The crystal structure of superconducting FeSe$_{1-x}$Te$_x$ by pulsed neutron diffraction

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Abstract. A transition to a superconducting state was recently observed in the binary alloy of FeSe$_{1-x}$Te$_x$ system where $T_C$ rises with increasing $x$. The substitution of the larger Te for Se ion results in no additional charges but increases the internal chemical pressure. Earlier studies suggested that the crystal structure maintains the tetragonal $P4/nmm$ symmetry with the substitution of Te where the average bond angle, $\alpha$, decreases considerably from $\sim 104^\circ$ in FeSe to 100.5$^\circ$ in the mixed phase of FeSe$_{0.5}$Te$_{0.5}$. With the use of pulsed neutron power diffraction and the Rietveld analysis, the crystal structure refinement for FeSe$_{0.5}$Te$_{0.5}$ yielded very large thermal factors in the superconducting phase indicative of the presence of structural distortions that may be significant in understanding the electronic and magnetic properties of this system.

1. Introduction

The recent discovery of superconductivity in FeSe$_{1-x}$Te$_x$ has resulted in a simple binary system with tetrahedrally coordinated Fe layers, similar to the original FeAs oxy-pnictide based superconducting compounds [1]. While density functional calculations indicate this system is not an electron-phonon type superconductor [2-4], recent NMR measurements suggested that antiferromagnetic (AFM) fluctuations may even increase with $T_C$ in FeSe [5]. Additionally, the substitution of Se$^{2-}$ with Te$^{2-}$ implies that charge doping is not critical to raise $T_C$ in this class of superconductors, unlike in the case of high $T_C$ cuprates where hole or electron doping in the AFM parent lattice is needed to make the system superconducting. Although the mechanism of superconductivity is not well understood, and perhaps the role of magnetism is not solely important to the pairing mechanism, this is a new class of superconductors with distinctly unique properties from the cuprates and possibly with a new mechanism. At the same time, the application of external pressure can enhance $T_C$ directly implicating that the pairing mechanism is in some way influenced by the lattice structure. In particular, an interesting structural property relevant to the oxy-pnictide superconductors is that $T_C$ becomes a maximum when the Fe tetrahedra become most regular [6]. It thus appears that the crystal structure is a key element to the understanding of the ground state properties of the ferrous compounds. With the use of high resolution pulsed neutron powder diffraction, we investigated the crystal structures of FeSe and FeSe$_{0.5}$Te$_{0.5}$ above and below $T_C$. We find that nominally FeSe can be described using the tetragonal, $P4/nmm$ symmetry above $T_C$ and the orthorhombic symmetry $Cmma$ below. For FeSe$_{0.5}$Te$_{0.5}$, no clear structural transition is observed but the
thermal factors increase significantly below $T_C$ indicative of non-periodic structural distortions. Details of the refinement will be discussed.

2. Methods
The samples were prepared by solid-state reaction from Fe (99.9 %), Se (99.9 %), and Te (99.9 %). Stoichiometric amounts of the starting materials were mixed, and the pressured powders were sealed in an evacuated quartz tube and heated at 700°C for 24 hours. The details of sample preparation can be found in Ref. [7]. The pulsed neutron diffraction measurements were performed using the high intensity powder diffractometer (HIPD) of Los Alamos National Laboratory on polycrystalline samples of FeSe and FeSe$_{0.5}$Te$_{0.5}$ at temperatures above and below the superconducting transition. The Rietveld crystallographic method of analysis was used to determine the crystal structure.

3. Results and Discussion
Stoichiometric $\alpha$-FeSe is superconducting with a $T_C \sim 7$ K. Consistent with earlier findings, the crystal symmetry above $T_C$ is tetragonal and the refined parameters are summarized in Table 1(a). This

![Figure 1](image)

Figure 1 The diffractograms at 70 K (left) and 7 K (right) of FeSe with a $T_C$ of ~ 7 K, are compared to a tetragonal and orthorhombic crystal model, respectively. The difference is shown as well.

| Table 1 | (a) The refined parameters for FeSe at 70 K using the $P4/nmm$ space group. The lattice constants are given by $a = b = 3.75993(3)$ Å and $c = 5.48220(6)$ Å. Rp = 3.31 % and wRp = 5.74 %. |
|---------|------------------------------------------------------------------------------------------------|
| Atom    | Site | x     | y     | z       | U11     | U22     | U33 (Å$^2$) | Frac |
| Fe      | 2a   | 0.75  | 0.25  | 0       | 0.0017(3) | 0.0017(3) | 0.0028(4) | 1.0 |
| Se      | 2c   | 0.25  | 0.25  | 0.26628 | 0.0008(3) | 0.0008(3) | 0.0033(6) | 1.0 |

(b) The refined parameters for FeSe at 7 K using the $Cmna$ space group. The lattice constants are given by $a = 5.32491(5)$ Å, $b = 5.30890(1)$ Å, and $c = 5.47905(1)$ Å. Rp = 3.36 % and wRp = 5.76 %.

| Atom | Site | x     | y     | z       | U11     | U22     | U33 (Å$^2$) | Frac |
|------|------|-------|-------|---------|---------|---------|------------|------|
| Fe   | 4a   | 0.25  | 0     | 0       | 0.0007(8) | 0.0003(1) | 0.0013(4) | 1.0 |
| Se   | 4g   | 0     | 0.25  | 0.26598 | 0.005(1) | 0.005(1) | 0.0033(5) | 1.0 |
particular sample contained about 16% of the Fe$_7$Se$_8$ phase [see Ref. [7] for details of the refinement of the impurity phase]. Anisotropic thermal factors were used in the refinement that showed a tendency for larger $<U>$ factors along the c-axis. The diffraction data are compared to a model calculated using the $P4/nmm$ symmetry as shown in Fig. 1a. With cooling, a subtle structural change is observed. Recently it was reported that this change is due to a structural transition to an orthorhombic symmetry, $Cmcm$ [8]. The result of the comparison between the 7 K data to this crystal symmetry is shown in Fig. 1(b) and the parameters are summarized in Table 1(b). Note that the thermal factors increase below $T_C$.

With the substitution of Te for Se, it is presumed that no structural transition is observed below $T_C$ and that the symmetry remains in the tetragonal phase of $P4/nmm$. The refinement results are summarized in Table 2(a) and (b). This is different from the FeSe discussed above. At the same time, the absence of a structural transition is analogous to the LaO$_{1-x}$F$_x$FeAs that also showed no structural transition when the system entered the superconducting regime [9]. This effect was in turn correlated with the absence of long-range antiferromagnetic order in the superconducting state and the onset of a spin-density wave (SDW). Shown in Fig. 2 are the diffraction patterns at 8 and 16 K compared to the tetragonal crystal symmetry. The fits are reasonable. However, with cooling, we observed that the thermal factors, $<U>$ Å$^2$, increase in an uncharacteristic way, indicating that atomic distortions are enhanced in the superconducting phase. In most solids upon cooling, the thermal factors are reduced because of the decrease in thermal vibrations. The increase in thermal factors is probably in response to local lattice distortions that may be key to the superconducting mechanism. This calls for a study of the local atomic structure that can directly probe that local lattice without the assumption of crystal periodicity.

4. Summary
In the Fe-Se-Te system, $T_C$ is enhanced by changing the ionic size from Se to Te with no additional charges added to the system. This is uniquely different from the cuprate superconductors where the onset of superconductivity is coupled with either hole or electron doping. The negative pressure induced by substituting the larger Te for Se is what probably drives the tetrahedra to become more regular. This also changes the bond angle between the Se-Fe-Se ions that is in turn linked to the higher $T_C$ in the doped system. At the same time, the large thermal factors observed in the refined structural parameters below $T_C$ suggest that local distortions are present that are not manifested in the long-range symmetry.
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Table 2: (a) The refined parameters for FeSe_{0.5}Te_{0.5} using space group P4/nmm at 16 K. a = 3.791266 Å and c = 5.939199 Å; R_p = 4.17 %, wR_p = 5.85 %;

| Atom | Site | x   | y   | z     | U (Å^2) | Frac |
|------|------|-----|-----|-------|---------|------|
| Fe(1) | 2a   | 0.75 | 0.25| 0     | 0.0015(2) | 1.0  |
| Se/Te | 2c   | 0.25 | 0.25| 0.266902 | 0.0029(1) | 1.0  |
| Fe(2) | 2c   | 0.25 | 0.25| 0.808282 | 0.0081(1) | 0.03 |

(b) The refined parameters for FeSe_{0.5}Te_{0.5} at 8 K using the P4/nmm space group. The lattice constants are given by a = 3.79151(1) Å and c = 5.93898(0) Å. R_p = 4.12 % and wR_p = 5.89 %.

| Atom | Site | x   | y   | z     | U (Å^2) | Frac |
|------|------|-----|-----|-------|---------|------|
| Fe(1) | 2a   | 0.75 | 0.25| 0     | 0.0109(4) | 1.0  |
| Se/Te | 2c   | 0.25 | 0.25| 0.267573 | 0.0113(8) | 1.0  |
| Fe(2) | 2c   | 0.25 | 0.25| 0.808282 | 0.0081(1) | 0.03 |