Investigation of Oxidation States and Crystal Structure Modulation in the New Superconductor $FeSe_x$

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Small changes in the composition of the Se are observed to influence the crystal structure and transport properties of crystals of $FeSe_x$. X-ray absorption near edge structures spectroscopy (XANES) was used to investigate the electronic structure of these crystals. While Fe K-edge XANES shows a superposition of FeSe and Fe oxide like spectrum the Se K-edge XANES does not show any oxidation. The room-temperature XANES spectra derive an average valency of +1.82 for Fe and -2.18 for Se. The present studies indicate crystal distortion and a *p* hole variation at the Se site that my lead to itinerant electrons which in turn may be one of the sources responsible for the observed superconducting behavior in these crystals. These results indicate a predominantly Fe 3d character in this system.

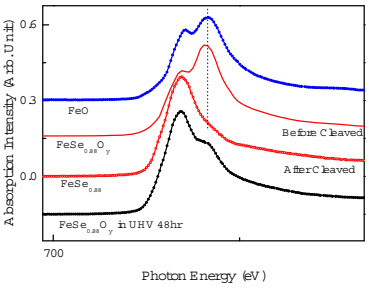

Fig. 1: The Fe L_3-edge spectra with before ($FeSe_xO_y$, solid red line) and after cleaved ($FeSe_{0.88}$, cycle red line) and the FeO standards. As the cleaved crystal stays in the UHV chamber, the oxidation state was observed (dottedline is guided the eyes).

Soft x-ray absorption spectra in Fe L-edge (Fig. 1) and O K-edge were recorded at the beamline 20A (HSGM) of NSRRC and beamline 8 of ALS. Total-electron-yield (TEY) mode was used for data collections. To further understand the valence states and the crystal symmetry distortion of the atomic structure. We also measured the Fe and Se K-edge at 17C and 01C hard x-ray beamline in NSRRC. Shown in Fig. 2 and Fig. 3

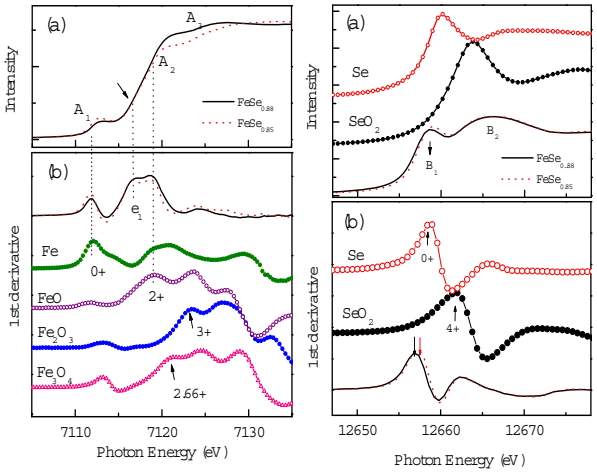

Fig. 2: (left) (a) Fe K-edge (1*s*➔4*p*) spectra of $FeSe_x$ as a functiom of Se content, (b) shows the first derivative based on the absorption spectra and along with the different valence states of Fe-foil, FeO, Fe_2O_3 and Fe_3O_4 standard samples. Figure 3 (right) (a)The Se K-edge (1*s*➔4*p*) absorption spectra of a series of $FeSe_x$ as a functiom of Se content along with SeO_2 and Se metal. (b) shows the first derivative based on the absorption spectra.

The lattice distortion observed is confirmed in the XANES measurements and is found to lead to itinerant holes/electrons. This in turn is seen to influence the T_c of the samples. The separation of the Fe in the plane was found to decrease from the 4*p* orbital to varying (modulating) coordination geometry. The spectra reflect a predominantly metallic Fe character even though oxygen was found on the surface of the crystals incorporated during handling. The spectral evidence confirms that Se defects are leading to an increase at the 4*p* hole count and in an unchanged structure chain in the Se sites. Such symmetry in the tetragonal $FeSe_x$ would lead to an increase in the *p* holes due to Fe 3*d*–Se 2*p* hybridization resulting in a decreasing covalence.