# Superparamagnetic behavior of MOCVD grown ZnO:Co films

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**Abstract.** Temperature and field dependences of magnetization have been measured for Co-doped ZnO films with different Co content grown by MOCVD on sapphire substrates. Measured field dependences of magnetization show ferromagnetic-like hysteresis loops and paramagnetic contribution. Coercive field decreases with an increase of Co content and temperature. The difference between temperature dependences of magnetization measured in zero field cooling and field cooling conditions was observed in the temperature range from 2 K to 300 K indicating superparamagnetic behaviour of the films. The distribution of blocking temperatures extracted from the temperature dependences of magnetization is broad and shifts to the low blocking temperatures with an increase of Co content

## 1 Introduction

Due to their specific transport and magnetic properties diluted magnetic semiconductors such as ZnO doped with transition metal ions attract a considerable interest of scientific society. In particular ZnO and ZnO:Co materials reveal weak ferromagnetic-like behavior persisting up to room temperatures [1-2]. This behavior remains the subject of discussion until now due to irregular dependence of magnetic properties on preparation method and on concentration of cobalt [1-7]. This irregularity points to the significant role of paramagnetic defects in the magnetic properties of undoped and Co-doped ZnO.

In this work we present the results of the investigation of magnetic properties of ZnO thin films (180-590 nm) doped with Co (1.5-7.2 at%) grown by MOCVD on crystalline sapphire substrates.

## 2. Experimental

The method and conditions of films preparation were described in our previous work where the conducting properties of the films have been reported [8]. In brief the films were grown on single crystalline sapphire (R-$Al_2O_3$) substrates. Volatile β_diketonates of metals (anhydrous acetylacetonates $Zn(C_5H_7O_2)_2$ and $Co(C_5H_7O_2)_2$ were used as precursors in the MOCVD process. The deposition temperature was 600°C. The composition of the films and their thickness were determined by X-ray structural microanalysis. Thickness and Co-content of investigated films are listed in table 1.

According to X-ray diffraction data investigated films crystallize in the hexagonal wurtzite structure. No second phases were detected up to the maximal concentration of Co.

**Table 1.** Thickness and Co content in investigated films

| Film thickness, nm | Co content, at. % |
|---|---|
| 180 | 1.5 |
| 380 | 6.3 |
| 590 | 7.1 |

The preferred orientation of ZnO (110) is observed, but the X-ray diffraction patterns of the films contain additional reflections corresponding to other orientations of wurtzite ZnO. The number and intensity of these reflections increase with the cobalt concentration and film thickness.

Substitution of $Zn^{2+}$ by $Co^{2+}$ in wurtzite structure was confirmed by X-ray absorption spectroscopy (XAS) using synchrotron radiation (the synchrotron radiation center was BESSY II, RGBL, Berlin). However it does not completely eliminate a possibility of embedding the cobalt ions in octahedral interstices of the wurtzite structure, which is implicitly supported by the slight increase in the wurtzite lattice parameter observed upon an increase of the cobalt concentration [9].

Field and temperature dependences of magnetization were measured using Squid magnetometer VSM (Quantum Design, USA, Model: SVSM-050). Field dependences of magnetizations were recorded with a sweep rate 50 Oe/s. The temperature sweep rate was 4 K/min during the measurements of temperature dependences of magnetization.

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## 3. Results

Field dependences of magnetization measured for the film with 1.5 at. % and 6.3 at. % Co is shown in figures 1 and 2. Diamagnetic susceptibility of substrates was determined from the slope of magnetization dependence on magnetic field at 300 K in magnetic fields above 8 kOe. Then diamagnetic contribution to the magnetization was subtracted from measured magnetization. Magnetization of the films was calculated per formula unit (ZnO)

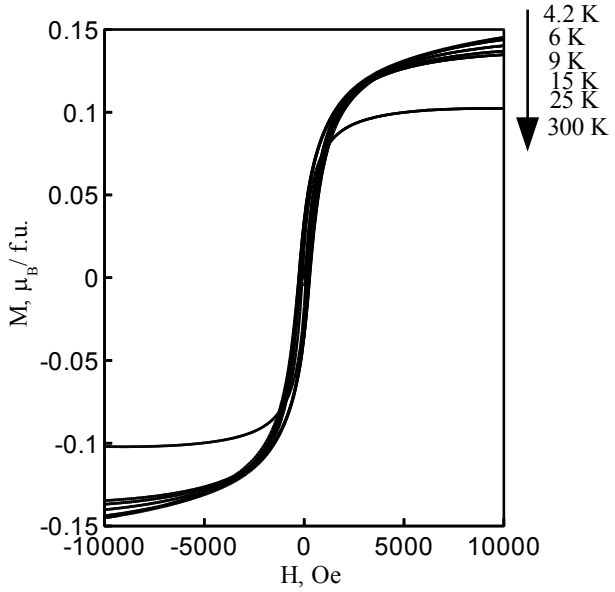


**Fig. 1.** Magnetization vs. magnetic field for the film with 1.5 at. % Co content

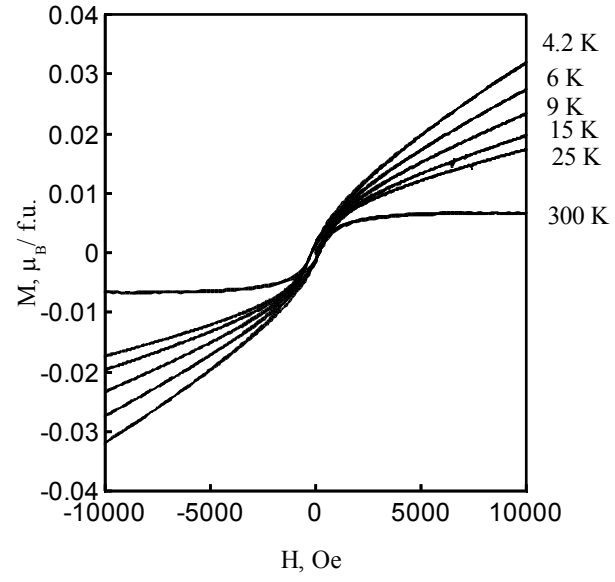


**Fig. 2.** Magnetization vs. magnetic field for the film with 6.3 at. % Co content

For all films clearly seen hysteresis loop is observed in the temperature range from 4.2 to 300 K. The coercive field decreases with an increase Co concentration. The magnitude of the hysteresis loop is significantly larger for the film with at. 1.5 % Co content than for the films with 6.3 at. % and 7.1 at. % Co.

At temperatures below 25 K magnetization increases nearly linearly with an increase of applied field in magnetic fields from 6 kOe to 10 kOe for the films with 6.3 at % Co and 7.1 at % Co, correspondingly. In this fields and temperature range hysteresis was not observed for these films. For the film with 1.5 at. % Co field dependences of magnetization are close to linear in magnetic field from 8 kOe to 10 kOe.

Temperature dependences of magnetization measured in magnetic field 200 Oe are shown in figures 3 and 4.

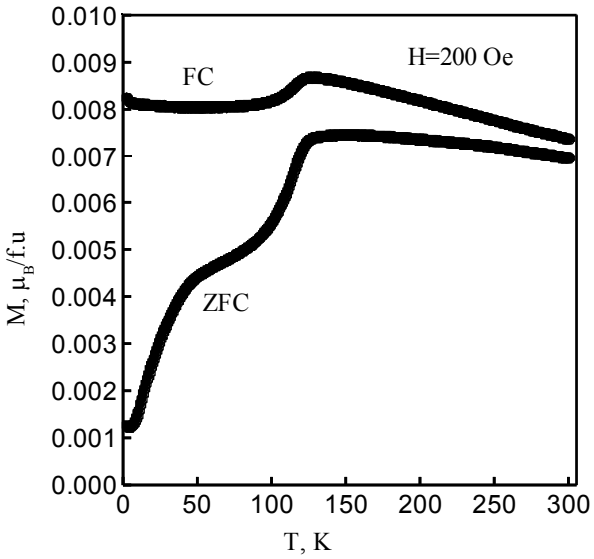


**Fig. 3.** Magnetization vs. temperature for the film with 1.5 at. % Co content

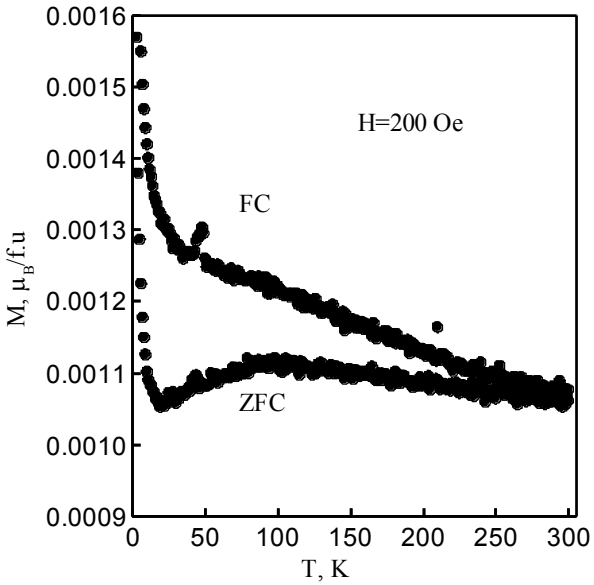


**Fig. 4.** Magnetization vs. temperature for the film with 6.3 at. % Co content

The temperature dependencies of magnetization measured in zero field cooling (ZFC) and filed cooling (FC) regimes differs for all investigated films at temperatures up to 300 K. The most pronounced difference was observed for the film with 1.5 at. % cobalt.

## 4. Discussion

Saturation magnetization at 300 K for the film with 1.5 at. % Co content significantly exceeds the maximum possible saturation magnetization originating from $Co^{2+}$ ions. Thus observed hysteresis loop for this film should at least partially originate from paramagnetic defects present in ZnO. This is consistent with the observation of ferromagnetic-like hysteresis loops in MOCVD grown on $MgAlO_2$ substrates undoped ZnO films [10]. For the films with 6.3 % and 7.1 % Co content saturation magnetization measured at 300 K is several times smaller than for the film with 1.5 % Co and than the maximum saturation magnetization of$Co^{2+}$ ions This suggests that Co impurity affects paramagnetic defects in ZnO.

The observation of hysteresis loops and the difference between magnetization values measured in ZFC and FC conditions points to the super paramagnetic contribution to the magnetization [11-13]. The properties of superparamagnetic materials are essentially determined by blocking temperature $T_B$. This temperature is directly related to the activation energy of the reorientation of magnetic moments of magnetically ordered nanoparticles or nanoclusters. Typically different nanoclusters have different blocking temperature. The following expression was derived for the calculation of blocking temperature distribution $p(T_B)$ from the temperature dependence of magnetization [12,13]:

$$p(T_B) = k\left[\frac{1}{T_B}\frac{d}{dT}\left(M_{ZFC}(T) - M_{FC}(T)\right)\right]_{T=T_B}$$

where $k$ is the temperature independent coefficient, $M_{ZFC}(T)$, $M_{FC}(T)$ is the magnetization measured in ZFC and FC conditions correspondingly.

In figure 5 we plot the derivative of the difference between $M_{ZFC}(T)$ and $M_{FC}(T)$ divided by temperature as a function of temperature. For the film with 1.5 at. % Co content two maxima at 8 K and 110 K are clearly seen in figure 5. For the films with 6.3 at. % Co and at. 7.1 % Co the distribution of blocking temperatures is shifted to lower temperatures. No maxima of $p(T_B)$ can be seen for these films in the temperature range from 2 K to 300 K. The two maxima in the distribution of blocking temperature for the sample with at. 1.5 % Co content may indicate the presence of two different types of magnetic clusters in this film. The peculiarity near 100 K in the temperature dependences of magnetization is seen for both FC and ZFC measurement condition. Therefore it can be manifestation of intrinsic transition within magnetic clusters. For instance charge state of defects responsible for magnetism can vary with temperature due to thermal activation of electrons to the states with higher energy. The strong reduction of electrical conductivity with an increase of Co content was reported earlier for these films [8]. This typically means the change of Fermi level position and charge state of defects and thus their magnetic properties. According to X-ray diffraction data the structure of the investigated films changes significantly with an increase of Co content. Therefore concentration of paramagnetic defects in the films should vary significantly even with small variation of cobalt concentration. This can explain disappearance of the clusters with long blocking time in the samples with high cobalt concentration. Additionally interaction between $Co^{2+}$ ions and paramagnetic defects can decrease blocking temperature.

The variation of coercive field $H_c$ with temperature is shown in figure 6. The coercive field decreases with an increase of temperature for all films at temperatures above 15 K. For the films with 6.3 at. % and 7.1 at % of Co maximum in $H_c(T)$ dependence is observed below 15 K. This maximum most probably originates from linear paramagnetic contribution to the field dependence of magnetization.

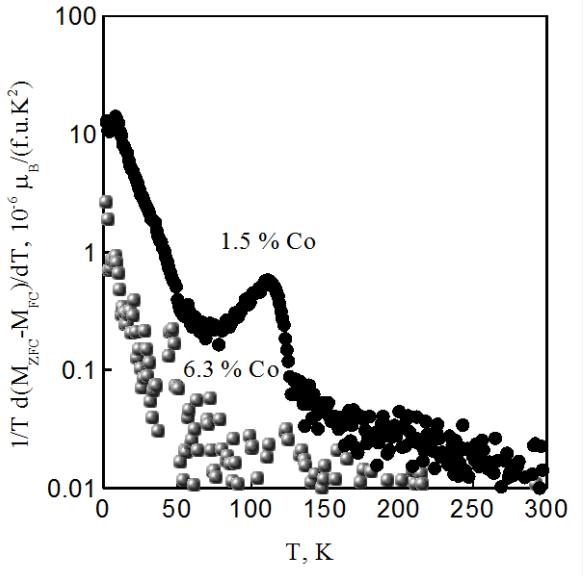


**Fig. 5.** Blocking temperature distribution ($1/Td/dT(M_{ZFC}$-$M_{FC})$) for the films with 1.5 % and 6.3 % Co

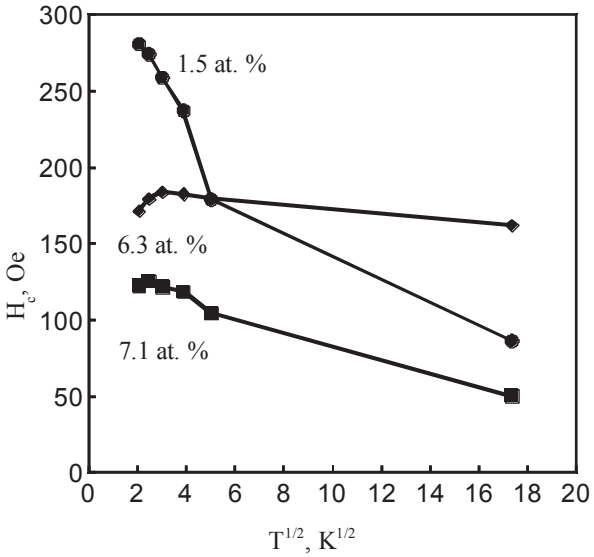


**Fig. 6.** Temperature dependence of coercive force for investigated films.

For ensemble of non-interacting magnetic nanoparticles coercive field decreases with temperature increase as square root approaching zero value at blocking temperature [13,14]. For investigated films coercive field decreases with temperature slower than it would be expected for distribution of blocking times (fig. 5). In particular a finite value of coercive field was obtained for all investigated films at 300 K. At this temperature the difference between magnetization measured in ZFC and FC conditions is zero within the accuracy of the measurements for the films with 6.3 at % and 7.1 at. % of cobalt concentration. Therefore ferromagnetic contribution can present in the measured magnetization especially in the films with high cobalt concentration.

In figure 7 the inverse magnetic susceptibility $(dM/dH)^{-1}$ calculated for field dependence of magnetization in magnetic field 10 kOe.

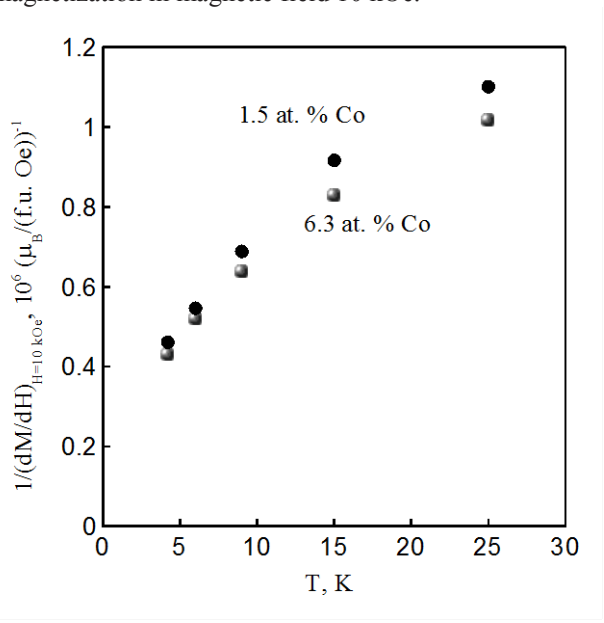


**Fig. 7.** Temperature dependence of the inverse magnetic susceptibility $(dM/dH)^{-1}$ calculated from the field dependence of magnetization in magnetic field 10 kOe.

At temperatures from 4,2 K to 15 K the dependence is close to linear. The corresponding straight line crosses temperature axis at -5.5 K for the film with 1.5 at % Co and – 5.9 K for the film with 6.3 at. % Co. The deviation from linear dependence at higher temperatures can originate from the rest of diamagnetic contribution. The magnitude of susceptibility calculated at 10 kOe is larger for the films with 6.3 at % Co and 7.1 at % Co than for the film with 1.5 at. % Co. However the difference is not proportional to the cobalt concentration. Therefore we associate the susceptibility at 10 kOe with the paramagnetic contribution to the magnetization then this paramagnetic contribution cannot be directly explained by the presence of additional $Co^{2+}$ ions. Defect states in ZnO should also contribute to the paramagnetic properties of investigated films.

## 5. Summary

The analysis of field and temperature dependence of the magnetization of investigated films shows that measured magnetization contains superpamagnetic, paramagnetic and probably ferromagnetic contributions.

Defects of ZnO structure play significant role in magnetic properties of investigated films especially for the film with 1.5 at. % of Co content. These defects contribute to paramagnetic and superparamagnetic properties of investigated films.

Cobalt impurity affects the magnetic properties of the films essentially indirectly by variation of the defects concentration and charge state and probably by interaction of $Co^{2+}$ ions with defect states.

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