BL-6C/2013G605

Three-dimensional atomic image of Bi_2Te_3:Mn topological insulator

Shinya Hosokawa[1,*], Yuuki Ideguchi[1], Kenji Kamimura[1], Koji Kimura[1], Naohisa Happo[2], Kouichi Hayashi[3,†], Mamoru Kitaura[4], Akimasa Ohnishi[4], and Minoru Sasaki[4]
[1]Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan
[2]Graduate School of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan
[3]Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan
[4]Department of Physics, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan

To investigate structures around the impurity sites in a Mn-doped Bi_2Te_3 topological insulator, Mn $K\alpha$ x-ray fluorescence holography (XFH) measurements were carried out on $Bi_2Te_3Mn_{0.1}$ single crystal at 100 and 300 K. At 300 K, only images of the second-neighboring atoms are observed on the (001) plane, indicating that the Mn atoms are substituted with the Bi or Te atoms and the nearest-neighboring atoms has strong positional fluctuations in the angular direction. Besides these images, more intense images are detected at the half positions from the central Mn atoms at 100 K. By combining with XAFS data, it was suggested that a majority of the Mn impurity atoms are located at the edges of Te triangles formed on the layer surface.

1 Introduction

In the past, Bi_2Te_3 was well-known as a thermoelectric material having a large value of thermopower. Nowadays, this material has also achieved much attention as a topological insulator (TI), where the so-called Dirac electrons with an almost zero mass can conduct on the surface of this material [1]. For this reason, Bi_2Te_3 is promising as a raw material for future computer systems of very fast and energy saving.

Recently, Kim *et al*. [2] found that $Bi_2Te_3Fe_x$ alloys have an excellent TI behavior at $x = 0.03 - 0.10$. They observed two interesting TI features that the lifetime of the TI properties is extremely long and the Dirac electrons are not scattered by Fe impurities. Mn-doped Bi_2Te_3 alloys also show excellent TI properties [3] similar to $Bi_2Te_3Fe_x$ alloys.

Then an important question arises from the structural point of view; where are the impurity atoms located in the Bi_2Te_3 crystal for showing such TI properties? The undoped Bi_2Te_3 has a layer structure with a hexagonal form [4]. The interlayer positions would be most plausible, but there is no special reason to exclude the possibilities of substitutions with Bi or Te atoms or interstitial positions in the layer.

Structural characterization around impurities is one of the most difficult issues to study the structure of materials. Detailed data collections and proper models are necessary to perform single crystal structure analysis using intense x-ray or neutron source. XAFS gives mostly one-dimensional information on the nearest neighboring atoms, and the information on the second- or distant-neighboring atoms is very poor. A proper model is again essential.

X-ray fluorescence holography (XFH) is a newly developed technique for atom-resolved structural characterizations of materials, and enables one to draw three-dimensional (3D) atomic images around a specific element emitting fluorescent x-rays [5]. Owing to an interference between direct incident x-rays and those scattered by surrounding atoms, the fluorescent x-ray intensity from the emitter slightly modulates with incident x-ray angles by about 0.1 %, from which 3D images of neighboring toms can be obtained by simple Fourier transforms without any special atomic models. This technique has, in particular, an excellent potential for investigating local structures around impurity atoms [6].

We carried out a Mn $K\alpha$ XFH measurement on $Bi_2Te_3Mn_{0.1}$ single crystal at room temperature [7]. The reconstructed atomic images around the central Mn atom show only a hexagonal configuration of the second-neighboring atoms on the (001) plane. Subsequently, we have performed the same experiment at a low temperature of 100 K, which shows a different feature that strong atomic images appear at positions with a much nearer distance from the central Mn atoms. In this paper, we report the results of the recent XFH experiment at 100 K, and discuss a possible interpretation of the positions of the Mn impurity atoms in combination with our recent XAFS data.

2 Experiment

A single crystal of $Bi_2Te_3Mn_{0.1}$ was grown by a modified Bridgeman method, where appropriate amounts of Bi_2Te_3 and Mn powders were melted and crystallized in an evacuated quartz ampoule several times by slow cooling. The sample was cooled from 850 to 550°C with a cooling rate of 10°C/h. The crystal was cut and polished so as to have a flat (001) surface larger than 3×3 mm^2. The crystallinity was examined by taking a Laue photograph, and the concentration and homogeneity were confirmed over the sample within the experimental errors by an electron-probe micro-analysis.

A Mn *Ka* XFH measurement on $Bi_2Te_3Mn_{0.1}$ was carried out at 100 K using a cryostream apparatus at BL-6C of the Photon Factory in the High Energy Accelerator Research Organization (PF-KEK), Tsukuba, Japan. The sample was placed on a two-axes table of a diffractometer. The measurement was performed in

inverse mode by changing two axes, the exit angle of $0° \leq \theta \leq 75°$ in steps of 1.00° and the azimuthal angle of $0° \leq \phi \leq 360°$ in steps of about 0.35°. Incident x-rays were focused onto the (001) surface of the sample. Mn $K\alpha$ fluorescent x-rays were collected using an avalanche photodiode detector with a cylindrical graphite crystal energy analyzer. The XFH signals were recorded at eight different incident x-ray energies from 7.0 to 10.5 keV in steps of 0.5 keV. Details of the experimental setup are given elsewhere [5].

Holographic oscillation data were obtained by subtracting the background from the fluorescent x-ray intensities. An extension of the hologram data was carried out using the crystal symmetries of the hexagonal structure [4] and the measured x-ray standing wave lines. From the hologram patterns, 3D atomic configuration images were reconstructed using Barton's algorithm [8] by superimposing the holograms with eight different incident x-ray energies, which can highly suppress the appearance of twin images.

3 Results and Discussion

Figure 1 shows the resonstructed atomic images of $Bi_2Te_3Mn_{0.1}$ single crystal at (a) 300 K [7] and (b) 100 K on the (001) plane around the central Mn atoms marked by the circles in the figures. The image intensities were normalized to that of the strongest images at 100 K, and are shown as the color bars besides the figures. As a guide for eyes, intersections of dashed lines indicate ideal positions of the neighboring atoms obtained from diffraction measurement on the undoped Bi_2Te_3 crystal [4] provided that the Mn atoms are located at a Bi or Te position. In the crystal structure, all of atoms on the (001) plane are the same element, Bi or Te, depending on the z values along the c axis.

In Fig. 1(a) at 300 K, clear six atomic images are observed near the ideal positions of the second neighboring atoms in the hexagonal lattice. Thus, some of the Mn impurity atoms should be located at a substitutional position of Bi or Te atoms in the original Bi_2Te_3 crystal. The local lattice constant around the Mn impurity is slightly larger than that of the undoped Bi_2Te_3 crystal.

As seen in Fig. 1(b) at 100 K, new and strong atomic images are observed at the middle positions of the hexagonal lattice from the central Mn atom. The distance of the atomic images from the central Mn atom is about 0.25 nm, which is much shorter than the shortest Ge-Te interatomic length of 0.3063 nm. Our new XAFS experiment near the Mn K edge confirmed such a short interatomic distance around the Mn atoms [9]. Therefore, it is concluded that these Mn impurity atoms are not at any substitutional positions.

Since the XAFS data indicate that the nearest neighbors are not light Mn atoms but heavy Bi or Te atoms owing to a characteristic feature of the backscattering amplitude with k, most plausible positions of the Mn impurities for these images would be the interstitial position, i.e., the edges of triangles formed on the hexagonal layer. The Bi-Bi or Te-Te second neighboring interatomic length in the undoped Bi_2Te_3 crystal is 0.4388 nm, and a large lattice expansion around the Mn impurity is expected by about 0.03 nm. Thus, the most plausible impurity site would be at the Te triangle sites in the surface of the layes, which allow such large distortions observed by the present XFH and XAFS data [9].

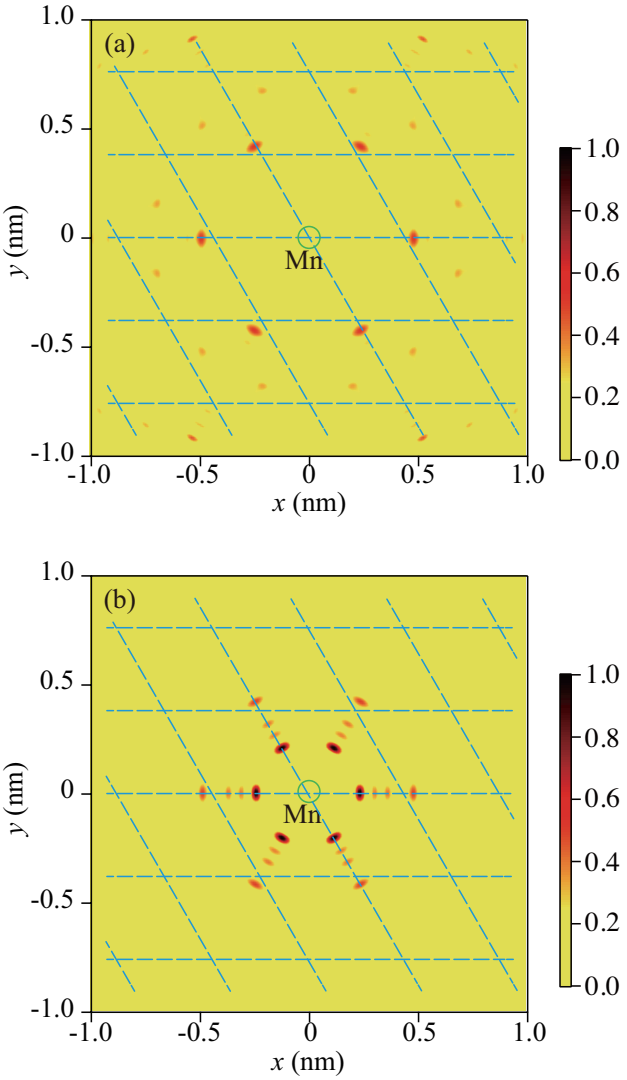

Fig. 1: Atomic images of a $Bi_2Te_3Mn_{0.1}$ single crystal at 300 K [7] and 100 K on the (001) plane around the central Mn atom obtained from the Mn $K\alpha$ XFH measurement.

For the further understandings of the Mn impurity sites in the $Bi_2Te_3Mn_{0.1}$ single crystal, a detailed comparison between the XANES data and the corresponding FEFF analysis using cluster models would be helpful, which is now in progress.

Acknowledgement

The authors thank Professor S. Sasaki and Dr. M. Okube for the support of the XFH experiments. The experiments were performed at BL-6C (No. 2013G605). This work was supported by Grant-in-Aid for Scientific

Research on Innovative Areas “3D Active-Site Science” (No. 26105006).

References

[1] H.-J. Kim *et al*., *Phys. Rev. B* **84**, 125144 (2011).
[2] H.-J. Kim *et al*., *Phys. Rev. Lett.* **110**, 136601 (2013).
[3] S. Sasaki *et al*., *private communication*.
[4] Y. Feutelais et al., *Mater. Res. Bull.* **28**, 591 (1993).
[5] K. Hayashi *et al*., *J. Phys.: Condens. Matter* **24**, 093201 (2012).
[6] S. Hosokawa *et al*., *Phys. Rev. B* **87**, 094104 (2013).
[7] S. Hosokawa *et al*., *J. Phys.: Conf. Ser.* **502**, 012024 (2014).
[8] J. J. Barton, *Phys. Rev. Lett.* **67**, 3106 (1991).
[9] S. Hosokawa *et al., Phys. Rev. B, in preparation*.

*hosokawa@sci.kumamoto-u.ac.jp. †Present address: Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan.