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# Presence of Room Temperature Ferromagnetism in $\text{Co}^{2+}$ Doped $\text{TiO}_2$ Nanoparticles Synthesized through Shape Transformation

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New approach for synthesis of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles showing room temperature ferromagnetic behavior, through shape transformation of hydrothermally treated scrolled titania nanotubes in the presence of  $\text{Co}^{2+}$  ions is described. The XRD and ICP measurements demonstrated successful incorporation of 0.46 at. %  $\text{Co}^{2+}$  ions in preserved anatase crystal structure of  $\text{TiO}_2$  nanoparticles, without presence of Co-oxide clustering, metallic Co, or various Co-Ti oxide species. HRTEM measurements revealed that majority of the nanoparticles have polygonal shapes with average dimension of  $\sim 6\text{--}10\text{ nm}$ . Obtained value of 3.06 eV for band gap energy of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles explained altered optical properties of  $\text{TiO}_2$  matrix and indicates narrowing of the electronic properties in respect to the undoped anatase  $\text{TiO}_2$  nanomaterials. The  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanocrystals enabled synthesis of optically transparent film that shows room temperature ferromagnetic ordering with a saturation magnetic moment of  $0.25\text{ }\mu\text{B}$  per Co atom. The proposed explanation for room temperature ferromagnetic behavior is based on the presence of critical amount of oxygen vacancies that mediate interaction between  $\text{Co}^{2+}$  spins trapped in the lattice structure of titania nanoparticles with undercoordinated surface defect sites.

## 1. Introduction

The development of spin-based electronic (spintronics) devices has recently attracted a great deal of attention. The possibility of simultaneous control of charge currents and spin polarized currents in those systems might provide new qualities to information processing technologies. Nanoscale diluted magnetic semiconductors (DMS) are the main components of proposed spintronic devices. DMS are the mostly II-VI or III-V compounds, in which the host cations are replaced with magnetic impurities up to a few atomic percent. Some of those materials exhibit interesting magnetic and magnetooptical behavior characterized by a high-Curie-temperature ferromagnetism. Theoretical predictions have identified wide band metal oxide semiconductors ( $\text{ZnO}$  and  $\text{TiO}_2$ ) as good candidates for the host materials, which, after doping with transition metal ions, could support room temperature ferromagnetism. Consequently, those doped semiconductors can be used for the development of the spin-based electronics devices.<sup>1</sup> Recently, DMSs such as Co doped  $\text{TiO}_2$ , Fe doped  $\text{TiO}_2$ , and Mn and Co doped  $\text{ZnO}$  have been reported to show the room temperature ferromagnetism.<sup>2</sup>

$\text{TiO}_2$  is a well-known wide band gap (3.2 eV) semiconductor and as such has the potential for a wide range of applications. As inexpensive, nontoxic and biocompatible material,  $\text{TiO}_2$  is one of the most important photocatalysts.<sup>3</sup> In addition, Co doped  $\text{TiO}_2$  is promising for the spintronics applications due to the excellent optical transmission in the visible and near-infrared regions and high n-type carrier mobility.<sup>4</sup>

Since Matsumoto et al.'s<sup>5</sup> discovery of high  $T_c$  ferromagnetism in  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  anatase films, there was an expansion of experimental and theoretical work focused on transition metal doped  $\text{TiO}_2$  as a ferromagnetic material. However, most of the research was confined on the thin films,<sup>5–10</sup> whereas there was significantly less focus on the transition metal doped nanoparticles.<sup>11–13</sup> Paucity of the published research on a synthesis of the free-standing high-quality nanoparticles doped with the transition metal ions is related to a number of challenges such as high surface to volume ratio, requests for uniform size distribution of the nanocrystals, as well as successful doping, i.e., control of exact position of the dopant ions within a crystal. The last condition is the most important one and hardest to satisfy. The main obstacle to successful doping is, according to the classical nucleation model, due to the kinetic noncompetitiveness between the nucleation process of doped crystals and the nucleation process of pure crystals.<sup>14,15</sup> According to this model, an increase of the ratio between the dopant and host radius and charge incompatibility reduces the probability for the critical nucleus formation containing impurity ions. The nucleation process in a mixed solution of precursor ions is ruled most frequently by a favorable reaction pathway that leads toward formation of the critical nucleus made up of pure host material. For example, during the synthesis of  $\text{Co}^{2+}$  doped  $\text{ZnO}$  as reported by Gamelin et al.,<sup>16</sup> the addition of 2%  $\text{Co}^{2+}$  ions to the starting solution eliminates 35% of the nucleation events in comparison to pure  $\text{ZnO}$ ; the result was explained by an increase in the activation energy and critical radius of the nuclei upon introduction of the impurity ions.<sup>16</sup>

In this paper we report on the preparation procedure of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles through shape transformation by solution chemical route. Using titania nanotubes in the presence of  $\text{Co}^{2+}$  ions as precursors for the synthesis of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$

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nanoparticles, we eliminated the driving force problem that arises from the increase in the activation energy for nanocrystal nucleation in the presence of the dopant ions and consequent exclusion of the  $\text{Co}^{2+}$  ions during nanoparticle growth. The shape transformation from nanotubes into nanoparticles in the presence of  $\text{Co}^{2+}$  ions using extended hydrothermal treatment induces structural reorganization, while at the same time avoiding the nucleation stage and problems related to it.

Shape, size, and crystal structure of the  $\text{Co}^{2+}$  doped titania nanoparticles were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. The optical characterization of a powdered sample of the  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles was made by UV-vis reflection spectroscopy. The magnetic properties of films made of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles were explored using a superconducting quantum interference device (SQUID) magnetometer. Doped semiconductor nanoparticles obtained by the described synthetic procedure can be easily processed and incorporated into various matrixes.

## 2. Experimental Methods

All chemicals were reagent-grade and used as received. The pH was adjusted using hydrochloric acid (Sigma Aldrich, Germany). Titania nanotubes were synthesized by using P25  $\text{TiO}_2$  powder (Degussa, Frankfurt, Germany) as a precursor in a hydrothermal process described elsewhere.<sup>17</sup> Co doped  $\text{TiO}_2$  nanoparticles were synthesized using hydrothermal treatment of a suspension containing  $3 \times 10^{-2}$  M titania nanotubes at pH 3 as the starting materials in the presence of  $6.3 \times 10^{-3}$  M  $\text{CoCl}_2$  (Kemika, Zagreb, Croatia). The suspension was stirred for 4 h followed by a 60 min hydrothermal treatment at 250 °C. Transparent colloidal solution of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles was obtained after efficient redispersion of hydrothermally synthesized powder using ultrasonic horn (200 W). Excess of  $\text{Co}^{2+}$  ions was removed by dialysis against acidified water (pH 3) at 4 °C for 3 days. For dialysis process was used Spectra/Por Dialysis Membrane, MWCO: 3,500 (Spectrum Laboratories, Inc., Rancho Dominguez, CA).

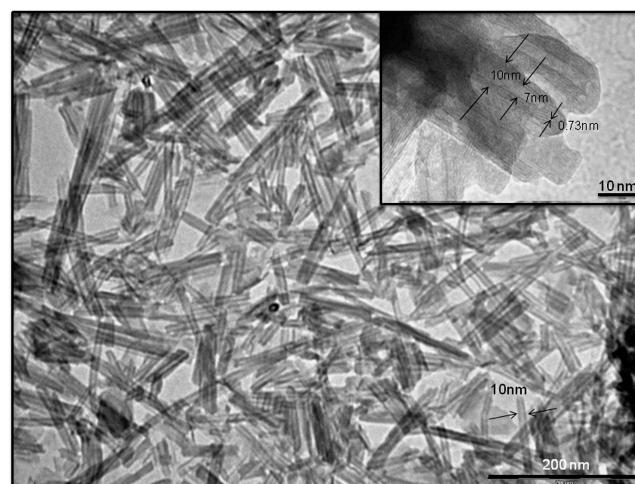
Films for magnetic measurements are prepared by spin coating of dialyzed colloidal dispersion of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles onto a glass substrate. After each deposition of dispersion, the sample was annealed in air for 2 min at 200 °C.

**2.1. Apparatus.** Morphology of the titania nanotubes was characterized using Hitachi H-7000 FA TEM with a W filament at a high tension of up to 125 kV, whereas the size and shape of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanocrystals were determined by conventional, JEOL 200CX, and high resolution transmission electron microscopy (HREM), Phillips CM200 with a FEG, at 200 kV.

Reflection spectrum of  $\text{Co}^{2+}:\text{TiO}_2$  powder was recorded at room temperature using a Thermo Scientific Evolution 600 UV-vis spectrophotometer.

The percentage ratio of  $\text{Co}^{2+}$  ions to  $\text{Ti}^{4+}$  ions in doped nanoparticles was determined using ICP Emission Spectrometer: ICAP 6000 series (Thermo Electron Corporation). Prior to the ICP measurements, the powdered sample was dissolved in 2 mL of concentrated sulfuric acid. The concentration of  $\text{Co}^{2+}$  ions was 0.46 at % compared with the amount of  $\text{Ti}^{4+}$  ions.

The X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance diffractometer in theta/theta reflection geometry with parallel beam optics achieved by multilayer Göbel mirror. Diffraction data for a structure analysis were collected in  $2\theta$  range from 10° to 80° with steps of 0.05° and 10 s counting time per step.



**Figure 1.** TEM images of scrolled titania nanotubes. Inset: at higher magnification.

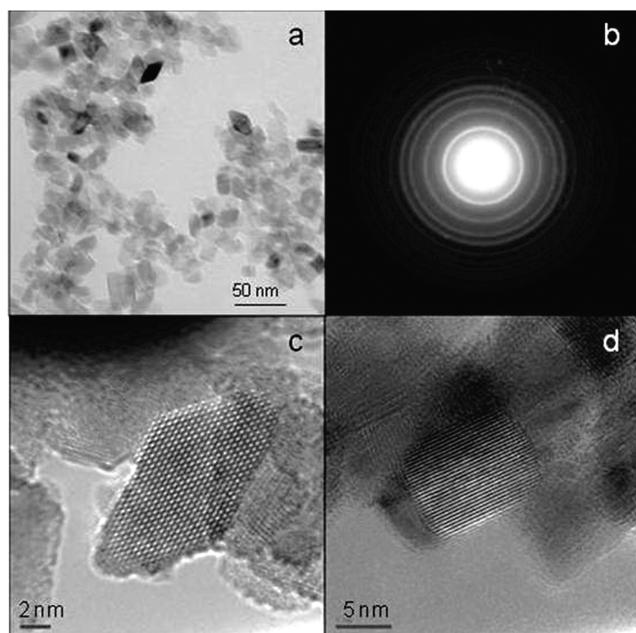
The field dependence of the magnetic moment of our samples was measured with a superconducting quantum interference device magnetometer (Quantum Design). The magnetic field was applied parallel to the film surface. The measured magnetization at 300 K was corrected for the diamagnetic background of the glass substrate (derived from high-field dependence magnetization data).

## 3. Results and Discussion

We exploited the potential for systematic shape manipulation of titania nanotubes by the additional hydrothermal treatment for the synthesis of a new class of nanostructured diluted magnetic oxide (DMO) materials.<sup>18</sup>

As an initial step in the procedure, we produced scrolled titania nanotubes from a hydrothermally treated dispersion of commercial  $\text{TiO}_2$  powder in proton deficient aqueous solution according to procedure reported by Kasuga et al.<sup>17</sup> Typical morphology of the titania nanotubes is shown in the Figure 1. The inset in Figure 1 is a conventional TEM image of the same region at a higher magnification, which reveals an open-ended multiwall morphology of the scrolled nanotubes. The uniform size distribution of nanotubes, a few hundred nanometers in length with the outer diameter of about 10 nm and inner diameter of about 7 nm, is confirmed by conventional TEM measurements. The interwall spacing is quite large, about 0.73 nm. The nanotubes are characterized by quasianatase, axially symmetric, and distorted octahedral coordination with a large fraction of five-coordinated sites on the surface.<sup>19</sup> Those surface sites generally appear as an accommodation of objects in nanoscale regime for high curvature and surface reconstruction.<sup>20</sup> It is characteristic of the multiwall, scrolled titania nanotubes, such as we observed, to have a large fraction (~40%) of highly reactive undercoordinated interior and exterior Ti atoms.<sup>19</sup> This material represents an ideal precursor for the reshaping and synthesis of Co doped  $\text{TiO}_2$  nanoparticles.

The undercoordinated, square-pyramidal structure ( $C_{4v}$ ) of surface defect sites that terminate layers of titania nanotubes can be exploited for strong adsorption of ions from surrounding media. In the previous study we showed that the bigger portion of the undercoordinated sites was located on the interface between the layers that constituted the scrolled nanotubes.<sup>19</sup> The charging of undercoordinated sites with protons, lithium, or manganese ions leads toward the complete or partial exfoliation of nanotubes.<sup>19,21</sup> Simultaneously, a nanotube unscrolling into



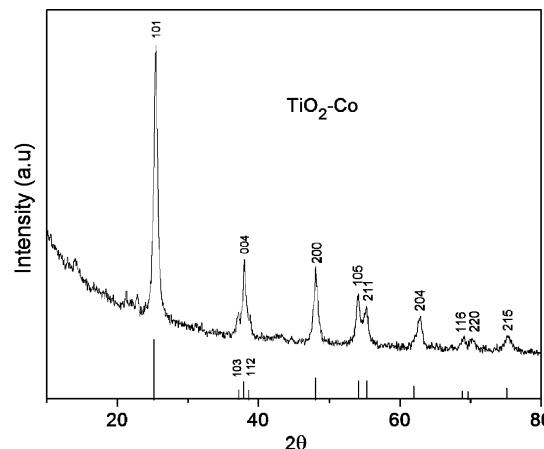
**Figure 2.** (a) TEM image of Co<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles; (b) SAED pattern; (c and d) HREM images of the Co<sup>2+</sup>:TiO<sub>2</sub> nanocrystals.

sheet-like structure as a consequence of charge disbalance between the layers is conformation of the ions adsorption at undercoordinated sites. Those sites at the interior walls of nanotubes are accessible for transition metal ions, due to the order of magnitude bigger interwall spacing in comparison to the atomic dimension. It was also observed that addition of cobalt ions (from CoCl<sub>2</sub>) in nanotubes dispersion in concentration higher than 0.1 M induces their partial unrolling.

We conducted the hydrothermal treatment on the dispersion of the titania nanotubes in the presence of Co<sup>2+</sup> ions in order to produce internally doped Co:TiO<sub>2</sub> nanoparticles through encapsulation of nanotube's surface-bound Co ions with extra layers of TiO<sub>2</sub> during shape transformation. The result of such reaction route, where the shape transformation is followed by the change in the crystalline domain, is dispersion of Co<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles, Figure 2a.

In Figure 2a it can be noted that some of the nanoparticles exhibit darker contrast as a result of the orientation corresponding to strong diffracting conditions and not due the difference in chemical composition. Selected area electron diffraction pattern (SAED) of the nanoparticles, Figure 2b, shows a ring pattern typical for the anatase crystal phase of TiO<sub>2</sub>. In addition, perfection of the pattern and the rings suggests the random orientation of the nanoparticles. Majority of the nanoparticles have faceted, polygonal shape. As the particle size decreases the fraction of the facets parallel to the close packed planes increases, Figure 2, panels c and d. Although the length of the nanoparticles varies in the wider range, the particle width is in the 6–10 nm range.

In another study,<sup>18</sup> we showed that from the titania nanotubes, due to suitable ratio of surface and bulk coordinatively unsaturated Ti sites, the anatase TiO<sub>2</sub> nanocrystallites can be produced in a range of sizes and shapes (faceted and bricklike particles with exposed flat surfaces, and rods) by manipulation of reaction conditions such as concentration, temperature, pH and time of the hydrothermal process. Those nanoparticles have different crystallinity domain, aspect ratios and surface structure. It is expected that the faceted nanoparticles, synthesized in the presence of Co<sup>2+</sup> ions, have more ordered crystalline structure as the fraction of coordinatively unsaturated Ti sites ( $C_{4v}$ ), is



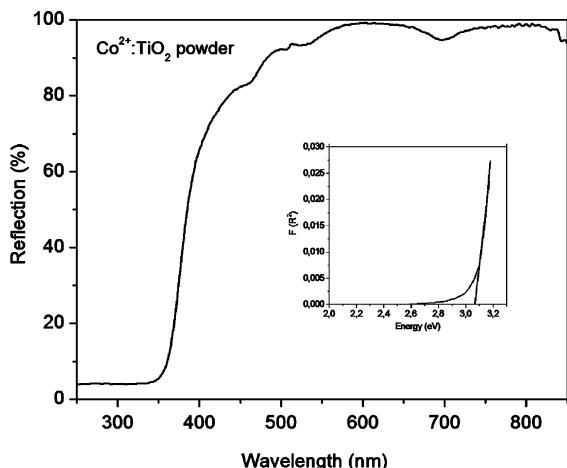
**Figure 3.** X-ray powder diffraction of Co<sup>2+</sup>:TiO<sub>2</sub> nanoparticles. Bragg peak positions, Miller indices, and peak intensities for anatase TiO<sub>2</sub> are included for reference.

generally smaller in the faceted particles than in the nanotubes and spherical particles ( $d < 20$  nm).<sup>18</sup> In the same time, those undercoordinated surface sites in doped faceted nanoparticles represent possible positions for dopant ions with different coordinative nature compared to those in particle core. HREM characterization of the Co<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles, Figure 2c and 2d, confirmed that they are internally defect free, although some twinned particles were observed. Neither SAED nor TEM characterization indicate any traces of the Co segregations in any form.

Results of the powder X-ray diffraction analysis of Co<sup>2+</sup> doped TiO<sub>2</sub> nanocrystals confirmed the existence of a homogeneous anatase phase with the isotropic dopant distribution, Figure 3.

All diffraction peaks characteristic for the anatase crystal lattice with the preserved intensity ratio are present. The intensity ratio is as expected for the random orientation of the anatase nanocrystals, the finding in agreement with electron diffraction result. There are no peaks that would indicate the presence of the rutile phase. In addition, X-ray data do not show any inhomogeneity caused by the presence of CoO clustering, metallic Co, and various Co-Ti oxide species. The lack of the overall disturbance of anatase crystal structure still leaves possibility for local distortions caused by incorporation of Co<sup>2+</sup> ions either at substitutional sites or at interstitial sites.

According to Vegard's law statistical substitution of dopant ions within host crystal lattice structure lead to a lattice contraction or expansion. The observed slight shifts of (004) and (200) peaks positions to lower angles ( $2\theta = 37.996$  and  $48.078$ , respectively), Figure 3, are caused by an increase of the  $d$  values (2.366 and 1.889 Å) for the (004) and (200) lattices in the Co doped TiO<sub>2</sub> nanoparticles in comparison with  $d$ -values (2.361 and 1.883 Å) of the (004) and (200) lattices in bare TiO<sub>2</sub> nanocrystals<sup>21</sup> obtained using the same synthetic procedure. The particularly clear shift to lower angle ( $2\theta = 25.436$ ) is observed for (101) peak due to an increase of the  $d$  value for the (101) lattice (3.499 Å) in doped nanoparticles in comparison with  $d$  value (3.489 Å) of the (101) lattice in bare TiO<sub>2</sub> nanocrystals.<sup>21</sup> Such increases in the  $d$ -spacing indicate the slight elongation of the unit cell along  $c$  axis and  $a$  axis caused by substitution of Ti<sup>4+</sup> with larger cation. Indeed, the ionic radius of the low spin state Co<sup>2+</sup> is 0.79 Å, the value slightly higher than of the Ti<sup>4+</sup> (0.745 Å) when they are both in octahedral coordination.<sup>22</sup> Although Co<sup>2+</sup> ions have slightly larger diameter and significantly different charge from Ti<sup>4+</sup> this is not an obstacle for the

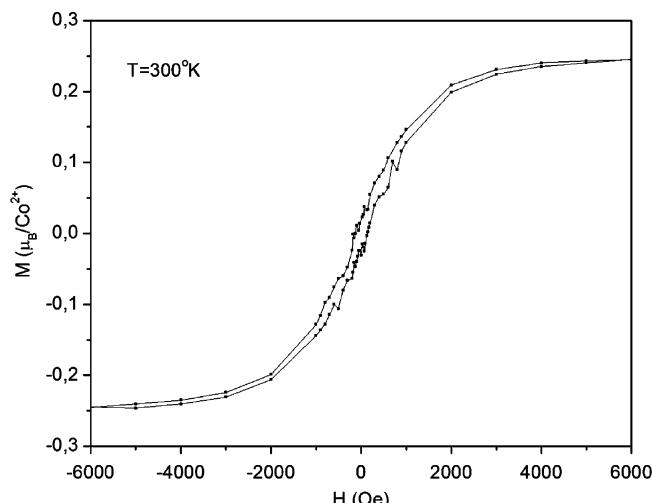


**Figure 4.** Reflection spectrum of powder of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles; Inset: band gap calculation.

successful incorporation into the anatase lattice, due to the possibility of the bond lengths shortening that occurs in titania matrix after doping with transition metal ions.<sup>21</sup> Based on a similar analysis of peak position that was reported for the Co doped  $\text{TiO}_2$  thin films and Co doped  $\text{TiO}_2$  nanotubes,<sup>4,23</sup> the observed slight shifts of the peaks positions are proof of the successfully incorporated larger  $\text{Co}^{2+}$  ions into the anatase lattice. The observed absence of the significant change in the lattice parameter of the  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanocrystals with respect to an undoped  $\text{TiO}_2$  can be expected according to work of Manivannan et al.<sup>24</sup> which claims that the lattice spacing does not change significantly even if the Co ions dissolves in  $\text{TiO}_2$  lattice in much higher concentration compared to the concentration used in our experiment.

ICP analysis showed that the dopant concentration was 0.46 at % with respect to the amount of  $\text{Ti}^{4+}$ . This value is much lower than the initial dopant concentration (21 at %) prior to the additional hydrothermal treatment of nanotubes. The observed difference can be attributed to the removal of the excess of cobalt ions during postsynthetic dialysis process applied on the colloidal solution of the  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles. In addition, dialysis process of dispersion of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles against water at pH 3 opens up opportunity for removal of the dopant ions that substitute Ti atoms in the undercoordinated coordination environment of reconstructed surfaces. Dopant ions from these sites are weakly bound to the anatase lattice and can be easily removed leaving the residual strongly bound  $\text{Co}^{2+}$  ions that are octahedrally coordinated in the core of nanoparticles.<sup>21</sup> Results of the additional ICP measurements after the repeated dialysis showed an unchanged amount of  $\text{Co}^{2+}$  ions indicating that dopant ions cannot be quantitatively excluded from the  $\text{TiO}_2$  critical nuclei. Retainment of the  $\text{Co}^{2+}$  ions in the core of the nanoparticles is of importance, as transition metal ions substituting the Ti atoms in the titania nanoparticle's core contribute to their magnetic behavior.<sup>21</sup>

The optical properties of powdered sample of the  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles were measured in a reflection mode, Figure 4. Direct influence of the incorporated dopant ions on the optical properties of the  $\text{TiO}_2$  is revealed by increased absorbance and shift of the onset of absorption to 405 nm. This shift is a sign of the slight change of the band gap position and in the same time presents the positioning indication of the Co atoms energy levels within the band gap region of  $\text{TiO}_2$  matrix. Therefore, Co ions incorporated into the  $\text{TiO}_2$  lattice can participate in the light-induced charge-transfer processes.



**Figure 5.** Isothermal magnetization of the film made of 0.46 at%  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles recorded at room temperature

In order to calculate the band gap energy of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles, we used a plot of  $F(R)^2$  versus  $E$  (eV); the linear part of the curve was extrapolated to  $F(R)^2 = 0$  revealing the band gap energy (inset in the Figure 4). The term  $F(R)$  corresponds to the Kubelka–Munk value obtained from the relation

$$F(R) = (1 - R)^2/2R \quad (1)$$

where the  $R$  is the percentage of reflectance obtained from spectrum in Figure 4.<sup>25,26</sup> The extracted value of 3.06 eV (405 nm) for the band gap energy of  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles supports the observed altered optical properties of the  $\text{TiO}_2$  matrix, which still remains transparent in the visible and near-infrared regions. This value also indicates narrowing of the electronic properties in comparison with the pure anatase  $\text{TiO}_2$  nanomaterials, whose band gap energy is 3.2 eV.

For the optically transparent film made of 0.46%  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles, the magnetic response was measured at room temperature. In order to provide a long-range magnetic ordering and better connection between the nanoparticles in the synthesized film, a spin coating technique under oxidizing conditions was applied. It is well-known that aggregation density of DMS nanocrystals has direct influence on magnetic properties.<sup>16,27</sup> The influence of interfacial or grain-boundary defects on appearance of room-temperature ferromagnetism in the set of transition metal-doped oxide nanoparticles is recognized by Gamelin et al.<sup>27</sup> Their work also revealed that ferromagnetism in DMS nanocrystals can be activated by the fusion of defects from the nanocrystal interior to the interface and the randomization of the dopant ions.<sup>28</sup>

The measurement of the magnetization of a film made of 0.46%  $\text{Co}^{2+}$  doped  $\text{TiO}_2$  nanoparticles, as a function of magnetic field strength ( $H$ ), was carried out in superconducting quantum interference device (SQUID) magnetometer.

The in plane hysteresis loop (Figure 5) represents distinct evidence, although response is weak, of the ferromagnetic ordering at room temperature (300 K). A low saturation moment of  $M_S = 0.25$  Bohr magnetons ( $\mu_B$ ) per  $\text{Co}^{2+}$  ion was observed. The coercive field was found to be  $H_C \sim 150$  Oe, with remanence of  $M_R \sim 0.02$  ( $\mu_B$ )/ $\text{Co}^{2+}$  ion. Relatively high external field (>4000 Oe) is necessary to saturate the magnetization. The cobalt clustering as the reason for the observed ferromagnetic signal was additionally ruled out by absence of blocking temperature in ZFC curve obtained through the measurements

of zero-field-cooled/field-cooled (ZFC/FC) temperature dependences of magnetization at 100 Oe (not shown). The room temperature paramagnetic contribution (evaluated to be less than 40% from low temperature magnetization) was not subtracted.

As a result of X-ray diffraction analysis, Figure 3 showed the absence of any peaks that would indicate segregation of Co in a metallic form or as oxide precipitate in the characterized specimens. The implication is that the observed ferromagnetism of the film, Figure 5, is an intrinsic property of Co<sup>2+</sup> ion doped TiO<sub>2</sub> nanoparticles.

The appearance of ferromagnetism in the Co doped TiO<sub>2</sub> lattice also strongly depends on the formation and distribution of donor type defects such as oxygen vacancies and their tendency to form complexes with the Co atoms.<sup>29,30</sup> According to Huang et al., O<sup>2-</sup> vacancy ensures charge neutrality in the system for each Co<sup>2+</sup> which substitutes for a Ti<sup>4+</sup> ion.<sup>4</sup> Further, the additional role of the vacancies in the system is to mediate interaction between Co<sup>2+</sup> spins. On the other hand, an increase in oxygen content within the unit crystal cell induces suppression of ferromagnetism.<sup>4</sup>

The explanation of observed room temperature ferromagnetism in faceted 0.46 at % Co<sup>2+</sup> doped TiO<sub>2</sub> nanocrystals synthesized by the shape transformation of the nanotubes can be found in the simultaneous existence of the undercoordinated surface defect sites and octahedrally coordinated Co<sup>2+</sup> ions in the nanoparticles core. Those surface defect sites present coordinatively unsaturated surface Ti atoms with square pyramidal structure ( $C_{4v}$  pentacoordinated) characterized with oxygen atoms deficiency. According to the Coey's model of indirect exchange<sup>31</sup> and total energy calculations by Chambers et al.,<sup>29</sup> the oxygen vacancies which present donor type defects in diluted magnetic semiconductors are the requisite elements for the appearance of ferromagnetism due to its correlations with conductivity. Additionally, formation of interfacial n-type defects owing to the nanocrystal aggregation in the film also increases the possibility for ferromagnetic behavior.<sup>32,33</sup>

#### 4. Conclusions

In this work we present a new approach for synthesis of Co<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles through shape transformation of titania nanotubes in the presence of Co<sup>2+</sup> ions in additional hydrothermal treatment. The XRD and HRTEM measurements data demonstrated successful incorporation of 0.46 at % Co<sup>2+</sup> ions into preserved anatase crystal structure of TiO<sub>2</sub> nanoparticles, without the presence of CoO clustering, metallic Co, or various Co-Ti oxide species. The Co<sup>2+</sup> doped TiO<sub>2</sub> nanocrystals enabled the synthesis of an optically transparent film that shows room-temperature ferromagnetic ordering with a saturation magnetic moment of 0.25  $\mu_B$  per Co atom. The proposed explanation for room temperature ferromagnetic behavior is based on the presence of a critical amount of oxygen vacancies that mediate interaction between Co<sup>2+</sup> spins in the lattice structure of doped titania nanoparticles characterized with the presence of undercoordinated surface defect sites.

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