1. ZnO – based solid solutions

1.1. ZnO as matrix of diluted magnetic semiconductor

Although magnetic semiconductors have long been known [1], the manufacturing of a semiconductor-ferromagnetic hybrid [2] with a Curie temperature $T_C$ (the paramagnetic transition temperature) higher than 400-450 K remains a challenge. Zinc oxide - the semiconductor-piezoelectric with wide band gap 3.3 eV and high excitation binding energy of 60 meV - has attracted special attention as matrix for obtaining the high $T_C$ ferromagnetic DMS - diluted magnetic semiconductor materials. Firstly Dietl et al. [3] proposed that
$\text{ZnO}$-based solid solutions with wurtzite structure and $p$-type conductivity could exhibit ferromagnetism above room temperature upon doping with transition elements (on the order 5% or more), than after short time Sato et al. [4] predicted that ferromagnetic state could be organized in $n$-type $\text{ZnO}$-matrix by Fe, Co and Ni-ions. However, only solubility of $\text{Co}^{3+}$ in $\text{ZnO}$ is significant and many experimenters [5] had analyzed $\text{Zn}_{1-x}\text{Co}_x\text{O}$-materials from viewpoint of practical applications in spintronic devices. But the contradictory date was obtained for $\text{Zn}_{1-x}\text{Co}_x\text{O}$: ferro-, antiferro-, paramagnetic and spin-glass behavior at room temperature.

1.2. **Phase equilibria in the $\text{Zn} – \text{Co} – \text{O}$ system**

We have changed the common approach to $\text{Zn}_{1-x}\text{Co}_x\text{O}$. The consideration within framework of binary system $\text{ZnO} – \text{CoO}$ [5] is non-sufficient approximation for these solid solutions and the concentration diagram of ternary system $\text{Zn} – \text{Co} – \text{O}$ was drawn using our data and literature data (Figure 1). It was exhibited that crystal solutions based on $\text{ZnO}$, $\text{CoO}$ and $\text{Co}_3\text{O}_4$ possesses different oxygen nonstoichiometry at fixed $\text{Zn}/\text{Co}$ ratio.

Powder X-ray diffraction shows that the $\text{CoO}$ solubility in wurtzite $\text{ZnO}$ reaches 20 mol %; the boundary compositions of the solid solution vary with temperature. The solubility of cobalt oxides in $\text{ZnO}$ is noticeable above 1173 K; at 1173 K, homogeneous samples of nominal composition $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}_{1+\delta}$ are

![Figure 1. Concentration phase diagram for the $\text{Zn} – \text{Co} – \text{O}$ system.](image)
obtained; at 1273 K, of nominal composition $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}_{1+\delta}$; and at 1373 K, $\text{Zn}_{0.8}\text{Co}_{0.2}\text{O}_{1+\delta}$.

The oxygen content $1+\delta$ has an influence on spintronic properties of homogeneous $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$ and depends from partial oxygen pressure during the synthesis, annealing and cooling. It was shown that $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$ solid solutions with different composition participate in four monovariant equilibria with oxygen. For the first time the metastable clusterization in $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$ with wurtzite structure was found.

It is known that the oxygen concentration in CoO- and $\text{Co}_2\text{O}_3$ -based crystalline phases, which is dictated by the partial oxygen pressure, varies within several atomic percents and to a great extent determines the electrophysical properties of cobalt oxides. If we ignore the possibility of mutual clustering of solid solutions of the Zn-Co-O system and if we consider homogeneous materials only, the oxygen nonstoichiometry can noticeably affect the semiconductor and magnetic parameters of three-component crystals.

1.3. Magnetic ordering in $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$

It is yet impossible to control the properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$ through setting $\delta$. We chose another factor of influence, namely, doping one more magnetic ion into the wurtzite structure of $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$. Because iron and nickel do not substitute for even 1% zinc in this solid solution, we chose lanthanide oxides for a systemic investigation. The antiferromagnetic ordering in $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$ with wurtzite structure is very stable and keeps after partial substitution Zn$^{2+}$ by Pr, Nd, Sm and Eu ferromagnetic ions in $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}_{1+\delta}$ solid solution up to composition $\text{Zn}_{0.8}\text{Co}_{0.1}\text{Eu}_{0.03}\text{O}_{1+\delta}$.

Ponderomotive force measurements (Figure 2) and $\mu$SR techniques indicate three magnetic transitions: ferro – antiferro I ($T_c < 10$ K), antiferro I – antiferro II ($T_{\text{tr}} \sim 100$ K) and antiferro II – paramagnetic ($T_N \sim 625$ K). The conductivity and dielectric constant via temperature measurements have achieved the break-out near 650 K.

The anomalies observed on the $1/\chi = f(T)$ and $\sigma = f(T)$ curves in the range of the temperatures studied may indicate that not only the magnetic order but also the crystal structure changes.

A likely explanation is the ability of ZnO to form metastable polymorphs with sphalerite (zinc blende) or NaCl structures. Lanthanide doping confirmed the possibility of crystal disorder in $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$. In spite of the fact that different research groups reported about ferromagnetism [5], we detected the antiferromagnetic ordering at room temperature for homogeneous crystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}_{1+\delta}$. 
Our suggestions based on experimental data show that homogeneous Zn$_{1-x}$Co$_x$O$_{1+x/2}$ exhibit antiferromagnetic behavior, whereas inhomogeneous materials from the system Zn – Co – O with Co clusters might be the source of the room-temperature ferromagnetism.

Figure 2. Reverse magnetization vs. temperature curve for a sample with the nominal composition Zn$_{0.95}$Co$_{0.05}$O$_{1+x/2}$

References