MLF Experimental Report	提出日 Date of Report 2, April, 2013
課題番号 Project No. 2012B0048 実験課題名 Title of experiment Magnetic structure on electron-doped VO2 実験責任者名 Name of principal investigator Daisuke Okuyama 所属 Affiliation CMRG, ASI, RIKEN	装置責任者 Name of responsible person Touru Ishigaki 装置名 Name of Instrument/(BL No.) iMATERIA 実施日 Date of Experiment 21, January, 2013

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.

W-doped VO_2: ($V_{0.85}W_{0.15}O_2$) powder

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 the rutile-type VO_2, the metal-insulator phase transition takes place accompanying the structure phase transition with the V-dimerized distortion. Then, the magnetic ordering of V ions is not observed down to lowest temperature. In the W-doped VO_2/TiO_2 ($V_{1-x}W_xO_2$) thin-film, in which V^{4+} is partially substituted by W^{6+} with doping the electron in V ion, the W-doped dependence of the transition temperature of metal-insulator transition was extensively studied. With increasing x-value, the ground state changes from smaller-x insulator to metal and then to another larger-x insulator. In contrast, the little study of the bulk sample of W-doped VO_2 has been investigated only at the composition near Insulator due to the difficulty of synthesizing the sample. Recently, we successfully synthesized rutile-type $V_{1-x}W_xO_2$ powder sample for larger-x insulator phase at x=0.15. In this sample, the huge decrease of the magnetization induced by the formation of the V-dimer (spin-Peierls transition) is no longer observed, but the antiferromagnetic like anomaly of magnetization is observed at low temperature as shown. To clarify the origin of the observed anomaly and determine the magnetic ground state, we performed powder neutron diffraction experiment at low temperature.

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

The four-gram $V_{0.85}W_{0.15}O_2$ powder sample was filled in V cylinder cell, and mounted on He-closed cycle refrigerator of iMATERIA. The obtained diffraction data are shown in Fig. 1. The indexes of Fig. 1 are calculated by using the tetragonal $P4_2/mnm$ symmetry. At 90 K (blue line), the observed diffraction data can be well explained by the nuclear scattering from tetragonal $P4_2/mnm$ symmetry, which is same with that of the metallic phase of VO_2. Below T_{MI}~70 K (red line), we cannot unfortunately observe the additional magnetic diffraction. However, we found structural phase transition, as shown Fig. 1. The (1 0 1) and (1 1 1) reflections are split into two peaks, which indicate that the structural phase transition from tetragonal to monoclinic. In the synchrotron x-ray experiment of $V_{0.89}W_{0.11}O_2$ thin-film, the forbidden (*h* 0 *l*) with *h*+*l*=odd and (0 0 *l*) with *l*=odd reflections are observed. Then, the possible monoclinic space group from the subgroup of $P4_2/mnm$ is Pm, Pc, P2/m, C2/m, or P2/c. From the simulation by using these candidates, it is clarified that the most reasonable space group is C2/m. In this space group, V ions have two different sites, which indicates a possibility of charge disproportionation. In the larger-*x* insulator phase, the driving mechanism of insulator phase is still debated. If two V sites have different bond valence sums, a charge ordering of V ions may take place. Therefore, we think there is a possibility of charge-ordering-induced (Mott-Hubbard-type) mechanism of insulator phase for this larger-*x* (*x*=0.15) W-doped VO_2, in contrast to Spin-Peierls-type mechanism for smaller-*x* (same with bulk VO_2) insulator phase.

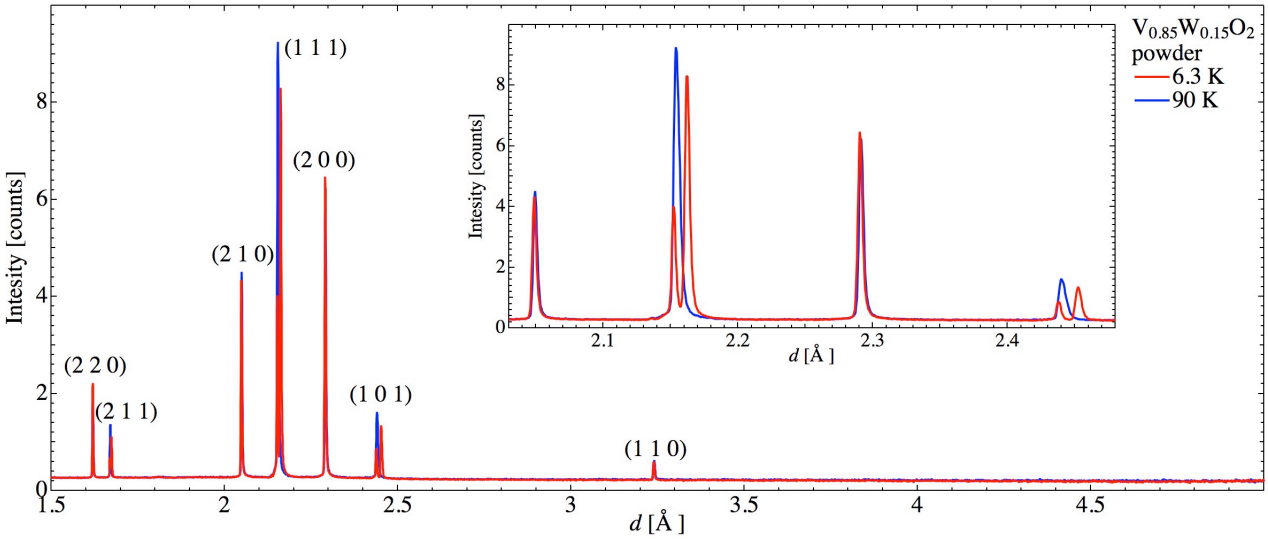

Fig. 1: The neutron diffraction profiles at 6.3 K (red) and 90 K (blue). The anomaly of the magnetization curve was observed at ~70 K.