茨城県 IBARAKI Prefectural Government **MLF Experimental Report**	提出日(Date of Report)
課題番号(Project No.) 2020PM3003 実験課題名(Title of experiment) 電子物性現象の学術研究 実験責任者名(Name of principal investigator) 大山研司 所属(Affiliation) 茨城大学大学院理工学研究科	装置責任者(Name of responsible person) 石垣徹 装置名(Name of Instrument : BL No.) iMATERIA: BL20 実施日(Date of Experiment) 2020/4/16-4/17

実験目的、試料、実験方法、利用の結果得られた主なデータ、考察、及び結論を記述して下さい。
実験結果などの内容をわかりやすくするため、適宜図表添付して下さい。
Please report experimental aim, samples, experimental method, results, discussion and conclusions. Please add figures and tables for better explanation.

1. 実験目的(Objectives of experiment)

We focus magnetic ground state in a chromic material $CoMoO_4$. This compound has been investigated in views of various application to catalysis and electric capacitance [1, 2]. There are two crystal structure phases α- and β-$CoMoO_4$, which are transformed by temperature and pressure variations [3-5]. It is interesting that the structural phase transition is accompanied by visible color variation, corresponding to thermochromic and piezochromic behaviors. The chromic phenomenon and magnetic ground state are caused by electronic state variation in the transition. The aim of this study is to clarify the magnetic ordered structures of $CoMoO_4$ using the precise neutron diffraction (ND) at BL20 iMATERIA, MLF, J-PARC

2. 試料及び実験方法

Sample(s), chemical compositions and experimental procedure

2.1 試料 (sample(s))

Powder sample of $CoMoO_4$ which was synthesized using the solid state reaction at Fukui University.

2.2 実験方法(Experimental procedure)

The ND measurements for the powder samples were conducted using the pulsed neutron diffractometer iMATERIA installed at BL20 of the Materials and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Complex (J-PARC). Sample temperature was controlled using a closed-cycle helium refrigerator. The diffraction data as a function of the *d* value for inter-planer distance were measured at the several detector banks SE, LA35, and LA15 with the neutron time-of-flight method.

3. 実験結果及び考察（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 results and discussion. If you failed to conduct experiment as planned, please describe reasons.

The ND study on magnetic phase transitions in $CoMoO_4$ was conducted. The compound exhibits a first-order structural phase transition between 233 and 723 K with a huge hysteresis, which is an origin of thermochromic behavior [3-5]. The low-temperature dominant α-phase of $CoMoO_4$ undergoes two other phase transitions at 6 and 12 K, as was revealed by specific-heat measurements [6]. The ND data revealed that an incommensurate magnetic structure sets in at 12 K, the propagation vector of which depends strongly on temperature down to 6 K. Figure 1 shows the ND data in the *d* range between 6.0 and 7.0 Å. The strong peak at 6.26 Å is (1, 1, 0) of α-phase, and that at 6.74 Å is nuclear reflection (1, 1, 0) and (0, 0, 1) nuclear reflections. These are independent of temperature below 15 K. Below 12 K, a small peak emerges at 6.53 Å, which shifts to the smaller *d* side with decreasing temperature. The incommensurate peak is attributed to an antiferromagnetic structure. At 6 K, the antiferromagnetic structure locks into a commensurate one characterized by the propagation vector $\boldsymbol{k}_\alpha$ = (1/2, 0, 1/2) located at 6.47 Å. The high-temperature dominant phase β-$CoMoO_4$ remains even in the low-temperature region, as described above. The β-phase also exhibits an antiferromagnetic ordered phase below 9 K, characterized by $\boldsymbol{k}_\beta$ = (0, 0, 1/2) located at 6.58 Å. These antiferromagnetic structures are associated with magnetic correlations within an edge-sharing two-triangle Co sublattice forming a quasi-two-dimensional planes, which give rise to magnetically frustrated state.

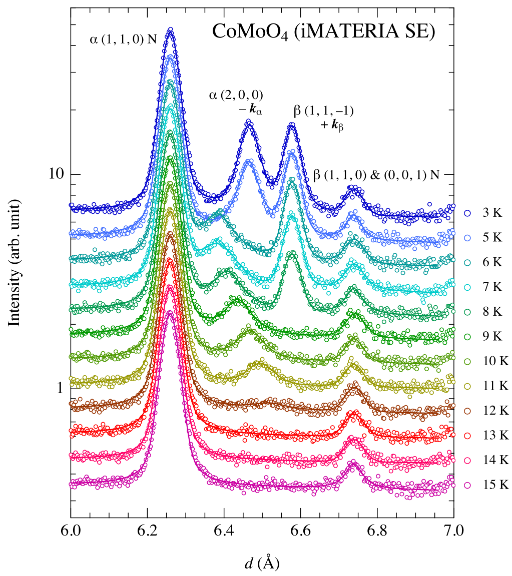

Fig. 1 Detailed temperature dependencies of the neutron powder diffraction pattern of $CoMoO_4$.

[1] R. A. Ross and M. R. Jeanes, Ind. Eng. Chem., Prod. Res. Develop., **13**, 102 (1974). [2] Y. Chen et al., Nanoscale **7**, 15159 (2015). [3] L. C. Robertson et al., Inorg. Chem. **50**, 2878 (2011). [4] L. Righetti et al., ACS Appl. Mater. Interfaces **3**, 1319 (2011). [5] G. W. Smith and J. A. Ibers, Acta Cryst. **19**, 269 (1965). [6] H. Ehrenberg et al., J. Magn. Magn. Mater. **135**, 335 (1994).

4. 結論(Conclusions)

The antiferromagnetic ordered state in the α phase is characterized by the incommensurate-commensurate transition at 6 K, while the magnetic ordered structure of the β phase is a commensurate one. The magnetic ordered structures in the both crystal-structure phases are considered to consist of noncollinear magnetic-moment arrangements at the Co sites forming the edge-sharing two triangle lattice, on which the antiferromagnetic interaction causes a frustration.