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Modification of the Magnetic and Electronic Properties of Ordered Arrays of (II, Mn)VI Quantum Wires Due to Reduced Lateral Dimensions

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We present a novel way of synthesising highly ordered arrays of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ quantum wires with lateral dimensions of 3 nm separated by 2 nm SiO_2 barriers by incorporating the (II, Mn)VI semiconductor with $0 \leq x \leq 1$ into the pore system of mesoporous MCM-41 SiO_2 matrices. The electronic and excitonic properties were studied using photoluminescence and photoluminescence excitation spectroscopy at low temperatures and in magnetic fields up to 7.5 T. Due to the quantum confinement of the excitons in the wires an increase of the direct band gap by about 200 meV for (Cd, Mn)S and by about 350 meV for (Cd, Mn)Se is observed. In addition, we observe a much stronger, p-d hybridisation related band gap bowing as a function of Mn-concentration in the wires compared to bulk. This effect is related to the increase of the band gap due to the quantum confinement which shifts the p-like valence band edge closer to the Mn-3d-related states in the valence band. Surprisingly, the s,p-d exchange induced giant Zeeman splitting of the excitons in the (Cd, Mn)Se wires compared to those in bulk material appears to be very small. The magnetic properties of the samples were studied by SQUID and electron paramagnetic resonance measurements in the temperature range from 2 to 300 K. Compared to the bulk (II, Mn)VI compounds, a reduced antiferromagnetic coupling between the magnetic moments of the Mn^{2+} ions is found. For $x > 0.8$, a suppression of the paramagnetic to antiferromagnetic phase transition of the Mn-system is observed because the lateral dimensions of the wires are smaller than the magnetic length scale of the antiferromagnetic ordering.

Introduction Several different approaches for fabricating ordered arrays of semiconductor nanostructures such as quantum dots and quantum wires have been developed (for reviews see [1, 2]). These methods range from lithographic patterning techniques on 2D structures followed by etching procedures to self-organised growth of the nanostructures. A major obstacle in the fabrication of arrays of nanostructures is to obtain

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simultaneously a high degree of order of the array, a high density and small lateral dimensions of the nanostructures with a sharp size distribution. We have recently introduced a novel way of fabricating ordered arrays of magnetic nanowires by synthesising (II,Mn)VI semiconductors inside the pores of mesoporous MCM-41 (Mobil Composition of Matter) SiO_2 matrices [3–5]. The good crystalline quality of the (II,Mn)VI wires and the high degree of order of the arrays allows one to study the effects of the reduction of the lateral dimensions on magnetic and electronic properties of the diluted magnetic semiconductor.

Experimental We have fabricated regular dense arrays of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ quantum wires with diameters of 3 nm and $0 \leq x \leq 0.3$ as well as $0.8 \leq x \leq 1$. The synthesis of the pristine MCM-41 SiO_2 matrices and their impregnation with the (II,Mn)VI semiconductor is described in Ref. [5]. X-ray diffraction as well as TEM studies reveal the hexagonal structure of the arrays (space group p6m). Physisorption measurements confirm the filling of the pores with the (II,Mn)VI compound. Photoluminescence (PL) and PL excitation spectroscopy (PLE) at liquid helium temperatures and in magnetic fields up to 7 T were performed to study the electronic and excitonic properties of the diluted magnetic wires. Electron paramagnetic resonance (EPR) and SQUID measurements at temperatures from 2 to 300 K were used to investigate the magnetic properties of the wires.

Results and Discussion Figure 1 summarises PL and PLE results of the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires. The PL spectra for $x \leq 0.3$ consist of several bands where the band at the highest energy corresponds to the excitonic band gap emission (Fig. 1c). The band gap absorption in PLE is Stokes-shifted. The PL bands at lower energies originate from lowest internal 3d shell transitions of Mn^{2+} . The PL spectrum of the MnSe wires is similar to bulk and corresponds to the $^4\text{T}_1 \rightarrow ^6\text{A}_1$ internal transition of the Mn^{2+} 3d-shell. Figures 1a and 3a show comparisons of the energy positions of the band gaps of

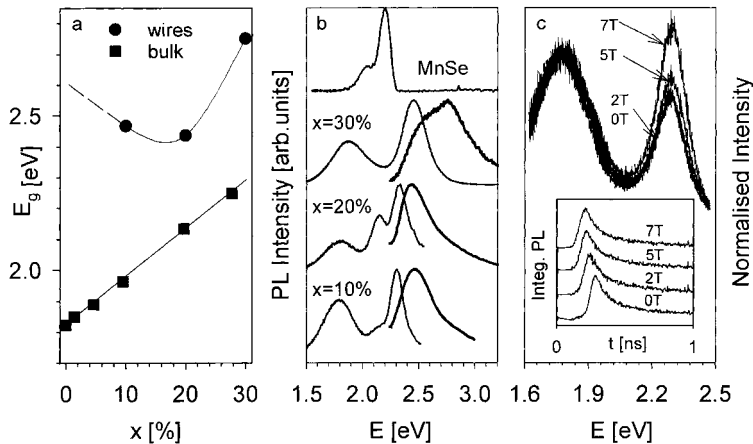


Fig. 1. a) Band gap of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ bulk [6] and $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires at 10 K; b) PL (thin lines) and PLE (thick lines) of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires at 10 K; c) PL of $\text{Cd}_{0.9}\text{Mn}_{0.1}\text{Se}$ wires at various magnetic fields at 2 K, inset: Time-dependence of the integrated excitonic PL

bulk and wires for $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$, respectively. Due to the quantum confinement of the excitons in the wires an increase of the direct band gap by about 200 meV for (Cd,Mn)S and by about 350 meV for (Cd,Mn)Se is observed. The larger blue shift for (Cd,Mn)Se is due to the larger exciton Bohr radius. For both systems a strong bowing is observed for the band gaps of the wires indicating an increased s,p–d exchange interaction. The effect is similar to the increased bowing observed in the bulk (II,Mn)VI compounds when increasing the band gap by changing the group-VI anion from Te to Se to S [7]. Surprisingly, the magnetic field-induced giant Zeeman splitting is rather small as shown by the rather negligible red-shift of the excitonic PL with field for the $\text{Cd}_{0.9}\text{Mn}_{0.1}\text{Se}$ wire sample in Fig. 1c and for $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ wire samples in Ref. [4]. The PL decay-time of 160 ps for the band highest in energy confirms its excitonic character. PL intensity as well as decay times hardly change with increasing magnetic field, i.e., only a slight increase of the excitonic PL compared to the Mn-related PL band is observed. Thus, the energy transfer from the band states into the Mn-3d shell in these samples is only weakly affected by the magnetic field.

Figure 2 presents EPR results of the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires. The EPR spectra for $x \leq 0.3$ consisting of a sextett of sharp lines on a broad background are typical for exchange coupled Mn^{2+} in (II, Mn)VI alloys [8]. The sharp lines are due to hyperfine transitions of the Zeeman-split $m_S = -1/2$ and $m_S = +1/2$ levels of the ${}^6\text{A}_1$ ground state of the Mn^{2+} 3d-shell. The total intensity I as well as the line width ΔH of the integral EPR signal of the Mn^{2+} absorption are sensitive probes of the spin–spin correlations of the Mn^{2+} ions [9]. In the paramagnetic phase, the magnetic susceptibility $\chi \propto I \propto (T + \theta)^{-1}$, where T is the temperature and θ reflects the antiferromagnetic coupling between the Mn^{2+} ions (Figs. 2c and 3c). The θ -values obtained for $\text{Cd}_{1-x}\text{Mn}_x\text{Y}$ ($\text{Y} = \text{S}, \text{Se}$) wires are smaller than for bulk. Also, in bulk MnSe and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ for $x > 0.8$ a phase transition occurs from paramagnetic to antiferromagnetic with decreasing temperature. The Néel-temperatures (determined by EPR) are indicated for bulk rocksalt and zincblende MnSe and MnS by the arrows in Figs. 2b and 3b, respectively. There is no indi-

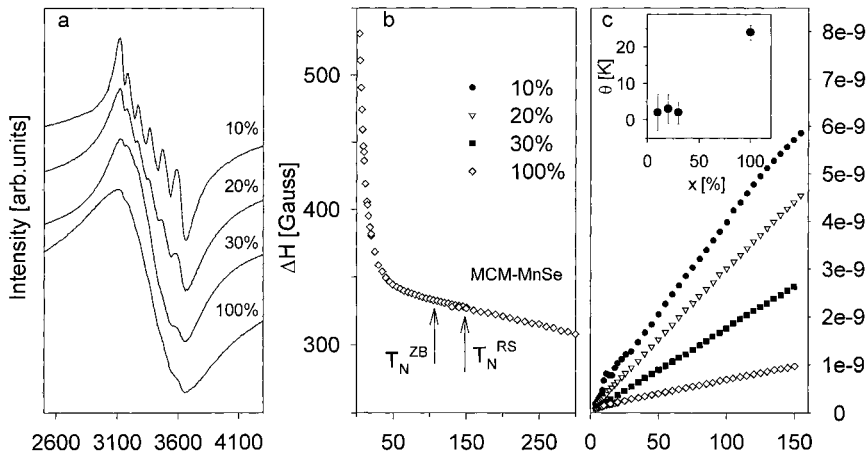


Fig. 2. a) EPR spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires in MCM-41 SiO_2 at 4 K; b) EPR line width of MnSe wires vs. temperature; c) inverse intensity of EPR signals of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires vs. temperature, inset: corresponding Curie-Weiss parameters θ

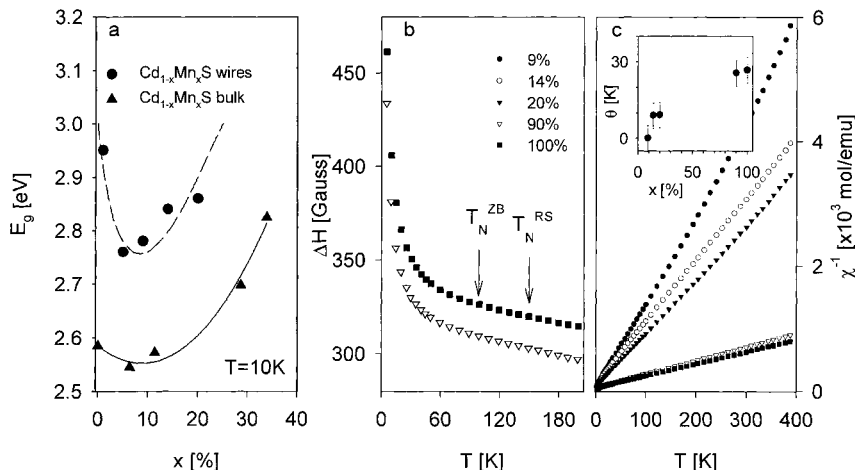


Fig. 3. a) Band gap of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ bulk [10] and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ wire samples at 10 K; b) EPR line width vs. temperature of MnS and $\text{Cd}_{0.1}\text{Mn}_{0.9}\text{S}$ wires; c) inverse magnetic susceptibility of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ wires vs. temperature, inset: corresponding Curie-Weiss parameters θ

cation for the occurrence of such a phase transition in the MnSe and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ wires with $x \geq 0.9$ down to 2 K. Neither ΔH nor T^{-1} diverge to infinity at a finite temperature or show cusp-like features in Fig. 2b as well as in Figs. 3b and c. This indicates that the lateral dimensions of the wires are smaller than the magnetic length scale of the antiferromagnetic order.

Conclusions High-quality nanostructures can be formed inside the pore system of MCM-41 SiO_2 matrices. Electronic as well as magnetic properties of the host-guest compounds MCM-41 $\text{SiO}_2/\text{Cd}_{1-x}\text{Mn}_x\text{Y}$ ($Y = \text{S}, \text{Se}$) are strongly modified compared to bulk.

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