The Pressure Effects on Electronic Structure of Iron Chalcogenide Superconductors \( \text{FeSe}_{1-x}\text{Te}_x \)

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We study the electronic structure of iron-based superconductors \( \text{FeSe}_{1-x}\text{Te}_x \) within the density functional theory. We pay particular attention to the pressure effects on the Fermi surface (FS) topology, which seem to be correlated with a critical superconducting temperature \( T_C \) of iron chalcogenides and pnictides. A reduction of the FS nesting between hole and electron cylinders with increasing pressure is observed, which can lead to higher values of \( T_C \). The tellurium substitution into selenium sites yields FS changes similar to the pressure effect.

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I. INTRODUCTION

Iron chalcogenides \( \text{FeSe}_{1-x}\text{Te}_x \) are members of promising family of Fe-based high temperature superconductors1. Non-stoichiometric \( \text{Fe}_{1+x}\text{Se}_x \) have been found to be superconducting at 8K2. Tellurium substitution into selenium sites raises the critical temperature \( T_C \) in \( \text{FeSe}_{1-x}\text{Te}_x \) up to 15K for \( x = 0.5 \)3–5. Additionally, \( T_C \) increases to 37K for \( \text{FeSe}_{0.5}\text{Te}_{0.5} \) and to 26K for \( \text{FeSe}_{0.5}\text{Te}_{0.5} \) under external pressure. On the other hand, the end member \( \text{FeTe} \) \((x = 1)\) is no longer superconducting, but shows antiferromagnetic phase at low temperatures. Disorder has also influence on chalcogenide properties. It can be introduced by excess iron atoms (deficiency of selenium) in \( \text{Fe}_{1+x}\text{Se}_x \) (\( \text{FeSe}_{1-x} \)) layer13 or by doping with Ni, Co and Cu into Fe sites14–18. Recently, ternary compounds \( \text{A}_x\text{Fe}_2\text{Se}_2 \) with alkali metal \( A = \text{K}, \text{Rb}, \text{Tl}, \text{Cs} \) between FeSe layers have been investigated due to promising \( T_C > 30\text{K} \)19–22.

These compounds containing no arsenic atoms, unlike pnictide superconductors, are particularly important for applications. They are also convenient for theoretical investigations because of simple both chemical compositions and crystal structures.

The main aim of this paper is to examine the pressure effect on electronic structure of \( \text{FeSe}_{1-x}\text{Te}_x \) in the normal state within the density functional theory (DFT) calculations. We describe our computational methods and give structural parameters obtained by a geometry optimization under pressure for \( \text{FeSe} \) and \( \text{FeSe}_{0.5}\text{Te}_{0.5} \) compositions in the tetragonal phase of the PbO-type (P4/nmm). The results of band structure calculations corresponding to ambient and higher pressures are presented. We are especially interested in the changes of the Fermi surface (FS) topology under pressure, which is suspected to be correlated with superconducting temperatures of iron chalcogenides and pnictides.

II. COMPUTATIONAL DETAILS

We have studied \( \text{FeSe}_{1-x}\text{Te}_x \) superconductors with \( x = 0 \) and 0.5 displayed in Fig. 1. All calculations were performed in the framework of DFT within the local-density approximation (LDA) of the exchange-correlation potential. We used the based on plane-waves and PAW (Projector Augmented Wave) Methods QUANTUM-ESPRESSO code23 and ABINIT24 to optimize both lattice parameters and atomic positions in the unit cell. Then we employed the FPLO (full-potential local-orbital) code25 to calculate all electronic properties of \( \text{FeSe}_{1-x}\text{Te}_x \) under external pressure.

The following valence configurations were used in our calculations: \( 3d^84s^24p^6, 3d^{10}4s^24p^4 \) and \( 4d^{10}5s^25p^4 \) for Fe, Se and Te, respectively. Total energy of considered systems was converged with accuracy to \( 10^{-4}\text{Ry} \) for the plane waves energy 50Ry cut-off. The \( 12 \times 12 \times 12 \) (196 points) \( k \)-point mesh in the non-equivalent part of the Brillouin zone was sufficient.

The first step of the analysis was geometry relaxation of the \( \text{FeSe}_{1-x}\text{Te}_x \) crystal structure in the tetragonal phase, which was performed with 0.05GPa convergence criterion on the pressure (\( 10^{-3}\text{Ry/Bohr} \) on forces). The calculated lattice parameters at ambient pressure are pre-
TABLE I: Experimental and calculated lattice constants $a$, $c$, and free $z_{Se/Te}$ parameters of FeSe and FeSe$_{0.5}$Te$_{0.5}$ at $p = 0$. The bulk moduli $B_0$ obtained from the third-order Birch-Murnaghan equation of state.

| Material          | $a$ [Å] | $c$ [Å] | $z_{Se/Te}$ | $B_0$ [GPa] |
|-------------------|---------|---------|-------------|-------------|
| FeSe (exp.)       | 3.7742  | 5.4545  | 0.266       | 30.7        |
| FeSe (opt.)       | 3.5963  | 5.4310  | 0.256       | 32.9        |
| Fe$_{0.03}$Se$_{0.97}$Te$_{0.43}$ (exp.) | 3.8007  | 5.9926  | 0.274       | 36.6        |
| FeSe$_{0.5}$Te$_{0.5}$ (exp.) | 3.8003  | 5.9540  | 0.256/0.285 | 33.6        |
| FeSe$_{0.5}$Te$_{0.5}$ (opt.) | 3.6546  | 5.6847  | 0.238/0.289 | 33.6        |

*aAccording to 7,8,12 and 30, respectively.

FIG. 2: Calculated pressure evolution of the lattice parameters $a$, $c$ (a and d) as well as the chalcogen atom distance from the iron plane (b and e) for FeSe and FeSe$_{0.5}$Te$_{0.5}$. Their corresponding unit cell-volume changes vs. pressure (squares), fitted to the equation of states (lines), are shown in parts (c and f), respectively.

FIG. 3: The electronic band structures of FeSe along high-symmetry lines at $p = 9$ GPa.

FIG. 4: The total and orbital projected electronic DOS for (a) FeSe and (b) FeSe$_{0.5}$Te$_{0.5}$ at ambient and higher pressures.

III. ELECTRONIC STRUCTURE

The electronic structure of FeSe$_{1-x}$Te$_x$ near the Fermi energy contains mainly the Fe-3d states 26 as can be seen from the distinct orbital character of bands (Fig. 3 for FeSe at $p \approx 9$ GPa) as well as orbital-projected densities of states (DOS) plotted in Fig. 4. However, the bands at the Fermi level ($E_F$) have also contributions from the $p_z$ orbitals, which indicates that Te/Se- $p$ orbitals may play a substantial role in superconductivity as well. A higher DOS at $E_F$ is observed in FeSe$_{0.5}$Te$_{0.5}$ than in FeSe. This suggests a small increase of electronic den-
FIG. 5: The Fermi surface sheets of FeSe (drawn separately for each of five bands) at (a) 0 and (b) 9 GPa.

FIG. 6: Changes in the Fermi surface nesting between electron and hole sheets of FeSe under external pressure.

In both compounds, the densities at the Fermi energy are slightly enhanced under pressure. Zero pressure values of DOS at \( E_F \) are 1.49 eV\(^{-1} \) for FeSe and 1.73 eV\(^{-1} \) for FeSe\(_{0.5}\)Te\(_{0.5}\). At pressures corresponding to the maximum critical temperatures, the densities are equal to 1.54 eV\(^{-1} \) (\( p \approx 9 \) GPa) and 1.77 eV\(^{-1} \) (\( p \approx 2 \) GPa), respectively.

In general, the Fermi surface of FeSe\(_{1-x}\)Te\(_x\) compounds exists in five bands and consists of two electron cylinders \( \delta \) and \( \delta' \), centred at the M point, and three hole-like sheets around the \( \Gamma \) point - two outer cylinders and one inner closed pocket (labelled as \( \alpha \), \( \beta \), \( \gamma \)). Figure 5 visualizes all FS sheets for FeSe under ambient and higher pressures. The electron and hole cylinders are separated by the nesting vector close to \( q = [\pi, \pi, 0] \) (Fig. 6). Due to this fact, the spin-density waves (SDW) can compete with the superconducting (s-wave-type) pairing. Under external pressure, the cylinders are more corrugated and the FS nesting is suppressed\(^9\).

In turn, the Fermi surface sheets in FeSe\(_{0.5}\)Te\(_{0.5}\) (not shown) have also more 3-dimensional character in comparison with FeSe system and the cylinders yield more imperfect nesting upon increasing pressure. Thus, both tellurium substitution and external pressure have the similar effects on electronic structure of iron chalcogenides in the tetragonal phase.

IV. CONCLUSIONS

We have studied the effect of external pressure on both crystal and electronic structures of FeSe\(_{1-x}\)Te\(_x\) superconductors. The influence of tellurium content was also investigated. Correlations between critical temperature, lattice parameters and topology of the Fermi surface were observed. The increase of pressure as well as Te substitution raise the values of \( z_{\text{Se/Te}} \) causing suppression of the Fermi surface nesting.

In FeSe\(_{0.5}\)Te\(_{0.5}\) at \( p = 0 \), due to the reduced FS nesting, a possible SDW state becomes more unstable than in FeSe. Hence, the superconducting phase can appear at an earlier stage in the former system. In both compounds, the imperfect FS nesting of the corrugated cylinders is enhanced with increasing pressure, which can lead to higher values of \( T_c \).

The orbital character of bands and projected DOS confirm that the electronic structure near the Fermi energy consists of Fe-3\( d \) electrons being slightly hybridized with chalcogenide 3p/4p states. A higher DOS at the Fermi level is observed under pressure, which usually improves superconducting properties.

In previous experiments, critical temperature reaches maximum under finite pressures and then structural phase transitions take place\(^7,9,12\). Therefore, the observed \( T_c \)-increase seems to be caused by the pressure-induced changes in the tetragonal phase. When this phase begins to diminish, the trend is reversed (\( T_c \) decreases). Ab initio investigations of such effects will be undertaken in the future.
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