Oxygen Vacancies in a (TiCo)O$_2$ Ferromagnet Revealed from EXAFS

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1 Introduction

Transition-metal doped oxides are promising candidates for a room temperature ferromagnetic semiconductor which is a key material to spintronics devices [1]. Several models have been proposed for ferromagnetism of the oxides in which defects, especially oxygen vacancies, play a role [2]. However, there is few direct observation for the oxygen vacancies. This report concentrates on observing the oxygen vacancies directly by EXAFS.

2 Experiment

We selected a rutile-type TiO$_2$ (99.99%) as a matrix and a normal spinel-type Co$_3$O$_4$ (99.9%) as a dopant. They mixed in the ratio of 3 at% Co and were ground for several hours using a ball mill. The mixture was calcined at 800 ºC for 5 hours in air. Hereafter we refer to the specimen thus obtained as (Ti$_{0.97}$Co$_{0.03}$)O$_2$.

EXAFS, X-ray diffraction and magnetic measurements were carried out for the specimen with references TiO$_2$ and Co$_3$O$_4$ at 300 K.

3 Results and Discussion

We have confirmed by conventional x-ray diffraction and SPring-8 synchrotron powder x-ray diffraction measurements that (Ti$_{0.97}$Co$_{0.03}$)O$_2$ is a single phase with a rutile-type structure as same as that of the TiO$_2$ matrix. Magnetization measurements shows that (Ti$_{0.97}$Co$_{0.03}$)O$_2$ has a coercive force of 0.02 T characteristic of ferromagnetism at 300 K while TiO$_2$ is paramagnetic.

Figure 1 shows the absolute values of radial structure functions of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ near both Co and Ti K edges and TiO$_2$ near Ti K edge without a difference of the phase shift. From the EXAFS fit a central Ti atom in the rutile-type TiO$_2$ has six oxygen neighbors at 1.96 Å, two Ti atoms at 2.96 Å and eight Ti next neighbours at 3.56 Å, which are completely the same interatomic distances as those of x-ray diffraction. The radial structure function of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ at the Co K edge shows the three peaks corresponding to the first Co-O, the first Co-Ti and the second Co-Ti pairs as indicated by the arrow. The features of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ near both Co and Ti K edges are as same as those of TiO$_2$ at the Ti K edge. This implies that Co atoms in (Ti$_{0.97}$Co$_{0.03}$)O$_2$ are located on the Ti sites of TiO$_2$. It should be noted that (Ti$_{0.97}$Co$_{0.03}$)O$_2$ forms no Co clusters because there is not any peaks around 2.0 Å. In (Ti$_{0.97}$Co$_{0.03}$)O$_2$ the interatomic distances of Co-O and Co-Ti pairs are a little different from those of the Ti-O and Ti-Ti counterparts.

Another striking feature of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ is about the oxygen around the Co site. The Co-O peak of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ is much lower than the Ti-O peaks of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ and TiO$_2$. This means that the coordination number of oxygen around Co in (Ti$_{0.97}$Co$_{0.03}$)O$_2$ is less than six. We have obtained the coordination number of oxygen around the Ti atom to be six and that the Ti^{4+} sites are substituted by Co^{3+} or Co^{2+} ions. Therefore we conclude that there are oxygen vacancies only around Co atoms in (Ti$_{0.97}$Co$_{0.03}$)O$_2$ due to the electroneutrality [3].
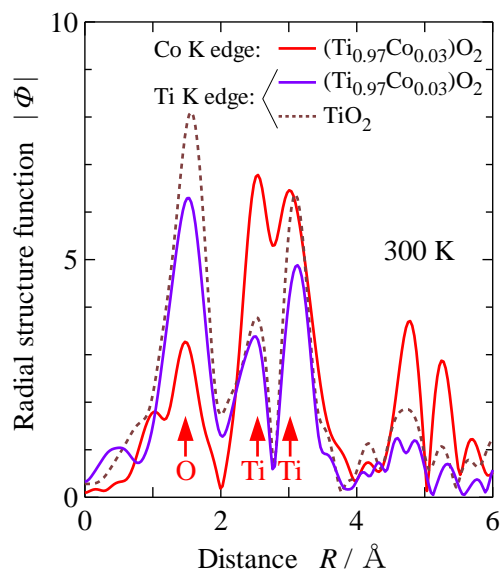

Fig. 1: Radial structure function of (Ti$_{0.97}$Co$_{0.03}$)O$_2$ with references Co$_3$O$_4$ and CoTiO$_3$ for the Co K edge at 300 K.

References
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