

pubs.acs.org/journal/apchd5

Excitons at the Phase Transition of 2D Hybrid Perovskites

Jonas D. Ziegler, Kai-Qiang Lin, Barbara Meisinger, Xiangzhou Zhu, Manuel Kober-Czerny, Pabitra K. Nayak, Cecilia Vona, Takashi Taniguchi, Kenji Watanabe, Claudia Draxl, Henry J. Snaith, John M. Lupton, David A. Egger, and Alexey Chernikov*



ing their robust nature across the phase transition. These findings are unexpected in view of the associated substantial changes of the free carrier masses, strongly contrast broadly considered effective mass and drift-diffusion transport mechanisms, highlighting the unusual nature of excitons in 2D perovskites.

KEYWORDS: 2D perovskites, excitons, phase transition, diffusion

INTRODUCTION

Coulomb-bound electron-hole pairs, commonly known as excitons, dominate the optical response of nanostructured materials.¹ A prominent example is 2D Ruddlesden-Popper halide perovskites hosting tightly bound, mobile exciton quasiparticles.²⁻⁹ Excitons in 2D perovskites are primarily responsible for the absorption and emission of light, governing key material properties for high-efficiency photovoltaic and lighting applications.¹⁰⁻¹⁶ They combine very high binding energies up to 0.5 eV with sizable mobilities,¹⁷⁻¹⁹ exhibiting efficient transport from ambient conditions down to cryogenic temperatures.²⁰ These properties render the material system a promising platform for future optoelectronics and offer a rich playground to study fundamental physics of interacting quasiparticles.

In addition to strongly bound excitons, 2D halide perovskites incorporate soft organic components in their crystal lattice as well as feature highly efficient exciton—phonon coupling and possible polaronic effects.^{4,21-25} A particularly interesting phenomenon in this regard are the structural phase transitions^{26,27} that 2D perovskites inherit from their bulk counterparts. It involves temperature-induced changes of the crystal symmetry with more recent findings indicating a dynamic order—disorder transition.²⁸ Phase transitions in 2D perovskites often occur close to room temperature, strongly affect the optical properties,^{29,30} are sensitive to the layer thickness,⁵ and were recently shown to change the effective masses of the charge carriers.^{7,31} They represent a key feature of this class of materials with potential implications for the design of perovskite-based optoelectronic devices and their response to temperature.

However, in contrast to their 3D counterparts,³² the fundamental properties of excitons in 2D perovskites remain essentially unexplored at the phase transition. Although a recent study finds strong changes in the diamagnetic shifts⁷ attributed to changes of the exciton total mass, the impact of the phase transition on both binding energy and diffusion of excitons is not known. Moreover, the occurrence of a structural phase transition offers a unique opportunity to investigate fundamental properties of excitons including their transport behavior in a well-defined experimental scenario. This is particularly relevant for the case of 2D halide perovskites, as the excitons represent a considerable challenge for appropriate descriptions, exacerbated by their intermediate Wannier– Frenkel nature and the strong coupling to phonons.

Received: July 5, 2022 Published: October 18, 2022





Here, we address these questions by studying excitonic properties across a structural phase transition in a 2D perovskite. Combining non-linear spectroscopy with transient microscopy, we determine temperature-dependent exciton binding energies and monitor exciton diffusion at temperatures directly above and below the phase transition. First-principles calculations demonstrate changes of the carrier masses between the two phases that are concurrent with modification of the single-particle band gap accounting for the observed spectral shift. Surprisingly, both exciton binding energies and the diffusion coefficients are found to be constant between low- and high-temperature phases. These results strongly suggest that excitonic properties do not trivially scale with free carrier masses, challenging the appropriate description of excitons and their dynamics in 2D halide perovskites.

RESULTS

In our study, we used thin layers exfoliated from 2D butylammonium lead iodide crystals, (n = 1) BA₂PbI₄, with about 50 nm thickness, encapsulated between hBN layers for environmental protection³³ and transferred onto SiO₂/Si substrates. The samples were placed into a helium-cooled microscopy cryostat for optical measurements. We used a 80 MHz tunable 140 fs Ti:Sapphire laser for excitation in photoluminescence (PL) experiments and a tungsten-halogen white light source for reflectance. The incident light was focused to a spot with about 1 μ m diameter. The PL was then either dispersed by a grating or deflected by a mirror to obtain spectrally and spatially resolved responses, respectively. A CCD sensor was used for time-integrated signals and we employed a streak camera for time-resolved detection; additional details are provided in Section S3 of Supporting Information.

Phase Transition in 2D Perovskites. The structure of the studied BA_2PbI_4 crystals is schematically illustrated in Figure 1a. The inorganic layers composed of PbI_4 octahedra host the electronic states forming conduction and valence bands at the fundamental band gap of the material. The organic chains between the layers effectively serve as barriers in this natural multi-quantum-well structure. The phase transition, driven by the ordering of the butylammonium chains, changes the relative alignment of the octahedra between the phases.²⁹ In the high-temperature (HT) phase, recent findings emphasize both strong anharmonic fluctuations of the tilt angle and indications of an order–disorder transition.²⁸ In the low-temperature (LT) phase, the octahedra become effectively locked at a larger average distortion angle δ^{31} as illustrated in Figure 1b.

The impact of the phase transition on the optical response of layered alkylammonium lead iodide perovskites is primarily associated with a spectral shift on the order of 100 meV.^{5,29} PL spectra of the studied BA₂PbI₄ samples presented in Figure 1c demonstrate this characteristic effect. As the temperature increases, the dominant exciton peak abruptly shifts to lower energies by 120 meV at about T = 270 K, corresponding to the known temperature range of the phase transition in this class of materials.^{27,29} In addition, the spectra exhibit a continuous, smooth increase of the spectral linewidth from thermal population of vibrational modes and increasingly rapid exciton—phonon scattering at higher temperatures.⁴

For a theoretical analysis, we perform electronic structure calculations using density functional theory (DFT). To this end, we utilize two different DFT codes: VASP,³⁴ implement-



Figure 1. Structural phase transition in 2D perovskites. (a) Schematic illustration of the layered structure of (n = 1) BA₂PbI₄, consisting of alternating organic (butylammonium, BA) and inorganic layers (PbI₄) with layer number *n*. (b) Illustration of thermally induced anharmonic fluctuations of the octahedral tilting in the HT phase, and an effective locking with a larger average distortion angle, δ , in the LT phase (LT). (c) Measured PL spectra of an hBN-encapsulated BA₂PbI₄ thin layer for different temperatures across the phase transition at $T_{\rm PT} = 270$ K.

ing the projector augmented wave potentials³⁵ that uses a plane-wave basis set, and the all-electron full-potential code exciting,³⁶ based on the linearized augmented plane-wave method. We first apply the PBE functional,³⁷ augmented by van der Waals corrections calculated with the Tkatchenko-Scheffler method³⁸ to describe exchange-correlation interactions and include the effects of spin-orbit coupling (SOC). Following previous work,³¹ we show the main changes of the electronic band structure across the phase transition in Figure 2. The electronic band gap between the HT and LT phase differs substantially by 240 meV. Also, SOC has a substantial contribution as verified by additional calculations for a model structure where the BA cations are replaced by Cs (see Supporting Information, Section S2). More specifically, without accounting for SOC we find that the gap changes by only about 110 meV going from the LT to the HT phase.



Figure 2. Electronic band structure across the phase transition. The Kohn–Sham band energies, computed by PBE including SOC are shown between Γ and S (S = 0.5 0.5 0) for the optimized crystal structures of BA₂PbI₄. The VBM of both phases are aligned at zero. The trends in the differences of the band gap and effective masses are consistent between PBE and HSE06 (see Supporting Information, Section S2).



Figure 3. Temperature-dependent exciton binding energy. (a) Two-photon PL excitation (TPLE) and PL spectra of BA₂PbI₄ at T = 5 K. The reflectance contrast spectrum corresponding to the changes of reflectance relative to the substrate is presented in the same graph for comparison. (b) PL and TPLE spectra measured for the LT and HT phases at T = 260 K and T = 275 K, respectively. The spectra are corrected for changes in the effective absorption due to the multi-layer interference effects. The energy separation between ground and excited states Δ_{2p-1s} , proportional to the respective exciton binding energy, is indicated by the dashed lines. (c) Temperature-dependent Δ_{2p-1s} and the corresponding exciton binding energy E_{b} , indicated on the right *y*-axis. For this analysis, the 1s energy was determined from reflectance contrast to exclude any influence of the temperature-dependent Stokes shift, presented in the inset. The error bars are estimated from the fits.

Using the same procedure, we also perform calculations with the hybrid functional $HSE06^{39}$ as implemented in *exciting*.⁴⁰ As expected, the HSE06 functional has a strong impact on the band gap, increasing it in both phases by ~0.6 eV closer to experimental values, yet does not strongly alter the change across the phase transition. Similarly, the absolute values of the effective masses that are substantially lower in the HT phase are confirmed by both PBE and HSE06 calculations.

Hence, based on various electronic structure methods, we find that part of the experimentally observed energy shift can already be attributed to effects that occur at the single-particle level. Specifically, it is a direct consequence of the changes in the average out-of-plane distortion angle of PbI₄ octahedra:³¹ a smaller distortion angle in the HT phase leads to a stronger electronic coupling between individual octahedra and hence to a larger bandwidth and a smaller band gap. For the same reason, the effective masses are substantially smaller in the HT than in the LT phase, which is in line with previous measurements of the diamagnetic shifts and theoretical work.⁷ Moreover, by lifting certain degeneracies of the Pb s states in the valence band and Pb p states in the conduction band, SOC manifests itself in additional changes of the band gap and effective masses. Altogether, when assuming Wanniertype excitons and band-like transport, one would expect both exciton binding energy and exciton diffusion to change accordingly across the phase transition.

Exciton Binding Energy. To measure exciton binding energy as a function of temperature across the phase transition, we employed two-photon photoluminescence excitation (TPLE) spectroscopy; details of the setup are given in Supporting Information, Section S3 and ref 41. The PL signal of the ground-state exciton above 2.3 eV was detected as a function of the laser photon energy tuned between 1.24 and 1.77 eV. In this spectral range, exciton states with p-type orbital symmetry determine two-photon absorption⁴² and the resulting TPLE signal is usually dominated by the 2p transition.^{42–44} The advantage of TPLE, in contrast to linear spectroscopy, is the suppression of direct optical transitions allowing us to detect spectrally broad, weaker signals from excited exciton states both at low and elevated temperatures. An exemplary TPLE spectrum of a BA_2PbI_4 sample is presented in Figure 3a together with the corresponding PL data at a lattice temperature of 5 K. Both the ground and excited states are in good agreement with the measured reflectance contrast spectrum, shown for direct comparison. The analysis of the reflectance spectra using a transfer matrix approach further allows us to correct the measured TPLE spectra for effective two-photon absorption from multi-layer interferences (see Supporting Information, Section S6).

The strongest resonance in the reflectance spectra and the high-energy peak of the PL at 2.54 eV stems from the groundstate exciton transition (1s). The reflectance features weaker replica on the high-energy side. These can arise from multilayer interference effects and are also in the energy range of reported phonon sidebands^{21,24} mimicking the low-energy side of the PL at 5 K (c.f. Figure 1b). The maximum of the TPLE spectrum at 2.87 eV corresponds to the 2p energy with the high-energy flank attributed to weaker contributions of 3p, 4p,... and so forth resonances. In addition, the 2p peak closely corresponds to the energy of the 2p transition weakly visible in the reflectance spectrum. The energy separation between 2p and 1p as well as the near-degeneracy of 2p and 2p excited states are consistent with large exciton binding energies and the properties of excited states in 2D perovskites.^{3,5,6,8}

Figure 3b presents PL and TPLE spectra for two temperatures close to the structural phase transition in the HT and LT regime. At these elevated temperatures, the 1s and 2p resonances broaden and their energy separation slightly increases in comparison to the 5 K data. The main difference between HT and LT spectra is a shift of both ground and excited state peaks to lower energies of about 120 ± 10 meV. The absence of LT and HT peaks in high- and low-temperature spectra, respectively, confirms the absence of phase mixing. The magnitude of the shift is thus essentially the same as for the single-photon PL presented in Figure 1c, compared to values between 110 and 240 meV predicted by first-principles calculations (c.f. Figure 2). Their relative separation Δ_{2p-1st} however, remains constant.



Article

Figure 4. Exciton diffusion at the phase transition. (a) Representative streak camera image of the spatially and time-resolved exciton emission for the LT phase (T = 260 K). The data are normalized at each time step. (b) Extracted change of the mean-squared displacement $\Delta\sigma^2$ for the LT and HT phases as a function of time. Diffusion coefficients are obtained from the slope $\Delta\sigma^2(t)$ indicated by solid lines. (c) Temperature-dependent PL linewidth determined from Lorentz fits presented as full width at half-maximum, corresponding to the change of the exciton—phonon scattering rate. (d) Summary of measured exciton diffusion coefficients (N = 29) across the phase transition for the two phases in the temperature range between 260 and 274 K. Measurement series obtained on the same sample and sample positions are represented by the same symbols. Estimated values from a semi-classical drift-diffusion model based on calculated effective masses and scattering times obtained from PL linewidths are indicated.

Temperature-dependent values for Δ_{2p-1s} are summarized in Figure 3c. In order to exclude an influence of the temperaturedependent Stokes shift, presented in the inset, the 1s energy is determined from reflectance contrast instead of PL. The Stokes shift is on the order of 20 meV for both LT and HT regions at the phase transition and changes smoothly as a function of temperature. The exciton binding energy E_b is then estimated by taking advantage of linear scaling with the energy separation Δ_{2p-1s} . We use the relationship $E_b = 1.2 \times \Delta_{2p-1s}$ from the literature⁸ and present temperature-dependent binding energy on the right *y*-axis in Figure 3c.

The absolute values for the exciton binding energy around 400 meV in BA₂PbI₄ correspond well to the previously reported low-temperature results.^{3,5,6} Interestingly, however, the binding energy does not change between LT and HT phases across the phase transition. This result is rather surprising because the reduced effective mass $\mu = m_{\rm h} m_{\rm e} / (m_{\rm h} +$ $m_{\rm e}$) (see Figure 2) changes from 0.15 (LT) to 0.11 m_0 (HT) across the phase transition. Because the exciton binding energy typically scales with the reduced mass in the Wannier model, these changes should lead to a substantial decrease of the binding energy in the HT phase. Interestingly, the exciton binding energy is not only constant between LT and HT phases but also appears to continuously increase with temperature up to 25% from 5 to 300 K. We note that if we neglect the influence of the Stokes shift, the increase of the binding energy would appear even more pronounced.

Exciton Diffusion. Following the analysis of exciton binding energies, we examine the exciton diffusion—a process commonly expected to be affected by the *total* mass of the exciton. Experimentally, exciton propagation is monitored by detecting spatially and time-resolved PL for a series of temperatures across the phase transition. The samples are excited using energy densities from a few to several 10's of nJ/ cm^2 per pulse. We confirm the absence of density-dependent effects such as exciton—exciton annihilation⁴⁵ (see Supporting Information, Section S7) and perform a series of measurements on different samples and spot positions (see Supporting Information, Section S5). A typical streak camera image of the

time-dependent cross section along the *x* coordinate is shown in Figure 4a for the LT phase at T = 260 K. The signal is normalized at each time step, illustrating continuous broadening of the exciton cloud. For the analysis, the PL intensity profiles are fitted with Gaussian distributions $\propto \exp[-x^2/(2\sigma(t)^2)]$ at time intervals of $\Delta t = 100$ ps. The extracted timedependent change of the variance $\Delta\sigma(t)^2$ is presented in Figure 4b for LT and HT phases at the temperatures of 260 and 270 K, respectively. The corresponding phase and phase purity are verified prior to every single diffusion measurement at each temperature and sample position using spectrally resolved PL, as shown in Figure 1c (see Supporting Information, Sections S3 and S4).

As it is characteristic for diffusive propagation, the variance increases linearly with time for both LT and HT cases. In contrast to the spectral shift of the emission energy, however, the diffusion coefficients D extracted from the slope of $\Delta \sigma^2$ = $2Dt^{46}$ are essentially the same. This observation is accompanied by a nearly continuous increase of the exciton-phonon scattering rate with temperature, reflected in the change of the PL spectral linewidth⁴ as shown in Figure 4c. Within the framework of the semi-classical band-like propagation model, the diffusion coefficient scales with the temperature T, exciton mass $M_{\rm X}$, and scattering rate \hbar/τ as $D = (k_{\rm B} T \times \tau)/M_{\rm X}$. Here, the scattering time is obtained from the linewidth Γ as shown in Figure 4 (c) according to $\tau = \hbar/\Gamma$. As there is practically no change of the linewidth and therefore scattering time is constant across the phase transition, we would expect the diffusivity to follow the change of the total exciton mass by a factor of 1.5 (see Figure 2). In contrast to that, the nearly equal diffusion coefficients of the LT and HT phases mimic the lack of change in the exciton binding energy. Although the absolute values of the diffusion coefficients vary for different flakes and sample positions, possibly related to locally varying inhomogeneity of the energy landscape, the average values for individual measurement series remain nearly constant, as illustrated by Figure 4d. In contrast to the expectation borne from a semi-classical treatment that uses the calculated exciton masses (Figure 2) and scattering times (Figure 3c), we thus do

not find any systematic differences for the exciton diffusion between the two phases.

DISCUSSION

Excitons in 2D perovskites combine seemingly conflicting properties: on the one hand, they show large exciton binding energies that are typically associated with localized Frenkel-type states, whereas on the other hand, the relatively low effective masses and the efficient exciton transport suggest wavefunctions extending over many unit cells, which is typically a Wannier-type feature. The latter consideration also manifests itself in the successful application of effective mass models with modified thin-film Coulomb potentials in combination with first-principles calculations to describe key exciton properties such as binding energies and Bohr radii.^{3,6–9} These models typically involve parameters such as appropriate dielectric screening constants of the organic and inorganic layers and the reduced exciton mass.

Our study provides a unique opportunity to assess such models for BA₂PbI₄ because the phase transition is associated with a change in the average crystal structure, as mentioned above. Indeed we find, in line with previous work, that along with the change of the structure the band gap and effective masses of the system are also modified across the phase transition. Interestingly, although the band gap change is reflected in the spectral shift of the optical transition, the difference of the effective masses of the bare carriers does not manifest itself in any accompanying changes of the exciton binding energy and diffusion constant. Clearly, the canonical effective mass theory for these two key properties does not appear to be fully consistent with the experimental findings. This assessment is based on the bare carrier masses that we have calculated theoretically. This implies that we cannot rule out that the actual masses, renormalized by scattering mechanisms at the various temperatures, more appropriately reflect the demonstrated behavior across the phase transition. Because these masses are also challenging to determine in both experiment and theory, our work altogether demonstrates that our understanding of the exciton properties of 2D perovskites should be reconsidered, potentially along the following.

The observation of a constant exciton binding energy at the structural phase transition strongly implies that the dependence on the effective mass of the *free* carriers is substantially weaker than commonly assumed, especially in view of modified thin-film Coulomb potentials. It is conceivable that the exciton wavefunction could spread over a sufficiently large region of the reciprocal space beyond the effective mass approximation, where the effect of the phase transition on the band curvature may be reduced. It is further relevant to consider that a continuous, temperature-dependent change of the exciton binding energy has been observed in 3D perovskites.^{32,48,49} Among the possible explanations was the associated increase of the dielectric constant at increased temperatures.^{47,48} However, the exciton binding energies in 2D perovskites are on the order of many 100s of meV, more than an order of magnitude larger than in 3D systems (a few to several 10s meV). This should affect the relevant frequency range of the dielectric function⁵⁰ and may relate to the opposite behavior in 2D perovskites, where the exciton binding energy increases with temperature.

It is also possible that the exciton masses are either partially renormalized or even largely determined by polaronic effects that may not change too drastically at the phase transition. We also note that their influence on the experimentally determined values may generally depend on the interplay of magnetic fields and carrier—phonon coupling.^{51,52} The associated renormalization of the effective mass may also be connected to the observed increase of the exciton binding energy with increasing temperature.

Similar considerations can be suggested for exciton diffusion in BA₂PbI₄. In 3D halide perovskites, a dynamic disorder picture has been put forward, which takes into account the strong local fluctuations in the lattice away from the average structure and rationalizes key transport properties in this manner.53-55 While there are important differences between 3D and 2D perovskites, it is interesting that anharmonic fluctuations were recently demonstrated also for the 2D systems.²⁸ Because exciton diffusion appears to be essentially immune to changes in the effective mass of the average structure, one could speculate that it could also largely be governed by different expressions of polaronic effects, such as local fluctuations of the lattice. It is still intriguing, however, that the semi-classical description seems to account for temperature-dependent transport of free excitons in a related system, 2D phenylethylammonium lead iodide.²⁰ However, the general applicability of such models can be challenged in view of the exciton mean free path being typically smaller than their wave packet size, given by the de Broglie wavelength.^{55,56} The observed inadequacy of the semi-classical prediction for the change of the diffusion coefficients at the phase transition provides additional experimental evidence that alternative descriptions for the exciton transport in 2D perovskites should be explored.

CONCLUSIONS

In summary, we have studied the impact of the structural phase transition in 2D perovskites on the exciton properties. Temperature-dependent exciton binding energy and exciton diffusion were monitored across the phase transition using a combination of non-linear spectroscopy and time-resolved microscopy. Both exciton binding energy and exciton diffusion are found to be unaffected by the phase transition. These findings go beyond the expectations of the effective mass description of excitons and the semi-classical understanding of their transport. Our results highlight the unusual behavior of excitons in this class of materials and strongly motivate further developments for their description. Moreover, the robust nature of the excitons with respect to substantial changes of the crystal structure seems particularly promising from the perspective of applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.2c01035.

Additional information and optical pictures on the sample preparation, DFT calculations, two-photon PLE spectroscopy (experimental setup, temperature-dependent spectra, and analysis), temporal and spectral properties of mixed and pure phases, low temperature dynamics, and temperature-dependent PL and reflectance contrast (spectra and analysis) (PDF)

AUTHOR INFORMATION

Corresponding Author

Alexey Chernikov – Integrated Center for Applied Physics and Photonic Materials, Institute of Applied Physics and Würzburg-Dresden Cluster of Excellence ct.qmat, Technische Universität Dresden, Dresden 01062, Germany; Department of Physics, University of Regensburg, Regensburg 93053, Germany; orcid.org/0000-0002-9213-2777; Email: alexey.chernikov@tu-dresden.de

Authors

Jonas D. Ziegler – Integrated Center for Applied Physics and Photonic Materials, Institute of Applied Physics and Würzburg-Dresden Cluster of Excellence ct.qmat, Technische Universität Dresden, Dresden 01062, Germany; Department of Physics, University of Regensburg, Regensburg 93053, Germany

Kai-Qiang Lin – Department of Physics, University of Regensburg, Regensburg 93053, Germany

Barbara Meisinger – Department of Physics, University of Regensburg, Regensburg 93053, Germany

- Xiangzhou Zhu Department of Physics, Technical University of Munich, Garching 85748, Germany
- Manuel Kober-Czerny Department of Physics, Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom
- Pabitra K. Nayak Department of Physics, Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom; Tata Institute of Fundamental Research, Hyderabad 500046, India
- Cecilia Vona nstitut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin 12489, Germany
- Takashi Taniguchi International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Ibaraki 305-004, Japan; Orcid.org/0000-0002-1467-3105
- Kenji Watanabe Research Center for Functional Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305-004, Japan; © orcid.org/0000-0003-3701-8119

Claudia Draxl – nstitut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin 12489, Germany; orcid.org/0000-0003-3523-6657

Henry J. Snaith – Department of Physics, Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom; © orcid.org/0000-0001-8511-790X

John M. Lupton – Department of Physics, University of Regensburg, Regensburg 93053, Germany

David A. Egger – Department of Physics, Technical University of Munich, Garching 85748, Germany; orcid.org/0000-0001-8424-902X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsphotonics.2c01035

Funding

Financial support by the DFG via SPP2196 Priority Program (project-ID: 424709454) and Emmy Noether Initiative (CH 1672/1, project-ID: 287022282) as well as the Würzburg-Dresden Cluster of Excellence on Complexity and Topology in Quantum Matter ct.qmat (EXC 2147, project-ID 390858490) is gratefully acknowledged. D.A.E. acknowledges funding from the Alexander von Humboldt Foundation within the frame-work 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 DFG under Germany's Excellence Strategy—EXC 2089/1-390776260. K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan (grant number JPMXP0112101001) and JSPS KAKENHI (grant numbers 19H05790, 20H00354, and 21H05233). P.K.N. acknowledges support from the Department of Atomic Energy, Government of India, under project identification no. RTI 4007, SERB India core research grant (CRG/2020/003877) and Swarna Jayanti Fellowship, DST, India. C.V. acknowledges the North-German Supercomputing Alliance (HLRN) for providing computational resources.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank our colleagues Matan Menahem, Omer Yaffe, Mikhal Baranowski, and Paulina Plochocka for helpful discussion.

REFERENCES

(1) Haug, H.; Koch, S. W. Quantum Theory of the Optical and Electronic Properties of Semiconductors, 5th ed.; World Scientific, Singapore, 2009.

(2) Ishihara, T.; Takahashi, J.; Goto, T. Exciton state in twodimensional perovskite semiconductor (C10H21NH3)2PbI4. *Solid State Commun.* **1989**, *69*, 933–936.

(3) Tanaka, K.; Takahashi, T.; Kondo, T.; Umebayashi, T.; Asai, K.; Ema, K. Image charge effect on two-dimensional excitons in an inorganic-organic quantum-well crystal. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 045312.

(4) Gauthron, K.; Lauret, J.-S.; Doyennette, L.; Lanty, G.; Al Choueiry, A.; Zhang, S. J.; Brehier, A.; Largeau, L.; Mauguin, O.; Bloch, J.; Deleporte, E. Optical spectroscopy of two-dimensional layered (C6H5C2H4-NH3)2-PbI4 perovskite. *Opt. Express* **2010**, *18*, 5912.

(5) Yaffe, O.; Chernikov, A.; Norman, Z. M.; Zhong, Y.; Velauthapillai, A.; van der Zande, A.; Owen, J. S.; Heinz, T. F. Excitons in ultrathin organic-inorganic perovskite crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 045414.

(6) Blancon, J.-C.; et al. Scaling law for excitons in 2D perovskite quantum wells. *Nat. Commun.* **2018**, *9*, 2254.

(7) Baranowski, M.; Zelewski, S. J.; Kepenekian, M.; Traoré, B.; Urban, J. M.; Surrente, A.; Galkowski, K.; Maude, D. K.; Kuc, A.; Booker, E. P.; Kudrawiec, R.; Stranks, S. D.; Plochocka, P. Phase-Transition-Induced Carrier Mass Enhancement in 2D Ruddlesden– Popper Perovskites. *ACS Energy Lett.* **2019**, *4*, 2386–2392.

(8) Cho, Y.; Berkelbach, T. C. Optical Properties of Layered Hybrid Organic–Inorganic Halide Perovskites: A Tight-Binding GW-BSE Study. J. Phys. Chem. Lett. 2019, 10, 6189–6196.

(9) Cho, Y.; Greene, S. M.; Berkelbach, T. C. Simulations of Trions and Biexcitons in Layered Hybrid Organic-Inorganic Lead Halide Perovskites. *Phys. Rev. Lett.* **2021**, *126*, 216402.

(10) Kumar, Ś.; Jagielski, J.; Yakunin, S.; Rice, P.; Chiu, Y.-C.; Wang, M.; Nedelcu, G.; Kim, Y.; Lin, S.; Santos, E. J. G.; Kovalenko, M. V.; Shih, C.-J. Efficient Blue Electroluminescence Using Quantum-Confined Two-Dimensional Perovskites. *ACS Nano* **2016**, *10*, 9720–9729.

(11) Tsai, H.; et al. High-efficiency two-dimensional Ruddlesden– Popper perovskite solar cells. *Nature* **2016**, *536*, 312–316.

(12) Wang, N.; et al. Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. *Nat. Photonics* **2016**, *10*, 699–704.

(13) Tsai, H.; et al. Stable Light-Emitting Diodes Using Phase-Pure Ruddlesden-Popper Layered Perovskites. *Adv. Mater.* **2018**, *30*, 1704217.

(14) Chen, Y.; Sun, Y.; Peng, J.; Tang, J.; Zheng, K.; Liang, Z. 2D Ruddlesden-Popper Perovskites for Optoelectronics. *Adv. Mater.* **2018**, *30*, 1703487.

(15) Liang, C.; et al. Two-dimensional Ruddlesden–Popper layered perovskite solar cells based on phase-pure thin films. *Nat. Energy* **2021**, *6*, 38–45.

(16) Chen, H.; Lin, J.; Kang, J.; Kong, Q.; Lu, D.; Kang, J.; Lai, M.; Quan, L. N.; Lin, Z.; Jin, J.; Wang, L.; Toney, M. F.; Yang, P. Structural and spectral dynamics of single-crystalline Ruddlesden-Popper phase halide perovskite blue light-emitting diodes. *Sci. Adv.* **2020**, *6*, No. eaay4045.

(17) Deng, S.; Shi, E.; Yuan, L.; Jin, L.; Dou, L.; Huang, L. Longrange exciton transport and slow annihilation in two-dimensional hybrid perovskites. *Nat. Commun.* **2020**, *11*, 664.

(18) Seitz, M.; Magdaleno, A. J.; Alcázar-Cano, N.; Meléndez, M.; Lubbers, T. J.; Walraven, S. W.; Pakdel, S.; Prada, E.; Delgado-Buscalioni, R.; Prins, F. Exciton diffusion in two-dimensional metalhalide perovskites. *Nat. Commun.* **2020**, *11*, 2035.

(19) Xiao, K.; Yan, T.; Liu, Q.; Yang, S.; Kan, C.; Duan, R.; Liu, Z.; Cui, X. Many-body effect in optical properties of monolayer molybdenum diselenide. *J. Phys. Chem. Lett.* **2021**, *12*, 2555–2561.

(20) 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*, 6674–6681.

(21) Straus, D. B.; Hurtado Parra, S.; Iotov, N.; Gebhardt, J.; Rappe, A. M.; Subotnik, J. E.; Kikkawa, J. M.; Kagan, C. R. Direct Observation of Electron–Phonon Coupling and Slow Vibrational Relaxation in Organic–Inorganic Hybrid Perovskites. *J. Am. Chem. Soc.* **2016**, *138*, 13798–13801.

(22) Guo, Z.; Wu, X.; Zhu, T.; Zhu, X.; Huang, L. Electron–Phonon Scattering in Atomically Thin 2D Perovskites. *ACS Nano* **2016**, *10*, 9992–9998.

(23) Wright, A. D.; Verdi, C.; Milot, R. L.; Eperon, G. E.; Pérez-Osorio, M. A.; Snaith, H. J.; Giustino, F.; Johnston, M. B.; Herz, L. M. Electron-phonon coupling in hybrid lead halide perovskites. *Nat. Commun.* **2016**, *7*, 11755.

(24) Urban, J. M.; Chehade, G.; Dyksik, M.; Menahem, M.; Surrente, A.; Trippé-Allard, G.; Maude, D. K.; Garrot, D.; Yaffe, O.; Deleporte, E.; Plochocka, P.; Baranowski, M. Revealing Excitonic Phonon Coupling in (PEA) 2 (MA) n -1 Pb n I 3 n +1 2D Layered Perovskites. J. Phys. Chem. Lett. **2020**, 11, 5830–5835.

(25) Srimath Kandada, A. R.; Silva, C. Exciton Polarons in Two-Dimensional Hybrid Metal-Halide Perovskites. J. Phys. Chem. Lett. 2020, 11, 3173–3184.

(26) Kind, R. Structural phase transitions in perovskite layer structures. *Ferroelectrics* **1980**, *24*, 81–88.

(27) Billing, D. G.; Lemmerer, A. Synthesis, characterization and phase transitions in the inorganic—organic layered perovskite-type hybrids [(C n H 2 n + 1 NH 3) 2 PbI 4], n = 4, 5 and 6. Acta Crystallogr., Sect. B: Struct. Sci. 2007, 63, 735–747.

(28) Menahem, M.; Dai, Z.; Aharon, S.; Sharma, R.; Asher, M.; Diskin-Posner, Y.; Korobko, R.; Rappe, A. M.; Yaffe, O. Strongly Anharmonic Octahedral Tilting in Two-Dimensional Hybrid Halide Perovskites. *ACS Nano* **2021**, *15*, 10153–10162.

(29) Ishihara, T.; Takahashi, J.; Goto, T. Optical properties due to electronic transitions in two-dimensional semiconductors (CnH2n +1NH3)2PbI4. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *42*, 11099–11107.

(30) Martín-García, B.; Spirito, D.; Biffi, G.; Artyukhin, S.; Bonaccorso, F.; Krahne, R. Phase Transitions in Low-Dimensional Layered Double Perovskites: The Role of the Organic Moieties. *J. Phys. Chem. Lett.* **2021**, *12*, 280–286.

(31) Dyksik, M.; Duim, H.; Zhu, X.; Yang, Z.; Gen, M.; Kohama, Y.; Adjokatse, S.; Maude, D. K.; Loi, M. A.; Egger, D. A.; Baranowski, M.; Plochocka, P. Broad Tunability of Carrier Effective Masses in TwoDimensional Halide Perovskites. ACS Energy Lett. 2020, 5, 3609–3616.

(32) Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J. Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites. *Nat. Phys.* **2015**, *11*, 582–587.

(33) Seitz, M.; Gant, P.; Castellanos-Gomez, A.; Prins, F. Long-Term Stabilization of Two-Dimensional Perovskites by Encapsulation with Hexagonal Boron Nitride. *Nanomaterials* **2019**, *9*, 1120.

(34) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(35) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(36) Gulans, A.; Kontur, S.; Meisenbichler, C.; Nabok, D.; Pavone, P.; Rigamonti, S.; Sagmeister, S.; Werner, U.; Draxl, C. exciting: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory. *J. Phys.: Condens. Matter* **2014**, *26*, 363202.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(38) Tkatchenko, A.; Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(39) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.

(40) Vona, C.; Nabok, D.; Draxl, C. Electronic Structure of (Organic-)Inorganic Metal Halide Perovskites: The Dilemma of Choosing the Right Functional. *Adv. Theory Simul.* **2022**, *5*, 2100496.

(41) Lin, K.-Q.; et al. Narrow-band high-lying excitons with negative-mass electrons in monolayer WSe2. *Nat. Commun.* 2021, *12*, 5500.

(42) Wang, F.; Dukovic, G.; Brus, L. E.; Heinz, T. F. The optical resonances in carbon nanotubes arise from excitons. *Science* 2005, 308, 838–841.

(43) Ye, Z.; Cao, T.; O'Brien, K.; Zhu, H.; Yin, X.; Wang, Y.; Louie, S. G.; Zhang, X. Probing excitonic dark states in single-layer tungsten disulphide. *Nature* **2014**, *513*, 214–218.

(44) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. Bright and dark singlet excitons via linear and two-photon spectroscopy in monolayer transition-metal dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 085413.

(45) Warren, J. T.; O'Hara, K. E.; Wolfe, J. P. Two-body decay of thermalized excitons in CuO2. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2000, 61, 8215–8223.

(46) Ginsberg, N. S.; Tisdale, W. A. Spatially Resolved Photogenerated Exciton and Charge Transport in Emerging Semiconductors. *Annu. Rev. Phys. Chem.* **2020**, *71*, 1–30.

(47) Guo, Y.; Yaffe, O.; Hull, T. D.; Owen, J. S.; Reichman, D. R.; Brus, L. E. Dynamic emission Stokes shift and liquid-like dielectric solvation of band edge carriers in lead-halide perovskites. *Nat. Commun.* **2019**, *10*, 1175.

(48) Yamada, Y.; Nakamura, T.; Endo, M.; Wakamiya, A.; Kanemitsu, Y. Photoelectronic Responses in Solution-Processed Perovskite CH₃NH₃PbI₃ Solar Cells Studied by Photoluminescence and Photoabsorption Spectroscopy. *IEEE J. Photovoltaics* **2015**, *5*, 401–405.

(49) Even, J.; Pedesseau, L.; Katan, C. Analysis of Multivalley and Multibandgap Absorption and Enhancement of Free Carriers Related to Exciton Screening in Hybrid Perovskites. *J. Phys. Chem. C* 2014, *118*, 11566–11572.

(50) Glazov, M. M.; Chernikov, A. Breakdown of the Static Approximation for Free Carrier Screening of Excitons in Monolayer Semiconductors. *Phys. Status Solidi B* **2018**, 255, 1800216.

(51) Yamada, Y.; Mino, H.; Kawahara, T.; Oto, K.; Suzuura, H.; Kanemitsu, Y. Polaron Masses in CH₃NH₃PbX₃ Perovskites Determined by Landau Level Spectroscopy in Low Magnetic Fields. *Phys. Rev. Lett.* **2021**, *126*, 237401.

(52) Peeters, F. M.; Devreese, J. T. Magneto-optical absorption of polarons. *Phys. Rev. B* 1986, 34, 7246-7259.

(53) 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*, 8041–8046.

(54) 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*, 196601.

(55) Schilcher, M. J.; Robinson, P. J.; Abramovitch, D. J.; Tan, L. Z.; Rappe, A. M.; Reichman, D. R.; Egger, D. A. The Significance of Polarons and Dynamic Disorder in Halide Perovskites. *ACS Energy Lett.* **2021**, *6*, 2162–2173.

(56) Glazov, M. M. Quantum Interference Effect on Exciton Transport in Monolayer Semiconductors. *Phys. Rev. Lett.* **2020**, *124*, 166802.

Recommended by ACS

Effect of Electron–Phonon Coupling on the Color Purity of Two-Dimensional Ruddlesden–Popper Hybrid Lead Iodide Perovskites

Jing Li, Zhizhen Ye, et al. MARCH 23, 2023 THE JOURNAL OF PHYSICAL CHEMISTRY C

Lasing in Two-Dimensional Tin Perovskites

Ada Lilí Alvarado-Leaños, Annamaria Petrozza, et al. NOVEMBER 24, 2022 ACS NANO

READ 🗹

Luminescence Enhancement Due to Symmetry Breaking in Doped Halide Perovskite Nanocrystals

Ghada H. Ahmed, Sascha Feldmann, et al. AUGUST 17, 2022 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 🗹

Optimizing Broadband Emission in 2D Halide Perovskites

Carina Pareja-Rivera, Diego Solis-Ibarra, *et al.* AUGUST 09, 2022 CHEMISTRY OF MATERIALS READ

Get More Suggestions >