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Synthesis and some physical properties of the diluted magnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{O}$

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Abstract. Polycrystalline samples of cadmium–manganese mixed oxides $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ were synthesized by ceramic technology in a wide range of concentrations x ($0.05 \leq x \leq 0.90$). Their crystalline structures were investigated by the Rietveld profile method based on the x-ray powder diffraction measurements. All samples were found to be of sodium chloride structure type with lattice constants $a(x)$ slightly deviating from the Vegard law. Thermogravimetric analysis shows that samples are unstable above 500 K owing to the absorption of oxygen by MnO. Magnetic susceptibility $\chi(x, T)$ measurements made by the Faraday method indicated the presence of antiferromagnetic interactions between Mn^{2+} ions. In the paramagnetic region the Curie–Weiss law is obeyed with the linear dependence on the concentration of the effective paramagnetic temperature $\Theta(x)$ and Curie molar constant $C_M(x)$. From the analysis of the magnetic susceptibility data, values of the spin and the nearest-neighbour exchange integral were found to be $S = 2.6 \pm 0.1$ and $J_1/k_B = 11 \pm 1$ K, respectively.

1. Introduction

During the past two decades, semiconducting mixed crystals with controlled quantities of randomly distributed magnetic ions, referred to as diluted semimagnetic semiconductors (DMSCs) or semimagnetic semiconductors (SMSCs), have been extensively studied [1, 2]. Emergence of new features in both semiconducting and magnetic properties and the possibility of tuning them by varying the concentration of the magnetic ions offer new possibilities in numerous applications. These systems also prove to be convenient for establishing theories and their experimental verifications [2, 3].

The most thoroughly studied materials of this type are the $\text{A}_{1-x}^{\text{II}}\text{Mn}_x\text{B}^{\text{VI}}$ alloys where A^{II} and B^{VI} represent group II and group VI elements, respectively [1, 2]. Among these DMSCs mixed oxides have been the least investigated and, to our best knowledge, considerable attention has been given only to $\text{Mg}_{1-x}\text{Mn}_x\text{O}$ for small concentrations of Mn ions [4]. In this paper we present results of a studying on the crystalline structure, the thermal stability and some magnetic properties of the ternary semiconducting oxide $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ for a wide range of Mn concentrations x ($0.05 \leq x \leq 0.90$).

Constitutive oxides CdO and MnO are both wide-gap semiconductors with energy gaps $E_g = 2.4$ eV [5] and $E_g = 2.2$ eV [6], respectively. From the magnetic point of view, CdO is a diamagnetic whereas MnO is a type-2 antiferromagnetic below the Néel point $T_N = 122$ K [7]. The crystallochemical properties of CdO and MnO are very similar; they both crystallize in the space group $Fm3m$ in sodium chloride (NaCl) structure type with lattice constants $a(\text{CdO}) = 4.695$ Å and $a(\text{MnO}) = 4.444$ Å; also, Cd^{2+} and Mn^{2+} ions

have similar values of ionic radii (1.09 Å and 0.96 Å, respectively [8]) and electronegativities (1.7 and 1.5, respectively). These similarities offer the possibility of forming ternary mixed solid solutions of the constitutive oxides CdO and MnO.

2. Experimental methods and results

Polycrystalline samples of $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ were obtained by using a solid state reaction between the appropriate carbonates CdCO_3 (99.999% pure) and MnCO_3 (99.99% pure). Carbonates were chosen as starting compounds because of the prominent instability of MnO which absorbs oxygen even at room temperature. The starting compounds were mixed in appropriate molecular ratios and homogenized for at least 10 h. Samples were pressed into pellets under a pressure of 100 MPa and heat treated at 1100 K in an inert argon atmosphere for 8 h and then slowly cooled. The x-ray powder diffraction measurements showed all samples ($x = 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.80$ and 0.90) to be a single phase in the $Fm\bar{3}m$ space group of rock-salt type. Chemical analysis revealed that the variation in the actual composition is less than 5% of the nominal x -value.

The crystal structures of $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ samples for $0.10 \leq x \leq 0.90$ were refined by the use of the program package FULLPROF, based on the full-profile Rietveld [9] method. The x-ray diffraction data were obtained at room temperature with a Rigaku powder diffractometer with a rotation anticathode (Cu $K\alpha_{1,2}$ radiation) and a Philips goniometer. The basic characteristics of the refinement are listed in table 1. In the $Fm\bar{3}m$ space group of the rock-salt structure type the cations Mn^{2+} and Cd^{2+} occupy the (a) and the O^{2-} anions the (b) Wyckoff positions, with the same local symmetry and with fractional coordinates $[0, 0, 0]$ and $[1/2, 1/2, 1/2]$, respectively. Cations are octahedrally coordinated with six oxygen anions, i.e. O^{2-} with six cations. Since the fractional coordinates of the ions are fixed, we have refined the lattice constant $a(x)$ and temperature factors B for each concentration. The results are listed in table 2. The values obtained for $a(x)$ are depicted in figure 1 and one can see a slight deviation from the Vegard law $a(x) = Ax + B$, where $A = -0.255(7)$ Å and $B = 4.712(4)$ Å. The factors A and B were determined by the linear least-squares fit to the $a(x)$ data.

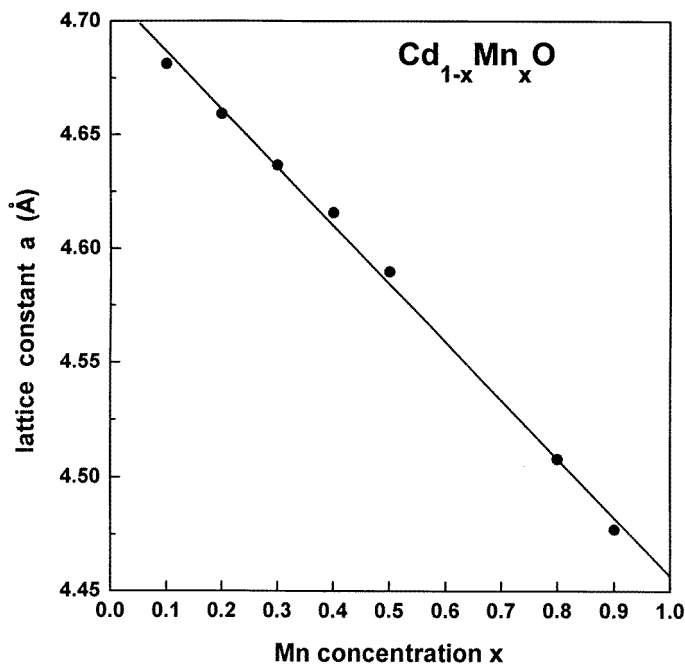
Table 1. Basic characteristics of the crystal data refinement for $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ (Crystal system, cubic, space group, $Fm\bar{3}m$; $\lambda_{\text{Cu } K\alpha_1} = 1.5406$ Å; $\lambda_{\text{Cu } K\alpha_2} = 1.5444$ Å). R_B is the Bragg factor; R_{wp} is the weighted profile factor.

x	2θ (deg)	Number of reflections	Number of fitting parameters	R_B (%)	R_{wp} (%)
0.10	30–120	22	8	3.77	9.64
0.20	30–120	22	8	3.77	8.76
0.30	30–125	22	8	4.45	8.01
0.40	30–125	22	8	4.65	7.65
0.50	30–125	22	8	4.61	6.58
0.80	30–130	22	8	2.64	3.97
0.90	32–132	22	8	4.80	3.08

The thermal stabilities of the samples were investigated using a Perkin–Elmer model TGS-2 thermogravimetric system. Samples were heated at a rate of 10 K min^{-1} in an oxygen flow and in the temperature range $300 \text{ K} \leq T \leq 1150 \text{ K}$. Mass changes of the samples as a function of the temperature are depicted in figure 2, for three different Mn

Table 2. Refined values of the crystal data for $Cd_{1-x}Mn_xO$.

x	a (Å)	B_a (Å ²)	B_b (Å ²)
0.10	4.6812(1)	0.41(3)	0.6(1)
0.20	4.6592(1)	0.61(3)	1.0(1)
0.30	4.6366(2)	0.54(3)	0.9(1)
0.40	4.6159(2)	0.35(3)	0.8(1)
0.50	4.5900(2)	0.45(3)	0.7(1)
0.80	4.5080(1)	0.45(4)	0.7(1)
0.90	4.4774(1)	0.49(4)	0.9(1)

**Figure 1.** The dependence of the lattice constant of $Cd_{1-x}Mn_xO$ samples on Mn concentration.

concentrations. One can see that all samples are stable up to the same temperature of approximately 500 K. The mass gain above this temperature points indicates an uptake of oxygen by MnO since CdO is stable in this temperature range.

Preliminary investigations of the magnetic properties of $Cd_{1-x}Mn_xO$ samples were carried out at room temperature and liquid-nitrogen temperature. Magnetic susceptibility measurements were made by the Faraday method in a DC field of 6 kOe. Experimental data were corrected for temperature-independent diamagnetic contributions $\chi_d = -3.4 \times 10^{-5} \text{ emu mol}^{-1}$ and $-2.60 \times 10^{-5} \text{ emu mol}^{-1}$ for CdO and MnO, respectively [9]. The values obtained for the molar magnetic susceptibilities $\chi_M(x)$ are depicted in figure 3. The solid curve through the room-temperature data represents the least-squares fit to the

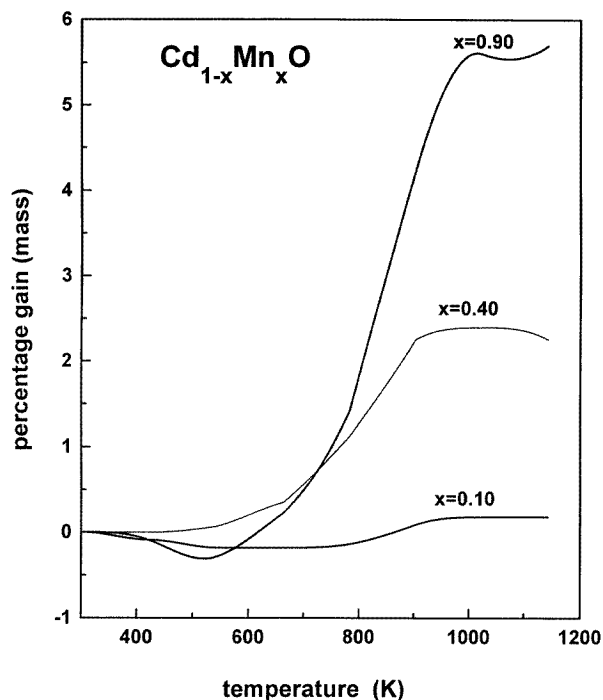


Figure 2. Thermograms of $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ samples for $x = 0.10, 0.40$ and 0.90 .

Curie–Weiss law for randomly diluted magnetic systems in the form

$$\chi_M(x, T) = \frac{C_M(x)}{T - \Theta(x)} = \frac{C_M x}{T - \Theta_0 x} \quad (1)$$

where C_M and Θ_0 denote the Curie molar constant and the Curie–Weiss paramagnetic temperature, respectively [3]. In this procedure, C_M and Θ_0 were treated as fitting parameters. The effective magnetic moment $\mu_{eff} = (8C_M)^{1/2}$ of Mn^{2+} ions is then calculated to be $\mu_{eff} = (6.0 \pm 0.1)\mu_B$, which is close to its free-ion value of $5.92\mu_B$ [9]. The value of the parameter $\Theta_0 = -610 \pm 20$ K represents the Curie–Weiss paramagnetic temperature of MnO and exhibits satisfactory agreement with the values found in the literature, namely $610 \text{ K} \leq |\Theta_p| \leq 690 \text{ K}$ [10]. It is noticeable that, at the liquid-nitrogen temperature, the values of $\chi_M(x)$ for higher Mn concentrations ($x \geq 0.50$) deviate from the Curie–Weiss law, which indicated that they are not in the paramagnetic region. This result is consistent with the theoretical claim that the Curie–Weiss law is valid when the paramagnetic temperature $|\Theta(x)|$ is substantially smaller than the measurement temperature T [3]. Since $|\Theta(x)|$ is directly correlated with the Néel temperature $T_N = 122$ K for pure MnO, it is obvious that the condition $|\Theta(x)| \ll 78$ K is not fulfilled for samples with high x . To provide this condition we have performed $\chi(x, T)$ measurements in the temperature range $290 \text{ K} \leq T \leq 500$ K, where the upper temperature limit was imposed by the thermal stability of the samples. Experimental conditions were the same as before and the temperature stability was ± 1 K.

The values obtained for the inverse molar magnetic susceptibilities $\chi_M^{-1}(x, T)$, corrected for diamagnetic contributions, are depicted in figure 4, where some concentrations are omitted for clarity. The straight lines represent least-square fits to the Curie–Weiss law in

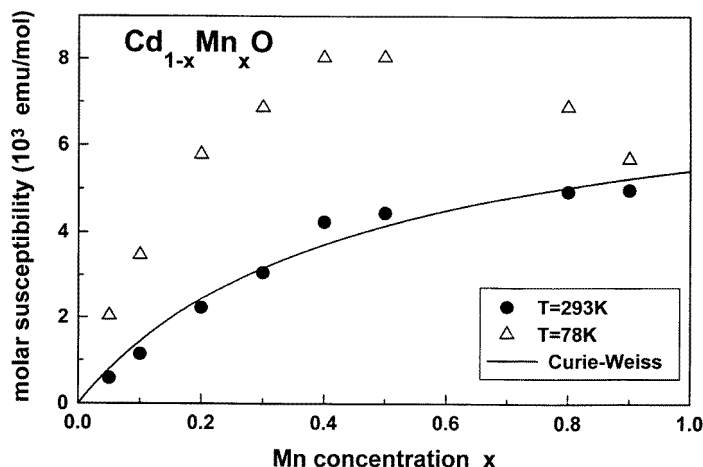


Figure 3. Molar magnetic susceptibility of $Cd_{1-x}Mn_xO$ samples at room temperature and liquid-nitrogen temperature.

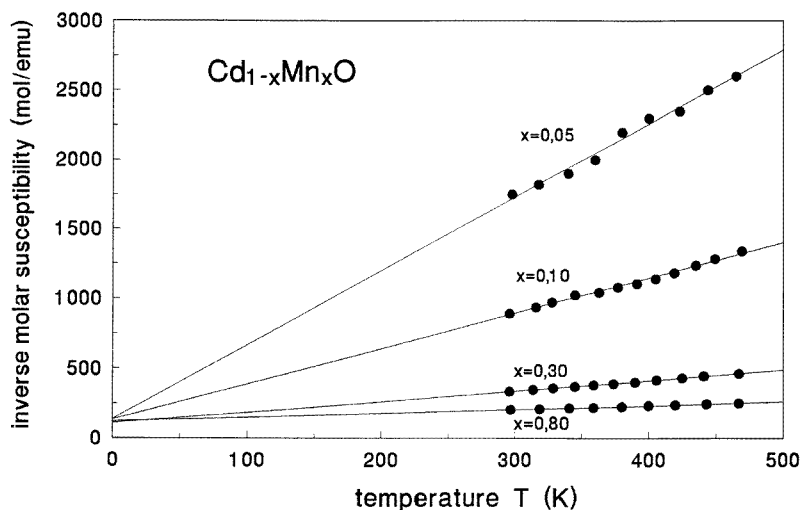


Figure 4. Temperature dependence of the inverse molar magnetic susceptibility of $Cd_{1-x}Mn_xO$ for $x = 0.05, 0.10, 0.30$ and 0.80 .

the form given in equation (1). The Curie molar constants $C_M(x)$ were obtained from the slopes of the lines and the effective Curie–Weiss temperatures $\Theta(x)$ by extrapolations to the T axis. Negative values of $\Theta(x)$ show the presence of antiferromagnetic interactions in all $Cd_{1-x}Mn_xO$ samples. For $T = 0$ all the straight lines in figure 4 have a common intercept on the y axis (within the fitting accuracy), i.e. $\chi_M^{-1}(T = 0)$ is independent of x which is in accordance with the theoretical predictions embodied in equation (1). The same behaviour was observed for all DMSCs of the $A_{1-x}^{II}Mn_xB^{VI}$ type [1–3].

The values obtained for $C_M(x)$ and $|\Theta(x)|$ are depicted in figure 5 and figure 6, respectively. The straight lines on these figures represent least-squares linear fits in

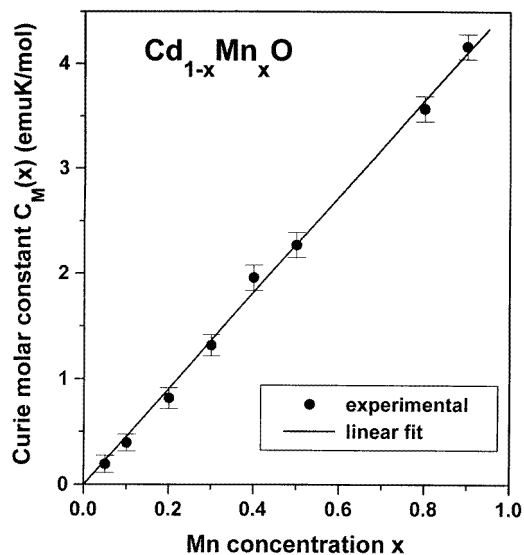


Figure 5. Concentration dependence of the Curie molar constant for $\text{Cd}_{1-x}\text{Mn}_x\text{O}$.

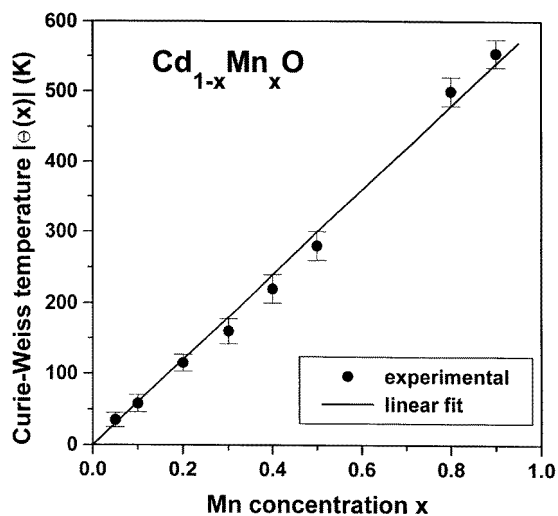


Figure 6. Concentration dependence of the Curie-Weiss paramagnetic temperature for $\text{Cd}_{1-x}\text{Mn}_x\text{O}$.

accordance with the theoretical predictions for randomly diluted magnetic systems [3]:

$$C_M(x) = (g\mu_B)^2 S(S+1) \frac{N_A}{3k_B} x \equiv C_M x \quad (2)$$

$$\Theta(x) = -\frac{1}{3k_B} S(S+1) \left(\sum_p J_p Z_p \right) x \equiv \Theta_0 x. \quad (3)$$

In these expressions, S denotes the spin of Mn^{2+} ions, J_p is the exchange integral of a pair of p -th neighbours and Z_p is the number of cations on the p th coordination sphere around

the given atom chosen as central. From the slopes of the fitted lines we have obtained values of C_M and Θ_0 and then, by the use of equations (2) and (3), values of the spin S and nearest-neighbour exchange integral J_1/k_B were inferred (table 3). The value of S was obtained in a straightforward manner from equation (2) to be $S = 2.6 \pm 0.1$ for Mn^{2+} spin ($3d^5$ configuration) and thus its atomic value $S = 5/2$ (Hund's rule fulfilled) can be taken as a good approximation in the regime where $C_M(x)$ linearly depends on x . To obtain the value of J_1/k_B a necessary simplification of equation (3) has been made on the basis of the range of superexchange Mn–O–Mn interaction. From electron paramagnetic resonance studies, it has been inferred that for Mn^{2+} in $\text{Mg}_{1-x}\text{Mn}_x\text{O}$ (NaCl structure) the values of J_1 and J_2 , the nearest-neighbour (NN) and next-nearest-neighbour (NNN) exchange integrals, respectively, are nearly equal [11]. A similar conclusion has been drawn from the magnetic susceptibility study on pure MnO [12]. Because of these results, in the sum in equation (3) we retain only terms with NN and NNN exchange integrals without distinguishing them, i.e. $J_1 = J_2$. Since Mn^{2+} ions form a FCC sublattice in the NaCl-type lattice of $\text{Cd}_{1-x}\text{Mn}_x\text{O}$, the numbers of NN and NNN cations are $Z_1 = 12$ and $Z_2 = 6$, respectively, and equation (3) reduces to

$$\Theta(x) = -6S(S+1)\frac{J_1}{k_B}x \equiv \Theta_0x. \quad (4)$$

By the use of equation (4) and the values obtained for S and Θ_0 (see table 3) the value of the NN exchange integral was calculated to be $J_1/k_B = 11 \pm 1$ K. This value is in a very good agreement with the NN exchange integral $J_1/k_B = 10 \pm 1$ K for Mn^{2+} found from the magnetic susceptibility measurements on pure MnO [12].

Table 3. Values of parameters for $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ determined from the magnetic susceptibility data.

C_M (emu K mol ⁻¹)	Θ_0 (K)	S	J_1/k_B (K)
4.5 ± 0.1	-600 ± 20	2.6 ± 0.1	11 ± 1

3. Summary

Polycrystalline samples of cadmium–manganese mixed oxides $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ were successfully synthesized by ceramic technology in a wide concentration range $0.05 \leq x \leq 0.90$. All samples crystallize in the same crystal type, sodium chloride, as do the constitutive oxides CdO and MnO.

Thermogravimetric analysis showed that all samples were stable up to the same temperature of 500 K. Since pure MnO absorbs oxygen even at room temperature, it can be concluded that CdO stabilizes MnO in $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ independently of their molar ratios. A similar behaviour was obtained for $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions [13].

Static magnetic susceptibility $\chi(x, T)$ measurements were made by the Faraday method in the temperature interval $290 \text{ K} \leq T \leq 500 \text{ K}$ in which the condition $|\Theta(x)| \ll T$ was fulfilled for all the samples. This allowed us to present experimental data via the Curie–Weiss law for randomly diluted magnetic systems given by equation (1). From the Curie molar constants $C_M(x)$, the effective spin S per Mn^{2+} ion is determined to be close to its atomic value of $5/2$. Analysis of the effective paramagnetic temperature $\Theta(x)$ data gave the value of the NN exchange integral $J_1/k_B = 11 \pm 1$ K. Finally, from the concentration

dependence of $C_M(x)$ and $\Theta(x)$ a conclusion on the distribution of magnetic ions can be inferred. According to the theory, the linear dependences given by equation (2) and (3) are valid under the assumption of a completely random distribution of magnetic atoms [3]. The data on $C_M(x)$ and $\Theta(x)$ depicted in figures 5 and 6, respectively, show a linear dependence on x in the whole concentration range $0.05 \leq x \leq 0.90$. Consequently, we can conclude that Mn^{2+} ions are randomly distributed over the cation sites in all $\text{Cd}_{1-x}\text{Mn}_x\text{O}$ samples.

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