MLF Experimental Report	提出日 Date of Report 15June 2015
課題番号 Project No. 2014B0313 実験課題名 Title of experiment Relationship between the crystal symmetry and the stability of stripe ordering in layered nickelates 実験責任者名 Name of principal investigator Yoichi Ikeda 所属 Affiliation Neutron Science Laboratory, ISSP, The Univ. of Tokyo	装置責任者 Name of responsible person T. Ishigaki 装置名 Name of Instrument/（BL No.） iMATERIA (BL20) 実施日 Date of Experiment (17:00) 24Mar. ~ (10:30) 27Mar. 2015

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.

Sample: $Nd_{5/3}Sr_{1/3}NiO4$ (powder)
1. HTT; annealed at 1200d'C * 6 times in air, I4/mmm structure at r.t., 3.88 g (2.4517 g cm^{-3})
2. LTO; melt-grown of HTT sample, 4.71 g (4.065 g cm^{-3})
3. LTT; annealed HTT sample at 600d'C-12h in reducing atmosphere, 4.67 g (2.9509 g cm^{-3})

Cell: Standard vanadium cell at iMATERIA (phi 6mm)
Option: 4He Closed-cycle refrigerator
Mode: Single flame in all measurements

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.

On the first day, we measured the powder neutron diffraction (PND) pattern of HTT sample at 4, 70, 150 and 300 K to confirm the preliminary X-ray powder diffraction results and to search the sign of the structural transformation at low temperatures for the HTT sample. Figure 1 and 2 show the PND pattern measured at 300 and 4 K, respectively. For the data sets of the BS bank, we employed a Rietveld refinement with the structure model of I4/mmm where the initial parameters were evaluated from the results of the powder X-ray diffraction measurement. As seen in these figures, no significant deviation from the tetragonal structure of I4/mmm was observed down to 4 K. These results indicate that the tetragonal structure of the HTT sample is maintained at low temperatures. However, the qualities of those fits (*S*) are not as good as that of the standard sample. These low quality of fit may result from the unknown Bragg peaks indicated by the blue asterisk * in these figures, and possibly a slight modification of the crystal structure at low temperatures. Indeed, as shown in Fig. 3, the significant broadening of the peak width of the (112) reflection was observed with decreasing temperature for the HTT sample.

This broadening of the (112) reflection may be indicative of the orthorhombic structural modification from the high-temperature tetragonal structure. It is also noteworthy that relatively large isotropic atomic displacement parameters were evaluated for the oxygen atom on the 4*e* site in a whole temperature range. This result may also be suggestive of the structural instability owing to the displacement of the oxygen atoms in the HTT sample. In order to verify the structure model for the HTT sample, we have to further examine the structure parameters and improve the quality of fit on the Rietveld analysis. To improve the quality of fit, it is also important to examine the cause of the weak Bragg peaks which cannot be indexed with the I4/mmm structure model.

On the second day, we measured the NPD pattern of the LTO sample between 4 and 300 K as a reference for the HTT sample. From these experiments, we confirmed that the low-temperature orthorhombic structure is maintained down to 4 K. However, the LTO sample contains the high-temperature tetragonal phase as a secondary phase, so that we have not succeeded in the Rietveld refinement for the data set of the LTO sample. Further examination of the stripe type charge spin order and the refinement of the structure parameters are now in progress.

On the third day, we measured the NPD pattern of the LTT sample between 4 and 300 K. The LTT sample was prepared by annealing the HTT sample in the reducing atmosphere to examine the influence of the oxygen atoms to the structure parameter. As shown in Fig. 5, the Bragg peak of the LTT sample splits into two peaks in contrast to that of the HTT sample. This result clearly indicates that the crystal structure of the LTT sample is modified from the high-temperature tetragonal structure, resulting from the change in the oxygen content by the reducing annealing. Further examination of the crystal structure of the LTT sample is now in progress.

[Request for the contact person]

In this experiment, we had difficulty in obtaining measured data within that day. This is because we could not extract the experimental data ourselves. To obtain the data, we have to request the data to the assistant of the experiment or the contact persons. Therefore, we could not plan and quickly determine the experimental sequence while examining the data. Improvements of the experimental-data extracting system are required. Such improvements may lighten the burden imposed on the contact persons.

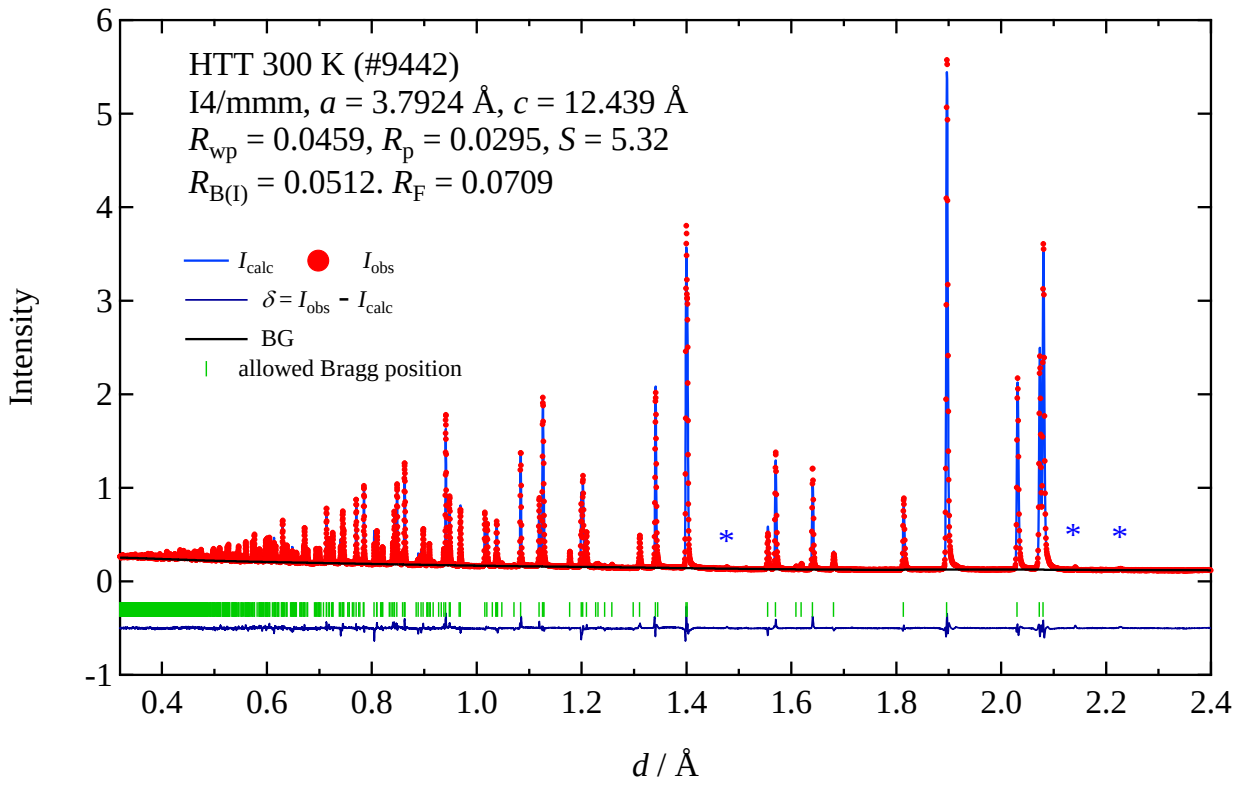

Fig 1 Powder neutron diffraction pattern and the result of a Rietveld refinement for the data set of the BS bank measured at 300 K.

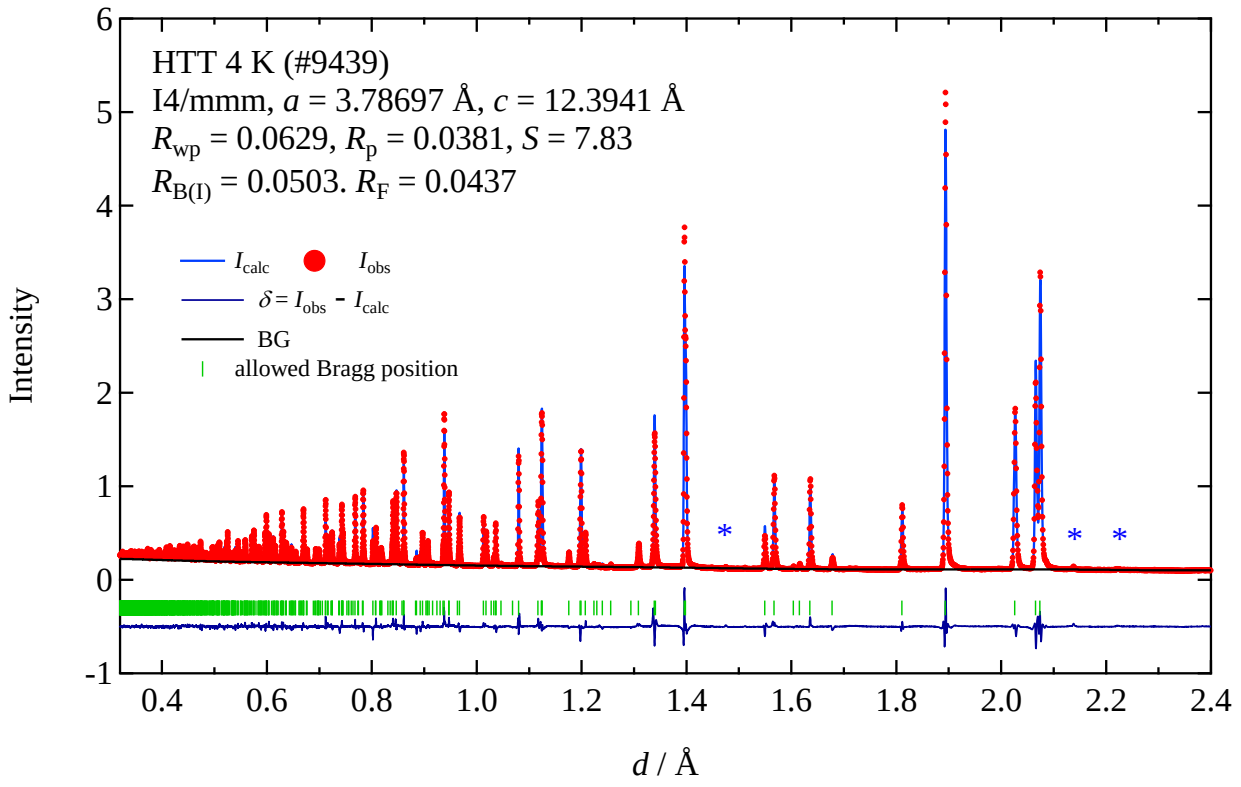

Fig 2 Powder neutron diffraction pattern and the result of a Rietveld refinement for the data set of the BS bank measured at 4 K.

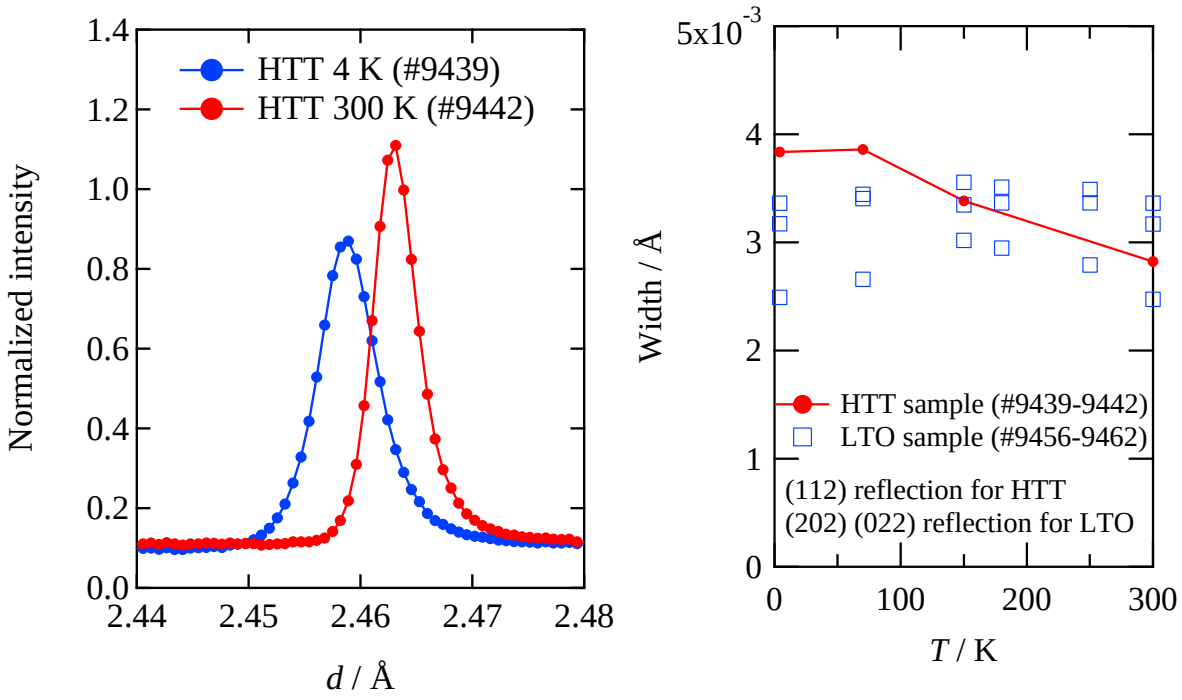

Fig. 3 (left panel) Peak profiles around d ~ 2.46 Å of the HTT sample measured at 4 and 300 K. (right panel) Peak width observed around d ~ 2.46 Å of the HTT (red-closed circles) and LTO (blue-open squares) samples. Corresponding Mirror indices in the Bragg peak in the left panel are 112 for I4/mmm space group, and 202-022 for F4/mmm space group.

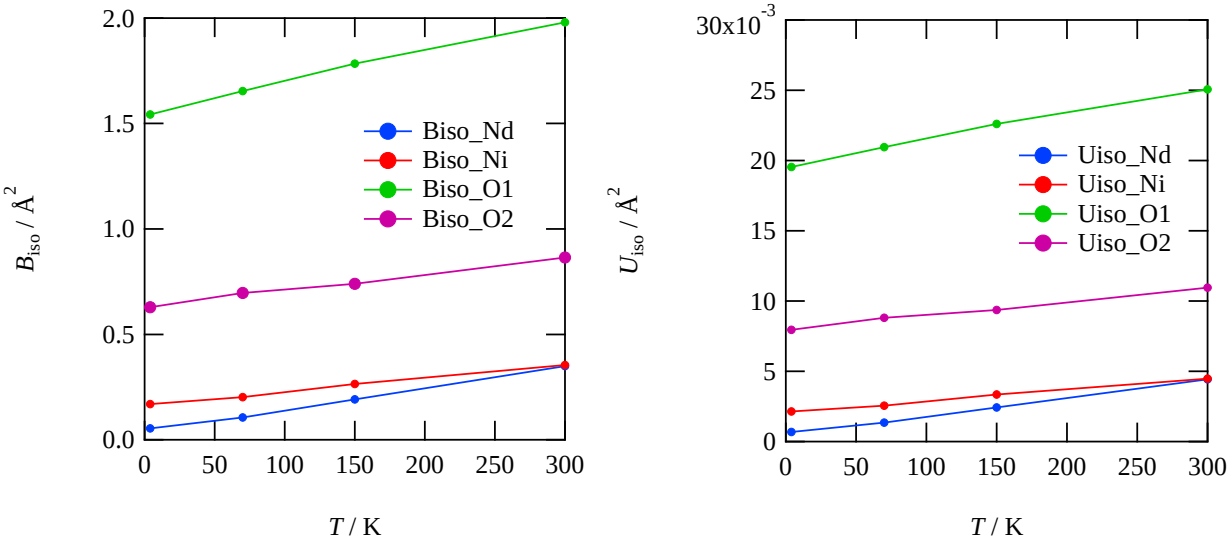

Fig. 4 Temperature dependence of the evaluated isotropic atomic displacement parameter of the HTT sample, where $U_{iso} = B_{iso}/8\pi$. O1 and O2 mean the oxygen atoms on the 4*e* and 4*c* site of I4/mmm, respectively.

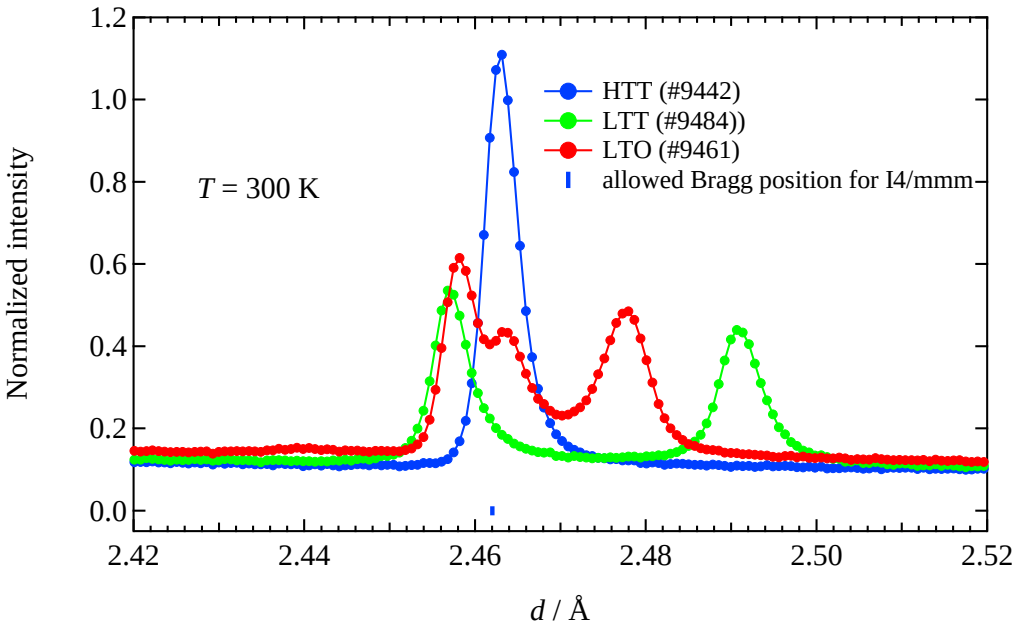

Fig. 5 Peak profiles around d ~ 2.46 Å of the HTT (blue), **LTT (light green)** and LTO (red) samples. The vertical blue bar indicate the allowed Bragg position of the (112) reflection for the high-temperature tetragonal structure (I4/mmm).

[Requests]

We want the upgrade in the support function of the Z-Rietvelt: specifically (i) add the export function of the list of the calculated results as a simple text form like the "*.lst" file of the RIETAN, which contains the structure factor F_{calc}, d-value (peak position), Mirror indices, multiplicity, and so on. This function may be quite important to check the simple typographical error of the structure model and verify the calculated results. (ii) Add the excluding function of arbitrary tof (d) regions from the fitting region. This function may support us to judge the influence of the spurious peaks in the data set to the fitting results. (iii) Add the configuration option of the export function of the "Igor" type file (graph size, offset values, and so on). (iv) Fix the bugs of the x-label in the exported Igor graph (d / us -> d / Å, etc). (v) Fix the bugs(?) of the indications in the exported tex file written about the refined structure model (e.g. the site symbol, atom names, space group, lattice constants and suffix of U_{ij}. In the current version 0.9.43.2, a question make ? (or blank) is output in above columns).