Investigation of the structural distortion in FeSe\textsubscript{x} crystals by X-ray absorption near edge structures (XANES) spectroscopy

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1. Introduction

Superconductivity in FeSe was attributed to the defects that may be caused due to Se deficiency \cite{1}. While this was contested support came from the theoretical analysis of the Se deficient crystal which revealed the presence of magnetic clusters around the Se vacancies \cite{2}. It was also observed that the resistivity curves exhibit a small hump around 100 K indicating a structure change. High resolution X-ray diffraction on both polycrystalline bulk and single crystals revealed an orthorhombic distortion starting from 105 K \cite{3}. The influence of Se deficiency was investigated by room temperature XANES studies which revealed a crystal structure modulation in which the distortion in the ab plane is larger than the c-axis \cite{4}. To further investigate the temperature variation of this distortion we measured the XANES spectra on Se deficient FeSe\textsubscript{x} crystals with x = 1 – 0.8. While the room temperature spectra reflect the distortion of the tetragonal lattice, the spectra at 77 K do not show this distortion but a possible change in the crystal structure. These results are presented here.

2. Results and discussion

Details of the FeSe\textsubscript{x} crystal growth are given elsewhere \cite{3}. The X-ray diffraction measurements were performed on a Phillips Xpert system, magnetic measurements were made on a Quantum Design SQUID magnetometer and the resistance measurements were made on a PPMS system of the same make. XANES measurements were made at National Synchrotron Radiation Research Center (NSRRC), Taiwan. The Fe K-edge spectra were recorded on crystals cleaved in situ in vacuum thereby removing the possibility of oxygen contamination due to handling. Crystals with x = 1, 0.95, 0.9, 0.85, 0.8 were used for the measurements. The spectra were recorded at 300, 200, 150, 120, 100 and 77 K. Of these, the spectra for x = 1, 0.9 and 0.8 and temperatures 200, 100 and 77 K are used in the discussion.

The Fe K-edge spectra exhibit three distinctive features marked A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} \cite{4} as shown in Figs. 1 and 2. The XRD patterns recorded on single crystals reveal an octahedral distortion starting from 125 K \cite{1,5} and almost complete at 50 K. So we recorded the spectra at 200 K to 77 K at different intervals to capture these changes associated with the structure on the XAS spectra.

Figs. 1 and 2 give the XAS Fe K-edge spectra of FeSe\textsubscript{x} crystals with x = 1, 0.9 and 0.8 which were recorded at 77, 100 and 200 K. The spectra exhibit three distinctive peaks marked A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} \cite{4}. The A\textsubscript{1} peak arises out of the Fe–Fe bonds. The A\textsubscript{2} peak is assigned to the Fe 4sp bond. Since the main features in XANES K-edge spectra can be displayed by multiple scattering of the absorption process, the spectra reveal the different orbital orientations, p\textsubscript{x}, p\textsubscript{y} and p\textsubscript{z} \cite{4}, it is seen that the variation with temperature of the peak A\textsubscript{2} is maximum for x = 0.9 indicating a possible concentration effect as x decreases. While this was contested the results at 77 K appear to be different from those at 200 K. The shapes of the spectra at A\textsubscript{3} peak are different.

The low temperature XRD patterns recorded on a mosaic of single crystals show the splitting of the (2 2 0) reflection indicative of the orthorhombic distortion which is showed in Fig. 3. The
XANES spectra also indicate the distortion. In addition, the Se deficiency also influences these spectra as well as crystal structure distortion. The distortion is maximum in the case of $x = 0.9$ and at 200 K in the range of temperatures where the spectra are recorded.

3. Conclusion

The structure distortions observed in the low temperature XRD patterns are observed to influence the XANES spectra on FeSe$_x$ crystals. The distortion is observed to be maximum when $x = 0.9$ and at 200 K temperature. The transition from tetragonal to orthorhombic structure appears to minimize the changes in the spectra as a function of energy.

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References