Pressure-dependent topological superconductivity on the surface of FeTe$_{0.5}$Se$_{0.5}$

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Abstract
FeTe$_{1-x}$Se$_x$ is a family of iron-based superconductors with its critical temperature ($T_c$) dependent on the composition of Se. A well-known $T_c$ is 14.5 K for $x = 0.45$, which exhibits an $s$-wave superconducting gap between the topological superconducting surfaces states. Exchange interaction between the electrons has been proposed as the mechanism behind the formation of Cooper pairs for the sample of FeTe$_{0.5}$Se$_{0.5}$. In this article we provide further proof that exchange interaction, and hence the associated $T_c$, depends on the applied pressure on FeTe$_{0.5}$Se$_{0.5}$. Using density functional calculations for electrons and phonons and the Bardeen–Cooper–Schrieffer (BCS) theory for superconductivity, we found that $T_c$ and superconducting gap for FeTe$_{0.5}$Se$_{0.5}$ soars under increasing compression, consistent with the results of experiment.

1. Introduction
Research has shown that FeTe$_{1-x}$Se$_x$ [1–19] is a superconductor with its $T_c$ dependent on $x$, the proportional content of Se. An especially interesting example is FeTe$_{0.55}$Se$_{0.45}$, which has been confirmed by spin-polarized and angle-resolved photoelectron spectroscopy [1] to have a Dirac cone associated with its (001) surface states. Each of the electrons populating the Dirac cone has its spin locked perpendicularly to the crystal momentum in preservation of the time-reversal symmetry. The experiment also reports an $s$-wave superconducting gap around 1.8 meV as the temperature is lowered down to 0 K. The moderate $T_c$ of 14.5 K and its connection to topological surface states make the iron-based superconductor an intriguing platform for the study of superconducting mechanism and suggest potential application in quantum computing using Majorana edge modes [20–22].

Theoretical analysis [1–3] of FeTe$_{0.55}$Se$_{0.45}$, which is only slightly different from FeTe$_{0.55}$Se$_{0.45}$ but much easier treated in computation, also confirms topological superconductivity. Dirac-cone type surface states within the gap of bulk states have been derived using density functional theory (DFT), and a $Z_2$ invariant equal to 1 is obtained by the parity of orbitals at time-reversal-invariant momenta in the first Brillouin zone. Antiferromagnetic (AFM) exchange interaction [4] or spin fluctuation [5] has been proposed for the mechanism of the unconventional superconductivity. Our previous calculation [3] based on DFT and maximally localized Wannier functions was able to extract the AFM exchange energy and used it as the attractive interaction between electrons of the Cooper pair in the BCS model. The derived $T_c$ and superconducting gap for FeTe$_{0.55}$Se$_{0.45}$ are close to those of FeTe$_{0.55}$Se$_{0.45}$, proving theoretically that singlet exchange mediated by phonons is the source of topological superconductivity for the compound.

2. Calculation of bulk electronic structure and surface states under pressure
According to one experiment [6] onset of superconductivity for FeTe$_{0.5}$Se$_{0.5}$ powders rises in temperature from 13.5 to 25.6 K under increasing pressure up to 2 GPa. Other iron-based superconductors also have higher $T_c$ under enhanced pressure. Relation between pressure and $T_c$ is therefore an important aspect in the research of superconductivity mechanism. In this article we provide more evidence that singlet exchange...
interaction between electrons is behind the rising $T_c$ of FeTe$_{0.5}$Se$_{0.5}$ under increasing pressure. We used experimentally determined lattice constants $a = b = 3.7933$ Å and $c = 5.9552$ Å [7] from powder-diffraction data for the tetragonal $P4/nmm$ crystal structure of FeTe$_{0.5}$Se$_{0.5}$. As will be seen, pressure
Figure 2. Compressed by uniaxial pressure of 1.08 GPa along the z axis, topological surface states of FeTe$_{0.5}$Se$_{0.5}$ are still separated from the projection of bulk states.

increases rapidly by compression along the z axis, with a and b kept constant. Throughout our investigation \textit{ab initio} DFT calculations were executed using the VASP code [23, 24] with general gradient approximation (GGA) [25] chosen for exchange–correlation functional, which helps straight comparison with references [2, 3].

Shown in figure 1(a) is a unit cell of bulk FeTe$_{0.5}$Se$_{0.5}$ under uniaxial pressure of 1.08 GPa, equivalent to the strain of $-2\%$ in the z direction (or $c = 5.8361$ Å). The cell contains four Fe atoms in the x–y plane and two atoms for each of Te and Se at alternate heights. Figure 1(b) is its electronic band structure plotted along major symmetry directions within the first Brillouin zone. As is the case for zero strain, a small band gap of 9.20 meV is found along the $\Gamma$–Z or (001) direction in the zoomed-in part of the bands within the rectangle. The gap is opened by spin–orbit interaction and is only slightly larger than that of previous calculation [3] without compression. Blue solid spheres in the $\Gamma$–Z panel clearly indicate that Te $p_z$ orbital contributes more to the band than does Se $p_z$ orbital (red circles), reflecting the importance of Te substitution. Contributions from d orbitals of Fe is illustrated by the example of $d_{xy}$ orbital (blue spheres) in figure 1(c), where the band inversion and substantial $p$–$d$ hybridization can be inferred. Since the band structure and its composition of orbitals remain largely intact under the pressure, its topological nature stays the same as that with zero strain.

Surface states of FeTe$_{0.5}$Se$_{0.5}$ were calculated by using maximally localized Wannier functions [26] with tight-binding parameters obtained from the bulk results, including five d orbitals from Fe and three p orbitals from each of Se and Te. By increasing the number of layers in the calculation, convergent surface states emerge in the gap of bulk states. Figure 2 is the band structure for 67 layers of FeTe$_{0.5}$Se$_{0.5}$ at 1.08 GPa, where a Dirac cone is still readily identified by its separation from the projection of bulk bands under the pressure. Each of the two crossing bands is occupied by electrons with spin opposite to that of the other, preserving time-reversal symmetry.

The robust spin texture is illustrated by the valence band (figure 3(a)) and conduction band (figure 3(b)) for k points near the $\Gamma$ point in the $k_x$–$k_y$ plane, where contours of equi-energy curves were obtained from a seven-layer calculation and each arrow specifies the in-plane spin component of the electron.

3. Exchange interaction and the BCS model under pressure

Exchange energy $V$ of a pair of electrons was derived from the energy difference between singlet and triplet states as expressed in the following equation,
Figure 3. Spin texture of seven layers of the compressed FeTe$_{0.5}$Se$_{0.5}$ as shown in figure 1 is plotted for (a) the valence band and (b) the conduction band in energy-momentum topography within an energy window shown at right. Each arrow represents the direction of electron spin associated with a $k$ point in the $k_x$–$k_y$ plane.

\[ E_s - E_t = 2 \iint \psi_k^*(\mathbf{r})\psi_k^*(\mathbf{r}') \frac{e^2}{\varepsilon |\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{r}')\psi_k(\mathbf{r}) d^3r d^3r' = -2V, \]  

where $E_s$ ($E_t$) is the total energy of the two electrons from intralayer Fe atoms at singlet (triplet) state and $\psi_k(\mathbf{r})$ is the Bloch wave function for an electron with crystal momentum $\mathbf{k}$. The two-particle Coulomb interaction $\frac{e^2}{\varepsilon |\mathbf{r} - \mathbf{r}'|}$, with $e$ the absolute value of the electron charge and $\varepsilon$ the dielectric constant, indicates the origin of the exchange interaction. Calculated exchange energy using GGA functional at 1.08 GPa for nearest neighbors ($J_1$) of electrons is $-15.4$ meV, whose magnitude is considerably higher than the value ($-11.8$ meV) without the associated strain [3]. Exchange energy for second nearest neighbors ($J_2$) is $-12.9$ meV, which is also stronger in magnitude than $J_2$ at zero pressure. For third nearest neighbors, exchange interaction is typically one order of magnitude smaller than $J_1$ or $J_2$ because of more screening by the presence of another Fe atom half way in between.

Exchange energy strengthens as FeTe$_{0.5}$Se$_{0.5}$ is further compressed along the $z$ axis. Figure 4 reveals a linear relationship between the pressure in the $z$ direction and $|J_1|$ (squares), and an almost linear plot for $|J_2|$ (spheres), up to the pressure of 1.867 GPa. The strengthened exchange energy is caused mainly by increased hybridization between the interlayer $p_z$ orbital and intralayer $d$ orbitals as a result of a shortened
lattice constant $c$. The stronger exchange energy in turn helps precipitate the condensation of Cooper pairs of electrons whose Hamiltonian $H$ is formulated in the BCS theory for $s$-wave superconductivity:

$$H = \sum_{k,m} \varepsilon_k a_{k,m}^+ a_{k,m} - V \sum_{k,k'} a_{k,\uparrow}^+ a_{k',\downarrow} a_{-k',\uparrow} a_{-k,\downarrow},$$

where $a_{k,m}^+$ ($a_{k,m}$) is the creation (annihilation) operator for the quasi-particle (electron) with crystal momentum $k$ and spin $m$ ($\uparrow$ for up and $\downarrow$ for down) and $\varepsilon_k$ is the associated mean one-particle energy. Two-particle interaction is represented by the attractive exchange energy $-V$ for Cooper pairs, which is mediated by phonons having the transferred momentum $k-k'$.

Phonon dispersion curves of FeTe$_{0.5}$Se$_{0.5}$ at 1.08 GPa are presented in figure 5 with three acoustic and 21 optical phonon bands along symmetry directions calculated from the VASP code. Using the Debye model, the derived Debye frequency $\omega_D$ and associated phonon energy are $2.68 \times 10^{13}$ s$^{-1}$ and 17.6 meV respectively. In the BCS model Cooper pairs are formed by electrons inside the energy range between $\mu - \hbar \omega_D$ and $\mu + \hbar \omega_D$, where $\hbar$ is reduced Planck constant and $\mu$ is the chemical potential or, on approaching 0 K, the Fermi level $\varepsilon_F$.

The superconducting gap at 0 K denoted by $\Delta(0)$ is calculated from $2\hbar \omega_D e^{-1/\lambda}$, where $\lambda$ is the strength of electron–phonon coupling and equal to $V$ multiplied by $N(\varepsilon_F)$, the latter being single spin electronic density of states per unit volume at the Fermi level. Using $|J_1|$ for $V$ (15.4 meV) and the calculated $N(\varepsilon_F)$ (29.67 eV$^{-1}$) for FeTe$_{0.5}$Se$_{0.5}$ at 1.08 GPa, we obtain 0.46 for $\lambda$, which is significantly larger than the value of 0.36 at zero pressure and suggests stronger coupling between the electrons and phonons [4, 8].

Critical temperature is calculated from the equation $k_B T_c = 1.13\hbar \omega_D e^{-1/\lambda}$, where $k_B$ is Boltzmann’s constant. Under uniaxial compression along the $z$ axis, $T_c$ rises from 16.0 K to 25.8 K as the pressure increases from zero to 1.08 GPa. Variation of $T_c$ and $\Delta(0)$ with respect to pressure is depicted in figure 6. Both have a slower rise followed by a linear section with higher slopes, which then turn sharply upward and at approximately 1.83 GPa attaining a highest $T_c$ of 36.1 K and largest $\Delta(0)$ of 5.50 meV. Values of $T_c$ in figure 6 tend to be higher than those reported in reference [6] and another paper [19]. One likely reason is that surface atoms have fewer neighbors and thus suffer less screening. Larger screened exchange energy from the calculation contributes to stronger electron–phonon coupling and thus pushes $T_c$ higher.

Figure 7(a) depicts part of the energy bands of FeTe$_{0.5}$Se$_{0.5}$ at 1.83 GPa, in which the surface states are on the brink to be incorporated into the bulk bands under the corresponding strain of $-3.25\%$. It is after this critical point that both $T_c$ and $\Delta(0)$ start to decline due to severe distortion and swift disappearance of Dirac cone from further compression, making previous formulation of topological superconductivity inapplicable. Given as an example is the band structure of FeTe$_{0.5}$Se$_{0.5}$ at 1.90 GPa plotted in figure 7(b), in which all surface states are completely consumed by the bulk bands as a result of the high pressure.
4. Magnitude and direction of pressure

Powders of FeTe$_{0.5}$Se$_{0.5}$ used in experiment as described in reference [6] may be compressed from one or more directions other than the $z$ axis and still achieve a rise of $T_c$, which, however, cannot be as high as the value obtained from uniaxial compression along the $z$ direction. As previously pointed out, exchange interaction depends heavily on the hybridization of $p_z$ and $d$ orbitals. Applying pressure along the $z$ axis increases the overlap of wave functions most directly and therefore raises $T_c$ rapidly.

Shown in figure 8 is the band structure of FeTe$_{0.5}$Se$_{0.5}$ compressed in the three ($x$, $y$, and $z$) axes with a uniform strain of $-0.12\%$, which causes a rapid rise of pressure to 2.08 GPa. Dirac cone and non-trivial topological property maintain their existence, but both $|J_1|$ (12.7 meV) and $|J_2|$ (12.0 meV) have a very limited increase from those at zero pressure, so do $\Delta(0)$ (2.69 meV) and $T_c$ (17.7 K). If the same pressure is
applied along the z axis solely, all surface states vanish and conditions of topological superconductivity no longer qualify, as the pressure mentioned in figure 7(b) has demonstrated.

Figure 9 depicts $T_c$ vs pressure for simultaneous compression along the three axes. As pressure is increased, $T_c$ drops almost linearly as that reported in reference [6] and topological surface states can be maintained up to approximately 7.2 GPa. Values of $T_c$ in this figure, however, are smaller than the experimental ones, indicating that the sample is either compressed along different directions or overwhelmed by bulk superconductivity.

Recent experiments [27–29] suggest that the interplay of ferromagnetism (FM), paramagnetism, topology, and superconductivity may contribute to time-reversal symmetry breaking on the surface of FeTe$_{1-x}$Se$_x$. Our calculation also indicates that FeTe$_{0.5}$Se$_{0.5}$ under uniform compression of 10.4 GPa ($-5\%$ strain) is about to lose AFM, with only a small magnetic moment of 0.1 $\mu_B$ left for each Fe atom.

Figure 7. Band structure of FeTe$_{0.5}$Se$_{0.5}$ compressed along the z axis at (a) 1.83 GPa and (b) 1.90 GPa. All surface states are merged into the bulk bands in (b).
There seems to be a competition between the AFM phase and FM phase in the superconducting realm of FeTe$_{1-x}$Se$_x$. Further exploration could look into this intriguing picture and try to include the competition mechanism.

5. Conclusion

We have used s-wave BCS model to study FeTe$_{0.5}$Se$_{0.5}$ under pressure by extracting relevant parameters from first-principles DFT calculations and maximally localized Wannier functions. The results clearly indicate that screened singlet exchange interaction is behind the topological superconductivity of FeTe$_{0.5}$Se$_{0.5}$, having higher $T_c$ under higher pressure. $T_c$ can be raised as high as 36.1 K if the pressure is uniaxial in the $z$ axis and not greater than 1.83 GPa. Compression of FeTe$_{0.5}$Se$_{0.5}$ in other directions, however, do not attain such a high critical temperature. The study also suggests there may be more superconductors whose properties can be explored through the aspect of exchange interaction.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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