Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites

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Solar cells based on the organic–inorganic tri-halide perovskite family of materials have shown significant progress recently, offering the prospect of low-cost solar energy from devices that are very simple to process. Fundamental to understanding the operation of these devices is the exciton binding energy, which has proved both difficult to measure directly and controversial. We demonstrate that by using very high magnetic fields it is possible to make an accurate and direct spectroscopic measurement of the exciton binding energy, which we find to be only 16 meV at low temperatures, over three times smaller than has been previously assumed. In the room-temperature phase we show that the binding energy falls to even smaller values of only a few millielectronvolts, which explains their excellent device performance as being due to spontaneous free-carrier generation following light absorption. Additionally, we determine the excitonic reduced effective mass to be 0.104 $m_e$ (where $m_e$ is the electron mass), significantly smaller than previously estimated experimentally but in good agreement with recent calculations. Our work provides crucial information about the photophysics of these materials, which will in turn allow improved optoelectronic device operation and better understanding of their electronic properties.

The recent rapid development of perovskite solar cells is revolutionizing the photovoltaic research field, with the latest certified power conversion efficiencies reaching over 20% (ref. 1). Initially developed from the concept of the nanostructured excitonic solar cell where there is no requirement for long-range charge or exciton diffusion1−4, it has now become clear that owing to the remarkable properties of the inorganic–organic perovskite family of materials $ABX_3$ (A = CH$_3$NH$_3$; B = Pb$^2+$; and $X =$ Cl$^-$, I$^-$ and/or Br$^-$) these cells are capable of operating in a comparable configuration and with comparable performance to the best inorganic semiconductors5,6, where the solid absorber layer is sandwiched between n- and p-type charge selective contacts in a planar heterojunction configuration7,8. Despite this success, several fundamental properties of the organic lead tri-halide perovskites remain controversial and poorly known. In particular the binding energy of the excitons ($R^*$), bound electron–hole pairs that are the primary photoexcited species created in the absorption process, is vital to understanding the way that the cells function. The operating mechanisms depend on what fraction of excitons dissociate in the bulk material, giving rise to free-charge transport, or what fraction need to be dissociated at heterojunctions within the cells. Knowledge of the true exciton binding energy is also crucial for interpreting spectroscopic measurements based on these materials, such as time-resolved spectroscopy. Values for $R^*$ reported in the literature cover a broad range from 2 to 55 meV (refs 11–17), with the larger values being initially adopted and a growing number of reports suggesting a wide range of lower values15–17. In addition, basic parameters such as the effective masses of electrons and holes also remain to be directly measured in the archetypical material CH$_3$NH$_3$PbI$_3$. A number of calculations of the band structure in the literature are able to reproduce the observed bandgaps14,18,19 and these suggest that the conduction and valence bands are essentially isotropic and symmetrical14,18,19. A direct measurement of the exciton binding energy and effective masses is therefore crucial for our current understanding and for future development of this remarkable class of materials.

In this work we describe the use of very high-field interband magneto-absorption studies that allow us, unlike previous photoluminescence measurements20, to make an accurate study of the family of free-exciton states, which are the relevant excitations created in photovoltaic devices. In the low-temperature orthorhombic phase we establish that the exciton binding energy is only 16 meV, which is significantly smaller than has been previously assumed. We also investigate the room-temperature tetragonal phase, which occurs above 160 K (refs 11,19), where we find the striking result that the binding energy falls to only a few millielectronvolts. Our measurements give an accurate and independent value for the reduced effective mass and, in addition, show that the essentially symmetric and isotropic conduction and valence bands of the organic–inorganic lead tri-halide perovskites make them model semiconductors to demonstrate the optical properties of excitons in a high magnetic field.

In Fig. 1 we summarize the results of transmission measurements of a ∼300-nm-thick polycrystalline film of CH$_3$NH$_3$PbI$_3$, deposited directly on a glass substrate, measured at 2 K in magnetic fields of up to 65 T in the Faraday configuration using a long (500 ms) pulsed field magnet. Close to the band edge (~1.6 eV), the spectra are dominated by the hydrogen-like exciton states and at higher energies the free-carrier behaviour of the conduction and valence bands gives rise to a series of interband transitions between the van

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Figure 1 | Magnetic field dependence of the optical density for the perovskite CH$_3$NH$_3$PbI$_3$. a. A sequence of optical density (Log(1/Transmission))
spectra measured during a single pulse of the magnetic field. For easier comparison the spectra are offset. The arrows show the energies for the Landau
level absorptions at 65 T. b,c. Sequences of ratios of the transmission in magnetic field T(B) to that measured at zero field T(0), which improves the
resolution of smaller field-dependent features and where the resonant absorption features correspond to minima. b shows the 2s absorption visible at
lower fields and c shows the Landau levels seen at higher fields. The dashed arrows show the magnetic field evolution of the excitonic (b) and Landau level
(c) absorptions as plotted in Fig. 2. The feature highlighted at 2.03 eV in c is a band-edge absorption from a previously undetected higher-energy band
edge and will be the subject of a future publication.

Hove singularities at the bottom of the Landau levels with energies given by:

$$E(B) = E_g + (N + 1/2)\hbar\omega_c \pm 1/2g_{eff}\mu_B B$$

where $E_g$ is the energy gap, $N = 0, 1, 2, 3\ldots$ is the Landau quantum number, $\omega_c = eB/m^*$, $B$ is the applied magnetic field, $e$ is the
elementary charge, $m^*$ is the reduced effective mass of the exciton given by $1/m^* = 1/m_e^* + 1/m_h^*$, where $m_e$ and $m_h$ are the electron and
hole effective masses respectively, $g_{eff}$ is the effective $g$-factor for the Zeeman splitting, and $\mu_B$ is the Bohr magneton. In the present case
we use unpolarized light so that the last term is ignored. In contrast to the early magneto-optical studies on this material$^{12,13}$, our spectra show a clearly resolved 1s exciton at 1.64 eV, which has a large
diamagnetic shift, significantly larger than the peak width and larger than the values observed previously$^{12,13}$. In addition, the spectra we show in Fig. 1 demonstrate several important new features as the field is increased. By 65 T there is a clear sequence of 5 well-resolved Landau level transitions that develop in magnetic fields above 30 T. Furthermore, a small shoulder develops on the high-energy side of the 1s exciton peak, which we identify as the 2s exciton absorption. The appearance of the Landau levels and the 2s exciton state can be seen more clearly by taking the ratio of the high-field spectra to zero field as shown in Fig. 1b,c, where the resonant absorptions
become minima in the ratio of transmission. This shows that the 2s state is clearly visible as a weak but gradually growing absorption in the range 10–35 T. Above 20 T a second absorption grows much more rapidly, which we attribute to a combination of the 2p exciton and the first of the free-electron interband Landau level transitions. The 2p exciton transition is forbidden at zero magnetic field but becomes allowed at high fields owing to the reconstruction of the hydrogenic energy levels that occurs once the cyclotron energy exceeds the exciton binding energy ($\hbar\omega_c > R^*$; ref. 21). At high fields the conventional atomic quantum numbers ($n, l$) are no longer valid and this state is renamed as (1, 0) corresponding to the strongest bound state associated with the $N = 1$ Landau level.

The separation between the sequence of Landau levels visible directly in the absorption spectrum at 65 T immediately allows us to estimate the reduced effective mass to be $m^* \approx 0.1 m_e$, to within a few per cent accuracy, and the separation of the 1s and 2s states at low field (15 meV at 10 T) allows us to estimate an excitonic binding energy, $R^*$, of order 20 meV, which is consistent with the condition $\hbar\omega_c > R^*$ for fields above 14 T in agreement with our preliminary analysis of Fig. 1b. We will present a more detailed fitting to the full family of transitions below, which allows us to deduce a precise value of $R^*$ being $16 \pm 2$ meV. The values for the effective mass are in good agreement with recent calculations$^{14,18}$ and smaller than previous experimental estimates. The excitonic binding energy is
much smaller than the early spectroscopic values\(^{12,13}\) of 30–50 meV although in good agreement with a recently calculated theoretical value\(^{15}\) that takes into account the frequency-dependent refractive index of the perovskite.

We now perform a full fitting, where we also include data taken up to 150 T using a fast-pulse single-turn magnetic field system at a fixed photon energy. To extract accurate values for the effective mass and exciton binding energy from the magnetic field dependence of the transition energies it is important to use full numerical calculations for the magnetic-field-dependent transitions as the data cover a wide range from the low- to the high-magnetic-field limits and no analytical solution exists for the hydrogen atom in a high magnetic field. To do this, we use numerical values\(^{21}\) that scale the most strongly bound excitonic energy levels \(E_{\text{ex}}(\gamma)\) by the use of the dimensionless parameter \(\gamma = h\omega / 2R^*\). This allows us to fit the complete range of magnetic field values. In addition to the excitonic transitions, the higher-energy transitions are known\(^{22}\) to become dominated by simple interband transitions between free-carrier Landau levels as described above. Figure 2 shows the full fan diagram of measured transition energies, together with the calculated transition energies for the excitonic and free-electron transitions and a schematic of the optically allowed transitions observed. The values for the effective mass and exciton binding energy are then adjusted to globally fit the data. In practice the two parameters are dominated by very different parts of the data set and are not strongly interdependent.

The observation of the 2s transition places strong constraints on the exciton binding energy, and the slope and separation of the high-field, high-quantum-number Landau levels strongly constrain the reduced effective mass value. Further confirmation of the exciton binding energy comes from our simultaneous fitting of the diamagnetic shift of the 1s state, as shown in the inset to Fig. 2a, where the binding energy is now also strongly constrained by the accurately determined effective mass. We conclude that the excitonic transitions dominate for the \(N = 0\) landau level (1s, 2s) and the \(N = 1\) (1, 0) level up to \(\sim 50\) T, and free electrons dominate for \(N = 1\) above 50 T and for all higher Landau levels. In the intermediate region a weak splitting of the \(N = 1\) level can just be detected where both transitions are occurring. This clear demonstration of the interchange between excitonic and interband free-carrier transitions is usually masked in more conventional semiconductors by complications brought about by additional degeneracies, such as the light and heavy holes present in III–V or II–VI materials\(^{22,23}\), and is an illustration that in addition to their potential in applications, the organic–inorganic metal trihalide perovskites can also act as excellent model semiconductors.

A further interesting observation from the fan charts in Fig. 2 is that the Landau level separations are not significantly decreasing at higher energies (and in a related observation the Landau level fans show good linearity). This suggests that the approximation of a constant effective mass is good for a wide range of band energies and non-parabolicity effects are relatively small compared with some predictions\(^{24}\).

The value deduced for the effective mass of \(m^* = 0.104 \pm 0.003 m_e\) is remarkably close to that of 0.099\(m_e^*\) predicted recently by Menendez-Proupin et al.\(^{14}\) who have adjusted the amount of exchange coupling to match the experimentally measured values of the bandgap, and Umari et al.\(^{15}\), who find 0.11\(m_e^*\). We find the exciton binding energy \((R^*)\) to be 16 ± 2 meV, in contrast to the earlier values of 37–50 meV reported in refs 12, 13, also determined at 4 K, which were deduced by fitting only the 1s state without an independent measurement of the effective mass and using

![Figure 2 | Energy ‘fan’ diagrams.](image-url)
only a low-magnetic-field approximation and with much poorer experimental resolution. Our value here is also strongly supported by the extrapolation of the free-electron transitions to zero magnetic field, which fixes the excitonic continuum.

Several authors have pointed out that using lower mass values ($0.1 m_e$) and depending on whether the low- ($\epsilon = 25.7$) or high- ($\epsilon = 5.6$) frequency dielectric constant is used, the conventional Wannier–Mott hydrogenic model gives values for the excitonic binding energy ($R = m^* e^2/2\hbar^2 \epsilon^2$) anywhere from 2 to 50 meV. In practice the exciton binding energies are comparable to several of the phonon modes and so it is likely that the appropriate dielectric constant at the equivalent frequency will be intermediate between the low- and high-frequency limits or could approach the low-frequency limit as discussed for CsSnX$_2$ perovskites. Our values of $R$ and $m^*$ suggest a value of $\epsilon \approx 9$ assuming the hydrogenic model. In fact Even et al. have recently argued from fitting the lineshape of the low-temperature absorption that the exciton binding energy as discussed above.

We show the optical density spectra taken in the long-pulse system in Fig. 4a, which shows that the 1s exciton has considerably more broadening and as a result it is much harder to make an accurate analysis of the diamagnetic shift of the 1s transition energy, in comparison with that of the lower-temperature phase. The exciton binding energy is more difficult to fit precisely because the absolute energy of the 1s exciton state is less certain and would need to be fitted with a knowledge of the scattering processes and the dielectric function. A detailed examination of the 1s exciton absorption spectra, as in the low-temperature diagram, indicates that the transition becomes much more resolved at higher magnetic fields and actually moves down in energy at first (dashed line, Fig. 4a). Both the increase in intensity and the reduction in transition energy with increasing field suggest that the exciton binding energy is increasing with the magnetic field. We attribute this to a decrease in dielectric constant resulting from the additional magnetic binding of the exciton.

Using only the high-field ($B > 50$ T) spectra where Landau levels can be observed and the 1s exciton peak is well formed, we estimate a binding energy of the order of 10–12 meV in high magnetic fields. We extrapolate the high-energy free-carrier Landau levels to a band-edge energy very close to the apparent 1s exciton peak at $B = 0$, which allows us to conclude that the exciton binding energy is much smaller at zero magnetic field, with a value less than our measurement uncertainty of a few millielectronvolts. This strongly supports the suggestion by Even et al. that the binding energy is reduced to values of order 5 meV above the phase transition to the orthorhombic phase and the recent analysis of Yamada et al. that there is a decrease to around 6 meV at room temperature.

The overall picture is that there is a critical collapse of the exciton binding energy as a function of both increasing temperature and decreasing magnetic field. As the temperature increases, any fall in structural phase transitions from cubic ($T > 350$ K) to tetragonal ($T > 145$ K) to orthorhombic (low $T$) that result in changes in band structure and bandgap. The tetragonal (room temperature) and orthorhombic phases have similar band structures, with almost symmetric and isotropic direct bandgaps at the $\Gamma$-point, with the bandgap increasing by $\sim 100$ meV at the phase transition to the orthorhombic phase, although the magnitude of the bandgap change is dependent on the growth process. Although the band structures are very similar the phase transition may be expected to produce significant changes in the phonon structure and consequently may significantly affect the dielectric constant and hence the exciton binding energy as discussed above.

In Fig. 3, we extend the interband magneto-optical spectra up to 150 T using a fast-pulse single-turn magnetic field system, which shows the magnetic-field-dependent transmission for a series of temperatures at a fixed photon energy. From this data it is very easy to observe the influence of the lower-temperature phase change. Two strong transmission minima can be observed in the low-temperature data that begin to move towards lower field values as the temperature increases. This is because the perovskite bandgap increases with increasing temperature, causing the interband magneto-optical transitions at a fixed energy to shift towards lower magnetic field values. Above 140 K there is a sudden rapid shift upwards of the resonance fields caused by the structural phase transition to the high-temperature tetragonal phase, which has a lower bandgap. We then repeat the magneto-optical study in this tetragonal phase using the fast-pulse system as we show in Fig. 3b.

We show the optical density spectra taken in the long-pulse system in Fig. 4a, which shows that the 1s exciton has considerably more broadening and as a result it is much harder to make an accurate analysis of the diamagnetic shift of the 1s transition energy, in comparison with that of the lower-temperature phase. The exciton binding energy is more difficult to fit precisely because the absolute energy of the 1s exciton state is less certain and would need to be fitted with a knowledge of the scattering processes and the dielectric function. A detailed examination of the 1s exciton absorption spectra, as in the low-temperature diagram, indicates that the transition becomes much more resolved at higher magnetic fields and actually moves down in energy at first (dashed line, Fig. 4a). Both the increase in intensity and the reduction in transition energy with increasing field suggest that the exciton binding energy is increasing with the magnetic field. We attribute this to a decrease in dielectric constant resulting from the additional magnetic binding of the exciton.
binding energy decreases the frequency of motion of the electron and hole bound in the exciton leading to increased contributions to the dielectric constant from the many phonon modes and molecular rotations present in these materials. The fall in binding energy leads to a further increase in dielectric constant and the binding energy collapses to a value close to that predicted by using the low-frequency dielectric constant, giving a value of a few meV. When a magnetic field is applied the process is partly reversed owing to the additional cyclotron motion which causes an increase in the binding energies. Similarly low exciton binding energies due to a frequency-dependent dielectric constant have been predicted in the CsSnX₃ (X = I, Br, Cl) perovskite halide semiconductors, which have very similar band and crystal structures to the organic–inorganic lead tri-halide perovskites studied here, previously leading to significant experimental controversy. An immediate consequence of the temperature and magnetic field dependence of the exciton binding energy is that the interpretation of the earlier literature measurements as giving an exciton binding energy of 30–50 meV, which are based on the assumption of a constant binding energy as a function of magnetic field or temperature, will be invalidated. Hence, our measurements show that the exciton binding energies are much smaller than previously concluded and explain why the properties of the organic–inorganic perovskites in the room-temperature phase will be dominated by free-carrier behaviour as suggested by more recent time-resolved studies.

We also show in Fig. 4 the temperature dependence of the magnetic-field position of the N = 1 Landau level resonance, compared with the temperature dependence of the bandgap as deduced from the film absorption. The sudden shift in resonance position of 63 T at the phase transition temperature can be shown to be equivalent to a change in bandgap of 105 meV from the slope of the N = 1 resonance (1.67 meV T⁻¹), consistent with the 100 meV change in bandgap deduced from absorption. This confirms that the magneto-spectroscopy is measuring the same fundamental band structure as the optical absorption.

Our basic conclusion is that the excitonic binding energy in the low-temperature phase of the organic–inorganic perovskite, CH₃NH₃PbI₃, is much smaller (16 ± 2 meV) than has previously been estimated and is comparable to conventional III–V semiconductors with a similar bandgap. Our measurements in the room-temperature phase suggest that there is a critical collapse of the exciton binding energies at higher temperatures, as predicted, due to the frequency-dependent dielectric constant. By room temperature, the appropriate binding energy will be only a few millielectronvolts and the photovoltaic device performance is essentially a free-carrier phenomenon. This result conclusively shows that the very impressive performance of photovoltaic devices using this material can be attributed to the spontaneous generation of free electrons and holes following photoabsorption, thereby also resolving the apparent contradiction between initial reports of sizeable exciton binding energy values (30–50 meV) and recent reports of free-carrier behaviour. The reason for the difference between our observations and previous estimates of the binding energy is primarily the combination of higher quality, much more crystalline films, and the use of very high magnetic

Figure 4 | Transmission in high-temperature tetragonal phase. a, Optical density, with the dashed line showing the anomalous behaviour of the 1s exciton transition. The arrows show the positions of the excitonic and Landau level absorptions as plotted in b, b, Fan diagram using data from long-pulse fixed-field spectra (black circles) and fixed-energy fast-field-sweep data (red stars). The calculated transition energies are shown for the free-electron and hole levels (solid lines) and the excitonic transitions (dashed lines). c, Temperature-dependent bandgaps and resonance positions for the N = 1 inter-Landau level transition.
fields. This has enabled us to measure multiple excitonic transitions that allow precise spectroscopic measurements, in contrast to previous works that have relied exclusively on measuring the 1s exciton and require assumptions to be made about the dielectric constant and effective masses \(^{11,13}\). The effective mass values of \(\sim 0.1m_e\), which we have determined, are in good agreement with recent calculations \(^{14,18,19}\) but are also significantly lower than the earlier experimental estimates \(^{12,15}\).

**Methods**

Methods and any associated references are available in the online version of the paper.

Received 30 January 2015; accepted 6 May 2015; published online 15 June 2015

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Acknowledgements

The authors thank: Meso-superstructured Hybrid Solar Cells—MESCO NMP-2013-SMAL-7 604032 project. H.J.S thanks for financial support the Engineering and Physical Sciences Research Council (EPSRC), and the European Research Council (ERC-StG 2011 HYPER Project no. 279881). S. Stranks thanks Worcester College, Oxford, for additional financial support. P.P. thanks ANR JCJC project milliPICS, Region Midi-Pyrenees contract MERS 13053031. A. Miyata thanks the JSPS postdoctoral fellowships for research abroad for support. This work was supported by EuroMagNETII under the EU contract No. 228043.

Author contributions

A.Miyata, A.Mitioglu, P.P., O.P. and R.I.N collected and analysed the data. J.T.W.W. and S.D.S. prepared the samples. All authors contributed to the interpretation and the manuscript preparation. R.I.N. supervised and initiated the project.

Additional information

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Competing financial interests

The authors declare no competing financial interests.
Methods

Samples were prepared on glass substrates cleaned sequentially in hallmanex, acetone, isopropanol and O₂ plasma. The polycrystalline CH₃NH₃PbI₃ perovskite films were deposited in a nitrogen-filled glovebox following the interdiffusion preparation methods described previously. In brief, a PbI₂ layer was first deposited on cleaned glass by spin-coating (speed/ramp = 6,000 r.p.m./6,000 r.p.m. s⁻¹, time = 35 s) from a precursor solution of PbI₂ in DMF with a concentration of 450 mg ml⁻¹, followed by drying at 70 °C for 5 min. Then the MAI layer was deposited on dried PbI₂ film by spin-coating (speed/ramp = 6,000 r.p.m./6,000 r.p.m. s⁻¹, time = 35 s) from a precursor solution of MAI in isopropanol with a concentration of 50 mg ml⁻¹, followed by annealing at 100 °C for 1 h. The perovskite films were sealed by spin-coating a layer of the insulating polymer poly(methyl methacrylate) (PMMA; 10 mg ml⁻¹, speed/ramp = 1,000 r.p.m./1,000 r.p.m. s⁻¹, time = 60 s) on top to ensure air and moisture insensitivity.

The magneto-optical measurements have been performed using 70 T long-duration and 150 T short-duration pulsed magnets in the high magnetic field laboratory in Toulouse. For the long-pulsed measurements (~500 ms duration) the sample was immersed in liquid or gaseous helium in a cryostat. A tungsten halogen lamp was used to provide a broad spectrum in the visible and near-infrared range. The absorption was measured in the Faraday configuration in which k, the wave propagation vector, is parallel to the magnetic field B. A nitrogen-cooled CCD (charge-coupled device) array coupled to a spectrometer collected the light transmitted through the sample. The exposure time was 3 ms to limit variations in the magnetic field during acquisition. Thirty spectra were taken during a 70 T shot of the magnetic field. The magnetic field was measured using a calibrated pick-up coil. All spectra were normalized to both the incident intensity and by the zero field transmission to produce absolute and differential transmission spectra. For the short-duration (10 μs) pulsed measurements a series of diode and Ti-sapphire laser lines was sent through and collected from the sample using fibre optics and detected using a fast (100 MHz) silicon detector and a high-speed digital oscilloscope. The sample was mounted inside a non-conducting helium flow cryostat and was cooled separately for each measurement. The magnetic fields were generated by a semidestructive single-turn coil system using 10 mm coils.

References

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