Oxygen vacancy-induced room-temperature ferromagnetism in D–D neutron irradiated single-crystal TiO_2 (001) rutile*

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Remarkable room temperature ferromagnetism in pure single-crystal rutile TiO_2 (001) samples irradiated by D–D neutron has been investigated. By combining X-ray diffraction and positron annihilation lifetime, the contracted lattice has been clearly identified in irradiated TiO_2, where Ti^{4+} ions can be easily reduced to the state of Ti^{3+}. As there were no magnetic impurities that could contaminate the samples during the whole procedure, some Ti^{3+} ions reside on interstitial or substituted sites accompanied by oxygen vacancies should be responsible for the ferromagnetism.

Keywords: D–D neutron, single-crystal TiO_2, defects, d^0 magnetism

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1. Introduction

High Curie temperature ferromagnetism in diluted magnetic semiconductor (DMS) oxides, including TiO_2,[1–3] has been the focus of recent research in the field of spintronics regarding the ability to accommodate both charge and spin degrees of freedom to increase the density of information stored in the same material.[4–6] Following the first observation of room-temperature ferromagnetism (RTFM) in Co-doped TiO_2,[1] transition metal-doped TiO_2 matrices have received much attention, since stable RTFM was observed in several typical ions-doped TiO_2.[7–11] However, the magnetic properties are extremely sensitive to sample preparation methods,[9,12] conditions, and even measurement techniques, lack of reproducibility is still an open question to determine whether the origin of RTFM is intrinsic or extrinsic. Actually, oxygen vacancies (V_O) can easily be created when TiO_2 samples are doped with dopants, and there seems to be more controversies for TiO_2 to account for RTFM[13] since a new phenomenon called d^0 magnetism was first introduced by Coey's group.[14–16] So far, RTFM has been observed experimentally in various undoped systems of TiO_2. Hong *et al.*[17] reported a large magnetic moment in pure TiO_2 films, RTFM that may depend on thickness of films was mediated mostly by interfacial V_O, the results are supported by pure films of TiO_2 annealed in vacuum.[18] V_O in reduced TiO_2 pure powders without Ti^{3+} or Ti^{2+} ions detected were claimed to give magnetic behavior, as proposed by Zhao *et al.*[19] To avoid any impurities effects, single-crystals rutile TiO_2 (SCR) were irradiated with oxygen ions, and Ti^{3+} ions from the reduced Ti^{4+} were associated with RTFM.[20] As a matter of fact, ferromagnetic orders in undoped films as well as powders are not stable when stored in air,[18] that may be the reason why Ti^{3+} ions can be detected in single-crystal TiO_2 rather than the powders.[19,20] Recently, we have reported optical properties of D–D neutron (2.5 MeV) irradiation effects on Co-doped ZnO wafers.[21] The Co metal and oxide clusters were dissolved with a great number of induced defects coherently throughout the wafers after the irradiation. In addition, no other effects, neutron-induced nuclear reaction for example, were detected.

In this paper, we demonstrate RTFM in SCR induced by D–D neutrons, structural and magnetic properties were investigated to explore the origin of magnetism. D–D neutrons can easily pass through SCR leaving defects distributed homogeneously. And what is more, it was proved to be a much cleaner way of creating defects[21] than other ions[22] (e.g., N–, Ar–), because neutron activation cross sections at 2.5 MeV in SCR are very low and can be neglected (data from National Nuclear Date Center). Our results strongly suggest that V_O should be related to RTFM in SCR, for the samples are pure enough after D–D neutron irradiation.

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2. Experiment

Commercial pure TiO_2 (001) rutile single crystals with a same size of 10 mm×10 mm×0.5 mm from MaTecK were irradiated with 2.5-MeV D–D neutrons with a dose of 2.9×10^{10} cm^{-2} at room temperature. All the samples were investigated using an NaI (Tl) detector immediately after the irradiation, and no obvious radioactivity was observed. Alternating Field Gradient Magnetometer (AGM), X-ray Diffraction (XRD, Cu $K\alpha$), Positron Annihilation Lifetime (PAL, fitted by the analysis program LifeTime-9.0), X-ray Photoelectron Spectroscopy (XPS), and Ultraviolet-visible absorption spectra (UV-Vis) were employed to characterize magnetic, structural, chemical, and optical properties of the irradiated samples. All the measurements were performed at room temperature.

3. Results and discussion

Magnetization measurement of neutron-irradiated SCR is shown in Figs. 1(a) and 1(b). As no magnetic moment was observed in unirradiated pure SCR, here we provide an AGM measured result of SCR implanted with Cu ions (70 keV, 5×10^{15} cm^{-2}) to evaluate the RTFM. Cu ion implantation can also induce lots of V_O and RTFM,[23] but the projected range of Cu in SCR is only 33 nm as calculated by SRIM code (Stopping and Range of Ions in Matter), namely, somewhat like a rutile thin film with numerous defects deposited on an SCR substrate.[20] Hysteresis loops in both of the samples can be observed clearly, the saturation magnetic moment M_S of as-implanted sample is higher than that of neutron-irradiated, interestingly, M_S of neutron-irradiated sample is about 10^5 times higher when we normalized the data. Therefore, we must suggest that one D–D neutron which can penetrate SCR easily would create more defects on average than a 70-keV Cu ion did, and RTFM extraordinarily depends on the concentration of V_O in SCR.

The effects of neutron irradiation on the structural properties of the SCR samples are quite pronounced as shown in Fig. 2. Only (002) diffraction peak was found before and after the irradiation (diffraction angles from 10° to 80°, parts of the data are not shown), no additional impurity phase was present. Due to the bad crystallinity, (002) diffraction peak became broadened after neutron irradiation. One remarkable characteristic is that the (002) peak shifts to a small extent towards higher diffraction angles after neutron irradiation. Considering that displacement energies for O in rutile are approximately two times smaller than for Ti,[24] it indicates that irradiation conditions would be favorable to formation of V_O over titanium vacancies. As sketched in the inset of Fig. 2, with increasing V_O, lattice distortion in direction to c axis and a weaker (002) peak would become more and more conspicuous.

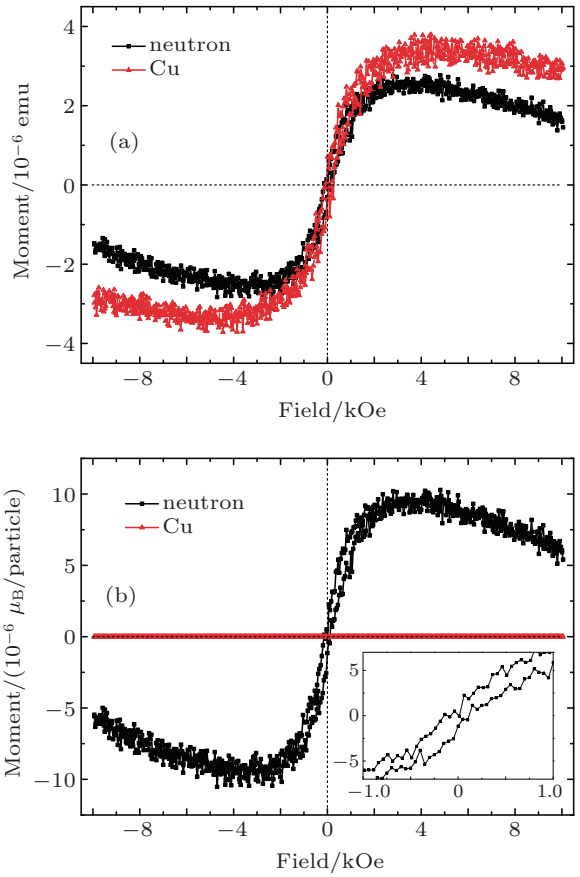


Fig. 1. (color online) (a) M–H curves for samples irradiated with neutrons and implanted with Cu ions. (b) The data normalized by particle dose. Inset shows low field region of irradiated SCR. The unit 1 Oe = 79.5775 A·m^{-1}.

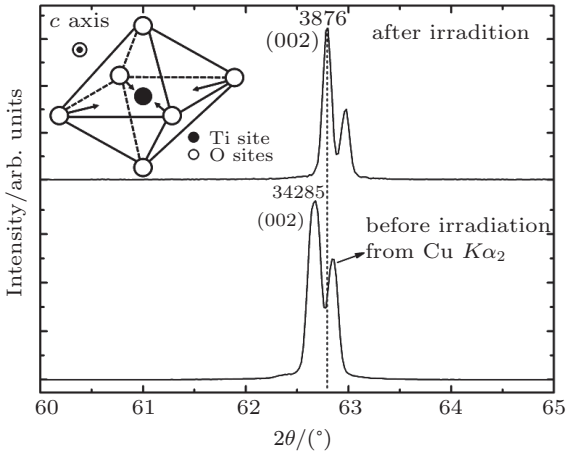


Fig. 2. XRD patterns of the sample before and after D–D neutron irradiation. Inset shows the schematic diagram of electrostatic attraction between induced V_O at equatorial oxygen sites and V_{Ti} at central titanium site.

Contraction in cell volume upon XRD data was further studied by PAL. We analyzed the data using a two-state trapping model,[25] two components of τ_1 and τ_2 are attributed to positron lifetimes in bulk and one defect. According to this model,

$$\tau_m = I_1\tau_1 + I_2\tau_2, \quad (1)$$

$$\tau_2 = \tau_{\text{trap}}, \quad (2)$$

$$\tau_{\text{bulk}}^{-1} = I_1 \tau_1^{-1} + I_2 \tau_2^{-1}, \quad (3)$$

the results are listed in Table 1. The change of a charge state in a titanium vacancy before and after neutron irradiation can become visible in the trapped position lifetime.[26] The value of τ_2, compared with unirradiated SCR, decreases significantly, which implies a proof of increased valence electron density at positron annihilation site.

Table 1. Parameters of positron lifetime and Doppler broadening spectra.

Sample	τ_1/ps	I_1/%	τ_2/ps	I_2/%	τ_m/ps	τ_{bulk}/ps	$\tau_{\text{trap}}/\tau_{\text{bulk}}$	S-parameter
Before irradiation	143.3	83.5	202.0	16.5	153.0	150.5	1.342	0.563043
After irradiation	121.0	32.3	164.5	67.7	150.4	147.4	1.116	0.562482

Neutron irradiation can lead to reduction effects and oxygen deficiencies of rutile samples, the oxygen gradually coming out and escaping from the surface region of the irradiated samples induces an increase of the average electron density as told by the average lifetime τ_m.[27] The number of oxygen vacancies surrounding a titanium vacancy definitely becomes more after the irradiation, a weaker screening of electron density should be one of the reasons for decreased τ_2.[28] The other one, obviously, the open volume of a titanium vacancy can be determined by the ratio of $\tau_{\text{trap}}/\tau_{\text{bulk}}$,[29] it is clear that the ratio varies from 1.342 to 1.116 corresponding to divacancy and monovacancy respectively, the data from PAL have highly reflected XRD results. In order to facilitate the analysis of PAL, Doppler broadening measurements on samples before and after neutron irradiation were carried out. The ratio gives characteristic information about surroundings of positron annihilation site. As shown in Table 1, the decrease of S-parameter suggests that the probability of a positron annihilating with high momentum core electrons gets higher, however, each titanium vacancy is surrounded only by oxygen atoms and more induced oxygen vacancies in the first coordination shell, the increased concentration of titanium vacancies and valence election density should give us an increased S-parameter after neutron irradiation. This result implies that positrons get annihilation with a new type defect and probably annihilate with 3d electrons[30,31] of Ti^{3+}–V_O defect complexes originated during the neutron irradiation. When one trapped electron in oxygen vacancy constitutes an F^+ center, the unpaired electron tends to occupy interstitial or substitutional Ti 3d orbit, the reduction conditions are favorable to reducing Ti^{4+} to Ti^{3+} state and forming Ti^{3+}–V_O defect complexes.

The formation of V_O in bulk plays an important role in RTFM, it is believed that RTFM arises from not only the structural defects but also the charge redistribution.[32] To verify the existence of Ti^{3+}–V_O defect complexes, XPS measurement was performed to determine chemical states of Ti in irradiated SCR. Even though XPS can analyze only the surface region of the samples, the observed results are quite evident. XPS wide scan in the binding energy range 0 to 1000 eV confirmed that, apart from unavoidable carbon contamination, no other magnetic elements, i.e., Fe, Co, Ni, were detected. Figure 3 shows XPS spectra of Ti 2p for SCR before and after neutron irradiation. The core level binding energy of Ti $2p_{3/2}$ of SCR before neutron irradiation is approximately at 458.5 eV with 5.7-eV distance between Ti $2p_{1/2}$, and the two peaks of irradiated SCR are located at 459.1 eV and 464.6 eV with a peak separation of 5.5 eV, assigned to Ti^{4+} in SCR.[33] The asymmetric curves of Ti 2p were fitted with mixed Gaussian–Lorentzian functions. Ti 2p peaks were deconvoluted into four peaks, two valence states of Ti $2p_{3/2}$ and $2p_{1/2}$. According to the fitting results of Ti 2p, no Ti^{3+} ions were detected, however, about 30% of Ti^{4+} ions were reduced to Ti^{3+} state after neutron irradiation as shown in Figs. 3(a) and 3(b). The increase in the V_O density may lead to a higher binding energy of Ti 2p level by 0.6 eV, which is strictly represented by a lack of overlap between the electron distributions of Ti and O. In such a case, V_O was required to compensate the formation of Ti^{3+} ions in SCR. Compared to stoichiometric rutile, neutron-irradiated SCR is $Ti_{0.3}^{3+}Ti_{0.7}^{4+}O_{1.85}$ (surface region) as considered by charge balance. A deficit of oxygen can be compensated by oxygen vacancies or lower valence states of interstitial or substitutional titanium ions, following this, we could deduce that Ti^{3+}–V_O defect complexes are in large quantities in irradiated samples.

Figure 4(a) shows UV-Vis of the sample before and after neutron irradiation. The absorption edges of the sample before and after the irradiation are 419 nm and 415 nm. It is known that the valence band and conduction band consist of both the Ti 3d and O 2p orbitals (hybrid orbitals), the presence of oxygen vacancies (or F^+) in SCR can give rise to a shift of Fermi level to conduction band, and an increase in the V_O in SCR brings about a blueshift of optical band gap as shown in Fig. 4(b).[34] F^+ center is a deep donor with a transition energy of 1.61 eV ($\sim$ 770 nm) to conduction band bottom,[35] we believe that a weak peak at 770 nm is probably due to the F^+ center in reduced SCR.

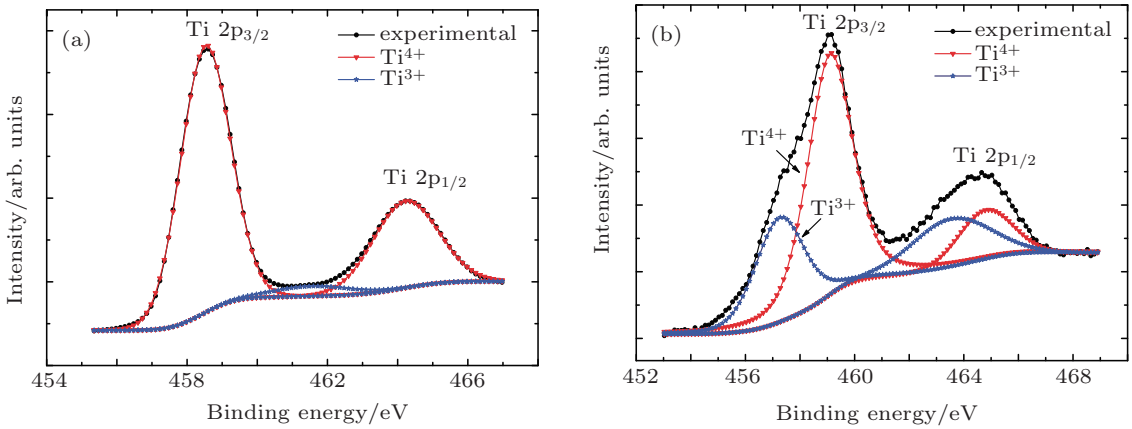


Fig. 3. (color online) XPS core level spectra of Ti 2p levels of SCR (a) before and (b) after neutron irradiation. Curves were fitted using XPS peak software.

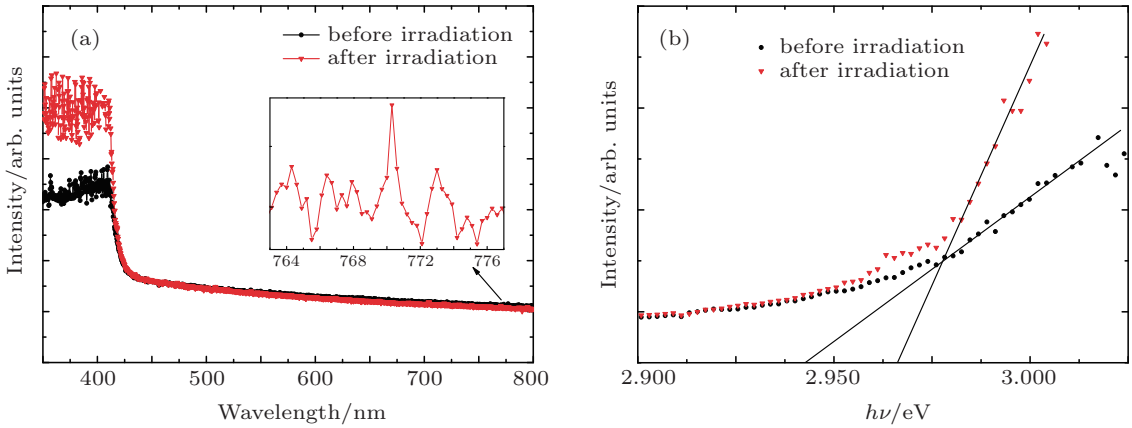


Fig. 4. (color online) (a) UV-Vis for samples before and after neutron irradiation. (b) Curves of the transformed Kubelka–Munk function values versus $h\upsilon$. Inset is the long wavelength region.

D–D neutrons which are deemed to be clean defect generators induce strongly reduced conditions for RTFM. The origin of RTFM in neutron-irradiated SCR directly correlates with V_O, Cu-doped SCR sample has attested to the fact that magnetization depends on the concentration of V_O. An electron captured by oxygen vacancy which forms a bound magnetic polaron (BMP) with an oppositely directed spin between the coupling Ti^{3+} ions can cause RTFM.[36] Furthermore, the presence of Ti^{3+}–V_O defect complexes has been identified, the BMP model in this paper is quite appropriate. However, the reduction conditions induced by D–D neutrons are satisfied with Stoner splitting of the Ti 3d band which can also favor ferromagnetism,[37] thus a further study is advisable to investigate the source of the room temperature ferromagnetism.

4. Conclusion

In summary, we have investigated the origin of RTFM in D–D neutron-irradiated single-crystal rutile TiO_2 (001), the samples irradiated with D–D neutrons exhibit RTFM which can be associated with oxygen vacancies. We make sure that the RTFM in neutron-irradiated TiO_2 single crystals is intrinsic rather than any impurities.

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