ESRF	**Experiment title:** EXAFS study of Sb and Mn dopants in Bi_2Se_3 topological insulators	**Experiment number**: HC-2424
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Report:

The aim of the experiment was to determine the crystallographic sites of Sb and Mn dopants intercalated in Bi_2S_3 topological insulators (TIs) single crystals. This goal was achieved by probing EXAFS spectra at Se, Sb and Mn *K* absorption edges as well as Bi L_3 absorption edge. The measurements were performed on BM23 beamline on ex-situ cleaved samples placed inside a cryostat cooled down to 10K. All the spectra were collected in partial fluorescence mode using Vortex SDD. We have probed the following main set of samples:

- Bi_2Se_3,
- $(Bi_2Se_3)_{0.8}(Sb_2Se_3)_{0.2}$,
- $Bi_{1.9}Mn_{0.1}Se_3$,
- $(Bi_2Se_3)_{0.9}Mn_{0.1}$

We have also proposed to measure angular dependent XANES spectra. However, the preliminary test performed on Sb K edge of Sb in $(Bi_2Se_3)_{0.8}(Sb_2Se_3)_{0.2}$ have not revealed a significant dependence. Therefore, we made decision to measure EXAFS spectra of additional samples in order to track the possible evolution of doping sites with the stoichiometry of the crystals. The set of additional samples consisted of:

- $Bi_{1.8}Mn_{0.2}Se_3$,
- $Bi_{1.85}Mn_{0.15}Se_3$,
- $(Bi_2Se_3)_{0.96}Mn_{0.04}$
- $Bi_{1.98}Fe_{0.02}Se_3$,
- $(Bi_2Se_3)_{0.9}(Bi_2S_3)_{0.1}$,
- Bi_2Te_3,
- Sb_2Te_3.

Standard data evaluation procedure of EXAFS spectra was performed using ATHENA software. Based on the crystallographic information obtained from the ICSD database and FEFF calculations we determined the crystallographic model of reference materials, pristine Bi_2Se_3 and Bi_2Te_3 crystals. Crystal structure of Bi_2X_3 (X=Se,Te) is described by $R\bar{3}m$ space group. The quintuple layers (QL), consisting of five atomic planes of X–Bi–X–Bi–X, are separated by a van der Waals gap. We assume, that doping atoms may substitute Bi or X sites as well as to enter the crystal structure in a tetrahedral (T_d vdW) or octahedral (O_h vdW) interstitial sites within van der Waals gap. In addition and octahedral sites within QL layers (Oh QL). The model of reference samples were used to generate the scattering paths for fitting the predicted structure to experimental data. This part of analysis were performed in ARTEMIS software.

Figure 1 and table 1 shows the results of the combined fits performed on Bi_2Se_3 and $(Bi_2Se_3)_{0.8}(Sb_2Se_3)_{0.2}$. Fitted were hexagonal unit cell parameters (a, c) and crystallographic coordinates within the unit cell. Results of the fits clearly indicate predominant substitutional character of Sb dopants leading to a negligible modification of the unit cell parameters along with a slight (by 2%) of the Sb crystal coordinates (local crystal distortion).

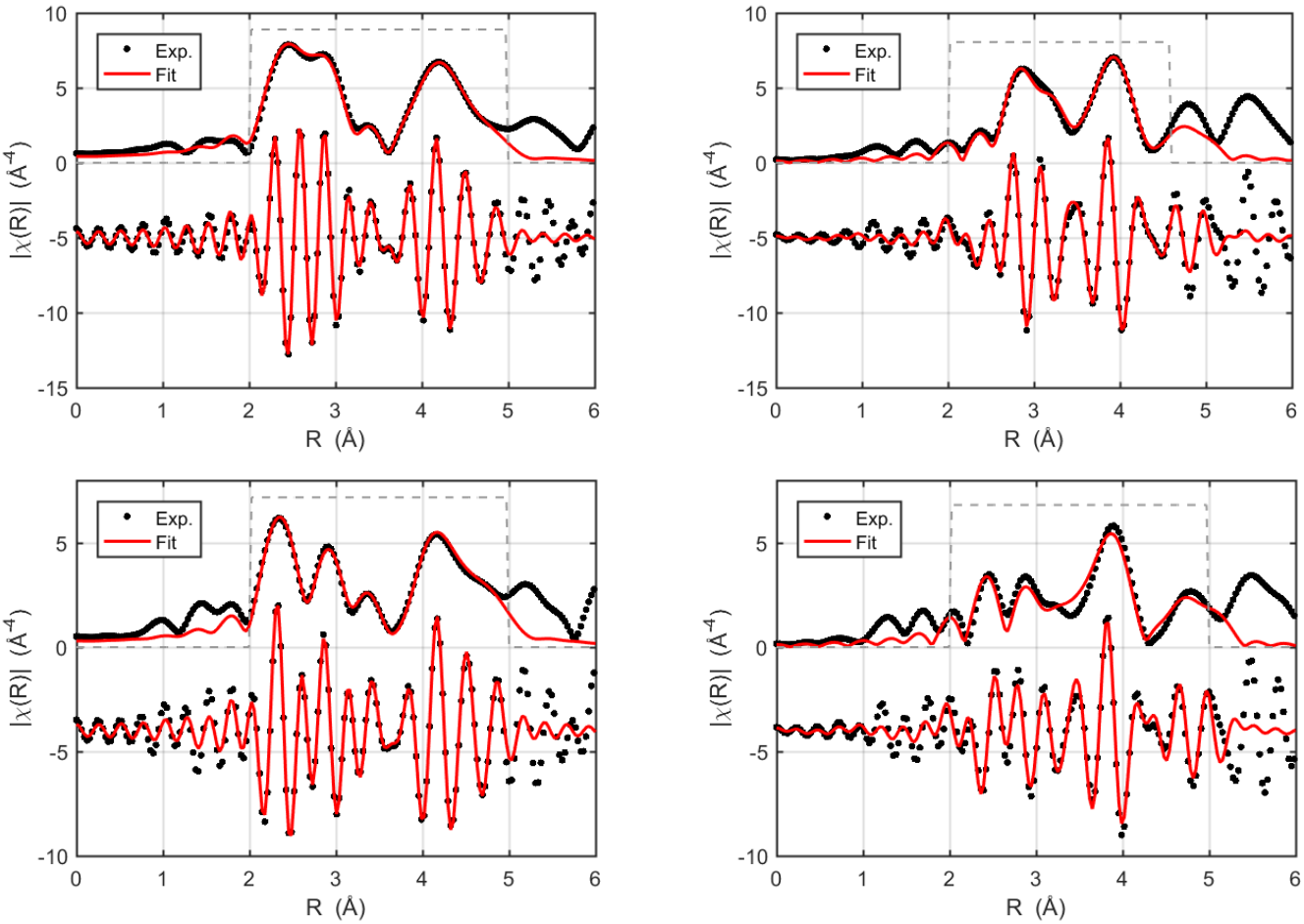

Figure 1. Comparison of the EXAFS fits performed on data acquired from Bi_2Se_3 (top row) and $(Bi_2Se_3)_{0.8}(Sb_2Se_3)_{0.2}$ (bottom row) single crystals probed at Bi L_3 (left column) and Se K (right column) edges. Presented are the results of combined fits that use the same set of dependent parameters on both edges. Fits were performed to the parameter space of k from 3 to 12.5 $Å^{-1}$, and R from 2 to 5 Å (three coordination shells, seven/eight independent paths). The following parameters were fitted: a and c crystal units, Bi/Sb and Se crystallographic coordinates, E_0 and S^2 parameters independent for each edge and path, respectively.

Table 1. Quantitative results of the fits shown in figure 1 along with the crystallographic parameters of Bi2Se3 sited in ICSD database by S. Nakajima et al.

Sample	Model fitted	Unit cell parameters		Crystallographic coordinates		
		a	c	Bi1	Se1	Se2
Bi_2Se_3	S. Nakajima	4.1383	28.5760	0.4010	0.0000	0.2104
$(Bi_2Se_3)_{0.8}(Sb_2Se_3)_{0.2}$	Bi substitution	4.1353	28.4528	0.3999	0.0000	0.2107
S. Nakajima (ICSD 42545)		4.1430	28.6360	0.3985	0.0000	0.2115

Analysis performed on Mn K-edge EXAFS spectra only revealed that dopants are distributed among different sites expected. First approximation fits, shown in figure 2, were performed under assumptions that dopants are randomly distributed within the volume of the crystal, i.e. dimers or trimers occupying next interstitial or substitutional sites are negligible. They revealed that $(Bi_2Se_3)_{1-x}Mn_x$ crystals exhibit quasi uniform distribution of dopants among all the sites considered, while in $Bi_{2-x}Mn_xSe_3$ samples Mn dopants occupy predominantly substitutional and/or O_h vdW sites.

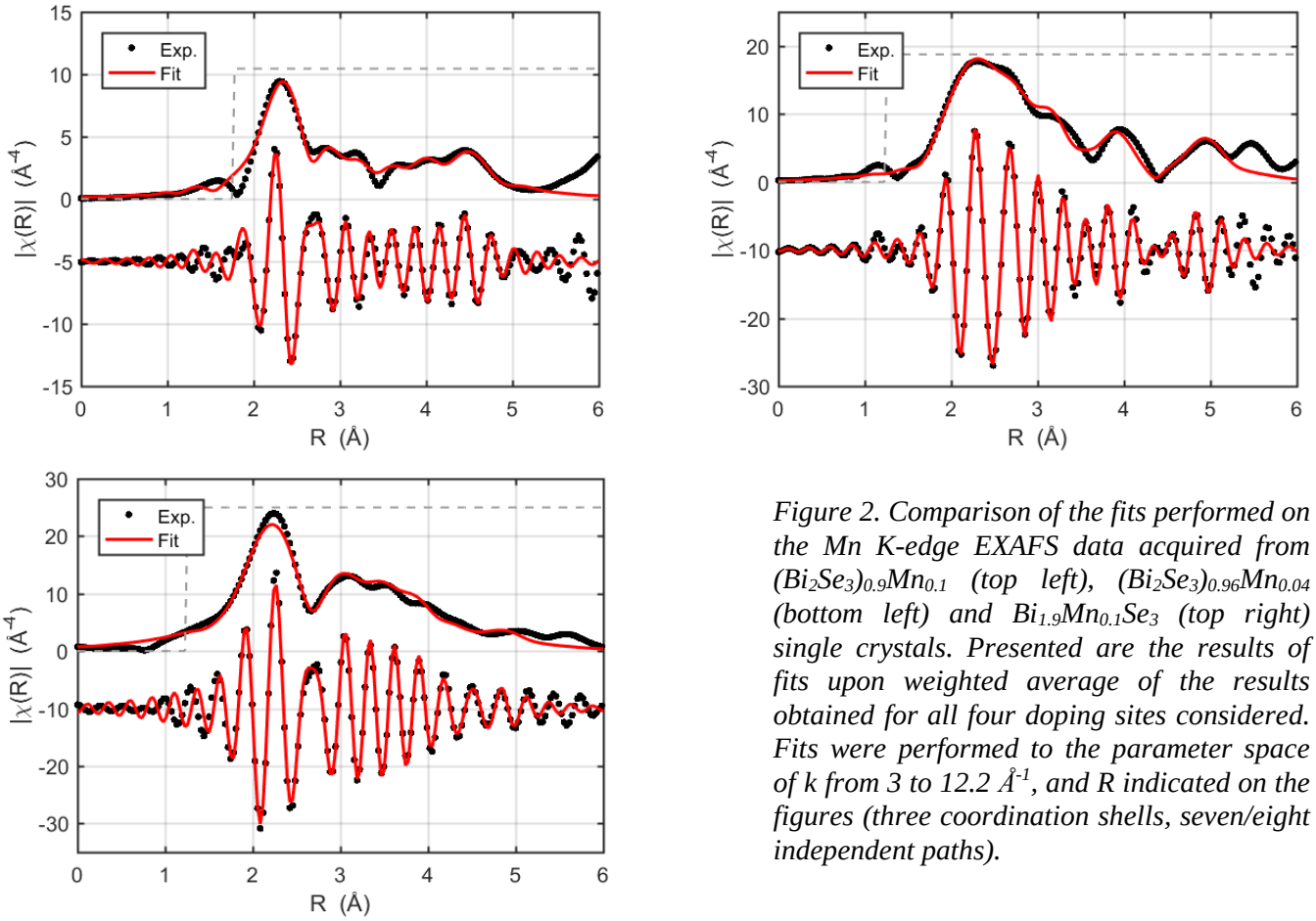

Figure 2. Comparison of the fits performed on the Mn K-edge EXAFS data acquired from $(Bi_2Se_3)_{0.9}Mn_{0.1}$ (top left), $(Bi_2Se_3)_{0.96}Mn_{0.04}$ (bottom left) and $Bi_{1.9}Mn_{0.1}Se_3$ (top right) single crystals. Presented are the results of fits upon weighted average of the results obtained for all four doping sites considered. Fits were performed to the parameter space of k from 3 to 12.2 $Å^{-1}$, and R indicated on the figures (three coordination shells, seven/eight independent paths).

Selected results of the experiment were presented during ESRF User Meeting 2017 by Krzysztof Maćkosz – poster no 17, *Local structure of dopants in Bi_2Se_3 and Bi_2Te_3 single crystals*.

Combined analysis of Mn doped samples is still on-going. While the manuscript describing results of EXAFS analysis of S and Sb doped samples, combined with STM and ARPES data, is being prepared.