Mössbauer Study of Ti$_{1-x}$Co$_x$Fe$_2$O$_2$


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Mössbauer spectra of Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ (0.01 ≤ x, y ≤ 0.05) prepared with $^{57}$Fe enriched iron have been taken at various temperatures ranging from 80 to 300 K. The Mössbauer spectrum of Ti$_0.94$Co$_{0.06}$Fe$_{0.05}$O$_2$ consists of a ferromagnetic (six-Lorentzian), a paramagnetic phase (doublet) and amorphous phase over all temperature ranges. Isomer shifts indicate Fe$^{3+}$ for the ferromagnetic phase and the paramagnetic phase of Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ samples. It is noted that the magnetic hyperfine field of ferromagnetic phase had the value about 1.5 times as large as that of α-Fe. The XRD data for Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ showed mainly rutile phase with tetragonal structures without any segregation of Co and Fe into particulates within the instrumental resolution limit. The magnetic moment per (Co+Fe) atom in Ti$_{0.94}$Co$_{0.06}$Fe$_{0.05}$O$_2$ under the applied field of 1 T was estimated to be about 0.332μB which is ten times as large as that of Ti$_{0.9}$Co$_{0.1}$O$_2$, 0.024μB per Co atom, suggesting a high spin configuration of Co and Fe ions.

Key words: magnetic semiconductors, rutile, low spin

I. Introduction

There has been much attention paid to diluted magnetic semiconductors (DMS) in the last decade, but the origin of ferromagnetism in semiconductor remains an issue of discussions [1, 2]. Recently, cobalt-doped anatase titanium dioxide, Ti$_{1-x}$Co$_x$O$_2$, thin films were reported to be ferromagnetic even above 400 K [1] with a 0.32/Co magnetic moment, and the magnetic ordering was explained in terms of the carrier-induced ferromagnetism [3] as in the III-V based DMS.

Chambers et al. [4, 5] reproduced the ferromagnetism of Ti$_{1-x}$Co$_x$O$_2$. It was reported that the moment is as high as 1.25/Co, and claimed that the ferromagnetism strongly depends on the oxygen deficiency [4, 5]. These results seem to show that the ferromagnetism in Ti$_{1-x}$Co$_x$O$_2$ is originated from the ordered low spin Co$^{3+}$ state due to the charge carriers induced by oxygen defects. However, considering the fact that the ferromagnetism strongly depends on the growth condition [5], the possibility of the Co segregation cannot be excluded in this system [6]. Furthermore, it was reported that the anatase TiO$_2$ is a crystalline defected easily [7]. Rutile is known to be the most stable phase. Due to its scientific and practical importance, TiO$_2$ rutile has been the subject of many experimental and theoretical investigations.

The purpose of this study is to carry out Mössbauer, X-ray and magnetic-susceptibility measurements on rutile Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ (0.01 ≤ x, y ≤ 0.05) to examine magnetic properties and separated contribution of the ferromagnetic and paramagnetic phases to the magnetization.

II. Experiment

Synthesis of Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ sample was accomplished by the following direct-composition method. The starting materials were TiO$_2$, CoO, and Fe$_2$O$_3$ powders of 99.999, 99.999, and 99.9 % purities, respectively. Mixtures of the proper proportions of the elements sealed in evacuated quartz ampoule were heated at 900°C for one day and then slowly cooled down to room temperature at a rate of 10°C/h. In order to obtain single phase material, it was necessary to grind the sample after the first firing and to press the powders into pellets before annealing them for a second time in evacuated and sealed quartz ampoule. Mössbauer spectra were achieved using a conventional Mössbauer spectrometer of the electromechanical type with 50 mCi $^{57}$Co(Rh) source. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder and clamped between two thin boron nitride plates. Magnetic susceptibility measurements were performed with the vibrating sample magnetometer (VSM).

III. Results and Discussion

Figure 1 shows an X-ray diffraction patterns for Ti$_{1-x}$Co$_x$Fe$_2$O$_2$ (x, y=0.03, 0.05) at room temperature. X-
ray-diffraction patterns of Ti_{0.99}Fe_{0.01}O_2 were obtained with Cu Kα radiation. The XRD data for Ti_{1-x-y}Co_xFe_yO_2 showed mainly rutile phase with tetragonal structures, CoTiO_3 and Fe_2TiO_5 second phase without any segregation of Co and Fe into particulates within the instrumental resolution limit. It is noteworthy that the trace of metallic Co or Fe phase was not observed from XRD patterns for rutile Ti_{1-x-y}Co_xFe_yO_2. This result is consistent with that of the XRD for the rutile phase Ti_{1-x}Co_xO_2 (0.01≤x≤0.12) films fabricated by Park et al. [8].

When the same concentration of Co and Fe was co-doped into TiO_2, CoTiO_3 second phase showed more obvious peaks than those of Fe_2TiO_5. It seems that in TiO_2 structure Co ions easily combined into CoTiO_3 because the free combining energy of Co ion is lower than that of Fe ions.

Hysteresis (M-H) curves measured at room temperature for the rutile Ti_{0.97}Co_{0.03}O_2, Ti_{0.97}Fe_{0.03}O_2, and Ti_{0.96}Co_{0.04}Fe_{0.02}O_2 are shown in Fig. 2. Magnetization was highly enhanced when TiO_2 was co-doped by the same concentration of Co and Fe in comparison to the substitution of Co or Fe only into TiO_2. The magnetic hysteresis curves showed an obvious ferromagnetic behaviour. And the magnetic moment per (Co+Fe) atom in Ti_{0.96}Co_{0.04}Fe_{0.02}O_2 under the applied field of 1 T was estimated to be about 0.332μB which is ten times as large as that of Ti_{0.97}Co_{0.03}O_2, 0.024μB per Co atom. The observed magnetic moment of the rutile Ti_{1-x-y}Co_xFe_yO_2 seems to suggest a high spin configuration of Co and Fe ions [8].

Figure 3 shows some of the Mössbauer spectra of...
Tl0.94Co0.06Fe0.03O2 at various absorber temperatures ranging from 80 to 300 K.

The Mössbauer spectrum of Tl0.94Co0.06Fe0.03O2 consists of a ferromagnetic (six-Lorentzian), a paramagnetic (doublet) and amorphous phase (Fe2TiO3) over all temperature ranges. Using a least-squares computer program [9], the separation of the ferromagnetic phase (six-Lorentzian) and the paramagnetic phase (doublet) of the Tl0.94Co0.06Fe0.03O2 Mössbauer spectrum was achieved. The widths that are assumed to be the same in respective subspectra and over all absorption areas of the spectra are independently varied as free parameters.

The magnetic hyperfine field of the ferromagnetic phase in the Tl0.94Co0.06Fe0.03O2 is found to be 491 kOe, whereas that of α-Fe be 330 kOe at room temperature [10]. It is noted that the magnetic hyperfine fields of the ferromagnetic phase in the Tl0.94Co0.06Fe0.03O2 had the value about 1.5 times as large as that of α-Fe. The isomer shift at room temperature for the ferromagnetic phase of Tl0.94Co0.06Fe0.03O2 are found to be 0.22 mm/s relative to the Fe, which is consistent with the high spin Fe3+ charge state [11]. The isomer shift for the paramagnetic phase of Tl0.94Co0.06Fe0.03O2 indicates Fe2+. Those results indicate that the Fe impurities substituted into Ti atoms instead of the formation of iron clusters.

IV. Conclusions

We investigated the ferromagnetism observed in rutile phase Tl1-xCoFe2O5 (0.01≤x, y≤0.05) using X-ray, VSM and Mössbauer spectroscopy. The XRD data for Tl1-xCoFe2O5 showed mainly rutile phase with tetragonal structures, CoTiO3 and Fe2TiO3 second phase without any segregation of Co and Fe into particulates within the instrumental resolution limit. The magnetic hysteresis curves showed an obvious ferromagnetic behaviour. And the magnetic moment per (Co+Fe) atom in Tl0.94Co0.06Fe0.03O2 under the applied field of 1 T was estimated to be about 0.332μB which is ten times as large as that of Tl0.97Co0.03O2, 0.024μB per Co atom, suggesting a high spin configuration of Co and Fe ions.

The magnetic hyperfine field for the ferromagnetic phase Tl0.94Co0.06Fe0.03O2 had the value about 1.5 times as large as that of α-Fe. The isomer shift at room temperature for the ferromagnetic phase of Tl0.94Co0.06Fe0.03O2 are found to be 0.22 mm/s relative to the Fe, which is consistent with the high spin Fe3+ charge state.

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References