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Three-dimensional atomic images of Tl-based thermoelectric materials by x-ray fluorescence holography

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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, 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 phase. With increasing temperature, a phase transition takes place at about 140°C to a normal phase, where the Tl atoms locate at the periodic positions of the corresponding $InSe_4$ frame. At the same time, this material looses the excellent thermopower. Thus, it is assumed that such a complicated structural one-dimensionality of this material and a spatial randomness of the Tl atoms are behind its huge thermoelectric power.

X-ray fluorescence holography (XFH) is a newly developed technique that enables one to draw three-dimensional (3D) atomic images around a specific element emitting fluorescent x-rays. From our recent studies [2,3], it has been established that in relation to the theoretical calculation, magnitudes of the randomness of specific neighboring atoms can be determined. In this article, we report results of XFH measurements on $TlInSe_2$, and discuss the spatial fluctuations of Tl atoms.

Experimental procedure

The measurements were performed on $TlInSe_2$ single crystal for the incommensurate phase at room temperature at the beamline BL6C of the PF/KEK and BL12B2 of the SPring-8. The sample with a (110) surface and a surface size of larger than 5x10 mm^2 was placed on the two-axes table of a diffractometer. The measurements were carried out by rotating the two axes, $0° < \theta < 70°$ in steps of 1° and $0° < \phi < 360°$ in steps of 0.35°, of the sample. The fluorescent x-rays were collected with a fast APD detector, available for more than one million cps, with a cylindrical graphite crystal energy analyzer. The holograms were recorded at thirteen incident x-ray energies. To suppress false images, a 3D atomic image was reconstructed using Barton's algorithm [4].

Results and discussion

The atomic images on the (001) plane are depicted in Fig. 1, where only the Tl and In atoms locate. In the figure, expected atomic positions for the Tl and In atoms are indicated by circles. Although many artifacts are still seen in the image, the In atoms are clearly visible at the proper positions. However, the Tl images are observed very weakly. Since the x-ray scattering by Tl atoms (Z = 81) is much stronger than that by the In atoms (Z = 49), this result should be closely related to the spatial randomness of the Tl atoms in the incommensurate phase of this material. A detailed theoretical interpretation is now in progress for estimating the positional randomness of each element at each neighboring site from the obtained images.

References

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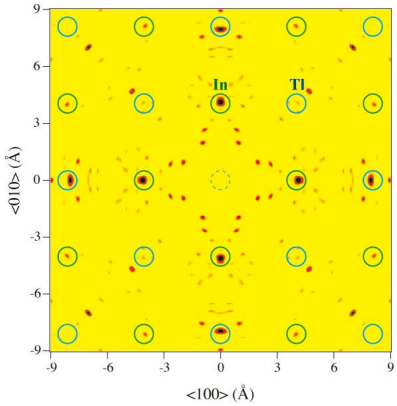

Fig. 1 The obtained atomic image on the (001) plane, z = 0 from the central Tl atom.