

Magnetic properties of bulk $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ single crystals

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Magnetic properties of bulk $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ single crystals

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Manganese and cobalt-doped ZnO have been produced using a modified melt-growth technique. X-ray diffraction measurements indicate that the samples are high-quality single crystals with ω -2θ full width at half maximum values of 78 arc sec for the undoped ZnO and 252 arc sec for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=0.05$). The lattice parameter of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ was observed to increase with Mn concentration. Transmission measurements showed systematic variations dominated by absorption from interatomic Mn^{2+} and Co^{2+} transitions. No evidence of diluted magnetic semiconductor mean-field ferromagnetic behavior was observed in any of these nominally noncarrier-doped samples. The magnetic properties instead showed paramagnetic behavior for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ dominated by an antiferromagnetic Mn–Mn exchange interaction at low temperatures. $\text{Zn}_{1-x}\text{Co}_x\text{O}$ showed hysteresis that was attributed to superparamagnetic Co clusters embedded in a diamagnetic ZnO matrix. It has been shown that in the bulk single-crystal form, intrinsic and noncarrier-doped $\text{Zn}_{1-x}\text{TM}_x\text{O}$ is not ferromagnetic; thus creative processing and doping techniques are necessary to achieve practical ferromagnetism in these materials.

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INTRODUCTION

Ferromagnetic semiconductors are anticipated to be an enabling component of the next-generation spintronic devices.¹ An additional degree of freedom and functionality can be integrated into existing semiconductor devices by combining the dissimilar properties of ferromagnetism and semiconductivity, with applications ranging from nonvolatile memory to quantum computation. Both the II–VI and III–V semiconductor systems have compounds which can be made ferromagnetic by the addition of small amounts of an interior third period transition-metal element,² though this behavior is generally restricted to cryogenic temperatures. Theoretical predictions using the mean-field model for ferromagnetism suggest that ZnO and GaN are room-temperature ferromagnetic dilute magnetic semiconductors (DMS) when doped with sufficient quantities of holes (3.5×10^{20}) and Mn (3.5%).³ Subsequent density-functional calculations also predict ferromagnetism in transition-metal alloys of ZnO

through a double-exchange mechanism, though not necessarily requiring additional free carriers at high (25%) alloy concentrations.⁴

The II–VI semiconductors make an attractive alternative to the introduction of transition metals relative to the III–V semiconductors, as predictions indicate a larger solid solubility (on the order of tens of percent)⁵ for nominally isovalent transition metal for zinc substitutions in this wurtzite lattice. This has led to the production of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ exhibiting ferromagnetism by numerous methods, including pulsed laser deposition,^{6–8} ion implantation,^{9,10} molecular-beam epitaxy,¹¹ and solid-state reaction.^{12,13} These experiments have been plagued by highly process-dependent properties very often with minimal reproducibility.⁶ There are also several reports for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ that do not exhibit ferromagnetic behavior.^{14,15} Recent results have also provided evidence that the ferromagnetism in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ is not an inherent property of the system but could be due to secondary phases or clusters.¹⁶ To date, it has been difficult to ascertain whether this ferromagnetism is an intrinsic property of the material or an artifact of certain production methods. This problem is further complicated in

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thin-film measurements, as any magnetic signature from the substrate can significantly contribute to the measured signal.

In this work, the magnetic and other properties of transition-metal-doped melt-grown single crystals of ZnO are reported. Bulk crystals, compared to epilayers, can aid in understanding the mechanism of ferromagnetism independent of substrate effects. Using single-crystal growth techniques, uniform dopant distributions can be achieved within the solubility limit of the material. The magnetic signature in thin epitaxial layers can also be influenced by dislocation and strain effects. Bulk crystals can also provide homoepitaxial substrates for spintronic device processing for both ZnO and near-lattice matched heteroepitaxial substrates for ferromagnetic GaMnN grown by either molecular-beam epitaxy¹⁷ (MBE) or metalorganic chemical vapor deposition (MOCVD).¹⁸ This work shows that, as expected by theory, undoped $\text{Zn}_{1-x}\text{TM}_x\text{O}$ is not ferromagnetic—even though ferromagneticlike signals can be observed.

EXPERIMENTAL DETAILS

Single crystals were grown by a modified melt-growth technique described elsewhere.¹⁹ Varying doping levels of Mn and Co were incorporated into the ZnO crystals during the growth process. It should be noted that in this instance, doping levels imply incorporation of these impurities at lattice concentration. This work focuses on a systematic series of three Mn-doped samples with increasing doping concentration. Target Mn concentrations from the stoichiometric ratio of reactants used in the crystal growth were 0.04%, 1%, 3%, and 5% for samples labeled as sample A, B, C, and D, respectively. The samples were cut from the crystals perpendicular to the crystallographic *c* axis and double-side polished. In addition, cobalt-doped $\text{Zn}_{1-x}\text{Co}_x\text{O}$ crystals with 1% and 3% cobalt were also grown for this study. High-resolution x-ray diffraction (XRD) was performed on the single-crystal samples using a Philips X'Pert PRO MRD four-circle diffractometer. Ultraviolet-visible transmission measurements were performed using a Varian-Cary 300 spectrometer from 200 to 800 nm. Secondary-ion-mass spectroscopy was performed using an Atomika Instruments Ion Microprobe A-DIDA 3000 on the as-grown crystals and compared with a Mn^+ -implanted calibration sample. Magnetic property measurements were performed with a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer from 2 to 300 K.

RESULTS

X-ray diffraction 2θ - ω scans performed on both undoped and transition-metal (TM)-doped ZnO showed that the as-grown material was a completely oriented single crystal, as no peaks attributable to second phase formation were observed. Only *c*-axis (002) and (004) peaks were visible in the 2θ - ω scans at doping levels up to 5% Mn and 3% Co, as shown in Fig. 1. The measured *c*-axis lattice parameter was 5.207 Å in the undoped sample, but increased with Mn incorporation to a value of 5.211 Å at the 5% doping level. This difference in these values is close to the experimental error in the measurement, though by using multiple *c*-axis

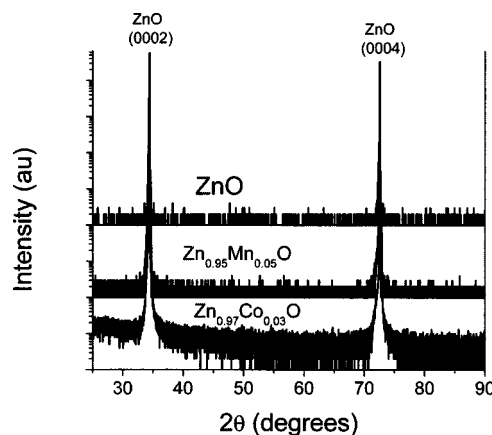


FIG. 1. 2θ - ω diffraction pattern from *c*-axis cut, $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, $\text{Zn}_{1-x}\text{Co}_x\text{O}$, and ZnO samples, showing only basal plane reflections and no secondary phase formation, even in the most heavily alloyed samples.

reflections and a Bradley-Jay extrapolation function, a larger *c*-axis lattice parameter was observed for all of the Mn-doped samples. An increase in lattice parameter was not conclusively identified in the Co-doped sample, owing to the more similar Zn^{2+} and Co^{2+} tetrahedral ionic radii. Phi scans from the asymmetric (102) reflections clearly revealed the six-fold symmetry of the wurtzite structure. Crystal quality was observed to decrease with increasing transition-metal concentration as evidenced by the 2θ - ω scan linewidths, increasing from 78 arc sec in the undoped sample to 252 arc sec at 5% Mn. In addition, peak asymmetry increased on the low angle side as the transition-metal elements were added, indicating the likely incorporation of Mn/Co interstitial atoms into the crystal lattice with increasing doping concentration.

Secondary-ion-mass spectroscopy (SIMS) performed on the samples is shown in Fig. 2. The peaked curve in Fig. 2 is a reference sample implanted with 3×10^{16} Mn ions at 200 keV. In comparison with the ion-implanted sample which shows a peaked distribution, the as-grown crystals show a uniform dopant distribution with depth throughout the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ crystal. The Mn concentrations of the samples were found to be 0.2%, 0.6%, and 1.6% from these curves.

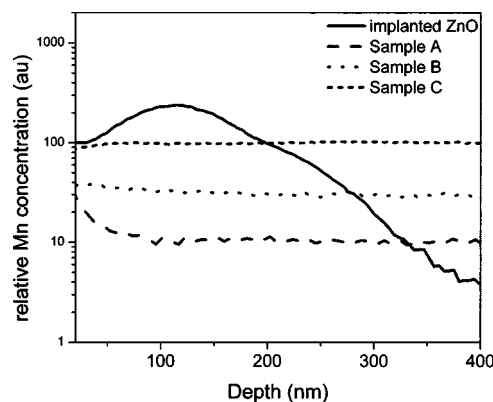


FIG. 2. Secondary-ion-mass spectroscopy spectra for the implanted and bulk $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ samples. The peaked curve is a reference sample implanted with 3×10^{16} Mn ions at 200 keV. In comparison with the ion-implanted sample, the as-grown crystals show a uniform dopant distribution with depth throughout the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ crystal.

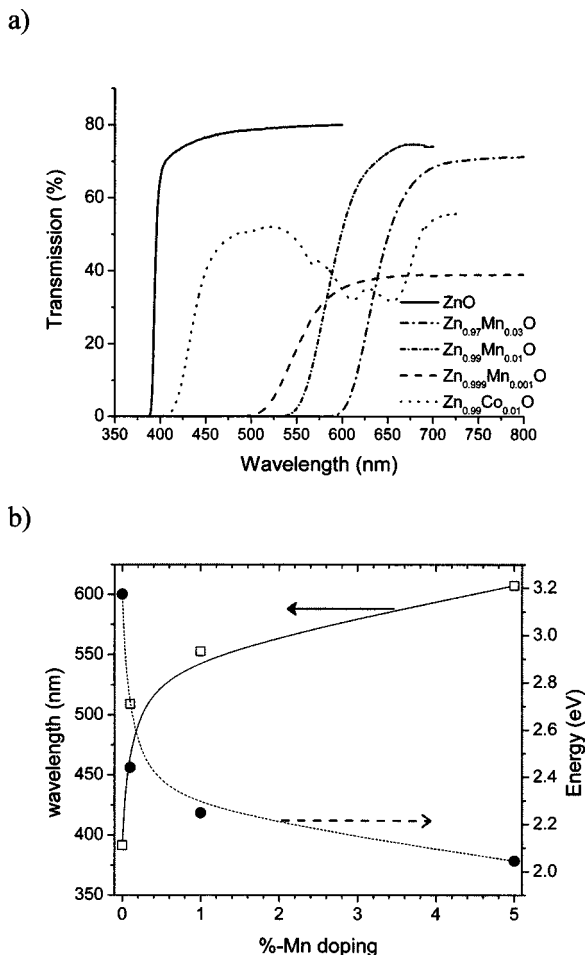


FIG. 3. (a) Transmission spectra from undoped, $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ single crystals of varying doping concentrations. The corresponding concentrations are (ZnO, solid; $\text{Zn}_{0.97}\text{Mn}_{0.03}\text{O}$, long-dashed dot; $\text{Zn}_{0.999}\text{Mn}_{0.001}\text{O}$, dashed; $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$, short-dashed dot; and $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$, dotted). The undoped ZnO sample shows a sharp cutoff at 391 nm. Characteristic absorption in the visible region due to the individual transition-metal dopant transitions are clearly visible. (b) The extrapolated absorption edge in bulk $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ crystals with increasing doping level plotted as a function of wavelength and energy. The lines are intended as a guide for the eye.

These values are slightly different from those expected from the growth conditions due to the limitations of SIMS for quantization at alloying concentrations. Still, these results demonstrate the utility of this modified melt-growth technique in producing high-quality, uniformly alloyed, single crystals of ZnO.

The most prevalent feature about the individual transparent crystals of the transition-metal-doped ZnO is the distinct, brilliant color with varying transition-metal doping. The cobalt-doped samples show a striking green color, which deepens with increasing cobalt incorporation. Similarly, the Mn-doped samples possess a range of reddish colors, from a pale orange for the samples doped at <0.1% Mn to a deep red for the samples doped at closer to 5% alloying content. The UV-visible transition measurements taken from these samples confirm that these trends are attributed to interatomic transitions within the divalent transition-metal dopant atoms. Figure 3 shows the transmission results for the bulk crystals. The undoped ZnO crystal shows a sharp absorption edge at 391.4 nm (3.17 eV). The absorption edge shifts non-

linearly from 500 nm at 0.04% to 552.7 nm at 1% to 607.5 nm at 5% with increasing Mn concentration, as shown in Fig. 3. This absorption can be attributed to the overlapping $\text{Mn}^{2+} d^5$ crystal-field transitions from the ground state ${}^6A_1(S)$ to ${}^4T_1(G)$, ${}^4T_2(G)$, ${}^4A_1(G)$, and ${}^4E(G)$. These transitions have been seen in thin-film and bulk absorption and cathodoluminescence (CL) measurements.²⁰ The $\text{Zn}_{1-x}\text{Co}_x\text{O}$ sample also shows distinctive character with doping of the transition-metal element that differs from the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ due to the partially full nature of the d orbitals in the high-spin d^7 state. The Co-doped sample shows an absorption cutoff at 415.3 nm, near a CL peak in the previously grown ZnO and attributed to the ${}^6A_1(S) \rightarrow {}^4T_1(G)$ transition.⁵ Also prevalent are two absorption maxima centered at 605 and 655 nm, which are due to the $d-d$ transitions in the high-spin d^7 state of the Co^{2+} ions, as has been previously observed in thin-film samples as ${}^4A_2(F) \rightarrow {}^2E(G)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$.⁵ These two transitions lead to stronger absorption in the red at 605 and 655 nm, which when combined with the violet region absorption cutoff at 415 nm explains the deep green color in these samples.

The magnetic behavior of these materials is of critical importance for spintronic applications. Figure 4 shows the magnetization versus the temperature plot for the three samples of increasing Mn doping concentration (samples A, B, and C, respectively) taken at 100 K. Also included in these figures to give an estimate of the magnetization involved in the system are the lines indicating the expected magnetization behavior based on the diamagnetic volume susceptibility of ZnO, the paramagnetic susceptibility of MnO, and the noninteracting mixture of 99% ZnO–1% MnO. The 100-K temperature is above the most likely ferromagnetic oxide contaminant, the spinel Mn_3O_4 , which has a Curie temperature of 46 K. Linear, paramagnetic behavior is observed for samples B and C, due to the incorporation of the Mn atoms. In the most lightly doped sample A, the 100- and 300-K curves show a diamagnetic behavior, due to the nominally temperature-independent diamagnetic contribution from the ZnO becoming dominant over the smaller temperature-dependent paramagnetic Mn contribution. At 5 K, the most lightly doped sample shows a macroscopically diamagnetic behavior because of the $1/T$ dependence of the paramagnetic signal becoming a larger influence than the temperature-independent diamagnetic ZnO signal. In addition, no hysteresis is observed at 5 K, indicating the exclusion of any ferrimagnetic oxide second phase.

The inverse magnetic susceptibility of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ is shown at the lower half of Fig. 4. It is clear from this Curie–Weiss plot that a linear behavior is observed at elevated temperature. There is a slight deviation from linear behavior at low temperature due to the antiferromagnetic Mn–Mn exchange interactions. After performing the required correction²¹ for the diamagnetic background, the extrapolated intercept with the x axis gives a $\Theta = -33.6$ K. Assuming only nearest-neighbor interactions and Mn in the $5/2$ spin state and fitting to a Curie–Weiss-type function, the exchange integral can be calculated to be

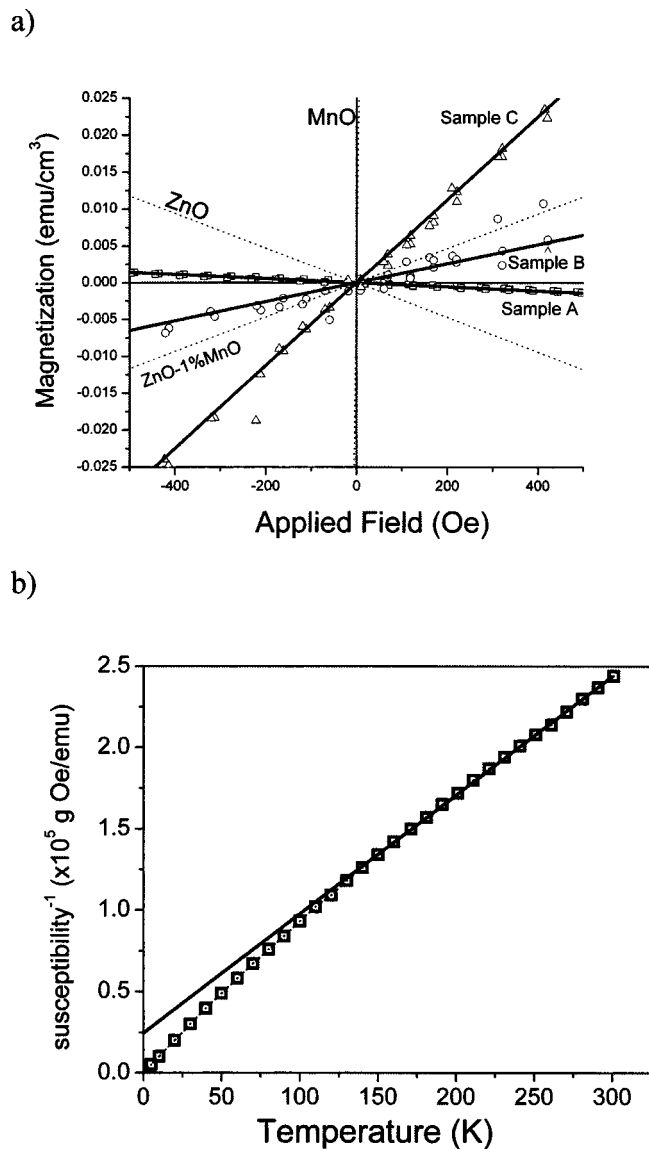


FIG. 4. (a) The top plot shows the 100-K magnetization plot for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ for samples A ($x=0.0004$), B ($x=.01$), and C ($x=.03$). No hysteresis is observed in the magnetization curves for any of these samples. The dotted lines show the expected behavior for ZnO, MnO, and a linear mixture of ZnO-1% MnO for comparison. (b) The bottom figure shows a Curie-Weiss plot of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ for sample C. A deviation from nominal paramagnetic behavior is observed at low temperatures. The extrapolated intercept of the linear high-temperature region is at $\Theta = -33.6$ K.

$$J_1 = \frac{3k_B\theta_0}{2z(S)(S+1)}.$$

The exchange integral J_1/k_B is calculated to be -17.2 K when using $z=12$ as the number of nearest neighbors in the wurtzite lattice and correcting for the atomic fraction of Mn. This calculated value is similar to the -15 K observed with Mn-Mn in heavily alloyed ($x=0.36$) $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ grown by pulsed laser deposition.¹⁵ The less pronounced deviation from linearity and smaller magnitude of the temperature intercept are indicative of the dilute nature of the Mn atoms, such that the average distance between Mn is large and fewer participate in the superexchange process. If the Mn atoms are distributed randomly on Zn sites, at this concentration, only one-sixth of the Mn atoms would have a single nearest-

neighbor Mn atom on an adjacent Zn site for a 1.5% doping level. For a randomly distributed alloy where all transition metals are on substitutional sites, the expectation value for nearest-neighbor occupancy is only $\langle z \rangle = 0.36$. For $x=0.36$, $\langle z \rangle$ is 4.32, which is 12 times that of the dilute case. Thus, the lower observed temperature intercept would be expected for the dilute case and is consistent in magnitude with the previously grown thin-film samples.

These results indicate that the dominant exchange mechanism is superexchange, which is consistent with samples grown by other high-temperature techniques and with other Mn-doped II-VI compounds.²¹ For comparison, the J_1/k_B for the other II-VI compounds are -13.7 and -11.8 K for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$.²¹ The larger exchange integral would be expected based on the reduced interatomic distances in ZnO relative to the other II-VI materials, which results in a stronger antiferromagnetic coupling among Mn atoms in nearest-neighbor sites.

The high-spin ($S=5/2$) Mn^{2+} spin state configuration is observed in other tetrahedrally coordinated Mn in II-VI semiconductors,²² and can be verified in ZnO using the Curie-Weiss law, $\chi = C/T - \Theta$. The Curie constant is related to the Bohr magnetons per Mn ion through the relation $C = p_{\text{eff}} \mu_B N_{\text{avo}} x / 3k_B$, where p_{eff} is the Bohr magneton number. From the calculation of the Curie constant, the estimated Bohr magneton number for Mn is $5.4 \mu_B/\text{Mn atom}$, which indicates that the Mn is in the high-spin state ($S=5/2$) as expected.

Ferromagnetism is not anticipated in either the mean-field or double-exchange model without an additional p -type doping in this system. There is no intentional carrier doping in these samples, although a background n -type electrical conductivity typical of ZnO has been confirmed through electrical property measurements. Photoluminescence in these samples exhibited a broad green band emission centered around 550 nm, which is typically attributed to intrinsic defect transitions in the doped material. The large doping levels, however, quenched any cathodoluminescence in these samples. These findings do not preclude double exchange at higher doping levels and/or indirect exchange becoming dominant in the presence of free carriers, which could lead to ferromagnetism in these samples. This will be investigated in due course.

The magnetic behavior of the cobalt-doped material is considerably different from that of in the Mn-doped crystals, as seen in Fig. 5. In this curve, clear evidence of hysteresis is observed in this loop for $\text{Zn}_{1-x}\text{Co}_x\text{O}$. The curve is reminiscent of uncorrected curves for thin-film DMS, where the diamagnetic contribution of the substrate is significantly larger than the film and is usually subtracted. In this case, there is no substrate contribution. The ZnO background does lead to a large diamagnetic contribution, but if the entire material consisted of a ferromagnetically coupled Co-based dilute magnetic semiconductor, the expected magnetization should be significantly larger than the $\sim 10^{-4}$ emu/g (less than $0.01 \mu_B/\text{Co}$) observed in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ crystal. The negative slope in the diamagnetic region is less than that anticipated from pure ZnO, indicating a paramagnetic contribution from the remaining cobalt atoms. A closer examination of the

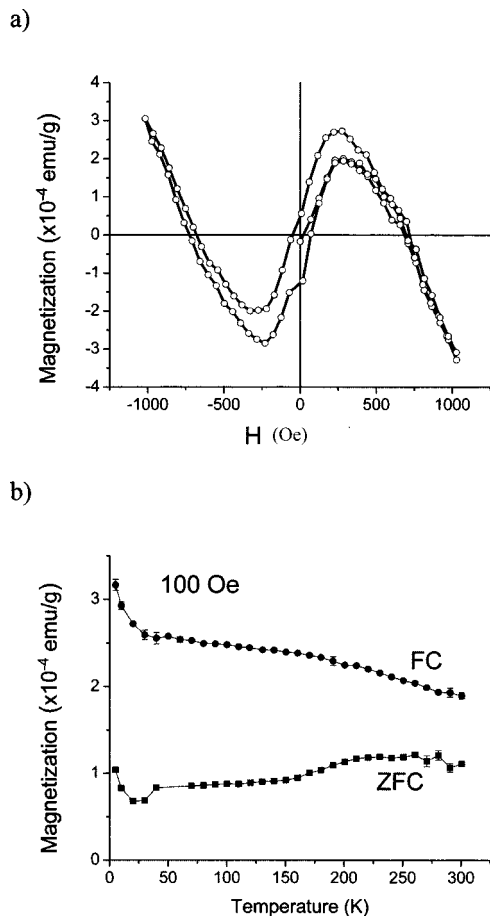


FIG. 5. (a) The top figure shows the room-temperature magnetization vs the applied field plot for a lightly doped $\text{Zn}_{1-x}\text{Co}_x\text{O}$ sample ($x=0.01$). Hysteresis is clearly evident in this curve at low fields, but it is quickly overwhelmed by the diamagnetic ZnO signal at even moderate fields (0.1 T). (b) The bottom diagram shows the difference in the field-cooled (FC) and zero-field-cooled (ZFC) magnetization vs the temperature plots taken at 100 Oe for the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x=0.01$) sample.

field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves in Fig. 5 taken at 100 Oe shows a superparamagnetic-cluster-type behavior of these two curves. The extrapolated slopes versus the temperature are of opposite signs in the ZFC and FC curves and there is a significant deviation in these two values. Similar behavior has been reported previously in suspended Co particles in ZnO ¹⁶ as well as MnAs nanoparticles in $(\text{Zn}_{1-x}\text{Mn}_x)_3\text{As}_2$.²³ Thus, the observed hysteresis is most likely due to nanoscale paramagnetic Co clusters below the blocking temperature or surface magnetic phases, with the remaining dissolved isolated Co^{2+} atoms providing a paramagnetic contribution. Though it is difficult to extract due to the masking effects of the Co clusters, it is reasonable to assume that the dominant exchange mechanism here is also antiferromagnetic superexchange, similar to that found above in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and that observed in $\text{Zn}_{1-x}\text{Co}_x\text{S}$ and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$.²⁴ These findings would also be consistent with the recent density-functional calculations for dilute, intrinsic $\text{Zn}_{1-x}\text{Co}_x\text{O}$.²⁵

DISCUSSION

Because of the complexity of this materials system, it is crucial for future devices to understand the materials system

beginning with the baseline noncodoped material. In this work, we see the utility of employing the bulk single crystals relative to thin films in understanding the fundamental material properties in the system. The transmission properties in this case are dominated by the crystal-field transitions of the transition-metal elements. The magnetic properties are dominated by the individual exchange elements of the transition metals. In the absence of strain confinement effects and itinerant carriers, this exchange is due to an antiferromagnetic coupling between adjacent transition-metal atoms. The macroscopic electronic properties are controlled by intrinsic defects within the ZnO lattice and are not present in sufficient quantities to produce carrier mediated ferromagnetism for nominally non-carrier-doped material.

Thus, in order to optimize these materials for ferromagnetic applications, it is worthwhile to consider ZnO as an extension of the Zn-VI series of DMS. For instance, ZnMnTe can become ferromagnetic through carrier introduction with *p*-type codoping.²⁶ In addition, strain effects in epilayers may play a crucial role in stabilizing ferromagnetism²⁷ in these structures and may lead to ferromagnetism in low-dimensional II-VI DMS.²⁸ Future efforts should focus on optimizing these properties in the II-VI systems while taking into account that the dominant exchange mechanism is antiferromagnetic superexchange and even in the near-equilibrium bulk growth case, clustering is possible and may lead to observed ferromagnetism not attributable to DMS behavior.

The elevated temperature growth process used in this study is close to equilibrium. In a substitutional alloy, near-equilibrium processes would be expected to yield random arrangement of atoms, provided there is no negative interaction energy from the coupling of adjacent transition-metal atoms. Ferromagnetic ZnO-based wide-band-gap DMS, however, have generally been produced using highly nonequilibrium techniques that promote abnormal transition-metal distributions. This is in contrast with the III-V DMS, where highly nonequilibrium conditions are required for growth to promote uniform dopant distribution and avoid clustering that leads to non-DMS related ferromagnetism. The assertion that random Mn and Co substituents in the ZnO lattice leads to ferromagnetism should be reevaluated, as the ferromagnetism may instead be configurational due to artifacts in the lower-temperature growth processes. This work demonstrates that the intrinsic, undoped $\text{Zn}_{1-x}\text{TM}_x\text{O}$ is not ferromagnetic, and that creative processing and doping techniques are necessary to achieve practical ferromagnetism in these materials.

CONCLUSIONS

High-quality single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ have been grown by a modified melt-growth technique. The crystals were single phase and of good structural quality as indicated by x-ray linewidth of less than 100 arc sec in the undoped samples, with slight increases upon transition-metal doping. The bulk optical properties are dominated by the Mn^{2+} and Co^{2+} cations in the d^5 and d^7 high-spin configurations, respectively, in a strong tetrahedral

field. The magnetic properties in this system are dominated by antiferromagnetic superexchange between nearest-neighbor transition elements, which is consistent with the behavior in the other II-IV dilute magnetic semiconductor systems. Though magnetic hysteresis is observed at room temperature in the Co-doped samples, this is likely due to a clustering mechanism and may not be useful directly in spintronic devices. Further work is needed in order to understand the effects leading to ferromagnetic behavior in thin films of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ so that they may be optimized for future device applications.

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