt{2\hbar/m\omega_{\text{LO}}} \quad (4)$$

$$m^* = m_b \left(1 - \frac{\alpha}{6} \right)^{-1} \quad (5)$$

For stronger coupling, a different (non-perturbative) approach is usually required (for example, see Refs. [96] and [97]).

Small polarons exhibit thermally activated hopping transport, but temperature-dependent mobility measurements have given a $T^{-1.5-1.6}$ dependence,^[46,98,99] indicative of acoustic phonon scattering.^[100] Calculations have shown that, considering the influence of spin-orbit coupling, optical phonon scattering would reproduce the correct temperature dependence.^[73] We note that Fröhlich's polaron theory was initially derived for a single-phonon mode but can be extended to multiple LO modes by using an oscillator intensity-weighted averaging of the LO phonon energy, which lowers the effective phonon energy and thereby increases the coupling strength.^[71,101] Table 2 summarizes the reported values for polaron parameters α , m^* , and r_p , as well as the calculated exciton radius and binding energies, r_{exc} and E_{br} for common MHPs.

Table 2. Reported values for the coupling constant α , effective mass m^* with respect to free carrier band mass m_b , radius of the polaron r_p , and magnitude of the polaron energy $E_0 = \alpha\hbar\omega_{\text{LO}}$ in different OIHPs.^[a]

Material	α	m^*	r_p [Å]	E_0 [meV]	$\hbar\omega_{\text{LO}}$ [meV]	E_b [meV] ^[b]	Ref. ^[b]
GaAs	0.068	1.01	40	2.5	36	4.7	[104]
MAPbCl ₃	2.17	1.48	27	60	28	85	[87]
MAPbBr ₃	1.69	1.35	43	36	21	62 (60)	[87] ([105])
MAPbI ₃	1.72	1.36	51	28	16.5	54 (40)	[87] ([105])

[a] For comparison we calculated the upper limit of the exciton binding energy $E_b = 13.6\mu/\epsilon_\infty^2$ by using a reduced mass $\mu = 0.1$ ^[103] and the optical dielectric constant ϵ_∞ from Ref. [87]. [b] Values in parentheses correspond to experimental values with references given.

Further experimental evidence for strong electron–phonon coupling comes from temperature-dependent PL spectroscopy. The temperature dependence of the PL linewidth $\Gamma(T)$, in the case of broadening by scattering from acoustic (AC) and LO phonons, is described by Equation (6):

$$\Gamma(T) = \Gamma_0 + \gamma_{\text{AC}}T + \gamma_{\text{LO}}/[\exp(E_{\text{LO}}/K_B T)] \quad (6)$$

Whereas acoustic broadening has been shown to be small for OIHPs, LO broadening shows significant energies of $\gamma_{\text{LO}} = 60\text{--}90 \text{ meV}$.^[69,102] These findings are supported by first-principles calculation of the electron-phonon self-energy $\Sigma \approx 50 \text{ meV}$, which is close to the transition point in the Brillouin zone (Figure 5).

4. Conclusions

A close survey of recent studies indicates that a large polaron (Fröhlich polaron) is most appropriate to describe charge carriers at room temperature in bulk MHPs. Excitonic behavior can be only expected for strongly confined MHP structures rather than bulk MHP structures. This picture is compatible with the overall low carrier mobility compared to conventional inorganic semiconductors and the $T^{-1.5-1.6}$ temperature-dependence of the mobility. Polaron radii are large ($r_p > 20 \text{ Å}$) and polaron

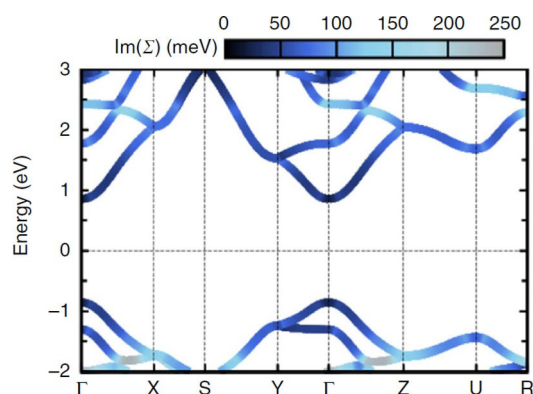


Figure 5. First-principles electron-phonon self-energy for MAPbI₃. The magnitude of the imaginary part of the self-energy $\text{Im}(\Sigma)$ is shown on top of the GW band structure and amounts to approximately 50 meV, close to the Γ point. Adapted from Ref. [69] with permission of the Nature Publishing Group.

masses overall around 20–50% heavier than the calculated effective charge carrier band masses.

The low first-order recombination defect in bulk materials is satisfyingly explained by the high formation energy of deep defects. The second-order recombination rate defies kinetic theory by orders of magnitude, as can be expected from the band-type transport in MHPs. High Auger recombination rates can be rationalized by taking into account the soft nature, direct-to-indirect band-gap transitions, and low Debye temperatures of MHP materials. The presented data also indicates that essentially static, zero-Kelvin calculations in the framework of density functional theory have to be analyzed with exceptional scrutiny when attempting to correlate it with experiments conducted at close to room temperature.

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Conflict of interest

The authors declare no conflict of interest.

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