Photoluminescence lifetime of nanocrystalline ZnS:Mn^{2+}

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It is beyond common understanding that the photoluminescence lifetime of the transition $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} doped in ZnS decreases dramatically by five orders of magnitude from bulk to nanocrystal since the magnetic interactions which usually make the spin-forbidden transition allowed cannot be so strong. In this paper, we present a possible mechanism involving the exchange Coulomb interaction between the *d* electrons of Mn^{2+} and the electrons of the host. Assuming that the spin of the ground state of the host is not zero, and that the exchange Coulomb interaction causes mixing between the excited $^4T_1$ state of Mn^{2+} and a certain excited state of the host whose energy is slightly higher than that of the $^4T_1$ state of Mn^{2+}, we demonstrate that the spin-forbidden transition could be almost allowed. Moreover, the mixing degree increases as the particle size of the nanocrystal decreases. A numerical estimation about this mechanism agrees with the experimental results of optical and magnetical properties. [S0163-1829(98)02544-2]

I. INTRODUCTION

The luminescent properties of nanosized materials have attracted considerable interest in recent years. Semiconductor nanocrystals have an increased energy band gap and a blue-shifted spectrum, which result from quantum confinement.[1] Nanosized materials doped with transition metals or rare-earth elements have increased quenching concentration since the resonant energy transfer among the luminescent centers is blocked by the boundary of nanosized particles.[2]

The most significant and puzzling finding thus far is that the photoluminescence (PL) lifetime of nanocrystalline ZnS:Mn^{2+} is at least five orders of magnitude shorter than that of the bulk crystal while still yielding a considerably high external luminescent quantum efficiency (see Table I or Ref. 3 for details). Recent experiments done by Sooklal *et al.* likely indicate that decreased particle size results in a decreased lifetime for aqueous colloidal ZnS:Mn^{2+}.[4] Similar phenomenon were also observed in our recent experiment on nanocrystalline thin-film $ZnSiO_4$:Mn^{2+}, the decay time of which drops from several ms to several tens of ns. All these findings verify that there exists an obviously unusual fast transition component in the luminescent decay of this kind of transition-metal-doped nanocrystals. To seek explanation of this phenomenon, a suggestion was proposed that quantum confinement could cause strong mixing of the *sp* electrons of the host ZnS and dopant Mn^{2+} with the *d* electrons of dopant, and that this mixing could change the spin-forbidden transition to an allowed one.[3] However, the unusual mechanism of how the spin-forbidden transition could be allowed in such degree is still not clear, since it is well known that the spin-orbit interaction or the magnetic dipole interaction with radiative field, which includes the spin of *d* electron of Mn^{2+}, cannot be so strong as to change the spin-forbidden transition to an allowed one. In this paper, we will show a mechanism to solve the ''relaxation of the forbiddenness'' puzzle. Firstly, we analyze the origin of the puzzle from the standpoint of crystal-field theory. We then present a model including the exchange interaction between the orbits of Mn^{2+} and ZnS and give a numerical estimation of the model. Finally, we give further experimental supports.

TABLE I. PL properties of nanocrystalline and bulk ZnS:Mn^{2+}.

Sample	Nanocrystalline ZnS:Mn^{2+}	Bulk ZnS:Mn^{2+}
E_g	4.2 eV	3.66 eV
Excitation peak	265 nm (4.68 eV)	332 nm (3.73 eV)
Full width at half maximum (FWHM) of excitation peak	2 eV	0.5 eV
Emission peak	590 nm (2.10 eV)	584 nm (2.12 eV)
FWHM of emission peak	0.33 eV	0.23 eV
Lifetime	20.5 ns, 3.7 ns	1.8 ms
Quantum efficiency	18%	unknown

II. ORIGIN OF THE PUZZLE

Let us first analyze the luminescence mechanism of crystalline ZnS:Mn^{2+}. The energy-level structure and luminescent transition of Mn^{2+} doped in ZnS can be described by a crystal-field Hamiltonian under T_d symmetry, i.e.,

$$H = H_0 + H^c_{\text{even}} + H^c_{\text{odd}} + H_{sl}, \tag{1}$$

where H_0, H^c_{even}, H^c_{odd}, and H_{sl} are quasifree ion, even crystal field, odd crystal field and spin-orbit interaction Hamiltonian, respectively. The energy-level structure of Mn^{2+} is mainly determined by $H_0 + H^c_{\text{even}}$. H^c_{odd} and H_{sl} result in states of mixed parity and spin, respectively. Under T_d symmetry, the luminescent transition of $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} is spin-forbidden while the weak interaction H_{sl} makes the transition slightly allowed. The forbiddenness caused by the parity selection rule is largely relaxed due to the parity mixing caused by the strong interaction H^c_{odd} under T_d symmetry. The oscillator strength of the electric dipole transition $^4T_1 \rightarrow {}^6A_1$ is estimated as follows (magnetic dipole transition is too weak to be considered):

$$P_e = P_e^0 \left| \frac{\langle H^c_{\text{odd}} \rangle}{\Delta(n'l')} \right|^2 \left| \frac{\langle H_{sl} \rangle}{E(^4T_1) - E(^6A_1)} \right|^2, \tag{2}$$

where P_e^0 is the oscillator strength of allowed electric dipole transition, whose order of magnitude is 1. As for visible light, the corresponding luminescence lifetime is about 1 ns. $\langle H^c_{\text{odd}} \rangle$ is the matrix element of H^c_{odd} between d^5-electron states [such as $(3d)^5\ {}^6A_1$] and excited states with opposite parity (such as $(3d)^4(4p)^6A_1$). Under T_d symmetry, $\langle H^c_{\text{odd}} \rangle \approx 10^4\ \text{cm}^{-1}$, which has the same order of magnitude as $\langle H^c_{\text{even}} \rangle$, since the system has no inversion symmetry; $\Delta(n'l')$ is the energy difference between the d^5 states and the excited states with opposite parity mentioned above, whose value is about $5 \times 10^4 - 10^5 cm^{-1}$; $\langle H_{sl} \rangle$ is the matrix element of H_{sl} between $^6A_1$ and $^4T_1$ states, with the order of magnitude of $10^2\ \text{cm}^{-1}$; $E(^4T_1) - E(^6A_1) \approx 1.7 \times 10^4\ \text{cm}^{-1}$. Thus, we have the estimation $P_e \sim 10^{-6}$, which corresponds to a luminescence lifetime of ms order of magnitude (Table I). Therefore, the small decay rate (radiative and nonradiative) of the $^4T_1 \rightarrow {}^6A_1$ transition is mainly because H_{sl} is too weak. From the viewpoint of cubic crystal-field picture, the domain parts of $^6A_1$ and $^4T_1$ states are $|(e\uparrow)^2(t_2\uparrow)^3\ {}^6A_1 M_s a_1\rangle$ and $|(e\uparrow)^2(e\downarrow)^1(t_2\uparrow)^2\ {}^4T_1 M_s \gamma\rangle$, respectively, so the transition between the two states is essentially a spin-forbidden one-electron transition $|e\downarrow\rangle \rightarrow |t_2\uparrow\rangle$.

Now let us compare the structural properties of bulk crystal and nanocrystalline ZnS:Mn^{2+}. In both kinds of ZnS:Mn^{2+}, Mn^{2+} substitutes for Zn^{2+} and has T_d site symmetry; Mn^{2+} has a stronger interaction with host than Zn^{2+}, since the radius of Mn^{2+} (0.80 Å) is larger than that of Zn^{2+} (0.74 Å). Extended x-ray absorption fine structure experiments show that the distance between Mn^{2+} and its S^{2-} ligands of nanocrystallite contracts only 1–3% compared to that of a bulk one, while the bond angles have no distinct change.[5] A nanosized particle of 2–3 nm has only 100–300 primitive cells, about half of which distribute near its surface. Under a simple hypothesis that the probability of Mn^{2+} occupying each primitive cell is equal, there are at least half of the Mn^{2+} ions whose S^{2-} ligands are located on the surface. The local environment and the electronic structure of this kind of Mn^{2+} will be obviously different from those of the bulk ones. It is also possible that there are defects in nanocrystalline particles, as is in bulk crystal, which will have effect on the luminescent properties of nanocrystalline ZnS:Mn^{2+}.

We will meet difficulties if we try ascribing the fast decay of Mn^{2+} in nanocrystal to the change of environment only. Assuming that the host remains ''static'' during the transition process, the change of environment of Mn^{2+} only affects the symmetry of crystal field and crystal-field parameters while there is no notable effect on H_{sl}. Thus, only the energy-level positions are affected but the transition remains spin forbidden. Therefore, we cannot explain the significant change of luminescence lifetime observed in experiment. However, the difficulty here is a hint that separating Mn^{2+} ions from the host is not a proper model.

III. THE EXCHANGE INTERACTION MODEL

The fast decay of luminescence of nanocrystalline ZnS:Mn^{2+}, no matter by radiative transition or nonradiative relaxation, needs a complete relaxation of the forbiddenness caused by the spin selection rule. As has been stated above, it is impossible to relax this forbiddenness by the weak magnetic interactions including the *d*-electron spin operator of Mn^{2+}, such as spin-orbit interaction, so this relaxation must involve some kind of strong electric interaction. Since electric interactions do not change the total spin of Mn^{2+} ion, we need to consider Mn^{2+} and host ZnS as a coupled system and assume that the spin orientation of the host could be changed during the luminescent transition. Since there is no remarkable change of the emission peak position for nanocrystalline ZnS:Mn^{2+}, as compared to the bulk crystal, it is

natural to assume that there is no significant change of energy of the host when its spin orientation changes during the radiative transition. It is impossible for a perfect ZnS crystal (doped with Mn^{2+} as equal-electron impurity) to change its spin orientation without changing its energy, since its ground state has zero-spin. However, it is possible for nanocrystalline ZnS:Mn^{2+} to have nonzero-spin ground state, whose energy is not much concerned with its spin orientation, considering the fact that surface, boundary, and defects such as dangling bonds exist in nanosize particles. The stationary states of a Mn^{2+}-ZnS system are mixtures of products of the host states and d^5 crystal-field state of Mn^{2+}. The total spin S of Mn^{2+}-ZnS states must be the same when they are mixed (via exchange Coulomb interaction, etc.) to form stationary states and S remains unchanged during the electric dipole transition between these stationary states, while the spin of the crystal-field states of Mn^{2+} is allowed to change.

Here we give a qualitative demonstration. For simplicity, we only consider two states of Mn^{2+}: ${}^6A_1(M_s)$ and ${}^4T_1(M_s)$. The latter can be thought of as a state $|\frac{3}{2}M_s T_1\gamma\rangle$. Here γ, denoting a suitable combination of the components of the three-folded degenerated orbit state T_1, is omitted for simplicity. A host state of nanocrystal is described by a single-electron state $\psi(m_s)$, which has spin $s=1/2$ and $m_s=\pm 1/2$. The other part of the host state is a background whose spin is zero and not concerned with the transition process. The valence and conduction band of nanocrystalline ZnS with particle size of about 2–3 nm is constructed by discrete levels with large energy intervals in between. Two single-electron states of host are considered in our discussion: $\psi_v(m_s)$ and $\psi_f(m_s)$. The former can be thought as a spin-unpaired bond electronic state on top of the valence band. The latter can be considered as an excited state of the host resulting from an electron occupying $\psi_v(m_s)$ moving to a certain local state around Mn^{2+}, for example, a deep defect energy state.

A state of the Mn^{2+}-ZnS system is an eigenstate of total spin, so the stationary ground state can be written as

$$|GSS_z\rangle=\sum_{M_s m_s} {}^6A_1(M_s)\psi_v(m_s)\langle\tfrac{5}{2}M_s\tfrac{1}{2}m_s|SS_z\rangle, \qquad (3)$$

where S could be 2 or 3, corresponding to a stationary state in which the spins of the host and Mn^{2+} are antiparallel (ϕ_1 for simplicity) [Fig. 1(a)] or parallel. The two states with different S will have a very small energy difference:

$$\begin{aligned}E_G(S=3)-E_G(S=2)&=-\frac{6}{5}\sum_\gamma\int\psi_\gamma^*(1)\psi_v^*(2)\left(\frac{e^2}{r_{12}}\right)\psi_\gamma(2)\psi_v(1)d^3r_1d^3r_2\\&\approx-\frac{6}{5N}\sum_\gamma\int\psi_\gamma^*(1)W_v^*(2)\left(\frac{e^2}{r_{12}}\right)\psi_\gamma(2)W_v(1)d^3r_1d^3r_2\\&=-\frac{6}{5N}J_{00}, \qquad (4)\end{aligned}$$

where γ is the notation of the d-electron state of Mn^{2+}, W_v is the Wannier function of valence band, and N is the number of primitive cells in a certain nanocrystal. For a typical particle with the size of 3 nm, $N\approx 300$. The second step of the derivation of Eq. (4) takes the localization of the d-electron of Mn^{2+} and Wannier function into account.

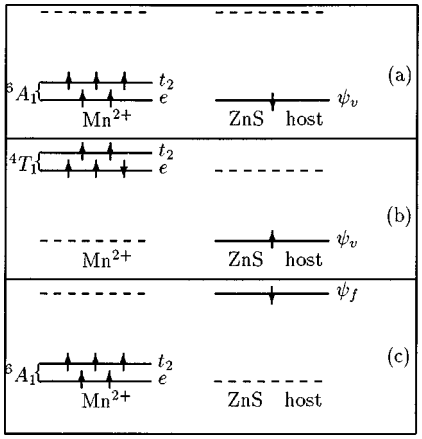

FIG. 1. Three representative states with $S=2$ of nanocrystalline ZnS:Mn^{2+}, (a) ϕ_1, (b) ϕ_2, (c) ϕ_3.

The exchange integral J_{00} for ZnS is unavailable. Comparing with the analogous values for $Cd_xMn_{1-x}Se$ and $Hg_xMn_{1-x}Se$,[6] we estimate it to be about 1 eV. Thus, we get the splitting of the ground states $|E_G(S=3)-E_G(S=2)|\approx 10^{-3}-10^{-2}$ eV.

When Mn^{2+} is at the excited state ${}^4T_1$ and the host is at the ground state, the system state can be written as:

$$|MSS_z\rangle=\sum_{M_s m_s} {}^4T_1(M_s)\psi_v(m_s)\langle\tfrac{3}{2}M_s\tfrac{1}{2}m_s|SS_z\rangle, \qquad (5)$$

where S could be 1 or 2 (ϕ_2 for simplicity) [Fig. 1(b)]. Analogous to ϕ_1, there is also a splitting of 10^{-3}–10^{-2} eV between the two states with different S.

Although the total spins of ϕ_1 and ϕ_2 are the same, the matrix elements of the electric dipole transition between them remain zero because the two states ${}^6A_1$ and ${}^4T_1$ of Mn^{2+} have different spins, i.e., the direct transition between the two states is still spin forbidden.

Consider a third state $|\phi_3\rangle$ in which the host is at the state $\psi_f(m_s)$ and Mn^{2+} is at the ground state:

$$|HSS_z\rangle=\sum_{M_s m_s} {}^6A_1(M_s)\psi_f(m_s)\langle\tfrac{5}{2}M_s\tfrac{1}{2}m_s|SS_z\rangle, \qquad (6)$$

where S could be 2 or 3. The $S=2$ case (ϕ_3 for simplicity) is shown on Fig. 1(c).

Since ϕ_2 and ϕ_3 have the same total spin, there is a nonzero exchange Coulomb interaction matrix element $Q_{\rm exc}$ between them. $Q_{\rm exc}$ is not concerned with the actual value of S_z and can be a real value if the normalization factors of ϕ_2 and ϕ_3 are properly chosen:

$$Q_{\rm exc}=\langle\phi_3|H_{\rm coul}|\phi_2\rangle. \qquad (7)$$

$Q_{\rm exc}$ is the same order of magnitude as

$$J=\int\psi_f^*(1^-)\psi_{t_2}^*(2^+)\left(\frac{e^2}{r_{12}}\right)\psi_v(2^+)\psi_e(1^-)d^3r_1d^3r_2, \qquad (8)$$

where $(\pm)$ denotes $m_s=\pm 1/2$. Since ψ_f is localized around Mn^{2+}, the overlap of ψ_f and ψ_e is significant. There is also

a considerable overlap between ψ_v and ψ_{t_2} in nanosized particles. Therefore J is not zero and of great importance. For simplicity, we only consider the mixing of ϕ_2 and ϕ_3 and get the following equation:

$$\begin{pmatrix} E_2 & Q_{\rm exc} \\ Q_{\rm exc} & E_3 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = E\begin{pmatrix} a \\ b \end{pmatrix}. \tag{9}$$

It is easy to get the eigenvalue

$$E_{\pm} = \frac{(E_2+E_3) \pm \sqrt{(E_3-E_2)^2+4Q_{\rm exc}^2}}{2}, \tag{10}$$

and the corresponding stationary excited states Φ_1, Φ_2. The stationary excited state with lower energy is

$$\begin{aligned} |\Phi_1\rangle &= \cos\theta\phi_2 + \sin\theta\phi_3, \\ \tan\theta &= \frac{(E_3-E_2)-\sqrt{(E_3-E_2)^2+4Q_{\rm exc}^2}}{2Q_{\rm exc}}. \end{aligned} \tag{11}$$

The matrix element of electric dipole transition between $|\Phi_1\rangle$ and $|\phi_1\rangle$ is

$$\left\langle \Phi_1 \middle| \sum \vec{r}_i \middle| \phi_1 \right\rangle = \sin\theta \langle \psi_f | \vec{r} | \psi_v \rangle, \tag{12}$$

where $\langle \psi_f|\vec{r}|\psi_v\rangle = \langle \psi_f(m_s)|\vec{r}|\psi_v(m_s)\rangle$ and is independent on m_s. It is evident now that the luminescent transition ${}^4T_1 \rightarrow {}^6A_1$ of nanocrystalline ZnS:Mn^{2+} borrows in fact the matrix element $\langle \psi_f|\vec{r}|\psi_v\rangle$ of the spin-allowed electric dipole transition between single-electron states of the host, so we get the radiative decay time

$$\tau_{\rm rad} = \tau_0 / \sin^2\theta, \tag{13}$$

where τ_0 is the radiative lifetime of the allowed electric dipole transition, the magnitude of which is about 1 ns. If the mixing caused by exchange Coulomb interaction gives $\sin^2\theta$ to be several percent, $\tau_{\rm rad}$ will be several tens of ns, which is comparable with the experimental decay time (including the contributions from both radiative and nonradiative relaxation process) $\tau_1 = 20.5$ ns and $\tau_2 = 3.7$ ns.

Here we give an estimation on the mixing rate. The exchange Coulomb interaction is a short-ranged interaction so the exchange integral J is roughly proportional to the probability of the electron in the state ψ_v moving about the luminescent Mn^{2+} ion. Assuming this probability equal in each primitive cell, and noting that defect state ψ_f is agglomerated around Mn^{2+}, we have $Q_{\rm exc} \sim J_0/\sqrt{N}$, where J_0 is obtained from J in Eq. (8) by replacing $\psi_v(2^+)$ by Wannier function $W_v(2^+)$ of the valence band. Usually, J_0 has the same order of magnitude as J_{00} in Eq. (4),[7] i.e., $J_0 \sim 1$ eV. Since both ψ_f and W_v are localized around Mn^{2+}, we can expand them in sp orbits of Mn^{2+} and the nearest ligands S^{2-}. Thus, J_0 is a proper-weighted summation of exchange integrals involving sp orbits of Mn^{2+} and S^{2-} and d orbits of Mn^{2+}. These integrals can be calculated by DV-X_α program (a discrete variational calculation based on local-density functional X_α approximation[8]). Some of the absolute value of these integrals can be as large as several electron volts. Thus, we estimate $J_0 \sim 1$ eV. Therefore, for a particle with the size of 3 nm, $Q_{\rm exc} \approx 0.1$ eV. Note that $E_2 = 2.1$ eV and usually the deep defect energy level E_3 is about 1 eV below the bottom of conduction band, we get $E_3 - E_2 \approx 0.5$ eV. Therefore, $\sin^2\theta$ is several percent, as has been estimated above. From the above discussion, we can see that the observed fast decay time of Mn^{2+} needs restrictions on the energy band structure of the semiconductor host. The energy shift due to exchange interaction J, i.e., $\Delta E_2 = -Q_{exc}^2/(E_3-E_2)$, combining with the shifts of E_1 and E_2 in the order of magnitude of J_{00}/N, is approximately to be -10^{-2} eV, which is comparable with the 0.02 eV redshift of emission peak observed in experiment.[3]

IV. EXPLANATION OF OTHER EXPERIMENTAL RESULTS

As has been demonstrated above, the lowest states of the Mn^{2+}-ZnS system is composed of two near-degenerated states with $S = 2$ and 3. There is considerable electron population on both states even at several tens of Kelvin. This feature will affect the electron paramagnetic resonance (EPR) spectra of nanocrystlline ZnS:Mn^{2+}. However, the crystal-field splitting (fine structure), which can be used to determine the total spin of the system, was not observed in experiment due to the random orientation of nanocrystalline particles in the sample.[9] In the EPR experiment, two sets of hyperfine splitting structures were observed in the Q band, which was ascribed to two kinds of Mn^{2+} sites: one inside of the nanocrystal and the other near the surface. However, two different values of the hyperfine splitting parameter A, one is 1.4 times of the other, were used in the explanation of the EPR spectra. It is suspectable that A varies so much in the same sample. Besides, the value of the fine splitting parameter D used to explain one set of the hyperfine splitting spectrum is very large. This implies that the crystal-field parameter $B_2^0 \sim 1000$ cm^{-1},[10] which should be zero under T_d symmetry. Thus, a great shift of the emission peak (above 0.1 eV) should be observed, which was actually not observed in the PL spectrum. In our model, the hyperfine splitting can be described by

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{S}'\cdot\mathbf{I} = g\beta\mathbf{H}\cdot\mathbf{S} + A_{\rm eff}(S)\mathbf{S}\cdot\mathbf{I}, \tag{14}$$

where $S = 2$ or 3 is the quantum number of the total spin $\mathbf{S}$ of the Mn^{2+}-ZnS system, $\mathbf{S}'$ is the spin of Mn^{2+} and

$$A_{\rm eff} = \frac{\langle S' \tfrac{1}{2} S \| \mathbf{S}' \| S \tfrac{1}{2} S \rangle}{\langle S \tfrac{1}{2} S \| \mathbf{S} \| S' \tfrac{1}{2} S \rangle} A = \left(\frac{1}{2} + \frac{4}{S(S+1)} \right) A. \tag{15}$$

Therefore, $A_{\rm eff}(2)/A_{\rm eff}(3) = 1.4$, which is exactly the ratio of the two values of parameter A got from EPR experiment.[9]

Note that apart from the fast transition excitation state ψ_1, there are some other excitation states, e.g., $|M1S_z\rangle$, $|H3S_z\rangle$, and Φ_2. $|M1S_z\rangle$ has almost the same energy level as Φ_1, while the transition from this state to the ground state is almost spin-forbidden (the forbiddenness could be partly relaxed by magnetic interaction). The energy on $|M1S_z\rangle$ could also be transfered to Φ_1 (a spin-forbidden process) and then to the ground state. Since the two ways from $|M1S_z\rangle$ to the ground state are both almost spin-forbidden, a slow decay component should be accompanied

with the fast decay component already observed in nanocrystalline ZnS:Mn^{2+}. The energy of Φ_2 is a little higher than Φ_1. Thus, a direct transition from this state to the ground state could not be observed since the energy could be easily transfered to Φ_1 with assistance of phonons. The energy of $|H3S_z\rangle$ is 1 eV higher than that of Φ_1 or Φ_2. The direct transition from $|H3S_z\rangle$ to the ground state $|G3S_z\rangle$ is spin-allowed. If energy is pumped to this state, blue (or green) emission should be observed. This is verified by the experiment done by Sooklal *et al.*[4]

V. CONCLUSION

In conclusion, we give a discussion on how the luminescence lifetime of ZnS:Mn^{2+} is shortened by five orders of magnitude from bulk to nanocrystal. It is assumed that in nanocrystalline ZnS:Mn^{2+}, the ground state of ZnS has non-zero spin, and that the exchange Coulomb interaction causes significant mixing between the $^4T_1$ state of Mn^{2+} and an excited state of ZnS. This mixing grows stronger as the particle size decreases. Therefore, the $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} could be spin allowed in particles with 2–3 nm scale. This causes the increment of probability of both electric dipole radiative transition and electric dipole nonradiative transition, which result in the fast decay of nanocrystalline ZnS:Mn^{2+}. This mechanism also agrees with the results of EPR experiment and other luminscent properties of nanosized ZnS:Mn^{2+}.

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[10] Note that the splitting of $^6A_1$ states of Mn^{2+} due to D is equivalent to the contribution of a fourth-order interaction including H_{sl} and H^c. At least two matrix elements of the fourth order interaction are H_{sl}. Therefore, we have

$$D \ll \left| \frac{\langle H_{sl} \rangle}{E(^4T_1) - E(^6A_1)} \right|^2 B_2^0 < 10^{-4} B_2^0,$$

i.e.,

$$B_2^0 > 1000 \text{ cm}^1.$$