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Electron spin resonance investigation of the substitution of Fe^{3+} for Ti^{4+} ions in rutile TiO_2 single crystal*

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A Fe doped rutile TiO_2 single crystal is grown in an O_2 atmosphere by the floating zone technique. Electron spin resonance (ESR) spectra clearly demonstrate that Fe^{3+} ions are substituted for the Ti^{4+} ions in the rutile TiO_2 matrix. Magnetization measurements reveal that the Fe:TiO_2 crystal shows paramagnetic behaviour in a temperature range from 5 K to 350 K. The Fe^{3+} ions possess weak magnetic anisotropy with an easy axis along the c axis. The annealed Fe:TiO_2 crystal shows spin-glass-like behaviours due to the aggregation of the ferromagnetic clusters.

Keywords: rutile, electron spin resonance, diluted magnetic semiconductors
PACC: 7550P, 3320B, 7550L

1. Introduction

Diluted magnetic semiconductors, in which a fraction of nonmagnetic elements are replaced by magnetic transition metal (TM) ions, have been extensively studied.[1,2] Because of their high Curie temperature (T_c) and excellent transparency in the visible region, diluted magnetic semiconductor oxides (DMSOs) have attracted a great deal of attention in recent years.[3,4] It was reported that room-temperature ferromagnetism could be achieved in Fe doped rutile TiO_2 (Fe:TiO_2).[5,6] However, the microscopic origin of the ferromagnetism has been subjected to heated arguments. Extrinsic effects, such as ferromagnetic cluster and impurity phases, have been found to be responsible for the magnetic response in several cases.[7] So it is of fundamental importance to determine the local crystal structure and the electronic state of the doped Fe ions in rutile TiO_2. However, most of the previous studies of the Fe:TiO_2 have focused on thin films and polycrystalline materials. Owing to the interference with substrate and/or grain boundary, it is difficult to accurately identify the local crystal structure of the doped TM ions. The growth of Fe:TiO_2 single crystals in equilibrium conditions is expected to produce segregation-free and homogeneous samples, at least for low doping concentrations.[8,9] Compared with the films and the polycrystalline materials, the single crystal can facilitate us to gain an insight into the origin of the ferromagnetism in the DMSOs. In this work, a rutile Fe:TiO_2 single crystal of high quality is grown and the local environment of the Fe ions is studied by electron spin resonance. Magnetzation measurement reveals that the isolated Fe ion possesses weak anisotropy with an easy axis along the c axis. After being annealed in vacuum, the Fe^{3+} ions begin to segregate to form ferromagnetic clusters.

2. Experimental

Fe:TiO_2 single crystals were fabricated by using the floating zone method in the O_2 atmosphere at a pressure of 0.5 MPa. The nominal composition of Fe in the crystal accounts for 3%. X-ray diffraction (XRD) and back-reflection Laue XRD experiments were performed to check the crystallization and determine the crystallographic direction. An electron spin resonance (ESR) measurement was made at 77 K with an x-band spectrometer (JEOL JES–FA200) at a microwave frequency of about 9.0 GHz. A cuboid piece of Fe:TiO_2 single crystal perpendicular to the c axis was cut off for the magnetization measurement, which was performed by using a superconducting quantum interference device (SQUID) magnetometer. As a comparison, a piece of crystal was sealed in an evacuated

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quartz ampoule and annealed at 1000 °C for 4 days.

3. Results and discussion

As-prepared Fe:TiO_2 crystal is stinking reddish in colour. Figure 1 shows the XRD patterns of as-prepared Fe:TiO_2 crystal. The powder XRD pattern of the Fe:TiO_2 crystal shows the peaks corresponding to rutile phases. No segregation of Fe oxide or the impurity phase is detectable within the instrumental resolution limit. The values of lattice parameters fitted by using the powder XRD pattern are $a = 0.4599$ nm and $b = 0.2961$ nm, which are a bit larger than those of TiO_2 ($a = 0.4584$ nm and $c = 0.2953$ nm). Since the radius of the Fe^{3+} ions is larger than that of the Ti^{4+} ions, the expansion of the unit cell implies that the Fe ions are incorporated into the rutile lattices.[10] Figures 1(b) and 1(c) shows the XRD patterns along the R (001) and the R (110) directions, respectively. The narrow diffraction peaks demonstrate the high quality of the crystal.

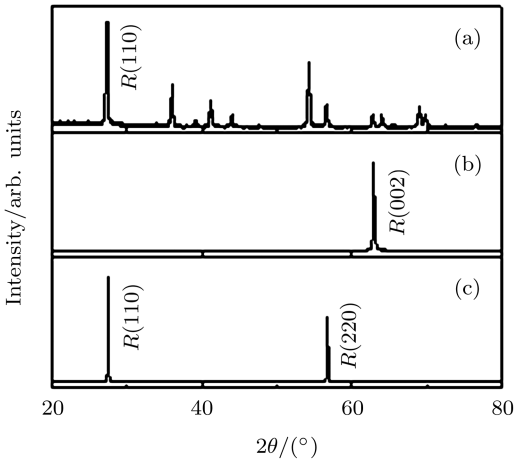


Fig.1. Powder XRD pattern of an as-prepared Fe:TiO_2 single crystal (a) and XRD patterns of Fe:TiO_2 along the c axis (b) and (110) axis (c).

ESR is an efficient method of investigating the electronic state of doping ion in various crystals. The unit cell of rutile contains two equivalent lattice sites of local orthorhombic (D_{2h}) symmetry. These two equivalent centres are perpendicular to each other and also perpendicular to the tetragonal axis of the crystal structure. In the case where Fe^{3+} ions are substituted for Ti^{4+} ions located at the oxygen octahedral centers, there should be expected two equivalent sets of paramagnetic centres in the crystal. The ESR spectra observed for the Fe:TiO_2 crystal during the rotation of the DC field in the (001) plane at 77 K are presented in Fig.2(a). The ESR spectra are strongly anisotropic in an available magnetic field range of 0–800 kA/m. The observed ESR spectra are caused by the trivalent paramagnetic Fe^{3+} ions. The ground state of free Fe^{3+} ions ($3d^5$) is ^6S, which is a nondegenerate orbital singlet. The Fe^{3+} ion with $S = 5/2$ in a distorted octahedron field of the rutile TiO_2 host lattice can be described by the following spin Hamiltonian:[11,12]

$$\begin{aligned} H &= g\beta H \cdot S + D\left(S_z^2 - \frac{35}{12}\right) \\ &\quad + E(S_x^2 - S_y^2) + \frac{a}{6}\left(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16}\right) \\ &\quad + \frac{7}{36}F\left(S_z^4 - \frac{95}{14}S_z^2 + \frac{81}{16}\right), \end{aligned} \tag{1}$$

where g is the spectroscopic splitting factor; β is the Bohr magneton; H is the applied magnetic field; S_x, S_y and S_z are the components of the electron spin operator; D is the second-order axial zero-field splitting parameter; E is the second-order rhombic zero-field splitting parameter; a and F are the cubic and the fourth-order axial zero-field splitting parameters, respectively. Figure 2(b) shows the calculated curves from expression (1). The derived spin Hamitonian parameters are $g = 2.0$, $D = 23.22$ GHz, $E = 2.73$ GHz, $a = 0.2139$ GH, and $F = -0.9905$ GHz, which are in agreement with the previous results in Ref.[11]. The Fe^{3+} ions are definitely substituted for the Ti^{4+} ions and are incorporated into the rutile lattice. To maintain charge neutrality, oxygen vacancies should be generated to accommodate Fe^{3+} ions in rutile. But

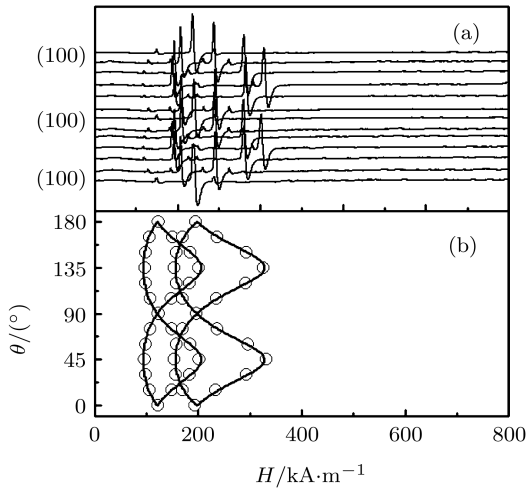


Fig.2. Measured (a) and calculated (b) curves of the ESR spectrum of an as-grown Fe:TiO_2 single crystal with H rotating in the (001) plane at 77 K.

no evidence indicates that the oxygen vacancies are near the Fe^{3+} ions, which is different from the previ-

ous results.[13]

The temperature dependence of the inverse magnetic susceptibility ($1/\chi$) in a field of 160 kA/m is shown in Fig.3(a). From 5 K to 300 K the curve in both the c axis and the (110) direction shows a typical paramagnetic behaviour and displays a typical Curie–Weiss behaviour

$$\chi = \frac{C}{T-\theta}. \tag{2}$$

The derived Curie–Weiss temperature θ is about 0.1 K for both of the directions. This implies that almost no exchange interaction occurs among the Fe^{3+} ions, which is in agreement with the ESR result. But the $1/\chi$ along the c axis is much smaller in the whole temperature range. Figure 3(b) shows the magnetization curve of the Fe:TiO_2 crystal, measured at 5 K. The magnetization curve shows typical paramagnetic behaviour and magnetocrystalline anisotropic behaviour. The magnetization along the c axis is greater than that along the (110) direction. The magnetic moment prefers to lie along the c axis. Similar results are reported in the $Zn_{1-x}Co_xO$ crystal. It is suggested that tetrahedral coordination of Co leads to the distortion of the Co ions electronic clouds. The change of spin-orbital coupling energy induced by spin rotation behaves as the change of magnetocystalline anisotropy energy.[1,14]

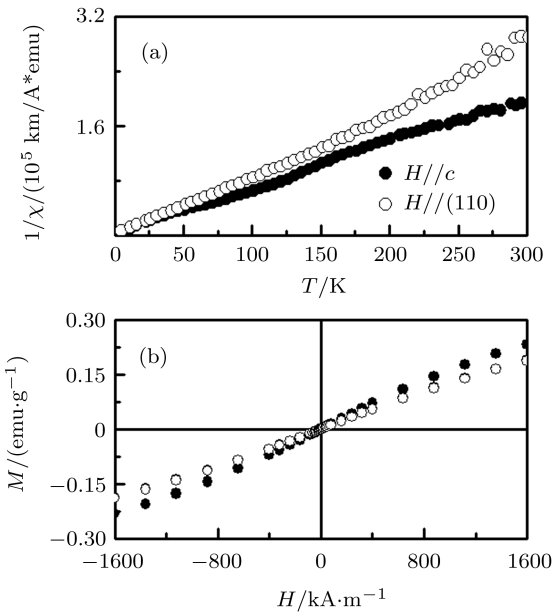


Fig.3. The temperature dependence of $1/\chi$ parallel to the c axis and the (110) direction in a field of 160 kA/m (a) and the magnetization curve of an as-prepared Fe:TiO_2 crystal at 5 K (b).

It has been reported that the oxygen vacancies are crucial for ferromagnetism and the annealing of the sample in vacuum can greatly enhance the magnetic property of the Fe doped rutile.[15,16] The ESR spectrum of the annealed Fe:TiO_2 crystal is almost identical to that of the as-prepared crystal. But some changes in the ESR spectrum occur for the annealed crystal. Figure 4 shows the ESR spectra along the (100) direction for both the as-prepared and the annealed Fe:TiO_2 single crystals at 77 K. It can be seen that the substitutional Fe^{3+} ions still exist after annealing. Nevertheless, a new absorption around 304 kA/m, correspondingly $g = 1.68$, appears. These imply the structure change of the crystal, which may lead to the change of the magnetic state.

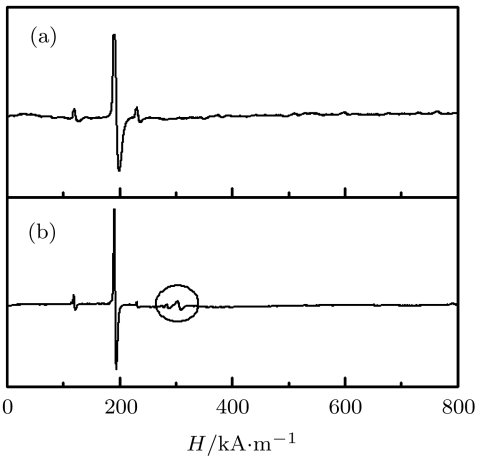


Fig.4. ESR spectra at 77 K in the direction parallel to the (100) axis for as-prepared (a) and annealed Fe:TiO_2 crystals (b).

Figure 5(a) shows the ZFC and the FC magnetization curves measured at 16 kA/m for the annealed sample. There is a distinct bifurcation of the ZFC and the FC starting at 40 K. The Fe:TiO_2 crystal changes from the paramagnetic state to spin-glass-like behaviour and the magnetization is enhanced significantly.[17] Considering the ESR spectrum of the annealed crystal, a portion of Fe^{3+} ions segregates to form nanoscale ferromagnetic clusters in the annealing process. Obviously, there should be a paramagnetic contribution of Fe^{3+} ions as well. In Fig.5(b), we show the hysteresis curve at 5 K of the annealed crystal. A large coercivity for the field up to 336 kA/m is observed for the annealed sample. The magnetization is not saturated for the field up to 1600 kA/m, which may partly be due to the paramagnetic signal of substitutional Fe^{3+} ions.

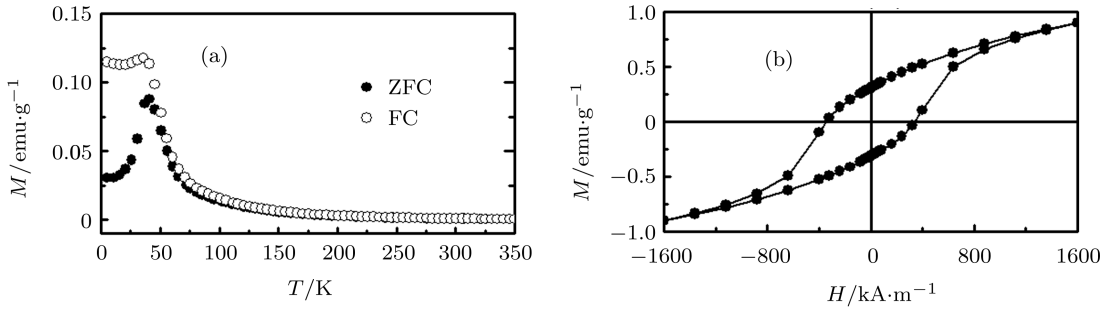


Fig.5. The ZFC and the FC magnetization curves at 16 kA/m for the annealed Fe:TiO_2 single crystal with H in the direction parallel to the c axis (a) and the magnetization curve of annealed Fe:TiO_2 crystal along the c axis at 5 K (b).

4. Conclusion

Rutile Fe:TiO_2 single crystals are grown by the floating zone technique. ESR measurements confirm that the Fe^{3+} ions are substituted for the Ti^{4+} ions and incorporated into the TiO_2 lattices. Magnetization measurement reveals that these Fe^{3+} ions show paramagnetic behaviour in a temperature range from 5 K to 350 K with an easy axis along the c axis. A spin-glass-like behaviour is observed in the Fe:TiO_2 crystal annealed in vacuum, owing to the formation of nanoscaled ferromagnetic clusters.

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