

Above Room Temperature Ferromagnetism in Co- and V-Doped TiO₂ — Revealing the Different Contributions of Defects and Impurities

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Abstract We report recent experimental results on the magnetic, magnetotransport, and magneto-optical properties of Co- and V-doped TiO_{2-δ} magnetic oxides at the doping level around 1 at. %. The samples were prepared using rf magnetron sputtering in identical conditions that allows to compare the mechanisms of above-room-temperature ferromagnetism observed in both cases of doping. In spite of the comparable values of magnetic moment around $1 \div 2.5 \mu_B$ per 3d impurity derived from macroscopic magnetic measurements for both systems, the magneto-optical response

of TiO_{2-δ}:V was at least 2 orders of magnitude weaker. The anomalous Hall effect was absent in V-doped TiO_{2-δ}, and no appreciable magnetic moment on V impurities was found by X-ray magnetic circular dichroism (XMCD) technique in contrast to Co-doped TiO_{2-δ}. The obtained experimental data indicate dissimilar origin of intrinsic ferromagnetism in TiO_{2-δ}:Co and TiO_{2-δ}:V.

Keywords Doped TiO₂ · Magnetic semiconductors · Oxygen vacancy · Defect-induced ferromagnetism

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1 Introduction

The tuning of physical properties of solids to realize a desired functionality is always a challenge. In the case of semiconductors the last decades were devoted to the creation, understanding and manipulation of ferromagnetism in doped semiconducting materials. The utilization of spin functionality hand in hand with electrical charge-based electronics opens the wide field of phenomena combining brand-new physics and extensive potential for applications in the next generation logic device and storage. One of the most interesting and practical-related phenomena observed in oxide magnetic semiconductors is magnetization switched by electrical field (electric field induced ferromagnetism) in Co-doped TiO₂. Reversible transition from paramagnetic to ferromagnetic state at room temperature [1] offers promise for future semiconductor spintronics operating at room temperature, such as a gate-tunable magnetization inversion [2]. TiO₂-based magnetic semiconductors have found the applications related to electronic nonvolatile memory devices and in particular to nanoelectronic memristor devices (see the patent [3])

In spite of great advances in recent years in this area [4] the origin of the above and below room temperature ferromagnetism (RTFM) in dilute magnetic semiconductors (DMS) and oxides remains a controversial issue [5]. For exception of GaAs:Mn, the mechanism of the long-range magnetic order in the most of studied DMS doped with transition metal (TM) or nontransition metal impurities as well as even undoped ones is still under debates [6–9].

The wide bandgap semiconducting oxide TiO_2 is especially interesting as a host for DMS due to well-known special properties of this material [10]. Doped with $3d$ TM, for example, with Co, V, or Fe TiO_2 as well as doped with nonmagnetic impurities [11] exhibits a ferromagnetic behavior up to 800 K and more. The most studied case is Co-doped TiO_2 , the ferromagnetism in this material was firstly observed in [12]. Later the RTFM in TiO_2 :V was reported by Hong et al. [13, 14]. There is a stable interest to bulk TiO_2 -based DMS [15] and nanomaterials (thin films [16], nanoparticles [17], nanowires [18], nanotubes [19]) during the last years.

In the case of $\text{TiO}_{2-\delta}$:TM several explanations of RTFM were suggested: carrier-mediated ferromagnetism [5, 6, 20], superexchange [21], percolation network of magnetic polarons [7, 22], charge transfer ferromagnetism of Stoner-type in the impurity band [23], and magnetism of dangling bonds [24]. Each of these models meets serious difficulties in explaining all available experimental data. For example, the carrier-mediated ferromagnetism is the most popular point of view but it fails in explaining ferromagnetism in dielectric $\text{TiO}_{2-\delta}$:Co [25] and extra large magnetic moment per Co impurity at low doping [26]. Moreover, one of the main difficulties in the understanding of RTFM in TiO_2 -based DMS is due to the dependence of their properties on many conditions of fabrication and the slight difference in structure, which was confirmed in many experimental works as well as theoretically [27]. At the same time there is abundant evidence in the literature pointing to the absence of magnetic order in doped oxides [28–30].

Many recently published results show the importance of oxygen vacancies (V_O) [31] both for doped and undoped films. The effect of V_O on the magnetic properties of undoped TiO_2 was studied theoretically as well as experimentally [32–34], and ferromagnetism up to 880 K was observed [34]. However, there is also a lack of consensus in opinions — for example, Yang and coauthors have shown that the state of TiO_2 should be antiferromagnetic due to excess electrons introduced by an oxygen vacancy [35]. In case of doped TiO_2 the magnetic properties can be tuned with the changing of amounts of defects, for instance, with the hydrogenation [36]. In [37] vacancies V_O in Co-doped TiO_2 were shown to be mediating the ferromagnetism

while the Co clusters are the key factor for inducing the superparamagnetism in host TiO_2

In this paper we report the last experimental results on magnetic, magnetotransport and magneto-optical (MO) properties of $\text{TiO}_{2-\delta}$:Co and $\text{TiO}_{2-\delta}$:V thin films with a small fraction (~ 1 at. %) of TM. For $\text{TiO}_{2-\delta}$:Co we succeeded to obtain the anomalous Hall effect (AHE) contribution that in addition to the large MO response and well pronounced magnetic hysteresis at room temperature confirms the presence of intrinsic ferromagnetism in this system. Measurements show also magnetic hysteresis at room temperature for $\text{TiO}_{2-\delta}$:V with the same level of the coercivity and comparable with $\text{TiO}_{2-\delta}$:Co level of magnetic moment per $3d$ impurity, but $\text{TiO}_{2-\delta}$:V possesses 2 orders of magnitude weaker MO response. These data clearly demonstrate that the only one mechanism cannot be responsible for RTFM in $\text{TiO}_{2-\delta}$ doped with $3d$ TM and here we discuss the possible contributions to magnetization.

2 Experimental Methods

$\text{TiO}_{2-\delta}$:Co and $\text{TiO}_{2-\delta}$:V thin films of 300 nm thickness were deposited on LaAlO_3 (001) and rutile substrates at 550 and 650 °C by rf magnetron sputtering of metallic alloy targets in the argon–oxygen atmosphere at oxygen partial pressures of $2 \cdot 10^{-6} - 2 \cdot 10^{-4}$ Torr. By variation of oxygen partial pressure during the sputtering process different structural phases of $\text{TiO}_{2-\delta}$ can be adjusted. In the present study we report results for two samples: $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ (pure anatase) and $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ (mixture of anatase and rutile).

The sample structures and cluster formation have been checked by standard X-ray diffraction (XRD) analysis. To check the possible secondary parasitic magnetic phases in V-doped TiO_2 films energy-dispersive X-ray (EDX) analysis has been performed at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) with high-resolution scanning electron microscope Hitachi S-4800 with microanalysis system (INCA, Oxford Instruments).

Magnetic measurements have been performed with vibrating sample magnetometer (VSM) magnetometer (LakeShore 7407, 16 kOe, MSU) at room temperature and superconducting quantum interference device (SQUID) magnetometer (Cryogenics 600, 50 kOe, HZDR) at the temperature range of 4–300 K. MO spectra have been measured in the transversal Kerr effect (TKE) geometry by the dynamic method in the 0.5–4.5 eV energy range under the external magnetic fields up to 3 kOe at room temperature. Magnetotransport properties have been studied by the four-probe method at 77–300 K in magnetic field up to 18 kOe.

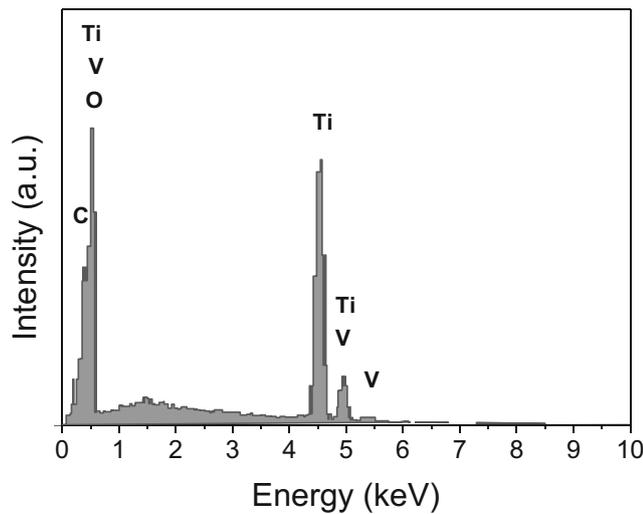


Fig. 1 EDX spectrum of $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ thin film with mixed structure “anatase + rutile”

3 Results

3.1 Structural Analysis

XRD analysis revealed the anatase structure of Co-doped TiO_2 film. The V-doped TiO_2 film was shown to be a mixture of anatase and rutile. Accordingly to XRD patterns there was no evidence of Co and V clusters present in studied films. This conclusion is also confirmed with SQUID and X-ray magnetic circular dichroism (XMCD)/X-ray absorption near edge structure (XANES) investigation (will be discussed below).

Previously it has been discovered [38] that the magnetic and MO properties of $\text{TiO}_2:\text{Co}$ DMS depend strongly on the film structure: the TKE signal is much larger and has several peculiarities of the spectra for anatase while for rutile it is

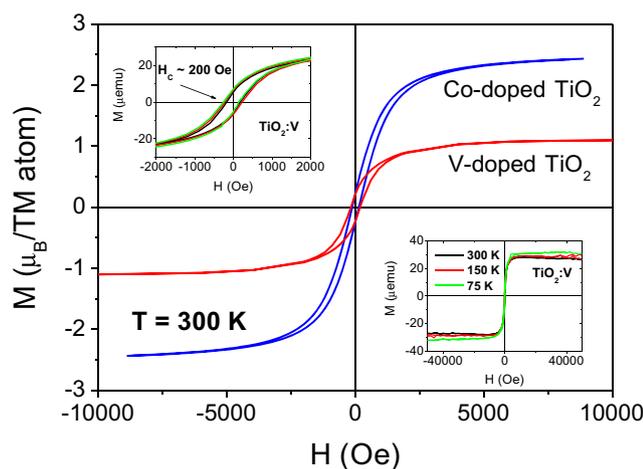


Fig. 2 Magnetic moment per TM atom versus magnetic field curves at room temperature for Co- and V-doped TiO_2 thin films

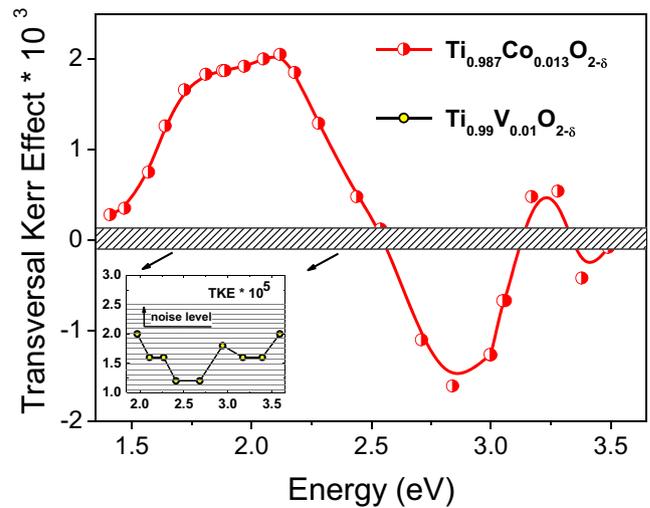


Fig. 3 TKE spectra of Co- and V-doped $\text{TiO}_{2-\delta}$ films

not. For $\text{TiO}_2:\text{V}$ films the magnetic properties do not depend so crucially on the matrix structure [39], so our comparison of these DMS with different crystal structures is rather accurate.

The EDX spectrum of $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ sample (Fig. 1) demonstrates the absence of $K_{\alpha,\beta}$ fluorescent lines of iron and cobalt ($6 \div 7 \text{ keV}$), and only Ti, O and V lines are observed. Due to the low V concentration only the K_{α} line of vanadium (4.95 keV) is well resolved and K_{β} line (5.43 keV) has a nondetectable intensity.

3.2 $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$

The magnetic hysteresis of studied film at room temperature is presented in Fig. 2. The coercive field of about 200 Oe is rather typical for $\text{TiO}_{2-\delta}:\text{Co}$ systems with different concentrations of impurities [40]. A similar value was observed in

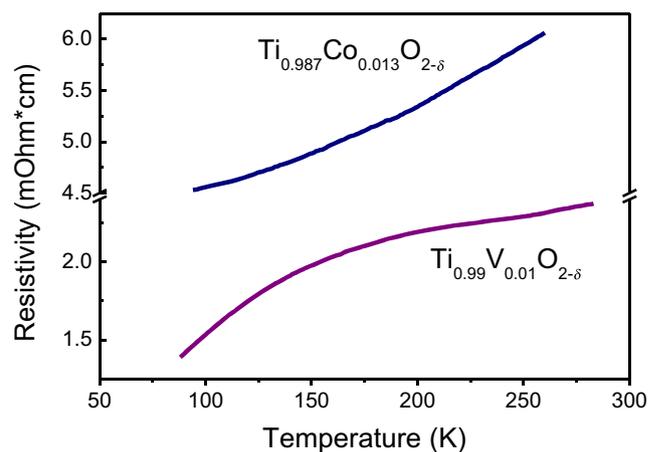


Fig. 4 The temperature dependence of electrical resistivity $\rho(T)$ of $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ and $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$

[41], where FM in Co-doped TiO_2 polycrystalline thin films originates from a combined effect of the oxygen vacancies and TM doping at 0.5 % concentration. The average magnetic moment per Co atom determined from the saturation magnetization at 300 K is about $2.5 \mu_B$, which is higher than the cobalt magnetic moment in bulk $1.7 \mu_B/\text{Co}^{2+}$ obviously excluding possible segregation of Co metal, and slightly exceeds the most of available in literature data (see [8]). Superparamagnetic behavior was not observed in measured zero-field-cooled (ZFC)/field-cooled (FC) curves, and this supports the results of XRD proving the absence of Co nanoparticles [42].

Earlier it was shown that TKE spectrum of $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ produced with magnetron sputtering differs from the spectra of metallic Co clusters in nonmagnetic $\text{TiO}_{2-\delta}$ matrix [38, 43] and TKE signal is larger than for pure Co thin film. This confirms the results of XRD analysis about the absence of metallic Co clusters in $\text{TiO}_{2-\delta}$ at the concentrations around 1 at. %. Additional peaks in TKE spectra for anatase (Fig. 3) at low Co concentration can be an evidence of new spin-polarized states inside the bandgap leading to new MO transitions.

The temperature dependence of electrical resistivity $\rho(T)$ reveals a “metallic” character from 90 to 300 K (Fig. 4), which means all impurities are activated at $T > 90$ K and therefore the carrier concentration n does not change too much in the studied temperature range. This conclusion is confirmed by Hall effect measurements which are simplified due to the relatively low resistivity of this sample. The measured Hall resistivity at 90 K is presented at Fig. 5.

The Hall resistivity ρ_H in ferromagnetic material can be written as follows:

$$\rho_H = R_0 B_z + 4\pi R_S M_z, \quad (1)$$

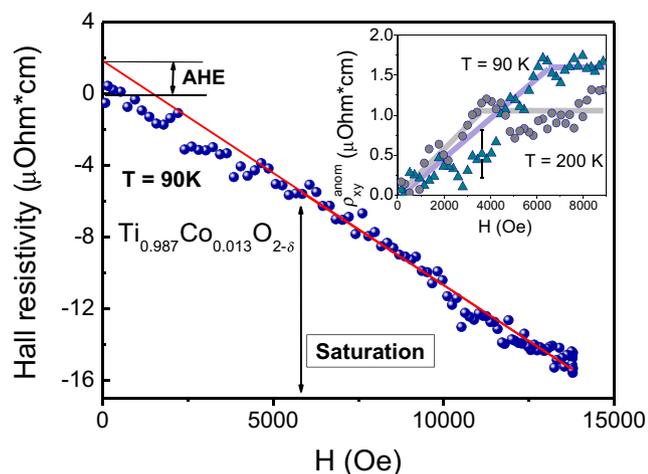


Fig. 5 Hall resistivity of $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ measured at 90 K. *Inset:* The anomalous Hall resistivity of $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ $\rho_{xy}^{\text{anom}}(H)$ versus magnetic field measured at 90 K (triangles) and 200 K (circles)

where the first term describes the ordinary Hall effect and the second term is the AHE contribution. R_S is the AHE coefficient, and M_z and B_z are the magnetization and magnetic induction components, respectively. To separate ordinary and AHE contributions we subtracted the linearly approximated high field part of the curve (Fig. 5) from the measured magnetic field dependence of the Hall resistivity. The obtained results are shown at Fig. 5 where the magnetic field dependences of the AHE resistivity ρ_{xy}^{anom} at 90 and 200 K are presented. Curves demonstrate saturation at 6,000 and 4,000 Oe, which are approximately the same as for $M(H)$ curve (Fig. 2). The negative ordinary Hall effect contribution corresponds to the electron type of conductivity. The following parameters have been found at room temperature: $R_0 = -1.3 \cdot 10^{-9} \Omega \cdot \text{cm}/\text{G}$, $R_S = 1.6 \cdot 10^{-7} \Omega \cdot \text{cm}/\text{G}$, carrier concentration $n = 4 \cdot 10^{19} \text{ cm}^{-3}$, and mobility $\mu = 21 \text{ cm}^2/\text{V} \cdot \text{s}$. It is interesting to note that the ratio $R_S/\rho^2 = 4.5 \cdot 10^{-3} \text{ 1/G} \cdot \Omega \cdot \text{cm}$ for the studied sample is much larger than one for the sample $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ prepared by laser ablation $R_S/\rho^2 = 1.2 \cdot 10^{-5} \text{ 1/G} \cdot \Omega \cdot \text{cm}$ [44]. This means that neither side-jump mechanism nor intrinsic mechanism [45] is responsible for AHE in $\text{TiO}_{2-\delta}:\text{Co}$, since R_S/ρ^2 should be constant for these mechanisms. Besides, the empirical but not supported by theory relation $R_S/\rho^{1.6} = \text{const}$ for the systems with high resistivity [6, 46] is also invalid for studied samples. Perhaps, there is no universal correlation between AHE and resistivity in highly resistive systems.

Previously, the valence state and local magnetic moment carried by Co impurities in rutile $\text{Ti}_{0.92}\text{Co}_{0.08}\text{O}_{2-\delta}$ prepared in our group [40] have been checked by element-selective XANES and XMCD techniques at the ESRF (Grenoble, France). No difference in XMCD spectra shape recorded in soft and hard X-rays ranges has been found that endorses the hypothesis about the unique charge state of Co atoms either near the surface or in the bulk of the sample.

The shape of the XANES and XMCD spectra at the Co L3 edge clearly demonstrated that Co atoms in the sample are in nonmetallic state. In [47] the same shape of XMCD spectra was found and related to the Co^{2+} ions that replace the Ti^{4+} ions. Thus, for studied $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$ we can conclude that Co^{2+} in the TiO_2 matrix substitutes Ti^{4+} ions and no Co clusters are responsible for magnetic properties of this material.

3.3 $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$

The studied $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ sample exhibits the clear magnetic hysteresis (Fig. 2) at room temperature with the same level of the coercivity (~ 200 Oe) as for $\text{Ti}_{0.987}\text{Co}_{0.013}\text{O}_{2-\delta}$.

Saturation magnetization at room temperature corresponds to $\sim 1.1 \mu_B$ per vanadium atom. This value differs

from the results obtained by Hong et al [13] and our preliminary results [39], where the larger magnetic moment per vanadium impurity was found for higher V content. Thereby it is particularly interesting to compare the magnetic properties of identically grown Co- and V-doped TiO_2 films at low dopant concentration.

Since neither bulk vanadium nor its oxides are ferromagnetic it is hard to believe that possible vanadium clusters can be above room temperature ferromagnetic. The performed XRD analysis and microscopy have not shown the presence of detectable amount of vanadium clusters. Hysteresis loops additionally measured at 150 and 75 K have not shown the significant changes in the saturated magnetization. ZFC/FC curves recorded by SQUID (not shown) confirm the ferromagnetic ordering in the sample and do not reveal the superparamagnetic behavior. We can also exclude that the ferromagnetic behavior of the studied $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ sample is due to possible parasitic phases because of the results of EDX analysis and discussed underneath spectroscopy.

Unexpectedly, the MO signal has not been found for the $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ sample with 300 nm thickness: the value of TKE signal was on the noise level (Fig. 3). So, in spite of a rather strong magnetic moment per impurity atom estimated from magnetometry data, more sensitive MO spectroscopy surprisingly could not confirm the magnetic behavior of this system. We also were unable to detect any nonlinearity in the field dependence of Hall resistivity that indicates the negligible AHE.

Our previous experience with element-selective XANES and XMCD spectroscopy that has been applied for $\text{Ti}_{0.97}\text{V}_{0.03}\text{O}_{2-\delta}$ DMS [39] revealed the absence of XMCD signal at the V K-edge even if the TKE was detected. Normally, this XMCD result means that vanadium atoms have no local orbital magnetic moment associated with the $2p$ shell at least at the level of $2 \cdot 10^{-5} \mu_B$. The same result was obtained for $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ thin film. The shape of XANES spectra at the V K-edge is significantly different and shifted along the energy scale from the reference spectrum of vanadium foil that confirms the idea about the ionic state of V atoms.

Thus, the absence of magnetic signal probed by XMCD, TKE and Hall effect measurements could have a principal nature.

4 Discussion

The value of magnetic moment per impurity atom derived from the macroscopic magnetization data can be determined by at least three different contributions. The first is local polarization of $3d$ impurity (spin and orbital magnetic moments). The second one is magnetic polarization related to oxygen vacancies. Finally, the last contribution

to magnetic polarization is determined by structural defects which create a local anisotropy (such as crystallographic imperfections, etc.) As it follows from detailed investigation using VSM and SQUID magnetometry, TKE spectroscopy, element-selective analysis and AHE in TiO_2 doped with Co and V the different contributions play the major role.

In $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ the local magnetic polarization of vanadium is absent and V ions do not carry magnetic moment, so the main causes of magnetism might be defects or oxygen vacancies. It was shown [48] that oxygen vacancies in TiO_2 create a charge imbalance which causes the deviation from stoichiometric TiO_2 with the potential to generate Ti^{3+} ions. Every Ti^{3+} ion with one unpaired $3d$ electron provides the local magnetic moment. Taking into account that since both MO signal and AHE are negligible in $\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_{2-\delta}$ we can conclude that spin-orbit interaction is very small. It confirms defect-driven magnetization and charge transfer model [23] if the impurity band with Stoner-type ferromagnetism appears due to light impurities. Since the formation of the impurity band, its position in the gap and density of states are very sensitive to many parameters [23], it becomes clear why samples produced with the different methods and/or with different conditions exhibited completely different properties.

In the case of $\text{Ti}_{0.087}\text{Co}_{0.013}\text{O}_{2-\delta}$ the local magnetic polarization of cobalt ions is rather strong, so the influence of defects is not so crucial. This could explain why positions of cobalt atoms as well as Co concentration in the $\text{TiO}_{2-\delta}$ matrix influence strongly on either MO spectra or macroscopic magnetization. Nevertheless, in the case of lower concentrations of cobalt in insulating $\text{TiO}_2:\text{Co}$ thin films the role of different defects becomes more important and the value of magnetic moment could achieve huge values up to $22.9 \mu_B/\text{Co}$ [49].

The principal difference between Co- and V-doped $\text{TiO}_{2-\delta}$ films with the same concentration (~ 1 at. %) has been revealed with TKE spectroscopy: the intraionic optical transitions were observed in $\text{TiO}_2:\text{Co}$, that is the evidence of new spin-polarized states appeared inside the bandgap due to the incorporation of Co ions into the octahedral complex of oxygen. In the case of V-doped films the TKE signal was not observed. Together with results of all other performed studies we can conclude about the defect-induced nature of ferromagnetism in $\text{TiO}_2:\text{V}$ at a low concentration of dopant.

5 Conclusions

The magnetic, magnetotransport and MO properties of $\text{TiO}_{2-\delta}:\text{Co}$ and $\text{TiO}_{2-\delta}:\text{V}$ thin films with a small fraction (~ 1 at. %) of TM produced by rf magnetron sputtering under identical conditions were studied. The role of several

different mechanisms of magnetic ordering has been considered and shown to be important. The essential features like the strong MO response and AHE have been found for Co-doped films which depend on the concentration and the film structure contrary to the V-doping.

It has been found that the mechanism of RTFM in TM-doped TiO₂ films is determined not only with the crystal structure and dopant concentration but also with the type of 3d impurity. While for TiO_{2-δ}:V the magnetic properties are determined mainly by defects in TiO_{2-δ}:Co magnetic moments of Co play a main role

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