Spin-polarized Mn\(^{2+}\) emission from Manganese-doped colloidal nanocrystals

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We report magneto-photoluminescence studies of strongly quantum-confined “0-D” diluted magnetic semiconductors (DMS), realized in Mn\(^{2+}\)-doped ZnSe/CdSe core/shell colloidal nanocrystals. In marked contrast to their 3-D (bulk), 2-D (quantum well), 1-D (quantum wire), and 0-D (self-assembled quantum dot) DMS counterparts, the ubiquitous yellow emission band from internal d-d (\(\Pi_1 \rightarrow \Pi_0\) A\(_1\)) transitions of the Mn\(^{2+}\) ions in these nanocrystals is not suppressed in applied magnetic fields and does become circularly polarized. This polarization tracks the Mn\(^{2+}\) magnetization, and is accompanied by a sizable energy splitting between right- and left-circular emission components that scales with the exciton-Mn sp-d coupling strength (which, in turn, is tunable with nanocrystal size). These data highlight the influence of strong quantum confinement on both the excitation and the emission mechanisms of magnetic ions in DMS nano-materials.

The coupling between band electrons and local magnetic moments underpins many fascinating phenomena in condensed matter physics. In semiconductors, these couplings are simply realized and often studied in diluted magnetic semiconductors (DMS) \([1–3]\), where the strong sp-d exchange interactions between electron/hole spins and the embedded magnetic atoms (typically Mn) can lead, for example, to giant exciton g-factors, magnetic polarons, or carrier-mediated ferromagnetism in both II-VI and III-V materials. To address how sp-d interactions are affected – and potentially controlled – by quantum confinement and wavefunction engineering, advances in molecular-beam epitaxy (MBE) and colloidal synthesis have focused considerable attention on DMS systems of reduced dimensionality: 2-D quantum wells, 1-D wires, and 0-D epitaxial dots and (even smaller) nanocrystals. Recent studies indicate substantial influence arising from even single Mn atoms \([4, 5]\), and suggest that the sp-d exchange ‘constants’ themselves are modified \([5, 10]\).

A defining feature of wide-gap A\(_1\)B\(_{1-}x\)Mn\(_x\)B\(_{VI}\) DMSs (\(E_g > 2.2\) eV) is a prominent yellow photoluminescence (PL) band centered at \(\sim 2.1\) eV, that originates from internal (\(\Pi_1 \rightarrow \Pi_0\) A\(_1\)) transitions within excited 3d\(^2\) shells of the Mn\(^{2+}\) ions \([1, 2]\). That is, a band-edge exciton can either recombine radiatively with rate \(k_{R}\), or transfer its energy to a Mn\(^{2+}\) ion via an Auger-like process (described below) with rate \(k_{Mn}\) that depends on the exciton-Mn coupling. It is known that at low temperatures and in magnetic fields, this Mn\(^{2+}\) PL band is suppressed and remains unpolarized, while the band-edge exciton PL increases and circularly polarizes. This universal behavior has been observed in DMS crystals, epilayers, quantum wells, quantum wires, and in epitaxial quantum dots \([1, 2, 11, 12]\). To date however, the magneto-optical and polarization properties of this Mn\(^{2+}\) PL have not been reported in colloidal DMS nanocrystals, despite widespread technological interest in their use as efficient phosphors \([19]\) or spintronic materials \([20]\) and despite being materials that evince the strongest quantum confinement and potentially largest exciton-Mn coupling.

Here we measure the magneto-PL properties of Mn\(^{2+}\)-doped ZnSe/CdSe core/shell colloidal nanocrystals. In stark contrast to their 3-D (bulk), 2-D (quantum well), 1-D (wires and rods) and even their 0-D (epitaxial quantum dot) DMS counterparts, the yellow Mn\(^{2+}\) PL band in these nanocrystals is not suppressed in applied magnetic fields and does develop a sizable circular polarization. This polarization tracks the magnetization of the embedded Mn\(^{2+}\) atoms, and is accompanied by an unexpectedly large energy splitting between right- and left-circular PL components that scales with the overall strength of the sp-d interaction (which, in turn, we tune with CdSe shell thickness). These data highlight the critical role of strong quantum confinement on both the excitation and the emission of Mn\(^{2+}\) atoms in DMS nano-materials.

Mn\(^{2+}\)-doped ZnSe/CdSe core/shell nanocrystals (NCs) were grown using colloidal methods \([5, 21]\). All ZnSe cores have 17 \(\AA\) radii. Five doping levels yielded cores averaging \(\langle n_{Mn}\rangle=0.8, 1.6, 2.6, 5.2, \) and 9.6 Mn\(^{2+}\) ions/core (average Mn concentration up to \(\sim 2\%\)), as determined by inductively-coupled plasma optical emission spectroscopy. Nonmagnetic (undoped) cores were also grown. Ensembles of cores were then overcoated with CdSe shells of thickness 0-6 (\(\pm 2\) \(\AA\)), which reduces quantum confinement and lowers the NC band-edge from 3 eV to \(\sim 2.4\) eV. Nonresonant magneto-PL was measured using weak 3.06 or 3.81 eV laser excitation (100 µW/cm\(^2\)) in the Faraday geometry (\(B||k\)), with dilute NC films mounted in the variable-temperature insert of a 8 T magnet. Importantly, magnetic circular dichroism (MCD) spectroscopy was also performed on all films to measure the Zeeman splitting of the 1S (band-edge) exciton absorption peak. All Mn-doped NCs show enhanced Zeeman splittings that follow Brillouin (\(B_{5/2}\)) functions, indicating strong sp-d coupling of the bands to the paramagnetic, spin-5/2 Mn\(^{2+}\) ions \([3, 10, 20]\). This provides an independent measure of the Mn\(^{2+}\) magnetization within a given NC sample.
FIG. 1: (a,b) Magneto-PL from bulk ZnMnSe at 4 K, showing conventional DMS behavior. The yellow $^4T_1 \rightarrow ^6A_1$ Mn$^{2+}$ PL at $\sim$2.1 eV is suppressed by magnetic fields and remains unpolarized, while 2.8 eV exciton PL (scaled down 15×) increases. Similar behavior is found in 3D, 2D, 1D, and 0D DMS grown by MBE. (c,d) The contrasting magneto-PL from Mn:ZnSe/CdSe nanocrystals ($n_{Mn}$=2.6 Mn/core; $T=1.8$ K). The Mn$^{2+}$ PL is not suppressed by magnetic fields, and does develop a sizable circular polarization (and, exciton PL never appears). The dashed line shows the NC absorption.

and allows to compare the overall strength of the $sp$-$d$ interaction between samples. Quantum confinement and $sp$-$d$ coupling fall rapidly with increasing shell thickness as previously observed $^{10}$, however these NCs do not exhibit $sp$-$d$ inversion since the NC band-edges did not fall below $\sim$2.4 eV.

To most clearly present the new aspects of the Mn$^{2+}$ PL from these NCs, we first show, by way of comparison, the characteristic magneto-PL from a traditional wide-gap II-VI DMS. Fig. 1(a) shows PL from a Zn$_{0.92}$Mn$_{0.08}$Se epilayer grown by MBE. At 0 T, the broad Mn$^{2+}$ PL band is clearly visible at $\sim$2.1 eV, as is the PL from exciton recombination at the 2.8 eV band-edge. With applied magnetic field the Mn$^{2+}$ PL is rapidly and equally suppressed in both $\sigma^{\pm}$ circular polarizations (Fig. 1b), while the exciton PL increases many-fold and becomes completely $\sigma^{+}$ polarized. We observed similar behavior in a variety of other DMS epilayers and quantum wells.

This behavior – a suppression of the un-polarized Mn$^{2+}$ PL and an enhancement and polarization of the exciton PL – is a universal characteristic of all non-resonant magneto-PL studies of DMS materials reported to date, aspects of which have been reported in bulk crystals $^{1,2,11,13}$, in quantum wells $^{14}$, quantum wires $^{15}$, and in “self-assembled” epitaxial quantum dots $^{16}$.

Although the precise mechanism of energy transfer from excitons to the Mn$^{2+}$ 3d$^5$ shell is still debated $^{13,14,18,22}$, its marked field dependence indicates a spin-dependent excitation transfer as detailed by Nawrocki $^{22}$ and later refined by Chernenko $^{18}$. The relevant selection rules require that energy transfer conserves the spin projection of the Mn$^{+}$ exciton system along $B$, $S_{Mn}^{z}$ + $\sigma^{\pm}$. Using standard notation $^{1,2}$, the spin-aligned ground state of the half-filled Mn$^{2+}$ 3d$^5$ shell ($^6A_1$) has total spin $S_{Mn}^{z}$=$5/2$, whilst the lowest crystal-field-split excited states ($^4T_1$, $^4T_2$, $^4A_1$, $^4E$) have one flipped spin and therefore $S_{Mn}^{z}$=$3/2$. Applied fields Zeeman-split these levels [inset, Fig. 1(b)]. “Bright” excitons (with total spin $\sigma^{\pm}$) PL is rapidly and equally suppressed by magnetic fields, and therefore they cannot excite Mn$^{2+}$ out of $S_{Mn}^{z}$=$5/2$ levels. However, the -5/2 level becomes predominantly populated as the paramagnetic Mn$^{2+}$ polarize in applied magnetic fields. Concurrently, in the Faraday geometry, excitons rapidly populate the lowest $J_z$=$-1$ bright state $^{18}$. These effects suppress the exciton-Mn energy transfer rate $k_{Mn}$ and therefore suppress (enhance) the Mn$^{2+}$ (exciton) PL. In contrast, “dark” ($J_z=$±2) excitons have $s_{Mn}^{\pm}$ = ±1 and can excite the $S_{Mn}^{z}$=$5/2$ ground state; this explains why, e.g., PL intensities in epitaxial dots are relatively unaffected in the Voigt geometry ($B,\perp k$, $B\parallel$ dot axis), where bright and dark excitons become mixed $^{18}$.

Once the Mn$^{2+}$ 3d$^5$ shell is excited, relaxation to the $^4T_1$ level proceeds quickly $^{18}$. From this point, however, radiative transitions to the $^6A_1$ ground state are nominally spin-forbidden. However, weak spin-orbit couplings of the $^4T_1$ levels soften these selection rules $^{1,2}$, allowing phonon-assisted Mn$^{2+}$ PL at $\sim$2.1 eV.

In marked contrast to the conventional behavior just described, Figs. 1(c,d) show magneto-PL from Mn:ZnSe/CdSe nanocrystals. At zero field, only the Mn$^{2+}$ PL band is visible – exciton PL is entirely quenched (undoped but otherwise identical NCs do show strong exciton PL at $\sim$2.7 eV; not shown). Thus, energy transfer from excitons to the Mn$^{2+}$ ions is quite efficient in these NCs even though the average Mn concentration is <1%. More importantly, the Mn$^{2+}$ PL band is not suppressed in applied magnetic fields – rather, it develops a pronounced circular polarization of $\sim$30%. To our knowledge, this behavior has no precedent in any non-resonant PL study of $^{11}I_{x}^{x-Mn_x}By_{VI}$ materials reported to date $^{11,14,18}$. These data therefore provide a first indication that, in contrast to typical DMS materials, the Mn$^{2+}$ PL from DMS nanocrystals is more than merely a byproduct of exciton-Mn energy transfer. Rather, the data point to the fundamentally different character of both the Mn$^{2+}$ excitation and emission process in strongly quantum-confined systems which, as elucidated below, can actually be used to reveal spin physics and $sp$-$d$ interactions in nanoscale DMS materials.

We note that these new findings are unrelated to
the circularly-polarized exciton PL reported in large Mn:CdSe NCs [20]. By design, excitons in large Mn:CdSe NCs have energies <2.1 eV, so that energy transfer to the Mn

It is also evident in Fig. 1(c) that exciton PL at the NC band edge never appears in applied magnetic fields to 6 T (and even in ultrahigh fields to 55 T; not shown). Again, this stands in marked contrast to conventional DMSs [1, 2, 11–18], where band-edge PL increases dramatically with field because the exciton-Mn energy transfer rate \(k_Mn\) is suppressed. Thus, exciton-Mn energy transfer remains surprisingly efficient in these NCs, even when the Mn

Importantly, Figure 2 reveals that the circular polarization of the Mn

Moreover, while \(\Delta E\) is found to be largely independent of \(\langle n_{Mn}\rangle\), it does depend on the degree of quantum confinement in these core-shell NCs, which we can tune by varying the CdSe shell thickness. Figure 3(c) shows \(\Delta E\) measured in a series of NCs with identical Mn:ZnSe cores, but with increasing CdSe shell thickness. While still following a Brillouin function, the saturation amplitude of \(\Delta E\) is considerably reduced when the CdSe shell is thicker. Crucially, the reduction in \(\Delta E\) is almost perfectly echoed by the similar reduction of the \(sp-d\) coupling strength in the same three samples (as measured by MCD via the 1S Zeeman splitting). As shown previously [10], thicker CdSe shells cause the conduction- and valence-band wavefunctions to occupy larger volumes, thereby reducing their overlap with the embedded Mn

Perhaps most interestingly, and again in contrast to conventional DMS materials, we find that the Mn

not change \(\Delta E\) appreciably. As such, \(\Delta E\) saturates by only a few tesla at low temperatures – but at large values of order 5–10 meV, which greatly exceeds the typical linear Zeeman shifts expected of Mn

FIG. 2: (a) The circular polarization \((CP)\) of the Mn

\[\begin{array}{c|c}
T=1.8 K & T=4 K \\
\hline
\langle n_{Mn}\rangle=0.8 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=9.6 K & T=20 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=40 K & T=55 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=60 K & T=300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=60-300 K & T=60-300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=60-300 K & T=60-300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
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T=60-300 K & T=60-300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
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\[\begin{array}{c|c}
T=60-300 K & T=60-300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
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1.0 & 1.1 \\
\end{array} \]

\[\begin{array}{c|c}
T=60-300 K & T=60-300 K \\
\hline
\langle n_{Mn}\rangle=1.6 Mn/core & \langle n_{Mn}\rangle=1.6 Mn/core \\
\hline
0 & 0.1 \\
0.2 & 0.3 \\
0.4 & 0.5 \\
0.6 & 0.7 \\
0.8 & 0.9 \\
1.0 & 1.1 \\
\end{array} \]
While awaiting a formal theoretical underpinning of these effects, we anticipate that studies of single Mn-doped NCs will help unravel the nature of this coupling, as will measurements of ultrafast exciton dynamics as a function of NC size, B, and Mn$^{2+}$ doping. The role of any excess charge in these NCs, and how it may influence the polarization and energy of Mn$^{2+}$ emission, also merits investigation [28].

In summary, these studies reveal that the processes of both Mn$^{2+}$ excitation and Mn$^{2+}$ emission are essentially different in colloidal DMS nanocrystals as compared to conventional DMS materials. Magnetic fields do not suppress the efficient exciton-Mn energy transfer, implicating the potential role of dark excitons in these NCs. Further, the circular Mn PL polarization and unexpectedly large energy splitting (that scales with sp-d coupling strength) highlights the critical influence of strong quantum confinement and suggests their use as powerful probes of spin interactions in nanoscale DMS materials. This work was supported by the DOE Basic Energy Sciences Chem., Bio- and Geosciences Division. We thank N. Samarth for the ZnMnSe epilayers, and J. Gaj, D. Yakovlev, and Al. Efros for valuable discussions.

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