Bismuth chalcogenides doped with transition metals – structural investigations

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Bismuth chalcogenides, e.g. Bi_2Te_3 and Bi_2Se_3, where studied for decades as a promising thermoelectric materials. Their structure is built from ”quintuple layers” – Te/Se-Bi-Te/Se-Bi-Te/Se hexagonal atomic planes separated by van der Waals gap. Recently the interest in these materials were renewed due to discovery of surface states protected by time reversal symmetry that are resistant to impurities, defects, and geometry deformations - the property characteristic for topological insulators (TIs). Doping with magnetic elements can produce bulk ferromagnetic ordering and thus breaks time-reversal symmetry that leads to exotic electron transport phenomena. Controlling magnetic properties of TIs is a prerequisite for applications and development of devices.

Theoretical predictions and recent experiments show that long range magnetic order in bismuth chalcogenides can be achieved upon proximity effect or substitutional doping into bismuth site. Our goal is to systematically determine the location and population of transition metal dopants in bismuth chalcogenides single crystals grown with Bridgman method.

We have studied single crystals of Bi_2Te_3 and Bi_2Se_3 doped with Co, Mn and Fe. Angle resolved XANES (and XNLD) has been collected at K-edges of dopants at SuperXAS beamline at Swiss Light Source. Theoretical modelling of the spectra of dopants in substitutional sites and interstitial sites were performed by means of FEFF and FDMNES.

Significant, gradual changes in the spectral shape depending on the x-ray polarization direction with respect to crystal c-axis are visible in the experimental spectra of all the crystals studied. On the other hand, the general shape of the spectra is significantly different for distinct types of dopants. It indicates that the distribution of dopants in bismuth chalcogenide structure is not random, but the dominant sites are specific for dopants. Qualitative data analysis aided by preliminary simulations results indicates that:

- Fe doped into Bi_2Se_3 preferentially occupies tetrahedral interstitial sites within van der Waals gap,
- Mn doped into Bi_2Se_3 and Bi_2Te_3 preferentially occupies octahedral interstitial sites within van der Waals gap and also likely substitutes Bi,
- Co doped into Bi_2Te_3 preferentially occupies tetrahedral interstitial sites within van der Waals gap. In the case of Co doping precipitation of another phase was also observed.

Angle resolved XANES measurements provide additional information that can help in determination of the dopant sites. However our preliminary findings indicate that while there is preferential occupation of certain site, characteristic for each kind of dopant, other sites are likely occupied too.

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