Direct Measurement of the Exciton Binding Energy and Effective Masses for Charge carriers in an Organic-Inorganic Tri-halide Perovskite

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Solar cells based on the organic-inorganic tri-halide perovskite family of materials have shown remarkable 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

[1]

25 **their excellent device performance due to spontaneous free carrier generation following**

26 **light absorption. Additionally, we determine the excitonic reduced effective mass to be**

27 **$0.104m_e$ (where m_e is the electron mass), significantly smaller than previously estimated**

28 **experimentally but in good agreement with recent calculations. Our work provides crucial**

29 **information about the photophysics of these materials, which will in turn allow improved**

30 **optoelectronic device operation and better understanding of their electronic properties**

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32

33 The recent rapid development of perovskite solar cells is revolutionizing the photovoltatic (PV)

34 research field, with the latest certified power conversion efficiencies reaching over 20% [1].

35 Initially developed from the concept of the nanostructured excitonic solar cell where there is no

36 requirement for long range charge or exciton diffusion [1-8], it has now become clear that due to

37 the remarkable properties of the inorganic-organic perovskite family of materials ABX_3

38 ($A=CH_3NH_3^+$; $B=Pb^{2+}$; and $X = Cl^-$, I^- and/or Br^-) these cells[2-10] are capable of operating in a

39 comparable configuration and with comparable performance to the best inorganic

40 semiconductors, [7, 9,10] where the solid absorber layer is sandwiched between n- and p-type

41 charge selective contacts in a planar heterojunction configuration [7-8]. Despite this success

42 several fundamental properties of the organic lead tri-halide perovskites remain controversial and

43 poorly known. In particular the binding energy of the excitons (R*), bound electron-hole pairs

44 that are the primary photoexcited species created in the absorption process, is vital to

45 understanding the way that the cells function. The operating mechanisms depend upon what

46 fraction of excitons dissociate in the bulk material, giving rise to free charge transport, or what

47 fraction need to be dissociated at heterojunctions within the cells. Knowledge of the true exciton

48   binding energy is also crucial for interpreting spectroscopic measurements based on these

49   materials, such as time-resolved spectroscopy. Values for R* reported in the literature cover a

50   broad range from 2 to 55 meV[11-17], with the larger values being initially adopted and a growing

51   number of reports suggesting a wide range of lower values[15-17]. In addition basic parameters such

52   as the effective masses of electrons and holes also remain to be directly measured in the

53   archetypical material $CH_3NH_3PbI_3$. A number of calculations of the band structure in the

54   literature are able to reproduce the observed band gaps[14,18,19] and these suggest that the

55   conduction and valence bands are essentially isotropic and symmetrical[14,18,19]. A direct

56   measurement of the exciton binding energy and effective masses is therefore crucial for our

57   current understanding and for future development of this remarkable class of materials.

58   In this work we describe the use of very high field inter-band magneto-absorption studies which

59   allow us, unlike previous PhotoLuminescence measurements[20], to make an accurate study of the

60   family of free exciton states, which are the relevant excitations created in PV devices. In the low

61   temperature orthorhombic phase we establish that the exciton binding energy is only 16 meV,

62   which is significantly smaller than has been previously assumed. We also investigate the room

63   temperature tetragonal phase, which occurs above 160K[11,19], where we find the striking result

64   that the binding energy falls to only a few millielectron volts. Our measurements give an

65   accurate and independent value for the reduced effective mass and in addition, show that the

66   essentially symmetric and isotropic conduction and valence bands of the organic-inorganic lead

67   tri-halide perovskites makes them model semiconductors to demonstrate the optical properties of

68   excitons in a high magnetic field.

69

70   In Fig. 1 we summarize the results of transmission measurements of a ~300-nm thick

71   polycrystalline film of $CH_3NH_3PbI_3$, deposited directly on a glass substrate, measured at 2 K in

72   magnetic fields of up to 65 T in the Faraday configuration using a long (500ms) pulsed field

73   magnet. Close to the band edge (~1.6 eV), the spectra are dominated by the hydrogen-like

74   exciton states and at higher energies the free carrier behaviour of the conduction and valence

75   bands gives rise to a series of interband transitions between the van Hove singularities at the

76   bottom of the Landau levels with energies given by:

77    $$E(B) = E_g + \left(N + \frac{1}{2}\right)\hbar\omega_c \pm \frac{1}{2}\,g_{eff}\mu_B B,$$

78   where E_g is the energy gap, N=0,1,2,3.. is the Landau quantum number, $\omega_c = eB/m^*$, B is the

79   applied magnetic field, e is the elementary charge, m* is the reduced effective mass of the

80   exciton given by, $1/m^*=1/m^*_e+1/m^*_h$, where m_e and m_h are the electron and hole effective

81   masses respectively, g_{eff} is the effective g-factor for the Zeeman splitting, and μ_B is the Bohr

82   magneton. In the present case we use unpolarised light so that the last term is ignored. In contrast

83   to the early magneto-optical studies on this material[12,13] our spectra show a clearly resolved 1s

84   exciton at 1.64 eV, which has a large diamagnetic shift, significantly larger than the peak width

85   and larger than the values observed previously[12,13]. In addition, the spectra we show in Fig. 1

86   demonstrate several important new features as the field is increased. By 65T there is a clear

87   sequence of 5 well-resolved Landau level transitions which develop in magnetic fields above

88   30T. Furthermore, a small shoulder develops on the high energy side of the 1s exciton peak

89   which we identify as the 2s exciton absorption. The appearance of the Landau levels and the 2s

90   exciton state can be seen more clearly by taking the ratio of the high field spectra to zero field as

91   shown in Fig. 1b and 1c, where the resonant absorptions become minima in the ratio of

92   transmission. This shows that the 2s state is clearly visible as a weak but gradually growing

[4]

93 absorption in the range 10 - 35 T.   Above 20 T a second absorption grows much more rapidly

94 which we attribute to a combination of the 2p exciton and the first of the free-electron inter-band

95 Landau level transitions. The 2p exciton transition is forbidden at zero magnetic field but

96 becomes allowed at high fields due to the re-construction of the hydrogenic energy levels which

97 occurs once the cyclotron energy exceeds the exciton binding energy ($\hbar\omega_c > R^*$) [21]. At high

98 fields the conventional atomic quantum numbers (n, l) are no longer valid and this state is

99 renamed as (1,0) corresponding to the strongest bound state associated with the N=1 Landau

100 level.

101

102 The separation between the sequence of Landau levels visible directly in the absorption spectrum

103 at 65T immediately allows us to estimate the reduced effective mass to be $m^* \approx 0.1\ m_e$ to within

104 a few per cent accuracy, while the separation of the 1s and 2s states at low field (15 meV at 10 T)

105 allows us to estimate an excitonic binding energy, R^*, of order 20 meV, which is consistent with

106 the condition $\hbar\omega_c > R^*$ for fields above 14T in agreement with our preliminary analysis of fig.

107 1b. We will present a more detailed fitting to the full family of transitions below, which allows

108 us to deduce a precise value of R^* being 16±2 meV.   The values for the effective mass are in

109 good agreement with recent calculations[14,18] and somewhat smaller than previous experimental

110 estimates. The excitonic binding energy is much smaller than the early spectroscopic values[12,13]

111 of 30-50 meV although in good agreement with a recently calculated theoretical value[15] which

112 takes into account the frequency dependent refractive index of the perovskite.

113

114 We now perform a full fitting, where we also include data taken up to 150T using a fast pulse

115 single turn magnetic field system at a fixed photon energy. In order to extract accurate values for

116   the effective mass and exciton binding energy from the magnetic field dependence of the

117   transition energies it is important to use full numerical calculations for the magnetic field

118   dependent transitions as the data cover a wide range from the low to the high magnetic field

119   limits and no analytical solution exists for the hydrogen atom in a high magnetic field. To do this

120   we use the values calculated by Makado and Magill[21] which scale the most strongly bound

121   excitonic energy levels $E_{n,0}(\gamma)$ by the use of the dimensionless parameter $\gamma=\hbar\omega_c/2R^*$. This

122   allows us to fit the complete range of magnetic field values. In addition to the excitonic

123   transitions, the higher energy transitions are known[22] to become dominated by simple interband

124   transitions between free carrier Landau levels as described above. Fig. 2 shows the full fan

125   diagram of measured transition energies, together with the calculated transition energies for the

126   excitonic and free electron transitions and a schematic of the optically allowed transitions

127   observed. The values for the effective mass and exciton binding energy are then adjusted to

128   globally fit the data. In practice the two parameters are dominated by very different parts of the

129   data set and are not strongly interdependent.

130

131   The observation of the 2s transition places strong constraints upon the exciton binding energy,

132   while the slope and separation of the high field, high quantum number Landau levels strongly

133   constrain the reduced effective mass value. Further confirmation of the exciton binding energy

134   comes from our simultaneous fitting of the diamagnetic shift of the 1s state, as shown in the inset

135   to Fig. 2a, where the binding energy is now also strongly constrained by the accurately

136   determined effective mass. We conclude that the excitonic transitions dominate for the N=0

137   landau level (1s, 2s) and the N=1 (1,0) level up to ~50T, and free electrons dominate for N=1

138   above 50T and for all higher Landau levels. In the intermediate region a weak splitting of the

139 N=1 level can just be detected where both transitions are occurring. This clear demonstration of

140 the interchange between excitonic and interband free carrier transitions is usually masked in

141 more conventional semiconductors by complications brought about by additional degeneracies,

142 such as the light and heavy holes present in III-V or II-VI materials[22,23] and is an illustration that

143 in addition to their potential in applications, the organic-inorganic metal tri-halide perovskites

144 can also act as excellent model semiconductors. A further interesting observation from the fan

145 charts in Fig. 2 is that the Landau level separations are not significantly decreasing at higher

146 energies (and in a related observation the Landau level fans show good linearity). This suggests

147 that the approximation of a constant effective mass is good for a wide range of band energies and

148 non-parabolicity effects are relatively small compared with some predictions[24].

149   The value deduced for the effective mass of $m^*=0.104\pm0.003$ m_e is remarkably close to

150 that of 0.099 m_e predicted recently by Menendez et al [14] who have adjusted the amount of

151 exchange coupling in order to match the experimentally measured values of the band gap, and

152 Umari et al[18], who find 0.11 me. We find the exciton binding energy (R*) to be 16±2 meV, in

153 contrast to the earlier values of 37 to 50 meV reported in [12,13], also determined at 4K, which

154 were deduced by fitting only the 1s state without an independent measurement of the effective

155 mass and using only a low magnetic field approximation and with much poorer experimental

156 resolution. Our value here is also strongly supported by the extrapolation of the free electron

157 transitions to zero magnetic field, which fixes the excitonic continuum.

158   Several authors [14-17] have pointed out that using lower mass values (0.1 m_e) and

159 depending on whether the low ($\varepsilon = 25.7$) or high ($\varepsilon = 5.6$) frequency dielectric constant is

160 used[18,24] the conventional Wannier-Mott Hydrogenic model gives values for the excitonic

161 binding energy ($R^*=m^*e^4/2\hbar^2\varepsilon^2$) anywhere from 2 -50 meV. In practice the exciton binding

[7]

162   energies are comparable to several of the phonon modes[25] and so it is likely that the appropriate

163   dielectric constant at the equivalent frequency will be intermediate between the low and high

164   frequency limits or could approach the low frequency limit as discussed by Huang and

165   Lambrecht [23] for $CsSnX_3$ perovskites. Our values of R* and m* suggest a value of $\varepsilon \approx 9$

166   assuming the hydrogenic model. In fact Even et al [15] have recently argued from fitting the

167   lineshape of the low temperature absorption that the exciton binding energy should be on the

168   order of 15 meV, and that as a result of the new rotational motion of the $CH_3NH_3^+$ cations in the

169   high temperature phase there is an additional contribution to the dielectric screening which

170   makes the exciton binding energy fall discontinuously to 5 meV at the transition to the high

171   temperature phase where the photovoltaic cells operate. In a similar analysis of the temperature

172   dependent absorption, Yamada et al[16] conclude that the exciton binding energy decreases

173   continuously from 30 meV at 13K to 6 meV at 300K.

174

175   An important factor in understanding the band structure of the organic-inorganic lead tri-halide

176   perovskite is the presence of structural phase transitions from cubic (T>350K) to tetragonal

177   (T>145K) to orthorhombic (low T) which result in changes in band structure and band gap[11,19].

178   The tetragonal (room temperature) and orthorhombic phases have similar band structures, with

179   almost symmetric and isotropic direct band gaps at the Γ-point, with the band gap increasing by

180   ~100 meV at the phase transition to the orthorhombic phase[11,15, 16, 27], although the magnitude of

181   the band gap change is dependent on the growth process[15, 16]. Although the band structures are

182   very similar the phase transition may be expected to produce significant changes in the phonon

183   structure and consequently may significantly affect the dielectric constant and hence the exciton

184   binding energy as discussed above.

185

186   In Fig. 3, we extend the interband magneto-optical spectra up to 150T using a fast pulse single

187   turn magnetic field system, which shows the magnetic field dependent transmission for a series

188   of temperatures at a fixed photon energy. From this data it is very easy to observe the influence

189   of the lower temperature phase change. Two strong transmission minima can be observed in the

190   low temperature data which begin to move towards lower field values as the temperature

191   increases. This is because the perovskite band gap increases [13] with increasing temperature,

192   causing the interband magneto-optical transitions at a fixed energy to shift towards lower

193   magnetic field values. Above 140K there is a sudden rapid shift upwards of the resonance fields

194   caused by the structural phase transition to the high temperature tetragonal phase, which has a

195   lower band gap. We then repeat the magneto-optical study in this tetragonal phase using the fast

196   pulse system as we show in fig. 3b. At these temperatures, significantly fewer resonances are

197   resolved, but it is still possible to observe several different inter-Landau level transitions and it is

198   possible to construct a good fan diagram(fig. 4b). This shows that the effective mass is

199   essentially the same ($m^*=0.104\pm0.005\ m_e$) as at low temperature in the orthorhombic phase,

200   although the band gap is slightly (~50 meV) smaller than at 2K.

201

202   We show the optical density spectra taken in the long pulse system in Fig. 4a, which shows that

203   the 1s exciton has considerably more broadening and as a result it is much harder to make an

204   accurate analysis of the diamagnetic shift of the 1s transition energy, in comparison to that of the

205   lower temperature phase. The exciton binding energy is more difficult to fit precisely because the

206   absolute energy of the 1s exciton state is less certain and would need to be fitted with a

207   knowledge of the scattering processes and the dielectric function. A detailed examination of the

208 1s exciton absorption spectra, as in fig. 4a, shows that there is an anomalous behavior in which

209 the transition becomes much more resolved at higher magnetic fields and actually moves down

210 in energy at first (dashed line, fig. 4a). Both the increase in intensity and the reduction in

211 transition energy with increasing field suggest that the exciton binding energy is increasing with

212 the magnetic field. We attribute this to a decrease in dielectric constant resulting from the

213 additional magnetic binding of the exciton.

214

215   Using only the high field (B>50 T) spectra where Landau levels can be observed and the 1s

216 exciton peak is well formed, we estimate a binding energy on the order of 10-12 meV *in high*

217 *magnetic fields*. We extrapolate the high energy free carrier Landau levels to a band edge energy

218 very close to the apparent 1s exciton peak at B=0 which allows us to conclude that the exciton

219 binding energy is much smaller at zero magnetic field, with a value less than our measurement

220 uncertainty of a few meV. This strongly supports the suggestion by Even et al[15] that the binding

221 energy is reduced to values of order 5 meV above the phase transition to the orthorhombic phase

222 and the recent analysis of Yamada et al [16] that there is a decrease to around 6meV at room

223 temperature.

224

225 The overall picture is that there is a critical collapse of the exciton binding energy as a function

226 of both increasing temperature and decreasing magnetic field. As the temperature increases any

227 fall in binding energy decreases the frequency of motion of the electron and hole bound in the

228 exciton leading to increased contributions to the dielectric constant from the many phonon

229 modes and molecular rotations present in these materials. The fall in binding energy leads to a

230 further increase in dielectric constant and the binding energy collapses to a value close to that

231   predicted by using the low frequency dielectric constant, giving a value of a few meV. When a

232   magnetic field is applied the process is partly reversed due to the additional cyclotron motion

233   which increases the binding energies. Similarly low exciton binding energies due to a frequency

234   dependent dielectric constant have been predicted [26] in the $CsSnX_3$ (X = I, Br, Cl) perovskite

235   halide semiconductors which have very similar band and crystal structures to the organic-

236   inorganic lead tri-halide perovskites studied here, previously leading to significant experimental

237   controversy [26,28]. An immediate consequence of the temperature and magnetic field dependence

238   of the exciton binding energy is that the interpretation of the earlier literature measurements as

239   giving an exciton binding energy of 30-50 meV, which are based on the assumption of a constant

240   binding energy as a function of magnetic field [12,13], or temperature [11], will be invalidated. Hence,

241   our measurements show that the exciton binding energies are much smaller than previously

242   concluded and explain why the properties of the organic-inorganic perovskites in the room

243   temperature phase will be dominated by free carrier behavior as suggested by more recent time

244   resolved studies[17,20,25,27,30,31].

245

246   We also show in Fig. 4 the temperature dependence of the magnetic field position of the N=1

247   Landau level resonance, compared with the temperature dependence of the band gap as deduced

248   from the film absorption. The sudden shift in resonance position of 63T at the phase transition

249   temperature can be shown to be equivalent to a change in band gap of 105 meV from the slope of

250   the N=1 resonance (1.67 meV/T), consistent with the 100 meV change in band gap deduced from

251   absorption. This confirms that the magneto-spectroscopy is measuring the same fundamental

252   band structure as the optical absorption.

253

254 Our basic conclusion is that the excitonic binding energy in the low temperature phase of the

255 organic-inorganic perovskite, $CH_3NH_3PbI_3$ is much smaller (16 ± 2 meV) than has previously

256 been estimated and is comparable to conventional III-V semiconductors with a similar band

257 gap[29]. Our measurements in the room temperature phase suggest that there is a critical collapse

258 of the exciton binding energies at higher temperatures, as has been predicted by Even et al [15], due

259 to the frequency dependent dielectric constant. By room temperature the appropriate binding

260 energy will be only a few milli-electron-volts and the photovoltaic device performance is

261 essentially a free carrier phenomenon. This result conclusively shows that the very impressive

262 performance of PV devices using this material[1-10] can be attributed to the spontaneous generation

263 of free electrons and holes following photo-absorption, thereby also resolving the apparent

264 contradiction between initial reports of sizeable exciton binding energy values (30-50 meV) and

265 recent reports of free carrier behavior [16,17,20,25,30-32] . The reason for the difference between our

266 observations and previous estimates of the binding energy is primarily the combination of higher

267 quality, much more crystalline films, and the use of very high magnetic fields. This has enabled

268 us to measure multiple excitonic transitions which allow precise spectroscopic measurements, in

269 contrast to previous works which have relied exclusively on measuring the 1s exciton and require

270 assumptions to be made about the dielectric constant and effective masses[11-13, 17]. The effective

271 mass values of ~0.1 m_e, which we have determined, are in good agreement with recent

272 calculations [14,18,19,24] but are also significantly lower than the earlier experimental estimates [12,13].

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364 **Author contribution**

365 Atsuhiko Miyata, Anatolie Mitioglu, P.P, O.P and R.J.N collected and analysed the data. J. T-

366 W. W. and S.D.S. prepared the samples. All authors contributed to the interpretation and the

367 manuscript preparation. R.J.N. supervised and initiated the project.

368

369 **Figure captions**

370

371 **Figure 1: Magnetic field dependence of the optical density for the perovskite** $CH_3NH_3PbI_3$

372 (a) A sequence of optical density (Log(1/transmission)) spectra measured during a single pulse

[17]

373   of the magnetic field. To improve the resolution of smaller field dependent features (b) and (c)

374   show sequences of ratios of the transmission in magnetic field T(B) to that measured at zero field

375   T(0), where the resonant absorption features correspond to minima. For easier comparison

376   spectra are offset. The feature highlighted at 2.03 eV is a band edge absorption from a

377   previously undetected higher energy band edge and will be the subject of a future publication.

378

379   **Figure 2: Energy 'Fan' diagrams.** (**a**) Full fan using data from long pulse fixed field spectra

380   (black circles) and fixed energy fast field sweep data (red stars). The calculated transition

381   energies are shown for the free electron and hole levels (solid lines) and the excitonic transitions

382   (dashed lines). Inset to (a) lower fields measured using fixed field spectra. (b) shows a schematic

383   of the energy levels and transitions between the free electron and hole levels (solid lines) and the

384   excitonic transitions (dashed lines).

385

386   **Figure 3: Single turn coil results.** Plots of the magneto-transmission measured using a single

387   turn fast pulse magnetic field, with schematic of the experimental system. For better comparison

388   spectra are offset. (a) shows the temperature dependence with the arrows indicating the position

389   of the N=1 inter Landau level transition. The inset shows a schematic of the single turn

390   experimental system showing the coil and its firing circuit, the sample and the optical fiber

391   illumination and collection system. (b) shows the transmission spectra in the tetragonal

392   (intermediate temperature) phase with spectra measured for different wavelengths in the

393   temperature range 155 – 190 K. The linked arrows show the positions of the N=1 and N=2

394   transitions.

395 **Figure 4: Transmission in high temperature tetragonal phase** (**a**) optical density, with the

396 dashed line showing the anomalous behavior of the 1s exciton transition. (**b**) fan diagram. (**c**)

397 Temperature dependent band gaps and resonance positions for the N=1 inter-Landau level

398 transition.

399

400

401

Methods

403 Samples were prepared on glass substrates cleaned sequentially in hallmanex, acetone,

404 isopropanol and O_2 plasma. The polycrystalline $CH_3NH_3PbI_3$ perovskite films were deposited in

405 a nitrogen-filled glovebox following the interdiffusion preparation methods described

406 previously[5]. In brief, a PbI_2 layer was first deposited on cleaned glass by spin-coating

407 (speed/ramp = 6000rpm/6000 rpm/s, time = 35s) from a precursor solution of PbI_2 in DMF with

408 concentration of 450 mg/ml, followed by drying at 70°C for 5 min. Then the MAI layer was

409 deposited on dried PbI_2 film by spin-coating (speed/ramp = 6000rpm/6000 rpm/s, time = 35s)

410 from a precursor solution of MAI in isopropanol with concentration of 50 mg/ml, followed by

411 annealing at 100°C for 1 hour. The perovskite films were sealed by spin-coating a layer of the

412 insulating polymer poly(methyl methacrylate) (PMMA; 10 mg/ml, speed/ramp = 1000rpm/1000

413 rpm/s, time = 60s) on top in order to ensure air-and moisture-insensitivity.

414

415 The magneto-optical measurements have been performed using 70 T long-duration and 150T

416 short duration pulsed magnets in the high magnetic field laboratory in Toulouse. For the long

417   pulsed measurements (~500 ms duration) the sample was immersed in liquid or gaseous helium

418   in a cryostat. A tungsten halogen lamp was used to provide broad spectrum in the visible and

419   near infra-red range. The absorption was measured in the Faraday configuration in which k, the

420   wave propagation vector is parallel to the magnetic field B. A nitrogen cooled CCD array

421   coupled to a spectrometer collected the light transmitted through the sample. The exposure time

422   was 3 ms in order to limit variations in the magnetic field during acquisition. Thirty spectra were

423   taken during a 70 T shot of the magnetic field. The magnetic field was measured using a

424   calibrated pick-up coil. All spectra were normalized to both the incident intensity and by the zero

425   field transmission to produce absolute and differential transmission spectra.   For the short

426   duration (10μs) pulsed measurements a series of diode and Ti-Sapphire laser lines was sent

427   through and collected from the sample using fiber optics and detected using a fast (100MHz)

428   silicon detector and high speed digital oscilloscope[33]. The sample was mounted inside a non-

429   conducting helium flow cryostat and was cooled separately for each measurement. The magnetic

430   fields were generated by a semi-destructive single turn coil system using 10mm coils[33,34].

431

(a) R* = 16 meV, m* = 0.104. Inset axis labels: Energy (eV) ranging 1.64–1.70, B (T) ranging 10–40. Main plot: Energy (eV) vs Magnetic Field (T), with curves labeled N=0, N=1, N=2, N=3, N=4.

(b) Energy vs B schematic.

(a) 1.771 eV

8.5 K

29 K

61 K

115 K

140 K

155 K

180 K

210 K

Transmission (arb. units)

B(T)

(b)

1.959 eV   N=2

1.850 eV

1.810 eV

N=1

1.771 eV

1.746 eV

1.722 eV

Transmission (arb. units)

B(T)

(a) 1s 161K 65 T 0T

(b) Tetragonal Phase $m^* = 0.104$ $R^* = 12$

(c)