MLF Experimental Report	提出日 Date of Report 2017.6.5.
課題番号 Project No. 2016B0062 実験課題名 Title of experiment Role of disorders in the reduction of thermal conductivity for the intermetallic compounds with disordered Na atoms in helical tunnels 実験責任者名 Name of principal investigator Takahiro Yamada 所属 Affiliation Tohoku University	装置責任者 Name of responsible person Shuki Tori 装置名 Name of Instrument/（BL No.） Super High Resolution Powder Diffractometer (SuperHRPD) / BL 08 実施日Date of Experiment 2017/02/11 ~ 2017/02/14

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.

Ternary intermetallic compound in Na-Ga-Sn system, $Na_{2+x}Ga_{2+x}Sn_{4-x}$, x=0.0, 0.19, powder (in vanadium cells)

Ternary intermetallic compound in Na-In-Sn system, $Na_2In_2Sn_4$, powder (in a vanadium cell)

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.

Experimental method

Time-of-flight (TOF) neutron powder diffraction data of ternary intermetallic compounds in Na-Ga-Sn and Na-In-Sn systems, which can be considered as candidates for thermoelectric materials due to the low thermal conductivities, were measured by a high-resolution neutron powder diffractometer Super-HRPD installed at the beam line BL08 of J-PARC facility. The powdered samples of the intermetallic compounds, $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.0, 0.19) and $Na_2In_2Sn_4$ which were prepared by solid state reaction in Tohoku University, were sealed into vanadium cylindrical cells with a diameter of 6 mm and a height of 60 mm in a glove box filled with a helium atmosphere. The sample cells were installed in a closed-cycle helium cryostat. The TOF neutron powder diffraction measurements were performed at approximately 10, 50, 100, 200, and 280 K for each sample in order to get information on the atomic displacement parameters (ADPs) for Na atom, of which the static and/or dynamic positional disorders probably play an important role in the reduction of lattice thermal conductivity of the compounds. The crystal structures varying temperature were analyzed using a Rietveld analysis program, Z-Rietveld (ver. 1.0.0).

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

Results

The measured diffraction patterns of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0 and 0.19) and $Na_2In_2Sn_4$ were explained well by reported crystal structures having tunnel frameworks formed by Ga/Sn or In/Sn atoms with a hexagonal cell [1] and an orthorhombic cell [2], respectively. The anisotropic atomic displacement parameters (ADPs) were successfully refined for Na and Ga/Sn sites of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.19), while only isotropic ADPs could be refined for those of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0). The difference in the analytical results for the ADPs are probably due to the crystallinity of the powdered samples. Unfortunately, the measured diffraction data of $Na_2In_2Sn_4$ were statistically poor for the analysis of ADPs of Na atoms due to the anomalously large neutron mass absorption of the In atom.

The refined equivalent isotropic ADPs, U_{eq}, of Na site and Ga/Sn site of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.19) were plotted in Figure 1. The values of U_{eq} at 12–282 K are over five times larger than the those of the Ga/Sn site. The U_{eq} values are consistent with the values of the ADPs of Na atom determined from the single crystal X-ray diffraction data measured for $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.24) at 93–303 K [1]. The characteristic Einstein temperature (θ_E) and disorder parameter (d) of Na atom estimated from the ADPs in the measurement range were θ_E = 110(2) K and d_{Na} = 0.156(7) Å, which were closed to the values (θ_E = 105 K and d_{Na} = 0.16 Å) obtained from the single crystal XRD [1]. They indicated that the compound with x = 0.19 has both of the dynamic and static positional disorder of Na atoms in the Na site.

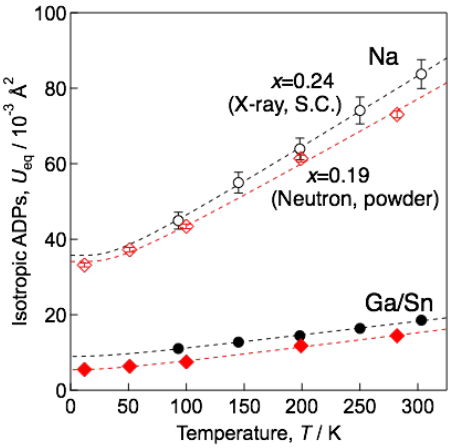

Fig. 1. Isotropic ADPs of Na (open marks) and Ga/Sn (close marks) sites refined from powder neutron diffraction of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ with x = 0.19 (diamonds). The data refined from single crystal X-ray diffraction of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ with x = 0.24 (circles) in Ref. 1 were drawn.

Figure 2 shows the well-refined crystal structures of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.19) at 282 K and 12 K drawing with anisotropic atomic displacement ellipsoids perpendicular to and along tunnel direction. The displacement ellipsoids of the Na site largely elongate along the tunnels, whereas the ellipsoids of Ga/Sn site are almost spherical. The volume of the Na site ellipsoids was larger than the volume of Ga/Sn site ones, and became smaller with keeping the elongated shape until at 12 K. They indicate that large static disorder was existed along tunnel direction even at low temperature.

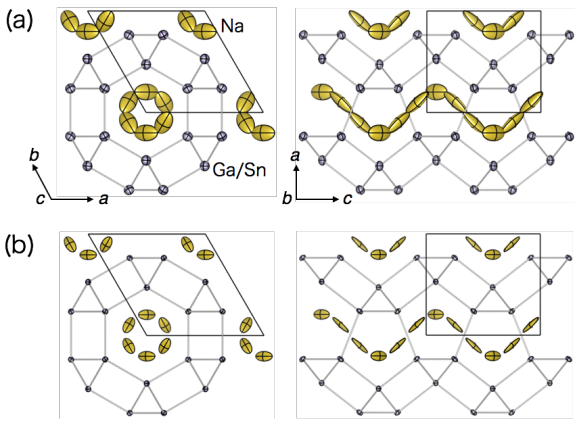

Fig. 2. Crystal structures of $Na_{2+x}Ga_{2+x}Sn_{4-x}$ (x = 0.19) at 282 K (a) and 12 K (b). Displacement ellipsoids are drawn at 75% probability level.

More detailed structural analysis considering the possibility of the distortion of the hexagonal lattice, which was suggested by a slight broadening of some peaks, are now in progress.

References

[1] T. Yamada, H. Yamane, H. Nagai, *Adv. Mater.*, **27**, 4708 (2015).

[2] W. Blase, G. Cordier, R. Knipe, R. Schmidt, *Z. Naturforsch.* **44b**, 505 (1989).