MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2014B0254 実験課題名 Title of experiment Phonon Dynamics of thermoelectric tetrahedrite 実験責任者名 Name of principal investigator Koichiro Suekuni 所属 Affiliation Hiroshima University	装置責任者 Name of responsible person Kenji Nakajima 装置名 Name of Instrument/（BL No.） AMATERAS/BL14 実施日 Date of Experiment April 24th – 30th, 2015 June 5th, 2016

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.

Tetrahedrite : $Cu_{12}Sb_4S_{13}$, $Cu_{10}Zn_2Sb_4S_{13}$; powders
Tennantite : $Cu_{12}As_4S_{13}$, $Cu_{10}Zn_2As_4S_{13}$; powders
Colusite : $Cu_{23}Zn_3V_2Sn_6S_{32}$; powders

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 present work, we have studied phonon structures of above-listed Cu-S based synthetic minerals, tetrahedrites, tennantites, and colusite, by means of inelastic neutron scattering (INS). The tetrahedrites and tennantites have been attracting much attention as thermoelectric materials due to their large Seebeck coefficients and low lattice thermal conductivities. [1, 2] For the “pristine” tetrahedrite $Cu_{12}Sb_4S_{13}$ and tennanite $Cu_{12}As_4S_{13}$, furthermore, much attention have been paid for their metal-semiconductor transition (MST) at low-temperatures. [1, 3] At room temperature, these two synthetic minerals and their Zn-substituted systems have body-centered cubic (bcc) structures composed of three units: $(Cu/Zn)S_4$ tetrahedron, CuS_3 trigonal plane, and $(Sb/As)S_3$ trigonal pyramid. Our previous x-ray structural analysis on a tetrahedrite revealed that the Cu atom in sulfur triangle vibrates with a large atomic displacement parameter perpendicular to the plane as shown in Fig. 1. [2] Such a large-amplitude vibration is referred to as “rattling”. Our present INS study has aimed at the direct observation of phonon structure involving out-of-plane rattling of Cu atoms, leading to understanding of mechanisms of the low thermal conductivity and the MST. The results were compared with that for the colusite consisting of tetrahedral units, CuS_4, VS_4, and SnS_4, where the anions are vibrating with smaller amplitude than that in CuS_3.

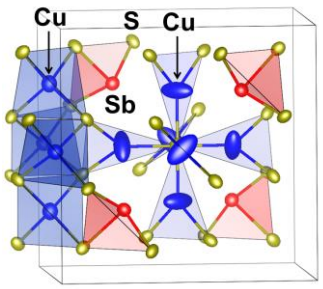

Fig. 1 Structural units of tetrahedraite $Cu_{12}Sb_4S_{13}$.

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

We used powdered samples of 12-15 g for the INS measurements. The powders were molded into a pellet form (Fig. 2) by using a hydraulic press machine. Five pellets wrapped by an aluminum foil were attached to the bottom of a top-loading-type refrigerator (Fig. 2). The measurements were performed at temperatures between 290 K and 10 K for 2-5 hour. The incident energy E_i of neutron beam was set at approximately 5, 9, 20, and 70 meV.

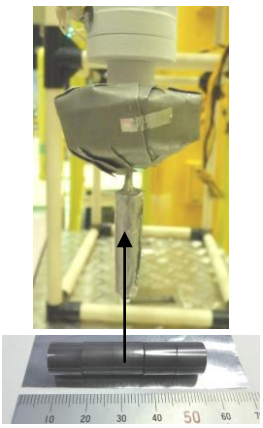

Fig. 2 Sample pellets attached to the bottom of a refrigerator.

The sets of INS data for $E_i \cong 9$ meV at 290 K for the tetrahedrites $Cu_{12}Sb_4S_{13}$ (Sb) and $Cu_{10}Zn_2Sb_4S_{13}$ (ZnSb), and the tennanites $Cu_{12}As_4S_{13}$ (As) and $Cu_{10}Zn_2As_4S_{13}$ (ZnAs) are shown in Fig. 3. This figure shows energy (E) and momentum transfer (Q) dependence of the scattering intensity. The data of Sb, ZbSb, and ZnAs exhibit distinct intensities at $E \cong 3$ meV. The low-energy modes are likely attributed to the out-of-plane rattling of Cu atom in the sulfur triangle. In fact, such a mode is absent at energies below 7 meV for $Cu_{23}Zn_3V_2Sn_6S_{32}$ without rattling Cu atoms. The INS data in Fig. 3 also show that strong arc-shaped intensity arises from a point, (Q, E) $\cong$ (2 Å^{-1}, 0.5 eV), which is close to a position of Bragg peak with strongest intensity. We therefore ascribe the arc line in the figure to the longitudinal acoustic phonon. In order to investigate the rattling modes of Cu atoms with eliminating the contribution of acoustic phonon, we extracted the data in the Q range between 0.9 and 1.3 Å^{-1} and then integrated. As shown in Fig. 4, the integrated intensity shows a peak, whose position shifts to higher energy on going from As to Sb, ZnAs to ZnSb. The order of energy is consistent with an order of the lattice parameter. This fact suggests that the characteristic energy of rattling mode increases with increasing the size of sulfur triangle. Indeed, first-principles phonon structure calculations have proposed that the rattling modes become more stabilized in a unit cell with expanded volume. [4] To elucidate the relationship between local structure around rattling Cu atom and phonon dynamics, a systematic study of crystal structures of the tetrahedrites and tennantites are ongoing.

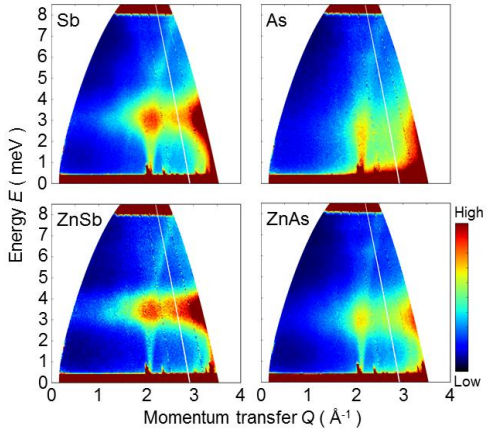

Fig. 3 INS data at 290 K for tetrahedrites (Sb, ZnSb) and tennantites (As, ZnAs).

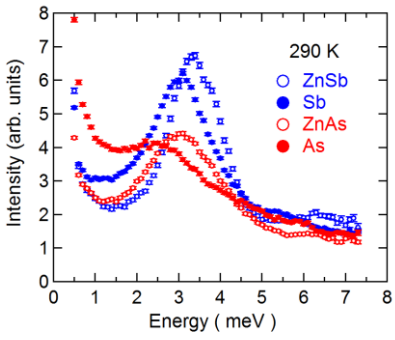

Fig. 4 Energy dependence of integrated intensity in the Q range of 0.9-1.3 Å^{-1} at 290 K for tetrahedrites (Sb, ZnSb) and tennantites (As, ZnAs).

Thus, our INS studies have demonstrated the existence of low-energy localized modes being ascribed to the rattling. Such low-frequency phonon branches open new paths for the occurrence of Umklapp scattering of heat-carrying acoustic phonon, leading to the reduced lattice thermal conductivity.

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

Temperature dependences of rattling modes for samples with Sb, ZnSb, As, and ZnAs are presented in Fig. 5. For the Sb sample, characteristic energy of the rattling mode (peak energy) decreases upon cooling to 150 K, which is a hallmark of anharmonic nature of the rattling. The relative intensity at $E \leq 1$ meV rises with decreasing temperature. Existence of such an overdamped mode implies instability of phonon and crystal structures. With further cooling across the MST transition at T_{MST} = 85 K, the phonon structure dramatically changed. More specifically, the overdamped mode diminished and a peak appeared at around 2 meV, suggesting a structural transformation. Indeed, our synchrotron X-ray diffraction study revealed that the MST is concomitant with the structural change from the room-temperature bcc cell to a body-centered tetragonal supercell. [3] The INS data specify the origin of the structural phase transition as the instability of rattling mode.

For the sample with As, as shown in Figs. 3-5, the phonon spectrum is broad even at 290 K compared with the other three samples. Furthermore, a steep rise at $E \leq 1$ meV indicates the instability of rattling mode. On cooling below T_{MST} = 124 K, the intensity at $E \leq 4$ meV is abruptly diminished. Hence, a rattling-induced structural transformation occurs at T_{MST} like in the Sb sample.

Zn-substituted systems show gradual changes in the phonon spectra as shown in Fig. 5. For the ZnSb sample, with decreasing temperature, the peak shifts to lower energy and changes to a peak with a shoulder. Therefore, there are at least two modes at $E \leq 4$ meV. The energy of 2 meV at the maximum agrees with a characteristic energy of localized mode evaluated from a specific heat analysis. [5] For the ZnAs sample, the peak energy decreases upon cooling, then increases below 100 K. Mechanisms of the complicated behavior need to be clarified by the x-ray structural analysis.

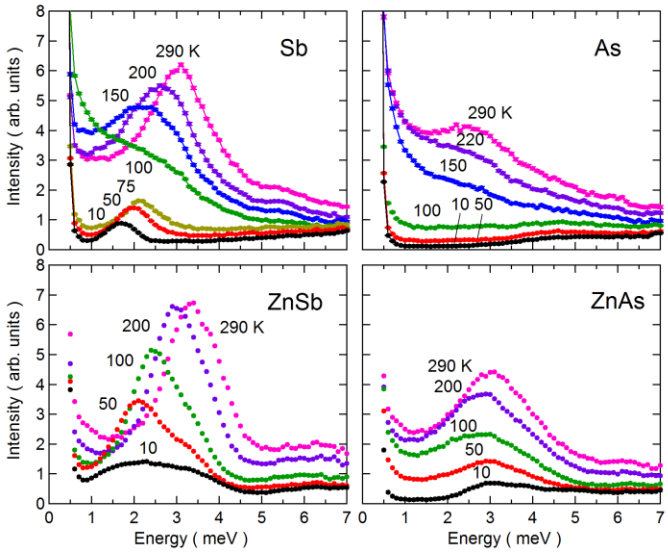

Fig. 5 Temperature dependence of low-energy mode for the tetrahedrites (Sb, ZnSb) and the tennantites (As, ZnAs).

Summing up, we have done INS measurements on the synthetic minerals: tetrahedrites and tennantites with rattling Cu atoms, and colusite without rattling atoms. We found low-energy modes with anharmonic nature in the former two minerals, but not in the latter one. Therefore, we attributed the low-energy modes to the out-of-plane rattling of Cu atoms. The phonon Umklapp scattering via the low-lying modes probably results in the low lattice thermal conductivity. Furthermore, for the pristine systems, we revealed the drastic change of the rattling modes upon cooling through T_{MST}. This result indicates that the MST concomitant with the structural transformation is induced by the instability of rattling mode.

[1] K. Suekuni *et al.*, Appl. Phys. Express **5**, 051201 (2012). [2] K. Suekuni *et al.*, J. Appl. Phys. **113**, 043712 (2013).
[3] H. I. Tanaka and K. Suekuni *et al.*, J. Phys. Soc. Jpn. **85**, 014703 (2016).
[4] X. Lu *et al.*, Adv. Energy Mater. 3, 342 (2013). [5] K. Suekuni *et al.*, J. Phys. Soc. Jpn. 84 103601 (2015).