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Light-Induced Spontaneous Magnetization in Doped Colloidal Quantum Dots

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An attractive approach to controlling spin effects in semiconductor nanostructures for applications in electronics is the use of light to generate, manipulate, or read out spins. Here, we demonstrate spontaneous photoinduced polarization of manganese(II) spins in doped colloidal cadmium selenide quantum dots. Photoexcitation generates large dopant-carrier exchange fields, enhanced by strong spatial confinement, that lead to giant Zeeman splittings of the semiconductor band structure in the absence of applied magnetic fields. These internal exchange fields allow spontaneous magnetic saturation of the manganese(II) spins to be achieved at zero external magnetic field up to ~50 kelvin. Photomagnetic effects are observed all the way up to room temperature.

uture spintronics and spin-photonics technologies will require a portfolio of techniques for manipulating spins in semiconductor nanostructures (1). One approach is to tailor magnetic exchange interactions between charge carriers and embedded magnetic impurity ions within the semiconductor (1-3), which can lead to the formation of a magnetically ordered state, the socalled magnetic polaron (1, 4). Among the most notable phenomena yet discovered in diluted magnetic semiconductors (DMSs) is the so-called excitonic magnetic polaron (EMP) (Fig. 1A) (5-14), in which charge carrier photoexcitation initiates magnetic polaron formation. EMPs are greatly enhanced by exciton spatial localization (4, 14), a notion that has motivated numerous investigations into epitaxial DMS nanostructures (8, 10-13). Despite more than 40 years of magnetic polaron

studies (15) and its recent renaissance because of its implications for quantum information processing (16, 17) and ferromagnetism in semiconductors (18), EMP signatures have still only been observed below ~30 K, too cold for most practical applications. Furthermore, the experimental exchange fields of only a few tesla contrast with theoretical predictions of exchange fields on the order of 100 T and above (4, 19); magnetic saturation has not been achieved experimentally without the use of strong external magnetic fields at cryogenic temperatures. The data obtained to date thus suggest that EMPs are a low-temperature phenomenon too weak to support spontaneous magnetic saturation.

Recently, chemical syntheses have opened alternative routes to doped semiconductor nanostructures complementary to epitaxially grown materials (Fig. 1, B and C); their spherical zerodimensional geometries provide even greater exciton spatial confinement than in quantum-well heterostructures or self-assembled quantum dots (QDs), and they can be purified, processed, and incorporated into device architectures with the use

of techniques traditionally associated only with molecular species (20-22). Until very recently, however, available colloidal Mn²⁺-doped semiconductor nanocrystals suffered from exciton quenching by rapid energy transfer to Mn2+ after nanocrystal photoexcitation (23). This energy transfer is faster than Mn²⁺ spin reorientation, and it hinders EMP formation (12, 24). Colloidal Mn²⁺:CdSe QDs can now be prepared so that their excitonic photoluminescence (PL) (Fig. 1D) is not quenched by energy transfer to Mn²⁺ because their excitonic energy levels can be tuned to lie below all Mn^{2+} electronic excited states (22, 23). The elimination of $QD \rightarrow Mn^{2+}$ energy transfer allows the observation of excitonic PL with 10 K decay times of $\tau_{\rm em} \sim 100$ ns (25). Previous magnetic circular dichroism and magnetic circularly polarized luminescence experiments have already demonstrated that these long-lived excitons coexist with strong Mn²⁺-exciton magnetic exchange coupling (23).

Here, we demonstrate spontaneous photoinduced polarization of Mn^{2+} spins in colloidal doped CdSe nanocrystals. Very large effective internal magnetic fields were observed that lead to complete magnetization of the nanocrystals in the absence of an external magnetic field at temperatures up to ~50 K, with signatures of photomagnetization observable up to room temperature. These large spin effects can be attributed to the strong zero-dimensional exciton confinement achieved in colloidal doped nanocrystals.

We examined the PL of colloidal Mn²⁺:CdSe DMS QDs as a function of temperature and time (26). Representative variable-temperature PL results are shown in Fig. 1D for diameter d = 4.3 nm, 4.5% Mn²⁺:CdSe QDs. Even at room temperature, the excitonic PL maximum shifts to lower energy as the temperature is lowered, in stark contrast with the Varshni-like temperature dependence that is typically observed with colloidal CdSe QDs (27) and other semiconductors, in which the PL energy

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increases approximately linearly with decreasing temperature in the range of 100 to 300 K and then plateaus. For comparison, Fig. 1E shows PL data for undoped CdSe QDs prepared and measured in an identical fashion. The absorption spectra of the Mn²⁺:CdSe and undoped CdSe QDs both follow Varshni-like temperature dependence (Fig. 1F), as does the PL of the undoped CdSe QDs.

The data in Fig. 1D thus indicate a PL Stokes shift (ΔE , representing shift of the excitonic PL maximum from the excitonic absorption maximum at the same temperature) for the Mn²⁺:CdSe QDs that increases with decreasing temperature, starting already at room temperature (Fig. 1F). This anomalous temperature dependence reflects stabilization of the exciton by Mn²⁺ through a mechanism that is strongly temperature dependent. In epitaxial DMSs, a similar anomalous temperature dependent. In epitaxial DMSs, a similar anomalous temperature dependence has been observed at $T < \sim 30$ K that reflects partial Mn²⁺ spin alignment in the effective exchange field (B_{eff}) of the exciton (*11, 12*). The largest B_{eff} observed in such measurements has been ~3.5 T (*11*).

The data from Fig. 1F are replotted in Fig. 2A as ΔE versus 1/T (where T is temperature), along with similar data for two other colloidal Mn²⁺:CdSe QD samples of different diameters. The resulting plots all show a clear 1/T dependence of ΔE at high temperatures (Curie regime) that saturates at temperatures below ~50 K. As in previous analyses (11, 12, 24), we fit these data to a simple isotropic $S = \frac{5}{2}$ Brillouin function (Eq. 1) to estimate the effective exchange field (B_{eff}) acting on the paramagnetic Mn^{2+} ions within the nanocrystals. In Eq. 1, the $Mn^{2+}g$ factor $g_{Mn} =$ 2.00, $\mu_{\rm B}$ = Bohr magneton, k = Boltzmann constant, and C is a scaling constant proportional to the number of Mn^{2+} per QD (see below). B_{eff} is thus determined by the curvature of the data set, not its height. As illustrated in Fig. 2B, the data from Fig. 1F are reproduced well with $B_{\rm eff} \approx 75$ T (solid red line). This value of $B_{\rm eff}$ is more than one order of magnitude greater than those reported previously. For comparison, the dashed lines in Fig. 2B show the behavior expected from Eq. 1 for various values of $B_{\rm eff}$. As detailed below, $B_{\rm eff}$ here is a phenomenological value with contributions from two major sources, but it is nevertheless extraordinarily large in these colloids.

$$\Delta E = C \left\{ \frac{(2S+1)}{2S} \operatorname{coth} \left[(2S+1) \left(\frac{g_{\mathrm{Mn}} \mu_{\mathrm{B}} B_{\mathrm{eff}}}{2kT} \right) \right] - \frac{1}{2S} \operatorname{coth} \left(\frac{g_{\mathrm{Mn}} \mu_{\mathrm{B}} B_{\mathrm{eff}}}{2kT} \right) \right\}$$
(1)

All samples show similar saturation of ΔE with temperature. Figure 2C plots $B_{\rm eff}$ versus $1/V_{\rm QD}$ from analysis of the data in Fig. 2A using Eq. 1, where $V_{\rm QD}$ is the Mn²⁺:CdSe QD volume. These data yield a straight line that intersects the origin, demonstrating a strong influence of nanocrystal diameter on $B_{\rm eff}$. The exceptionally large values of $B_{\rm eff}$ shown in Fig. 2, compared with those of self-assembled DMS QDs or bulk DMSs (7, 11, 12, 24), can be attributed to increased exciton spatial confinement within these colloidal Mn^{2+} :CdSe QDs, with B_{eff} increasing by ~50% upon reduction of the QD diameter from 5.0 to 4.3 nm.

All of these colloidal Mn²⁺:CdSe QDs show saturation persisting as high as ~50 K ($1/T \approx$ 0.02 K⁻¹). The signature EMP temperature dependence of ΔE is even still clearly observed in all samples up to room temperature ($1/T \approx$ 0.003 K⁻¹) (26). Spontaneous magnetic saturation under the exchange field of an exciton has never been reported in any EMP study. In all previous investigations, $B_{\rm eff}$ induces only partial magnetization but is insufficient to completely align the Mn²⁺ spins, even at liquid helium temperatures. For example, B_{eff} of 3.5 T induces only 75% magnetization at 5 K and only 10% magnetization at 50 K (Fig. 2B) (*11*).

A more detailed picture of these EMPs is obtained from time-resolved PL (TRPL) measurements. Figure 3, A and B, shows TRPL data for doped and undoped CdSe QDs measured at 5 K. The Mn²⁺:CdSe QDs show a large PL redshift within the first few nanoseconds after the laser pulse. The entire PL band shifts in a similar way with time. Relaxation dynamics on



Fig. 1. Colloidal Mn^{2+} :CdSe QDs and their continuous-wave PL. (**A**) Schematic illustration of photoinduced magnetization of magnetic impurities in the effective magnetic field of a confined exciton. Blue arrows indicate Mn^{2+} dopant spins, the yellow arrow indicates the exciton, and the blue curly lines indicate surface capping ligands. (**B**) Transmission electron microscopy image of an isolated colloidal Mn^{2+} :CdSe QD. (**C**) Photograph of a colloidal Mn^{2+} :CdSe QD suspension in ambient room light and in the dark with unfocused laser irradiation. Variable-temperature continuous-wave PL spectra of colloidal (**D**) d = 4.3 nm 4.5% Mn^{2+} :CdSe and (**E**) undoped d = 4.0 nm CdSe QDs at different temperatures. From top to bottom: 5 [in (E)], 8, 30, 50, 70, 100, 120, 150, 170, 200, 225, 250, 275, and 295 K. (**F**) Absorption and PL peak maxima for d = 5.0 nm 4.2% Mn^{2+} :CdSe QDs. The PL of the undoped QDs follows Varshni-like behavior, but for the Mn^{2+} :CdSe QDs, it decreases in energy with decreasing temperature. See (*26*) for experimental details.



Fig. 2. Analysis of continuous-wave PL Stokes shifts. (**A**) PL Stokes shifts versus 1/T for three separate Mn^{2+} :CdSe QD samples of different diameters (red triangles, d = 4.3 nm, 4.5% Mn²⁺; red squares, d = 4.7 nm, 1.4% Mn²⁺; and blue circles, d = 5.0 nm, 4.2% Mn²⁺). (**B**) Fit of the d = 5.0 nm 4.2% Mn²⁺:CdSe QD Stokes shifts to a modified S = 5/2 Brillouin function (Eq. 1) with B_{eff} as the only floating variable, from which B_{eff} of 75 T is estimated (solid red line). The dashed lines illustrate other values of B_{eff} including 3.5 T, the largest B_{eff} recorded from analogous data for epitaxially grown QDs (11). (**C**) B_{eff} values obtained from fitting the data in part (A), plotted versus the inverse QD volumes ($1/V_{QD}$). All reported Mn²⁺ concentrations are actual incorporated concentrations (26).

several different time scales are evident from these data. A very fast relaxation of ~50 meV (less than ~10 ps) can be seen from the difference between absorption and t = 0 PL energies (Figs. 1C and 3C). A similar fast Stokes shift is observed in the undoped CdSe QDs of Fig. 3A, and continuous-wave PL measurements also show Stokes shifts of 50 to 80 meV for the same undoped nanocrystals. Similar Stokes shifts have been described for other undoped colloidal CdSe nanocrystals (~25 to 95 meV) and attributed to relaxation among exciton fine-structure levels (28, 29). This shift is not related to the EMP, and thus, we do not consider it further.

The two dominant relaxation processes in the Mn²⁺:CdSe QDs can be seen more clearly in Fig. 3C, where the 5 K PL maximum is plotted versus time. A fast relaxation of ~100 meV is observed within a few hundreds of picoseconds [similar to EMP formation times reported previously ($\tau_{\rm mp}$ ~ 50 to 250 ps) (6, 10, 12, 13)], followed by a slow relaxation over several nanoseconds that converges to the continuous-wave Stokes shifts at long times. The fast relaxation accounts for approximately half of the total continuous-wave Stokes shift and is attributed to EMP formation. The TRPL data also allow the temperature dependence of this EMP formation energy (E_{mp}) to be analyzed. For comparison with Fig. 1F, Fig. 3D illustrates the PL energies measured at t = 0, 1, and 13 ns after thelaser pulse for the same particles as described by

Fig. 1F. Plotting the 1-ns Stokes shifts versus 1/T yields a Brillouin-like saturation magnetization curve (Fig. 3E) similar to that of the total continuous-wave Stokes shift (Fig. 2B). Fitting this curve to Eq. 1 yields best-fit parameters of $B_{\rm eff} \approx 40$ T and $\Delta E = 80$ meV, which can now be associated with magnetic polaron formation (i.e., $B_{\rm eff} \approx B_{\rm mp}$, $\Delta E \approx E_{\rm mp}$), as in previous studies.

The expected temperature dependence of $E_{\rm mp}$ can also be estimated from Eq. 1 and previously reported parameters, with no fitting. EMP formation is primarily the result of kinetic $e_{\rm VB}^- - {\rm Mn}^{2+}$ exchange, which is typically about four to six times stronger than the $e_{\rm CB}^- - {\rm Mn}^{2+}$ interaction. $B_{\rm mp}$ can thus be described in terms of the isotropic mean-field $e_{\rm VB}^- - {\rm Mn}^{2+}$ exchange energy $(N_0\beta)$ with the use of Eq. 2 (9). Here, $V_{\rm ex}$ is the exciton localization volume, and N_0 is the cation density.

$$B_{\rm mp} \approx \frac{|N_0\beta|}{2\mu_{\rm B}g_{\rm Mn}} \cdot \frac{1}{N_0 V_{\rm ex}}$$
(2)

Because of the large surface confinement potential, $V_{\rm ex}$ is substantially smaller than $V_{\rm QD}$. An infinite spherical potential–well calculation yields $V_{\rm ex} = 23.2$ nm³ for d = 5 nm CdSe QD. From Eq. 2 and $N_0\beta = -1.3$ eV (4), a value of $B_{\rm mp} \approx 14$ T is calculated. In addition, the magnitude of $E_{\rm mp}$ can be calculated. The prefactor from Eq. 1 is $C \approx \frac{1}{2}|x_{\rm eff}N_0\beta S|$, where $x_{\rm eff}$ is the effective



Fig. 3. TRPL data. TRPL spectra for (**A**) *d* = 5.0 nm 4.2% Mn²⁺:CdSe and (**B**) undoped *d* = 4.0 nm CdSe QDs at cryogenic temperatures. The vertical dashed line indicates the PL energy 13 ns after the laser pulse. The Mn²⁺:CdSe QD PL shows a large red shift after the laser pulse, whereas the CdSe QD PL shows only a small red shift. (**C**) 5-K PL energy maximum versus time for the same Mn²⁺:CdSe QDs, emphasizing EMP formation ($\tau_{mp} \approx 50$ to 500 ps, blue line with long dashes) and reorientation ($\tau_{slow} \approx 2$ to 20 ns, blue line with short dashes) time scales of the multi-exponential decay. The PL energy converges to that observed in continuous-wave measurements (1.88 eV, *t* = ∞). The red line shows a fitted tri-exponential decay ($\tau_1 = 10$ ps, $\tau_2 = 570$ ps, $\tau_3 = 20$ ns) for illustration. Vertical dotted lines indicate timeline discontinuities. (**D**) Mn²⁺:CdSe QD PL maximum versus temperature, measured ~0, 1, and 13 ns after the laser pulse. (**E**) Mn²⁺:CdSe QD PL Stokes shift at 1 ns versus 1/*T*. The dashed line shows the predicted temperature dependence calculated from Eqs. 1 and 2 with the reported value of $N_0\beta$, as described in the text. This calculation yields $B_{mp} = 14$ T and $E_{mp} = 68$ meV.

 Mn^{2+} concentration and $S = \frac{5}{2}$, again neglecting the weak e_{CB}^- – Mn²⁺ interaction. At saturation, a value of $E_{\rm mp} \approx 68$ meV is calculated, assuming all Mn^{2+} contribute (i.e., $x_{eff} = 0.042$). The predicted temperature dependence of ΔE calculated from Eq. 1 using just these values is depicted in Fig. 3E, alongside the 1-ns PL data. The predicted curve agrees reasonably well with experiment, supporting assignment of this fast relaxation as EMP formation, but it also reveals that the isotropic EMP model alone is not sufficient to explain the data. In particular, the greater-than-predicted Stokes shifts observed at elevated temperatures indicate a contribution to the 1-ns data from the slower relaxation process that is also observed in Fig. 3, C and D, which is not accounted for in Eqs. 1 and 2.

The additional slow relaxation (several tens of millielectron volts) takes place with a time constant τ_{slow} of ~2 to 20 ns (Fig. 3, C and D). A similar slow EMP relaxation has occasionally been observed in other DMSs and attributed to various possible effects, from exciton localization to intersystem crossing (10, 30), but its precise origin is uncertain. Regardless of its origin, this component is associated with the EMP because it is not observed in undoped CdSe QDs and because it shows a similar Brillouin-like saturation at low temperatures. We favor an interpretation in which τ_{slow} arises from EMP directional reorientation within a potential energy surface that is warped by anisotropy. The time scale of this relaxation is similar to that of EMP reorientation by an applied magnetic field in $Cd_{1-x}Mn_x$ Te epilayers ($\tau \sim 2$ ns) (7). The EMP anisotropy energy is similar to those observed in Cd_{1-x}Mn_xTe digital quantumwell structures (8) and predicted for unstrained $Cd_{1-x}Mn_xTe(31)$, in both cases originating from the anisotropy of the hole effective mass. The analogy between anisotropic magnetic polarons and single-molecule magnets has also been described theoretically (17). In our samples, the hexagonal crystal field anisotropy of wurtzite CdSe probably dominates this surface warping, but nanocrystal shape anisotropy is also expected to contribute substantially. This anisotropy model accounts for the time scale of the slow relaxation, as well as the observation that the total EMP stabilization energy at long times (more than ~140 meV, see Figs. 2A and 3A) exceeds what would be possible in the isotropic limit (Fig. 3E).

 $\tau_{\rm slow}$ is slower than the typical exciton recombination times of self-assembled DMS QDs ($\tau_{\rm em} \sim$ 300 to 600 ps at 2 K) (12), suggesting that EMP relaxation magnitudes in those materials may be limited by their relatively fast exciton recombination kinetics. In contrast, $\tau_{\rm em} \sim 100$ ns at 10 K and $\tau_{\rm em} \sim 30$ ns at room temperature for these colloidal DMS QDs (25), allowing EMP relaxation dynamics to be probed in the absence of competing recombination processes, even at elevated temperatures. This exceptionally long $\tau_{\rm em}$ is itself also important, because it suggests that the dark-bright formalism used to describe exciton fine-structure splittings in undoped QDs (28) may still be applicable in these Mn²⁺:CdSe QDs,

despite the strong Mn^{2+} -exciton exchange coupling. In colloidal CdSe QDs, these long τ_{em} arise from confinement-enhanced electron-hole exchange interactions (28), and thus they have the same ultimate origin as the exceptionally large B_{mp} values shown in Figs. 2 and 3.

The conclusions presented above are summarized in Fig. 4. Figure 4A shows a plot of energy versus magnetization in a magnetic analog of the single-configurational-coordinate (SCC) diagrams typically used to represent electron-nuclear reorganization after photoexcitation. Much like the SCC diagrams, this magnetic coordinate diagram is valid to the extent that magnetic effects are slow relative to electronic transitions. In this diagram, the DMS QDs in their dark-adapted state reside at $\langle S_{\phi} \rangle \approx 0$, having only small magnetization fluctuations around zero and no time-averaged magnetization. Photoexcitation generates an excited state that is unstable with respect to magnetization along a random direction ϕ , defined by some combination of the direction of spontaneous Mn²⁺ fluctuation magnetization at the instant of photoexcitation and the initial hole spin orientation, and results in spontaneous relaxation either to the right or to the left of $\langle S_{\phi} \rangle = 0$ in Fig. 4A via magnetization of the Mn²⁺ sublattice. Magnetic saturation is reached

only if B_{mp} is sufficiently large, and even then only if τ_{mp} is sufficiently fast compared with exciton recombination (τ_{em}). This spontaneous magnetization takes place within a few hundred picoseconds and is followed by slower directional reorientation of the entire EMP (with $\tau_{slow} > 2$ ns) within a potential energy surface warped by anisotropy. Figure 4B illustrates such a warped surface for the case of axial anisotropy, where ϕ represents the initial magnetization direction, and θ and ε represent the two unique magnetization orientations.

The competition among concurrent excitedstate magnetization and exciton recombination dynamics is summarized schematically in Fig. 4C. Upon exciton recombination, the system returns vertically to a nonequilibrated ground state having $|\langle S_{\phi} \rangle| > 0$, and it thermalizes slowly back to $\langle S_{\phi} \rangle \approx 0$ with $\tau_{\rm MnSLR} \sim 0.1 \ \mu s$ – ms (where $\tau_{\rm MnSLR}$ is the Mn²⁺ spin-lattice relaxation time constant) (6, 13). If the system is excited again before ground-state thermalization, the excited state is already displaced relative to $\langle S_{\phi} \rangle = 0$ because the excitation occurs vertically; such spin accumulation has been observed previously (32). In the present experiments, the average time between excitation events (>100 \mu s) greatly exceeds the estimated Mn²⁺ spin-lattice relaxa-



Fig. 4. Competition among dynamic relaxation processes. (**A**) Magnetic coordinate diagram illustrating spontaneous Mn^{2+} magnetization under the exchange field of the exciton, oriented along a random initial coordinate ϕ . The orange and blue lines represent the upper and lower Zeeman components, respectively, of the lowest excitonic level. Magnetization occurs with τ_{mp} and competes with τ_{em} . After exciton recombination (with τ_{em}), the Mn^{2+} spin sublattice relaxes back to zero net magnetization with τ_{MnSLR} . ΔE_{Zeeman} , the total excitonic Zeeman splitting energy; *h*, Planck's constant; v, frequency. (**B**) Schematic illustration of the effect of anisotropy on the excited-state potential energy surfaces described in (A) for a hypothetical case of axial anisotropy, where θ and ε represent the two unique magnetization orientations. The orange and blue surfaces represent the upper and lower Zeeman components, respectively. Lower-symmetry anisotropies will cause more ruffling. (**C**) Schematic summary of all competing dynamics within (B). Photoexcitation of a dark-adapted Mn^{2+} :CdSe QD initiates EMP formation. Fast relaxation occurs with τ_{mp} along a random initial direction ϕ and is followed by slow reorientation toward ε with τ_{slow} to minimize total energy. These kinetics are in competition with τ_{em} . After recombination, the system returns to its dark-adapted form with τ_{MnSLR} .

tion time $(\tau_{MnSLR} \sim 0.1 \ \mu s)$ (13), and spin accumulation is not anticipated.

Future investigation into these and related DMS QDs can be anticipated to reveal new possibilities for spin manipulation in semiconductor nanostructures. In particular, the combination of such strong photomagnetic effects with colloidal processability may now allow incorporation of new spin effects like EMPs (which were previously accessible only in epitaxial DMSs) into molecular devices via spin-coat processing, self-assembly, or other related "soft" chemical techniques that have become mainstays of nanotechnology.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/325/5943/973/DC1 Materials and Methods

Fig. S1 References

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