Defect types and room-temperature ferromagnetism in undoped rutile TiO_2 single crystals*

Li Dong-Xiang(李东翔)[a)b)], Qin Xiu-Bo(秦秀波)[c)†], Zheng Li-Rong(郑黎荣)[d)], Li Yu-Xiao(李玉晓)[b)], Cao Xing-Zhong(曹兴忠)[a)], Li Zhuo-Xin(李卓昕)[a)], Yang Jing(杨 静)[a)], and Wang Bao-Yi(王宝义)[a)]

[a)] *Key Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*
[b)] *School of Physical Engineering, Zhengzhou University, Zhengzhou* 450001, *China*
[c)] *Research Center for Application of Nuclear Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*
[d)] *Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*

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Room-temperature ferromagnetism has been experimentally observed in annealed rutile TiO_2 single crystals when a magnetic field is applied parallel to the sample plane. By combining X-ray absorption near the edge structure spectrum and positron annihilation lifetime spectroscopy, Ti^{3+}–V_O defect complexes (or clusters) have been identified in annealed crystals at a high vacuum. We elucidate that the unpaired 3d electrons in Ti^{3+} ions provide the observed room-temperature ferromagnetism. In addition, excess oxygen ions in the TiO_2 lattice could induce a number of Ti vacancies which obviously increase magnetic moments.

Keywords: annealing, oxygen vacancies, Ti^{3+}–V_O defect complexes, ferromagnetism

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1. Introduction

Dilute magnetic semiconductors (DMSs) with magnetic and semiconducting properties are regarded as new generation materials due to their potential applications in spintronic devices.[1–5] Since the first discovery of room-temperature ferromagnetism (RTFM) in Co-doped anatase TiO_2 thin films,[6] several studies have been performed on the magnetism of TiO_2 doped with transitional metals (TMs), such as Mn, V, Cr, Nb, Fe, and Ni. Different research groups[7–10] learned about the magnetic properties of TM-doped TiO_2 samples using the first-principles method, but the origin of ferromagnetism in magnetic-transition-element-doped oxide semiconductors is still under debate as to whether ferromagnetism is intrinsic[11,12] or whether it comes from the precipitation of magnetic clusters.[13] Recently, Coey's group[14] reported on magnetism observed in HfO_2 thin films on sapphire or silicon substrates. Hong *et al*.[15] and Yoon *et al*.[16] reported room-temperature ferromagnetism in pure TiO_2 films. These results are surprising and have generated great interest in this new phenomenon, also known as d^0 magnetism.[17] Its appearance can exclude the influence of magnetic elements (imported by doping transitional metal) from the origins of ferromagnetism.

First-principles calculations indicated that the ferromagnetism of undoped rutile TiO_2 largely originates from the d orbitals of low-charge-state Ti ions converted from Ti^{4+} ions induced by the surface oxygen vacancies.[18] However, few experimental studies of exploring the origin of room-temperature ferromagnetism in undoped TiO_2 single crystals exist. In this study, the influence of annealing temperature in a high vacuum on structure and magnetism has been addressed. We aim to answer two questions: (i) what is the defect types of undoped TiO_2 single crystals annealed in a high vacuum; (ii) what is the origin of room-temperature ferromagnetism after high-temperature annealing.

2. Experiments

Commercial rutile TiO_2 single crystals were obtained from the Institute of Shanghai Optics and Fine Mechanics, Chinese Academy of Sciences. The size of the samples was $5\times5\times0.5$ mm^3, corresponding to a mass of 53.25 mg. Some samples were annealed in a vacuum annealing furnace (vacuum: 10^{-4}–10^{-5} Pa) from 1023 to 1273 K for 1 h. The structure and magnetism of TiO_2 single crystals were characterized by X-ray diffraction (XRD), X-ray absorption near the edge structure (XANES) spectrum, and superconducting quantum interference device (quantum design MPMS-XL5) at room temperature. The XANES analyses were performed on the beam lines 1W1B from the Beijing Synchrotron Radiation Facility (BSRF). Positron annihilation lifetime spectroscopy (PALS) was used to probe the vacancy-type defects of TiO_2 single crystals with ^{22}Na as the positron source. Two of the same samples were tightly clamped on both sides of ^{22}Na radioactive sources, forming a sandwich structure. The prompt time resolution of the system was 190 ps. Each spectrum con-

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†Corresponding author. E-mail: qinxb@ihep.ac.cn

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tains a total number of 2×10^6. The lifetime spectra were deconvoluted by using the code LT 9.0 software.

3. Results and discussion

The annealed samples in a high vacuum changed from transparent to dark-blue, which are most likely to be related to F^+ centers (the electrons in singly occupied oxygen vacancies).[19] The XRD patterns of virgin and annealed TiO_2 single crystals can be indexed to a pure rutile phase. No impurity phases were detected within the detection limits of the instrument. A representative XRD spectrum with an annealed TiO_2 single crystal in a high vacuum at 1273 K is shown in Fig. 1.

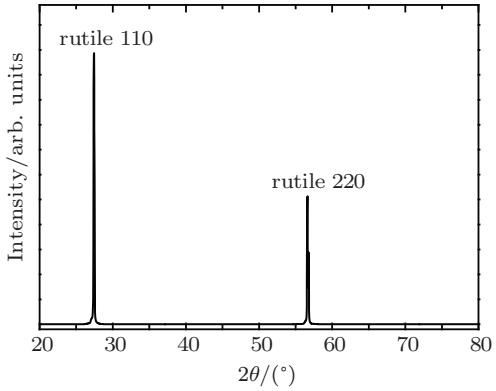


Fig. 1. XRD spectrum of the TiO_2 single crystal annealed in a high vacuum at 1273 K.

The pre-edge peaks of the XANES spectra of annealed samples in a high vacuum contain three major features denoted as A1, A2, and A3, as shown in Fig. 2(a). The three protrusions near 4970 eV are related to the 3d electrons of Ti.[20] The origin of the A2 and A3 features are attributed to 1s→3d transitions and assigned to $1s\rightarrow2t_{2g}$ and $1s\rightarrow3e_g$ transitions in an octahedral field, respectively.[21] The origin of the A1 peak is less clear, but it is also believed to be associated with Ti 3d–4p hybridized states.[21] The Ti pre-edge XANES signals allow us to obtain complementary information on the feature of Ti–O bonding by studying the variation of the pre-edge peaks.

Normalized derivative spectra of annealed samples in a high vacuum are shown in Fig. 2(b). The dashed line indicates the highest peak corresponding to the energy value. We obtained a value of 4978.692 eV (E_0) for the annealed TiO_2 single crystals in a high vacuum. This value is between the Ti^{4+} absorption edge at 4979.8 eV and the $Ti^{3.4+}$ absorption edge at 4977.2 eV.[22] The presence of a Ti^{3+} species is very likely after high-temperature annealing. It is possibly associated with oxygen vacancies due to

$$4Ti^{4+} + O^{2-} \rightarrow 4Ti^{4+} + 2e^- + V + 0.5O_2$$
$$\rightarrow 2Ti^{4+} + 2Ti^{3+} + V + 0.5O_2,$$

where V represents an empty position (anion-vacant site) originating from the removal of O^{2-} from the lattice, and here represents an oxygen ion vacancy.

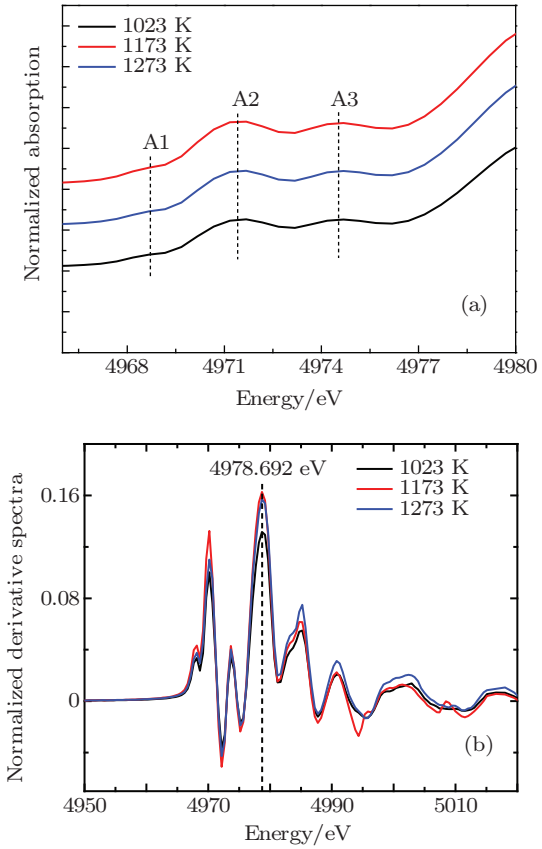


Fig. 2. (color online) Normalized XANES spectra at the Ti K-edge for annealed TiO_2 single crystals in a high vacuum: (a) pre-edge peak spectra. All spectra are plotted on the same vertical scale and displaced vertically for clarity. (b) Normalized derivative spectra.

Fitting results of positron lifetime spectra for annealed samples in a high vacuum are shown in Table 1. The positron annihilation lifetime spectroscopy of TiO_2 single crystals yields three distinct lifetime components: τ_1, τ_2, and τ_3, with relative intensities I_1, I_2, and I_3. The value of τ_2 is a major concern in reflecting size and types of defects (vacancies and/or complexes). Its relative intensity (I_2) gives more information on the distribution of these defects. It is well known that defects of efficient positron trap primarily include titanium vacancies, negatively-charged and neutral vacancy-type defects in annealed TiO_2 single crystals. In addition, He *et al.*[23] and Nowotny *et al.*[24] have clarified that the annealed samples in a vacuum have a good deal of oxygen vacancies and few titanium vacancies. Titanium vacancies were not sensitive to positrons because of low densities. Then, the test results of both XANES and XRD indicated that changes in τ_2 and I_2 are related to Ti^{3+}–V_O defect complexes. With the increase of the annealing temperature from 1023 to 1173 K, τ_2 increases and I_2 accordingly decreases owing to the generation of more Ti^{3+}–V_O defect complexes and forming of defect clusters, respectively. However, τ_2 decreases and I_2 accordingly increases

when the annealing temperature rises to 1273 K, indicating that the aggregated defect clusters decompose into smaller defects. It is also shown that aggregated defect clusters in small depth move to the surface.

Table 1. LT9.0 fitting results of positron lifetime spectra for annealed samples.

Temperature/K	τ_1/ns	τ_2/ns	τ_3/ns	I_1/%	I_2/%	I_3 /%
1023	0.1560	0.377	1.854	86.65	9.88	3.47
1073	0.1572	0.390	1.920	88.98	7.88	3.14
1173	0.1568	0.400	1.915	89.46	7.57	2.96
1273	0.1507	0.309	1.807	86.70	10.4	2.92

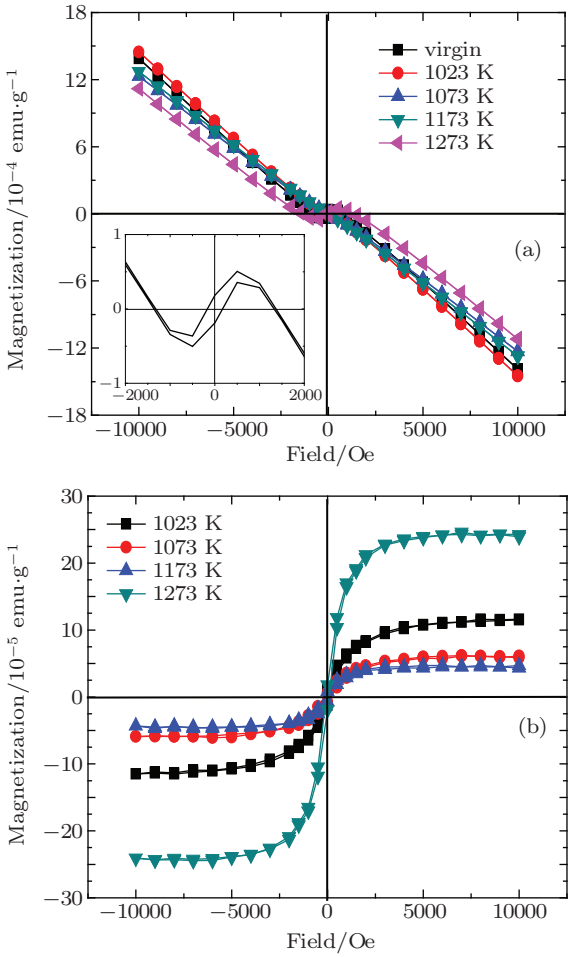


Fig. 3. (color online) (a) Original *M*–*H* curves of virgin and annealed TiO_2 single crystals at 300 K. The latter is annealed from 1023 to 1273 K in a high vacuum. Inset: the low-field part of the loop for the 1273 K annealed sample. (b) *M*–*H* loop after deducting the substrate signal.

Figure 3(a) shows the measured magnetic moments of TiO_2 single crystals at 300 K before and after annealing from 1023 to 1273 K in a high vacuum. All substrates display diamagnetic behavior[25] that is different from that of Zhou *et al*. (paramagnetic).[26] The inset shows the low-field part in an enlarged scale of the 1273 K annealed sample. The diamagnetism and ferromagnetism are proportional to the magnetic field. Figure 3(b) shows the annealing-fluence-dependent magnetization of TiO_2 single crystals after subtracting the diamagnetic background. The saturated magnetization first decreases gradually with increasing annealing temperature, and increases dramatically for the fluence at 1273 K. We also measured the hysteresis loops at 300 K to demonstrate their room-temperature ferromagnetism. When O is removed, the excess electrons are unpaired.[27] They can occupy the nearby localized Ti 3d orbit, and therefore convert Ti^{4+} ions to Ti^{3+} ions. The unpaired 3d electrons in Ti^{3+} ions provide vast spin magnetic moments which are definitely related to the observed ferromagnetism. The change in the saturated magnetization possibly depends on the aggregation and decomposition of Ti^{3+}–V_O defect complexes (or cluster), according to the results obtained from XRD, XANES, and PALS. With increasing annealing temperature, Ti^{3+}–V_O defect complexes gradually form clusters. Then, these clusters decompose into smaller defects at 1273 K. The change in the defect size is very consistent with the changing trend of saturation magnetization.

In order to check if the magnetism in annealed samples at a high vacuum is due to defects and/or oxygen vacancies, oxygen-annealing tests were made. Data of the oxygen-annealed TiO_2 single crystals at 1173 K, along with the data of annealed samples (HV) at 1273 K, are shown in Fig. 4. One can clearly see that annealing in an oxygen atmosphere for 2 h can reduce the magnetic moments of the annealed sample (HV) at 1273 K greatly. However, when we increase the duration of annealing up to 5–8 h, the saturation magnetization slowly increases. Finally, it is almost the same as the case of the 1273 K annealed sample (HV). In addition, we observed obvious hysteresis loops and change in color from dark-blue to transparent.

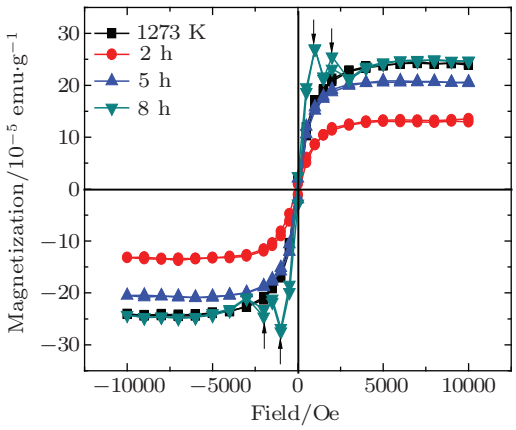


Fig. 4. (color online) Magnetization versus the magnetic field at 300 K for TiO_2 single crystals, annealed in O_2 at 1173 K for 2 h, 5 h, and 8 h. The anomalous protrusions in the curve are described by arrows. Note that the signals of substrates were removed.

When the sample undergoes a second annealing under oxygen conditions, oxygen exists as ions in the TiO_2 lattice. Therefore, Ti ions must provide corresponding electrons in order to maintain electrostatic balance, which makes the Ti

ions valence change. Ti ion valence may change from Ti^{3+} to Ti^{4+} when the annealing time is 2 h. Saturation magnetization decreases when unpaired 3d electrons reduce. After the annealing time increases to 5 and 8 h, excess oxygen ions in the TiO_2 lattice could induce a number of Ti vacancies that make saturation magnetization increase gradually. This evidence has clearly proven that the magnetism of annealed TiO_2 single crystals in a high vacuum indeed originates from oxygen vacancies: filling up vacancies could reduce unpaired 3d electrons in the TiO_2 lattice, and could weaken the saturation magnetization.

4. Conclusions

In summary, we have studied local atomic and electronic structures, defect types, and magnetism in annealed rutile TiO_2 single crystals by using XRD, XANES, PALS, and SQUID. The following conclusions can be drawn. (i) A lot of oxygen vacancies and especially Ti^{3+}–V_O defect complexes (or clusters) are formed in high-vacuum annealing samples. (ii) The second annealing in an oxygen atmosphere can further demonstrate that room-temperature ferromagnetism of annealed samples in a high vacuum is closely associated with oxygen vacancies. The unpaired 3d electrons in Ti^{3+} ions provide vast spin magnetic moments which are definitely related to the observed ferromagnetism. In addition, excess oxygen ions in the TiO_2 lattice could also induce a number of Ti vacancies which obviously increase the magnetic moments.

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