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# Ferromagnetism on a paramagnetic host background: the case of rutile TM:TiO<sub>2</sub> single crystals (TM = Cr, Mn, Fe, Co, Ni, Cu)

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## Abstract

Single crystals of TiO<sub>2</sub> rutile doped with Cr, Mn, Fe, Co, Ni, and Cu were grown with the flux method in a Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> melt. The samples, checked in their structural and phase homogeneity by x-ray diffraction and micro-Raman spectroscopy, were single-phase needle-shaped crystals several millimetres long. Paramagnetic and ferromagnetic behaviours at room temperature were observed and they are discussed also in connection with the magnetic properties of undoped TiO<sub>2</sub> crystals.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Recent advances in the search of transparent diluted magnetic oxides (DMOs) [1] have taken several directions, with a strong prevalence of studies on thin films grown with pulsed laser deposition, reactive sputtering, molecular beam epitaxy and, recently, ion implantation [2]. Their structural, magnetic and transport properties [3, 4] still present different behaviours for nominally identical stoichiometries and doping levels. It is generally assumed that only single-phase DMOs allow one to realize devices for spintronics applications, since the spin information is carried by the polarized carrier population. In fact, contrasting claims concerning the existence of ferromagnetism (FM) at room temperature (RT) in this class of materials have been reported. In this respect TiO<sub>2</sub> is rather important. FM in anatase and rutile phases of Co-doped TiO<sub>2</sub> was reported in early studies [5]. While later experiments confirmed these results [6–8], other authors ascribe the FM to Co metal precipitation [9, 10]. Furthermore, a recent study has pointed out the presence of both super-paramagnetism and the anomalous Hall

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effect in highly reduced Co-doped rutile thin films containing nanosized Co clusters [11]. In turn, FM with a Curie temperature  $T_C$  higher than 400 K has been observed in Co-doped  $\text{TiO}_2$  thin films grown by pulsed laser deposition and this has been ascribed to the matrix and not to Co segregation [12]. In this frame, the case of Mn doping is different because, as remarked also by Wang *et al* [13], no ferromagnetic phases in metallic Mn, Mn oxides or mixed Ti/Mn oxides are known above 40 K. A similar remark also holds for the mixed Ti/Cu oxides. Therefore, in these cases the detected FM cannot be related to metallic clusters or segregation. Some authors [14] suggest that the oxygen vacancies may play a crucial role for the appearance of FM in Cu-doped  $\text{TiO}_2$  and one effect of doping is just to increase their number. Besides, also in Co-doped  $\text{TiO}_2$  a strong interaction between Co and vacancies is invoked to explain the high Co magnetic moments and  $T_C$  values [15].

However, also because of the contrasting evidence, the mechanisms responsible for FM in DMOs are still under debate. Double-exchange and bound magnetic polaron formation are all potentially playing a role depending on the doping level, oxygen stoichiometry [16, 17] and the possibly related free charges. In addition, the effect of the host matrix alone on the magnetic properties has not yet been thoroughly clarified.

What has been reported above clearly illustrates the extreme difficulty in identifying the source of magnetic response in these systems and the need for careful identification of relevant phase(s). In this frame, the study of transition metal (TM)-doped single crystals has been virtually neglected. The use of pure rutile  $\text{TiO}_2$  single crystals has been limited to substrates for ion implantation [18] or Co thin-film evaporation [19]. Although unexplored in the case of DMOs, the growth of doped single crystals in equilibrium conditions (that can take typically several days) is expected to produce segregation-free and homogeneous samples, at least for low concentration of dopants, which can be profitably compared to samples produced in out-of-equilibrium conditions.

In the present study, we report on the magnetic properties of a set of rutile TM-doped  $\text{TiO}_2$  single crystals (TM = Cr, Mn, Fe, Co, Ni, and Cu) obtained with dopant incorporated into the rutile matrix during the equilibrium growth. Unlike most of published papers, that are focused on a single dopant, our choice of selecting several TM dopants allowed us to compare the magnetic properties of a homogeneous set of samples, which share the same single crystal host matrix. For all the samples we provide evidence, at room temperature, of paramagnetism (PM) and FM. The origin of magnetism in our single crystals is discussed by also considering the contribution to the magnetic properties arising from the undoped  $\text{TiO}_2$  host matrix.

## 2. Experimental details

The growth procedure involves the dissolution of the titanium dioxide  $\text{TiO}_2$  in molten  $\text{Na}_2\text{B}_4\text{O}_7$  at high temperature with spontaneous nucleation and crystal growth of  $\text{TiO}_2$  achieved by slow cooling ( $2^\circ\text{C h}^{-1}$ ) of the solution from 1100 to  $750^\circ\text{C}$  [20]. The choice of  $\text{Na}_2\text{B}_4\text{O}_7$  over other fluxes is known to favour the growth of transparent crystals with a light colour and compositions close to nominal  $\text{TiO}_2$  [20, 21], and is therefore suitable for the present magneto-optical applications, whilst other fluxes give rise to strongly coloured crystals [22]. The dopants were added as nitrates. The concentration of TM was nominally 5 at.% in  $\text{TiO}_2$ , although, as we will discuss below, the actual concentration is about or below 1%. The crystals grew in the form of needles elongated in the direction of the crystallographic  $c$ -axis and their size was approximately  $0.10 \times 0.05 \times 5.00 \text{ mm}^3$ . Among our samples, only the Cr-doped one is non-transparent and dark.

Micro-Raman spectra were collected at RT by a Dilor Labram spectrograph with a HeNe laser (632.8 nm) as exciting source and a light power less than 10 mW at the sample. The

microscope coupled confocally to the spectrograph with a 100× objective of numerical aperture 0.9 and a confocal hole opened at 200 μm yields a depth of focus of about 2.5 μm.

Powder x-ray diffraction (XRD) patterns were collected with a Thermo ARL X'tra diffractometer equipped with a Thermo Electron solid state detector in the  $2\theta$  range 10°–90° using Cu K $\alpha$  radiation. Single-crystal diffraction data were collected with a Philips PW1100 diffractometer using Mo K $\alpha$  radiation.

Microanalyses (energy dispersive x-ray analysis: EDX) were performed with a Phenix EDX spectrometer connected to a Philips 515 scanning electron microscope (SEM).

Static magnetic moments were measured at 500 and 2000 Oe from 352 to 2 K with a SQUID Quantum Design magnetometer. Magnetization loops were collected at RT for magnetic fields ( $H$ ) ranging between 0 and  $\pm 4000$  Oe.

### 3. Results and discussion

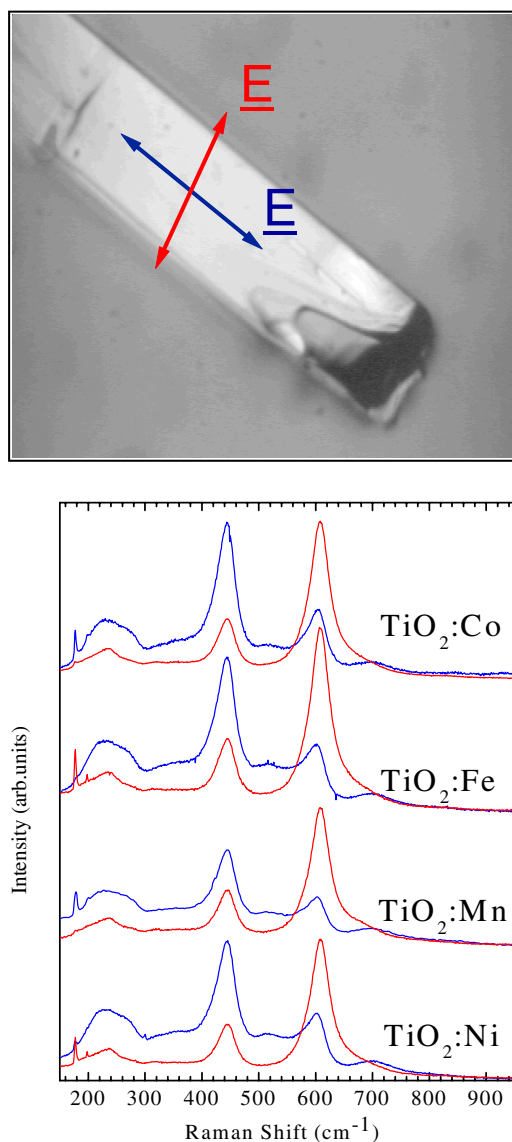
In figure 1 the micro-Raman spectra of some TM:TiO<sub>2</sub> single crystals are shown. The intensity, wavenumber and polarization dependence of the observed bands are in good agreement with the data reported in the literature for the pure compound [23]. Indeed rutile TiO<sub>2</sub> belongs to the D<sub>4h</sub> space group (no. 136) and the main Raman signals are due to the E<sub>g</sub> mode at  $\sim 445$  cm<sup>-1</sup> and to the A<sub>g</sub> mode at  $\sim 610$  cm<sup>-1</sup>. The broad band at 235 cm<sup>-1</sup> is probably due to multi-phonon process rather than a fundamental one-phonon process. It is important to notice that in all cases the TM doping does not cause relevant changes in the Raman spectra. In addition, if we consider the linewidth of the A<sub>g</sub> mode at  $\sim 610$  cm<sup>-1</sup>, we obtain from a best-fitting procedure a value of  $\sim 43$  cm<sup>-1</sup> for all the samples. Similar values have been obtained for pure TiO<sub>2</sub> bulk single crystals [24]. These observations suggest a comparable good quality in terms of crystalline structure for our samples. The spectra have also been collected from different points of each crystal: no difference was detected during micro-Raman mapping, which indicates that the samples can be regarded as homogeneous on a micrometric scale. The same result was achieved by optical inspection through the confocal microscope, which allowed us also to explore the in-depth homogeneity.

The TM doping concentration was evaluated by an EDX probe. The results indicate a concentration of Mn ions of less than 1% in the Mn:TiO<sub>2</sub> sample, and a concentration of Cr ions of about 0.5% in the Cr:TiO<sub>2</sub> sample. For the other samples the impurity concentration was below the probe sensitivity. No evidence of other contaminants was found within the experimental resolution.

Further evidence of the crystalline structure has been obtained by XRD analysis from both single crystals and powders prepared by grinding the single crystals. All samples showed an XRD pattern ascribed to the TiO<sub>2</sub> rutile phase. Moreover, no evidence of other crystalline phase was detected. In particular, no reflection from the TiO<sub>2</sub> anatase phase was found, in agreement with micro-Raman results. Attempts to evaluate the TM impurity concentration from a refinement of both powder and single crystal data did not provide any evidence of TM effects, due to the low concentration of impurities.

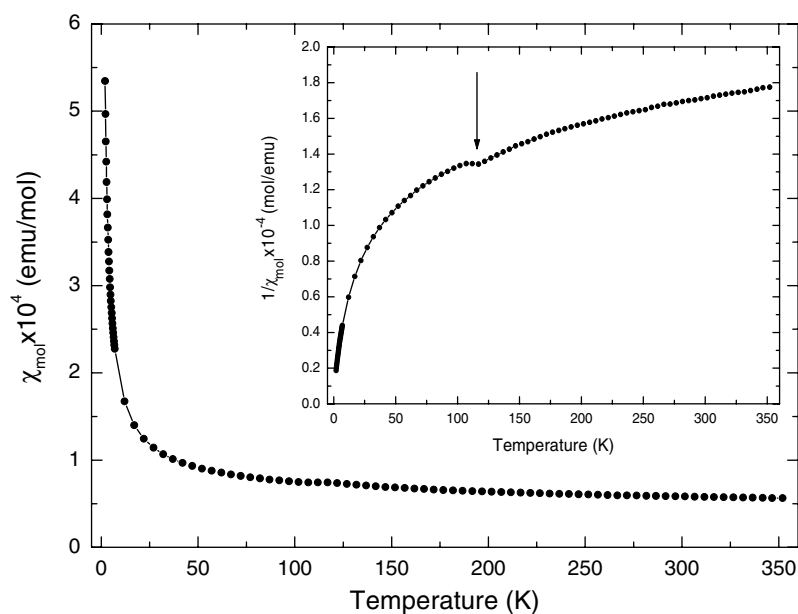
The lattice parameters of the pure TiO<sub>2</sub> sample were  $a = 4.5925(9)$  and  $c = 2.9583(4)$  Å. For the doped samples the same lattice parameters, within experimental error, were measured, which indicates that the doping level was not high enough to induce relevant structural distortions.

The magnetic moment plotted as a function of temperature shows, for all the considered samples, an overall behaviour closely resembling that of a paramagnet. As an example, figure 2 shows the molar magnetic susceptibility ( $\chi_{\text{mol}}$ ) of Co:TiO<sub>2</sub>, so far the most studied rutile-based DMO single crystals, as obtained by applying a 500 Oe magnetic field parallel to the



**Figure 1.** Top panel: image of a representative TM:TiO<sub>2</sub> crystal obtained by the microscope coupled with the Raman spectrometer. The width of the crystal is about 0.1 mm. The arrows indicate the two configurations for light polarization used in Raman measurements. Bottom panel: micro-Raman spectra of representative TM:TiO<sub>2</sub> crystals measured with two different light polarizations with respect to the crystal's *c*-axis. The red and blue curves are obtained with light polarization perpendicular and parallel to the *c*-axis, respectively (see panel above).

crystal's *c*-axis. However, deviations from the expected linear behaviour of the  $1/\chi_{\text{mol}}$  curve (inset of figure 2) were observed, suggesting the presence of a magnetic phase. Furthermore, a discontinuity, evidenced by the vertical arrow, at about 110 K is quite similar to that observed by Keys and Muly in reduced rutile crystals [25]. This finding suggests that the doped TiO<sub>2</sub> crystals can be oxygen deficient, in agreement with previous results on rutile crystals obtained from borate fluxes [21], as expected when Ti<sup>4+</sup> cations are partially replaced by divalent or

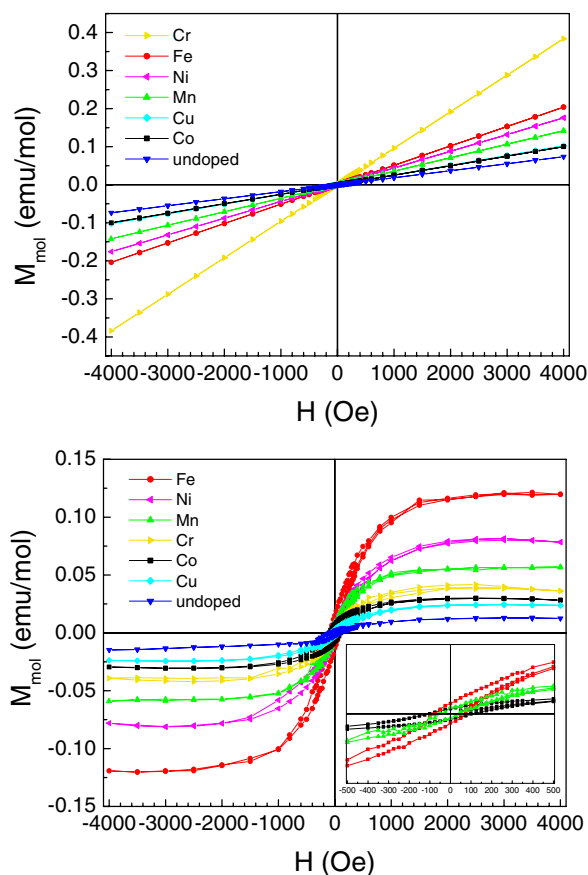


**Figure 2.**  $\chi_{\text{mol}}$  versus  $T$  detected for the Co:TiO<sub>2</sub> crystals. In the inset  $1/\chi_{\text{mol}}$  versus  $T$  is reported.

trivalent ions. We remark that, as reported in [25], the presence of a very high oxygen vacancy concentration in TiO<sub>2</sub> gives rise to an antiferromagnetic behaviour.

To verify the presence of the magnetic phase and the kind of magnetic order, static molar magnetization ( $M_{\text{mol}}$ ) versus  $H$  curves have been collected at RT with  $H$  applied parallel to the crystal's  $c$ -axis. After subtraction of the paramagnetic contribution, hysteresis loops have been extracted from the experimental data so that, for all the samples, including the undoped TiO<sub>2</sub>, a superposition of a ferromagnetic (hysteretic cycle, figure 3 (bottom panel)) and paramagnetic behaviour (figure 3 (top panel)) is evidenced.

From the data shown in figure 3 (top panel), it is possible to estimate the concentration of the ions contributing to the paramagnetic behaviour. By considering the most probable oxidation states for the TM ions, that is Cr<sup>3+</sup> (spin 3/2), Mn<sup>4+</sup> (spin 3/2), Fe<sup>3+</sup> (spin 5/2), Co<sup>2+</sup> and Ni<sup>3+</sup> in high spin configuration (spin 3/2) and Cu<sup>2+</sup> (spin 1/2), the resulting molar concentrations are respectively 1.24%, 0.27%, 0.22%, 0.11%, 0.41%, and 0.57%. These values have been obtained by taking into account the contribution of the undoped TiO<sub>2</sub> crystals (figure 3 (top panel)), for which the already present PM can be ascribed both to oxygen sub-stoichiometry (which yields Ti<sup>3+</sup> paramagnetic ions) and to the presence of unwanted paramagnetic impurities. These concentration data are in fair agreement with the estimation provided by the EDX analysis, but for Cr doping. Indeed, we observe that, among our samples, the paramagnetic susceptibility of the Cr-doped sample is the highest. This is the only sample that is non-transparent and dark, possibly due to the presence of a very high amount of oxygen vacancies. As consequence, a higher amount of paramagnetic Ti<sup>3+</sup> ions could be present in this sample, so invalidating the evaluation of Cr<sup>3+</sup> concentration determined from the paramagnetic data. Finally, concerning Fe and Mn doping, we observe that the estimated Fe-ion concentration agrees with preliminary Mössbauer measurements indicating a dopant concentration well below 1%, while the concentration of Mn ions agrees with that estimated from x-ray photoemission spectra [26].



**Figure 3.** Top panel: paramagnetic contributions at RT of the TM:TiO<sub>2</sub> and undoped TiO<sub>2</sub> crystals. Bottom panel: hysteresis curves at RT of the TM:TiO<sub>2</sub> and undoped TiO<sub>2</sub> crystals. Inset: enlarged view of the hysteresis cycles of Mn, Fe and Co:TiO<sub>2</sub> crystals (same symbols of the figure).

From the hysteresis loops the molar saturation magnetization  $M_{\text{Smol}}$  is deduced. It is interesting to note that the undoped TiO<sub>2</sub> sample also shows a hysteresis curve that we ascribe to contamination, with a value for  $M_{\text{Smol}}$  of about 0.013 emu mol<sup>-1</sup>. Once this value is subtracted from those measured for the TM-doped samples, the values of  $M_{\text{Smol}}$  result in being about 0.029 emu mol<sup>-1</sup> for Cr, 0.044 for Mn, 0.110 for Fe, 0.017 for Co, 0.069 for Ni and 0.012 for Cu. From these data the amount of the magnetic ions involved in FM can be estimated: by assuming again Cr<sup>3+</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup> and high spin Co<sup>2+</sup> and Ni<sup>3+</sup> ions, and a parallel spin alignment in the host matrix, the lowest limit for the magnetic ions contributing to the ferromagnetic ordering at RT results in being about  $1 \times 10^{-4}$  to  $4 \times 10^{-4}$  molar per cent. Therefore, the low  $M_{\text{Smol}}$  value has to be ascribed to a low fraction of TM ions involved in ferromagnetic ordering, while most of them remain in a paramagnetic state.

In spite of very low amount of ‘ferromagnetic ions’, it was also possible to measure the coercive fields  $H_c$ . The following values have been obtained:  $H_c \cong 50$  Oe for Cr:TiO<sub>2</sub>, Mn:TiO<sub>2</sub> and Ni:TiO<sub>2</sub>,  $H_c \cong 75$  Oe for Fe:TiO<sub>2</sub> and Cu:TiO<sub>2</sub>,  $H_c \cong 100$  Oe for Co:TiO<sub>2</sub> (see the details of loops at low fields for Mn, Fe and Co:TiO<sub>2</sub> reported, as examples, in the inset of figure 3 (bottom panel)). We point out here the narrow range of  $H_c$  values for the

**Table 1.** Valence of the TM impurity, number of unpaired 3d electrons, remanent magnetization (expressed in  $\text{emu mol}^{-1}$  or normalized to the value measured for  $\text{Cu}:\text{TiO}_2$ ) for the set of TM-doped  $\text{TiO}_2$  rutile single crystals.

Sample	TM ion valence	Unpaired 3d electron spins	Remanent magnetization ( $\text{emu mol}^{-1}$ )	Remanent magnetization (normalized to Cu value)
$\text{Cr}:\text{TiO}_2$	+3	$\uparrow\uparrow\uparrow (3/2)$	0.0028	0.97
$\text{Cr}:\text{TiO}_2$	+5	$\uparrow (1/2)$	0.0028	0.97
$\text{Mn}:\text{TiO}_2$	+4	$\uparrow\uparrow\uparrow (3/2)$	0.0097	3.34
$\text{Fe}:\text{TiO}_2$	+3	$\uparrow\uparrow\uparrow\uparrow (5/2)$	0.0149	5.14
$\text{Co}:\text{TiO}_2$	+2 (H.S.)	$\uparrow\uparrow\uparrow (3/2)$	0.0074	2.55
$\text{Ni}:\text{TiO}_2$	+3 (H.S.)	$\uparrow\uparrow\uparrow (3/2)$	0.0064	2.21
$\text{Cu}:\text{TiO}_2$	+2	$\uparrow (1/2)$	0.0029	1.00

different doping ions, also including the  $H_c$  value obtained for the undoped  $\text{TiO}_2$  ( $H_c \cong 85 \text{ Oe}$ ). Besides, these values are in agreement with those reported in the literature for thin films (see for example [2, 13]): this is rather surprising if we consider that the magnetic properties should be strongly dependent on the sample dimensionality, as well as on the  $\text{TiO}_2$  phase. Anyway, this very narrow range of the  $H_c$  values allows us to at least exclude, as the origin of FM, the segregation of metallic Fe, Co, and Ni phases because they would yield in principle different  $H_c$  values and this can suggest a common origin for the FM observed in our samples.

When TM ions, of whichever kind, are introduced into the  $\text{TiO}_2$  matrix, the  $M_{\text{Smol}}$  values are always larger than that found for the pure  $\text{TiO}_2$  crystal. Therefore, despite the evidence of FM in the undoped  $\text{TiO}_2$  crystals and despite the low concentration of dopant ions, a contribution to FM related to TM doping can be considered. A possible origin is a static fluctuation in the local concentration of ions. Indeed, an increase of the local concentration can favour FM, whereas very low local concentration prevents any magnetic ordering. But, in this frame, the case of Mn doping is itself conflicting because no FM phases in Mn oxides or mixed Ti/Mn oxides are known above 40 K [13], and similar remarks also hold for the Cu and mixed Ti/Cu oxides. Therefore, at least in Mn- or Cu-doped samples, the detected FM has to be related to ions diluted into the matrix. Moreover, our data extend recent observations on Cu-doped  $\text{TiO}_2$ : while in [14] FM in Cu-doped anatase is reported, we provide evidence of FM also in Cu-doped rutile.

It is interesting to note that the remanent magnetization in most cases increases with the number of 3d unpaired electrons. This is true for Fe, Mn, Ni, Co, and Cu doping, while deviations from this behaviour are only found for Cr doping (see table 1).

For example,  $\text{Cu}^{2+}$  has one unpaired electron, whereas  $\text{Fe}^{3+}$  has five unpaired electrons in the 3d shell. The ratio between the number of unpaired electrons in iron and copper is 5, and the ratio between the remanent magnetization for samples with these impurities is 5.14.  $\text{Mn}^{4+}$  has three unpaired electrons, and the ratio between the remanent magnetization of  $\text{Mn}^{4+}$  and  $\text{Cu}^{2+}$  is 3.34.

In the case of  $\text{Cr}^{3+}$  ( $3d^3$  ion), the scaling relation is not obeyed, while an agreement is found by assuming a  $\text{Cr}^{5+}$  ( $3d^1$  ion) impurity. This oxidation state is not well known in simple Cr compounds, but many oxide lattices containing chromium may, when suitably oxidized or reduced, contain  $\text{Cr}^{5+}$  [27].

We can assume the dependence of remanent magnetization on the number of unpaired d electrons as a further indication that magnetic ordering is related to the kind of magnetic ion introduced into the lattice as an impurity.



In conclusion, rutile TiO<sub>2</sub> single crystals doped with a large choice of TM ions have been grown and a superposition of ferromagnetic and paramagnetic behaviour was observed at room temperature in all the samples. The possible contribution of the dopant TM ions to the two different magnetic phases was evaluated: only a small fraction of ions is involved in ferromagnetic ordering at room temperature, taking into account the magnetic contamination observed already in the undoped TiO<sub>2</sub> matrix. Finally, a correlation is found between the measured remanent magnetization and the number of unpaired d electrons in the magnetic ions.

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