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XAFS studies of $TlInSe_2$ and spatial fluctuations in the incommensurate-commensurate phase transition range

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1 Introduction

Ternary Tl-compounds with TlSe-type structure, such as $TlInSe_2$ attract much attention because of their extremely large thermoelectric power, small thermal conductivity, and relatively large electrical conductivity. Thus, $TlInSe_2$ with expected figures of merit for an excellent thermoelectric performance are foreseen as a member of a new class of thermoelectric materials [1].

$TlInSe_2$ has a rather complex tetragonal layer-chain structure (space group I4/mcm) at room temperature as shown in Fig. 1, which can be described as a set of $InSe_4$ chains extended along the *c*-axis and connected with each other through one dimensional chains of Tl atoms. At room temperature, Tl atoms are believed to deviate from the periodicity of the $InSe_4$ frameworks, showing an incommensurate (IC) phase.

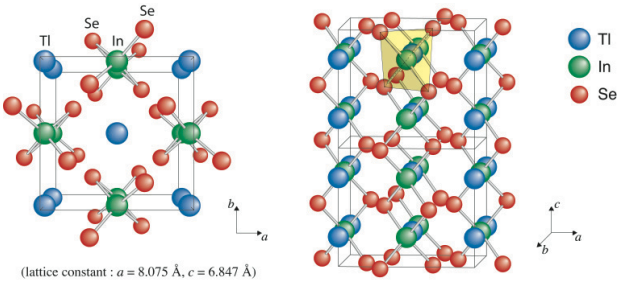

Fig. 1: Crystal structure of $TlInSe_2$.

From our recent x-ray fluorescence holography (XFH) experiment at room temperature, it was found that the Tl atoms have extremely large spatial fluctuations, which were discussed in relation to the IC phase of this material [2,3].

In this study, we have started to perform a series of structural measurements of $TlInSe_2$ by means of XFH, x-ray diffraction (XD), and XFH at low temperatures down to 25 K [4], where an IC-commensurate phase transition takes place.

2 Experiment

Single crystalline $TlInSe_2$ was grown by a modified Bridgeman method [1]. The well-ground powder of the sample was mixed with BN fine powder and pressed into a pellet with a diameter of 13 mm.

The XAFS experiments were performed using a usual transmission mode in the temperature range down to 25 K close to the Tl L_{II} edge (14.698 keV) at BL9C/PF and the In *K* edge (27.940 keV) at NW10A/PF-AR. The obtained data were analyzed by using FEFF8 code to calculate the bond lengths, the coordination number, and the mean-square displacement.

3 Results and Discussion

Figure 2 shows the Tl L_{II} XAFS signal multiplied by k^2 of $TlInSe_2$ measured at 25 K. As seen in the figure, a good quality of the XAFS oscillation was obtained, and the same qualities of the data were evaluated in the whole temperature range. From a preliminary analysis, the neighboring Tl and In atoms can be clearly seen at the appropriate positions in the Fourier transforms of the XAFS signal, whereas the Se neighboring atoms are hardly visible. Since the Tl L_I edge is located at $k \sim 13$ Å^{-1}, however, further careful analyses are necessary to discuss the local structures around the central Tl atoms in detail.

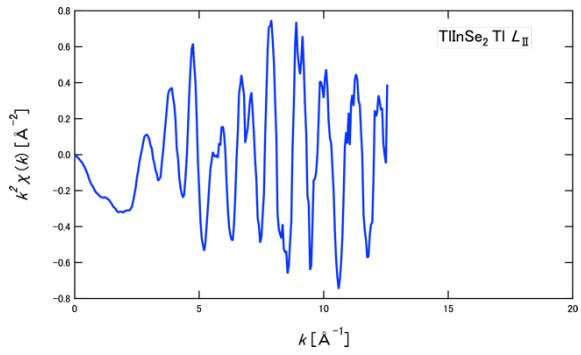

Fig. 2: Tl L_{II} XAFS signal of $TlInSe_2$ at 25 K.

Figure 3 shows the In *K* XAFS signal multiplied by k^2 of $TlInSe_2$ measured at 25 K. As seen in the figure, good quality of the XAFS oscillation was again obtained, and the same qualities of the data were evaluated in the whole

temperature range. From a preliminary analysis, the neighboring Se atoms can clearly be seen at the appropriate positions in the Fourier transforms of the XAFS signal, in contrast to those around the central Tl atoms in Fig. 2. The second-neighboring In atoms are also visible at the proper positions. Thus, it is concluded that the $InSe_4$ chain frame is firmly preserved. In combination with the Tl L_{II} XAFS data, positional fluctuations in the angular direction are expected for the Se atoms, which are consistent with the previous XFH result, where the images of the Se atoms are hardly visible.

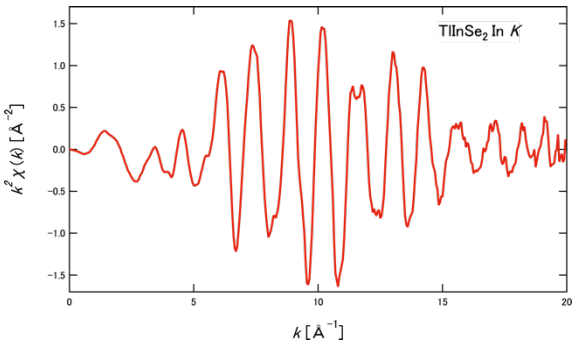

Fig. 3: In *K* XAFS signal of $TlInSe_2$ at 25 K.

Recent powder XD experiments revealed that the intensity and peak position of only the (231) Bragg peak largely change with decreasing temperature down to 200 K [5]. This finding may be related to temperature dependence of the positional fluctuations of Tl atoms in the IC phase. Detailed analysis of the present XAFS data are now in progress in combination with XD and XFH results.

Acknowledgement

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