MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012A0125 実験課題名 Title of experiment Ferromagnetic state of $LaCo_{1-x}Rh_xO_3$ induced by doping between two nonmagnetic end phases 実験責任者名 Name of principal investigator Yasui, Yukio 所属 Affiliation Meiji University	装置責任者 Name of responsible person Ishigaki, Toru 装置名 Name of Instrument/（BL No.） BL-20 実施日 Date of Experiment 2012/5/14 2012/6/15-6/16 2012/11/1-11/2

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

① $LaCo_{0.8}Rh_{0.2}O_3$

② Li_2ZrCuO_4

③ $Li_2Ru_{1-x}Ir_xO_3$ (x=0.1, 0.2, 0.3, 0.4)

④ $La_4BaCu_{5-x}Mn_xO_{13}$ (x=0, 0.2, 0.5)

Here, We report only the results of $LaCo_{0.8}Rh_{0.2}O_3$ (sample No. ①) as follows.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In $LaCoO_3$, the spin state of Co^{3+} ions changes with temperature. The Co^{3+} ($3d^6$) ion is surrounded with six octahedrally-coordinated O^{2-} ions, and the 3d orbitals split into the e_g orbitals in the higher energy level and the t_{2g} orbitals in the lower energy level. The Co^{3+} ion take the high-spin state (HS, $e_g^2 t_{2g}^4$, S=2), when the Hund coupling is larger than crystal field splitting, while it does the low-spin state (LS, t_{2g}^6, S=0) for the opposite condition. In addition, the intermediate-spin state (IS, $e_g^1 t_{2g}^5$, S=1) has been proposed by introducing a finite transfer between the e_g orbitals and O 2p orbitals. The ground state of Co^{3+} in $LaCoO_3$ is known as the LS below 100K, but excited states are contraversial at present, though many researcher have experimentally and theoretically studied this issue for many years. Recently, we have found the weak ferromagnetic ordering of $LaCo_{1-x}Rh_xO_3$ in the x range of $0.1 \leq x \leq 0.4$. The spin-state crossover affects not only the magnetic properties but also the structural properties. The detailed structural analysis is expected to reveal the spin-state of Co^{3+} through the distortion of the CoO_6 octahedron. Here, neutron diffraction for a polycrystalline sample of $LaCo_{0.8}Rh_{0.2}O_3$ has been carried out in order to investigate the structural properties related with the spin-state of Co^{3+} ions.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Neutron powder diffraction for $LaCo_{0.8}Rh_{0.2}O_3$ was carried out at 10K at iMATERIA, MLF, J-PARC, Japan. The obtained diffraction pattern was analyzed by Z-rietveld 0.9.37.2. Figure 1 shows the neutron diffraction pattern for $LaCo_{0.8}Rh_{0.2}O_3$ at 10 K and its analyzed results for the *Pnma* space group. Figure 2 shows the schematic figure of the obtained crystal structure of $LaCo_{0.8}Rh_{0.2}O_3$. The Tables 1 and 2 indicate the structural parameters and the bond lengths between Co^{3+} and O^{2-} ions of $LaCo_{0.8}Rh_{0.2}O_3$, respectively.

We discuss the relation between the spin-state of Co^{3+} and the shape of the $Co(Rh)O_6$ octahedron. The HS, IS, and LS Co^{3+} have 2, 1, and 0 electrons in e_g orbitals, respectively. The IS Co^{3+} ion has the Jahn-Teller instability at the e_g orbitals. Thus, when the CoO_6 octahedron contains the IS Co^{3+} ions, the bond lengths will have anisotropic values because of the Jahn-Teller distortion. On the other hand, when the CoO_6 octahedron contains the HS or LS Co^{3+} ions, the bond lengths are expected to be identical. The $Co(Rh)O_6$ octahedron can be regarded as an average of the isotropic RhO_6 octahedra and CoO_6 octahdra, and we simply assume that Rh substitution dilutes the distortion of CoO6 octahedron. If the IS model were valid for $LaCo_{0.8}Rh_{0.2}O_3$, the difference in the Co-O bond lengths, Δr is estimated to be 0.10 Å for the $Co(Rh)O_6$ octahedron. However, the observed Δr is 0.005 Å indicated in Table 2. Thus, we conclude that the spin-state of $LaCo_{0.8}Rh_{0.2}O_3$ is a mixed state consisting of the HS and LS Co^{3+} ions. This fact suggests that the HS Co^{3+} ions are thermally excited in addition to those stabilized by Rh^{3+} substitution.

Fig. 1

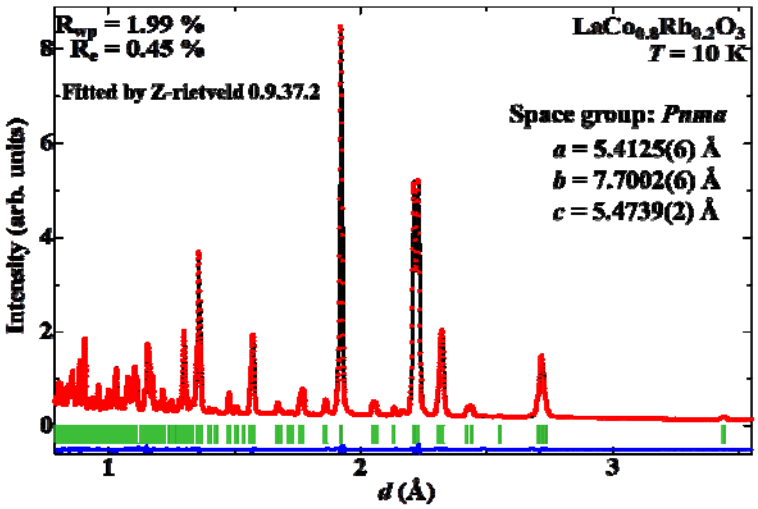

Fig. 1: Results of the powder neutron diffraction studies are shown for $LaCo_{0.8}Rh_{0.2}O_3$ at 10 K. The crosses indicate the observed data and the solid curves show the result of the Rietveld analysis. The Bragg positions are indicated by the vertical lines and the differences between the observed and calculated data are shown at the lowest part.

Fig. 2

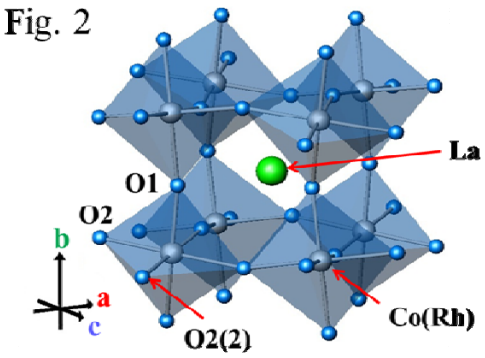

Fig. 2: Schematic figure of obtained crystal structure of $LaCo_{0.8}Rh_{0.2}O_3$.

Table 1. Atomic position of $LaCo_{0.8}Rh_{0.2}O_3$

	La	Co(Rh)	O1	O2
x	0.4753(2)	0	0.004(1)	0.2232(2)
y	0.25	0	0.25	0.0353(1)
z	0.5039(1)	0.5	0.4336(5)	0.7761(1)

Table 2. Bond lengths (Å)

Co-O1	1.9592(6)
Co-O2	1.9540(9)
Co-O2(2)	1.9545(6)