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EPR study of Mn-implanted single crystal TiO$_2$

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Abstract. Single crystals of manganese-implanted TiO$_2$ rutile have been investigated by electron paramagnetic resonance (EPR) technique at room temperature. ESR spectra have been interpreted to correspond to the transitions among the spin multiplet (S=3/2) of the paramagnetic Mn$^{4+}$ ion. Characteristic six-line hyper-fine splitting of the ESR spectra resulting from the spin I=5/2 of the Mn$^{55}$ nucleus has been observed. Analysis of EPR spectra shows that manganese in TiO$_2$ rutile host substitutes for Ti$^{4+}$ ions. Two equivalent Mn$^{4+}$ centers have been observed in the EPR spectra in correspondence with two equivalent octahedral positions of Ti ions in the rutile structure. Parameters of the crystal field of orthorhombic symmetry on the Mn$^{4+}$ centers have been obtained as result of computer modelling.

1. Introduction
The discovery of high-Curie temperature diluted magnetic oxides (various oxides doped by magnetic atoms, such as TiO$_2$, ZnO, SnO$_2$ and others) has attracted much attention due to their potential value for the development of the spintronic devices. A number of experimental works claim the room temperature ferromagnetism observed in various oxides. Despite of essential progress achieved in this field there is still an issue about either intrinsic or extrinsic magnetism is realized in these materials. It has been shown that the local environment of doped magnetic ions and oxygen defects have a drastic effect on the magnetic properties of these materials. There are a few theoretical calculations showing that the magnetic state of the doped ions is expected to be very sensitive to the local crystalline structure [1,2]. Therefore, there is a strong need in the studies that probe the local structure near the doped magnetic ion. On the other hand, Electron Paramagnetic Resonance (EPR) is well known technique to probe the local magnetic and structural properties of crystals. In particular, it is a very efficient method for the investigations of the local environment around a substitutional magnetic ion in various crystals [3,4].

In this study, the local structure of Mn ions in the single crystalline TiO$_2$ rutile doped by ion-beam implantation has been studied by EPR technique. The samples under study were (100) and (001) substrates implanted by Mn and annealed at very high temperature (T=950°C) to prevent manganese clusterization and to obtain highly diluted concentration of Mn ions in the TiO$_2$ host. We have shown that implantation with 40 keV Mn$^+$ ions with subsequent annealing at high temperature results in formation of the paramagnetic Mn$^{4+}$ centers substituting Ti$^{4+}$ ions in the rutile structure [1,2,5,10,11]. The parameters of spin Hamiltonian of the Mn$^{4+}$ ions in the implanted TiO$_2$ rutile crystals have been obtained and discussed.
2. Experimental procedures

Single crystalline (100) and (001) TiO$_2$ rutile substrates have been implanted on the ILU-3 ion accelerator (Kazan Physical-Technical Institute) with 40 keV Mn$^+$ ions to a fluence of $1.50 \times 10^{17}$ ions/cm$^2$ at ion current density of 8 µA/cm$^2$. The sample holder was cooled by flowing water during the implantation to prevent the samples from overheating. The implanted samples have been annealed at $T=950$°C in air during 1 hour. Structural studies have revealed that annealing procedure results in the diffusion of the most of manganese impurity out of the implanted layer with thickness of about 30 nm [3]. As another result of the post-implanting thermal treatment the samples has became transparent and the colour of samples has changed from dark-grey to light-orange.

The annealed samples have been studied by electron paramagnetic resonance (EPR) technique using Bruker EMX X-band spectrometer (9.8 GHz) at room temperature. Angular dependences of EPR spectra have been recorded with the static magnetic field rotated either in the plane of the plate-like samples ("in-plane" geometry) or in the two perpendicular planes ("out-of-plane" geometry) nearly coinciding with crystallographic planes of a substrate. That is in total there are three rotational planes for each sample to obtain the angular dependences of the EPR spectra.

3. Experimental results and discussion

For the both (001) and (100) manganese-doped TiO$_2$ rutile single crystals multi-line EPR spectra have been observed. The EPR spectra are strongly anisotropic with the resonance fields of the components up to 16 kG.

The typical EPR spectra observed for the (001) sample for the DC field applied along the [100], [001] and [110] crystal directions are shown in Fig. 1. The angular dependences of the resonance fields for the (001) sample on the rotation of the magnetic field in the (001) plane (in-plane geometry) and in the (100) plane (out-of-plane geometry) are presented in Fig.2a and Fig.2b, respectively. The angular dependences of the resonance fields for the (100) sample on the rotation of the DC field in the (001) plane (out-of-plane geometry) and in the (100) plane (in-plane geometry) are presented in Fig.3a and Fig.3b, respectively.

![Figure 1. Experimental EPR spectra for three symmetry direction of the Mn-implanted TiO$_2$ (001) sample. Narrow groups of lines belong to the Mn$^{4+}$ centers, single lines are due to Fe$^{3+}$ centers, and the broad lines is the background signal of the cavity and sample holder.](image-url)
A strong anisotropy of the EPR lines as well as typical six-line pattern of the Mn$_{55}$ hyperfine structure [1,2] clearly indicates that the observed EPR spectra are due to paramagnetic Mn ions. The (001) plane rotation patterns of both samples (Figs. 2&3) reveal a presence of at least two equivalent centers with symmetry axes perpendicular to each other. Besides, a set of additional EPR lines has been observed which EPR parameters and the resonance field dependence on angle unambiguously point to EPR of Fe$^{3+}$ ions. It should be noted that room temperature EPR is very sensitive to any small concentrations of the paramagnetic Fe$^{3+}$ centers [9]. Apparently the contamination by iron results from a non-perfect magnetic separation of ions in the implanter due to very close masses of the Fe and Mn atoms which are neighbours in the periodic table. EPR signal on Fe$^{3+}$ centers in the Fe-implanted TiO$_2$ crystals have been studied in details in our previous work [3]. In this work we pay attention to the manganese resonance signal only. Manganese in rutile has a large fine structure splitting, so that for the most of the crystal orientations the hyperfine structure patterns of various electronic transitions are well
separated from each other. Besides the manganese resonances could easily be distinguished from the Fe\(^{3+}\) signal by their characteristic hyperfine structure.

We found that the observed EPR manganese signal belongs to the Mn\(^{4+}\) centers substituting Ti atoms in the rutile lattice. Our theoretical analysis provides a set of the spin-Hamiltonian parameters which is very close to that of reported in the literature for Mn\(^{4+}\) ions in a bulk rutile crystal \[1,2,5,10,11\]. It should mentioned that both our and the literature data \[1,2\] indicate that in the recent works of D. Menzel \textit{et al} and F. Iacomi \textit{et al} \[6,7\] a wrong assignment of the single (without hyperfine structure!) EPR lines as the resonance signal of Mn\(^{4+}\) ions have been made. These lines should be attributed to other paramagnetic species (e.g. Fe\(^{3+}\)). Besides an assignment of the hyperfine lines at the central part of their spectra as due to Mn\(^{2+}\) ions is also suspicious.

It is known that the ground state of free Mn\(^{4+}\) ion (3d\(^3\) electronic configuration) is \(^4\)F. In the octahedral coordination the ground state of d\(^3\) ions is an orbital singlet. However as result of the spin-orbital coupling a fine structure splitting of spin quartet of the ground state with nearly isotropic g-factor is observed in the EPR of d\(^3\) ions \[8\]. Besides the hyperfine interaction of electron spin of Mn\(^{4+}\) with nuclear spin (I=5/2) results in the additional six-fold splitting of the spin levels. The unit cell of rutile contains two equivalent lattice sites of local orthorhombic (D\(_{2h}\)) symmetry. Thus, the spin Hamiltonian of the Mn\(^{4+}\) centers should include three terms which are: 1) the nearly isotropic Zeeman term, 2) the crystal field interaction of the orthorhombic symmetry and 3) hyperfine interaction of the manganese nuclear and electron spins \[8,12\]. For S=3/2, only terms involving the second orders of the spin operators are necessary:

\[
H = \beta H g S + D \left( S_z^2 - \frac{35}{12} \right) + E (S_x^2 - S_y^2) + I A S ,
\]

where g, D, E and A are the experimentally determined spin-Hamiltonian parameters. Experimental data reveals a very small anisotropy of the A tensor of the hyperfine interaction. It is also obvious from experimental spectra that the hyperfine interaction is much smaller than the Zeeman one, therefore we can extract nearly isotropic hyperfine constant directly from the splitting of the resonance lines in hyperfine patterns. Our estimations provide a nearly isotropic A = 78 G.

To obtain parameters of the fine structure splitting parameters of Mn\(^{4+}\) ions a computer modelling has been performed to simulate digitally the angular dependences of the resonance fields at an arbitrary rotation plane. The central positions of the hyperfine groups in the rotational patterns presented in Figs. 2&3 have been fitted. In order to extract the crystal field parameters more accurately the “in-plane” experimental patterns for both samples have been preferred in modelling due to the smallest misalignment between the rotational and crystalline planes during the in-plane measurements (<1 degree).

\[\text{Fig. 4.} \quad \text{On the left: the unit cell of the rutile lattice (O and Ti ions are shown by large dark and small bright spheres, respectively). On the right: mutual orientation of elongated TiO}_6\text{ octahedrons centered in the middle and corners of the TiO}_2\text{ unit cell.}\]
Before we proceed with the simulation results it is useful to look at the rutile crystalline structure. The crystal structure of rutile is shown in Fig. 4. There are two equivalent sites per unit cell. The local symmetry of each site is $D_{2h}$ and the principal axes of their spin-Hamiltonian parameters are perpendicular to each other and also perpendicular to the tetragonal axis of the crystal structure. Therefore, in the case of the substitutional Mn$^{4+}$ ions located on the Ti$^{4+}$ sites in the oxygen octahedrons centers one should expect two equivalent sets of paramagnetic centers in the crystal with principal axes given in Table 1. We observe 90° period of paramagnetic spectrum while turning the crystal around the c axis that proves that manganese atoms in fact substitute the Ti$^{4+}$ ions in the rutile lattice.

**Table 1** Principal axis directions of the Mn$^{4+}$ centers in the rutile crystal.

| Principal axes of the CF term | Crystalline directions | Sites   |
|-------------------------------|------------------------|---------|
| x                             | [110]                  | Site I  |
| y                             | [110]                  |         |
| z                             | [001]                  |         |
| x                             | [110]                  | Site II |
| y                             | [110]                  |         |
| z                             | [001]                  |         |

We have found that to simulate the experimental patterns of the most intense lines one have to use the same set CF parameters for each sort of the Mn$^{4+}$ paramagnetic centers with their principal axes as given in the Table 1. Results of the modelling are presented in Figs. 2&3 by solid lines. The best agreement has been obtained with values of CF parameters as given in Table 2.

**Table 2.** Crystal field parameters of the Mn$^{4+}$ centers

| D [G]       | E [G]   | A [G]  | $g_x$   | $g_y$   | $g_z$   |
|-------------|---------|--------|---------|---------|---------|
| 4290±20     | -1420±5 | 78±2   | 1.988±0.02 | 1.985±0.02 | 1.985±0.02 |

Thus, our analysis of EPR results with aid of computer modelling shows that high-temperature annealing treatment of the manganese-implanted TiO$_2$ rutile results in appearance of the paramagnetic Mn$^{4+}$ centers which substitute for the Ti$^{4+}$ ions in the rutile structure. Minor difference with the literature data on the bulk rutile crystal [1,2] may be attributed to the crystal structure imperfections of our Mn-implanted rutile samples (for instance, due to formation of oxygen vacancies and interstitial defects). We have to note also that in some recent publications a wrong assignment of the observed EPR lines as the resonance signal of Mn$^{4+}$ have been done [6,7].

4. Conclusion
We have established that the paramagnetic Mn$^{4+}$ ions formed as result of the Mn$^+$ ion-beam implantation of the single crystalline TiO$_2$ rutile substrates with following high-temperature annealing procedure. The local environment of orthorhombic symmetry on the doped Mn$^{4+}$ magnetic ions has been determined. Two equivalent Mn$^{4+}$ centers have been observed in the EPR spectra in correspondence with two equivalent octahedral positions of the Ti ions in the rutile structure. The spin
Hamiltonian parameters of the Mn$^{4+}$ centers in manganese-implanted rutile crystals have been obtained.

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