ESRF	**Experiment title:** The exact impurity positions of the topological insulator Bi2Te3Mn0.1 by site-selective resonant X-ray fluorescence holography	**Experiment number**: 02-02-858
Beamline: BM02	**Date of experiment**: from: 26.07.2018 to: 30.07.2018	**Date of report**: 10.09.2020
Shifts: 12	**Local contact(s)**: Marc De Boissieu, Nathalie Boudet, Gilbert Chahine	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jens R. Stellhorn*1, Maximilian Lederer*2, Lu Cong*2, S. Hosokawa1, M. de Boissieu*3, K. Hayashi2, W.-C. Pilgrim1

1Philipps-Universität Marburg, Fachbereich Chemie, Hans Meerwein Strasse, Marburg 35032, Germany
2Structural Physics Laboratory, Nagoya Institute of Technology, Japan
3 Science et Ingienerie des matériaux et procédés, St. Martin d'Heres, CEDEX

Report:

X-ray fluorescence holography (XFH) is a newly developed technique of structural characterization [1]. In general, by irradiating x-rays with an energy higher than the absorption edge of an element, an interference occurs between the direct incident X-rays and those scattered by surrounding atoms. As a result, a modulation in the fluorescent x-ray intensity from the emitter element is generated and a crystal angle dependence is obtained, which is called a hologram. By a simple 2D Fourier transform of the hologram, 3D real-space atomic images can be reconstructed around a specific element. Thus, XFH provides element selective 3D images, and is effective to obtain local structures around impurity atoms. In a resonant approach to XFH, called Resonant X-ray fluorescence holography (RXFH), the incident energy is varied over an absorption edge of a second element (with the energetically higher edge). The anomalous variation of the atomic form factors near the absorption edge can then be used to vary the contribution of a certain neighbouring atom and thus to provide element-selective information. The basis of the approach was outlined by Omori et al. [2]. The potential of combining XFH with anomalous dispersion terms was recently demonstrated by our group [3], using a slightly different approach intended for a valence-selective investigation in a sample of yttrium oxide with mixed redox states.

The experiments of this project were planned to establish the method of Resonant X-ray fluorescence holography (RXFH) at BM02 based on a sample of Mn: Bi_2Te_3. This is well-known as a thermoelectric material having a large value of thermopower, but has achieved much attention as a topological insulator, where the so-called Dirac electrons with an almost zero mass can conduct on the surface of this material.[4] The data should add to our previous structural analysis [5] and distinguish Bi from Te atoms in the structure. However, unexpected problems arised during the experiment: The energy resolution of the detecting system (consisting of a spherical analyzer crystal and a 2D XPAD area detector) could not discriminate the fluorescence line of Mn

(5.899 keV) from the second harmonic of the elastically scattered x-rays (13.422 keV +/-300 eV incident energy), owing to the special method-related constraints of setting the distance of the parts of the detecting system from the sample.

Despite the initial problems, we still succeeded to perform a RXFH experiment on a different sample. This sample was a quasi-crystal of $Al_{73}Ni_{12}Co_{15}$, which is an even more complex system, and the element-selective information accessible from RXFH are highly in demand. The aim is to separate contributions of the transition metal elements (Ni and Co) to examine if differences can be found in the nominally equivalent sites of the two elements. In this experiment, the Co *K*α fluorescent x-rays were recorded while setting the incident energy close to the Ni *K*-absorption edge at [Ni *K*]-333eV, -16eV, 0eV and +26eV, respectively. These energies correspond to characteristic relationship in the anomalous parts of the atomic form factors as illustrated in Fig. 1.

The corresponding reconstruction in real space is displayed in Fig. 2, in comparison with the 'standard' XFH reconstruction. The atomic images are located at the same sites as in the standard method, but the pure Ni sites are highly emphasized in the resonant approach. These results allow for the quantification of the relative occupations of the different transition metal atoms, which would be extremely challenging by alternative techniques.

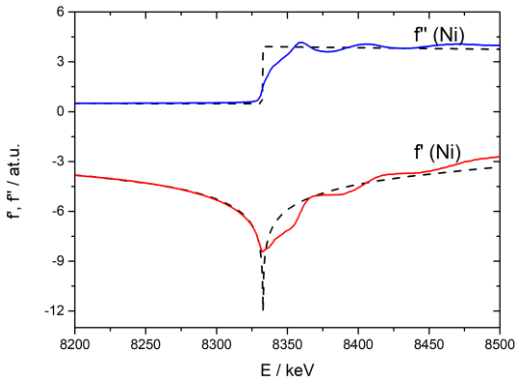

Fig. 1: Form factors for AlCoNi. Dashed lines are calculated from single atoms, and full lines are measured values.

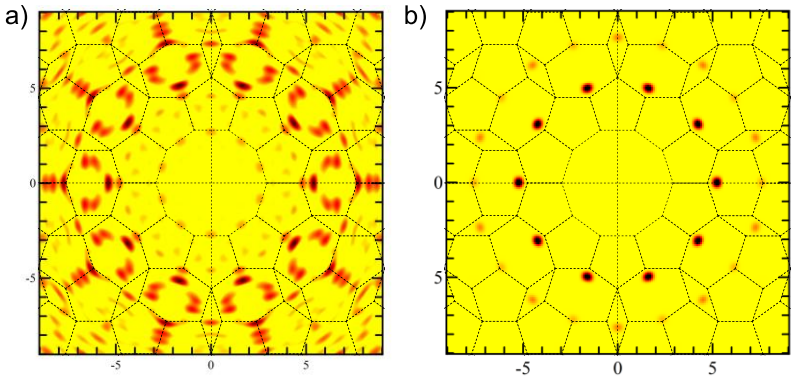

Fig. 2: Reconstructions of the average structure around Co. (a) from multi-energy XFH, (b) from resonant XFH.

[1] K. Hayashi et al., J. Phys.: Condens. Matter 24, 093201 (2012).
[2] S. Omori, L. Zhao, S. Marchesini, M. A. Van Hove, C. S. Fadley, Phys. Rev. B 65, 014106 (2001).
[3] J.R. Stellhorn et al., J. Appl. Cryst. 50, 1583-1589 (2017).
[4] H.-J. Kim et al., Phys. Rev. B 84, 125144 (2011).
[5] S. Hosokawa, J. R. Stellhorn et al., Phys Rev. B. 96, 214207 (2017).