Near-Edge Fine Structure Analysis of Copper in Cu-Bi$_2$Se$_3$ Topological Insulators

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Doped Topological Insulators have raised interest in the physics community because of the possible coupling/co-existence of the surface states with magnetic order induced by doping. For example, it has been observed that Cu doped Bi$_2$Se$_3$ is superconducting [1] below 10K. But, with more than one possible site, it is imperative to know where the dopant atom is present. So far [2] the valence state of Cu is used to determine this, and the common consensus is on Cu^{+1}. In this work, we use energy loss near-edge fine structure analysis (ELNES) [3] to observe the valence, local co-ordination and electronic structure around the dopant atom (Cu) in Cu-Bi$_2$Se$_3$. We use a Jeol 2010F to record the EEL spectra and the FEFF8.4 code [4] for ELNES simulations. The ARM200F and Nion UltraSTEM 100^{MC} were used to collect the HAADF-STEM images and Dr. Kirkland's STEMSLICE code to simulate the same. Commercial samples of Cu(I)Se [Cu$_2$Se] and Cu(II)Se [CuSe] were used as references.

Bi$_2$Se$_3$ are layered structures that peel off almost as easy as graphene. Since these were bulk-grown samples (not grown on substrates), we used the Leica UltraCut R ultramicrotome to prepare thin cross-sections to be studied using the TEM. The typical thicknesses of these samples were about 25-40nm. Fig (1a) shows the HAADF-STEM image of undoped Bi$_2$Se$_3$. The strongly scattered (bright) atoms correspond to Bi and the rest to Se. The quintuple layered structure is clearly visible with the van-der Waals gap separating each such set of five layers. Simulations for HAADF-STEM were performed simultaneously and the results overlaid onto the experimental data (with the red and blue circles signifying the positions of the atoms in the experiments). As we can note, the overlap is good, re-iterating the quality of the single crystals. Fig (1b) shows the HAADF-STEM image of Cu(II)Se reference sample (again with a simulated HAADF-STEM image overlaid). In this case, each bright blob is a dumbbell consisting of Cu and Se atoms. A line scan of the same, fig (1c), helps distinguish the Se columns from the Cu columns, with Se having higher intensity (as is expected due to the Z-dependence of HAADF-STEM intensities).

Fig (2a) shows the experimental EEL spectrum from Cu-Bi$_2$Se$_3$ (blue), Cu(I)Se (red) and Cu(II)Se (green). Cu L$_{2,3}$ transition is characterized by an edge at 930eV. Thus, fig (2a)-blue curve, confirms the presence of Cu in Bi$_2$Se$_3$ using EELS. The shape of the energy loss spectrum just beyond an ionization edge (ELNES) provides information about the valence and co-ordination around the atom of interest. In our case, we notice from fig (2a) that the near-edge structure of Cu-Bi$_2$Se$_3$ doesn't really match with either Cu(I)Se or Cu(II)Se. Therefore, we presume that the oxidation state of Cu is an intermediate value between '+1'and '+2'. Using FEFF, we simulate the ELNES for Cu(I)Se and Cu(II)Se. Cu(I)Se consists of twelve non-equivalent Cu sites (grouped into 4 as Type – A, B, C and D) as in fig(2b) and Cu(II)Se consists of two (Type A and B) as in Fig (2c). The blue curves in Fig (2b and 2c), thus, are the weighted average (W.A.) spectra, representing a combination of these unique spectra constituting each 'type'. The ELNES studies on Cu-Se reference samples thus clearly point to the limitations of fingerprinting based on the oxidation state of an atom – possible only if there is not more than one non-equivalent type of the atom in the material.

Thus to summarize, (i) we are able to detect the presence of Cu in Bi_2Se_3 using EELS. (ii) We infer first that the effective oxidation state of Cu in Bi_2Se_3 is not '+1' and is probably an intermediate value in between +1 and +2. (iii) The studies on the reference samples Cu(I)Se and Cu(II)Se reveal to us that the near edge structure is more sensitively determined by local atomic co-ordination than a specification of the oxidation state of an atom. (iv) We are working towards identifying the Cu position in Bi_2Se_3 with atomic spatial resolution using STEM-EELS with the Nion UltraSTEM.

References:
[1] Y.S. Hor et al., *Phys. Rev. Lett* 104, 057001, (2010)
[2] M. Kriener et al., *Phys. Rev. B* 84, 054513, (2011)
[3] James H. Paterson, Ondrej L. Krivanek, *Ultramicroscopy* 32, 4, 1990,
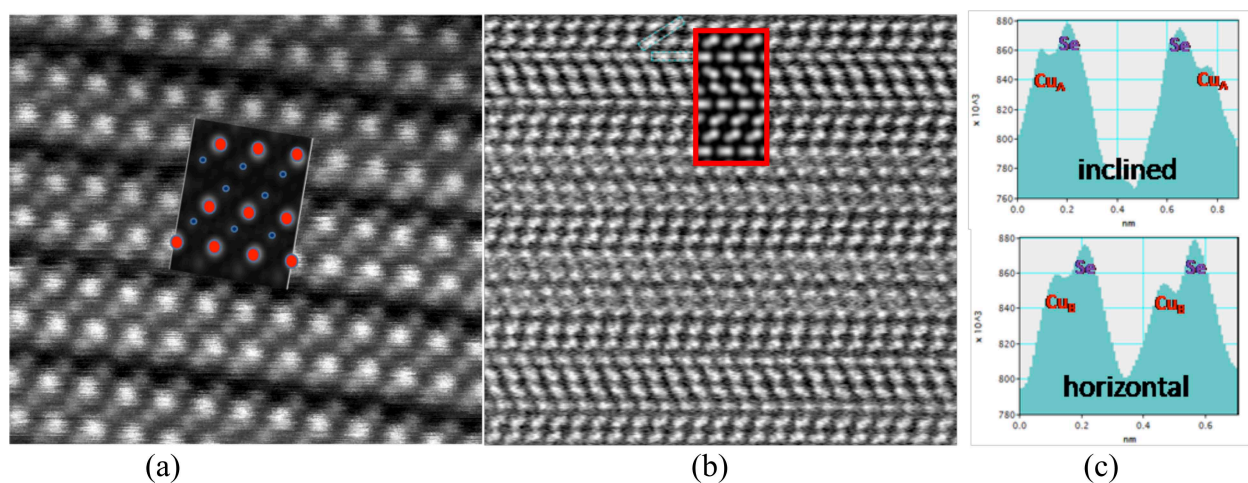[4] A.L. Ankudinov et al., *Phys. Rev. B* 58, 7565, (1998)

Figure 1. HAADF-STEM experimental image of **(a)** Bi2Se3 and **(b)** Cu(II)Se. A simulated HAADF-STEM image is overlaid to confirm the orientation and structure for both. **(c)** Line scan of the inclined and horizontal regions from (b) distinguishing the Se and Cu atoms in the dumb-bells.
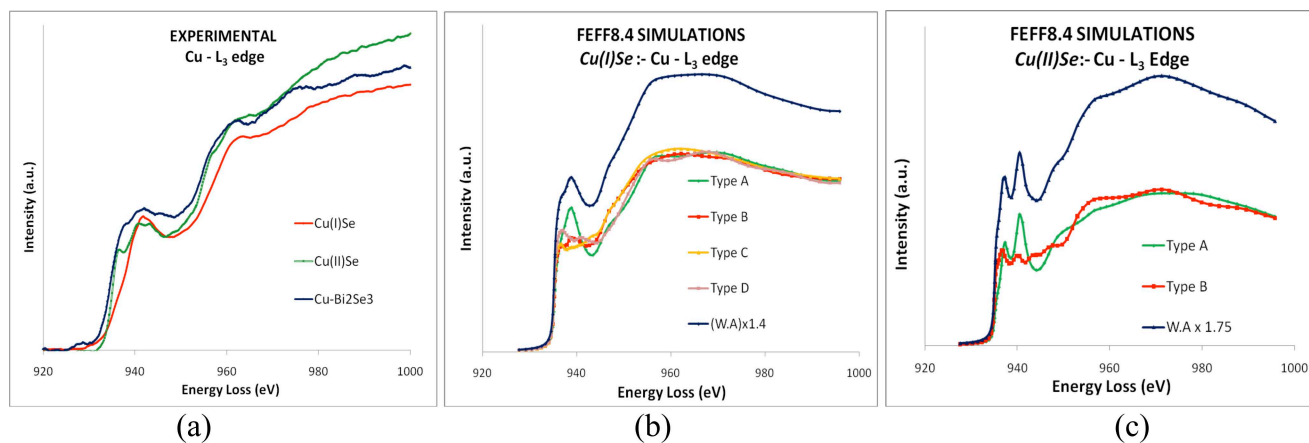

Figure 2. (a) Experimental EEL spectrum for $Cu-Bi_2Se_3$, Cu(I)Se and Cu(II)Se. FEFF8.4 simulated energy loss spectrum with the cumulative spectrum in blue for **(b)** Cu(I)Se, grouping 12 non-equivalent Cu sites to four types (A,B,C and D). **(c)** Cu(II)Se, with 2 non-equivalent Cu sites as types A and B.