INTRODUCTION

New functional material — diluted magnetic semiconductor (DMS) with the ferromagnetic transition temperature (Curie temperature: $T_C$) around 300K is the very desirable result for modern spintronics, optoelectronic and high-power electronic devices. It is important to understand the origin and nature of the ferromagnetism in DMS for successful synthesis of high-$T_C$ ferromagnetic DMSs. K.Sato et. al. [1] discuss zink oxide, as a promising material for semiconductors, doped with transitional metal (TM), which have high-$T_C$ and whose magnetic properties are controllable by changing carrier density. Ferromagnetic state of ZnO-based DMS might be described as ($Zn_{1-x}$, TM$_x$,O), in which the magnetic moments of all TM atoms are parallel and the system has a finite magnetization, where x is concentration of TM. The authors experimentally confirmed that high-$T_C$ are released in ZnO-based DMSs doped with V, Cr, Fe, Co or Ni. The stability of ferromagnetic state varies with the concentration of magnetic ion. So it is very important to investigate the magnetic properties with different concentrations of TM. According to the M. Mustaqima [2] Mn- and Co-doping ions in the ZnO matrix are usually the most promising systems for the fabrication of spintronic devices mainly because of their rich electron states and large substitutability of Zn in the lattice. Magnetic behavior of DMS strongly depends on concentration of dopand, spatial distribution of transitional metal in a crystal lattice and surface defects [2]. Many reports of ferromagnetism in the nanostructures of zinc oxide and thin films can be found in review articles [1, 2]. This paper is focused on nanoparticles because additional effects related to the high surface-to-volume ratio appear, making the ferromagnetic effects more complex but more interesting in nanoscale dimensions. Even pure zinc oxide has ferromagnetic state caused by deformations. There are some announcements about ferromagnetic state even in pure ZnO which are correlated with the experimental results presented in this paper. M. Mustaqima et.al [2] connects this ferromagnetic behavior to the surface defects. A few authors discussed ferromagnetism of un-doped ZnO in their papers [3-6]. Xu Zuo et al., using ab initio calculation based on density functional theory, showed that ferromagnetism in undoped ZnO is caused by oxygen interstitial and zinc vacancy. According to Ning Shuai [8] et al. room temperature ferromagnetism (RTFM) in pure ZnO originates from the intrinsic point defects such as oxygen vacancy ($V_{O}$), oxygen interstitial ($O_{i}$), zinc vacancy ($V_{Zn}$), and zinc interstitial ($Z_{al}$). Experimental conformation of RTFM in ZnO nanoparticles was reported by A. Sundaresan et.al [3].

Due to the large number of publications, it’s impossible to provide a full overview of this topic. This paper is focused on description of experimental obtaining of magnetization of pure,
of doped (meaning crystal lattice is doped with the one TM ion) and of co-doped (meaning crystal lattice is doped with the two TM ions) ZnO NPs with Co$^{2+}$ and Mn$^{2+}$. The ZnO NPs synthesised by microwave solvothermal syntheses were chosen for investigation because this method allow obtaining high quality nanocrystalline samples [8] and controlling the uniform size distribution [9-11], which is crucial for surface defects.

**Experimental**

The magnetisation was measured with the help of superconducting quantum interface device (SQUID) magnetometer. SQUID-type magnetometer, manufactured by Quantum Design, uses liquid helium cooled MPMS XL device, provides the sensitivity of 10−8 emu in the temperature range 2–300 K. Applied magnetic field, up to seven tesla value, was parallel to the surface of the samples at room-temperature.

All samples, namely ZnO, Zn$_{1-x}$Mn$_x$O$_2$, Zn$_{1-x}$Co$_x$O$_2$, Zn$_{1-x}$Mn$_x$O$_3$, Zn$_{1-x}$Co$_x$O$_3$, were obtained by microwave solvothermal synthesis and characterised with the use of the X-ray diffraction method, scanning electron microscopy, the parameters of the crystalline lattice, $a$ and $c$, were determined by the Rietveld method and reported in [7]. Specific surface area, the average particle size and density were investigated too. Chemical composition of the samples was obtained by inductively coupled plasma optical emission spectrometry (ICP-OES). The quantitative microanalysis of the Zn, Mn and Co content in the pressed NPs samples was performed using energy-dispersive spectrometry (EDS).

To eliminate unintentional metal contaminations the samples were carefully kept away from any magnetic materials during all the sample preparation process.

**RESULTS AND DISCUSSION**

The purity investigations and detail characterization of the samples like morphology, phase purity, lattice parameters, dopants content, skeleton density, specific surface area, average particle size, average crystallite size, crystallite size distribution are reported in [7]. The absence of the additional peaks in x-ray measurements indicates that ZnO NPs are free from any contaminations. Even more, ICP-OES and the quantitative microanalysis didn’t register any secondary phases.

Pure ZnO is diamagnetic oxide showing $d^0$ – magnetism. The rise of experimental confirmation [3],[6],[12] of ferromagnetism in pure zinc oxide forces theorists to develop theories for explaining the nature of this effect. From the first point of view it might be seen that undoped ZnO is diamagnetic. The straight line of magnetization, decreasing with the field increasing, is presented on the Fig.1. Magnetization measured at 2 K (blue spots) take place a little bit higher than magnetization measured at 300K. Magnetization symmetrically reflects with the reorientation of the magnetic field. Everything takes place according to quantum theory of magnetism except “s-shape shift” around 0 shown in the Fig.2a. Room temperature ferromagnetic effect, that is called “s-shape shift” in this paper, takes place even for undoped and low (less than 5%) doped nanoparticles. The distance between two lines $S = 0.0019$ emu/mg is estimated using Matlab with the “polyfit” function. The value of this “s-shape shift” is unique for every sample measured at given temperature and presented in the Table 1. The sample Zn$_{0.98}$Mn$_{0.01}$Co$_{0.01}$O has ferromagnetic “s-shape” behaviour in low magnetic field, measured at 300K but diamagnetic with the increasing of the field (Fig. 2b). The rest of all other two ions doped samples are paramagnetic at both temperatures in the range above 1 Tesla (Fig.4).

As it was mentioned in introduction Ning Shuai [12] et al. connect the room temperature ferromagnetism (RTF), in the thin ZnO films, with the intrinsic point defects like oxygen vacancy ($V_O$), oxygen interstitial ($O_I$), zinc vacancy ($V_Zn$), and zinc interstitial ($Zn_I$). Which kind of defect is responsible for the room temperature ferromagnetism (“s-shape shift” $S=0.0011$ - Table 1) in our sample is still an open question. It is well known fact, that oxygen vacancies have different electron states, such as $V_O$, $V_O^{+}$, and $V_O^{2+}$. Ning Shuai et. al evaluate the numbers of $V_O^{+}$ vacancies by EPR measurements indicating that $V_O$ and $V_O^{2+}$ have no net spin magnetic moments and cannot make any contribution to the ferromagnetism.

---

**Fig 1** The magnetization of undoped ZnO measured at 2K - blue dots and 300K - green dots as a function of magnetic field.

**Fig 2** The magnetization as a function of magnetic field a) undoped ZnO NPs measured at 2K, that are shown at fig1 but with increased scale. b) “s-shape shift” in the sample Zn$_{0.98}$Mn$_{0.01}$Co$_{0.01}$O at room temperature.

The magnetisation as a function of magnetic field is presented for 2K of undoped ZnO (at Fig.2a) because the shift is bigger than for 300K. The shift of the line around 0 is clearly seen at Fig2a. The shift of line does not look like “s-shape shift”, but it takes place even for 300K of undoped ZnO and evaluated by “polyfit” function of Matlab software, with the values $S_{300K}=0.0011$ and $S_{2K}=0.0019$, like for all others doped ZnO nanoparticles. A neglecting small value of $S_{300K}$: $S_{2K}$ confirm the purity and good crystalline structure of pure ZnO nanoparticles synthesized by solvothermal method [7 - 11].

The contamination of magnetic impurities is ruled out by X-ray diffraction (XRD) and argon inductively coupled plasma optical emission spectrometry (ICP-OES) methods [7]. Taking in account the authors studies [12] about ZnO thin films it might be assumed that oxygen vacancies $V_O^{+}$ are responsible...
for the low field (less one Tesla) ferromagnetic effect of undoped ZnO nanoparticles Fig2a. Since Xu Zuo et.al [5] explain the total magnetic moment of pure ZnO using ab initio calculation given by the supercell approach. They suggest that both oxygen interstitial \( I_0 \) and zinc interstitial \( V_Zn \) may induce ferromagnetism in pure wurtzite structure ZnO. According to Xu Zuo et.al, ZnO with oxygen interstitial is a ferromagnetic semiconductor implying equality of the integrals corresponding to the dominant ferromagnetic and antiferromagnetic superexchanges. While ZnO with \( V_Zn \) is a ferromagnetic metal.

The main goal of this paper is to describe the magnetization of ZnO nanoparticles applying different analytical techniques. Present the same measurement with different properties even of the measuring rate. Furthermore, it is possible to discuss the nature and stability of the state of the system, one crucial fact is missing. The same material can be described like superparamagnetic, ferromagnetic or ferrimagnetic depending on the type of measuring technique or even of the measuring rate. Furthermore, it is possible to present the same measurement with different properties applying different analytical techniques.

The most complicated magnetic behavior has material where one lattice is doped with two Co and Mn ions (Fig.4). \( Zn_{x_1}Mn_{x_2}Co_{y}O \) samples show “S shape shift” at the field below 1 Tesla in room temperatures, even 1% Co+1%Mn material which is diamagnetic (Fig.4a). 5%, 10% and 15% doped ZnO nanoparticles perform nonsaturation over 1T indicating superparamagnetic behavior at room temperatures. Paramagnetic contribution in 2K is so strong that magnetization increases rapidly showing nonsaturation (Fig.4b). The temperature dependence of \( Zn_{x_1}Mn_{x_2}Co_{y}O \) where \( x=15, y=15 \) (Fig.4c) and \( Zn_{x_1}Co_{y}O \) (Fig3d) where \( x=15, \) perform hysteresis, while other samples do not (Fig.3c).

Table 1 The value of the ferromagnetic effect – “s- shape shift” deepening on chemical composition of the ZnO, \( Zn_{1-x}Mn_xO \), Zn\( _{1-x}Co_yO \) \( Zn_{1-x}Mn_yCo_{2-y}O \) samples.

<table>
<thead>
<tr>
<th>Nominal values</th>
<th>Actual values</th>
<th>The height of S at 300K emu/g</th>
<th>The height of S at 2 K emu/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ZnO )</td>
<td>0.0011</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Mn_{0.2}O )</td>
<td>0.0046</td>
<td>0.0755</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Co_{0.2}O )</td>
<td>0.92234</td>
<td>0.0551</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Mn_{0.2}O )</td>
<td>5.674e-04</td>
<td>0.3409</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Co_{0.2}O )</td>
<td>2.7247</td>
<td>3.2862</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Mn_{0.2}O )</td>
<td>0.0602</td>
<td>0.1190</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Co_{0.2}O )</td>
<td>0.0043</td>
<td>0.3787</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Mn_{0.2}O )</td>
<td>0.3094</td>
<td>0.9767</td>
<td></td>
</tr>
<tr>
<td>( Zn_{0.8}Co_{0.2}O )</td>
<td>0.9244</td>
<td>1.2459</td>
<td></td>
</tr>
</tbody>
</table>

In a huge amount of modern articles, where chemists describe the dependence of magnetic properties on the type of synthesis, and theorists discuss the nature and stability of the state of the system, one crucial fact is missing. The same material can be described like superparamagnetic, ferromagnetic or ferrimagnetic depending on the type of measuring technique or even of the measuring rate. Furthermore, it is possible to present the same measurement with different properties applying different analytical techniques.

The height of shape shift” at the field below 1 Tesla on temperatures is diamagnetic. 15% Mn doped sample is paramagnetic at 2K with a small value of the “s-shape shift” \( S=0.0755 \), but diamagnetic contribution increases with the magnetic field over than 4 T (Fig.3a). Only 15% Mn doped sample has a paramagnetic behaviour, but with “s-shape shift” less than one: \( S=0.3409 \). While nanoparticles doped with Co ion have more complicated magnetic behaviour, because of higher substitution of Zn in the lattice (Fig.3b).

All \( Zn_{1-x}Co_{y}O \) samples have higher value of \( S \) in respective temperatures even for \( x=1 \) sample, which is diamagnetic at 300K. While 1% of Co doped sample at 2 K and 15% of Co at 300 K shows paramagnetism with the saturation over 1 T, the magnetisation with 15% of Co additive do not saturate at 2K.
magnetic ions incorporated into ZnO lattice. The total magnetic moment of each sample, measured by SQUID, consist of paramagnetic moment of the Co\(^{3+}\) (or/and Mn\(^{2+}\)) ion, contribution of ferromagnetic/ferrimagnetic (or superparamagnetic) phase and diamagnetic contribution. According to the mean field approximation theory the obtained magnetization of doped nanoparticles \(M(B,T)\) is the sum:
\[
M(B,T)=M(Zn,Co/Mn)O(B,T)+\chi_D(B,T)+C.
\]
(1)

Where \(M(Zn,Co/Mn)O(B,T)\) is the paramagnetic contributions of localised magnetic moments of Mn\(^{2+}\) or/and Co\(^{3+}\) ions, \(\chi_D\) is the diamagnetic contribution (of the ZnO lattice, parafilm, glue, plastic tube) and \(C\) is the ferromagnetic/ferrimagnetic contribution. Constant \(C\) of experimental results, presented in this paper, cannot be connected to the impurities of the components used during the synthesis because purity investigations obtained by XRD and ICP-OES methods didn’t register any foreign phase. Paramagnetic contributions of localised magnetic moments of ZnO nanoparticles doped with one ion (Mn\(^{2+}\) or/and Co\(^{3+}\)) could be presented with the next equation: \(M_{Zn,Co/Mn}O(B,T)\)=\(N\mu g S^*B(B,T)\), where \(B(\mu g S^*B\) is the Brillouin function with the spin \(S=5/2\) for Mn (or \(S=3/2\) for Co), \(g\)- is the \(g\)-factor, \(\mu g\)- Bohr magneton and \(N\) is the number of the Mn (or Co) centers.

Figure 5 presents the measured magnetisation of doped ZnO nanoparticles fitted with the equation (1), using “lsqcurvefit” function of the Matlab programming language.

Table 2 presents the fitting parameters of the samples with higher magnetic moment, namely Zn\(_{0.85}\)Mn\(_{0.15}\)O at 2K and 300K and Zn\(_{0.85}\)Mn\(_{0.15}\)O at 2K. There are tree fitting parameters in this model: \(A1=\chi_D^*B+C\), \(A2=N^*g^*\mu g\ast S\) and \(A3=\chi_D\). While Zn\(_{0.85}\)Mn\(_{0.15}\)O NPs at 2K (blue asterisks at fig.5) fit perfect Brillouin function with tree parameters, the magnetisation of Zn\(_{0.85}\)Mn\(_{0.15}\)O NPs do not.

<table>
<thead>
<tr>
<th>Table 2 fitting parameters of the measured magnetization fitted with Brillouin function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured magnetization for respective temperature</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Mn(</em>{0.15})O at 2K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Co(</em>{0.15})O at 2K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Co(</em>{0.15})O at 300K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Mn(</em>{0.15})Co(_{0.15})O at 2K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Mn(</em>{0.15})Co(_{0.15})O at 300K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Mn(</em>{0.15})Co(_{0.15})O at 30 K</td>
</tr>
<tr>
<td>Zn(<em>{0.85})Mn(</em>{0.15})Co(_{0.15})O at 300 K</td>
</tr>
</tbody>
</table>

It is an interesting question how to analyze the data with two co-doped ions in one crystal lattice? The magnetization data analysis of the nanoparticles doped with two ions is much more complicated because of the Mn-Co exchange interaction in the crystal lattice of ZnO. As it is seen from figure 4a and 4b, magnetic moment increases significant for NPs with the concentration of doped ions over 1% of the cobalt. Co ions increase the concentration of free carriers, thus enhance the spin coupling of the magnetic ions, and equivalently cause enhancement of magnetization. Magnetization obtained for Zn\(_{1-x}\)Co\(_{x}\)Mn\(_{1-x}\)O nanoparticles was fitted with the Brillouin function with tree parameters for the first time – Fig. 6. Whereas, there are two ions in one lattice, but Co has higher substitutionary (Table 1) SO Zn\(_{1-x}\)Co\(_{x}\)Mn\(_{1-x}\)O and Zn\(_{0.70}\)Mn\(_{0.15}\)Co\(_{0.15}\)O were fitted with the spin \(S=3/2\). Fitting parameters are presented in the table 2.

![Fig 5 Measured magnetization fitted with the Brillouin function shown as a black line with the respective spin. Green rhombs represent the Zn\(_{0.85}\)Co\(_{0.15}\)O NPs at 2K. Blue asterisks represent the Zn\(_{0.85}\)Mn\(_{0.15}\)O NPs at the temperature 2 Kelvin. Red rhombs represent the Zn\(_{0.85}\)Mn\(_{0.15}\)O NPs at 300K.](image)

![Fig 6 Measured magnetization fitted with the Brillouin function shown as a black line with the S=3/2. Green rhomb represent the data for Zn\(_{1-x}\)Co\(_{x}\)Mn\(_{1-x}\)O NPs at 2K. Blue asterisks represent the data for Zn\(_{1-x}\)Co\(_{x}\)Mn\(_{1-x}\)O NPs at 300K. a) Zn\(_{0.85}\)Mn\(_{0.15}\)Co\(_{0.15}\)O b) Zn\(_{0.85}\)Mn\(_{0.15}\)Co\(_{0.15}\)O](image)
Djerdl I [17] suggests that Co-Co interactions are rather in short range. The amount of antiferromagnetic Co-Co coupling increases with the increasing of concentration of Co ions in the lattice. Similar mechanism of antiferromagnetic interactions is for Mn-Mn coupling pairs. But Co ions take place the majority in replacing Zn ions in the lattice. That is why the spin was taken $S=3/2$ for the fitting of the experimental data in this paper. There is a possibility of inverse spinel formation, which could lead to the origin of ferromagnetism in antiferromagnetic interactions of two ions doped zinc oxide system. Further studies, theoretical and experimental, are still needed to clarify the magnetic behavior of ZnO nanoparticles doped with transitional metal ions.

CONCLUSIONS

Detail description of magnetic properties of these nanoparticles was reported for the first time. The present study provides a way to enhance the magnetisation by doping and co-doping crystal lattice of ZnO nanoparticle with transitional metal like Co$^{2+}$ and Mn$^{2+}$. Magnetic behavior of ZnO based DMS depends on the type of synthesis, concentration of magnetic ion, spatial distribution of transition metal in a crystal lattice, surface defects. Experimentally was confirmed that co-doped nanoparticles Zn$_{1-x-y}$Mn$_x$Co$_y$O, obtained by microwave solvothermal synthesis, is a very promising material for DMS. Combining our experimental results with the photoluminescence, EPR, electron density studies and theoretical calculations a great contribution to the understanding of ferromagnetic effects in ZnO based DMS will be done.

Acknowledgments

This research did not receive any specific grant from funding agencies in the public, commercial, of not-for-profit sectors.

References