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## Room temperature ferromagnetism in D-D neutron irradiated rutile $\text{TiO}_2$ single crystals

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Room temperature ferromagnetism (RTFM) was observed in unirradiated rutile  $\text{TiO}_2$  single crystals prepared by the floating zone method due to oxygen vacancy ( $\text{V}_\text{O}$ ) defects. D-D neutrons mainly collide elastically with  $\text{TiO}_2$ , producing  $\text{V}_\text{O}$ , titanium vacancies ( $\text{V}_\text{Ti}$ ) and other point defects; the density and kind of defect is related to the neutron irradiation fluence. D-D neutron irradiation is used to regulate the concentration and type of defect, avoiding impurity elements. As the irradiation fluence increases, the saturation magnetization ( $M_\text{s}$ ) first increases, then decreases and then increases. To verify the origin of RTFM, the CASTEP module was used to calculate the magnetic and structural properties of point defects in  $\text{TiO}_2$ .  $\text{V}_\text{O}$  induces a  $2.39 \mu_\text{B}$  magnetic moment,  $\text{Ti}^{3+}$  and  $\text{F}^+$  induce  $1.28 \mu_\text{B}$  and  $1.70 \mu_\text{B}$  magnetic moments, respectively, while  $\text{V}_\text{Ti}$  induces a magnetic moment of  $\sim 4 \mu_\text{B}$ . Combining experimental and theoretical results, increases in  $\text{V}_\text{O}$  concentration lead to  $M_\text{s}$  increases; more  $\text{V}_\text{O}$  combine with electrons to form  $\text{F}^+$ , inducing a smaller magnetic moment.  $\text{V}_\text{O}$  and  $\text{V}_\text{Ti}$  play a key role and  $M_\text{s}$  changes accordingly with larger fluence.  $\text{V}_\text{O}$ ,  $\text{F}^+$  and  $\text{V}_\text{Ti}$  are the most likely origins of RTFM.

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## 1 Introduction

$\text{TiO}_2$  is a versatile functional material that has important applications<sup>1–3</sup> in the fabrication of spintronics, optical coatings and solar cells.  $\text{TiO}_2$  doped with different ions has been synthesized<sup>4–6</sup> to modify its ferromagnetic and optical properties.  $\text{TiO}_2$  also has outstanding magnetic properties, showing RTFM in both ion-doped and undoped states. However, there is no consensus on the origin of magnetism of  $\text{TiO}_2$ , and some experimental results contradict each other. Kaspar *et al.*<sup>7</sup> pointed out that extended structural defects appear to be necessary to promote ferromagnetic ordering in  $\text{Cr:TiO}_2$ . Saadaoui *et al.*<sup>8</sup> found that the ferromagnetism is intrinsic and controlled by oxygen vacancies. Zheng *et al.*<sup>9</sup> reported that oxygen defects can be the dominating factor for increasing the saturation moment of Cu-doped  $\text{TiO}_2$  film. Zhou *et al.*<sup>10</sup> found that ferromagnetism was related to a lower level of  $\text{V}_\text{O}$  defects. Parras *et al.*<sup>11</sup> pointed out that the magnetic moment is indeed due to the  $\text{Ti}^{3+}$  ions induced by reduction. Wang *et al.*<sup>12</sup> reported that  $\text{V}_\text{Ti}$  could be the origin of RTFM.

Defects play an important role in the structural, magnetic and optical properties of semiconductor materials; in

particular, the intrinsic defects of  $\text{TiO}_2$  have the potential to induce spintronic properties at room temperature. Magnetic semiconductors with high Curie temperatures are expected to be used in spintronic materials with great potential applications because they can utilize both charge and spin degrees of freedom in a single component. Venhatesan and Coey *et al.*<sup>13</sup> reported that  $\text{HfO}_2$  films have high-temperature ferromagnetism and first proposed the concept of  $d^0$  magnetism. They avoided the interference of the second phase of magnetic elements in dilute magnetic semiconductors (DMS) and only studied the effect of intrinsic defects. Since then, many research groups have studied defects causing RTFM in  $\text{TiO}_2$ -based DMS materials.

In our previous work, the magnetic properties of Cu-doped  $\text{TiO}_2$  were investigated<sup>14,15</sup> by theoretical and experimental studies. RTFM may be induced by  $\text{V}_\text{O}$  or  $\text{Cu}^{2+}-\text{V}_\text{O}$ ; the effects of intrinsic defects and Cu-doping are ambiguous. The effects of  $\gamma$ -ray and D-D neutron irradiation<sup>16,17</sup> on the RTFM of  $\text{TiO}_2$  single crystals were initially explored. RTFM was observed, and  $\text{V}_\text{O}$  was the main origin of room temperature ferromagnetism. D-D neutrons mainly scatter with  $\text{TiO}_2$  single crystals; they have the right energy to cause vacancy defects, but not to produce a nuclear reaction at a higher energy or capture neutrons at a lower energy. Furthermore, because D-D neutron fluence could regulate the concentration and kind of defect, it is beneficial to explore the effect of intrinsic defects on RTFM properties. The effects of different defect concentrations and types on ferromagnetism can be obtained by adjusting the neutron fluence. Using D-D neutron irradiation has significant

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advantages over doping with other magnetic elements to clarify the origin of RTFM.

In this study, to illustrate the effect of intrinsic defects on magnetic and structural properties and optical band gap, D-D neutron irradiation was carried out to verify the effect of intrinsic defects in rutile  $\text{TiO}_2$  single crystals. In addition, we use the CASTEP module based on a density functional theory (DFT) method to calculate the magnetic properties of intrinsic vacancy defects. This lays a foundation for the application of  $\text{TiO}_2$  in photocatalysis and spintronics.

## 2 Materials and methods

Pure  $\text{TiO}_2$  single crystals from MaTeck prepared by the floating zone method with one side polished were cut to  $5 \times 10 \times 0.5 \text{ mm}^3$ . D-D neutron irradiation with fluences of  $0 \text{ n cm}^{-2}$ ,  $2 \times 10^9 \text{ n cm}^{-2}$ ,  $5 \times 10^9 \text{ n cm}^{-2}$ ,  $1 \times 10^{10} \text{ n cm}^{-2}$ , and  $2.5 \times 10^{10} \text{ n cm}^{-2}$  was used.

X-ray diffraction (XRD, D/Max-2400) with  $\text{Cu K}_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) was used to characterize the structure of  $\text{TiO}_2$ . The working voltage is 40 kV, the working current is 60 mA, the step length is  $0.02^\circ$ , the scanning speed is  $20^\circ \text{ min}^{-1}$ , and the scanning range is  $20\text{--}80^\circ$ . The excitation wavelength of the Raman spectrum is 532 nm, the laser power of the backscattering mode is 10 mW, and the spot size is  $2 \mu\text{m}$ . The Raman displacement range is  $100\text{--}1000 \text{ cm}^{-1}$  and the integral time is 10 s. Three points were selected from each sample for testing. A superconducting quantum interferometer (SQUID) was used to measure the M-H curves under an external magnetic field parallel to the surface of the sample. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI-5702 multi-functional electronic spectrometer. A conductive adhesive was used to stick the sample to the sample rack, with the polished surface facing out. The wide spectra (0–1000 eV), Ti (450–468 eV) and O (525–537 eV), and C (274–296 eV) fine spectra were tested, respectively. The photon energy of the X-ray source with Al as the anode material is 1486.6 eV. The photoluminescence (PL) source is a xenon lamp with an excitation source wavelength of 415 nm and a spectral range of 450–750 nm. Electron spin resonance (ESR) spectra were tested on a Bruker EMX plus at 2 K at the Steady High Magnetic Field Facilities, High Magnetic Field Laboratory, CAS. The samples were cut to  $2 \text{ mm} \times 2 \text{ mm}$  for testing. The magnetic field range is 2900–3900 G and the microwave frequency is 9.4 GHz. The ultraviolet visible (UV-vis) spectra were obtained in reflection mode with the measurement range of 300–700 nm.

## 3 Results and discussion

Fig. 1 represents the XRD patterns after neutron irradiation. There are  $\text{TiO}_2$  (002) and  $\text{Cu K}_\alpha$  peaks in the spectra. The full width at half maximum (FWHM) of the (002) peak is very small, indicating that the single crystals have high crystallinity. The (002) peak shows a small shift toward a small angle, which means that the lattice expands a little due to the repulsion force between the oxygen vacancies. Fig. 1(b) shows two small peaks

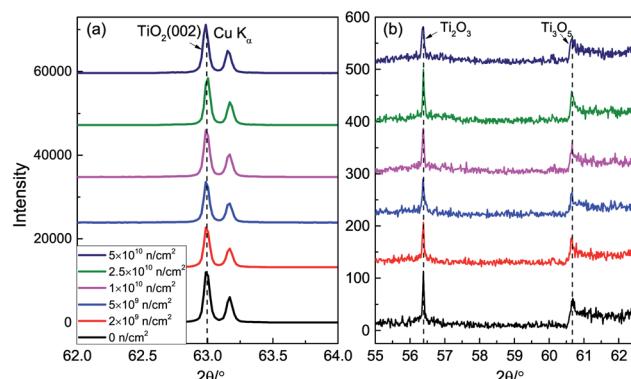


Fig. 1 XRD patterns; (a) (002) peak and (b) drawing of partial enlargement of  $\text{TiO}_2$  before and after neutron irradiation.

at  $56.4^\circ$  and  $60.7^\circ$ , corresponding to  $\text{Ti}_2\text{O}_3$  and  $\text{Ti}_3\text{O}_5$ , which indicates that  $\text{TiO}_2$  is non-stoichiometric.

The space group<sup>18</sup> of rutile  $\text{TiO}_2$  is  $D_{4h}^{14}$ , and the Raman-active vibrational energy levels are  $\text{B}_{1g}$  ( $143 \text{ cm}^{-1}$ ),  $\text{E}_g$  ( $447 \text{ cm}^{-1}$ ),  $\text{A}_{1g}$  ( $611 \text{ cm}^{-1}$ ), and  $\text{B}_{2g}$  ( $828 \text{ cm}^{-1}$ ). The scattering intensity is proportional to the number of corresponding molecules and is related to the smoothness of the surface and diffuse reflection. The Raman spectra of the samples before and after irradiation are presented in Fig. 2. There is an asymmetrical broad peak at  $235 \text{ cm}^{-1}$ , corresponding to the second-order scattering of phonons or internal disorder. The damage can be described by the FWHM of the  $\text{A}_{1g}$  peaks; as the irradiation fluence increases, the  $\text{A}_{1g}$  peak still maintains a good FWHM. No peak shift or new vibration level was observed, which indicates that no obvious lattice damage was caused by neutron irradiation.

Fig. 3 illustrates the M-H curves before and after D-D neutron irradiation. All the samples exhibit RTFM, including the unirradiated sample, which agrees with the experimental results<sup>19</sup> and our preliminary work.<sup>17</sup> Oxygen deficiencies are inevitably introduced in the preparation by the floating zone method;<sup>20,21</sup>  $\text{V}_\text{O}$  would induce a magnetic moment. Santara *et al.*<sup>19</sup> reported that  $\text{V}_\text{O}$  induced strong ferromagnetism at and

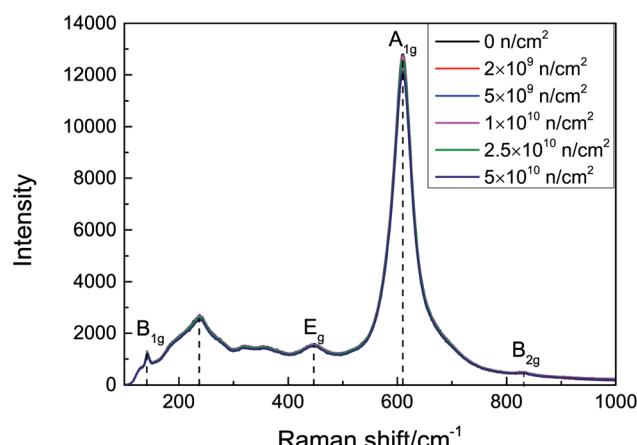


Fig. 2 Raman spectra of  $\text{TiO}_2$  before and after neutron irradiation.



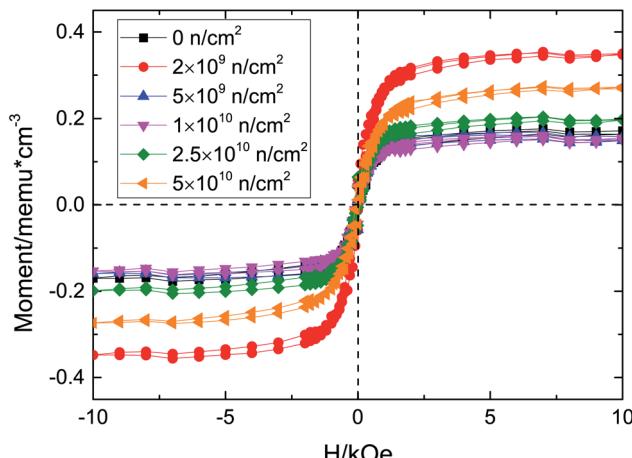


Fig. 3 M-H curves of  $\text{TiO}_2$  before and after neutron irradiation.

above room temperature in undoped  $\text{TiO}_2$  nanoporous nanoribbons. Furthermore, Kim *et al.*<sup>22</sup> pointed out that oxygen vacancy defects play an important role in the ferromagnetism of undoped rutile  $\text{TiO}_2$ . Moreover, our previous work,<sup>17</sup> using  $\gamma$ -ray irradiated  $\text{TiO}_2$ , also found that the origin of RTFM of unirradiated  $\text{TiO}_2$  single crystals was  $\text{V}_\text{O}$ ; thus the RTFM of unirradiated  $\text{TiO}_2$  is due to  $\text{V}_\text{O}$ . D-D neutron irradiation has advantages in regulating the concentrations and kinds of defect; because of its energy it only collides with atoms in elastic scattering and the nuclear reaction cross section is 0, so no nuclear reaction occurs. Therefore, D-D neutron irradiation has been used to regulate defect concentration and type to study changes of RTFM.

The maximum saturation magnetization ( $M_\text{s}$ ) is in the  $2 \times 10^9 \text{ n cm}^{-2}$  sample, while the  $M_\text{s}$  of the  $5 \times 10^9 \text{ n cm}^{-2}$  and  $1 \times 10^{10} \text{ n cm}^{-2}$  samples are almost equal to that of the unirradiated sample. Then, the  $M_\text{s}$  increased with the irradiation fluence, which means that there is an optimal value for  $\text{V}_\text{O}$  defect concentration. D-D neutron irradiation mainly causes point vacancy defects. Considering the XRD and Raman results and the physical process of D-D neutron irradiation of  $\text{TiO}_2$ , the ferromagnetism may due to vacancy defects, such as  $\text{V}_\text{O}$ ,  $\text{V}_\text{Ti}$ , and so on. In our previous work, we found that  $\text{V}_\text{O}$  could induce  $\sim 2 \mu_\text{B}$  magnetic moment, while  $\text{V}_\text{Ti}$  could introduce  $\sim 4 \mu_\text{B}$

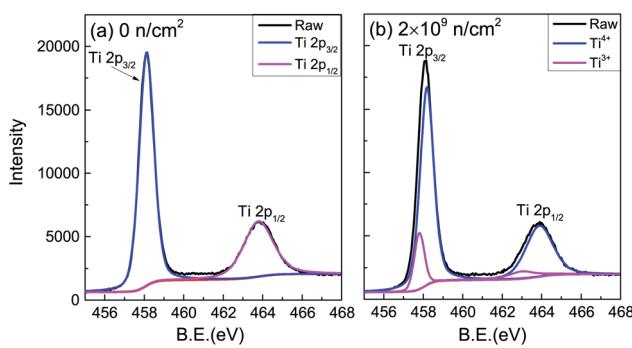


Fig. 4 XPS spectra of (a) raw and (b)  $2 \times 10^9 \text{ n cm}^{-2}$   $\text{TiO}_2$  samples.

magnetic moment, which we will verify below. After D-D neutron irradiation,  $\text{V}_\text{O}$  and  $\text{V}_\text{Ti}$  are induced due to the elastic collisions between neutrons and Ti and O atoms; these defects increase  $M_\text{s}$ . For the  $5 \times 10^9 \text{ n cm}^{-2}$  and  $1 \times 10^{10} \text{ n cm}^{-2}$  samples,  $M_\text{s}$  decreases on account of the compound defects that  $\text{V}_\text{O}$  make up with other defects,<sup>10</sup> e.g.,  $\text{F}^+$ ,  $\text{V}_\text{O}-\text{Ti}^{3+}$ ; these defects provide a smaller magnetic moment, so the total magnetic moment of the system is decreased. We preliminarily studied the Doppler broadening and positron annihilation spectroscopy<sup>16,23,24</sup> of Cu-doped and D-D neutron irradiated  $\text{TiO}_2$ , and  $\text{V}_\text{Ti}$  was found after spectral analysis.  $\text{V}_\text{Ti}$  would certainly be generated after D-D neutron irradiation of  $\text{TiO}_2$  single crystals. Below, we will further investigate the increase due to the  $\text{V}_\text{Ti}$  and  $\text{V}_\text{O}$  defects produced when the fluence increased for the  $2.5 \times 10^{10} \text{ n cm}^{-2}$  and  $5 \times 10^{10} \text{ n cm}^{-2}$  samples.

The valence of Ti after irradiation was characterized by XPS spectra.<sup>25-27</sup> Only Ti, O and C could be detected. Using C 1 s (284.6 eV) for charge correction, the Ti 2p core electron spectra of the unirradiated and  $2 \times 10^9 \text{ n cm}^{-2}$  samples are shown in Fig. 4. The peak separation fitting of the Ti 2p spectra was performed by the Gauss-Lorentz function. The  $\text{Ti}^{4+}$  2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies were 458.5 eV and 464.2 eV, respectively, and the energy level spacing<sup>28,29</sup> was 5.7 eV for  $\text{Ti}^{4+}$  and 5.2 eV for  $\text{Ti}^{3+}$ . After peak-differentiation and imitation, the unirradiated sample still showed +4 valence.  $\text{Ti}^{3+}$  was produced in irradiated  $\text{TiO}_2$ , proving that  $\text{V}_\text{O}$  was indirectly generated after irradiation.  $\text{Ti}^{3+}$  contributes a paramagnetic signal,<sup>30</sup> and the  $\text{Ti}^{3+}$  peak area shows no obvious change with the increased irradiation dose, which is inconsistent with the change of  $M_\text{s}$ .

To investigate the defect type after neutron irradiation, PL spectra are displayed in Fig. 5(a). After peak separation, the three main peaks are centered at 473 nm (2.62 eV), 600 nm (2.07 eV) and 820 nm (1.51 eV), as shown in Fig. 5(b). As the PL spectra are similar, we choose the  $2 \times 10^9 \text{ n cm}^{-2}$  sample for detailed analysis. In  $\text{TiO}_2$ , the electron trap state caused by  $\text{V}_\text{O}$  is about 0.5–1 eV below the bottom of the conduction band.<sup>31</sup> Therefore, the band peak at 473 nm is assigned to  $\text{V}_\text{O}$  and the deep level emission<sup>32,33</sup> of  $\text{V}_\text{O}$ , which is consistent with the first principles calculation below. The 600 nm luminescence peak is attributed to the consequence of polarization of the lattice ions surrounding the vacancy.<sup>34</sup> The peak at 818 nm might be

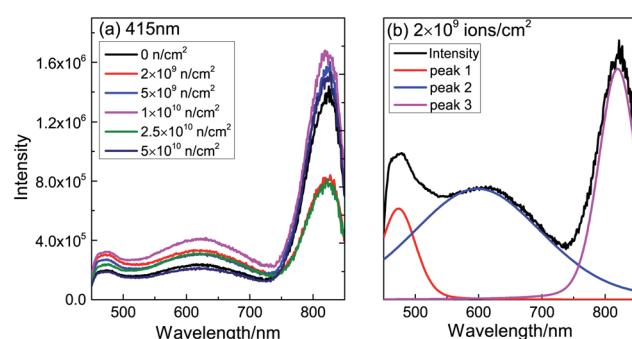


Fig. 5 (a) Raw PL spectra of  $\text{TiO}_2$  before and after neutron irradiation and (b) normalized PL spectra for  $2 \times 10^9 \text{ n cm}^{-2}$ .



Table 1 Peak area of PL spectra after peak fitting

Sample ( $\text{n cm}^{-2}$ )	473 nm	600 nm	820 nm
0	0.0777	0.3424	0.5798
$2 \times 10^9$	0.1195	0.5308	0.3496
$5 \times 10^9$	0.0889	0.3729	0.5382
$1 \times 10^{10}$	0.0871	0.4241	0.4888
$2.5 \times 10^{10}$	0.0970	0.5195	0.3835
$5 \times 10^{10}$	0.0751	0.2944	0.6305

a consequence of  $\text{Ti}^{3+}$  or  $\text{F}^+$  defects. Table 1 shows the area of the peaks after normalization. The area of the 473 nm peak is found to vary according to the change of  $M_s$ ; this is direct evidence that  $\text{V}_\text{O}$  causes RTFM. With the increase of neutron injection,  $\text{V}_\text{O}$  gradually forms an extinction center; more and more  $\text{V}_\text{O}$  combine with electrons to form  $\text{F}^+$ .<sup>35</sup>  $\text{F}^+$  induce a smaller magnetic moment, leading to a decrease in  $M_s$ . In a word,  $\text{V}_\text{O}$  was produced after neutron irradiation of  $\text{TiO}_2$ .

The CASTEP module was used to calculate the density of states (DOS) of  $\text{TiO}_2$ , which is based on a plane wave pseudo-potential method and DFT. The electron exchange correlation function is treated using a generalized gradient approximation

(GGA) exchange-correlation functional in the form of Perdew–Bede–Ernzerhof (PBE). GGA+U methods<sup>36,37</sup> were considered to give a proper description of the strong correlation effects. The Hubbard  $U$  was employed as  $U_{\text{Ti},\text{d}} = 6.47 \text{ eV}$ ,  $U_{\text{O},\text{p}} = 4.3 \text{ eV}$ . The Monkhorst–Pack scheme  $k$ -point mesh was  $2 \times 2 \times 3$  for the  $2 \times 2 \times 2$  supercell. The calculation ensured an energy convergence of  $1 \times 10^{-6} \text{ eV}$  per atom and the cut-off energy was 340 eV.

According to Fig. 6, we can find that the DOS of supercells with  $\text{V}_\text{O}$ ,  $\text{V}_{\text{Ti}}$ , and  $\text{F}^+$  defects are asymmetric, indicating that supercells with these defects have a magnetic moment. As displayed in Fig. 6(a), pure  $\text{TiO}_2$  has symmetric DOS and spin-zero ground states; it does not show magnetism.  $\text{V}_\text{O}$  defects could induce a magnetic moment in  $\text{TiO}_2$ , as shown in Fig. 6(b). We also calculated  $\text{F}^+$ ,  $\text{V}_{\text{Ti}}$ ,  $\text{V}_{\text{Ti}}^-$ ,  $\text{Ti}^{3+}$ ,  $\text{O}_\text{i}$ ,  $\text{Ti}_\text{i}$ ,  $\text{V}_\text{O}-\text{Ti}^{3+}$ , as shown in Fig. 6(c)–(i). The supercells with  $\text{F}^+$  and  $\text{Ti}^{3+}$  are found to have lower magnetic moments of  $1.28 \mu_\text{B}$  and  $1.70 \mu_\text{B}$ , respectively, while the supercell with  $\text{O}_\text{i}$  could not induce a magnetic moment. When there is  $\text{V}_{\text{Ti}}$  or  $\text{Ti}_\text{i}$ , its DOS is spin-polarized and the system has a magnetic moment of  $\sim 4 \mu_\text{B}$ . The supercell with  $\text{V}_\text{O}-\text{Ti}^{3+}$  induces a magnetic moment about the same as that of  $\text{V}_\text{O}$ .

The magnetic moment of the  $\text{V}_\text{O}$  system is  $2.39 \mu_\text{B}$ . The partial densities of states (PDOS) of Ti with  $\text{V}_\text{O}$  are shown in

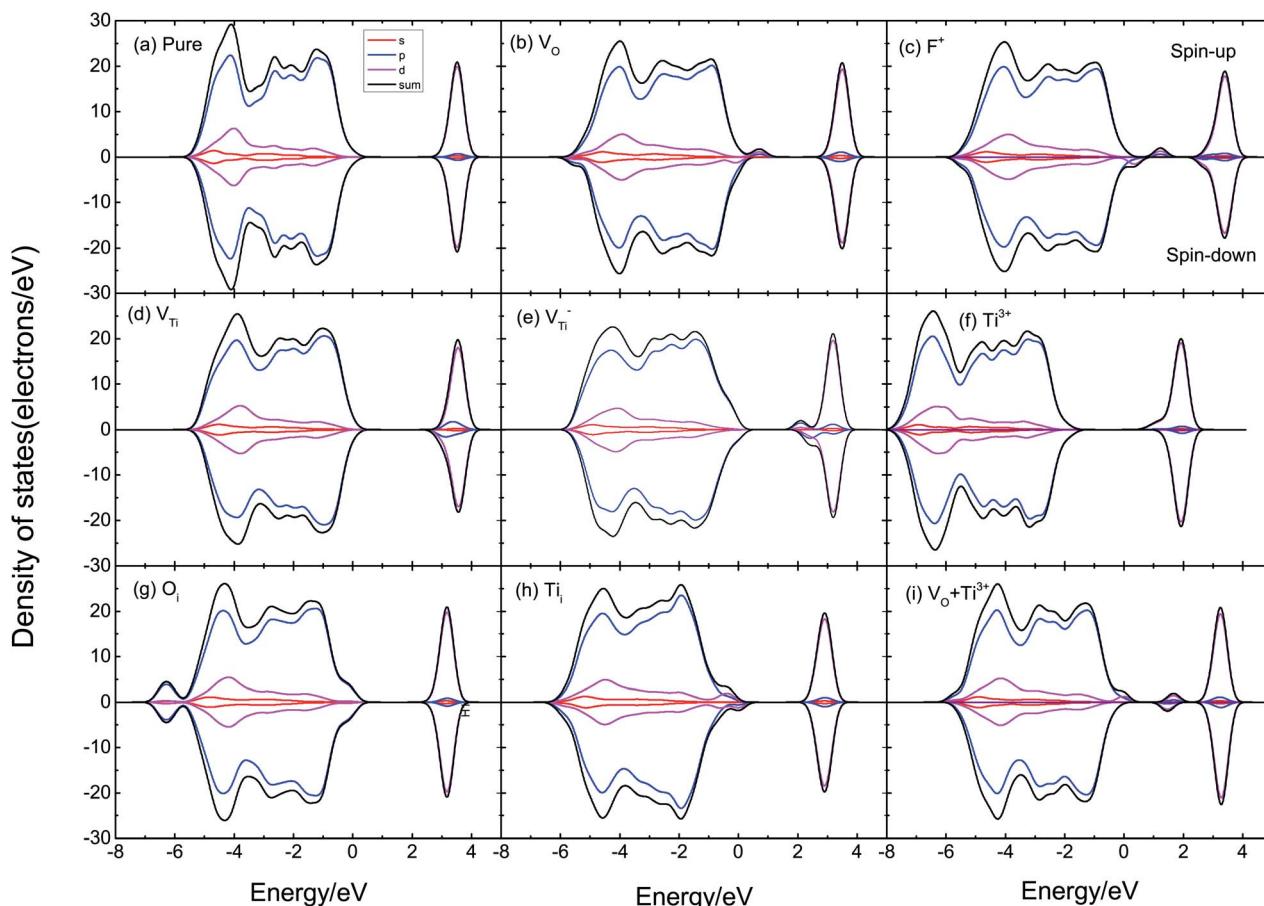


Fig. 6 Spin-polarized total and partial DOS of (a) pure  $\text{TiO}_2$ , (b) the  $\text{TiO}_2$  supercell with one  $\text{V}_\text{O}$ , (c) the  $\text{TiO}_2$  supercell with  $\text{F}^+$ , (d) the  $\text{TiO}_2$  supercell with  $\text{V}_{\text{Ti}}$ , (e) the  $\text{TiO}_2$  supercell with  $\text{V}_{\text{Ti}}^-$ , (f) the  $\text{TiO}_2$  supercell with  $\text{Ti}^{3+}$ , (g) the  $\text{TiO}_2$  supercell with  $\text{O}_\text{i}$ , (h) the  $\text{TiO}_2$  supercell with  $\text{Ti}_\text{i}$ , (i) the  $\text{TiO}_2$  supercell with  $\text{V}_\text{O}-\text{Ti}^{3+}$ .



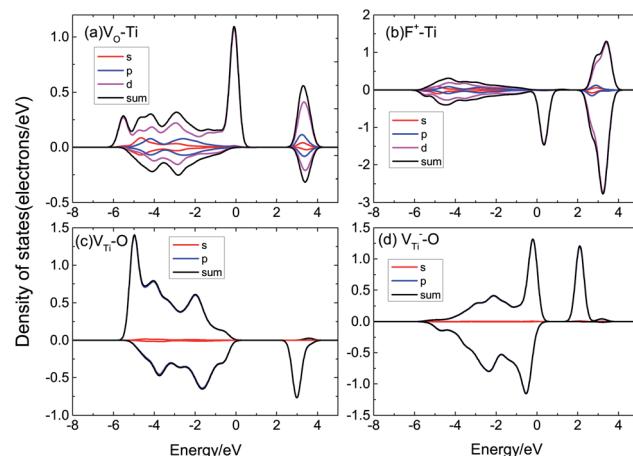
Fig. 7 The PDOS of (a) Ti of  $V_O$ , (b) Ti of  $F^+$ , (c) O of  $V_{Ti}$ , (d) O of  $V_{Ti}^-$ .

Fig. 7(a); the magnetic moment arises from the 3d orbital electrons of the Ti atoms around  $V_O$ . When there is  $V_O$ , the Ti atoms around  $V_O$  are repelled by the  $V_O$ , then the electron population of the Ti 3d orbital varies, causing spin-polarization in the system. It can be seen that  $F^+$  induces a  $1.28 \mu_B$  magnetic moment.  $F^+$  provides a lower magnetic moment than  $V_O$ , as shown in Fig. 7(b); its magnetic moment is also due to the asymmetric PDOS of the Ti 3d orbital.  $V_{Ti}$  can induce a  $4.53 \mu_B$  magnetic moment due to the O 2p orbital hybridization, as shown in Fig. 7(c). Fig. 7(d) shows the PDOS of O 2p of  $V_{Ti}^-$ . For Ti vacancies with various valence states, the titanium vacancy with negatively monovalent charge ( $V_{Ti}^-$ ) is more stable under different conditions.<sup>38</sup> According to our calculations,  $V_{Ti}^-$  induces  $\sim 4 \mu_B$  magnetic moment, which is almost consistent with the magnetic moment introduced by the neutral  $V_{Ti}$ .

Combining the above experimental and theoretical calculation results, we infer that the magnetism in  $TiO_2$  after D-D neutron irradiation is caused by  $V_O$ ,  $V_{Ti}$  and  $F^+$ . Besides, we also calculated the defect formation energies of these kinds of point and compound defects, as shown in Table 2. We used the following formula to calculate defect formation energy ( $E_f$ ):<sup>39-41</sup>

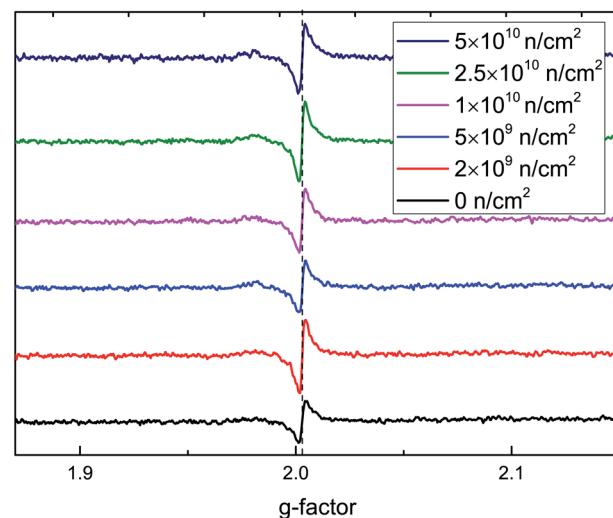
$$E_f = E_{(D)} - E_{(TiO_2)} + n_1\mu_{(O)} + n_2\mu_{(Ti)} + qE_F \quad (1)$$

$$E_{(TiO_2)} = \mu_{(Ti)} + 2\mu_{(O)} \quad (2)$$

$E_{(D)}$  is the total energy of the supercell with defects ( $V_O$ , or  $V_{Ti}$ , ...),  $E_{(TiO_2)}$  is the total energy of pure rutile  $TiO_2$ ,  $n_1$  and  $n_2$  are the number of removed O (or Ti) atoms, and  $\mu$  is the chemical potential energy. In the O-rich case,  $\mu_{(O)}$  is half of  $\mu_{(O_2)}$ ,  $\mu_{(O)} = -430$  eV;  $\mu_{(Ti)}$  can be calculated from formula (2),  $\mu_{(Ti)} = -1612.04$  eV. In the O-poor case,  $\mu_{(Ti)}$  is equal to the metal Ti,

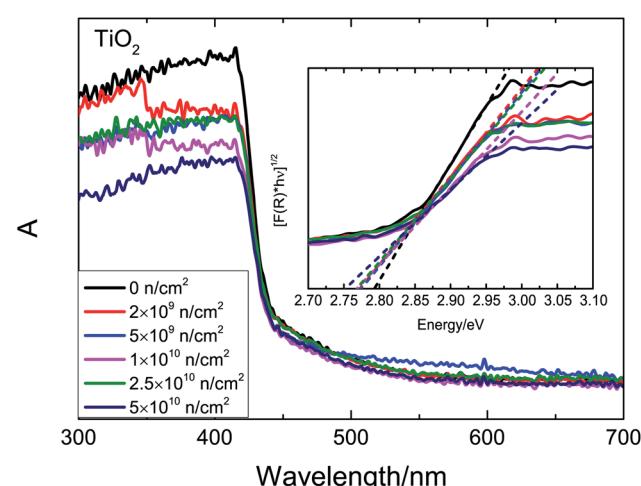
Table 2 Formation energy of  $TiO_2$  with neutral intrinsic defects

$E_f$ /eV	$V_O$	$V_{Ti}$	$O_i$	$Ti_i$
O-rich	7.00	0.57	0.58	11.89
O-poor	2.41	8.62	5.17	2.71

Fig. 8 ESR spectra of  $TiO_2$  before and after neutron irradiation.

and  $\mu_{(Ti)}^{\text{metal}} = -1602.85$  eV;  $\mu_{(O)}$  can be calculated from formula (2),  $\mu_{(O)} = -434.58$  eV.  $q$  is the charge of the defects, and the Fermi level  $E_F$  is the energy of the electron reservoir, referenced to the valence-band maximum (VBM).

The results were different in the O-rich and O-poor cases.  $V_O$  is more easily formed than  $V_{Ti}$  in terms of the energy of dislocation threshold and defect formation. Therefore, it is easier to form  $V_O$ ,  $V_{Ti}$ ,  $F^+$ ,  $Ti^{3+}$  and  $V_O-Ti^{3+}$  than  $Ti_i$  defects in the atmosphere, and the most likely origin of magnetism in  $TiO_2$  is  $V_O$ ,  $V_{Ti}$ ,  $F^+$  and  $Ti^{3+}$ . For unirradiated  $TiO_2$ , native  $V_O$  defects induced RTFM. After D-D neutron irradiation, the defect concentration increases with the irradiation fluence, and the defect type also changes. More and more  $V_O$  and  $V_{Ti}$  provide conditions for the formation of other defects;  $Ti^{3+}$ ,  $F^+$  and other compound defects ( $V_O + Ti^{3+}$  and so on) are produced, and the density of these defects becomes higher and higher with the increase of neutron irradiation fluence. We also found that  $V_O$  can induce a  $2.39 \mu_B$  magnetic moment.  $Ti^{3+}$  and  $F^+$  defects

Fig. 9 UV-Vis spectra of  $TiO_2$  before and after neutron irradiation.

introduce smaller magnetic moments that cause the RTFM of the  $5 \times 10^9 \text{ n cm}^{-2}$  and  $1 \times 10^{10} \text{ n cm}^{-2}$  samples to decrease. Bao *et al.*<sup>42</sup> proposed that the RTFM may be due to the formation of  $\text{V}_{\text{Ti}}$  from the substitution of Ga for Ti, and  $\text{V}_{\text{Ti}}$  was verified by positron annihilation spectroscopy. Qin *et al.*<sup>43</sup> reported that the RTFM is attributed to  $\text{V}_{\text{Ti}}$  and  $\text{N}_{\text{O}}$  defects in the rutile structure. Then, more  $\text{V}_{\text{Ti}}$  and  $\text{V}_{\text{O}}$  play a key role in increasing the RTFM of the  $2.5 \times 10^{10} \text{ n cm}^{-2}$  and  $5 \times 10^{10} \text{ n cm}^{-2}$  samples.

To further verify that the RTFM is caused by  $\text{V}_{\text{O}}$  defects, ESR spectra at 2 K are shown in Fig. 8. A peak was found around a g-factor of 2.003, which was assigned to an oxygen vacancy binding a single electron<sup>44</sup> in rutile  $\text{TiO}_2$ . The signal intensity first increases and then decreases, then increases with the increase in irradiation fluence, which is in accordance with the M–H curves. From the above analysis, the highest concentration of  $\text{V}_{\text{O}}$  is induced by  $2 \times 10^9 \text{ n cm}^{-2}$ ; it also causes the greatest changes in magnetism.

The UV-Vis absorption spectra after irradiation are shown in Fig. 9. According to first-principles calculations, a strong absorption at 420 nm is inherent. The optical band gap ( $E_g$ ) is estimated by the K–M function. The  $E_g$  decreases gradually with the increase in fluence. Based on our previous analysis and theoretical research,<sup>14,45</sup>  $\text{V}_{\text{O}}$ ,  $\text{V}_{\text{Ti}}$  and  $\text{V}_{\text{O}}\text{-Ti}^{3+}$  defects introduce unpaired states in the band gap, which could narrow the band gap. As the fluence increases, ever larger concentrations of defects and ever thicker defect states imply an ever narrower band gap. With the increase in irradiation fluence, the total defect concentration increases, and the change of defect types causes the  $M_s$  to change.

## 4 Conclusion

In summary, we found that the origin of RTFM of unirradiated  $\text{TiO}_2$  is  $\text{V}_{\text{O}}$ . D–D neutron irradiation was used to engineer the defect concentration and type. After D–D neutron irradiation, the  $M_s$  increases with the increasing concentration of  $\text{V}_{\text{O}}$  and  $\text{V}_{\text{Ti}}$ . As the neutron irradiation fluence increases, more and more  $\text{V}_{\text{O}}$  combine electrons to form  $\text{F}^+$ .  $\text{F}^+$  induce a smaller magnetic moment, leading to a decrease in  $M_s$ . With further increases of the irradiation fluence,  $\text{V}_{\text{Ti}}$  and  $\text{V}_{\text{O}}$  play an important role in increasing the magnetic moment. Therefore, RTFM is caused by  $\text{V}_{\text{O}}$ ,  $\text{F}^+$ , and  $\text{V}_{\text{Ti}}$ . The optimal fluence of D–D neutron irradiation remains to be further explored.

## Conflicts of interest

There are no conflicts to declare.

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