Structural Phase Diagram of $Cu_xFe_{1-x}Se_{0.85}$ and Its Relation to Superconductivity

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Among all substituent alternatives, transition metals especially those with unpaired 3d electrons, such as Mn, Co, Ni, and Cu, would be of even more attractive to researchers not only because of their comparable ionic (or atomic) sizes but also of issues arisen related to competition between ferromagnetism (or antiferromagnetism) and superconductivity, which leads to the understanding of the origin of the superconductivity in this type of materials. Figure 1 shows the structural evolution of $Cu_xFe_{1-x}Se_{0.85}$ as a function of Cu substitution obtained from Reitveld refinements of synchrotron X-ray and neutron powder diffraction data. Figure 1(a) shows the Se-Fe-Se bond angles (black and red) and Tc (blue) versus Cu contents at room temperature (solid one) and 6K (open one). The bond angles are defined as two angles in the tetrahedron as shown in Fig. 2. The results point out the tetrahedron which iron atom at centre was elongated along the c-direction. However, as compared with Fig. 1(b), which shows the slightly changes in lattice constants a and c with Cu substitution, the changes in bond angle suggests that the tetrahedral site of iron are more closed to be a regular tetrahedron (γ = 109.28°) from a c-direction elongated tetrahedron. This result is also committed as the bond distances reduce and enlarge respectively for Fe-Se and Fe-Fe as a function of Cu substitution, which are shown in Fig. 1(c). It implies that the substitutional Cu atoms might not only alter the chemical environment in iron plane, but as well extensively change the local density of states for each iron and selenium.

Temperature-dependent structural evolution of $Cu_xFe_{1-x}Se_{0.85}$ (x = 0.01 and 0.1) is shown in Fig. 1(d),(e) and (f). The difference between Cu context x = 0.01 and 0.1 conspicuously points out the cupper substitution not only increases the total unit cell volume, but also changes the behaviour of the coefficient of thermal expansion (α). Notice that all the lattice parameters, such as the volume at Fig. 1(d), could be fitted perfectly using a second-order polynomia. As compared with Fig. 1(e) and (f), it is easily to find that decreasing in temperature effectively reduces the spacing of c-axis and Fe-Se bond length. This is an indicative of that, in the low-temperature structure, the shorter bond length and more closed to regular tetrahedron are necessary for superconductivity. Moreover, as the Fe-Se bond shrinking, the overlaps between the orbital on neighbouring atoms will increase, which lead to an extended (broadened) conduction band. However, although the Cu substitution brings the same effect in FeSe system, the chemical substitution should take a major part and inhibit the formation of superconductivity. In fact, as shown Fig. 1(e) and (f), the structural distortion could be found around 50 K in $Cu_{0.01}Fe_{0.99}Se_{0.85}$, which was significantly suppressed from 100K in pure FeSe compound. The Mott-insulator (like) and metal to insulator transition are observed in the temperature-dependent resistivity of the $Cu_xFe_{1-x}Se_{0.85}$ samples. This might be caused by a similar manner that, in cuprates, almost all of the Cu ions are in 3d9 state and only one hole on each atom of the system. In $Cu_xFe_{1-x}S_{e0.85}$, there exists a barrier, as the content of Cu increases, for excitations to levels where two anti-parallel holes or electrons hopping between neighbouring site. The hopping probability (or hopping rate) is thus reduced due to the single occupancy of hopping electrons at Cu sites. This leads to localized spins and magnetism in the iron plane. The normal state susceptibility increases with Cu substitution (see Fig. 1c) provides substantial support since the increase in spin localization or trapping state would raise the ferromagnetic background. In this regard, the spin trapping state should be more complex when Cu substitution increases in the $Cu_xFe_{1-x}Se_{0.85}$ series and suppresses the superconducting behaviour as Cu concentration reaches 3%.

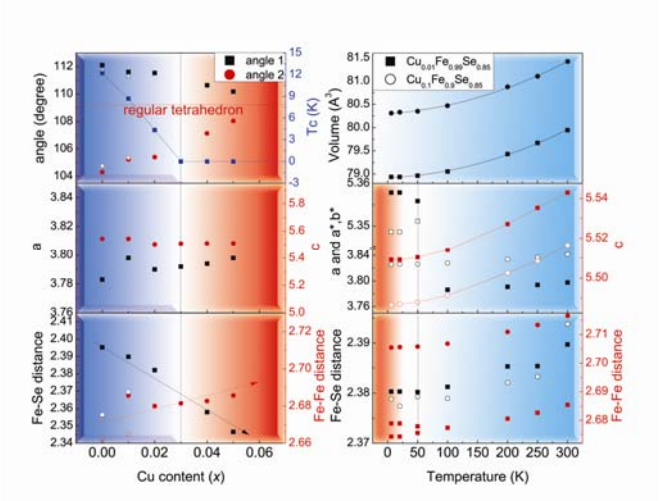

Fig. 1: Structural evolution of $Cu_xFe_{1-x}Se_{0.85}$ as a function of Cu substitution obtained from refinements of X-ray and Neutron diffraction data.

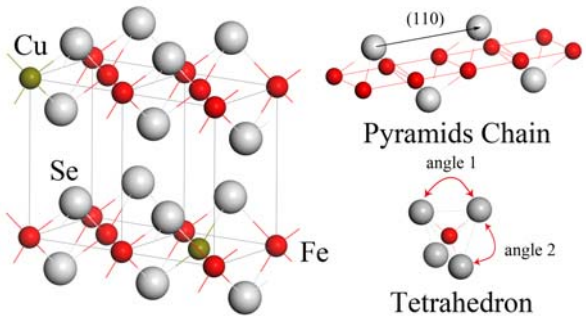

Fig. 2: The $Cu_xFe_{1-x}Se_{0.85}$ structure is sketched schematically as Fe (red), Cu (dark yellow) and Se (Gray) atoms.