X-ray absorption spectroscopy investigation of the electronic structure of superconducting FeSe$_x$ single crystals

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Abstract - X-ray absorption spectroscopy (XAS) Fe $K$-edge spectra of the FeSe$_x$ ($x=1–0.8$) single crystals cleaved \textit{in situ} under vacuum reveal characteristic Fe 4$p$ states and a lattice distortion. The Se $K$-edge spectra point to a strong Fe 3$d$-Se 4$p$ hybridization giving rise to itinerant charge carriers. A formal charge of $\sim 1.8+$ for Fe and $\sim 2.2–$ for Se was evaluated from these spectra in the FeSe$_x$ ($x=0.88$). The charge balance between Fe and Se is assigned to itinerant electrons located in the Fe-Se hybridization bond. As $x$ decreases the 4$p$ hole count increases and a crystal structure distortion is observed that in turn causes the Fe separation in the $ab$-plane to change from 4$p$ orbital to varying (modulating) coordination. Powder X-ray diffraction (XRD) measurements also show a slight increase in lattice parameters as $x$ decreases (increasing Se deficiency).

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Introduction. – Recent report of superconductivity in oxypnictides \cite{1–3} has generated a flurry of activity much akin to the cuprate superconductivity discovered in the 1980s. This has led to the discovery of several new compounds among which is the less toxic FeSe$_x$ \cite{4} that shows zero resistance at 8K which is dependent on Se deficiency and annealing at 400°C. While the 400°C anneal is found to reduce the non-superconducting NiAs-type hexagonal phase and increase the PbO-type tetragonal superconducting phase \cite{4–6} the role of Se deficiency is not well understood. On the other hand, the influence of fluorine doping \cite{1,7} and rare-earth substitutions \cite{8} on the superconductivity in the LaO$_{1-x}$F$_x$FeAs compounds have been investigated. The XAS \cite{9}, X-ray photoemission spectroscopy (XPS) \cite{10} and resonant X-ray inelastic scattering (RIXS) \cite{8} investigations show that the Fe 3$d$ states hybridize with the As 4$p$ states providing the itinerant charge carriers (electrons) responsible for superconductivity. Most of these studies suggest moderate-to-weak electronic correlations in this system. The photoemission spectroscopy (PES) measurements \cite{11} support the density of state (DOS) calculations on the FeSe$_x$ system and indicate the Fe-Se hybridization and itinerancy with weak-to-moderate electronic correlations \cite{12} while strong correlations have been suggested is some recent theoretical calculations \cite{13,14}. While fluorine substitution leads to electron doping in case of the LaO$_{1-x}$F$_x$FeAs system, how Se deficiency may bring in the mobile carriers in the FeSe$_x$ system leading to superconductivity is not clear. A detailed study of the FeSe$_x$ ($x=1–0.8$) crystals has been made using XAS Fe and Se $K$-edge spectra. The results presented here show a lattice distortion and Fe-Se hybridization that are probably responsible for producing itinerant charge carriers in this system. The lattice distortion was also confirmed by the powder X-ray diffraction (XRD) measurements.

Experimental. – FeSe$_x$ crystals were grown by the high-temperature solution method as described earlier \cite{5,6}. Crystals measuring 5 mm $\times$ 5 mm $\times$ 0.2 mm with (101) plate-like habit thus obtained were characterized for Se deficiency using a Philips Xpert XRD system and a Joel scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) (not presented here). The XAS measurements
at the Fe and Se K-edge were carried out on the 17C1 and 01C Wiggler beamlines at the National Synchrotron Radiation Reach Center (NSRRC) in Taiwan, operated at 1.5 GeV with a current of 200–240 mA. Si(111) crystals monochromators were used on both the beam lines giving an energy resolution $\Delta E/E$ better than $2 \times 10^{-4}$. The Fe and Se K-edge absorptions spectra were recorded by the fluorescence yield (FY) mode at room temperature using a Lytel detector [15]. All spectra were normalized to a unity step height in the absorption coefficient from well below to well above the edges. Standard Fe and Se metal foils and oxide powders, SeO$_2$, FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ were used for energy calibration and also for comparing different electronic valence states. Since surface oxidation was suspected the FeSe crystals were cleaved in situ in vacuum before recording the spectra. Even though we have studied a number of FeSe$_x$ crystals with $x = 1$ to 0.8 the results for only three compositions are presented here for comparison and clarity.

Results and discussion. –

Microstructure. To facilitate the discussion that follows the tetragonal crystal structure of FeSe and its building blocks, namely, Se-Fe tetrahedra and Fe-Se pyramidal sheets are shown in fig. 1(a). The electronic structure of the individual elements and FeSe$_x$ (indicating the hybridization band) are given in fig. 1(b). Figure 2 shows the XRD patterns of the FeSe$_x$ ($x = 0.9$, 0.88 and 0.85) crystals which are found to represent the superconducting FeSe phase. The patterns have been fitted to the P4/nmm and indexed in the figure. Weak hexagonal reflections are also seen among these. The main diffraction peak (101) shown expanded in the inset is found to shift to a lower 20 as $x$ decreases indicating an increase in the lattice parameters. The lattice parameters calculated from these patterns are $a = b = 3.771$ Å, $c = 5.528$ Å for $x = 0.9$, $a = b = 3.777$ Å, $c = 5.528$ Å for $x = 0.88$ and $a = b = 3.777$ Å, $c = 5.529$ Å for $x = 0.85$. It is observed that the $a = b$ parameter increases though very slightly as $x$ decreases. A much smaller change is seen in the $c$-parameter at the same time. Thus, the ab-plane variation is found to be larger than that of the c-axis. These lattice parameters are very close to those reported in literature for Se-deficient powders [4].

Formal charge of Fe and Se in the crystals. The transition metal Fe K-edge (1s $\rightarrow$ 4p) XAS spectra in fig. 3(a) are mostly related to the partial density of 4p states of the iron site (fig. 1(c)). The unoccupied states in the 3d (due to quadruple transition) and 4sp bands are sensitive to the local structure and the type of nearest neighbors [16–18]. These spectra could therefore be used to obtain information about the changes in the electronic states that may result from changes in the environment of the Fe ions such as Se vacancies in the present case. The Fe K-edge absorption spectra of FeSe$_x$ crystals are presented in fig. 3 along with the standards Fe, FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ and are normalized for the photon energy $\sim$100 eV above the absorption edge at $E_0 = 7112$ eV (the pure Fe K absorption edge energy). The spectra of the crystals appear to
X-ray absorption spectroscopy investigation of the electronic structure etc.

are in agreement with the results of Yang et al. [8] on Fe-pnictides 1111 and 122 systems and Lee et al. [20] using first-principles methods to study the FeSe$_x$ system. Thus the results presented here on the oxygen-free FeSe$_x$ crystals rule out the role of oxygen in superconductivity as is the case in the LaO$_{1-x}$Fe$_2$As system.

Three prominent features $A_1$, $A_2$ and $A_3$ are observed in these spectra (fig. 3(a)) of which the $A_1$ could be assigned to the 3d unoccupied states originating from the Fe-Fe bonds in metallic iron. The features $A_2$ and $A_3$ represent the unoccupied Fe 4$s$ states. The rising part of the broad feature $A_2$ ($\sim$7118.8 eV) appears as a broad peak labeled $e_1$ at $\sim$7116.8 eV, seen well separated in the first-derivative plots of these spectra given in fig. 3(b). It is not seen in those of the reference Fe metal foil or oxide powders and is a part of the Fe 4$s$ band. The $e_1$ feature appears at an energy between those of the Fe metal and FeO and therefore has its origin in a different interaction as will be seen. From these first-derivative plots, a formal charge of Fe was evaluated in conjunction with the three standards FeO(Fe$^{2+}$), Fe$_2$O$_3$(Fe$^{3+}$) and Fe$_3$O$_4$(Fe$^{2.66+}$). In addition we used the sine-function fitting of the broad feature $e_1$ (7113.84–7122.2 eV). By an extrapolation of the energy of FeSe$_{0.88}$ with those of the standards we obtained a formal charge of $\sim$1.8+ for Fe in these crystals thus establishing the electronic charge of Fe in the covalency (2+). It is also seen that the peak (energy) position is not increasing in energy as $x$ is decreased meaning that the effective charge (valence) of Fe does not change with $x$. This is consistent with the Fe L-edge spectra presented above as well as the RIXS analysis [19]. Thus the possible electronic configurations of Fe in the ground state could be written as 3$d^{6.2}$ or 3$d^{6.4}s^{0.2}$ indicating a mixture of monovalency (3$d^{6}4s^{1}$) and divalency (3$d^{5}$).

The Se K-edge spectra of the FeSe$_x$ crystals and Se and SeO$_2$ standards are presented in fig. 4(a) and the corresponding first-derivative plots are given in fig. 4(b) to highlight the energy changes in the spectra. The spectra represent mainly Se character without any trace of SeO$_2$, indicating the absence of oxidation even in the deeper layers of the FeSe$_x$ crystals. The spectra exhibit two peaks $B_1$ and $B_2$. The $B_1$ feature at photon energy around 12658 eV is formally assigned to the transitions 1$s$ $\rightarrow$ 4$p$ and shows a slight increase in intensity as well as shift to higher energy as $x$ is decreased. This indicates an increase in the Se 4$p$ unoccupied states i.e. in the upper Hubbard band (UHB). From the first-derivative plots a formal charge of $\sim$2.2– is obtained for Se in the $x$ = 0.88 crystal by interpolation with the energies of the standards Se and SeO$_2$ (as in the case of Fe). This is in agreement with a total charge of 0 when the formal charges of Fe and Se are added (Fe$^{1.8+}$ Se$^{2.2–}$). This establishes the electronic charge of Se in the covalency (2–).

Fe 3$d$–Se 4$p$ hybridization and superconductivity.

The excess negative charge of $\sim$0.2 seen on Se may be explained as follows. The electronic charge of Fe in the
covalent FeSe

above is in fact due to itinerant electrons in the Fe-Se hybridization bond and appears as a hole increase in the Se K-edge spectra. This could be confirmed from the Fe L-edge measurements on similar crystals. When we correlate this with the decreasing transition width in the resistance measurements (not shown here), it becomes apparent that that the charge carriers responsible for superconductivity are in fact itinerant electrons in a similar manner as the itinerant holes in the case of cuprates. Oxygen annealing in case of YBa2Cu3O6+δ is found to oxidize Cu4+ to Cu3+ through the hybridization of Cu 3d-O 2p states. The Cu3+ state has been assigned to the empty state in the Cu-O bonds that is also referred to as the 3d6L2 ligand state, where a hole is located in the oxygen ions surrounding a “Cu site” (L2 a ligand hole, tentatively label this as 3d6-like) [22]. These itinerant holes are responsible for superconductivity. In a similar manner in the case of FeSe, the Se deficiency is bringing a Fe 3d-Se 4p hybridization leading to itinerant electrons. It is also likely that the changes in bond lengths may also result in a reduction in the width of the resistive transition due to external pressure as reported by Mizuguchi et al. [23].

Lattice distortion, structure modulation. It is seen that the intensity of the A2 feature reduces as x is decreased which indicates a lattice distortion that increases with decreasing x. In addition the change in the A3 feature is larger than the A2 feature. Since multiple scattering in the XAS from p-orbitals could reveal the different orbital orientations and because of the nature of the p-orbitals i.e. px, py, and pz the A2 feature could be associated with pxy(σ) and A3 to pxz(π) orientations. This leads us to a speculation of a larger distortion in the ab-plane (Fe-Fe distance) compared to the c-axis. This is also seen from the XRD measurements (fig. 2) where the change in the a = b parameter is larger than that of the c-parameter (Fe-Se distance). Therefore, the Fe orbital structure changes from 4p to a varying (modulating) coordination as x is decreased. The broad feature B3, at ~20 eV above the Se K-edge appears at the same energy in all the FeSex spectra and is not affected by the Se deficiency and is assigned to the multiple scattering from the symmetrical Se 4p states in the coordination sphere that are correlated to the local structure of the Se ions [16]. This is consistent with the XRD result where the c-parameter is nearly unchanged. This becomes clear by looking at fig. 1 where Se is seen at the tip of the Fe-Se pyramid.

Since Se is located at the apex of the tetrahedral pyramid chain in the FeSex lattice (as shown in fig. 1), the removal of a Se ion with formal negative charge (−2) from the lattice would result in a Se vacancy with an effective positive charge and would cause repulsion to the surrounding positively charged Fe atoms. This is consistent with the distortion in the ab-plane discussed above. In addition the Fe atoms around the vacancy may act like magnetic clusters as pointed out by Lee et al. [20].

Fig. 4: (Color online) (a) The Se K-edge (1s → 4p) absorption spectra FeSex with different Se content along with the standards Se metal and SeO2 and (b) the first-derivative plots of the same spectra.

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Conclusion. — In conclusion a lattice distortion observed in the XAS Fe $K$-edge spectra of Se-deficient FeSe$_x$ crystals that may produce itinerant electrons in the Fe-Se hybridization bond seen in the Se $K$-edge spectra. The XRD measurements confirm this lattice distortion that increases with Se deficiency. The charge balance considerations from Se deficiency also result in itinerant electrons (in the Fe-Se hybridization bond). The increase in $x$ (itinerant electrons) is ascribed to the reduced lattice distortion (crystal structures that may produce itinerant electrons in the Fe-Se hybridization bond). The charge balance that increases with Se deficiency. The charge balance considerations from Se deficiency also result in itinerant electrons (in the Fe-Se hybridization bond). The increase in $x$ (itinerant electrons) is ascribed to the reduced lattice distortion (crystal structures that may produce itinerant electrons in the Fe-Se hybridization bond).

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