

 茨城県 <small>IBARAKI Prefectural Government</small>	MLF Experimental Report	提出日(Date of Report) 2021/11/15
課題番号(Project No.) 2019PM3008 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) 石垣 徹 所属(Affiliation) 茨城大学フロンティア応用原子科学研究センター		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) 2019/4/17-4/19

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)
<p>We investigate magnetic ground state in CoMoO_4, which has been investigated in views of various application to catalysis and electric capacitance [1, 2]. This material showse 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 chromic behaviors. The chromic phenomenon is caused by electronic state variation, and the magnetic ground state is also influenced by the structural 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</p>
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 evidenced by specific-heat measurements [6]. Figure 1 shows the ND data obtained using LA35 detector bank. Black line indicates the data taken at 20 K in the paramagnetic phase, which consists of nuclear reflections of α - and β -phase. The β -phase was suggested to appear only in the high-temperature phase, but the present result revealed that it survives even at 20 K. Green line is the data at 8 K in the intermediate state between 6 and 12 K. Several additional peaks appear, which are caused by the magnetic ordering phase transition. The peak positions indicate incommensurate magnetic propagation vectors, which was not reported in previous study [6]. The data at the lowest temperature (2-3 K), indicated by red line, show strong peaks, which are consistent with the propagation vector $k_\alpha = (1/2, 0, 1/2)$ for the antiferromagnetic structure reported in previous study [6]. However, some of tiny peaks seen only in the low-temperature data cannot be reproduced by the antiferromagnetic structure of α -phase phase. It is necessary to perform further ND measurement to reveal the detailed magnetic scattering signals with temperature variation.

[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).

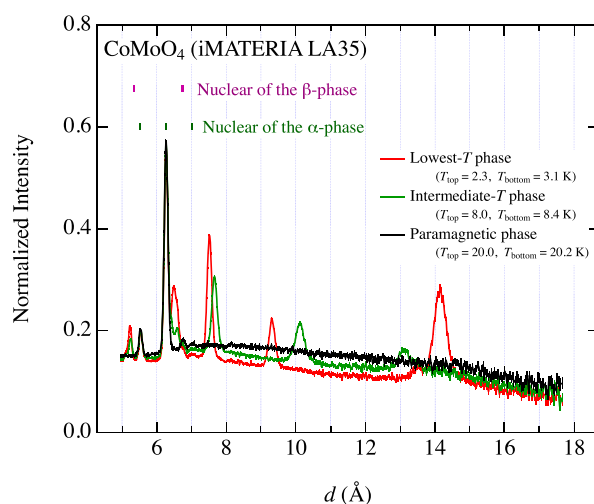


Fig. 1 Temperature dependence of ND pattern of CoMoO_4 obtained using LA35 detector bank.

4. 結論(Conclusions)

The CoMoO_4 shows a mixture of the two crystal-structure phases α and β , even at low temperatures, which contrasts with previous studies on the chromic behaviors. The α phase undergoes antiferromagnetic ordering phase transition, which is characterized by the incommensurate-commensurate transition. However, the magnetic Bragg reflections cannot be reproduced by the ordered structure reported previously. It is needed to conduct further ND measurements.