Structural and magnetic properties of transition metal substituted ZnO

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Structural and magnetic properties have been studied for polycrystalline Zn$_{1-x}$TM$_x$O, where TM (transition metal ions) = Mn, Fe, and Co. No bulk ferromagnetism was observed for single-phase materials, contrary to the existing theories. Single-phase samples demonstrate paramagnetic Curie-Weiss behavior with antiferromagnetic interactions, similar to other diluted magnetic semiconductors. Non-optimal synthesis conditions lead to formation of second phases that are responsible for spin-glass behavior (ZnMn$_2$O$_4$ impurity for Zn$_{1-x}$Mn$_x$O (S. Kolesnke et al., J. Supercond.: Incorp. Novel Magn. 15, 251 (2002))) or high-temperature ferromagnetic ordering (Co metal for Zn$_{1-x}$Co$_x$O with the Curie temperature $T_C > 800$ K or (Zn,Fe)$_3$O$_4$ for Zn$_{1-x}$Fe$_x$O with $T_C = 440$ K).

Keywords: Diluted magnetic semiconductors, ZnO, synthesis, ferromagnetism

I. INTRODUCTION

A widegap II-VI semiconductor, ZnO attracts attention as a material with possible application in optoelectronic devices such as solar cells, ultraviolet emitting diodes and transparent high-power electronic devices. The discovery of ferromagnetism at temperatures above 100 K in the III-V semiconductor Ga$_{1-x}$Mn$_x$As \(^1\) provided practical means to incorporate spin into semiconductor electronics. Theoretical predictions of room temperature ferromagnetism in diluted magnetic semiconductors \(^2\) recently focused attention on magnetic-ion-substituted ZnO with a wurtzite structure similar to GaAs. According to these calculations, room temperature ferromagnetism can exist in $p$-type doped Zn$_{1-x}$Mn$_x$O with 5%Mn and $3.5 \times 10^{20}$ holes per cm\(^3\). \textit{Ab initio} band calculations \(^3\) predict stability of ferromagnetism in $p$-type Zn$_{1-x}$Mn$_x$O, and antiferromagnetism in $n$-type Zn$_{1-x}$Mn$_x$O. Similar calculations predict a ferromagnetic phase for both carrier-undoped and $n$-type ZnO substituted with Fe, Co, or Ni. \(^4\) The parent compound ZnO without intentional carrier doping shows $n$-type conduction related to oxygen vacancies and Zn interstitials. \(^5\) The introduction of $p$-type conduction in ZnO is difficult. Several methods, including nitrogen doping \(^6\) and Ga and N codoping \(^7\) \(^8\), have been reported. Successful preparation of $p$-type ZnO could allow fabrication of transparent $p-n$ junctions and could enable synthesis of substituted ferromagnets.

Pulsed-laser deposited Zn$_{1-x}$Mn$_x$O thin films with up to 35% Mn show spin-glass behavior. \(^9\) We have previously shown for polycrystalline Zn$_{1-x}$Mn$_x$O that the spin-glass behavior can be induced by high-pressure oxygen annealing and it is related to precipitation of impurity phase ZnMnO$_3$. \(^10\) ZnO films doped with Co have been reported to be ferromagnetic with Curie temperature of about 280 K. \(^11\) However, Kim et al. pointed to the presence of Co clusters in their thin films as a reason for room temperature ferromagnetism. \(^12\) High-temperature ferromagnetism in thin films of Co-doped anatase TiO$_2$ \(^13\) has also been explained by the fact that cobalt is not substitutional for titanium in TiO$_2$. \(^14\) In this study, we investigate polycrystalline Zn$_{1-x}$TM$_x$O, where TM = Mn, Fe, and Co. We show that no high-temperature ferromagnetic ordering is present in single-phase samples. Ferromagnetism in these materials can be induced by second phases that may appear after non-optimal synthesis conditions.

II. EXPERIMENTAL METHODS

The Zn$_{1-x}$TM$_x$O samples in this study were prepared using a standard solid-state reaction technique. Mixtures of ZnO and MnO$_2$, Fe$_2$O$_3$, or Co$_3$O$_4$, for TM = Mn, Fe, and Co, respectively, were fired in air several times at elevated temperatures 900, 1000, 1100, and 1200°C with intermediate grindings. The samples were then annealed in an atmosphere of various gases (Ar, H$_2$, 1%H$_2$/Ar, or O$_2$ under high pressure of 600 bar). High pressure oxygen annealing was intended to produce $p$-type doped ZnO materials. Magnetic ac susceptibility and dc magnetization were measured using a Physical Property Measurement System and a Magnetic Property Measurement System (both Quantum Design) at temperatures up to 400 and 800 K, respectively. Energy dispersive x-ray spectroscopy (EDXS) analysis was performed by a Hitachi S-4700-II scanning electron microscope. Typically, 15-20 EDXS spectra were collected for each composition at various locations across the surface of a sintered pellet. Using the average Zn and TM cation contents, which were obtained from the EDXS spectra we determined the effective composition Zn$_{1-x}$TM$_x$O of the studied samples. X-ray diffraction experiments have been performed using a Rigaku x-ray diffractometer. We have analyzed the x-ray diffraction patterns using the Rietveld technique with the General Structure GSAS code. \(^15\) The refinements were done using the wurtzite hexagonal space group P6$_3$mc with (Zn,TM) atoms located at (2/3, 1/3, 0) and O atoms located at (2/3, 1/3, u). For both single-phase and multi-phase samples (where impurity peaks were observed), this was the only phase refined.
III. RELATIONSHIP BETWEEN SYNTHESIS CONDITIONS AND STRUCTURAL PROPERTIES

Single-phase samples can be synthesized in air for TM = Mn, and Co and in 1%H2/Ar for TM = Fe. X-ray diffraction data show that the Zn1−xTMxO samples are single-phase with the wurtzite structure up to a certain value of x. We estimated this value (the solubility limit) to be equal to 0.1, 0.1, and 0.2 for TM = Mn, Fe, and Co, respectively. Above the solubility limit, characteristic impurities can be observed by x-ray diffraction, namely ZnMn2O4, Fe2O or (Zn,Fe)3O4, and CoO for TM = Mn, Fe, and Co, respectively.

In Fig. 1 X-ray diffraction patterns are presented for Zn1−xFe2O after synthesis in 1%H2/Ar at 1000°C. The samples with x ≤ 0.1 are single-phase, and the presence of the second phase Fe2O can be observed for x ≥ 0.15. Wüstite Fe2O can typically be obtained in a slightly non-stoichiometric form with z < 1 depending on synthesis conditions; however, due to a very small amount of this phase in the Zn0.85Fe0.15O sample, we could not determine the value of z. Thus, we have separately prepared wüstite Fe2O by reduction of Fe2O3 in the same atmosphere, 1%H2/Ar at 1050°C, and obtained the compound with the rock-salt structure and lattice constant a = 4.3101 Å that is consistent with z = 0.95. Stability of Zn1−xFe2O and second phases are sensitive to changes of the synthesis temperature. The annealing of these samples in 1%H2/Ar at 950°C leads to precipitation of second phase (Zn,Fe)3O4, which accounts for room temperature ferromagnetism in multi-phase Zn1−xFe2O. Substitution of Fe in ZnO is not possible in air or at high pressure of oxygen at any temperature.

Fig. 2 shows x-ray diffraction patterns for the Zn0.8Co0.2O sample obtained from several annealing conditions. Various impurity peaks appear after annealing under reducing or strongly oxidizing conditions. These peaks are marked with stars in Fig. 2. After argon annealing at T = 1100°C, rock-salt-like antiferromagnetic CoO impurity is present. A slight reduction of Zn0.8Co0.2O in 1%H2/Ar at 1000°C leads to precipitation of Co metal, which causes a ferromagnetic contribution to the measured ac susceptibility and dc magnetization. High-pressure oxygen annealing at T = 1080°C induces spinel-like ZnCo2O4 impurity. High-pressure oxygen annealing was found, thus, to favor formation of compounds other than Zn1−xTMxO, for which TM ions display oxidation states higher than 2+.

Structural parameters of Zn1−xTMxO obtained from the Rietveld refinements are presented in Fig. 3. Open symbols in Fig. 3 denote the multi-phase compositions, i.e. the ones for which the presence of impurity peaks is observed in the X-ray diffraction data. The unit cell volume changes almost linearly with substitution of TM for single-phase compositions. This behavior is expected according to the difference between ionic radii r of tetrahedrally coordinated Zn2+ r = 0.60 Å and other transition metal TM2+ ions (r = 0.66, 0.63, and 0.58 Å for TM = Mn, Fe, and Co, respectively). The observed slight increase of the cell volume in case of TM = Co is inconsistent with the smaller ionic radius of Co than Zn estimated by Shamoon. This increase can not be explained either by the presence of Co3+ in Zn1−xCo2O as Co3+ is smaller than Co2+. Apparently, the ionic size of tetrahedrally coordinated Co2+ ion is larger than that of Zn2+. The u parameter (z-coordinate of the oxygen atoms) of the wurtzite structure of Zn1−xTMxO initially increases with increasing x, reaches its maximum close to the solubility limit, and subsequently decreases. The c/a ratio [Fig. 3(d)] decreases slightly at a similar rate for TM = Mn and Co, while it decreases much more rapidly for TM = Fe. This effect shows that Fe-doped ZnO is more anisotropic than ZnO doped with other transition metal ions. Ref. 17 has shown a phenomenological lin-
ear dependence \( u \propto (a/c)^2 \) for all undoped wurtzite-like compounds including ZnO. Our observation for transition metal doped ZnO is qualitatively consistent with this tendency up to the solubility limit. The coefficient of this linear dependence (varying from 9 to 34) is much higher than the reported value of 1/3.\[17\]

The effective TM content \( x_{\text{eff}} \) in Zn\(_{1-x}\)TM\(_x\)O determined from EDXS analysis is presented in Fig. 4. In our previous work\[10\], we have shown (based on the assumption that the ac susceptibility reflects spin-only behavior) that \( x_{\text{eff}} < x \) for TM = Mn (solid line in Fig. 4). Present EDXS data for TM = Mn confirm that result. For TM = Co, we observe a good agreement between the effective and nominal TM contents, within the experimental error. For TM = Fe, \( x_{\text{eff}} \simeq x \) for \( x = 0.05 \). However, for higher Fe concentration, \( x = 0.1 \), we observe \( x_{\text{eff}} \simeq 0.14 \). This larger effective Fe content than the starting content, \( x \), could arise from Zn volatilization during synthesis under reducing conditions in 1%H\(_2\)/Ar. We did not include this composition for the analysis of the magnetic properties of Zn\(_{1-x}\)Fe\(_x\)O.

**IV. MAGNETIC PROPERTIES**

Magnetic susceptibility is presented in Fig. 5 for Zn\(_{0.8}\)Co\(_{0.2}\)O. Here and throughout this paper, the diamagnetic ac susceptibility of -0.33 \( \times 10^{-6} \) emu/g for ZnO\[18\] was subtracted from the measured magnetic susceptibility. The ac susceptibility of the TM-doped ZnO resembles Curie-Weiss behavior which is also characteris-
After high-pressure oxygen annealing. After this anneal, a significant decrease of the ac susceptibility can be observed, which is correlated to the appearance of antiferromagnetic CoO impurity [Fig. 2(b)]. This behavior is characteristic to all studied TM-doped ZnO samples. These results, for TM = Mn, were presented elsewhere. [10] We have determined the parameters \( \Theta_0 \) and \( \Theta_0 \) for the studied TM-doped ZnO samples. The constant \( \Theta_0 \) contains both the spin of the TM\(^{2+} \) ions and the effective \( g_{\text{eff}} \) factor. Mn\(^{2+}\)-substituted ZnO was already discussed in Ref. [10].

Due to the half-filled 3d shell of Mn\(^{2+}\), its orbital momentum \( L = 0 \), the spin is \( S = 5/2 \), and the \( g_{\text{eff}} \) factor is very close to the free-spin value \( g = 2 \). This is similar to other Mn-based diluted magnetic semiconductors. For Co\(^{2+}\), the splitting of the energy levels due to the strong spin-orbit interaction results in an increase of the effective \( g_{\text{eff}} \) factor. The values of \( g_{\text{eff}} = 2.24 - 2.31 \) were reported for Co\(^{2+}\) in different diluted magnetic semiconductors. [22, 23, 24, 25, 26] An enhanced \( g_{\text{eff}} \) factor is also expected for Fe\(^{2+}\) due to its large orbital momentum \( (L = 2, S = 2) \). [27]

![FIG. 6: Inverse magnetic susceptibility for Zn\(_{1-x}\)Co\(_x\)O samples. The inset shows molar Curie constants \( C_M \) (full symbols) and Curie-Weiss temperatures \( \Theta \) (open symbols).](image)

In Table I, we compare the results determined from ac susceptibility for our samples with different TM\(^{2+}\). Here we assume the spin \( S \) to be equal to the theoretically expected value for each particular TM\(^{2+}\) ion. Our values of \( \Theta_0 \) and \( 2J_1/k_B \) are similar to other TM-containing semiconductors in case of TM = Mn [19, 21] and TM = Co. [26] The effective \( g_{\text{eff}} \) factors for TM = Co and Fe are substantially larger than the values from literature for other diluted magnetic semiconductors doped with respective TM\(^{2+}\) ions. The origin of this large \( g_{\text{eff}} \) factor is not clear at the moment. The presence of a small number of TM\(^{3+}\) in our samples (not detectable by X-ray

\[
\chi = \frac{C_M(x)}{T - \Theta(x)}, \tag{1}
\]

where \( \Theta(x) = \Theta_0 \cdot x \) is the Curie-Weiss temperature, \( C_M(x) = C_0 \cdot x \) is the molar Curie constant and \( C_0 \) is defined as

\[
C_0 = \frac{N(g_{\text{eff}}\mu_B)^2S(S+1)}{3k_B\rho}, \tag{2}
\]

\( N \) is the number of cations per unit volume, \( g_{\text{eff}} \) is the effective gyromagnetic factor of TM\(^{2+}\) ion, \( S \) is the spin, and \( \rho \) is the mass density calculated from the lattice parameters. The constant \( \Theta_0 \) is related to the exchange integral between the nearest TM neighbors \( J_1 \),

\[
\frac{2J_1}{k_B} = \frac{3\Theta_0}{zS(S+1)} \tag{3}
\]

where \( z = 12 \) is the number of nearest neighbors in the wurtzite structure of Zn\(_{1-x}\)TM\(_x\)O.

A linear fit to the inverse susceptibility data intersects the \( \chi^{-1} = 0 \) axis at a negative temperature. This result indicates the presence of antiferromagnetic interactions in the Zn\(_{1-x}\)TM\(_x\)O samples. At lower temperatures, inverse ac susceptibility deviates from the linear dependence toward a temperature close to zero. This is a result of additional antiferromagnetic interactions between the next nearest neighbor TM ions. [19]. The inset to Fig. 6 shows the molar Curie constants and the Curie-Weiss temperatures for Zn\(_{1-x}\)Co\(_x\)O. From linear fits of \( C_M \) and \( \Theta \) as a function of \( x \), we have determined the parameters \( C_0 \) and \( \Theta_0 \) for the studied TM-doped ZnO samples. The constant \( C_0 \) contains both the spin of the TM\(^{2+}\) ions and the effective \( g_{\text{eff}} \) factor. Mn\(^{2+}\)-substituted ZnO was already discussed in Ref. [10].

Due to the half-filled 3d shell of Mn\(^{2+}\), its orbital momentum \( L = 0 \), the spin is \( S = 5/2 \), and the \( g_{\text{eff}} \) factor is very close to the free-spin value \( g = 2 \). This is similar to other Mn-based diluted magnetic semiconductors. For Co\(^{2+}\), the splitting of the energy levels due to the strong spin-orbit interaction results in an increase of the effective \( g_{\text{eff}} \) factor. The values of \( g_{\text{eff}} = 2.24 - 2.31 \) were reported for Co\(^{2+}\) in different diluted magnetic semiconductors. [22, 23, 24, 25, 26] An enhanced \( g_{\text{eff}} \) factor is also expected for Fe\(^{2+}\) due to its large orbital momentum \( (L = 2, S = 2) \). [27]

| TM ion | \( \Theta_0 \) (K) | \( C_0 \) (emu K/mol) | \( 2J_1/k_B \) (K) | \( S \) | \( g_{\text{eff}} \) |
|--------|------------------|------------------|------------------|-------|---------|
| Mn     | -961 ± 49        | 4.1 ± 0.2        | -27.5 ± 1.4      | 5/2   | 2       |
| Fe     | -926 ± 26        | 6.0 ± 0.1        | -38.6 ± 1.1      | 2     | 2.83    |
| Co     | -951 ± 110       | 3.3 ± 0.1        | -63.4 ± 7.4      | 3/2   | 2.64    |

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diffusion (diffraction) is one possibility. These ions can increase the effective spin above the assumed value for TM$^{2+}$. This effect is especially crucial in the case of Fe substituted ZnO which we discuss below.

The influence of synthesis conditions on the structural and magnetic properties of Zn$_{0.95}$Fe$_{0.05}$O is illustrated in Fig. 7. The sample annealed at 950°C shows the presence of magnetite-like (Zn,Fe)$_3$O$_4$ impurity as displayed in the right inset. The ac susceptibility of this sample is much larger than the paramagnetic susceptibility of pure Zn$_{0.95}$Fe$_{0.05}$O (annealed at 1000°C). The temperature dependence of ac susceptibility for the sample containing (Zn,Fe)$_3$O$_4$ impurity is flat at higher temperatures, which is related to a ferromagnetic order with the Curie temperature equal to 440 K. A drop of the ac susceptibility around 20 K is probably related to the low temperature Verwey transformation, similar to the one observed in stoichiometric Fe$_3$O$_4$ at 120 K. The left inset to Fig. 7 shows the magnetization curves at $T = 300$ K for both samples. The (Zn,Fe)$_3$O$_4$-containing sample shows a narrow ferromagnetic hysteresis curve and the saturation magnetization close to 0.05$\mu_B$ per formula unit, which is equal to 1$\mu_B$ per substituting Fe ion. For ferrimagnetically coupled Fe ions in Fe$_3$O$_4$ one would expect the saturation magnetization 1.33$\mu_B$ per Fe ion. This suggests that most of the Fe in the multi-phase Zn$_{0.95}$Fe$_{0.05}$O sample is precipitated as a (Zn,Fe)$_3$O$_4$ impurity. The single-phase Zn$_{0.95}$Fe$_{0.05}$O sample shows a linear paramagnetic dependence on the magnetic field with a very small ferromagnetic hysteretic contribution. We were able to determine the magnitude of this ferromagnetic contribution by the following numerical procedure. Linear fits of the $M(H)$ data were performed in the high-field ranges 40 to 70 kOe and -40 to -70 kOe, where the ferromagnetic contribution to the magnetization is expected to be fully saturated. The average of the two fitted lines was subtracted from the measured $M(H)$ dependence. As a result, we obtained a small ferromagnetic hysteresis curve. The saturation magnetization of this ferromagnetic contribution gives an estimate for the upper limit of the ferromagnetic (Zn,Fe)$_3$O$_4$ impurity of 0.1%.

### V. SUMMARY

In summary, by studying structural and magnetic properties of transition metal substituted polycrystalline ZnO samples, we have found that no bulk ferromagnetism exists for single-phase materials, contrary to the existing theories. Stoichiometric samples demonstrate paramagnetic behavior with antiferromagnetic interactions similar to other semimagnetic semiconductors substituted with transition metal ions. Selected synthesis conditions lead to impurity-induced ferromagnetic order in Co and Fe-doped ZnO. Attempts to induce $p$-type doping by high-pressure oxygen synthesis lead to formation of secondary phases for which transition metals Mn, Fe, and Co exist in high oxidation states.

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