Fe-vacancy Ordering in Fe-Se Nano-structures and Its Role for Superconductivity

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Abstract

Ever since the discovery of FeSe superconductor, the exact chemical stoichiometry of the compound remains an unresolved issue. Previous studies showed that the superconducting property of $\beta$-Fe$_{1+\delta}$Se is very sensitive to its stoichiometry. In Fe-Se binary phase diagram, the PbO-type tetragonal structure only stabilized at Fe-rich side, while bulk superconductivity was observed in samples with $\delta$ close to 0.015. The recent discovered alkali/alkaline-intercalated iron selenide $A_{1-x}Fe_{2-y}Se_2$ superconductors with rich superconducting phases, where $A = K, Rb, Cs, Tl$, attracted great attention not only due to its high superconducting transition temperature ($T_c$, up to 46 K), but also because of their dissimilar characteristics as compared to other iron-based superconductors, especially its seemingly intrinsic multiphase nature, and the presence of iron vacancies and orders in the non-superconducting regime. The most frequently observed Fe-vacancy order in $A_{1-x}Fe_{2-y}Se_2$ is $\sqrt{5} \times \sqrt{5} \times 1$ superstructure, which yields a phase of $A_{0.8}Fe_{1.6}Se_2$ or $A_2Fe_4Se_5$. Experiment has further shown that the type of vacancy and magnetic orders is highly sensitive to the stoichiometry of $A_{1-x}Fe_{2-y}Se_2$.

The complexity of phases and phase separation during crystal preparation in $A_{1-x}Fe_{2-y}Se_2$ make it difficult to conclusively verify the phase-property relationship, even for the superconducting phases. $\beta$-Fe$_{1+\delta}$Se, on the other hand, has the simplest structure among all iron-based superconductor families. Several surprising results related to the Fe-Se system appeared in the literature during the past years, including the enhancement of $T_c$ to about 40 K under high pressure, and the intriguing extremely high $T_c$ (with superconducting energy gap of ~20 meV) in molecular beam epitaxy (MBE) grown single layer FeSe.

We have also demonstrated the presence of superconducting-like feature with $T_c$ close to 40 K in samples of nano-dimensional form. Therefore, it is quite natural to ask whether the presence of the complex phases observed in $A_{1-x}Fe_{2-y}Se_2$ compounds and Fe-vacancy order exist in samples without alkaline metals. Here we present the first discovery of iron vacancies and three types of vacancy orders in tetragonal $\beta$-Fe$_{1+\delta}$Se, characterized by analytical transmission electron microscopy (TEM). Our observations imply new phase diagram should be considered in the Fe-Se superconductors.
