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A Model on the Mn^{2+} Luminescence Band Redshift with Mn(Ⅱ) Doping and Aggregation within CdS:Mn Microwires *

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We report the microphoto-luminescence band redshifts with individual and multi-Mn(Ⅱ) ion emissions within CdS microwires. The localized exciton magnetic polarons (LEMPs) corresponding to the d–d optical transitions of Mn(Ⅱ) account for this shift. This LEMP emission from the double-, three- and four-Mn(Ⅱ) ions with ferromagnetic coupling after photoexcitation can happen in diluted magnetic semiconductors, except for the individual Mn(Ⅱ) doping. In addition, a simple spin-exchange polaronic model is established to account for these emission peaks well. Through this model, we can verify the local geometry of the Mn(Ⅱ) ions in CdS microwires.

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It is generally accepted that the carrier-spin interaction is the ferromagnetic origins in diluted magnetic semiconductors (DMSs).[1–3] There are also models of exchange interaction between transition metal (TM) ions[3,4] in DMS, although this coupling may form bound magnetic polaron,[5] mediated by the defects. Except for the above models, the clustering of TM ions[6,7] is also proposed and modeled to account for many magnetic properties of DMS for a long time. However, direct manifestation of a ferromagnetic cluster in DMS is not reported so far by microprobe techniques.

The models for ferromagnetism in DMS are usually proposed based on the different structural, conduction and magnetic experimental data, while the optical technique was seldom used for recently found DMS materials, which limited the better understanding of the microscopic interactions in DMS. Moreover, complicated elements, structure, preparation condition, and related interactions cause a variety of local magnetisms, which cannot be well described in a clear unified physics diagram. Until now the main difficulty in proposing a unified magnetism mechanism of DMS lies in obtaining a homogeneous sample, coexistence of complicated phases and shortage of nanoscale detection techniques.[8]

An optical technique is important to study the exchange interaction of TM ions. For the DMS, the doped magnetic ions and related photoinduced exciton could interact with each other to form an excitonic magnetic polaron (EMP) near the band edge, especially in TM-doped QDs. The DMS usually produces clear luminescence band in the red range of the free exciton emission line, which reflects the nature of local ferromagnetic interaction between TM ions.[9,10] This interaction between exciton and magnetic ions is weak due to the fact that EMPs are formed by *s*-type electrons and *p*-type holes and detectable only at low temperature. If the exciton is a localized one, i.e., concerning *d*–*d* transition of transition metal ions, the interaction between carriers and ion spin due to *p*–*d* hybridization becomes strong, at the same time the *d*–*d* transition becomes partially delocalized. We can call it the localized EMP (LEMP), and therefore the interaction from neighboring ion pairs could be detected by the optical and magnetic techniques to reflect their local magnetic coupling. If we can define the distance and locations of TM ions in DMS, we may obtain its local optical response and know more about its magnetic coupling nature. In fact there are a lot of reports on the EMP and related properties of Ⅱ–Ⅳ DMS.[11,12] Compared with other optical techniques, luminescence of magnetic excitons can be detected for their radiative recombination between electrons and holes, whether mobile or localized, gives a direct diagram of the spins that interact with electrons or holes, is further used for the modulation of its emission behavior by changing the local number, location, geometry and interactions of doped magnetic ions.[13,14]

In this Letter, we use the *d*–*d* radiation transition of Mn(Ⅱ) as a probe, to study the relations of LEMP energy with the location geometry of Mn(Ⅱ) ions doped in CdS microwires prepared in a CVD technique.[15] The products show multiple luminescence peaks in 560–800 nm on mass measurement. Except for the 575 nm peak of intrinsic transition of Mn(Ⅱ), other peaks were often assigned to the defects in the literature. Since these peaks can be present individually and shift with Mn concentration by single wire detection, the previous assignment by defects may be unsuitable. Moreover, the products also possess a ferromagnetic response by the magnetic measurements (see Figs. S1 and S2 in the support information, its Curie temperature T_c is strongly dependent on the individual product and Mn ion concentration). It is found that the Mn(Ⅱ) ions, doped in CdS microwires by replacing Cd(Ⅱ) ions, may aggregate to form many kinds of $(MnS)_n$ clusters containing a nat-

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ural number of Mn(Ⅱ) ions (namely, one, two, three, and so on) like other transition metal ions in DMS.[7,8] The d–d transition in one Mn ion, behaves much like a Frenkel exciton, which can aggregate in CdS matrices as the conjugated molecules in J-aggregates. For one microwire, we find that there is no clear interaction between any two neighboring MnS clusters, otherwise their luminescence will shift significantly, or diminish, even disappear at high doping. The LEMPs in these $(MnS)_n$ clusters are found to have emission energy depending on n, by the micro-photoluminescence technique on a single wire.[16] A model of hydrogen-like electron cloud (polaron) covering the cluster, in which Mn–Mn is ferromagnetically coupled,[13] is proposed to account for the emission peaks and LEMPs' character.

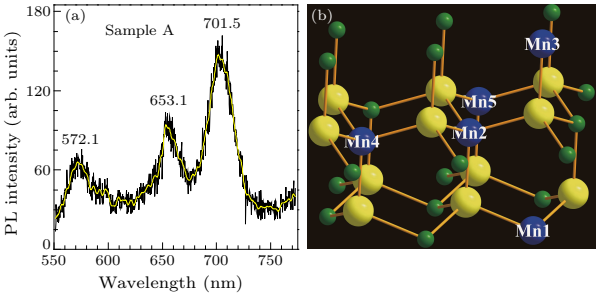


Fig. 1. (a) Luminescence of sample A excited by a cw laser with wavelength of 532 nm. (b) Location geometries of Mn(Ⅱ) ions correspond to the LEMP peaks of 572.1 nm, 653.1 nm, and 701.5 nm. Yellow and green spheres are S and Cd ions, respectively. Blue spheres denote Mn(Ⅱ) ions. For the individual Mn(Ⅱ) ion (namely, C1), except Mn1, other ions of Mn2 to Mn5 are still Cd ions; for two Mn(Ⅱ) ions case (namely, C2), except Mn1 and Mn2, other ions of Mn3, Mn4, and Mn5 are Cd ions; other cases are similar.

Figure 1(a) shows the luminescence of sample A of Mn-doped CdS microwires excited by a cw laser with wavelengths of 405 nm and 532 nm; the latter can only excite the Mn ions. Three LEMP-emission peaks appear. These three peaks actually can be found in three different samples individually if we tune their preparation condition, moreover its emission wavelength fluctuation is very small in about ±2 nm, and therefore, they may originate from the microstructural variation. The 572.1 nm peak is well known to originate from the $^4T_1(G) \rightarrow {}^6A_1(S)$ transition of individual Mn(Ⅱ) ion, and represents the LEMP emission in the MnS cluster with one Mn(Ⅱ) ion, while other peaks longer than the 572.1 nm peak result from the interactions of neighboring Mn ions. The peaks of 653.1 nm and 701.5 nm can be assigned to the LEMPs in the clusters with two and three Mn(Ⅱ) ions, respectively, which is ferromagnetically coupled with energy lowering. The local geometries of Mn(Ⅱ) ions are given in Fig. 1(b). The cluster with one Mn(Ⅱ) ion (C1) can be seen from Fig. 1(b) by taking Mn(Ⅱ) ions except Mn1 as Cd ions. The cluster with two Mn(Ⅱ) ions (C2) can also be seen from Fig. 1(b) by taking Mn(Ⅱ) ions except Mn1 and Mn2 as Cd ions. Other clusters C3, C4, and C5 are the same. For convenience, we call the LEMPs corresponding to 572.1 nm, 653.1 nm and 701.5 nm the LEMP1, LEMP2, and LEMP3, respectively. In the following, we will point out that LEMP1, LEMP2, and LEMP3 originate from C1, C2, and C3, respectively.

To confirm the above thought, we start from the following corrected Hamiltonian

$$H = \frac{P_e^2}{2m_e} - \frac{1}{4\pi\varepsilon}\frac{e^2}{r_e} + \alpha_e \boldsymbol{s}^{\mathrm{e}} \times \boldsymbol{S}(\boldsymbol{r}_e) + E_0 \qquad (1)$$

to describe the excited states, namely, LEMPs. Here E_0 denotes the fundamental splitting energy in d–d transition. Total spins of all Mn(Ⅱ) ions is $\boldsymbol{S}(\boldsymbol{r}_e) = \sum_j \delta(\boldsymbol{r}_e - \boldsymbol{R}_j)\boldsymbol{S}_j$, where $\delta(\boldsymbol{r}_e - \boldsymbol{R}_j)$ and $\boldsymbol{S}_j$ are the Dirac function and spin momentum of the jth Mn(Ⅱ) ion, $\boldsymbol{r}_e$ and $\boldsymbol{R}_j$ are the positions of the excited electron and jth Mn(Ⅱ) ion, respectively. The reason for introducing the second term in Eq. (1) is that one d-orbit hole is left after the photoexcitation of the electron in Mn(Ⅱ) ion d-orbit. In addition, the second term in Eq. (1) implies that Eq. (1) describes the case that the Mn(Ⅱ) ion located at the original point is excited and other Mn(Ⅱ) ions are not excited. The ground state of Eq. (1) has the following wavefunction form

$$\phi_\sigma(\boldsymbol{r}_e) = \sqrt{\frac{1}{\pi r_0^3}} e^{-r_e/r_0}|\sigma\rangle, \qquad (2)$$

where r_0 and $|\sigma\rangle$ are the radius and spin wave function of electrons, respectively.

Notice that the correlation between Mn(Ⅱ) ions is ferromagnetic when one d-orbit hole is excited. Therefore, all Mn(Ⅱ) ions in the cluster are correlated together by the manner of ferromagnetism after photoexcitation for its lower energy. In this view, the ground energy of the LEMPs in the Mn(Ⅱ) clusters with n Mn(Ⅱ) ions becomes

$$E_n = E_0 - \frac{e^2}{8\pi\varepsilon r_0} - \frac{\alpha_e}{r_0^3}\frac{5}{4\pi}\sum_{i=1}^{n} e^{-2R_n/r_0}. \qquad (3)$$

In the following, we determine α_e and r_0 through Eq. (3), using the energies of LEMPs when $n = 1$, 2, and 3. Notice that we set $R_1 = 0$ and thus Mn1 is excited (refer to Fig. 1(b)). From Fig. 1(a), we can find $E_1 - E_2 = 268.8$ meV and $E_2 - E_3 = 131.1$ meV. Recurring to Eq. (3) and the distances of $R_2 = 0.4134$ and $R_3 = 0.6749$ nm, we can obtain the parameters of α_e and r_0 to be 810.7 meV and 0.7277 nm, respectively.

Naturally, to demonstrate that the hydrogen-like model is right, we need to validate the applicability of α_e and r_0 to other cases, such as to the C4 case (refer to Fig. 1(b)). Fortunately, our experimental data support this description. In Fig. 2, we show the photoluminescence of another two Mn-doped CdS microwire samples (referred to samples B and C, respectively). These two samples are excited by the cw laser with wavelength of 532 nm. The energy difference between the peaks of 701.5 and 752.9 nm is about 120.7 meV, which agrees with the theoretical result, namely,

$$\frac{\alpha_e}{r_0^3}\frac{5}{4\pi}e^{-2R_4/r_0} = 116.9\,\mathrm{meV},$$

where $R_4 = 0.7161$ nm. Therefore, the hydrogen-like cloud model is in good accordance with the experimental data. This fact indicates that the LEMPs are localized in the Mn(Ⅱ) ion clusters and the typical radius can be described by $r_0 = 0.7277$ nm. In fact, the luminescence band of sample C is the superposition of three LEMP bands. Two of them originate from C4, and another originates from C5. This will be discussed in the following where we discuss the possible LEMP peaks in the Mn(Ⅱ) ion cluster.

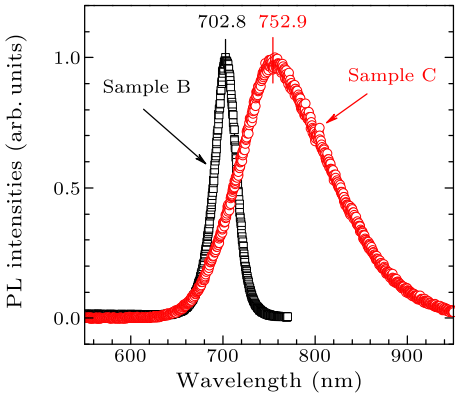


Fig. 2. Luminescence of two samples of Mn-CdS microwires (samples B and C). These samples are excited by cw lasers with wavelength of 532 nm.

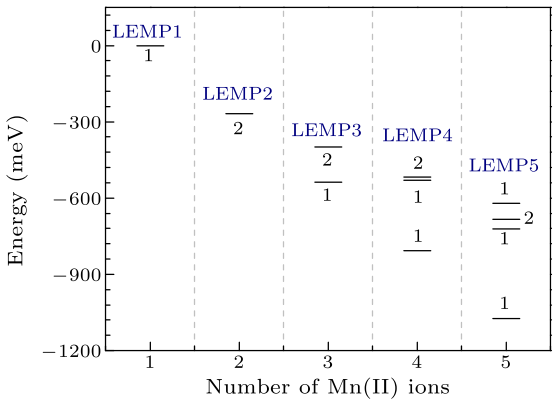


Fig. 3. Energy levels of LEMPs in Mn(Ⅱ) ion clusters in Mn-doped CdS microwires. Here the energy of LEMP1 being 2.1675 eV is set to be a reference. The numbers near the LEMP levels represent the ones of Mn(Ⅱ) ions excited from which the LEMPs have the same energies.

From the above discussions, we have confirmed that the hydrogen-like cloud model is valid to understand the LEMPs in DMS. Therefore, we can predict the possible peaks of LEMPs by more ions. In the above discussions, we always assume that the Mn(Ⅱ) ion at Mn1 is excited. Naturally, in the clusters of three or more Mn(Ⅱ) ions, Mn(Ⅱ) ions at other locations may also be excited. Notice that the absolute values of the coordinates of Mn(Ⅱ) ions generally are modified when we take different Mn(Ⅱ) ions as the origin of coordinates. Therefore, the excitations of other Mn(Ⅱ) ions possibly induce new LEMP peaks. For only one Mn(Ⅱ) ion exists in C1, only one type of LEMPs exists. In C2, the LEMPs excited from Mn1 and Mn2 are the same, due to the fact that the absolute distance between two Mn(Ⅱ) ions is the same. For the same reason, the LEMPs excited from Mn1 and Mn3 are the same as C3. However, when Mn2 is excited in C3, the LEMPs excited at Mn2 are different from the ones excited at Mn1 and Mn3. This means that there are two types of LEMPs in C3. In Fig. 3, we plot these relative energy levels. The numbers beside the levels represent the state number of Mn(Ⅱ) ions excited at which the LEMPs have the same energies. The energies of LEMPs excited at Mn2 in C3 are about 137.7 meV smaller than LEMP3. From Fig. 2, we can find that the full width at half maximum (FWHM) is about 61.9 meV, which is about half of 137.7 meV. Therefore, the PL spectra of sample B is mainly composed by the LEMPs excited at Mn1 or Mn3.

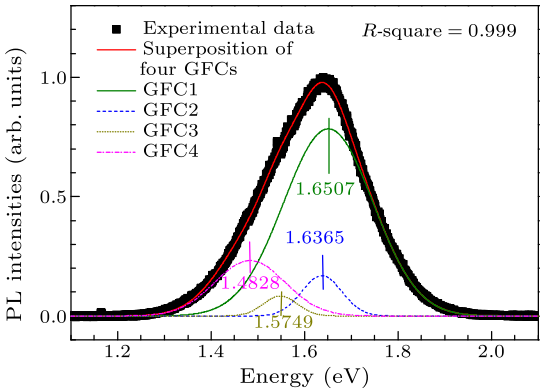


Fig. 4. Fitting of the PL spectral of Mn-doped CdS microwires (sample C). Here four Gaussian fitting curves (denoted as GFC1, GFC2, GFC3, and GFC4) are used. The peak positions of GFC1, GFC2, GFC3, and GFC4 are 1.6507 eV, 1.6365 eV, 1.5479 eV, and 1.4828, respectively, and their full widths at half maximum are 191.3 meV, 86.0 meV, 72.8 meV, and 151.0 meV, respectively.

For C4, the LEMPs excited at Mn1 and Mn3 have the same energies. While for the LEMPs at Mn2 and M4, their energies are about 289.6 meV and 14.1 meV lower than LEMP4, respectively. Due to the fact that the energy difference between the LEMPs at Mn1 (or Mn3) and Mn4 is very small, the band around 752.9 nm (1.6470 eV) is composed by these two kinds of LEMPs. To show this, we fit the PL spectra of sample C by four Gaussian fitting curves (denoted as GFC1, GFC2, GFC3, and GCF4, respectively), which are shown in Fig. 4. The fact of $R_{\text{square}} = 0.999$ indicates that the fitting process is applicable. In Fig. 3, the central positions of four Gaussian fitting curves, namely, GFC1, GFC2, GCF3, and GFC4, are 1.6507 eV, 1.6365 eV, 1.5479 eV, and 1.4828 eV, respectively. Notice that there are two Mn(Ⅱ) ion sites in one C4 (namely, Mn1 and Mn2) supporting the LEMPs of 1.6507 eV, while on the contrary, only one Mn(Ⅱ) ion site (namely, Mn4) supports the LEMPs of 1.6305 eV. Therefore, the PL intensity for the LEMPs of 1.6507 eV is stronger than that for the LEMPs of 1.6305 eV. The peak positions of 1.6507 eV and 1.6365 eV locate on the two sides of the experimental PL peak at 1.6470 eV (namely, 752.9 nm). Their

energy difference between 1.6507 eV and 1.6365 eV is about 14.2 meV, which agrees well with the theoretical value of 14.1 meV. In addition, the energy difference between the experimental peak at 701.5 nm (namely, 1.76764 eV for C3) and 1.6507 eV for C4 is about 116.94 meV, which closely approaches the theoretical value $\frac{\alpha_e}{r_0^3}\frac{5}{4\pi}e^{-2R_4/r_0} = 116.9$ meV. This indicates that the hydrogen-like cloud model is exactly applicable to explain the LEMP formation in Mn-doped CdS microwires.

The peaks fitted by GFC3 and GFC4 in Fig. 4 represent the LEMPs in C5 with five Mn ions. By analysis in detail, we find that the peaks of 1.4828 eV and 1.5749 eV in Fig. 4 represent the emission of LEMPs excited at Mn1 and Mn4 sites in C5, respectively. The geometry of C5 can be seen in Fig. 1(b). For C5, there are four LEMP levels (referred to Fig. 3). Similar to C4, there are two Mn(Ⅱ) ions in C5 supporting the LEMPs of 1.4828 eV, and only one Mn(Ⅱ) ion supports the LEMPs of 1.5749 eV. Thus the PL band for the LEMPs of 1.4828 eV is stronger than that for the LEMPs of 1.5749 eV.

Since the hydrogen-like model can well explain the PL peaks of the LEMPs in the Mn-doped CdS microwires, it can be used to determine the geometry of Mn ions doped in CdS microwires, and therefore, to discover the mechanism for how Mn(Ⅱ) ions are doped into CdS microwires. Notice that the PL spectrum of sample B (referred to Fig. 2) only covers the peak of 702.8 nm (namely, 1.7651 eV). Therefore, in sample B almost all Mn(Ⅱ) ions are doped in the manner of C3; and no coupling between any two $(MnS)_3$ clusters is observed. Due to the geometry complexity of multi-ions, the emission band always becomes broad if n is larger than 4, its accurate controlled incorporation in preparation becomes more difficult.

Based on the above discussion, we can deduce that the exciton from the d–d transition is not localized in individual Mn ions in CdS:Mn, the carriers in the exciton should be delocalized due to strong p–d exchange, and direct super-exchange ferromagnetic coupling dominates the Mn ion aggregation.[17] The ferromagnetic Mn–Mn coupling in the cluster (see Fig. S1 magnetic response of CdS:Mn microwire in support information) leads to a new peak at the redside of single ions, at the same time the peak from single ions disappears. This type of spectral variation of cluster levels and emissions[18] look like that in a molecular J-aggregate. Although this model does not consider the contribution of defects, its effects on the levels are still present with minor magnitudes. It is important that the magnitude dependence of spectral redshift on the aggregation number of Mn ions agrees well with our theoretical model.

In most DMS samples, the difficulty in understanding its magnetic mechanism lies in the inhomogeneity of TM ion number of clusters and their distributions. Even if their coupling is ferromagnetic, there are still problems in the spatial magnetic orientation within the sample to lead to complicated magnetic responses. It is very important to obtain the homogenously doped samples, which was possibly realized in the micrometer scaled structures, and their orientation was detected by the micro-photoluminescence technique. The above results indicate that this is a practical way to study the microscopic state of TM ions in DMS, and understand their spin coupling and magnetic mechanisms. Moreover, this kind of optical excitation with ferromagnetic coupling in micrometer size may be useful to study the behavior of magnetic excitons like BEC, spin-polarized emission, quantum modulation except for new light sources.

In conclusion, the doping processing influences the spatial distribution and micro-interactions of doped ions in nano- or micro-belt. In CdS:Mn microwires we find a clear manifestation of Mn ion cluster emission shift with the number of Mn ions, the spectral shift is related to the number of ions based on ferromagnetic coupling, like that in molecular aggregate. It is found that different n Mn ion clusters can be uniformly doped in CdS microbelt or wire. This quasi-1d structure supplies us with an important benchmark to study the microscopic mechanism of magnetism and spin-polarized emission processes in the near future.

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Mn^{2+} Luminescence band redshift with Mn(II) doping and aggregation within CdS:Mn microwires

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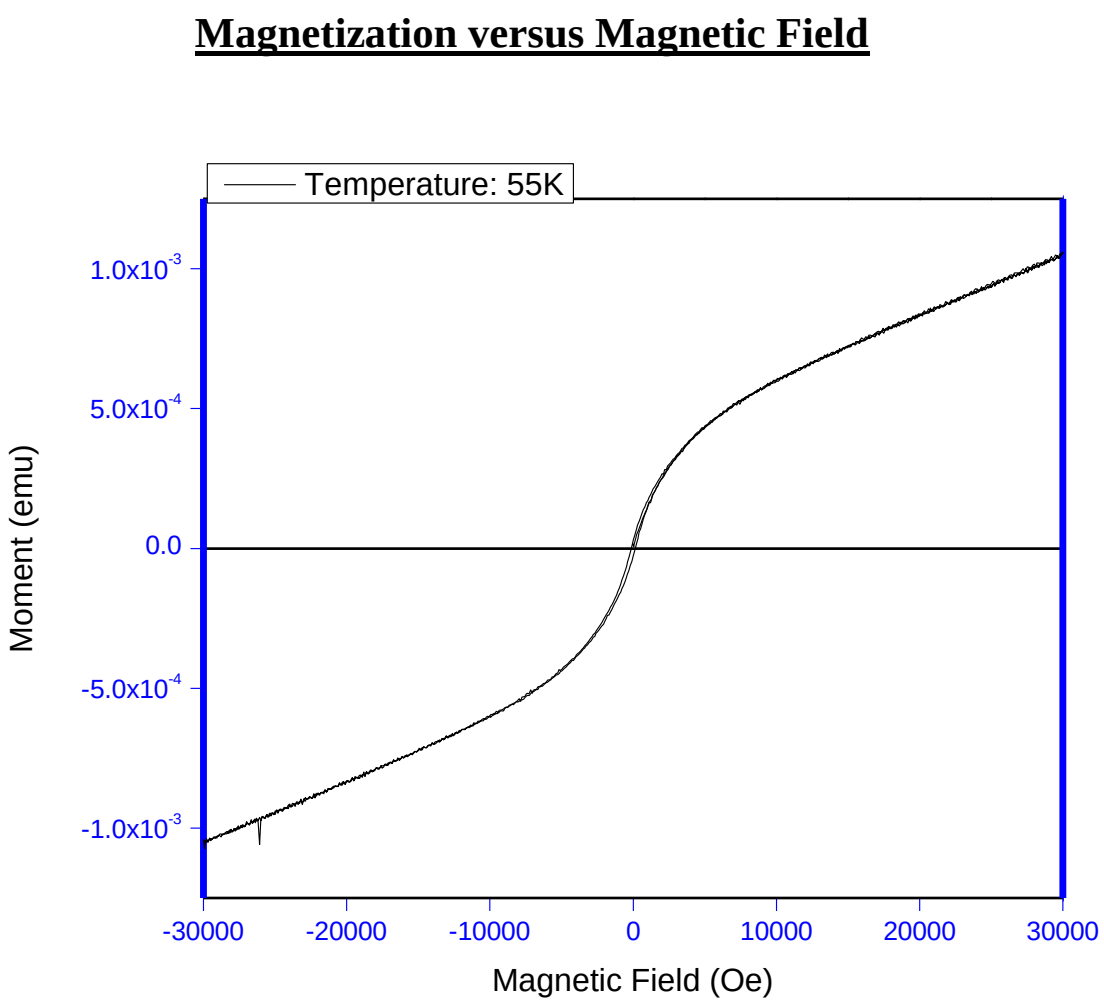


Figure S1 the magnetic properties of CdS:Mn microwires at 55K.

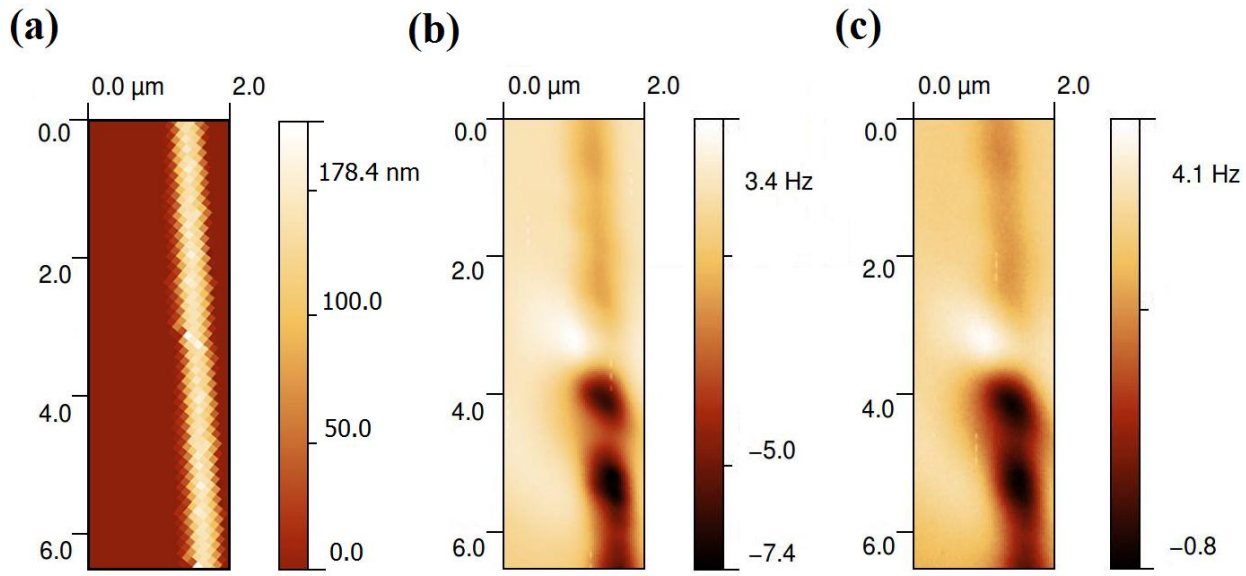


Figure S2. **AFM** Topographic image **(a)** at 5 K and the corresponding **MFM** magnetic imaging of the Mn(II) doped CdS single nanowire in constant height mode at 5K **(b)** 20 nm, **(c)** 100 nm above the sample.