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# Coherent Spin Dynamics of Electrons and Holes in CsPbBr<sub>3</sub> Colloidal Nanocrystals

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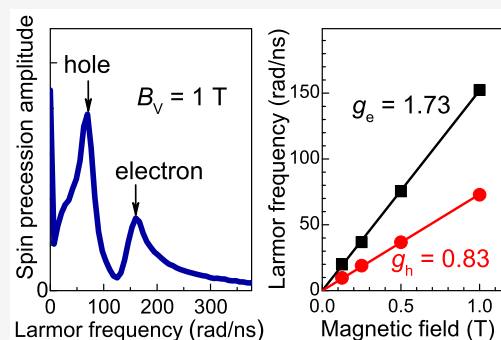
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Supporting Information

**ABSTRACT:** The spin dynamics in CsPbBr<sub>3</sub> 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  $\sim 600$  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 CsPbBr<sub>3</sub> 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, CsPbBr<sub>3</sub>, 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.<sup>1–6</sup> 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 CsPbX<sub>3</sub> (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.<sup>7–10</sup> 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,<sup>11</sup> and the importance of the Rashba effect was elaborated.<sup>12</sup> 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.<sup>13</sup> Anisotropic exciton Zeeman splitting in magnetic field was observed,<sup>14</sup> the coherent spin dynamics of holes were explored in CsPbBr<sub>3</sub>

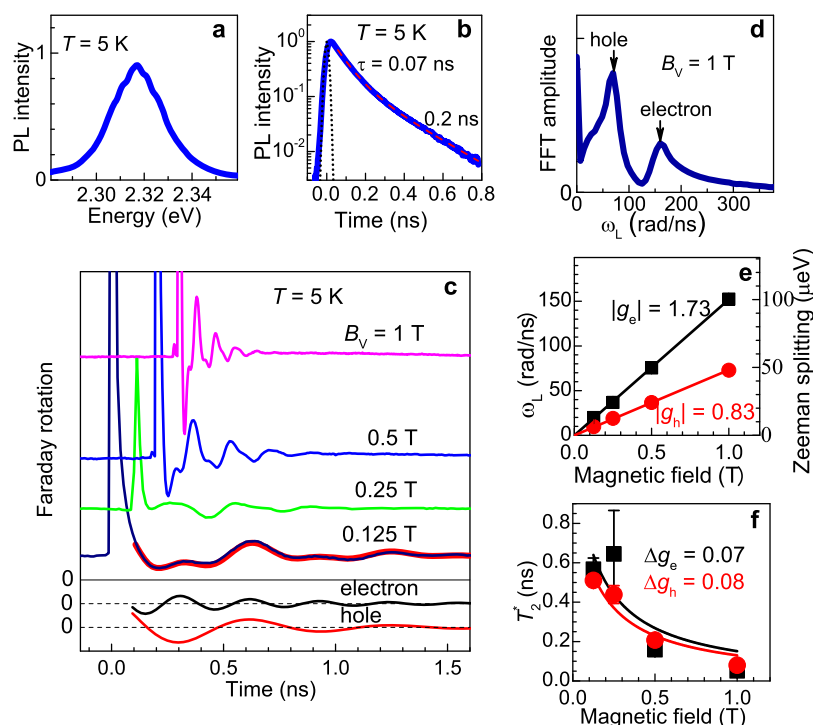
NCs,<sup>15</sup> and the picosecond spin dynamics of carriers were reported in CsPbI<sub>3</sub> NCs.<sup>16</sup>

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.<sup>17–25</sup>

Time-resolved pump–probe Faraday/Kerr rotation is an established technique for fulfilling the previously defined conditions for comprehensive spin physics studies of semiconductors,<sup>26,27</sup> 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.<sup>28–31</sup> Furthermore, its potential was recently demonstrated for CsPbBr<sub>3</sub> single crystals<sup>32</sup> and NCs<sup>15</sup> and for CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>1–x</sub>I<sub>3–x</sub> polycrystalline films.<sup>33</sup>

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**Figure 1.** (a) Photoluminescence spectrum of CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> NCs are  
76 compared with those in a polycrystalline film and a bulk single  
77 crystal.

## 78 ■ OPTICAL PROPERTIES OF NANOCRYSTALS

79 We study CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> NCs can be found in ref 13. It should be  
87 noted that whereas CsPbBr<sub>3</sub> NCs are known to crystallize in  
88 the cubic phase,<sup>3</sup> a recent report shows that they can exhibit  
89 tetragonal and orthorhombic phases at cryogenic temper-  
90 atures.<sup>11</sup> 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 CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> 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.<sup>11</sup> 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 CsPbBr<sub>3</sub> bulk crystals.<sup>32</sup> 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,<sup>13</sup> we measured  
110 polarized PL and recombination dynamics in high magnetic  
111 fields up to 30 T of similar CsPbBr<sub>3</sub> 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 technique<sup>27</sup> allows us to gain more information on the NC  
116 charging,<sup>30</sup> 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  $\mu_B$  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 CsPbBr<sub>3</sub> perovskites.<sup>32</sup> 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 CsPbBr<sub>3</sub> NCs,<sup>13</sup> 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 CsPbBr<sub>3</sub> bulk crystals;<sup>32</sup> 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 CsPbBr<sub>3</sub> NCs show that  
176 the zero-field exciton exchange splitting of neutral excitons is  
177  $\sim 0.6$  meV<sup>11</sup> and that most NCs at low temperatures have  
178 either tetragonal or orthorhombic crystal symmetry. Note that  
179 in rather similar FAPbBr<sub>3</sub> NCs the splitting is found to be in  
180 the range from 0.3 to 1.7 meV.<sup>10</sup> 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  $\sim 0.01$  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

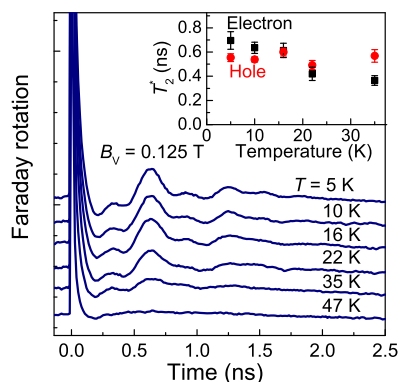
In NCs charged by either a single electron or a single hole, 195  
the ppFR signal is contributed by the spin dynamics of these 196  
resident carriers, limited only by their spin relaxation times. 197  
The spin coherence of the resident carriers is generated via 198  
photoexcitation of a charge exciton (trion) state, as studied in 199  
great detail for (In,Ga)As/GaAs epitaxially grown quantum 200  
dots.<sup>27,34</sup> 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 CsPbBr<sub>3</sub> 212  
and FAPbBr<sub>3</sub> NCs photocharging results in negative and 213  
positive loading of the NCs.<sup>35,36</sup> 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.<sup>37,38</sup> 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  
CsPbBr<sub>3</sub> single crystals.<sup>32</sup> 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 CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub>,<sup>32</sup> 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 CsPbBr<sub>3</sub>, 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.

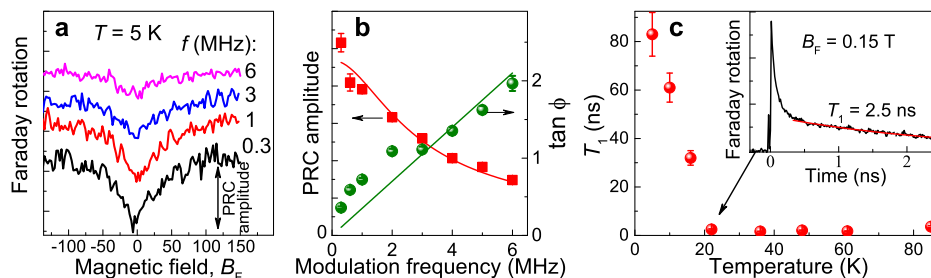
## 260 ■ LONGITUDINAL SPIN RELAXATION OF CARRIERS 261 IN NANOCRYSTALS

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).<sup>39</sup> 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  
CsPbBr<sub>3</sub> 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.<sup>32</sup> Therefore, we suggest  
that the PRC signal in CsPbBr<sub>3</sub> 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.<sup>32,39,40</sup> In addition, the detected signal is retarded by the  
phase,  $\phi$ , 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 CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> Perovskite Samples<sup>a</sup>

	nanocrystals	polycrystalline film	bulk <sup>32</sup>
electron <i>g</i> -factor, <i>g<sub>e</sub></i>	+1.73	+1.78	+1.96
hole <i>g</i> -factor, <i>g<sub>h</sub></i>	+0.83	+0.77	+0.75
exciton <i>g</i> -factor, <i>g<sub>X</sub></i>	+2.4 <sup>13</sup>		+2.35
electron spin dephasing time, <i>T<sub>2,e</sub></i> <sup>*</sup>	0.6–0.7 ns	0.25 ns	0.9–5.2 ns
hole spin dephasing time, <i>T<sub>2,h</sub></i> <sup>*</sup>	0.5 ns	0.4 ns	0.7–1.9 ns
longitudinal spin relaxation time, <i>T<sub>1</sub></i>	56–83 ns		32–53 ns

<sup>a</sup>Results for bulk CsPbBr<sub>3</sub> (single crystal) are taken from ref 32. *T<sub>2</sub>*<sup>\*</sup> values in NCs and bulk are given for *B<sub>V</sub>* = 0.125 T, and those in film are given for *B<sub>V</sub>* = 0.25 T.

the evaluated *T<sub>1</sub>* values for NCs are a few tens of nanoseconds longer than *T<sub>1</sub>* for the corresponding bulk perovskites;<sup>32</sup> see Table 1.

The longitudinal spin relaxation time, *T<sub>1</sub>*, 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, *T<sub>1</sub>* 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 CsPbBr<sub>3</sub> polycrystalline film. Its PL spectrum (Figure 4a) has an

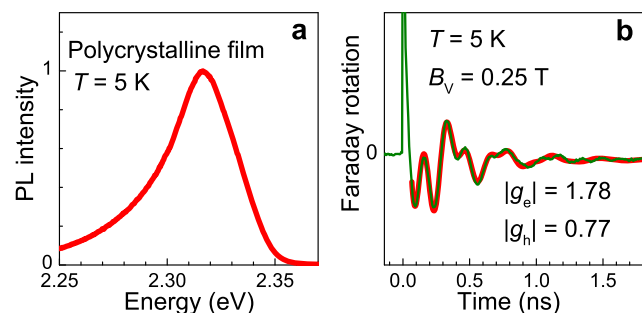


Figure 4. (a) Photoluminescence spectrum of the CsPbBr<sub>3</sub> polycrystalline film. (b) Coherent spin dynamics measured in the film at 2.330 eV for *B<sub>V</sub>* = 0.25 T. The panel gives experimental data (green line) and fit to the data (red line) with eq 1 and *S<sub>e</sub>*/*S<sub>h</sub>* = 0.75.

asymmetric shape with a low-energy tail, similar to the low-temperature emission of bulk CsPbBr<sub>3</sub>.<sup>32</sup> The spin precession monitored by ppFR is given in Figure 4b at *B<sub>V</sub>* = 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<sub>e</sub>*| = 1.78, *|g<sub>h</sub>*| = 0.77, *T<sub>2,e</sub>*<sup>\*</sup> = 0.25 ns, and *T<sub>2,h</sub>*<sup>\*</sup> = 0.4 ns. It is reasonable to suggest that similar to CsPbBr<sub>3</sub> bulk and NCs, *g<sub>e</sub>* > 0 and *g<sub>h</sub>* > 0 in the film.

### SUMMARY OF *g*-FACTORS AND SPIN RELAXATION TIMES IN CsPbBr<sub>3</sub> PEROVSKITE STRUCTURES

It is instructive to compare the *g*-factor values for CsPbBr<sub>3</sub> 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.<sup>41–43</sup> 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.<sup>32</sup>

In conclusion, we performed a detailed study of the electron and hole spin dynamics in CsPbBr<sub>3</sub> 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 *T<sub>2</sub>*<sup>\*</sup> 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 *T<sub>1</sub>* 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 CsPbBr<sub>3</sub> NCs and polycrystalline film, and Zeeman Hamiltonian and *g*-factors of charge carriers and excitons (PDF)

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## 398 Notes

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