



HAL
open science

Coherent Spin Dynamics of Electrons and Holes in CsPbBr₃ Colloidal Nanocrystals

Philipp S Grigoryev, Vasilii V Belykh, Dmitri R Yakovlev, Emmanuel
Lhuillier, Manfred Bayer

► **To cite this version:**

Philipp S Grigoryev, Vasilii V Belykh, Dmitri R Yakovlev, Emmanuel Lhuillier, Manfred Bayer. Coherent Spin Dynamics of Electrons and Holes in CsPbBr₃ Colloidal Nanocrystals. Nano Letters, 2021, 10.1021/acs.nanolett.1c03292 . hal-03360866

HAL Id: hal-03360866

<https://hal.science/hal-03360866v1>

Submitted on 1 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Coherent Spin Dynamics of Electrons and Holes in CsPbBr₃ Colloidal Nanocrystals

Philipp S. Grigoryev, Vasilii V. Belykh, Dmitri R. Yakovlev,* Emmanuel Lhuillier, and Manfred Bayer



Cite This: <https://doi.org/10.1021/acs.nanolett.1c03292>



Read Online

ACCESS |



Metrics & More



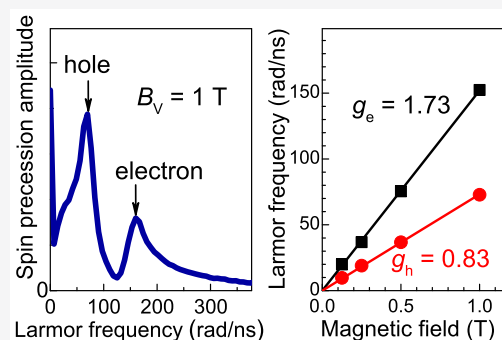
Article Recommendations



Supporting Information

ABSTRACT: The spin dynamics in CsPbBr₃ lead halide perovskite nanocrystals are studied by picosecond pump–probe Faraday rotation in an external magnetic field. Coherent Larmor precession of electrons and holes with spin dephasing times of ~ 600 ps is detected in a transversal magnetic field. The longitudinal spin relaxation time in weak magnetic fields reaches 80 ns at a temperature of 5 K. In this regime, the carrier spin dynamics is governed by nuclear spin fluctuations characterized by an effective hyperfine field strength of 25 mT. The Landé factors determining the carrier Zeeman splittings are $g_e = +1.73$ for electrons and $g_h = +0.83$ for holes. A comparison with a CsPbBr₃ polycrystalline film and bulk single crystals evidences that the spatial confinement of electrons and holes in the nanocrystals only slightly affects their g factors and spin dynamics.

KEYWORDS: Perovskite nanocrystals, CsPbBr₃, coherent spin dynamics, electron and hole g -factors, pump–probe time-resolved Faraday rotation



Lead halide perovskite nanocrystals (NCs) have only quite recently joined the rich family of semiconductor NCs grown by colloidal synthesis.^{1–6} They show a remarkable quantum yield up to 90% even for bare NCs, as surface states do not act detrimentally on the exciton emission efficiency. In these materials, the energies of surface states and of defects and impurities are not located within the band gap, which strongly suppresses channels for the nonradiative recombination of optical excitations in the vicinity of the band gap. This known phenomenon of the perovskites is often summed up as a defect-tolerant band structure. The inorganic lead halide perovskites CsPbX₃ (X = I, Br, or Cl) allow one to tune the band gap across a wide spectral range from the infrared up the ultraviolet by mixing the halogen composition. Further flexibility in NC band-gap tuning arises from the quantum confinement of the charge carriers, whereby details of the exciton fine structure are governed by the shape and size of the NC.^{7–10} Simple fabrication, a high quantum yield, and tunable optical properties also make lead halide perovskite NCs promising materials for spintronics applications. Still, only a few studies have been performed so far in this field. In particular, neutral and charged excitons in single NCs were identified by their Zeeman splitting in magnetic fields,¹¹ and the importance of the Rashba effect was elaborated.¹² Strong magnetic fields of 30 T allowed one to identify the influence of negatively charged excitons (trions) and dark excitons on the optical properties of NC ensemble.¹³ Anisotropic exciton Zeeman splitting in magnetic field was observed,¹⁴ the coherent spin dynamics of holes were explored in CsPbBr₃

NCs,¹⁵ and the picosecond spin dynamics of carriers were reported in CsPbI₃ NCs.¹⁶

To understand and interpret spin-dependent phenomena, precise knowledge of the values and signs of the charge-carrier g -factors is of key importance. Also, the characteristic time scales of the spin dynamics (longitudinal spin relaxation time, T_1 , spin coherence time, T_2 , and ensemble spin dephasing time, T_2^*) are needed. It is important that these parameters are measured directly and preferably on the same samples. Even for bulk lead halide perovskites, the published information is still fragmentary, often providing controversial conclusions.^{17–25}

Time-resolved pump–probe Faraday/Kerr rotation is an established technique for fulfilling the previously defined conditions for comprehensive spin physics studies of semiconductors,^{26,27} as it provides direct access to g -factors and the spin relaxation times. For example, it was successfully applied to colloidal II–VI semiconductor NCs.^{28–31} Furthermore, its potential was recently demonstrated for CsPbBr₃ single crystals³² and NCs¹⁵ and for CH₃NH₃PbCl_{1–x}I_{3–x} polycrystalline films.³³

Received: August 24, 2021

Revised: September 27, 2021

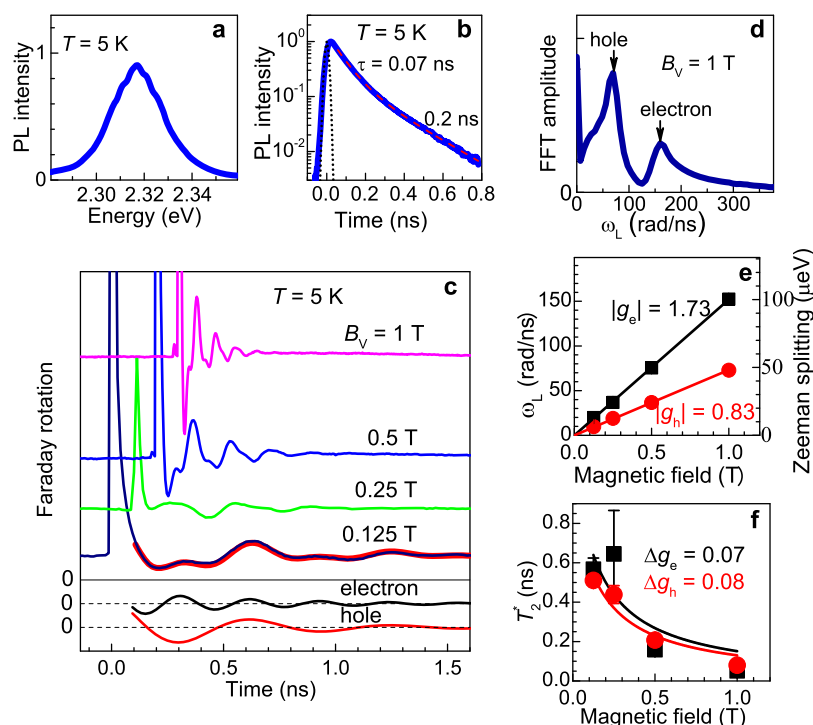


Figure 1. (a) Photoluminescence spectrum of CsPbBr₃ NCs. (b) Time-resolved recombination dynamics measured at the maximum of the PL line. The black dotted line shows the instrumental response function, whereas the red dashed line shows the double-exponential fit. (c) Coherent spin dynamics measured at 2.330 eV in different magnetic fields applied in Voigt geometry. The curves are shifted vertically and horizontally for clarity. The thick red line is a fit to the data at $B_V = 0.125$ T with eq 1 and $S_e/S_h = 0.5$. In the bottom, the black and red lines are the two components of the fit describing the electron and hole spin precession. (d) Fast Fourier transform (FFT) spectrum of the Faraday rotation dynamics at $B_V = 1$ T. (e) Magnetic field dependencies of the Larmor precession frequencies (corresponding Zeeman splittings are shown on the right axis) for electrons and holes. The error bars are within the data points. Solid lines are linear fits, giving $|g_e| = 1.73$ and $|g_h| = 0.83$. (f) Magnetic field dependencies of the spin dephasing times for electrons and holes. Lines are fits according to eq 2, with parameters given in the text.

68 In this Letter, we investigate the coherent spin dynamics of
69 electrons and holes in CsPbBr₃ NCs using time-resolved
70 pump–probe Faraday rotation (ppFR). We measure the
71 electron and hole g -factors, their spread within the NCs
72 ensemble, and the temperature dependence of the transverse
73 and longitudinal spin relaxation times. The carrier interaction
74 with the nuclear spins and its role in the spin dynamics are
75 studied. The spin dynamic parameters in CsPbBr₃ NCs are
76 compared with those in a polycrystalline film and a bulk single
77 crystal.

78 ■ OPTICAL PROPERTIES OF NANOCRYSTALS

79 We study CsPbBr₃ NCs dispersed in polymethyl methacrylate
80 (PMMA) and spin-coated on a glass coverslip. (For synthesis
81 details, see Section S2 in the Supporting Information.) The
82 NCs have a cubic shape with a typical size of 10 nm, which
83 slightly exceeds the exciton Bohr diameter of 7 nm. Therefore,
84 the excitons experience a rather weak size quantization.
85 Transmission electron microscopy images and optical spectra
86 of similar CsPbBr₃ NCs can be found in ref 13. It should be
87 noted that whereas CsPbBr₃ NCs are known to crystallize in
88 the cubic phase,³ a recent report shows that they can exhibit
89 tetragonal and orthorhombic phases at cryogenic temper-
90 atures.¹¹ Lower crystal symmetry will likely result in an
91 anisotropy of the charge-carrier g -factors.

92 To characterize the optical properties of the studied
93 CsPbBr₃ NCs, we measured the photoluminescence (PL)
94 spectrum and recombination dynamics at a temperature of $T =$
95 5 K; see Figure 1a,b. The results are typical for CsPbBr₃ NCs,

as reported in literature; see, for example, ref 13 and references
96 therein. The PL line has maximum at 2.317 eV and a full width
97 at half-maximum of 29 meV. It shows a fast recombination,
98 two-component dynamics with a decay of 0.07 and 0.2 ns
99 (Figure 1b), in line with the 0.2 ns decay measured in single
100 NC experiments.¹¹ We have checked that the application of
101 the magnetic field up to 6 T only slightly elongates the PL
102 decay. These decay times are considerably shorter than the
103 exciton decay time of 0.9 ns in CsPbBr₃ bulk crystals.³² In
104 general, the emission of an NC ensemble can be contributed
105 by neutral and charged NCs. Therefore, the PL can contain the
106 emission of neutral, negatively charged, and positively charged
107 excitons. The ratio of their populations depends on the
108 synthesis protocol, the sample preparation, and the optical
109 excitation conditions. In our previous study,¹³ we measured
110 polarized PL and recombination dynamics in high magnetic
111 fields up to 30 T of similar CsPbBr₃ NCs and concluded that at
112 liquid helium temperatures, the emission is mainly contributed
113 by negatively charged excitons with some contribution from
114 neutral excitons. The present study using the ppFR
115 technique²⁷ allows us to gain more information on the NC
116 charging,³⁰ as will be discussed as follows. 117

118 ■ COHERENT SPIN DYNAMICS OF ELECTRONS AND HOLES IN NANOCRYSTALS

119 To address the carrier spin dynamics, we use ppFR; see the
120 Methods in the Supporting Information. Here circularly
121 polarized pump pulses optically induce a carrier spin 122

123 polarization, while the linearly polarized probe pulses detect its
124 time evolution by varying their delay relative to the pump.

125 **Figure 1c** shows the spin dynamics measured for different
126 magnetic fields applied in the Voigt geometry (field orientation
127 perpendicular to the collinear pump and probe beams). The
128 Faraday rotation amplitude oscillates with time, reflecting the
129 coherent spin precession at the Larmor frequency about the
130 magnetic field. The precession frequency increases with
131 magnetic field strength, B_V , growing from 0.125 to 1 T.
132 Simultaneously, the signal decay accelerates. The modulations
133 in the oscillatory signal arise from the contribution of two
134 components with different precession frequencies, as con-
135 firmed in the fast Fourier transform (FFT) spectrum of the
136 dynamics in **Figure 1d**. Indeed, the Faraday rotation dynamics
137 can be well-fitted by the sum of two exponentially decaying
138 oscillations

$$A_{\text{FR}} = S_e \cos(\omega_{L,e}t) \exp(-t/T_{2,e}^*) + S_h \cos(\omega_{L,h}t) \exp(-t/T_{2,h}^*) \quad (1)$$

140 Here $S_{e(h)}$ is the amplitude of the electron (hole) spin signal,
141 $\omega_{L,e(h)}$ is the Larmor precession frequency of electrons (holes),
142 and $T_{2,e(h)}^*$ is the electron (hole) spin dephasing time. The
143 contributions of the two dynamics components at $B_V = 0.125$
144 T are shown separately in the bottom of **Figure 1c**. The fit
145 gives $T_{2,e}^* \approx 0.6$ ns and $T_{2,h}^* \approx 0.5$ ns with comparable
146 amplitudes of the electron and hole signals, $S_e/S_h \approx 0.5$. The
147 Larmor precession frequencies of both components increase
148 linearly with magnetic field (**Figure 1e**). By fitting them with
149 $\omega_{L,e(h)} = |g_{e(h)}| \mu_B B_V / \hbar$, where μ_B is the Bohr magneton and $g_{e(h)}$
150 is the electron (hole) g factor, we evaluate $|g_e| = 1.73$ and $|g_h| =$
151 0.83.

152 We attribute the high-frequency component with the g -
153 factor of 1.73 to the electron and the low-frequency
154 component with the g -factor of 0.83 to the hole by analogy
155 to bulk CsPbBr₃ perovskites.³² Note that our experimental
156 technique is not sensitive to the g -factor sign, which should be
157 determined using an alternate method. We use here the
158 knowledge of the exciton g -factor, $g_X = +2.4$, that we measured
159 in CsPbBr₃ NCs,¹³ and the fact that in lead halide perovskites,
160 $g_X = g_e + g_h$. This allows us to conclude that in the studied
161 NCs, both electron and hole g -factors are positive, similar to
162 CsPbBr₃ bulk crystals;³² for details see Section S4 in the
163 **Supporting Information**.

164 Let us clarify now the important question of whether neutral
165 or singly charged NCs are responsible for the ppFR signal. In
166 the case of neutral NCs, the signal should originate from the
167 photogenerated electrons and holes bound to neutral excitons.
168 There are two arguments that let us exclude this neutral
169 exciton scenario. First, the measured spin dynamics should
170 then be limited by the exciton recombination time, which is 0.2
171 ns for the studied NCs (**Figure 1b**). The measured spin
172 dephasing times of electrons (0.6 ns) and holes (0.5 ns) are
173 much longer than the exciton recombination time. The second
174 argument is related to the exciton fine structure. Magneto-
175 optical studies of emission from single CsPbBr₃ NCs show that
176 the zero-field exciton exchange splitting of neutral excitons is
177 ~ 0.6 meV¹¹ and that most NCs at low temperatures have
178 either tetragonal or orthorhombic crystal symmetry. Note that
179 in rather similar FAPbBr₃ NCs the splitting is found to be in
180 the range from 0.3 to 1.7 meV.¹⁰ The exciton exchange
181 interaction couples electron and hole spin so that the spins of

the electrons and holes forming the exciton do not precess 182
independently. This becomes possible only in strong magnetic 183
fields where the carrier Zeeman splitting exceeds the exchange 184
energy and the spin coupling is broken. One can see from the 185
right scale of **Figure 1e** that in the studied NCs, we detect 186
electron and hole spin precession in the low field regime with 187
Zeeman splittings of ~ 0.01 meV, that is, much smaller than the 188
neutral exciton exchange splitting. We conclude that neutral 189
NCs (i.e., neutral excitons) cannot contribute notably to the 190
coherent spin dynamics measured in the ppFR experiment. 191
Note that this conclusion contradicts the one of ref 15 that the 192
measured hole spin beats can be associated with a hole bound 193
to an exciton. 194

In NCs charged by either a single electron or a single hole, 195
the ppFR signal is contributed by the spin dynamics of these 196
resident carriers, limited only by their spin relaxation times. 197
The spin coherence of the resident carriers is generated via 198
photoexcitation of a charge exciton (trion) state, as studied in 199
great detail for (In,Ga)As/GaAs epitaxially grown quantum 200
dots.^{27,34} The exchange splitting is canceled in the trion and 201
obviously also cannot occur for the resident carrier left in an 202
NC after trion recombination. Therefore, the magnetic field 203
dependence of the Larmor precession frequency is expected to 204
be linear with zero energy offset at zero magnetic field. This is 205
exactly what we find in the experiment in **Figure 1e** for both 206
electrons and holes. On the basis of these arguments, we can 207
safely conclude that the ppFR signals originate from singly 208
charged NCs, both positively and negatively charged. From $S_e/$ 209
 $S_h \approx 0.5$, we suggest that the fractions of negatively and 210
positively charged NCs are comparable, with some preference 211
for the positively charged NCs. It was shown that in CsPbBr₃ 212
and FAPbBr₃ NCs photocharging results in negative and 213
positive loading of the NCs.^{35,36} This is consistent with the 214
Fermi level being close to the midpoint of the gap in Cs and 215
FA lead halide NCs, as demonstrated by photoemission 216
spectroscopy.^{37,38} 217

The spin dephasing times, of both electrons and holes, show 218
strong magnetic field dependences; see **Figure 1f**. The 219
dynamics shorten from 0.6 to 0.05 ns for electrons and from 220
0.5 to 0.08 ns for holes with increasing field up to 1 T. This 221
decrease is provided by the spin dephasing in the ensembles 222
with a dispersion of the g -factors, which translates to a spread 223
of the Larmor precession frequencies. It is described by the 224
following equation 225

$$\frac{1}{T_{2,e(h)}^*(B_V)} = \frac{1}{T_{2,e(h)}^*(0)} + \frac{\Delta g_{e(h)} \mu_B B_V}{\hbar} \quad (2)$$

Here $\Delta g_{e(h)}$ is the dispersion of electron (hole) g -factors. 227
 $T_{2,e(h)}^*(0)$ is the spin dephasing time at zero magnetic field, 228
which is limited by the spin coherence time, $T_{2,e(h)}$, of the 229
individual carriers and the spin relaxation mechanisms not 230
related to the g -factor dispersion, for example, the hyperfine 231
interaction with nuclear spin fluctuations. This equation gives 232
reasonable fits to the experimental dependencies of $T_{2,e(h)}^*(B_V)$ 233
with $T_{2,e}^*(0) = 1.2$ ns and $T_{2,h}^*(0) = 1.0$ ns and g -factor 234
spreads of $\Delta g_e = 0.07$ and $\Delta g_h = 0.08$. Note that the measured 235
 g -factor spreads are about two times larger than those in bulk 236
CsPbBr₃ single crystals.³² This may be related to the spread of 237
NC sizes and shapes, which determines the g factor and its 238
anisotropy. 239

240 Oscillating signals in the Faraday rotation dynamics are
241 detectable up to temperatures of 35 K, as shown in Figure 2.

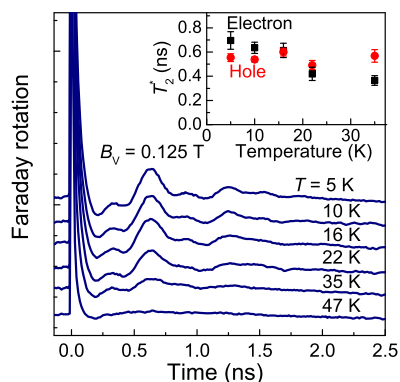


Figure 2. Dynamics of Faraday rotation signal in CsPbBr₃ NCs measured at 2.330 eV for different temperatures in $B_V = 0.125$ T. Data are shifted vertically for clarity. The inset shows the temperature dependence of the spin dephasing time for electrons and holes.

242 The amplitudes of both the electron and hole spin signals
243 gradually decrease with increasing temperature. That means
244 that the decrease in the signal amplitude is provided by a
245 decreasing efficiency of the optical spin polarization. On the
246 contrary, the spin dephasing times, shown in the inset of Figure
247 2, change only weakly in this temperature range. The hole
248 dephasing time remains almost constant at $T_{2,h}^* = 0.5$ ns,
249 whereas the electron time, $T_{2,e}^*$, slightly decreases from 0.7 to
250 0.4 ns. This is in contrast with the strong temperature
251 dependence of $T_{2,e}^*$ in bulk CsPbBr₃,³² where temperature
252 induces the delocalization of carriers and the activation of spin
253 relaxation mechanisms related to the spin–orbit coupling. On
254 the contrary, in NCs, carriers are localized at any temperature.
255 The other difference in NCs from bulk CsPbBr₃, presumably
256 related to the localization, is the much more homogeneous
257 spin dynamics for NCs (dephasing times and ratio between
258 electron and hole contributions) for different positions on the
259 sample.

260 ■ LONGITUDINAL SPIN RELAXATION OF CARRIERS 261 IN NANOCRYSTALS

262 Let us turn to experiments in the Faraday geometry where the
263 external magnetic field, B_F , is applied along the light wave
264 vectors. Consequently, the optically induced spin polarization

of carriers along the field direction does not show Larmor
precession. This allows one to measure the longitudinal spin
relaxation time, T_1 , and gather information on the nuclear spin
fluctuations.

The magnetic field dependence of the Faraday rotation
signal measured at a negative time delay of -1 ns is shown in
Figure 3a. The finite signal amplitude implies that the spin
relaxation time of carriers exceeds the repetition period of the
laser pulses, $T_R = 13.1$ ns. In fact, as we will show, it exceeds
several T_R periods and corresponds to a cumulative effect due
to repeated pulse application. In this experiment, the laser
helicity is kept constant, but the laser intensity is modulated
with frequencies in the $f = 0.3$ –6 MHz range. One can see that
at the low modulation frequency of 0.3 MHz (black line), the
signal amplitude has a minimum at zero magnetic field and
increases with the field increase. It thus corresponds to a so-
called polarization recovery curve (PRC).³⁹ The half width at
half-maximum of the PRC equals 25 mT, which is the
characteristic field of nuclear spin fluctuations acting on the
carriers via the hyperfine interaction. In our recent study of
CsPbBr₃ crystals, we showed experimentally and theoretically
that in lead halide perovskites, the holes in the valence band
have a considerably stronger hyperfine interaction compared
with the conduction band electrons.³² Therefore, we suggest
that the PRC signal in CsPbBr₃ NCs is mainly contributed by
the hole–nuclear hyperfine interaction.

When the pump modulation frequency is increased to 6
MHz, the PRC amplitude decreases; see Figure 3a. This is
evidence that the modulation period, $1/f$, is comparable to T_1
in this case, and the spin accumulation loses its efficiency.
Therefore, we used the spin inertia method to measure the
spin relaxation time, T_1 , in the longitudinal magnetic
field.^{32,39,40} In addition, the detected signal is retarded by the
phase, ϕ , which we also measure; see the Methods in the
Supporting Information for details. Figure 3b shows the PRC
amplitude and $\tan \phi$ as a function of the modulation frequency,
which gives us two ways to evaluate T_1 . Fitting the frequency
dependence of the PRC amplitude with the spin inertia
equation (Section S3 in the Supporting Information), we
obtain $T_1 = 83 \pm 9$ ns. The fit of the $\tan \phi$ dependence on f
with a linear equation (Section S4 in the Supporting
Information) gives $T_1 = 56 \pm 5$ ns. This difference in T_1 is
caused by the nonmonoexponential spin relaxation dynamics:
The amplitude of the spin polarization is more sensitive to the
slow component in the dynamics, whereas the retardation
phase is more dependent on the fast component. We note that

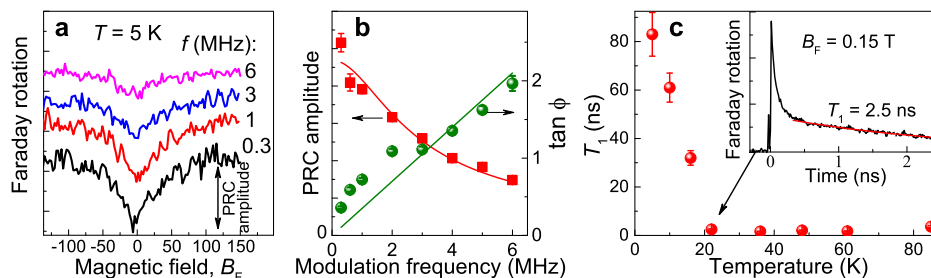


Figure 3. Spin dynamics of CsPbBr₃ NCs measured in longitudinal magnetic fields (Faraday geometry). (a) Polarization recovery curves measured at different pump modulation frequencies. Data are shifted vertically for clarity. $T = 5$ K. (b) PRC amplitude (red squares) and tangent of the retardation phase (green circles) as a function of the modulation frequency. Lines show fits with eqs S3 and S4 in the Supporting Information to the experimental data. $T = 5$ K. (c) Temperature dependence of the longitudinal spin relaxation time, T_1 . Inset shows the Faraday rotation signal dynamics in the longitudinal magnetic field, $B_F = 0.15$ T, at $T = 22$ K.

Table 1. Spin Parameters Measured for Different CsPbBr₃ Perovskite Samples^a

	nanocrystals	polycrystalline film	bulk ³²
electron <i>g</i> -factor, <i>g_e</i>	+1.73	+1.78	+1.96
hole <i>g</i> -factor, <i>g_h</i>	+0.83	+0.77	+0.75
exciton <i>g</i> -factor, <i>g_X</i>	+2.4 ¹³		+2.35
electron spin dephasing time, <i>T_{2,e}</i> [*]	0.6–0.7 ns	0.25 ns	0.9–5.2 ns
hole spin dephasing time, <i>T_{2,h}</i> [*]	0.5 ns	0.4 ns	0.7–1.9 ns
longitudinal spin relaxation time, <i>T₁</i>	56–83 ns		32–53 ns

^aResults for bulk CsPbBr₃ (single crystal) are taken from ref 32. *T₂*^{*} values in NCs and bulk are given for *B_V* = 0.125 T, and those in film are given for *B_V* = 0.25 T.

the evaluated *T₁* values for NCs are a few tens of nanoseconds longer than *T₁* for the corresponding bulk perovskites;³² see Table 1.

The longitudinal spin relaxation time, *T₁*, determined from the frequency dependence of the PRC amplitude is shown in Figure 3c as a function of temperature. It rapidly decreases with temperature and saturates at ~2 ns above 20 K. At temperatures higher than 20 K, *T₁* was measured by fitting the decay of the Faraday rotation signal with a single exponential function; see the inset of Figure 3c.

COHERENT SPIN DYNAMICS IN POLYCRYSTALLINE FILM

We also studied the coherent spin dynamics in a CsPbBr₃ polycrystalline film. Its PL spectrum (Figure 4a) has an

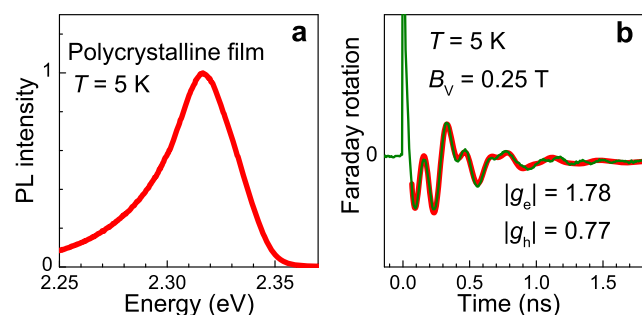


Figure 4. (a) Photoluminescence spectrum of the CsPbBr₃ polycrystalline film. (b) Coherent spin dynamics measured in the film at 2.330 eV for *B_V* = 0.25 T. The panel gives experimental data (green line) and fit to the data (red line) with eq 1 and *S_e*/*S_h* = 0.75.

asymmetric shape with a low-energy tail, similar to the low-temperature emission of bulk CsPbBr₃.³² The spin precession monitored by ppFR is given in Figure 4b at *B_V* = 0.25 T and *T* = 5 K. Similar to the NCs, it contains two Larmor precession frequencies, where a fit with eq 1 gives the following parameters: *|g_e|* = 1.78, *|g_h|* = 0.77, *T_{2,e}*^{*} = 0.25 ns, and *T_{2,h}*^{*} = 0.4 ns. It is reasonable to suggest that similar to CsPbBr₃ bulk and NCs, *g_e* > 0 and *g_h* > 0 in the film.

SUMMARY OF *g*-FACTORS AND SPIN RELAXATION TIMES IN CsPbBr₃ PEROVSKITE STRUCTURES

It is instructive to compare the *g*-factor values for CsPbBr₃ perovskite NCs, polycrystalline film, and bulk crystals (Table 1). We note a small but monotonic variation of the *g*-factors when going from NCs to film and further to bulk. The rather close *g*-factor values are related to the weak quantum confinement in the studied NCs, which is also confirmed by

their close energy positions of the PL emission. The behavior is in line with the well-known relation between the optical transition energy and the electron *g*-factor for semiconductors.^{41–43} The small effect of confinement on the spin properties of the compared samples is further confirmed by the similar range of spin relaxation times in NCs and bulk perovskites.³²

In conclusion, we performed a detailed study of the electron and hole spin dynamics in CsPbBr₃ perovskite NCs. Electron and hole *g*-factors of +1.73 and +0.83, respectively, have been measured from spin beats in the transverse magnetic field. The spin dephasing times *T₂*^{*} of ~1 ns considerably exceed the exciton recombination time, which has allowed us to attribute the measured spin dynamics to NCs singly charged with an electron or a hole. In the longitudinal magnetic field, a spin relaxation time *T₁* exceeding 80 ns has been measured. The influence of the carrier–nuclear hyperfine interaction, which controls the carrier spin dynamics at zero and weak magnetic fields, has been identified. Our study underlines that perovskite NCs have promising spin-dependent properties, very much comparable to the comprehensively studied epitaxially grown III–V quantum dots and colloiddally synthesized II–VI NCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03292>.

Details of experimental methods, synthesis and characterization of CsPbBr₃ NCs and polycrystalline film, and Zeeman Hamiltonian and *g*-factors of charge carriers and excitons (PDF)

AUTHOR INFORMATION

Corresponding Author

Dmitri R. Yakovlev – *Experimentelle Physik 2, Technische Universität Dortmund, 44221 Dortmund, Germany; P.N. Lebedev Physical Institute, Russian Academy of Sciences, 119991 Moscow, Russia; Ioffe Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia; orcid.org/0000-0001-7349-2745; Email: dmitri.yakovlev@tu-dortmund.de*

Authors

Philipp S. Grigoryev – *Spin Optics Laboratory, St. Petersburg State University, 199034 St. Petersburg, Russia; orcid.org/0000-0002-3349-062X*
 Vasilii V. Belykh – *Experimentelle Physik 2, Technische Universität Dortmund, 44221 Dortmund, Germany; P.N. Lebedev Physical Institute, Russian Academy of Sciences, 119991 Moscow, Russia; orcid.org/0000-0002-0032-748X*

389 Emmanuel Lhuillier – Sorbonne Université, CNRS, Institut
390 des NanoSciences de Paris, INSP, 75005 Paris, France;
391 orcid.org/0000-0003-2582-1422
392 Manfred Bayer – Experimentelle Physik 2, Technische
393 Universität Dortmund, 44221 Dortmund, Germany; Ioffe
394 Institute, Russian Academy of Sciences, 194021 St.
395 Petersburg, Russia; orcid.org/0000-0002-0893-5949

396 Complete contact information is available at:
397 <https://pubs.acs.org/10.1021/acs.nanolett.1c03292>

398 Notes

399 The authors declare no competing financial interest.

400 ■ ACKNOWLEDGMENTS

401 We thank M. M. Glazov, A. V. Rodina, and Al. L. Efros for
402 fruitful discussions. We acknowledge financial support by the
403 Deutsche Forschungsgemeinschaft via the SPP2196 Priority
404 Programme (Project YA 65/26-1) and the International
405 Collaborative Research Centre TRR160 (Project B1). The
406 research of V.V.B. and partially of D.R.Y. was supported by the
407 Government of the Russian Federation (contract no. 075-15-
408 2021-598 at the P.N. Lebedev Physical Institute). P.S.G.
409 acknowledges St. Petersburg State University for a research
410 grant 73031758. E.L. acknowledges the support of the ERC
411 starting grant blackQD (grant no. 756225) of the French state
412 funds managed by the ANR within the Investissements
413 d'Avenir programme under reference ANR-11-IDEX-0004-02
414 and, more specifically, within the framework of the Cluster of
415 Excellence MATISSE and by grant IPER-Nano2 (ANR-
416 18CE30-0023-01). M.B. acknowledges support by the Mercur
417 Foundation (grant Pe-2019-0022).

418 ■ REFERENCES

419 (1) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties
420 and potential optoelectronic applications of lead halide perovskite
421 nanocrystals. *Science* **2017**, *358*, 745–750.
422 (2) Chen, Q.; Wu, J.; Ou, X.; Huang, B.; Almutlaq, J.; Zhumekenov,
423 A. A.; Guan, X.; Han, S.; Liang, L.; Yi, Z.; Li, J.; Xie, X.; Wang, Y.; Li,
424 Y.; Fan, D.; Teh, D. B. L.; All, A. H.; Mohammed, O. F.; Bakr, O. M.;
425 Wu, T.; Bettinelli, M.; Yang, H.; Huang, W.; Liu, X. All-inorganic
426 perovskite nanocrystal scintillators. *Nature* **2018**, *561*, 88–93.
427 (3) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.;
428 Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V.
429 Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br,
430 and I): Novel optoelectronic materials showing bright emission with
431 wide color gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
432 (4) Akkerman, Q. A.; Rainó, G.; Kovalenko, M. V.; Manna, L.
433 Genesis, challenges and opportunities for colloidal lead halide
434 perovskite nanocrystals. *Nat. Mater.* **2018**, *17*, 394.
435 (5) Park, Y.-S.; Guo, S.; Makarov, N. S.; Klimov, V. I. Room
436 temperature single-photon emission from individual perovskite
437 quantum dots. *ACS Nano* **2015**, *9*, 10386–10393.
438 (6) Yu, B.; Zhang, C.; Chen, L.; Qin, Z.; Huang, X.; Wang, X.; Xiao,
439 M. Ultrafast dynamics of photoexcited carriers in perovskite
440 semiconductor nanocrystals. *Nanophotonics* **2021**, *10*, 1943–1965.
441 (7) Lin, J.; Gomez, L.; de Weerd, C.; Fujiwara, Y.; Gregorkiewicz,
442 T.; Suenaga, K. Direct observation of band structure modifications in
443 nanocrystals of CsPbBr₃ perovskite. *Nano Lett.* **2016**, *16*, 7198.
444 (8) Becker, M. A.; Vaxenburg, R.; Nedelcu, G.; Sercel, P. C.;
445 Shabaev, A.; Mehl, M. J.; Michopoulos, J. G.; Lambrakos, S. G.;
446 Bernstein, N.; Lyons, J. L.; Stöferle, T.; Mahrt, R. F.; Kovalenko, M.
447 V.; Norris, D. J.; Rainó, G.; Efros, A. L. Bright triplet excitons in
448 caesium lead halide perovskites. *Nature* **2018**, *553*, 189.
449 (9) Ramade, J.; Andriambarijaona, L. M.; Steinmetz, V.; Goubet,
450 N.; Legrand, L.; Barisien, T.; Bernardot, F.; Testelin, C.; Lhuillier, E.;

Bramati, A.; Chamorro, M. Fine structure of excitons and electron-
hole exchange energy in polymorphic CsPbBr₃ single nanocrystals. *451*
Nanoscale **2018**, *10*, 6393–6401. *452*
(10) Tamarat, Ph.; Bodnarchuk, M. I.; Trebbia, J.-B.; Erni, R.; *453*
Kovalenko, M. V.; Even, J.; Lounis, B. The ground exciton state of *454*
formamidinium lead bromide perovskite nanocrystals is a singlet dark *455*
state. *Nat. Mater.* **2019**, *18*, 717–724. *456*
(11) Fu, M.; Tamarat, P.; Huang, H.; Even, J.; Rogach, A. L.; Lounis, *457*
B. Neutral and charged exciton fine structure in single lead halide *458*
perovskite nanocrystals revealed by magneto-optical spectroscopy. *459*
Nano Lett. **2017**, *17*, 2895–2901. *460*
(12) Isarov, M.; Tan, L. Z.; Bodnarchuk, M. I.; Kovalenko, M. V.; *461*
Rappe, A. M.; Lifshitz, E. Rashba effect in a single colloidal CsPbBr₃ *462*
perovskite nanocrystal detected by magneto-optical measurements. *463*
Nano Lett. **2017**, *17*, 5020–5026. *464*
(13) Canneson, D.; Shornikova, E. V.; Yakovlev, D. R.; Rogge, T.; *465*
Mitioglu, A. A.; Ballottin, M. V.; Christianen, P. C. M.; Lhuillier, E.; *466*
Bayer, M.; Biadala, L. Negatively charged and dark excitons in *467*
CsPbBr₃ perovskite nanocrystals revealed by high magnetic fields. *468*
Nano Lett. **2017**, *17*, 6177–6183. *469*
(14) Nestoklon, M. O.; Goupalov, S. V.; Dzhioev, R. I.; Ken, O. S.; *470*
Korenev, V. L.; Kusrayev, Yu. G.; Sapega, V. F.; de Weerd, C.; Gomez, *471*
L.; Gregorkiewicz, T.; Lin, J.; Suenaga, K.; Fujiwara, Y.; Matyushkin, *472*
L. B.; Yassievich, I. N. Optical orientation and alignment of excitons *473*
in ensembles of inorganic perovskite nanocrystal. *Phys. Rev. B:* *474*
Condens. Matter Mater. Phys. **2018**, *97*, 235304. *475*
(15) Crane, M. J.; Jacoby, L. M.; Cohen, T. A.; Huang, Y.; *476*
Luscombe, C. K.; Gamelin, D. R. Coherent spin precession and *477*
lifetime-limited spin dephasing in CsPbBr₃ perovskite nanocrystals. *478*
Nano Lett. **2020**, *20*, 8626–8633. *479*
(16) Strohmair, S.; Dey, A.; Tong, Y.; Polavarapu, L.; Bohn, B. J.; *480*
Feldmann, J. Spin polarization dynamics of free charge carriers in *481*
CsPbI₃ nanocrystals. *Nano Lett.* **2020**, *20*, 4724–4730. *482*
(17) Giovanni, D.; Ma, H.; Chua, J.; Grätzel, M.; Ramesh, R.; *483*
Mhaisalkar, S.; Mathews, N.; Sum, T. C. Highly spin-polarized carrier *484*
dynamics and ultralarge photoinduced magnetization in CH₃NH₃PbI₃ *485*
perovskite thin films. *Nano Lett.* **2015**, *15*, 1553–1558. *486*
(18) Yu, Z. G. Effective-mass model and magneto-optical properties *487*
in hybrid perovskites. *Sci. Rep.* **2016**, *6*, 28576. *488*
(19) Zhang, C.; Sun, D.; Yu, Z.-G.; Sheng, C.-X.; McGill, S.; *489*
Semenov, D.; Vardeny, Z. V. Field-induced spin splitting and *490*
anomalous photoluminescence circular polarization in CH₃NH₃PbI₃ *491*
films at high magnetic field. *Phys. Rev. B: Condens. Matter Mater. Phys.* *492*
2018, *97*, 134412. *493*
(20) Wang, R.; Hu, S.; Yang, X.; Yan, X.; Li, H.; Sheng, C. Circularly *494*
polarized photoluminescence and Hanle effect measurements of spin *495*
relaxation in organic-inorganic hybrid perovskite films. *J. Mater. Chem.* *496*
2018, *6*, 2989–2995. *497*
(21) Hanrahan, M. P.; Men, L.; Rosales, B. A.; Vela, J.; Rossini, A. J. *498*
Sensitivity-enhanced ²⁰⁷Pb solid-state NMR spectroscopy for the *499*
rapid, non-destructive characterization of organolead halide perov- *500*
skites. *Chem. Mater.* **2018**, *30*, 7005–7015. *501*
(22) Wang, J.; Zhang, C.; Liu, H.; McLaughlin, R.; Zhai, Y.; *502*
Vardeny, S. R.; Liu, X.; McGill, S.; Semenov, D.; Guo, H.; *503*
Tsuchikawa, R.; Deshpande, V. V.; Sun, D.; Vardeny, Z. V. *504*
Spinoptoelectronic devices based on hybrid organic-inorganic *505*
trihalide perovskites. *Nat. Commun.* **2019**, *10*, 129. *506*
(23) Aebli, M.; Piveteau, L.; Nazarenko, O.; Benin, B. M.; Krieg, F.; *507*
Verel, R.; Kovalenko, M. V. Lead-halide scalar couplings in ²⁰⁷Pb *508*
NMR of APbX₃ perovskites (A = Cs, methylammonium, formami- *509*
dinium; X = Cl, Br, I). *Sci. Rep.* **2020**, *10*, 8229. *510*
(24) Zhou, M.; Sarmiento, J. S.; Fei, C.; Zhang, X.; Wang, H. Effect *511*
of composition on the spin relaxation of lead halide perovskites. *J.* *512*
Phys. Chem. Lett. **2020**, *11*, 1502–1507. *513*
(25) Mohd Yusoff, A. R. b.; Mahata, A.; Vasilopoulou, M.; Ullah, *514*
H.; Hu, B.; Jose da Silva, W.; Kurt Schneider, F.; Gao, P.; Ievlev, A. *515*
V.; Liu, Y.; Ovchinnikova, O. S.; De Angelis, F.; Khaja Nazeeruddin, *516*
M. Observation of large Rashba spin-orbit coupling at room *517*
temperature in compositionally engineered perovskite single crystals *518*
519

- 520 and application in high performance photodetectors. *Mater. Today*
521 **2021**, *46*, 18–27.
- 522 (26) *Semiconductor Spintronics and Quantum Computation*;
523 Awschalom, D. D.; Loss, D.; Samarth, N., Eds.; Springer: Berlin, 2002.
- 524 (27) Yakovlev, D. R.; Bayer, M. Chapter 6. Coherent Spin Dynamics
525 of Carriers. In *Spin Physics in Semiconductors*; Dyakonov, M. I., Ed.;
526 Springer International Publishing AG, 2017; pp 155–206.
- 527 (28) Gupta, J. A.; Awschalom, D. D.; Efros, Al. L.; Rodina, A. V.
528 Spin dynamics in semiconductor nanocrystals. *Phys. Rev. B: Condens.*
529 *Matter Mater. Phys.* **2002**, *66*, 125307.
- 530 (29) Fumani, A. K.; Berezovsky, J. Magnetic-field-dependent spin
531 decoherence and dephasing in room-temperature CdSe nanocrystal
532 quantum dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*,
533 155316.
- 534 (30) Feng, D. H.; Yakovlev, D. R.; Pavlov, V. V.; Rodina, A. V.;
535 Shornikova, E. V.; Mund, J.; Bayer, M. Dynamic evolution from
536 negative to positive photocharging in colloidal CdS quantum dots.
537 *Nano Lett.* **2017**, *17*, 2844–2851.
- 538 (31) Hu, R. R.; Yakovlev, D. R.; Liang, P.; Qiang, G.; Chen, C.; Jia,
539 T. Q.; Sun, Z. R.; Bayer, M.; Feng, D. H. Origin of two Larmor
540 frequencies in the coherent spin dynamics of colloidal CdSe quantum
541 dots revealed by controlled charging. *J. Phys. Chem. Lett.* **2019**, *10*,
542 3681–3687.
- 543 (32) Belykh, V. V.; Yakovlev, D. R.; Glazov, M. M.; Grigoryev, P. S.;
544 Hussain, M.; Rautert, J.; Dirin, D. N.; Kovalenko, M. V.; Bayer, M.
545 Coherent spin dynamics of electrons and holes in CsPbBr₃ perovskite
546 crystals. *Nat. Commun.* **2019**, *10*, 673.
- 547 (33) Odenthal, P.; Talmadge, W.; Gundlach, N.; Wang, R.; Zhang,
548 C.; Sun, D.; Yu, Z.-G.; Vally Vardeny, Z.; Li, Y. S. Spin-polarized
549 exciton quantum beating in hybrid organic-inorganic perovskites. *Nat.*
550 *Phys.* **2017**, *13*, 894–899.
- 551 (34) Greilich, A.; Oulton, R.; Zhukov, E. A.; Yugova, I. A.; Yakovlev,
552 D. R.; Bayer, M.; Shabaev, A.; Efros, Al. L.; Merkulov, I. A.;
553 Stavarache, V.; Reuter, D.; Wieck, A. Optical control of spin
554 coherence in singly charged (In,Ga)As/GaAs quantum dots. *Phys.*
555 *Rev. Lett.* **2006**, *96*, 227401.
- 556 (35) Yarita, M.; Aharen, T.; Tahara, H.; Saruyama, M.; Kawawaki,
557 T.; Sato, R.; Teranishi, T.; Kanemitsu, Y. Observation of positive and
558 negative trions in organic-inorganic hybrid perovskite nanocrystals.
559 *Phys. Rev. Mater.* **2018**, *2*, 116003.
- 560 (36) Nakahara, S.; Tahara, H.; Yumoto, G.; Kawawaki, T.;
561 Saruyama, M.; Sato, R.; Teranishi, T.; Kanemitsu, Y. Suppression of
562 trion formation in CsPbBr₃ perovskite nanocrystals by postsynthetic
563 surface modification. *J. Phys. Chem. C* **2018**, *122*, 22188–22193.
- 564 (37) Gréboval, C.; Rastogi, P.; Qu, J.; Chu, A.; Ramade, J.; Khalili,
565 A.; Dabard, C.; Dang, T. H.; Cruguel, H.; Ouerghi, A.; Witkowski, N.;
566 Silly, M. G.; Lhuillier, E. Direct observation of the electronic coupling
567 between absorbing and transport layer in quantum dot based solar cell
568 using time resolved photoemission. *J. Phys. Chem. C* **2020**, *124*,
569 23400.
- 570 (38) Mir, W. J.; Livache, C.; Goubet, N.; Martinez, B.; Jagtap, A.;
571 Chu, A.; Coutard, N.; Cruguel, H.; Barisien, T.; Ithurria, S.; Nag, A.;
572 Dubertret, B.; Ouerghi, A.; Silly, M. G.; Lhuillier, E. Strategy to
573 overcome recombination limited photocurrent generation in CsPbX₃
574 nanocrystal arrays. *Appl. Phys. Lett.* **2018**, *112*, 113503.
- 575 (39) Zhukov, E. A.; Kirstein, E.; Smirnov, D. S.; Yakovlev, D. R.;
576 Glazov, M. M.; Reuter, D.; Wieck, A. D.; Bayer, M.; Greilich, A. Spin
577 inertia of resident and photoexcited carriers in singly charged
578 quantum dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *98*,
579 No. 121304(R).
- 580 (40) Heisterkamp, F.; Zhukov, E. A.; Greilich, A.; Yakovlev, D. R.;
581 Korenev, V. L.; Pawlis, A.; Bayer, M. Longitudinal and transverse spin
582 dynamics of donor-bound electrons in fluorine-doped ZnSe: Spin
583 inertia versus Hanle effect. *Phys. Rev. B: Condens. Matter Mater. Phys.*
584 **2015**, *91*, 235432.
- 585 (41) Roth, L. M.; Lax, B.; Zwerdling, S. Theory of optical magneto-
586 absorption effects in semiconductors. *Phys. Rev.* **1959**, *114*, 90.
- 587 (42) Yugova, I. A.; Greilich, A.; Yakovlev, D. R.; Kiselev, A. A.;
588 Bayer, M.; Petrov, V. V.; Dolgikh, Yu. K.; Reuter, D.; Wieck, A. D.
- Universal behavior of the electron g-factor in GaAs/AlGaAs quantum
wells. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 245302.
- (43) Belykh, V. V.; Greilich, A.; Yakovlev, D. R.; Yacob, M.;
Reithmaier, J. P.; Benyoucef, M.; Bayer, M. Electron and hole g factors
in InAs/InAlGaAs self-assembled quantum dots emitting at telecom
wavelengths. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*,
165307.