Antiferromagnetic Interactions in Single Crystalline $Zn_{1-x}Co_xO$ Thin Films

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In a rather contradictory situation regarding magnetic data on Co-doped ZnO, we have succeeded in fabricating high-quality single crystalline $Zn_{1-x}Co_xO$ ($x = 0.003$–0.07) thin films. This gives us the possibility, for the first time, to examine the *intrinsic* magnetic properties of ZnO:Co at a quantitative level and therefore to address several unsolved problems, the major one being the nature of the Co-Co interaction in the ZnO structure.

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Manipulating the spin of an electron rather than its charge opens fascinating new routes for information storage and processing. A quantum computer operating on electron-spin qubits is probably one of the most appealing challenges in the new field of research and applications known as spintronics [1]. With the use of inherently quantum-mechanical effects, much faster computation can be achieved, as compared to its classical counterpart. Another particularly striking example of this emerging spintronics technology is the giant magnetoresistive read head for hard disk drives, which gave rise to a 100-fold increase in hard disk capacity during the last decade [2]. All devices of this kind are currently made of multilayer *metallic* hetero- or tunneling structures; however, the successful realization of the spin manipulation in *semiconductor* structures would open up the way to numerous totally new fields of applications including quantum information processing [3]. This is why diluted magnetic semiconductors (DMS) have become a focus of considerable interest in recent years.

DMS of the II-VI group, have attracted much attention as essential materials for practical semiconductor spintronic devices such as spin filters [2] or spin polarizers [4]. In particular, the theoretical predictions based on the local spin density approximation (LSDA), triggered extensive studies of ZnO:TM alloys with a special focus on ZnO:Co as the most promising candidate for a room-temperature ferromagnetic (FM) semiconductor [5]. Many experiments have been reported on this material fabricated by a variety of methods [6–19]; however, the magnetic properties of ZnO:Co still remain a controversial issue since the observed magnetic behavior appears to be strongly dependent on the preparation methods and is poorly reproducible.

Ferromagnetism was reported for thin films and bulk samples of ZnO:Co with a very large spread of spontaneous magnetic moment from 6.1 μ_B/Co to 0.01 μ_B/Co accompanied by a Curie temperature well above room temperature [6–11]. At the same time and with the use of practically the same preparation methods, the absence of ferromagnetism and paramagnetic behavior down to helium temperatures in ZnO:Co were claimed by many authors [12–19]. Interestingly, these last results seem to be less process dependent and most of them indicate dominant *antiferromagnetic* (AFM) interactions between Co^{2+} ions (negative sign of θ in the Curie-Weiss law) while a positive sign of $\theta(x)$ was also observed at low Co concentration [18,19]. It is worth noting that numerous secondary phases, such as metallic Co [11,15], CoO [15], Co_3O_4 [18], and $ZnCo_2O_4$ [15], were found to occur in this material, which further complicates the interpretation of experimental data.

On the theoretical side, the situation with ZnO:Co is not better. There exists a certain consensus that LSDA has difficulties when applied to the magnetic state of TM-doped ZnO, since it does not account for correlations between d electrons and leads almost "automatically" to a semimetallic FM ground state. Quite surprisingly, an improved version of LSDA, LSDA + U, which is supposed to be free from these deficiencies, leads to controversial results as regards the exchange constant sign between Co^{2+} ions in ZnO. Indeed, in their recent paper, Chanier *et al.* [20] show that the exchange constants, J^{out} and J^{in}, between nearest-neighbor (NN) Co^{2+} ions in the ZnO wurtzite structure are both negative (AFM) and have the values -9 and -21 K, respectively. In contrast, Lee and Chang [21] and Sluiter *et al.* [22] have detected a competition between FM J^{out} and AFM J^{in} in Co-doped ZnO. Quite close to this result are those of Risbud *et al.* who found that the FM and AFM ground state in ZnO:Co have almost the same energy.

In this Letter, we report the magnetic measurements we performed on single crystalline $Zn_{1-x}Co_xO$ thin films. The use of single crystalline films allows us to circumvent many problems inherent to polycrystalline samples (secondary phases, imperfections, surface and structural defects, etc.) and, for the first time, to perform a thorough analysis of the *intrinsic* magnetic properties of ZnO:Co at a quantitative level, thereby addressing most of the questions raised above. We first demonstrate the absence of ferromagnetism in these compounds. Next, by comparing the

magnetization measurements with our cluster model, we conclude decisively about the NN exchange constants, which we find both to be antiferromagnetic in this material. We also show that these conclusions hold even under strong n doping.

$Zn_{1-x}Co_xO$ thin films (x varying from 0.003 up to 0.07) were grown on sapphire substrates by plasma-assisted molecular-beam epitaxy (MBE) and had thicknesses of about 1 μm, the c axis of the wurtzite structure being perpendicular to the film plane. The conductivity of the films was n type, with residual carrier concentrations $n_e < 10^{18}$ cm^{-3}. For some of them, the electron doping level ($n_e \geq 10^{20}$ cm^{-3}) was controlled by *in situ* gallium doping ($Zn_{1-x}Co_xO$: Ga). Two-dimensional growth was achieved for a growth temperature of 560 °C (i.e., 50 °C higher than the optimal growth temperature used for ZnO), resulting in streaky reflection high-energy electron diffraction patterns and very smooth surfaces (rms $\leq$ 1 nm). The full widths at half maximum of the x-ray rocking curves measured in high-resolution ω scan position, were in the range of $\omega \sim 0.15°$ along (002), (105), and (−105). The low, identical values of ω measured both for (105) and (−105), indicated a large column diameter, close to 1 μm. The full width at half maximum along (101), measured in skew position, was ~0.75° corresponding to a twist value of ±0.5°. While the column diameters remained large, ω values were found to increase slightly and gradually with the Co concentration.

Magnetic measurements were performed using a Quantum Design MPMS XL magnetometer in magnetic fields up to 50 kOe and in the temperature range 2–300 K. Typically, the observed magnetic moment was relatively small, 10^{-3}–10^{-4} emu and, therefore, special attention was paid to the subtraction of spurious contributions. A pure ZnO film on a sapphire substrate and a sample holder were examined separately and their signals were subsequently subtracted from the total magnetic moment. The Co content x of the studied samples was determined by energy dispersive x-ray (EDX) microanalysis and was found to be quite uniform as the average dispersion Δx was around 0.003, for a large number of scanned "spots" ($N \simeq 30$). For the lowest concentration ($x < 0.005$), the x value was determined by magnetic measurements. Additionally, low-temperature EPR in the X band was used to check that Co^{2+} ions occupy tetrahedral substitutional sites in the wurtzite structure and to ensure the absence of secondary magnetic phases [23].

In order to facilitate the ensuing discussion, we first present our theoretical model. The $^4A_2$ ground state of an isolated Co^{2+} at a tetrahedral site of the ZnO host lattice is described by an $S = 3/2$ spin Hamiltonian determined by only three constants [19,23,24]: the two g factors, $g_{\|} = 2.236$ and $g_{\perp} = 2.277$, and the zero-field splitting constant $D = 2.76$ cm^{-1}, which are used in this work as fixed parameters.

As the Co concentration is increased, the role played by Co-Co interactions becomes more important and a model which considers an ensemble of isolated Co^{2+} fails. The most straightforward way to account for these interactions is provided by the so called nearest-neighbor cluster model [25–27]. In this model only the largest NN exchange constants are included and all other exchange constants are set equal to zero. As was demonstrated with ZnO:Mn [27], two groups of NN's have to be distinguished in the ZnO lattice: six "*in plane*" NN's which are in the same ab plane as the central cation (the corresponding exchange constant labeled J^{in}) and six "*out of plane*" NN's which are coupled to the central cation by J^{out}.

Here, four cluster types are considered (singles, pairs, open triangles, and closed triangles). This allows a quite accurate calculation of the magnetic moment for Co concentrations up to 0.05 (where 90% of all Co^{2+} spins are counted).

The magnetization of a cluster of type α is obtained from the usual equation: $M_\alpha(H,T) = (\partial F_\alpha/\partial H)_T$, where F_α is the free energy of the cluster found by exact numerical diagonalization of its Hamiltonian, which contains a Heisenberg exchange interaction term, a single-ion anisotropy, and the Zeeman energy. The field and temperature dependent magnetization thus becomes $M(H,T) = \sum_\alpha P_\alpha(x) M_\alpha(H,T)/N_\alpha$, where $P_\alpha(x)$ is the probability [25] that a Co^{2+} ion belongs to a cluster of type α, and N_α is the number of Co^{2+} ions in this cluster.

We now turn to the results of our magnetic measurements. In Fig. 1 we show the temperature dependence of the inverse static magnetic susceptibility, $\chi^{-1}(T)$, measured at $H = 10$ kOe and $H \perp c$ for three samples. The film for $x = 0.074$ was codoped with Ga in order to reach the electron concentration $n_e \approx 10^{20}$ cm^{-3}, which was further confirmed by electrical measurements. We found, however, that the n doping does not substantially affect the magnetic properties of ZnO:Co films. A linear increase of

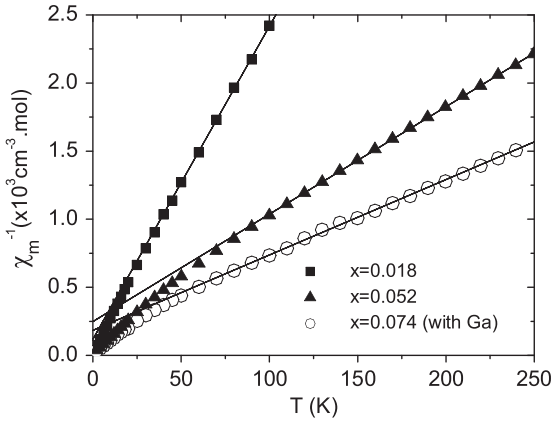

FIG. 1. Temperature dependence of the inverse magnetic susceptibility for $Zn_{1-x}Co_xO$ samples with $x = 0.018$, $x = 0.052$, and $x = 0.074$ taken at $H = 10$ kOe and $H \perp c$.

$\chi^{-1}(T)$ at higher temperatures was fitted to the Curie-Weiss law $\chi^{-1}(T) = [T - \theta(x)]/C(x)$. As a typical example, $\theta = -60 \pm 30$ K for $x = 0.074$ can be cited. An unusually large error bar arises mainly from the uncertainty in the background contribution because the ratio of the ZnO:Co signal to the background one is about $1/20$ at high temperatures. The situation becomes even worse at lower x rendering a proper determination of θ impossible. Therefore, we reach the conclusion that the accuracy of our measurements at high temperature is not sufficient to perform a quantitative analysis of the exchange interactions in $Zn_{1-x}Co_xO$ films. Moreover, it is quite clear that the value of θ cannot help much in obtaining NN exchange constants, since in $Zn_{1-x}Co_xO$ it also contains contributions from the single-ion anisotropy. As is shown below, the low-temperature magnetic measurements combined with the cluster model turn out to be much more informative from this point of view.

In Fig. 2 we show the magnetization of the $Zn_{1-x}Co_xO$ film with $x = 0.052$ as a function of magnetic field at $T = 2$ K. As expected from the results on weakly Co-doped ZnO films [23], the $M(H)$ curves reveal a considerable magnetic anisotropy of Co^{2+} in the wurtzite lattice (see the inset in Fig. 2). This could explain, at least in part, the difficulties in the interpretation of magnetic experiments on polycrystalline ZnO:Co samples when one uses a simple Brillouin function in order to fit $M(H)$ curves [12,17,18].

In order to probe the exchange interactions in ZnO:Co, we have compared the experimental data with the results of simulations performed using the following values for the NN exchange constants: $J^{in} = J^{out} = 0$, -5 K, -10 K and $J^{in} = -21$ K and $J^{out} = -9$ K, all other parameters being fixed. As seen from Fig. 2, a curve which corresponds to an ensemble of isolated Co^{2+} ions ($J^{in} = J^{out} = 0$) passes significantly higher as compared to the experimental data. A much better agreement is observed when one uses a negative and increasing value of J. The calculated $M(H)$ does not depend on J if both $|J^{in}|$ and $|J^{out}|$ exceed 10 K and remain negative. However, the closest curve to the experimental data still passes above the measured points.

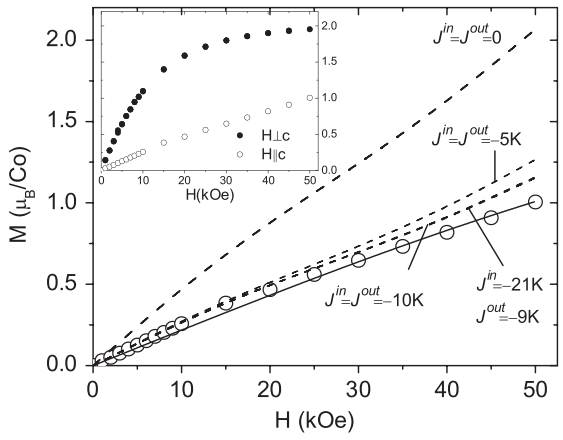

FIG. 2. M vs H plot for a $Zn_{1-x}Co_xO$ sample with $x = 0.052$ at $T = 2$ K and $H \parallel c$ (open circles). Dashed lines represent the calculated magnetization for $J^{out} = J^{in} = 0$, -5 K, -10 K, and $J^{out} = -9$ K, $J^{in} = -21$ K. The solid line is computed using $J^{out} = -9$ K, $J^{in} = -21$ K, and $T_0 = 3$ K. The inset shows $M(H)$ for both orientations, $H \parallel c$ and $H \perp c$.

Now we would like to improve our cluster model by taking into account weak exchange interactions between single Co^{2+} spins, which means that the effect of the distant-neighbor exchange interactions in the ZnO lattice must be considered in some way or another. To do this we shall use the effective-temperature approximation which corresponds physically to replacing the Curie susceptibility of noninteracting singles by the Curie-Weiss one, i.e., to replacing the actual temperature T by a higher effective temperature $T_{eff} = T + T_0$ [26,28]. Including this parameter in the model, a better match with the experimental data is obtained. The calculated curve for $T_0 = 3$ K and $J^{in} = -21$ K, $J^{out} = -9$ K is shown by the solid line in Fig. 2. Note that at low fields ($10 < H < 20$ kOe) there exists a small but reproducible "excess" of the experimental magnetization as compared with the calculated curve. We attribute this to particular magnetic states arising from weak interactions between distant neighbors.

Further evidence in favor of the existence of AFM Co-Co interactions in ZnO is provided by the $M(H)$ dependence on x. Figure 3 displays the experimental data for samples with $x = 0.003$, $x = 0.034$, and $x = 0.052$ taken at $T = 4$ K and $H \parallel c$, as well as the simulated curves. As above, the exchange constants were kept fixed at $J^{in} = -21$ K, $J^{out} = -9$ K, and T_0 was adjusted to obtain the best agreement. The slope of the $M(H)$ curves is seen to decrease continuously with increasing x, indicating that the magnetization per Co site decreases as the Co concentration is increased. This falloff in magnetization was earlier

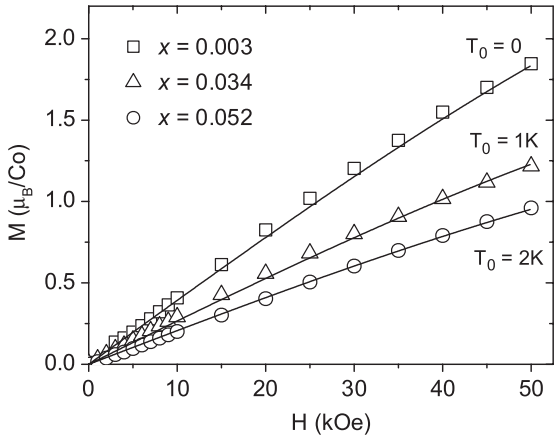

FIG. 3. M vs H plots for $Zn_{1-x}Co_xO$ films with $x = 0.003$ (squares), $x = 0.034$ (triangles) and $x = 0.052$ (circles) at $T = 4$ K and $H \parallel c$. Solid lines are calculations using $J^{in} = -21$ K and $J^{out} = -9$ K with T_0 as an adjustable parameter.

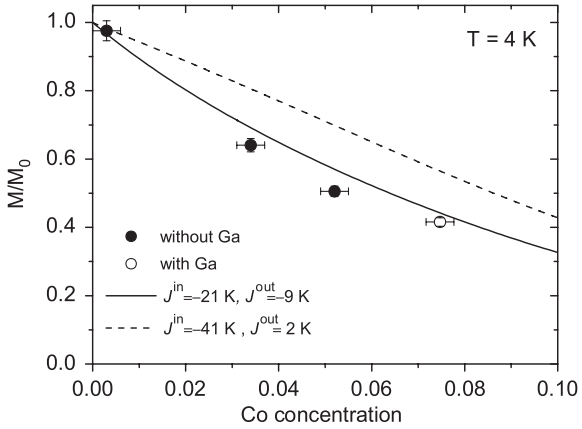

FIG. 4. Concentration dependence of magnetization measured at $T = 4$ K, $H \parallel c$ and $H = 50$ kOe for four $Zn_{1-x}Co_xO$ films with and without codoping with Ga. Solid and dashed lines correspond to the two scenarios discussed in the text.

observed in polycrystalline [12,14,16,18] ZnO:Co, where it was attributed to the formation of antiferromagnetic clusters of Co^{2+} ions. Note the increase of T_0 with the Co concentration, which is quite in line with the mean-field approximation [28,29].

We now return to the question regarding the sign of the exchange constants in ZnO:Co, namely, which of the theoretically suggested scenarios, (1) $J^{\text{in}} = -21$ K and $J^{\text{out}} = -9$ K according to Ref. [20], or (2) $J^{\text{in}} = -41$ K and $J^{\text{out}} = 2$ K according to Ref. [21], is realized in Co-doped ZnO? In fact we have already partly confirmed the former scenario, when analyzing the data in Fig. 2. Nevertheless, in order to render our analysis more convincing, we have plotted in Fig. 4 the observed magnetization at $H = 50$ kOe and $T = 4$ K divided by M_0, the calculated magnetization at $H = 50$ kOe, $T = 4$ K, and for $J^{\text{in}} = J^{\text{out}} = 0$, as a function of the Co concentration. The two scenarios are presented in Fig. 4, where the solid line corresponds to the first one and the dashed line represents the second [30]. Obviously, this is the case where both $J's$ are negative, which is realized in ZnO:Co. It is worth noting, once again, that, as follows from Fig. 4 and the above discussion, our ZnO:Co films which were codoped with Ga do not present any substantial difference in their magnetic behavior as compared with the Ga-free samples.

In summary, in a rather controversial situation regarding the magnetic data on Co-doped ZnO published so far in the literature, we have succeeded in preparing high-quality single crystalline $Zn_{1-x}Co_xO$ ($x = 0.003$–0.07) thin films grown by plasma-assisted MBE. We find that ZnO:Co is paramagnetic down to helium temperatures over the studied range of x. We focus then on the magnetization process at low temperature. In order to describe the reduction of the observed magnetization with increasing x, we have developed a phenomenological cluster model which is favorably compared with our experimental data. This has enabled us, by analyzing the concentration dependence of the ZnO:Co magnetization, to safely conclude about the NN exchange constants, J^{in} and J^{out}, which are found to be both antiferromagnetic and to exceed 10 K in this material. We also show that this conclusion holds even under strong n doping.

Clearly, the most interesting problem, which now remains open, is reproducible p doping and the way it affects the magnetic properties of Co-doped ZnO.

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[30] In fact, the dashed line also represents a set of J's suggested in [22], $J^{\text{in}} = -39$ K and $J^{\text{out}} = 30$ K.