ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

PERSPECTIVE

The Significance of Polarons and Dynamic Disorder in Halide Perovskites

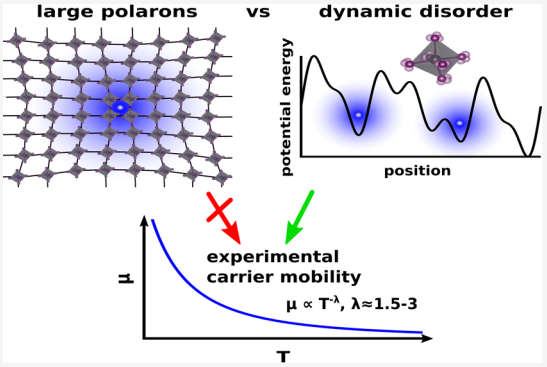
Maximilian J. Schilcher, Paul J. Robinson, David J. Abramovitch, Liang Z. Tan, Andrew M. Rappe, David R. Reichman, and David A. Egger*

Cite This: *ACS Energy Lett.* 2021, 6, 2162–2173

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: The development of halide perovskite semiconductors led to various technological breakthroughs in optoelectronics, in particular in the areas of photovoltaics and light-emitting diodes. Additionally, the study of their fundamental properties has uncovered intriguing puzzles that demand explanation. Polaronic effects associated with the coupling of electrons and holes to polar lattice vibrations are often invoked as a microscopic mechanism to explain various unusual experimental observations. While some form of polaronic behavior undoubtedly exists in these systems, several assumptions underlying standard models used to describe a polaron mechanism appear to be strongly violated in these materials. In this Perspective, we investigate the role of polaronic effects in halide perovskites and summarize signatures and failures of the polaron picture to explain physical characteristics of the materials. We highlight the importance of the complementary dynamic disorder concept that can rationalize various key properties of halide perovskites for which standard polaron and band-theory pictures of carrier transport fail.

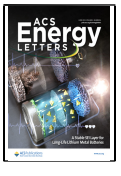


Halide perovskites (HaPs) hold great promise for the development of technological advances in energy science, such as the creation of highly efficient, inexpensive solution-processed solar cells, light-emitting diodes (LEDs), and other devices.[1−6] HaPs also have rather unique physical properties and thus present a number of intriguing puzzles for the scientific community that demand explanation.[7] In this Perspective, we focus on key phenomena that are particularly interesting scientifically and relevant practically, revolving around the electron−lattice coupling in HaPs. As ions move, the potential experienced by the excited carriers (electrons and holes) changes, coupling the dynamics of the ionic and electronic systems. This coupling becomes increasingly more important as temperature is raised.

Our discussion of electron−lattice coupling in HaPs starts from a description of the electronic structure and lattice dynamics. We then present an analysis of the role of polaronic effects in these materials. The polaron picture is used in the literature to address a wide range of related but still distinctly different electron−lattice coupling effects. Here, instead of presenting a detailed theoretical discussion, we will focus on the mechanisms contained in the underlying physical models of electron−lattice coupling and describe certain assumptions inherent to them. We will show that several of the assumptions that underlie standard polaron and carrier-transport treatments are strongly violated in HaP semiconductors at room temperature and above, which is the most important regime for optoelectronic applications. In particular, these materials show significant vibrational anharmonicity concurrent with large displacements in the ionic lattice as well as with nonlinearities in the electron−lattice interactions. Furthermore, we will argue that the mean free path of electrons and holes around room temperature is smaller than, or on the order of, the thermal (de Broglie) wavelengths of these carriers, which marks a violation of the well-known Mott−Ioffe−Regel criterion. This implies that the carrier-scattering mechanisms in HaPs cannot be described on the basis of the standard Boltzmann transport equation, which has been the conceptual basis to explain carrier transport in the most useful high-quality inorganic semiconductors.

These shortcomings in the conventional and simplest band-theory and polaron treatments lead to failures in explaining firmly established experimental results that include optical

Received: March 9, 2021
Accepted: May 6, 2021
Published: May 17, 2021



https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162–2173

absorption and charge-carrier transport in HaPs. But a complementary treatment, based on the concept of dynamic disorder, allows for the removal of the aforementioned constraints that limit the description of electron−lattice interaction mechanisms in HaPs. The dynamic disorder framework augments the canonical polaron and band-theory pictures and will be shown to properly rationalize the behavior found in the near-room-temperature, operationally important regimes for HaPs.

ELECTRONIC STRUCTURE AND LATTICE DYNAMICS

We briefly recall the electronic-structure and lattice-dynamics properties of HaPs. As discussed in previous articles,[5,8−10] typical HaPs exhibit *properties akin to the most useful high-quality inorganic bulk semiconductors*; namely, they have highly dispersive bands and small carrier masses, m^*, as determined from various calculations and experiments. In particular, the hole and electron effective masses have been found to be in the range of $0.15-0.25m_e$,[11−16] depending on the material composition and the details of the experiment or calculation. Hence, it takes relatively little effort to change carrier momentum in HaPs, which is a beneficial feature for electrical transport.

Interestingly, however, the *dynamical properties of the HaP ionic lattice are very different from those of typical high-quality inorganic semiconductors*,[7] which is related to the fact that HaPs are much softer mechanically.[17,18] As a consequence, it takes little effort to displace the halide and A-site ions from their equilibrium positions, and HaP lattice dynamics thus involve large ionic displacements in their highly coordinated octahedral networks. This is connected to the significant role played by anharmonic effects in HaPs around room temperature (see Figure 1).[19−38] For example, in $MAPbI_3$, octahedral and MA motions are highly anharmonic at room temperature, leading to a phonon mean free path of less than half a unit cell.[36,37] This means that rather than the spatially periodic, coherent phonons known from typical bulk semiconductors (e.g., Si and GaAs), lattice vibrations around room temperature in HaPs are localized in real space. Since HaPs are ionic materials, these large, localized atomic displacements (of cations as well as of the highly coordinated octahedral network, including large octahedral tilting) are associated with sizable electric fields.[39] This phenomenon has been dubbed "local polar fluctuations",[24] and it is very uncommon in the context of semiconductors and photovoltaic materials.[7] Other members of the HaP class, including lead-free variants, also display strong anharmonic effects, e.g., in the form of intrinsic rattlers.[40] The HaP structure compensates for its weak bonds by providing a highly coordinated network in which many weak bonds enable overall stability, so that the material can be thermodynamically stable despite being soft. This gives rise to the wide variety and large amplitude of the low-energy vibrations which generate local polar fluctuations and lead to the unusual electron−lattice interactions in HaPs that we discuss in this work.

APPLICATION OF THE TRADITIONAL POLARON PICTURE TO HaPs

Since the electronic structure of HaPs resembles that of typical crystalline inorganic semiconductors, the traditional band theory of transport using electron−phonon scattering, which

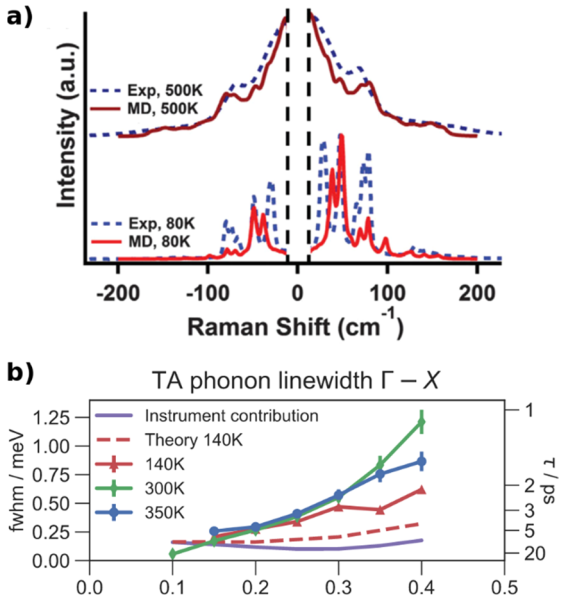


Figure 1. Selected evidence for the presence of strong anharmonic effects in HaPs. (a) Raman spectra of $CsPbBr_3$ computed from molecular dynamics (solid line) and measured experimentally (dashed line) at 500 and 80 K. The presence of a broad central peak in the Raman spectrum signals local polar fluctuations, which subsequently have also been detected in $MAPbI_3$ at room temperature.[37] Reprinted with permission from ref 24. Copyright 2017 The American Physical Society. (b) Phonon line widths and lifetimes of $MAPbI_3$ obtained from neutron scattering measurements and theoretical calculations along the Γ-to-X direction in the orthorhombic (140 K), tetragonal (300 K), and cubic (350 K) phases. That phonons show comparably small lifetimes, on the order of picoseconds, signals strong phonon−phonon interactions and anharmonicity that are detectable already around room temperature.[33] Reprinted with permission from ref 34. Copyright 2018 by Aryeh Gold-Parker.

has been developed for crystalline semiconductors,[41] would appear to be applicable in these materials as well. This theory starts from a knowledge of electronic-structure and lattice-dynamical properties to calculate the effects of electron−phonon scattering on carrier-transport characteristics.[42] Vibrations impact electronic levels because the atomic displacements from the ground-state lattice geometry change the potential energy for electrons and holes in the crystal, thus modifying their effective energies. An understanding of these electron−phonon scattering effects has been instrumental in microscopically rationalizing carrier mobilities in bulk Si and GaAs.[41] Note, however, that the traditional picture assumes small atomic displacements that only mildly affect the electronic structure. Consequently, the associated scattering theories typically apply assumptions such as (i) the harmonic approximation, i.e., that lattice dynamics are described by independent spatially periodic phonon modes; (ii) the use of linear electron−phonon coupling treated to lowest order in perturbation theory; and (iii) the (related) assumption that the effects of these vibrations on the electronic band structure are small compared to the band dispersion.[42] We note that recent work has argued that higher-order processes such as 2-phonon scattering, which are generally neglected in the band-theory approach outlined above, can have sizable scattering contributions, even in canonical systems such as GaAs.[43] One might expect these and related effects to be even more

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

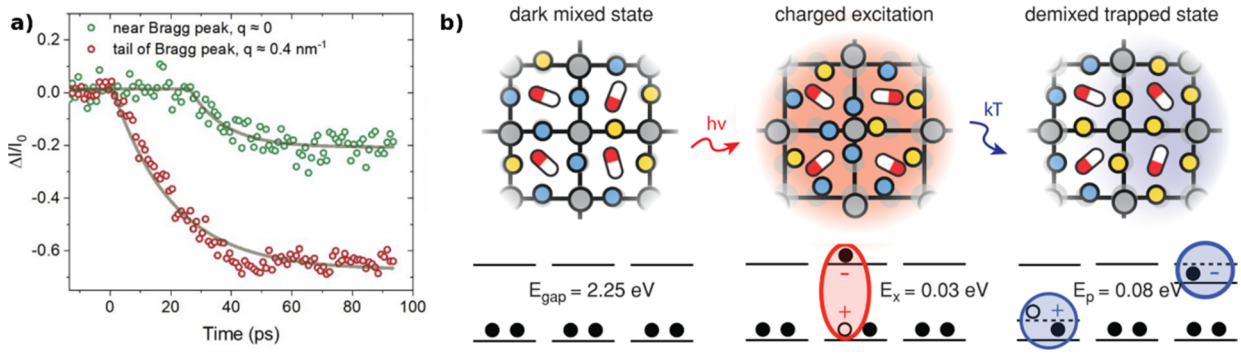


Figure 2. (a) Polaronic effects in the structural response of $MAPbBr_3$: transient X-ray diffuse scattering studies showing evidence for dynamic local strain fields following above-gap excitation. Reprinted with permission from ref 50, published under a CC BY 4.0 license. (b) Sketch of polaronic effects in the compositional segregation in mixed-halide HaPs: light illumination leads to polaron trapping, which induces sufficient strain that leads to a local phase separation around room temperature. In the figure, blue and yellow circles represent different halide species, and the energy scales involved with polaron formation and phase separation are also shown. Reprinted with permission from ref 52. Copyright 2017 American Chemical Society.

important in HaPs, where lattice displacements are unusually large.

As mentioned above, HaPs exhibit sufficiently low phonon energies that the vibrational modes of the material are heavily populated at room temperature. This is the case as well for the longitudinal optical (LO) phonon modes that are polar and involve sizable electrical fields, and are therefore typically the highest-energy lattice vibrations of relevance in semiconductors.[41] Note that the polar phonon modes in prototypical HaPs such as $MAPbI_3$ are much lower in energy than in, e.g., GaAs (16.5 vs 36.1 meV).[44] It is also noted that, comparing the two materials, the electric fields involved in the phonons are larger since the associated ionic screening is known to be larger; i.e., $1/\varepsilon^* = 1/\varepsilon_\infty - 1/\varepsilon_0$, where ε_∞ and ε_0 are the high-frequency and static dielectric constants, respectively, was calculated to be 0.17 in $MAPbI_3$ and 0.016 in GaAs.[44] The electric fields that result from the LO modes will substantially affect the potential energy of the electrons; i.e., one can expect the interaction between carriers and LO phonons—the so-called Fröhlich interaction[41,42,45]—to be important over a wide range of temperatures, including room temperature.[46] This interaction is theoretically depicted by the Fröhlich Hamiltonian, which describes the interaction between carriers in a parabolic band and one harmonic LO phonon via a linear (in the atomic displacement) coupling, with a strength measured by a dimensionless polaron coupling constant, α, which is dependent on the above-mentioned ionic screening as $\alpha \propto 1/\varepsilon^*$.

In the context of our discussion, the Fröhlich interaction is important for two reasons. First, it represents a scattering term in the band theory of carrier transport and the associated Boltzmann transport equation, and as such it is important to consider its impact on various physical quantities, e.g., the band gap and carrier mobility, as a function of temperature (see below). Second, via the Fröhlich Hamiltonian, this type of interaction can lead to the formation of a quasiparticle composed of both electronic and lattice degrees of freedom, which is called a polaron.[42] The polaron describes a charge carrier that is "dressed" with lattice deformations, such that an electron or hole carries with it the atomic displacements caused by the interaction.[47] According to their radii, these quasiparticles can be grouped into small and large polarons. Various studies have discussed that the intrinsic properties of prototype HaP materials, such as $MAPbI_3$ and $MAPbBr_3$, are such that large-polaron theory would apply. Application of it to HaPs describes polarons with sizes on the order of multiple unit cells and moderate coupling of $\alpha \approx 2$,[44,48] i.e., the intermediate coupling regime. The dressing of carriers should, by the standard theory of large polarons, lead to moderate polaronic mass enhancements that have been calculated to lie in the range of 30−50% around room temperature.[16,44,48,49]

Various further signatures of polaronic effects in the physical characteristics of HaPs have been discussed in the literature. For example, a recent study detected that polaronic effects are concurrent with the formation of a stress field which develops as a consequence of light absorption in $MAPbBr_3$ (see Figure 2a).[51] Another interesting aspect of polaronic behavior revolves around photoinduced compositional segregation in mixed-halide crystals that involves long-range movements of different halide ion types to different spatial locations in the sample, which was shown to be mediated by polaron formation (see Figure 2b).[52−54] In these studies, the standard Fröhlich Hamiltonian is *not* directly used, and thus the observed polaronic behavior possibly transcends the assumptions of harmonic phonons and linear electron−lattice coupling inherent to the model. We note in passing that various studies have discussed polaronic effects protecting carriers from recombining,[55−57] which must be reconciled with the picture of multiphonon recombination in which polaronic effects would actually increase non-radiative recombination rates.[58] It is furthermore interesting to note that a direct comparison of experimentally measured band masses in $MAPbBr_3$ and $CsPbBr_3$ shows[15,16] that they are similar, which would imply similar polaronic behavior across hybrid and all-inorganic HaPs. Finally, we also note important recent theoretical developments in first-principles calculations of polarons as described in, e.g., refs 59 and 60. To summarize, the above discussions motivate the polaron mechanism as a mediator of charge-carrier scattering in the transport characteristics of these systems. It is, however, important to stress that these observations do not prove that theories which invoke the underlying assumptions of the Fröhlich Hamiltonian or related models provide a correct microscopic description of electron−lattice effects in these materials.

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

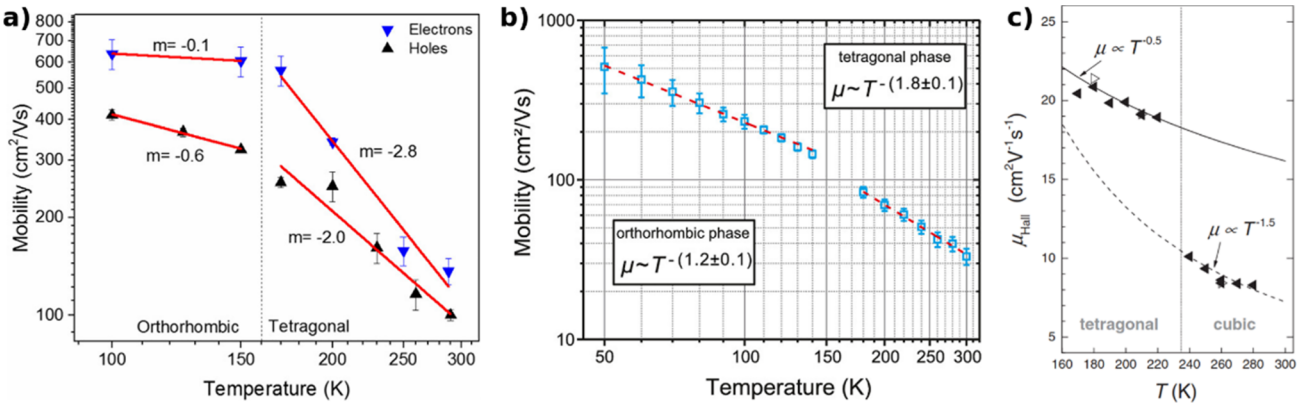


Figure 3. A selection of temperature-dependent mobility measurements performed for various HaP samples establishing $\mu \propto T^{-\gamma}$, with γ in the range of ≈1.5−3 around room temperature. (a) Time-of-flight measurements of $MAPbI_3$ single crystals. Reprinted with permission from ref 74. Copyright 2018 American Chemical Society. (b) All-optical measurements of large-crystal $MAPbI_3$ thin films. Reprinted with permission from ref 75. Copyright 2019 American Chemical Society. (c) Hall measurements of $MAPbBr_3$ single crystals. Reprinted with permission from ref 73. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

FAILURES OF THE TRADITIONAL POLARON PICTURE FOR HaPs

We will now discuss a series of observations pertinent for HaPs, which will establish the need to go beyond the traditional polaron picture as embodied directly in the Fröhlich Hamiltonian. We start this discussion with the temperature dependence of the semiconductor band gap, since it is a key observable for the quantification of electron−lattice interactions that naturally connects thermal vibrations to measurable electronic energies. The traditional picture of phonon-mediated band gap changes relies on the assumption that the atomic displacements themselves, and their effect on the electronic levels, are relatively small; i.e., one uses the aforementioned harmonic approximation and the low-order electron−phonon coupling expansion to calculate this quantity. The microscopic theory which encodes these assumptions, known as the Allen−Heine−Cardona (AHC) theory,[61,62] has proven to be valid for various prototypical inorganic semiconductors; in passing we mention ongoing and important efforts in further developing the theoretical framework in this direction, e.g., refs 63−66. However, for HaPs, a breakdown of the canonical approach has been discussed by Saidi et al.,[67] who demonstrate the importance of higher-order terms in the electron−lattice coupling of HaPs. It should be noted that the importance of such terms compared to temperature-dependent changes in the lattice structure in actual experiments is still under debate.[68] Nevertheless, the work of Saidi et al. illustrates that the truncation of electron−phonon coupling terms at low order, as found in both the AHC theory and the Fröhlich Hamiltonian, is at least *internally inconsistent*, as large changes to the temperature dependence of the band gap occur in a controlled theoretical setting when high-order coupling processes are included.

Perhaps the most salient observable quantifying electron−lattice interactions is the temperature dependence of the carrier mobility, μ, for which traditional transport theory predicts differences according to scattering by different types of phonons. For example, scattering of carriers by acoustic phonons generally follows a law of $\mu \propto T^{-1.5}$, whereas scattering by polar optical vibrations typically results in a shallower temperature dependence.[41] Recalling the above-discussed role of polar phonon modes in HaPs, it is surprising that various experiments covering a wide range of techniques and samples have firmly established $\mu \propto T^{-\gamma}$, with $\gamma \approx 1.5-3$ around room temperature (see Figure 3).[69−75] This seemingly contradicts the notion that interactions between charge carriers and polar optical phonon modes are dominant in HaPs around room temperature. Indeed, numerical modeling,[44,48,76,77] valid for certain well-defined limits of Fröhlich-type models, and/or the large-polaron mechanism have established that its temperature dependence for mobilities in HaPs is far too weak to explain experimental results; i.e., $\gamma \approx 0.5-1$ in these articles.

Perhaps most convincingly, exact numerical results now exist for carrier mobilities in the Fröhlich Hamiltonian for coupling strengths relevant for HaPs over a temperature range spanning several orders of magnitude.[78] These results are key for establishing very important physical features of electron−lattice interactions and carrier scattering in HaPs. Figure 2 of ref 78 clearly shows that, in the range of 200−400 K, the *exact temperature dependence of the polaron mobility* in the Fröhlich Hamiltonian is $\mu \propto T^{-0.5}$ for physical parameters that are representative of prototype HaPs,[79] in stark *disagreement* with experiments. The polaron mechanism, as described by the Fröhlich Hamiltonian and its variants, cannot successfully explain carrier transport in HaPs.

> The polaron mechanism, as described by the Fröhlich Hamiltonian and its variants, cannot successfully explain carrier transport in HaPs.

TIME AND LENGTH SCALES ASSOCIATED WITH CARRIER SCATTERING IN HaPs

We will now consider a simple estimation of the time and length scales at which carrier scattering occurs in HaPs at room temperature. A useful starting point for this discussion is the well-known relation $\mu = q_e\tau/m^*$, in which τ is the *average relaxation or scattering time of the carriers*. Using parameters from our above discussion that are representative of HaPs around room temperature, i.e., $\mu \approx 100$ cm^2/(Vs) and $m^* \approx 0.2\ m_e$, one finds very short scattering times of $\tau \approx 5$ fs. Such a scenario would seem to be relevant for realistic experimental

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

conditions in HaPs as well, as very rapid relaxation times of ≈4 fs have been reported from terahertz photoconductivity measurements of $MAPbI_3$ at room temperature,[72] which can be used to estimate *a very short carrier mean free path* of ≈0.8 nm. To put these numbers in perspective, it is worth recalling that relaxation times and mean free paths in the canonical high-quality semiconductor Si are much larger, i.e.., ≈60 fs and ≈10 nm,[81,82] respectively (see Figure 4). In HaPs, however, carrier scattering appears to occur on length scales that are on the order of one or only a few unit cells.

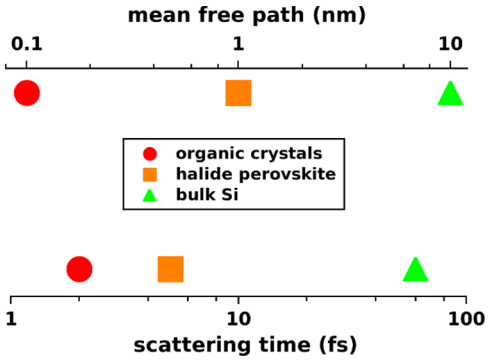


Figure 4. Illustration of the time and length scales that are relevant for carrier scattering in HaPs at room temperature. The figure shows estimates for the carrier mean free path and scattering time, plotted on a logarithmic scale, in comparison to those of organic crystals and the prototypical inorganic semiconductor silicon.

These estimates are useful to better understand the limitations of standard polaron and carrier-scattering theories for the case of HaPs. We again consider the aforementioned exact numerical results for the Fröhlich Hamiltonian,[78] because they demonstrate that, for the complete temperature range of relevance for practical optoelectronic applications of HaPs, the Mott−Ioffe−Regel criterion[83,84] is violated for systems with coupling strengths similar to those found in HaPs. In short, the Mott−Ioffe−Regel limit is surpassed whenever the mean free path of carriers is found to be smaller than the electron or hole (de Broglie) wavelength at a specific temperature. The above estimate of the mean free path of carriers in $MAPbI_3$ at room temperature of ≈0.8 nm strongly suggests that this is, indeed, the case. Violation of the Mott−Ioffe−Regel limit implies that carrier scattering (e.g., by lattice vibrations) destroys the coherence of electrons and holes because their mean free path would be smaller than their wavelength; as it has been put by Ioffe and Regel, the "electron waves fade out"[83] within the limits of their own wavelength. This scenario indicates a breakdown of the band-theory picture of carrier scattering as depicted by the Boltzmann transport equation in HaPs, which describes carriers as having well-defined energies or momenta due to being scattered only intermittently.

> This scenario indicates a breakdown of the band-theory picture of carrier scattering as depicted by the Boltzmann transport equation in HaPs.

Interestingly, recent theoretical work argues that $SrTiO_3$, a perovskite material with an effective Fröhlich coupling similar to that of HaPs,[85,86] falls in a similar category of "beyond quasiparticle" transport.[87] This work addresses the fact that lattice anharmonicity must be accounted for in this system, and that violation of the Mott−Ioffe−Regel criterion prevents the use of the standard Boltzmann transport equation. Indeed, the authors of ref 87 demonstrate that only with the treatment of lattice anharmonicity and a dynamical approach which accounts for incoherent processes missed by the Boltzmann transport equation can the magnitude and temperature dependence of transport in $SrTiO_3$ be described. Similarly, we argue that the violation of the Mott−Ioffe−Regel criterion together with the anharmonic HaP lattice motivates consideration of the dynamic disorder mechanism in these systems, which we now discuss.

> The violation of the Mott−Ioffe−Regel criterion together with the anharmonic HaP lattice motivates consideration of the dynamic disorder mechanism.

DYNAMIC DISORDER PICTURE OF ELECTRON−LATTICE INTERACTIONS

The appearance of anharmonic lattice dynamics and violation of the Mott−Ioffe−Regel criterion are reminiscent of behavior found in clean organic crystals such as oligoacenes and rubrene, which share important features with the HaP family.[88,89] The transport properties in these systems paradoxically embody aspects of band-like motion (typical in inorganic semiconductors) and incoherent hopping motion (characteristic of strongly disordered systems).[90] That such systems exhibit power-law temperature dependencies of the charge mobility on one hand,[88,89] along with very short carrier relaxation times and a violation of the Mott−Ioffe−Regel criterion on the other hand,[91] illustrates this puzzling duality. The dynamic disorder approach explains these features by positing that low-frequency vibrations of the lattice result in large fluctuations in the orbital overlaps between adjacent molecules, which transiently localize electrons and holes.[88−90,92−94] Thus, in organic crystals, the electron−lattice interaction involves a dynamic (time-dependent) disorder in the interactions between electronic carriers and the lattice.[95,96]

There are strong reasons to believe that HaPs should be described by the dynamic disorder picture as well. As emphasized above, HaPs are, like organic crystals,[97,98] notable for their slow, anharmonic lattice dynamics, the incoherent nature of their carrier relaxation (with the likely violation of the Mott−Ioffe−Regel condition), and their relatively low carrier mobilities, with magnitudes and temperature dependencies similar to those of high-quality organic crystals. Figure 4 shows that scattering times and mean free paths that have been calculated for the naphthalene crystal are ≈1 fs and ≈1 nm,[91] respectively, which suggests that HaPs could share certain similarities with organic crystals as far as the relevance of dynamic disorder as a mechanism for carrier scattering is concerned.[99] This picture has been pursued quantitatively by Mayers et al.[100] via the creation of a tight binding (TB) model, where the TB Hamiltonian is parametrized to density functional theory (DFT) in a DFT+TB scheme that describes how the band structure changes when the atoms are vibrating at finite temperature. This approach reveals the importance of dynamic disorder triggered by electron−lattice interactions in

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

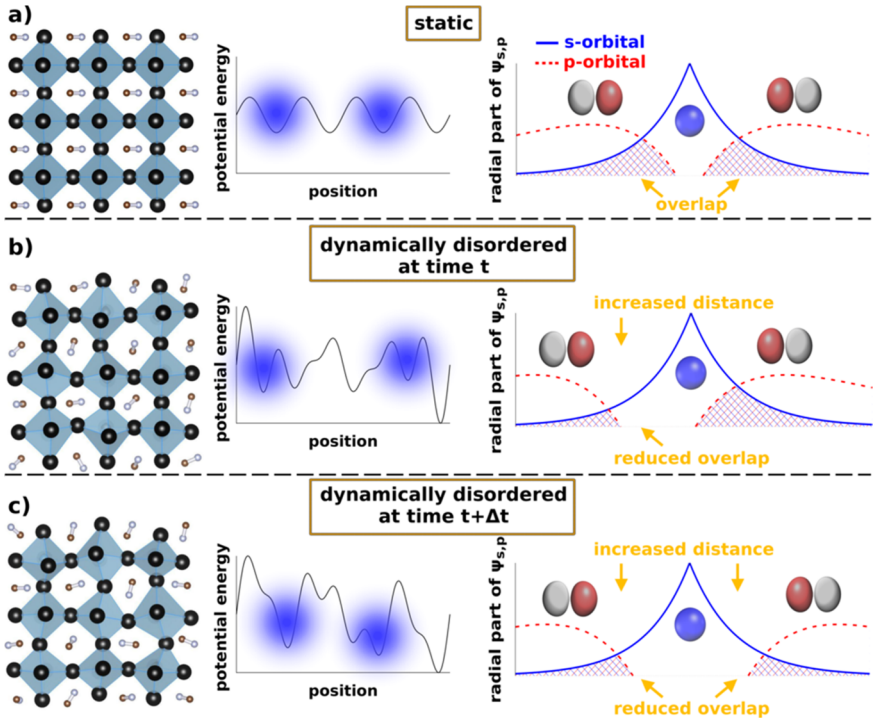


Figure 5. Illustration of dynamic disorder in electron−lattice interactions of HaPs. In the static scenario (a), a perfectly periodic lattice (left) leads to a periodic energy landscape for charge carriers (middle) and large overlap of electronic wave functions (right). Here, the radial part of an *s*-orbital (blue full line) and the same for a *p*-orbital (red-dashed curve) result in wave function overlap (blue-red dashed area). In the dynamic disorder scenario (b), at any given time *t* the atoms show large distortions from the ideal structure (left), which induces changes to the potential energy (middle) and leads to wave function overlap reductions (right). The latter is sketched as the reduction of overlap between *s*- and *p*-orbitals due to their increased distance. The disorder is dynamic because, at a later time $t + \Delta t$ (c), a different geometry distortion (left) leads to differently changed potential energy (middle) and differently reduced overlap (right). Note that the distortions, in general, may also lead to an increase of overlap but that a decrease is more likely to occur because bond elongation is more likely to occur than bond contraction.

the following manner. In the static and time-averaged HaP lattice (Figure 5a), perfect order of the lattice would lead to a periodic energy landscape for charge carriers and large overlap of electronic wave functions, e.g., the metal *s*- and halogen *p*-states hybridizing into the valence band. In *actual HaPs around room temperature* (Figure 5b), however, the lattice is far from this idealized, time-averaged geometry at any given time *t*. The associated atomic displacements induce changes to the potential energy for the carriers, and, just as importantly, they alter the wave function overlap since, e.g., the atoms are farther apart in a distorted structure than in the ideal one. The induced disorder is dynamic because, at a later time $t + \Delta t$ (Figure 5c), a different distortion may lead to a locally altered potential energy and different overlap. While there are lattice dynamics occurring at all time scales, for the dynamic disorder the slow evolution of the lead halide framework is most relevant. Thus, on relatively short time scales, it appears to the charge carrier that it is evolving in a statically disordered landscape. We note that "dynamic disorder" was used as a term to describe the rotational disorder of organic cations in HaPs;[96] see also a variety of previous theoretical investigations on the effect that the disordered MA cation has on HaP properties,[101,102] which focus on an aspect of the disorder apparent in these materials that is different from the one we highlight in this Perspective.

In the theoretical calculations of ref 100, the lattice dynamics lead to large fluctuations in the local energies and transfer integrals that are the ingredients of the TB Hamiltonian (see Figure 6). The resulting dynamic disorder picture formulated in ref 100 can be contrasted with the polaron models discussed earlier once various assumptions are made, which in view of Figure 6 are problematic for HaPs: namely, that the effect of lattice dynamics on the band structure is merely a small perturbation, and that the lattice dynamics themselves involve only small atomic displacements for which the harmonic

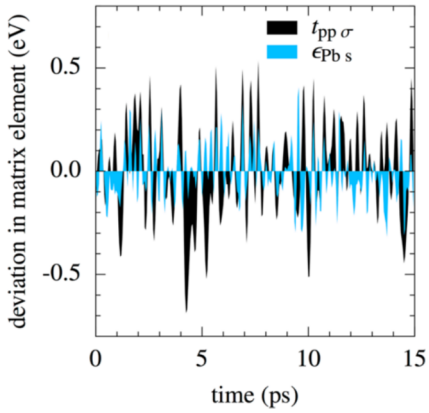


Figure 6. Example of dynamical fluctuations of local energies (blue) and transfer integrals (black) in $MAPbI_3$ at 300 K computed from the DFT-TB+MD method. Note that the fluctuations found for these two quantities are of similar magnitudes. Reprinted with permission from ref 100. Copyright 2018 American Chemical Society.

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

approximation is valid. Technically, this correspondence can be achieved by a linear Taylor expansion of the TB parameters in terms of the atomic displacements, along with an assumption of harmonic lattice motion. Such approximations would recapitulate a multi-mode version of the Fröhlich model, with the addition of off-diagonal fluctuations giving rise to (Peierls-type) coupling.[42] Instead, in ref 100, the non-linearity of the couplings is retained at the expense of treating the full anharmonic nuclear motion classically by molecular dynamics (MD), which is reasonable for high temperatures compared to the relevant phonon frequencies. Note that the approximation of classical lattice dynamics prevents true coherent polaron formation from being described, as the lattice can, at most, react to the *average* electronic dynamics.

The combination of DFT, TB, and classical MD (DFT+TB +MD) described above and developed in ref 100 successfully rationalizes diverse experimental behaviors with no adjustable parameters. In particular, the large fluctuations in off-diagonal TB parameters (i.e., the transfer integrals) reduces orbital overlap between adjacent HaP octahedra and transiently localizes carriers (see Figures 5 and 6). As shown in Figure 7a, a mobility of around $\mu \approx 100$ cm^2/(Vs) at room

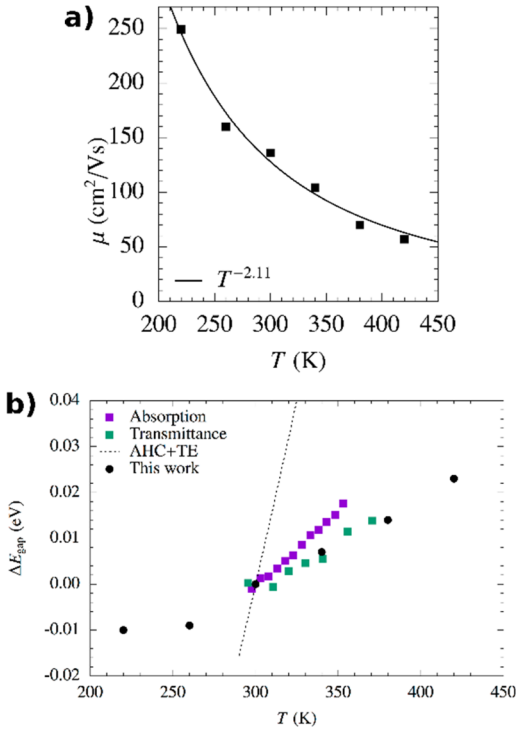


Figure 7. Carrier mobility (a) and changes in the band gap of $MAPbI_3$ (b) computed from the DFT-TB+MD method.[71,103,67] Reprinted with permission from ref 100. Copyright 2018 American Chemical Society.

temperature with a temperature dependence of $\mu \propto T^{-2}$ is obtained, consistent with the upper end of behavior observed in experiments. Interestingly, the exact solution of a theoretical model with the main ingredients found in the microscopic model of ref 100 has been put forward by Madhukar and Post.[104] These authors show that, in general, such models yield $\mu \propto a + bT^{-2}$, with a and b being material-dependent constants, which clearly can fit well the range of behaviors seen in experiments on HaPs. The temperature dependence of the band gap (see Figure 7b), a quantity we have discussed above, as well as the temperature dependence and magnitude of the width of the absorption threshold (known as the Urbach energy) in prototypical HaP materials, are shown to arise as a direct consequence of dynamic disorder in ref 100. In particular, the Urbach energy arises entirely from effective vibrational disorder correlated over only a very short length scale.[36,100,105] It is also illuminating to note that the "polaronic mass enhancements" discussed in the literature (see, e.g., refs 16 and 49) would be accessible to the dynamic disorder picture via computation of the impact that the thermal lattice fluctuations have on the (average) electronic band structure.

Independently, a similar dynamic disorder picture for HaPs has been put forward more recently by Lacroix et al.[106] Using a different parametrization of the dynamical TB approach and different means of extracting mobilities, they find room-temperature mobilities of similar magnitude, following an approximate $\mu \propto T^{-3/2}$ law at high temperatures, again consistent with experiments. Emphasizing the importance of disorder, both static and dynamic, these authors highlight the fact that the Boltzmann transport formalism neglects the type of localization effects described above, which are crucial for correctly describing the dynamics. In a related vein, they emphasize that at high temperatures, thermally excited vibrational motion naturally erases the effects of polaron formation. In particular, near room temperature, the energy broadening due to scattering by disorder becomes larger than the polaron formation energy, which would imply that polarons do not play a role at operationally relevant temperatures. The work of Mayers et al.,[100] as well as the work of Lacroix et al.,[106] illustrate that the dynamic disorder picture of transiently localized charge carriers in a slowly evolving electrostatic landscape that is driven by soft, anharmonic lattice dynamics in HaPs is consistent with diverse experimental observations. An interesting difference between these two articles concerns the detailed nature of the dynamic disorder present in HaPs, since ref 106 emphasizes the importance of diagonal disorder and ref 100 found the off-diagonal disorder to be more important for the temperature dependence of the mobility. Further investigation and clarification on this question will support the targeted materials design of HaPs showing desired optoelectronic properties.

> The dynamic disorder picture of transiently localized charge carriers in a slowly evolving electrostatic landscape that is driven by soft, anharmonic lattice dynamics in HaPs is consistent with diverse experimental observations.

CONCLUSIONS AND OPEN QUESTIONS

We have discussed the pertinent electron–lattice interaction mechanisms in HaPs in the most important temperature regimes for optoelectronic devices. Our analysis of the applicability and failures of the polaron picture, and the underlying physical models behind it, demonstrates that polaronic behavior of some form exists in HaPs. For example, signatures of polaronic effects were detected to be concurrent with the formation of a stress field developing upon light

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

absorption in $MAPbBr_3$[51] and to impact photoinduced compositional segregation in mixed-halide crystals that involves halide motion.[52−54] It is, however, important to stress that the appearance of such polaronic signatures cannot be used as a proof of the existence of polarons, as described by the Fröhlich Hamiltonian. This distinction is important because the picture arising from canonical polaron models, such as described by the Fröhlich Hamiltonian, appears incapable of explaining the established optical and charge-carrier characteristics of HaPs. Perhaps the most compelling evidence for this assessment is the set of recently published exact numerical data on the polaron mobility in the intermediate coupling regime that is relevant for HaPs.[78] These results show that the temperature dependence of the polaron mobility is incorrect compared to firmly established experimental findings, which is in line with numerical modeling of certain well-defined limits of the polaron mobility in HaPs.[44,48,76,77] Therefore, the Fröhlich polaron model cannot explain carrier scattering in HaPs. Emphasizing the soft, polar lattice of the HaPs and the associated local polar fluctuations that exist in these materials around room temperature, we argue that these failures are founded in several assumptions underlying the simplest polaron and band-theory pictures being violated in these materials. Perhaps the most important of these is the violation of the Mott−Ioffe−Regel criterion for electrons and holes in typical HaP compounds at and around room temperature, invalidating standard kinetic theory approaches to the description of their transport, similar to what has been discussed for the case of clean organic crystals.

The dynamic disorder picture is a complementary view of electron−lattice interactions that has been successful for describing carrier scattering in organic crystals and which appears to naturally apply to HaPs as well. It is important to stress that time and length scales associated with carrier scattering in HaPs are certainly not really comparable to those in organic crystals, see, e.g., Figure 4. But both material classes share that dynamic disorder can be invoked as a major factor in the carrier scattering mechanisms relevant around room temperature by the apparent failures of standard scattering mechanisms discussed above. The dynamic disorder approach puts forward a real-space description of electron−lattice interactions in HaPs which involves transient localization of band-edge carriers in the slowly evolving electrostatic potential. We argue that this mechanism subsumes standard polaronic treatments as formulated from, e.g., the Fröhlich Hamiltonian. However, the dynamic disorder mechanism goes beyond these descriptions by treating the full non-linearity of coupling parameters and the anharmonicity of the lattice in a natural way, which is required given the soft, low-frequency nature of the HaP lattice dynamics. As shown in refs 100 and 106, this viewpoint naturally provides explanations for puzzles which arise when electron−lattice interactions in HaPs are considered from standard band-theory approaches.

Various outstanding issues and directions remain open. First, other physically important systems that may be treated within the approach of refs 100 and 106 are worthy of investigation. In this regard, it is interesting to note that the *static* properties of colossal magnetoresistance materials with strong electron−lattice interactions, such as the rare-earth manganites, have been traditionally treated in a manner similar to that outlined here for the HaPs, in that the vibrational and spin degrees of freedom are treated completely classically.[107−110] The description of time-dependent behavior in such systems under analogous assumptions would connect naturally to the dynamic disorder picture of the HaPs. Furthermore, a recent experimental study on temperature-dependent exciton mobilities in a 2D HaP material showed that the Mott−Ioffe−Regel criterion is violated over a wide range of temperatures as well, which motivates investigations of the interplay between dynamic disorder and excitonic behavior in these systems.[111] Second, the properties of transiently localized band-edge carriers and the role played by spin−orbit coupling therein should be investigated in detail. This is potentially relevant because relativistic effects are known to be very important in HaPs,[112] which could influence the dynamical changes of the orbital overlaps that drive dynamic disorder and transient localization. Moreover, it would be interesting to better understand the potential impact of transient localization in some of the polaronic signatures that we have discussed here. It is also useful to note that the regime of transport, where mobility *decreases* with temperature because of dynamic disorder and transient localization,[113] can be contrasted to the more common case where localization leads to a mobility *increase* with temperature (e.g., as in hopping transport). Lastly, the proposed absence of large polarons at and around room temperature suggests that they do not play a significant role in a variety of important phenomena, such as non-radiative recombination of photoexcited carriers. The dynamic disorder models discussed here suggest that such polarons are largely undressed by thermally populated vibrational modes at high temperatures, and hence do not play a large role in electron−lattice effects around room temperature. On the other hand, it should be noted that these models do not treat quantum-mechanical aspects of ionic motion in a satisfactory manner and, thus, may not be suitable to describe some of the variants of polaronic behavior we addressed here. One possible way to improve upon this treatment is to note that the fully anharmonic problem studied in ref 100 can be mapped to a multi-mode Fröhlich-type model with effective harmonic phonons and temperature-dependent coupling constants.[114] This mapping, which makes use of linear-response theory, includes anharmonicity and non-linear couplings in an approximate manner and can be combined with the approach of predicting charge transport outlined in ref 87. Such an approach could enable the description of effects that capture both the physics of soft, anharmonic lattice dynamics in HaPs and the influence of incoherent scattering contributions, enabling the treatment of transport under conditions where the Mott−Ioffe−Regel criterion is violated, while at the same time affording a description of lower temperature behavior where polaron formation and the quantum treatment of phonons may play significant roles. The exploration of these and other directions in the near future will greatly enrich our understanding of the unique physics of HaPs and related solids.

AUTHOR INFORMATION

Corresponding Author

David A. Egger − *Department of Physics, Technical University of Munich, 85748 Garching, Germany;* orcid.org/0000-0001-8424-902X; Email: david.egger@tum.de

Authors

Maximilian J. Schilcher − *Department of Physics, Technical University of Munich, 85748 Garching, Germany*

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

Paul J. Robinson − *Department of Chemistry, Columbia University, New York 10027, United States;* orcid.org/0000-0003-0465-4979

David J. Abramovitch − *Department of Physics, University of California Berkeley, Berkeley, California 94720, United States*

Liang Z. Tan − *The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States;* orcid.org/0000-0003-4724-6369

Andrew M. Rappe − *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States;* orcid.org/0000-0003-4620-6496

David R. Reichman − *Department of Chemistry, Columbia University, New York 10027, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsenergylett.1c00506

Notes

The authors declare no competing financial interest.

Biographies

Maximilian Schilcher received his M.Sc. at the University of Augsburg and is currently a Ph.D. student at the Technical University of Munich. His research mainly focuses on the influence of dynamic disorder on optoelectronic properties of halide perovskites, using a combination of density functional theory and a large-scale tight-binding approach.

Paul J. Robinson received his B.S. in physics from the University of California, Los Angeles, in 2018 and is currently an NSF Graduate Research Fellow at Columbia University. His research interests are focused on creating and applying new methods to describe the quantum dynamics of electron−phonon coupled materials.

David Abramovitch is a student in the Department of Physics at the University of California, Berkeley. His research interests include electronic structure theory and electron−lattice interactions and are currently focused on tight-binding methods for finite-temperature halide perovskites.

Liang Tan received his Ph.D. in physics from the University of California, Berkeley. He is currently a Staff Scientist at Lawrence Berkeley National Laboratory. His research group focuses on first-principles calculations to study light−matter interactions at the nanoscale, for applications in optoelectronics, light harvesting, and quantum information (see https://liangtan.lbl.gov).

Andrew M. Rappe is currently Blanchard Professor of Chemistry at the University of Pennsylvania. His group studies physical phenomena in electronic and optical materials and uses these insights to design materials and processes. Current interests include bulk photovoltaic effects, heterogeneous catalysis, topological physics, polar phase transitions, and mechanochemistry (see https://web.sas.upenn.edu/rappegroup).

David Reichman is currently the Centennial Professor of Chemistry at Columbia University. Prior to arriving at Columbia, he was a professor at Harvard University. His group develops theory to understand the vibrational, optical, electronic, magnetic, and transport properties of novel condensed phase systems (see http://www.columbia.edu/cu/chemistry/groups/reichman).

David Egger received his Ph.D. in physics at the Technical University of Graz, Austria. Currently, he is an Assistant Professor of Physics at the Technical University of Munich. The research interests of his group are clustered around theoretical predictions of dynamic phenomena in energy and nanoscale materials at finite temperature (see www.theofem.de).

■ ACKNOWLEDGMENTS

D.A. was supported through the Center for Non-Perturbative Studies of Functional Materials funded by the Computational Materials Sciences Program of the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. L.Z.T. was supported by the Molecular Foundry, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. A.M.R. was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-FG02-07ER46431. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. D.R.R. acknowledges the support of NSF-CHE-1954791. P.J.R. acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant No. DGE-1644869. M.J.S. and D.A.E. acknowledge funding from the Alexander von Humboldt Foundation within the framework of the Sofja Kovalevskaja Award, endowed by the German Federal Ministry of Education and Research, the Technical University of Munich - Institute for Advanced Study, funded by the German Excellence Initiative and the European Union Seventh Framework Programme under Grant Agreement No. 291763, and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy - EXC 2089/1-390776260.

■ REFERENCES

(1) Snaith, H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4* (21), 3623−3630.

(2) Park, N.-G. Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell. *J. Phys. Chem. Lett.* **2013**, *4* (15), 2423−2429.

(3) Kazim, S.; Nazeeruddin, M. K.; Grätzel, M.; Ahmad, S. Perovskite as Light Harvester: A Game Changer in Photovoltaics. *Angew. Chem., Int. Ed.* **2014**, *53* (11), 2812−2824.

(4) Stranks, S. D.; Snaith, H. J. Metal-Halide Perovskites for Photovoltaic and Light-Emitting Devices. *Nat. Nanotechnol.* **2015**, *10* (5), 391−402.

(5) Brenner, T. M.; Egger, D. A.; Kronik, L.; Hodes, G.; Cahen, D. Hybrid Organic—Inorganic Perovskites: Low-Cost Semiconductors with Intriguing Charge-Transport Properties. *Nat. Rev. Mater.* **2016**, *1* (1), 15007.

(6) Li, W.; Wang, Z.; Deschler, F.; Gao, S.; Friend, R. H.; Cheetham, A. K. Chemically Diverse and Multifunctional Hybrid Organic−Inorganic Perovskites. *Nat. Rev. Mater.* **2017**, *2* (3), 16099.

(7) Egger, D. A.; Bera, A.; Cahen, D.; Hodes, G.; Kirchartz, T.; Kronik, L.; Lovrincic, R.; Rappe, A. M.; Reichman, D. R.; Yaffe, O. What Remains Unexplained about the Properties of Halide Perovskites? *Adv. Mater.* **2018**, *30*, 1800691.

(8) Brenner, T. M.; Egger, D. A.; Rappe, A. M.; Kronik, L.; Hodes, G.; Cahen, D. Are Mobilities in Hybrid Organic−Inorganic Halide Perovskites Actually "High"? *J. Phys. Chem. Lett.* **2015**, *6*, 4754−4757.

(9) Stoumpos, C. C.; Kanatzidis, M. G. Halide Perovskites: Poor Man's High-Performance Semiconductors. *Adv. Mater.* **2016**, *28* (28), 5778−5793.

(10) Herz, L. M. Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Lett.* **2017**, *2*, 1539−1548.

(11) Giorgi, G.; Fujisawa, J.-I.; Segawa, H.; Yamashita, K. Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis. *J. Phys. Chem. Lett.* **2013**, *4* (24), 4213−4216.
(12) Brivio, F.; Butler, K. T.; Walsh, A.; van Schilfgaarde, M. Relativistic Quasiparticle Self-Consistent Electronic Structure of Hybrid Halide Perovskite Photovoltaic Absorbers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89* (15), 155204.
(13) Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C. Lead Iodide Perovskite Light-Emitting Field-Effect Transistor. *Nat. Commun.* **2015**, *6* (1), 7383.
(14) Yang, J.-P.; Meissner, M.; Yamaguchi, T.; Zhang, X.-Y.; Ueba, T.; Cheng, L.-W.; Ideta, S.; Tanaka, K.; Zeng, X.-H.; Ueno, N.; Kera, S. Band Dispersion and Hole Effective Mass of Methylammonium Lead Iodide Perovskite. *Sol. RRL* **2018**, *2*, 1800132.
(15) Zu, F.; Amsalem, P.; Egger, D. A.; Wang, R.; Wolff, C. M.; Fang, H.; Loi, M. A.; Neher, D.; Kronik, L.; Duhm, S.; Koch, N. Constructing the Electronic Structure of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ Perovskite Thin Films from Single-Crystal Band Structure Measurements. *J. Phys. Chem. Lett.* **2019**, *10* (3), 601−609.
(16) Puppin, M.; Polishchuk, S.; Colonna, N.; Crepaldi, A.; Dirin, D. N.; Nazarenko, O.; De Gennaro, R.; Gatti, G.; Roth, S.; Barillot, T.; Poletto, L.; Xian, R. P.; Rettig, L.; Wolf, M.; Ernstorfer, R.; Kovalenko, M. V.; Marzari, N.; Grioni, M.; Chergui, M. Evidence of Large Polarons in Photoemission Band Mapping of the Perovskite Semiconductor $CsPbBr_3$. *Phys. Rev. Lett.* **2020**, *124* (20), 206402.
(17) Sun, S.; Fang, Y.; Kieslich, G.; White, T. J.; Cheetham, A. K. Mechanical Properties of Organic−Inorganic Halide Perovskites, $CH_3NH_3PbX_3$ (X = I, Br and Cl), by Nanoindentation. *J. Mater. Chem. A* **2015**, *3* (36), 18450−18455.
(18) Rakita, Y.; Cohen, S. R.; Kedem, N. K.; Hodes, G.; Cahen, D. Mechanical Properties of $APbX_3$ (A = Cs or CH_3NH_3; X = I or Br) Perovskite Single Crystals. *MRS Commun.* **2015**, *5* (4), 623−629.
(19) Whalley, L. D.; Skelton, J. M.; Frost, J. M.; Walsh, A. Phonon Anharmonicity, Lifetimes, and Thermal Transport in $CH_3NH_3PbI_3$ from Many-Body Perturbation Theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94* (22), 220301.
(20) Beecher, A. N.; Semonin, O. E.; Skelton, J. M.; Frost, J. M.; Terban, M. W.; Zhai, H.; Alatas, A.; Owen, J. S.; Walsh, A.; Billinge, S. J. L. Direct Observation of Dynamic Symmetry Breaking above Room Temperature in Methylammonium Lead Iodide Perovskite. *ACS Energy Lett.* **2016**, *1* (4), 880−887.
(21) Wang, M.; Lin, S. Anisotropic and Ultralow Phonon Thermal Transport in Organic−Inorganic Hybrid Perovskites: Atomistic Insights into Solar Cell Thermal Management and Thermoelectric Energy Conversion Efficiency. *Adv. Funct. Mater.* **2016**, *26* (29), 5297−5306.
(22) Fabini, D. H.; Laurita, G.; Bechtel, J. S.; Stoumpos, C. C.; Evans, H. A.; Kontos, A. G.; Raptis, Y. S.; Falaras, P.; Van der Ven, A.; Kanatzidis, M. G.; Seshadri, R. Dynamic Stereochemical Activity of the Sn^{2+} Lone Pair in Perovskite CsSnBr3. *J. Am. Chem. Soc.* **2016**, *138* (36), 11820−11832.
(23) Fabini, D. H.; Hogan, T.; Evans, H. A.; Stoumpos, C. C.; Kanatzidis, M. G.; Seshadri, R. Dielectric and Thermodynamic Signatures of Low-Temperature Glassy Dynamics in the Hybrid Perovskites $CH_3NH_3PbI_3$ and $HC(NH_2)_2PbI_3$. *J. Phys. Chem. Lett.* **2016**, *7* (3), 376−381.
(24) Yaffe, O.; Guo, Y.; Tan, L. Z.; Egger, D. A.; Hull, T.; Stoumpos, C. C.; Zheng, F.; Heinz, T. F.; Kronik, L.; Kanatzidis, M. G.; Owen, J. S.; Rappe, A. M.; Pimenta, M. A.; Brus, L. E. Local Polar Fluctuations in Lead Halide Perovskite Crystals. *Phys. Rev. Lett.* **2017**, *118* (13), 136001.
(25) Laurita, G.; Fabini, D. H.; Stoumpos, C. C.; Kanatzidis, M. G.; Seshadri, R. Chemical Tuning of Dynamic Cation Off-Centering in the Cubic Phases of Hybrid Tin and Lead Halide Perovskites. *Chem. Sci.* **2017**, *8* (8), 5628−5635.
(26) Brown, K. L.; Parker, S. F.; García, I. R.; Mukhopadhyay, S.; Sakai, V. G.; Stock, C. Molecular Orientational Melting within a Lead-Halide Octahedron Framework: The Order-Disorder Transition in $CH_3NH_3PbBr_3$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96* (17), 174111.
(27) Carignano, M. A.; Aravindh, S. A.; Roqan, I. S.; Even, J.; Katan, C. Critical Fluctuations and Anharmonicity in Lead Iodide Perovskites from Molecular Dynamics Supercell Simulations. *J. Phys. Chem. C* **2017**, *121* (38), 20729−20738.
(28) Wu, X.; Tan, L. Z.; Shen, X.; Hu, T.; Miyata, K.; Trinh, M. T.; Li, R.; Coffee, R.; Liu, S.; Egger, D. A.; Makasyuk, I.; Zheng, Q.; Fry, A.; Robinson, J. S.; Smith, M. D.; Guzelturk, B.; Karunadasa, H. I.; Wang, X.; Zhu, X.; Kronik, L.; Rappe, A. M.; Lindenberg, A. M. Light-Induced Picosecond Rotational Disordering of the Inorganic Sublattice in Hybrid Perovskites. *Sci. Adv.* **2017**, *3* (7), e1602388.
(29) Marronnier, A.; Lee, H.; Geffroy, B.; Even, J.; Bonnassieux, Y.; Roma, G. Structural Instabilities Related to Highly Anharmonic Phonons in Halide Perovskites. *J. Phys. Chem. Lett.* **2017**, *8* (12), 2659−2665.
(30) Marronnier, A.; Roma, G.; Boyer-Richard, S.; Pedesseau, L.; Jancu, J.-M.; Bonnassieux, Y.; Katan, C.; Stoumpos, C. C.; Kanatzidis, M. G.; Even, J. Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells. *ACS Nano* **2018**, *12* (4), 3477−3486.
(31) Rivett, J. P. H.; Tan, L. Z.; Price, M. B.; Bourelle, S. A.; Davis, N. J. L. K.; Xiao, J.; Zou, Y.; Middleton, R.; Sun, B.; Rappe, A. M.; Credgington, D.; Deschler, F. Long-Lived Polarization Memory in the Electronic States of Lead-Halide Perovskites from Local Structural Dynamics. *Nat. Commun.* **2018**, *9* (1), 3531.
(32) Wang, C.; Liu, Y.; Liu, S. F.; Li, B.; Chen, Y. Giant Phonon Tuning Effect via Pressure-Manipulated Polar Rotation in Perovskite $MAPbI_3$. *J. Phys. Chem. Lett.* **2018**, *9* (11), 3029−3034.
(33) Gold-Parker, A.; Gehring, P. M.; Skelton, J. M.; Smith, I. C.; Parshall, D.; Frost, J. M.; Karunadasa, H. I.; Walsh, A.; Toney, M. F. Acoustic Phonon Lifetimes Limit Thermal Transport in Methylammonium Lead Iodide. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (47), 11905−11910.
(34) Gold-Parker, A. *Slow and Fast Dynamic Processes in Hybrid Perovskite Solar Cell Materials*. Ph.D. Dissertation, Stanford University, Stanford, CA, 2018.
(35) Zhu, T.; Ertekin, E. Mixed Phononic and Non-Phononic Transport in Hybrid Lead Halide Perovskites: Glass-Crystal Duality, Dynamical Disorder, and Anharmonicity. *Energy Environ. Sci.* **2019**, *12* (1), 216−229.
(36) Gehrmann, C.; Egger, D. A. Dynamic Shortening of Disorder Potentials in Anharmonic Halide Perovskites. *Nat. Commun.* **2019**, *10* (1), 3141.
(37) Sharma, R.; Dai, Z.; Gao, L.; Brenner, T. M.; Yadgarov, L.; Zhang, J.; Rakita, Y.; Korobko, R.; Rappe, A. M.; Yaffe, O. Elucidating the Atomistic Origin of Anharmonicity in Tetragonal $CH_3NH_3PbI_3$ with Raman Scattering. *Phys. Rev. Mater.* **2020**, *4* (9), 092401.
(38) Fabini, D. H.; Seshadri, R.; Kanatzidis, M. G. The Underappreciated Lone Pair in Halide Perovskites Underpins Their Unusual Properties. *MRS Bull.* **2020**, *45* (6), 467−477.
(39) Cockayne, E.; Burton, B. P. Phonons and Static Dielectric Constant in $CaTiO_3$ from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62* (6), 3735−3743.
(40) Klarbring, J.; Hellman, O.; Abrikosov, I. A.; Simak, S. I. Anharmonicity and Ultralow Thermal Conductivity in Lead-Free Halide Double Perovskites. *Phys. Rev. Lett.* **2020**, *125* (4), 045701.
(41) Yu, P.; Cardona, M. *Fundamentals of Semiconductors: Physics and Materials Properties*, 4th ed.; Springer: Berlin, 2010.
(42) Mahan, G. D. *Many Particle Physics*, 3rd ed.; Plenum: New York, 2000.
(43) Lee, N.-E.; Zhou, J.-J.; Chen, H.-Y.; Bernardi, M. Ab Initio Electron-Two-Phonon Scattering in GaAs from next-to-Leading Order Perturbation Theory. *Nat. Commun.* **2020**, *11*, 1607.
(44) Sendner, M.; Nayak, P. K.; Egger, D. A.; Beck, S.; Müller, C.; Epding, B.; Kowalsky, W.; Kronik, L.; Snaith, H. J.; Pucci, A.; Lovrinčić, R. Optical Phonons in Methylammonium Lead Halide Perovskites and Implications for Charge Transport. *Mater. Horiz.* **2016**, *3* (6), 613−620.

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173

(45) Fröhlich, H. Electrons in Lattice Fields. *Adv. Phys.* **1954**, *3* (11), 325−361.
(46) Wright, A. D.; Verdi, C.; Milot, R.; Eperon, G.; Pérez-Osorio, M. A.; Snaith, H.; Giustino, F.; Johnston, M.; Herz, L. Electron−Phonon Coupling in Hybrid Lead Halide Perovskites. *Nat. Commun.* **2016**, *7*, 11755.
(47) In this work we will use the term "polaron" in a somewhat loose sense. In particular, we refer to "polaronic effects" as arising from microscopic assumptions, such as the assumptions of linear electron−phonon coupling and harmonic lattice motion, which are standard in the models traditionally employed to study polarons, even when the formation of a bound state composed of an electron and the vibrational degrees of freedom of the lattice does not explicitly arise.
(48) Frost, J. M. Calculating Polaron Mobility in Halide Perovskites. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96* (19), 195202.
(49) Schlipf, M.; Poncé, S.; Giustino, F. Carrier Lifetimes and Polaronic Mass Enhancement in the Hybrid Halide Perovskite $CH_3NH_3PbI_3$ from Multiphonon Fröhlich Coupling. *Phys. Rev. Lett.* **2018**, *121* (8), 086402.
(50) Guzelturk, B.; Winkler, T.; de Goor, T. V.; Smith, M. D.; Bourelle, S. A.; Feldmann, S.; Trigo, M.; Teitelbaum, S.; Steinrück, H.-G.; de la Pena, G. A.; Alonso-Mori, R.; Zhu, D.; Sato, T.; Karunadasa, H. I.; Toney, M. F.; Deschler, F.; Lindenberg, A. M. Visualization of Dynamic Polaronic Strain Fields in Hybrid Lead Halide Perovskites *arXiv Preprint* arXiv:2011.03103v1 [cond-mat.mtrl-sci], Nov 5, 2020. https://arxiv.org/abs/2011.03103v1 (accessed 2021-04-26).
(51) Guzelturk, B.; Winkler, T.; Van de Goor, T. W. J.; Smith, M. D.; Bourelle, S. A.; Feldmann, S.; Trigo, M.; Teitelbaum, S. W.; Steinrück, H.-G.; de la Pena, G. A.; Alonso-Mori, R.; Zhu, D.; Sato, T.; Karunadasa, H. I.; Toney, M. F.; Deschler, F.; Lindenberg, A. M. Visualization of Dynamic Polaronic Strain Fields in Hybrid Lead Halide Perovskites. *Nat. Mater.* **2021**, *20*, 618.
(52) Bischak, C. G.; Hetherington, C. L.; Wu, H.; Aloni, S.; Ogletree, D. F.; Limmer, D. T.; Ginsberg, N. S. Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites. *Nano Lett.* **2017**, *17*, 1028−1033.
(53) Bischak, C. G.; Wong, A. B.; Lin, E.; Limmer, D. T.; Yang, P.; Ginsberg, N. S. Tunable Polaron Distortions Control the Extent of Halide Demixing in Lead Halide Perovskites. *J. Phys. Chem. Lett.* **2018**, *9* (14), 3998−4005.
(54) Limmer, D. T.; Ginsberg, N. S. Photoinduced Phase Separation in the Lead Halides Is a Polaronic Effect. *J. Chem. Phys.* **2020**, *152*, 230901.
(55) Miyata, K.; Meggiolaro, D.; Trinh, M. T.; Joshi, P. P.; Mosconi, E.; Jones, S. C.; De Angelis, F.; Zhu, X.-Y. Large Polarons in Lead Halide Perovskites. *Sci. Adv.* **2017**, *3* (8), 1701217.
(56) Emin, D. Barrier to Recombination of Oppositely Charged Large Polarons. *J. Appl. Phys.* **2018**, *123* (5), 055105.
(57) Wiktor, J.; Ambrosio, F.; Pasquarello, A. Mechanism Suppressing Charge Recombination at Iodine Defects in $CH_3NH_3PbI_3$ by Polaron Formation. *J. Mater. Chem. A* **2018**, *6* (35), 16863−16867.
(58) Kirchartz, T.; Markvart, T.; Rau, U.; Egger, D. A. Impact of Small Phonon Energies on the Charge-Carrier Lifetimes in Metal-Halide Perovskites. *J. Phys. Chem. Lett.* **2018**, *9* (5), 939−946.
(59) Sio, W. H.; Verdi, C.; Poncé, S.; Giustino, F. Polarons from First Principles, without Supercells. *Phys. Rev. Lett.* **2019**, *122* (24), 246403.
(60) Sio, W. H.; Verdi, C.; Poncé, S.; Giustino, F. Ab Initio Theory of Polarons: Formalism and Applications. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2019**, *99* (23), 235139.
(61) Allen, P. B.; Heine, V. Theory of the Temperature Dependence of Electronic Band Structures. *J. Phys. C: Solid State Phys.* **1976**, *9* (12), 2305−2312.
(62) Allen, P. B.; Cardona, M. Temperature Dependence of the Direct Gap of Si and Ge. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1983**, *27* (8), 4760−4769.
(63) Monserrat, B.; Drummond, N. D.; Needs, R. J. Anharmonic Vibrational Properties in Periodic Systems: Energy, Electron-Phonon Coupling, and Stress. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87* (14), 144302.
(64) Zacharias, M.; Giustino, F. One-Shot Calculation of Temperature-Dependent Optical Spectra and Phonon-Induced Band-Gap Renormalization. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94* (7), 075125.
(65) Giustino, F. Electron-Phonon Interactions from First Principles. *Rev. Mod. Phys.* **2017**, *89* (1), 015003.
(66) Karsai, F.; Engel, M.; Flage-Larsen, E.; Kresse, G. Electron−Phonon Coupling in Semiconductors within the GW Approximation. *New J. Phys.* **2018**, *20* (12), 123008.
(67) Saidi, W. A.; Poncé, S.; Monserrat, B. Temperature Dependence of the Energy Levels of Methylammonium Lead Iodide Perovskite from First-Principles. *J. Phys. Chem. Lett.* **2016**, *7* (24), 5247−5252.
(68) Francisco-López, A.; Charles, B.; Weber, O. J.; Alonso, M. I.; Garriga, M.; Campoy-Quiles, M.; Weller, M. T.; Goñi, A. R. Equal Footing of Thermal Expansion and Electron-Phonon Interaction in the Temperature Dependence of Lead Halide Perovskite Band Gaps. *J. Phys. Chem. Lett.* **2019**, *10* (11), 2971−2977.
(69) Oga, H.; Saeki, A.; Ogomi, Y.; Hayase, S.; Seki, S. Improved Understanding of the Electronic and Energetic Landscapes of Perovskite Solar Cells: High Local Charge Carrier Mobility, Reduced Recombination, and Extremely Shallow Traps. *J. Am. Chem. Soc.* **2014**, *136* (39), 13818−13825.
(70) Savenije, T. J.; Ponseca, C. S.; Kunneman, L.; Abdellah, M.; Zheng, K.; Tian, Y.; Zhu, Q.; Canton, S. E.; Scheblykin, I. G.; Pullerits, T.; Yartsev, A.; Sundström, V. Thermally Activated Exciton Dissociation and Recombination Control the Carrier Dynamics in Organometal Halide Perovskite. *J. Phys. Chem. Lett.* **2014**, *5* (13), 2189−2194.
(71) Milot, R. L.; Eperon, G. E.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Temperature-Dependent Charge-Carrier Dynamics in $CH_3NH_3PbI_3$ Perovskite Thin Films. *Adv. Funct. Mater.* **2015**, *25* (39), 6218−6227.
(72) Karakus, M.; Jensen, S. A.; D'Angelo, F.; Turchinovich, D.; Bonn, M.; Cánovas, E. Phonon−Electron Scattering Limits Free Charge Mobility in Methylammonium Lead Iodide Perovskites. *J. Phys. Chem. Lett.* **2015**, *6*, 4991−4996.
(73) Yi, H. T.; Wu, X.; Zhu, X.; Podzorov, V. Intrinsic Charge Transport across Phase Transitions in Hybrid Organo-Inorganic Perovskites. *Adv. Mater.* **2016**, *28* (30), 6509−6514.
(74) Shrestha, S.; Matt, G. J.; Osvet, A.; Niesner, D.; Hock, R.; Brabec, C. J. Assessing Temperature Dependence of Drift Mobility in Methylammonium Lead Iodide Perovskite Single Crystals. *J. Phys. Chem. C* **2018**, *122*, 5935−5939.
(75) Biewald, A.; Giesbrecht, N.; Bein, T.; Docampo, P.; Hartschuh, A.; Ciesielski, R. Temperature-Dependent Ambipolar Charge Carrier Mobility in Large-Crystal Hybrid Halide Perovskite Thin Films. *ACS Appl. Mater. Interfaces* **2019**, *11*, 20838−20844.
(76) Wolf, M. J.; Irvine, L.; Walker, A. Quantifying Polaronic Effects on Charge-Carrier Scattering and Mobility in Lead−Halide Perovskites. *arXiv Preprint* arXiv:2003.00968v1 [cond-mat.mtrl-sci], March 2, 2020. https://arxiv.org/abs/2003.00968v1 (accessed 2021-04-26).
(77) Thongnum, A.; Pinsook, U. Polaron Transport in Hybrid $CH_3NH_3PbI_3$ Perovskite Thin Films. *Nanoscale* **2020**, *12* (26), 14112−14119.
(78) Mishchenko, A. S.; Pollet, L.; Prokof'ev, N. V.; Kumar, A.; Maslov, D. L.; Nagaosa, N. Polaron Mobility in the "Beyond Quasiparticles" Regime. *Phys. Rev. Lett.* **2019**, *123* (7), 076601.
(79) We use parameters from ref 80 for $CsPbBr_3$: $\alpha \approx 2.4$, $\omega_{LO}/T \approx 0.8$ at room temperature, in units where $k_B = \hbar = e = 1$. This is very close to the exact numerical data shown in Figure 2 of ref 78.
(80) Poncé, S.; Schlipf, M.; Giustino, F. Origin of Low Carrier Mobilities in Halide Perovskites. *ACS Energy Lett.* **2019**, *4*, 456−463.
(81) Titova, L. V.; Cocker, T. L.; Cooke, D. G.; Wang, X.; Meldrum, A.; Hegmann, F. A. Ultrafast Percolative Transport Dynamics in

Silicon Nanocrystal Films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *83* (8), 085403.
(82) Cooke, D. G.; Meldrum, A.; Uhd Jepsen, P. Ultrabroadband Terahertz Conductivity of Si Nanocrystal Films. *Appl. Phys. Lett.* **2012**, *101* (21), 211107.
(83) Ioffe, A. F.; Regel, A. R. Non-Crystalline, Amorphous and Liquid Electronic Semiconductors. *Prog. Semicond.* **1960**, *4* (89), 237−291.
(84) Mott, N. F. Conduction in Non-Crystalline Systems IX. the Minimum Metallic Conductivity. *Philos. Mag.* **1972**, *26* (4), 1015−1026.
(85) van Mechelen, J. L. M.; van der Marel, D.; Grimaldi, C.; Kuzmenko, A. B.; Armitage, N. P.; Reyren, N.; Hagemann, H.; Mazin, I. I. Electron-Phonon Interaction and Charge Carrier Mass Enhancement in $SrTiO_3$. *Phys. Rev. Lett.* **2008**, *100* (22), 226403.
(86) Devreese, J. T.; Klimin, S. N.; van Mechelen, J. L. M.; van der Marel, D. Many-Body Large Polaron Optical Conductivity in $SrTi_{1-x}Nb_xO_3$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81* (12), 125119.
(87) Zhou, J.-J.; Bernardi, M. Predicting Charge Transport in the Presence of Polarons: The beyond-Quasiparticle Regime in $SrTiO_3$. *Phys. Rev. Res.* **2019**, *1* (3), 033138.
(88) Gershenson, M. E.; Podzorov, V.; Morpurgo, A. F. Colloquium: Electronic Transport in Single-Crystal Organic Transistors. *Rev. Mod. Phys.* **2006**, *78* (3), 973−989.
(89) Fratini, S.; Nikolka, M.; Salleo, A.; Schweicher, G.; Sirringhaus, H. Charge Transport in High-Mobility Conjugated Polymers and Molecular Semiconductors. *Nat. Mater.* **2020**, *19* (5), 491−502.
(90) Troisi, A.; Orlandi, G. Charge-Transport Regime of Crystalline Organic Semiconductors: Diffusion Limited by Thermal Off-Diagonal Electronic Disorder. *Phys. Rev. Lett.* **2006**, *96* (8), 086601.
(91) Cheng, Y. C.; Silbey, R. J.; da Silva Filho, D. A.; Calbert, J. P.; Cornil, J.; Brédas, J. L. Three-Dimensional Band Structure and Bandlike Mobility in Oligoacene Single Crystals: A Theoretical Investigation. *J. Chem. Phys.* **2003**, *118* (8), 3764−3774.
(92) Fratini, S.; Mayou, D.; Ciuchi, S. The Transient Localization Scenario for Charge Transport in Crystalline Organic Materials. *Adv. Funct. Mater.* **2016**, *26* (14), 2292−2315.
(93) Fratini, S.; Ciuchi, S.; Mayou, D.; de Laissardière, G. T.; Troisi, A. A Map of High-Mobility Molecular Semiconductors. *Nat. Mater.* **2017**, *16* (10), 998−1002.
(94) Giannini, S.; Ziogos, O. G.; Carof, A.; Ellis, M.; Blumberger, J. Flickering Polarons Extending over Ten Nanometres Mediate Charge Transport in High-Mobility Organic Crystals. *Adv. Theory Simul.* **2020**, *3* (9), 2000093.
(95) Note that the term "dynamic disorder" has been applied in a seminal work by Poglitsch and Weber on HaPs, with a different meaning describing the disordered appearance of the organic cation in HaPs.[96]
(96) Poglitsch, A.; Weber, D. Dynamic Disorder in Methylammoniumtrihalogenoplumbates (II) Observed by Millimeter-wave Spectroscopy. *J. Chem. Phys.* **1987**, *87* (11), 6373−6378.
(97) Eggeman, A. S.; Illig, S.; Troisi, A.; Sirringhaus, H.; Midgley, P. A. Measurement of Molecular Motion in Organic Semiconductors by Thermal Diffuse Electron Scattering. *Nat. Mater.* **2013**, *12* (11), 1045−1049.
(98) Asher, M.; Angerer, D.; Korobko, R.; Diskin-Posner, Y.; Egger, D. A.; Yaffe, O. Anharmonic Lattice Vibrations in Small-Molecule Organic Semiconductors. *Adv. Mater.* **2020**, *32* (10), 1908028.
(99) Fetherolf, J. H.; Golež, D.; Berkelbach, T. C. A Unification of the Holstein Polaron and Dynamic Disorder Pictures of Charge Transport in Organic Crystals. *Phys. Rev. X* **2020**, *10* (2), 021062.
(100) Mayers, M. Z.; Tan, L. Z.; Egger, D. A.; Rappe, A. M.; Reichman, D. R. How Lattice and Charge Fluctuations Control Carrier Dynamics in Halide Perovskites. *Nano Lett.* **2018**, *18* (12), 8041−8046.
(101) Ma, J.; Wang, L.-W. Nanoscale Charge Localization Induced by Random Orientations of Organic Molecules in Hybrid Perovskite $CH_3NH_3PbI_3$. *Nano Lett.* **2015**, *15* (1), 248−253.
(102) Motta, C.; El-Mellouhi, F.; Kais, S.; Tabet, N.; Alharbi, F.; Sanvito, S. Revealing the Role of Organic Cations in Hybrid Halide Perovskite $CH_3NH_3PbI_3$. *Nat. Commun.* **2015**, *6* (1), 7026.
(103) Foley, B. J.; Marlowe, D. L.; Sun, K.; Saidi, W. A.; Scudiero, L.; Gupta, M. C.; Choi, J. J. Temperature Dependent Energy Levels of Methylammonium Lead Iodide Perovskite. *Appl. Phys. Lett.* **2015**, *106* (24), 243904.
(104) Madhukar, A.; Post, W. Exact Solution for the Diffusion of a Particle in a Medium with Site Diagonal and Off-Diagonal Dynamic Disorder. *Phys. Rev. Lett.* **1977**, *39* (22), 1424−1427.
(105) Greeff, C. W.; Glyde, H. R. Anomalous Urbach Tail in GaAs. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *51* (3), 1778−1783.
(106) Lacroix, A.; de Laissardière, G. T.; Quémerais, P.; Julien, J.-P.; Mayou, D. Modeling of Electronic Mobilities in Halide Perovskites: Adiabatic Quantum Localization Scenario. *Phys. Rev. Lett.* **2020**, *124* (19), 196601.
(107) Millis, A. J.; Mueller, R.; Shraiman, B. I. Fermi-Liquid-to-Polaron Crossover. I. General Results. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54* (8), 5389−5404.
(108) Millis, A. J.; Mueller, R.; Shraiman, B. I. Fermi-Liquid-to-Polaron Crossover. II. Double Exchange and the Physics of Colossal Magnetoresistance. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54* (8), 5405−5417.
(109) Vergés, J. A.; Martín-Mayor, V.; Brey, L. Lattice-Spin Mechanism in Colossal Magnetoresistive Manganites. *Phys. Rev. Lett.* **2002**, *88* (13), 136401.
(110) Şen, C.; Alvarez, G.; Dagotto, E. Competing Ferromagnetic and Charge-Ordered States in Models for Manganites: The Origin of the Colossal Magnetoresistance Effect. *Phys. Rev. Lett.* **2007**, *98* (12), 127202.
(111) Ziegler, J. D.; Zipfel, J.; Meisinger, B.; Menahem, M.; Zhu, X.; Taniguchi, T.; Watanabe, K.; Yaffe, O.; Egger, D. A.; Chernikov, A. Fast and Anomalous Exciton Diffusion in Two-Dimensional Hybrid Perovskites. *Nano Lett.* **2020**, *20* (9), 6674−6681.
(112) Even, J.; Pedesseau, L.; Jancu, J.-M.; Katan, C. Importance of Spin−Orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* **2013**, *4* (17), 2999−3005.
(113) Imry, Y. Possible Role of Incipient Anderson Localization in the Resistivities of Highly Disordered Metals. *Phys. Rev. Lett.* **1980**, *44* (7), 469−471.
(114) The linear-response spectral density approach discussed in ref 100, sec. S7, which maps the full, non-linear and anharmonic TB model onto an effective Fröhlich-like model with temperature-dependent coupling constants, is similar in spirit to the approach of ref 115, which has been employed along with a cumulant-based quantum mechanical framework for the accurate extraction of mobilities in $SrTiO_3$, see ref 87.
(115) Hellman, O.; Abrikosov, I. A.; Simak, S. I. Lattice Dynamics of Anharmonic Solids from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84* (18), 180301.

https://doi.org/10.1021/acsenergylett.1c00506
ACS Energy Lett. 2021, 6, 2162−2173