Co-doped rutile TiO$_{2-\delta}$ thin films studied by XANES and first principles calculations

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Abstract. The x-ray absorption near-edge structure (XANES) and first-principles calculations were employed to study the local structure and magnetic origin of Co-doped rutile TiO$_2$ thin film. It is found that the experimental Co $K$-edge XANES can be reproduced by the calculated spectrum of substitutional Co (Co$_{Ti}$) with O vacancy (V$_O$), suggesting the coexistence of Co$_{Ti}$ and V$_O$ in this system. First-principles total energy calculations further reveal that the O vacancy prefers to reside near the Co ion and substantially facilitates the impurity doping. The electronic structure analysis indicates that the O vacancy can mediate the ferromagnetic interaction between the Co$_{Ti}$ ions and thus is responsible for the observed room-temperature ferromagnetism in the Co-doped TiO$_{2-\delta}$ thin films.

1. Introduction

Dilute magnetic semiconductor (DMS) oxides are attracting increasingly interest due to their potential applications in spintronic devices [1]. Following the theoretical predications that room temperature (RT) ferromagnetism might exist in DMSs of wide-band-gap semiconductors like GaN and ZnO [2], transition-metal (TM) doped oxides have been identified as one of the most promising candidates. Especially, a recent discovery of RT ferromagnetism in Co-doped anatase and rutile TiO$_2$ by Matsumoto et al. [3,4] has motivated intensive studies on the Co:TiO$_2$ system.

Because of different preparation conditions, some investigators believe that the magnetism of TM:TiO$_2$ originates from the presence of TM clusters [5,6], while others treat the ferromagnetism as intrinsic [7,8]. On the other hand, the strong interaction between Co ions and O vacancy (V$_O$) in Co-doped TiO$_{2-\delta}$ was found to play an important role in the induction and stability of ferromagnetism [9,10]. Recently, first-principles calculations suggested that the interactions between Co(Fe) ion and V$_O$ in the Co(Fe):TiO$_2$ systems are strongly dependent on their separation distances [11,12]. Unfortunately, the relative spatial distribution and electronic properties of V$_O$ and Co ions in Co-doped TiO$_{2-\delta}$ is still an open question.

In this work, x-ray absorption near-edge structure spectroscopy (XANES) and the first-principles calculations were employed to study the local atomic and electronic structures in the Co:TiO$_{2-\delta}$ sample prepared by RT deposition method. The aim is to determine the occupation sites of Co and O vacancy and their correlations with the magnetic interactions between the substituted Co ions.

2. Experimental
The Co:TiO$_2$-$\delta$ thin film was prepared by RT deposition of Co on TiO$_2$ substrate, followed by high-temperature annealing in ultra-high vacuum (UHV). About 0.5-nm-thick Co overlayer was deposited on a clean TiO$_2$(100) surface at a rate of 1.0 Å/min under $\sim 5.0 \times 10^{-9}$ mbar. In situ annealing was performed at 700 °C for 30 min. X-ray photoelectron spectroscopy (XPS) measurement suggested that the oxidation state of Co ion in the film is +2. Furthermore, XPS depth profile analysis revealed that the effective Co:TiO$_2$-$\delta$ layer on TiO$_2$ substrate is about 30 nm, and the Co fraction is around 5%. Neither Co metal nor Co-rich rutile cluster was observed in the film. The superconducting quantum interference device (SQUID) magnetometer measurement shows that the saturation magnetic moment was 0.9 $\mu_b$/Co, by assuming that all the Co atoms contribute to the magnetization. The Co K-edge XANES spectra were collected at the beamline BL13B1 of Photon Factory (PF) of High Energy Accelerator Research Organization (KEK), Japan and the U7C beamline of National Synchrotron Radiation Laboratory of China.

3. Computational details
Our spin-polarized density-functional theory calculations were performed using a plane wave basis set with the projector augmented plane-wave (PAW) method [13] as implemented in the Vienna *ab initio* simulation package [14]. The exchange-correlation interaction was described within the generalized gradient approximation (GGA) [15]. To investigate Co distribution, supercell of 96 atoms ($2 \times 2 \times 2$) was used. The lattice constants and internal parameters were fully relaxed. The energy cutoff was set to 400 eV, and the convergence in energy and force were $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively. We calculate the formation energy to determine the relative stability of different configurations, for which the formation energy is expressed as

$$E_f = E_{\text{tot}} - E_{\text{ref}} - lE_{\text{Co}} + mE_{\text{Ti}} + nE_{\text{O}}$$

where $E_{\text{tot}}$ and $E_{\text{ref}}$ are the total energies of Co-doped TiO$_2$-$\delta$ and pure TiO$_2$ reference structure (as calculated with the same size supercell), respectively. Here, $E_{\text{Co}}$, $E_{\text{Ti}}$, and $E_{\text{O}}$, are the atom energies of Co, Ti, and O, while $l$, $m$, and $n$ are the numbers of doped Co, substituted Ti, and O vacancy [16].

4. Results and discussion
It is suggested that in the Co-doped TiO$_2$ films some native defects, for example, V$_O$ and Co interstitials (Co$_I$) are located at sites neighboring the substitutional Co ions. To study the local structures around Co in Co-doped TiO$_2$, we performed XANES calculations with FEFF8.4 code [17] at Co K-edge for three representative model clusters: the substitutional Co$_{Ti}$, interstitial Co$_I$, and Co$_{Ti}$+V$_O$. Figure 1 displays the Co K-edge XANES spectra of Co:TiO$_2$ and Co metal, along with the simulated XANES spectra for the above four model structures. First of all, the existence of metallic Co in the Co:TiO$_2$ sample can be easily excluded, since its XANES spectral shapes and edge positions are significantly different from those of the Co:TiO$_2$. Four peaks a, b, c and d can be observed in the Co K-edge XANES for the Co:TiO$_2$ film. From Fig. 1, we can find that these near edge features of Co:TiO$_2$ film can only be reproduced by FEFF8.4 calculation for the Co$_{Ti}$+V$_O$ model. When O vacancy is located beyond the nearest-neighbor of Co, the calculated XANES resembles that of the Co$_{Ti}$ model (not shown in Fig. 1). These results have confirmed that the Co ions were substitutionally incorporated into the TiO$_2$ lattice, and suggest that oxygen vacancy prefers to stay near the Co impurity.

Table 1 lists the calculated formation energies and magnetic moments for four representative models.

| Configuration      | $E_f$ (eV) | $M$ ($\mu_B$) |
|--------------------|------------|---------------|
| Co$_{Ti}$          | 4.58       | 0.88          |
| Co$_{Ti}$+V$_O$ (1.926 Å) | 1.16       | 1.01          |
| Co$_{Ti}$+V$_O$ (2.015 Å) | 1.88       | 1.00          |
| Co$_{Ti}$+V$_O$ (3.474 Å) | 1.94       | 1.00          |
reside near the Co dopant. This result is consistent with that figured out from the XANES measurements, demonstrating the presence of Co-V\textsubscript{O} complex in TiO\textsubscript{2} matrix both theoretically and experimentally.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure1.png}
\caption{Co K-edge XANES spectra of the Co:TiO\textsubscript{2} and Co metal, along with the calculated spectra for three model structures: Co\textsubscript{Ti}+V\textsubscript{O}, Co\textsubscript{Ti}, and Co\textsubscript{i}.
}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure2.png}
\caption{The calculated DOSs for (a) pure TiO\textsubscript{2}, (b) Co\textsubscript{Ti}, (c) Vo, and (d) Co\textsubscript{Ti}+V\textsubscript{O} models. The vertical dash line represents the Fermi level. The partial DOSs of Co 3d are in shade.
}
\end{figure}

Now, we explore the effects of the Vo on the magnetic interaction and electronic structure of the Co:TiO\textsubscript{2}. Figure 2 shows the calculated densities of states (DOSs) for three representative configurations including the Co\textsubscript{Ti}, Vo, and Co\textsubscript{Ti}+V\textsubscript{O} cases. For reference, the DOS for pure TiO\textsubscript{2} is also calculated [shown in Fig. 2(a)], which is in good agreement with that reported by others [18]. In the case of a Co atom substituted at the Ti site [Fig. 2(b)], the Co 3d levels are split into a doubly degenerate e\textsubscript{g} band and a triply degenerate t\textsubscript{2g} band due to the octahedral symmetry of Co atoms. The t\textsubscript{2g}\textsuperscript{↑} state is fully occupied, while the t\textsubscript{2g}\textsuperscript{↓} and e\textsubscript{g} bands remain only partly occupied. Correspondingly, the calculated Co K-edge XANES for the Co\textsubscript{Ti} model exhibits two pre-edge peaks which are similar to the Ti K-edge XANES, as indicated by arrows in Fig. 1. These two peaks arise from the hybridization between the unoccupied Co 3d (t\textsubscript{2g}\textsuperscript{↓} and e\textsubscript{g}) and O 2p states. As seen from Fig. 2(c), the O vacancy induces a donor state a\textsubscript{1} within the gap. This state sufficiently overlaps with the bottom of the conduction band, and therefore, the states induced by O vacancy are delocalized over the entire crystal, consistent with the result for oxygen-deficient TiO\textsubscript{2} [19]. When an O vacancy neighboring a Co ion is introduced, the e\textsubscript{g}\textsuperscript{↑} and t\textsubscript{2g}\textsuperscript{↑} bands are mixed due to the reduced crystal field in the pyramidal structure composed of five oxygen anions [Fig. 2(d)]. Moreover, Fig. 2(d) shows that the t\textsubscript{2g} bands and e\textsubscript{g}\textsuperscript{↑} band are basically occupied. This indicates that Co\textsubscript{Ti} adopts a low-spin configuration (t\textsubscript{2g}\textsuperscript{↑}e\textsubscript{g}\textsuperscript{↑},t\textsubscript{2g}\textsuperscript{↓}). Subsequently, the hybridization between the unoccupied Co 3d e\textsubscript{g} and O 2p states gives rise to the pre-edge peak a in the Co K-edge XANES spectrum. Moreover, Fig. 2(d) exhibits that this spin-split donor impurity band is hybridized evidently with the Co\textsubscript{Ti} 3d states. This suggests the existence of an exchange interaction between the delocalized states and Co ions within the carrier orbit. According to the resonant magnetic polaron (RMP) model [20,21], the delocalized band serves as an effective resonant magnetic polaron and can activate a long-ranged ferromagnetic interaction among the doped
Co ions. As a result, the ferromagnetic alignment between the Co ions in the Co:TiO$_2$-$\delta$ system is realized and thus enhances the saturated magnetic moment from 0.88 to 1.00 $\mu_B$/Co (Table 1).

5. Conclusions
In summary, by using XANES and first-principles calculations, we have studied the local atomic structure and magnetic origin of Co-doped TiO$_2$-$\delta$ film with RT ferromagnetism. Co $K$-edge XANES analysis together with total energy calculations revealed the formation of Co Ti$^{2+}$-Vo complex in the TiO$_2$ matrix. Based on our first-principles calculations, it is clarified that the impurity states induced by O vacancy are delocalized over the entire crystal, and the strong hybridization between the Vo$^{2+}$ induced spin-split donor impurity band and Co 3$d$ state might be responsible for the ferromagnetism origin of the Co:TiO$_2$-$\delta$ thin film.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (Grants No. 10605024, 10635060, 10725522, and 20701036). The authors would like to thank NSRL, BSRF, and Photon Factory for the synchrotron radiation beamtime.

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