Strain effects on the electronic structure of the iron selenide superconductor

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Abstract – The influence of various strains on the crystal and electronic structures of superconducting FeSe has been studied \textit{ab initio}. We consider changes in the Fermi surface nesting with a vector $Q = (0.5, 0.5) \times (2\pi/a)$ as crucial for rising superconductivity (SC) mediated by spin fluctuations (SF). Our results indicate that the $c$-axis–strained FeSe exhibits the most imperfect nesting, which enhances SF and, hence, also SC. In turn, the $ab$-plane compressive strain slightly weakens this nesting while the tensile strain destroys it completely. These findings are consistent with earlier reported experimental dependences of the superconducting transition temperatures on strain in FeSe thin films.

Introduction. – Iron chalcogenides draw wide interest because of their simple structure and possible applications. The iron selenide, FeSe, has been found to be superconducting below the transition temperature $T_c = 8$ K [1]. Although the pure FeTe is non-superconducting, $T_c$ is risen up to 15 K in the solid solutions FeSe$_{1-x}$Te$_x$ for $x = 0.5$ [2–4]. However, the highest $T_c$ of 37 K has been detected for bulk FeSe under hydrostatic pressure [5–9]. A comparable enhancement of $T_c$ up to more than 30 K was also reported for ternary compounds $A_x$Fe$_2$Se$_2$ with the alkali metals atoms $A$ (= K, Rb, Cs) located between Fe-Se layers [10–13], which can be explained by a chemical-pressure effect. Furthermore, superconductivity (SC) in a Cu-doped FeSe is restored by external pressure and at 7.8 GPa it reaches the maximum value of 31 K [14].

Also the influence of the non-hydrostatic strain on the superconducting properties of FeSe has been investigated experimentally. On the one hand, in lattice-mismatched epitaxial films of FeSe the tensile strain onset suppresses SC [15]. On the other hand, in similar films of FeSe$_{0.5}$Te$_{0.5}$, the uniaxial ($c$-axis) strain increases $T_c$ [16]. The SC properties may be also tuned by the control parameter of the Se deficit in FeSe$_{1-x}$ [17–19].

In recent years, the electronic structure of superconducting iron chalcogenides has intensively been studied both theoretically [20–24] and experimentally [8,21,25–27]. The authors of these works have postulated that in FeSe (and related 11-type systems) the multi-gap nature of SC is connected with the interband interactions between the holelike $\beta$ and electronlike $\delta$ Fermi surface (FS) sheets. In particular, SC can be mediated by antiferromagnetic spin fluctuations, observed experimentally by, e.g., NMR [28], which are driven by the imperfect nesting with the $q = (\pi, \pi)$ vector, spanning the above FS sheets in iron chalcogenides [20,22,23].

To our knowledge, this is the first theoretical study of the influence of strain on the electronic structure of FeSe. We focus mainly on both the qualitative and quantitative description of the nested area between the $\beta$ and $\delta$ FS sheets of FeSe under various kinds of strain in the unit cell (u.c.). The relation between our findings and available experimental data of the $T_c$ variations in the strained FeSe compound is discussed.

Computational details. – Band structure calculations for FeSe have been carried out in the framework of the density functional theory (DFT). A full theoretical optimization of the atomic positions and geometry of the tetragonal u.c. of the PbO-type ($P4/nmm$, No. 129) under various strains was performed with the Abinit package [29,30], using projector augmented-wave (PAW) pseudopotentials, generated with the Atompaw
This extreme accuracy of the self-consistent field (SCF) cycle and FS plots, respectively, reveals distinctly very subtle, very dense surface changes. Since the FS nesting properties of FeSe were previously computed the densities of states (DOSs) and the Fermi structure code [34], in the scalar-relativistic mode, to compute the densities of states (DOSs) and the Fermi surface changes. Since the FS nesting properties of FeSe are subtle, very dense k-point meshes in the Brillouin zone (BZ) were used, i.e., 64×64×64 and 256×256×256 for the self-consistent field (SCF) cycle and FS plots, respectively. This extreme accuracy of the k-point meshes allows for a detailed description of the FS features investigated here.

Finally, we determined numerically a nesting function:

\[ f_{\text{nest}}(\mathbf{q}) = \sum_{\mathbf{k},n,n'} \left( 1 - F^\beta_n(\mathbf{k}) \right) F^\delta_{n'}(\mathbf{k} + \mathbf{q}) \left( E^\beta_n(\mathbf{k}) - E^\delta_{n'}(\mathbf{k} + \mathbf{q}) \right), \]

where \( F^\beta_n \) and \( F^\delta_{n'} \) are the Fermi-Dirac functions of states \( n \) and \( n' \) in the bands \( \beta \) and \( \delta \), \( (F = 0 \text{ or } 1 \text{ for holes or electrons}) \), respectively. In turn, \( E^\beta_n \) and \( E^\delta_{n'} \) are the energy eigenvalues of these bands. The here considered \( f_{\text{nest}}(\mathbf{q}|\mathbf{Q}) \), were \( \mathbf{Q} = (0.5, 0.5) \times (2\pi/a) \) is the ideal nesting vector, reflects a frequency of occurrence of a given vector \( \mathbf{q} \sim (\pi/a) \) (having a length close or equal to \( \mathbf{Q} \)) in the k-space, spanning the FS sheets originating from the \( \beta \) and \( \delta \) bands.

**Results and discussion.**  The changes of the lattice parameters \( a \) and \( c \) in the tetragonal FeSe unit cell under hydrostatic pressure are displayed in fig. 1. This figure clearly shows that the LDA approach yielded reasonable results, being much better than those obtained by GGA (particularly for low pressure), compared with the available experimental data of ref. [8]. Hence, further only the LDA results will be presented. The variations of the parameters \( a \), \( c \), and free \( Z \) position of selenium atoms (\( Z_{\text{Se}} \)) in tetragonal FeSe u.c. calculated under hydrostatic pressure in comparison with those obtained for setting both \( ab \)-plane and \( c \)-axis compressive strains are presented in figs. 2 and 3. As demonstrated in fig. 2, the \( ab \)-plane compressive strain increases the \( c/a \) ratio while the hydrostatic pressure and \( ab \)-plane tensile strain (not displayed here) makes the opposite effects. Moreover, the \( c \)-axis compression is followed by changes in the u.c. geometry showing a strong tendency to become cubic above 3.5 GPa. Figure 3 illustrates results of the corresponding relaxations of the atomic position \( Z_{\text{Se}} \). This figure indicates that the largest increase of \( Z_{\text{Se}} \) takes place under the \( c \)-axis strain. The revealed here distinct anisotropic behavior of the FeSe lattice parameters is connected with its layered character.

Fig. 1: (Colour on-line) Variations of lattice parameters \( a \) and \( c \) of tetragonal FeSe u.c. with hydrostatic pressure, calculated by employing LDA and GGA approaches, compared with experimental data of ref. [8].

Fig. 2: (Colour on-line) Changes of lattice parameters \( a \) and \( c \) of tetragonal FeSe u.c. with different strain conditions.

Fig. 3: (Colour on-line) The same as in fig. 2 but for the free atomic \( Z_{\text{Se}} \) position.
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Fig. 4: (Colour on-line) Total DOSs plots of FeSe under various strain conditions.

Table 1: Calculated lattice parameters $a$, $c/a$ ratio, and free atomic position, $Z_{Se}$, in strained u.c. of FeSe.

| Strain (GPa)         | $a$ (nm) | $c/a$  | $Z_{Se}$ |
|----------------------|----------|--------|----------|
| unstrained (0 GPa)   | 0.3592   | 1.4988 | 0.2570   |
| hydrostatic (9 GPa)  | 0.3515   | 1.4018 | 0.2836   |
| $ab$-plane compressive (3 GPa) | 0.3505 | 1.5666 | 0.2612   |
| $ab$-plane tensile (3 GPa) | 0.3703 | 1.4089 | 0.2529   |
| $c$-axis compressive (1 GPa) | 0.3631 | 1.3849 | 0.2680   |

of the crystal structure along the $c$-axis, typical of iron chalcogenides. Our results show that the iron-selenium network in the $ab$-plane is more stable than that forming the interlayer connections of these planes along the $c$-axis. In general, these structural features have appeared to be characteristic of high-temperature superconductors.

The parameters $a$, $c/a$, and $Z_{Se}$, chosen to determine DOSs and FS nesting properties (depicted in figs. 4 and 6) are collected in table 1. It is worth underlining that the presented parameters obtained under hydrostatic pressure of 9 GPa correspond to the experimental conditions for which $T_c$ of FeSe reaches its maximum value. For the other considered cases of applied strain, because of a lack of measured structural data, they have been chosen arbitrarily to detect any modifications of the electronic structure that may explain the changes of $T_c$ observed in such forms of FeSe as, e.g., thin films [15].

As seen in fig. 4, any strain effects on the total DOSs at the Fermi level ($E_F$) seem to be irrelevant. However, it is worth noticing that both hydrostatic and $ab$-plane compressive strains make a shift of the whole DOS spectrum towards higher energies. In contrast, the $ab$-plane tensile and $c$-axis strains cause an opposite effect, which may lead to a rapid decrease of DOS at $E_F$ that, in turn, can suppress SC.

Since for FeSe, the $c$-axis strain has the most pronounced influence on the electronic structure, the corresponding FSs are presented in fig. 5. It is seen in this figure that above 2 GPa, a topological transition in the FS takes place when both the cylindrical $\beta$ and $\delta$ sheets around the $\Gamma$ and $M$ points, respectively, are split into smaller FS pockets. This effect is much stronger in comparison with that of hydrostatic pressure reported previously [22]. Therefore, in this work, we consider only small values of the $c$-axis strain to show an overall relation between the strain and electronic structure of FeSe.

Next, we consider quantitatively the nesting properties of the $\beta$ and $\delta$ FS sheets along the direction of $\mathbf{Q}$, being parallel to the $\Gamma M$ and $ZA$ lines as visualised in fig. 6. The numerical nesting function, $f_{nest}$, determined for these sheets of FeSe (defined in the previous section) is presented in fig. 7. Part (a) of this figure demonstrates that for the unstrained FS $f_{nest}$ reaches one pronounced maximum exactly at $\mathbf{Q}$, corresponding to the region in the vicinity of the $\Gamma M$ line, and the other maximum at $\mathbf{q}_1$ of a shorter length (0.625), dominating around the $ZA$ line. As is shown in fig. 7(b), the hydrostatic pressure diminishes the intensities of the peak at $\mathbf{Q}$ and $\mathbf{q}_1$ (the latter being shorter than $\mathbf{q}_1$ and also the range of length of possible spanning vectors $\mathbf{q}$ becomes much wider than in the unstrained FeSe. This effect may explain an
enhancement of spin fluctuations in FeSe. In unstrained FeSe, an antiferromagnetic spin ordering is stable on account of the high intensity peak at \( Q \) \[27\]. Thus, its instability, reflected by the smoothed \( f_{\text{nest}}(Q) \) (imperfect nesting), should lead to spin fluctuations being responsible for SC.

As visible in fig. 7(c) and (d), the \( ab \)-plane compressive and tensile strains act otherwise than hydrostatic pressure. The main peaks in the \( f_{\text{nest}} \) function, visible in these figure parts, being centered at close to \( Q \) (0.701) and shorter \( q_3 \) (0.635) vectors, respectively, have both distinctly higher magnitudes than those in the other cases. Thus, especially the onset of the tensile strain reflects a rapid change of the nesting properties (complete lack of nesting with \( Q \)). Since our results are limited to 3 GPa pressure, which corresponds to merely 2–3% of lattice mismatch, the FS nesting features of the MgO-based FeSe thin films \[15\] with even larger lattice parameters are expected to be considerably different from that in the unstrained bulk FeSe. Our results, supporting the spin-fluctuation scenario of the SC pairing mechanism, are in good agreement with the experimental studies on the suppression or absence of SC in the strained FeSe films \[15,17–19\].

Effects on the FS in FeSe similar to that of hydrostatic pressure are obtained for the \( c \)-axis strain, as seen in fig. 7(e). This influence is very strong and even relatively small values of pressure, \( e.g. \), 1 GPa (fig. 7(e)), cause a strong diminishing of the intensities of nesting with the \( Q \) vector. Hence, the enhancement of \( T_c \) in the relative \( c \)-axis–strained Fe\(_{0.5}\)Se\(_{0.5}\) thin films \[16\] may also be explained by a suppression of spin ordering and the occurrence of spin fluctuations.

It is apparent that the electronic structure of FeSe plays an important role in its SC, since there is a clear dependence of the \( T_c \)'s values, reported in the literature for various strained FeSe systems, on the here determined FS nesting features. Thus, our findings support also the general idea of spin-fluctuation–mediated SC in iron chalcogenides \[20,22,23,28\].

Conclusions. – The influence of various strains on the structural and electronic properties of the FeSe superconductor has been investigated from first principles. Our results show that large modifications of the FS nesting properties in this compound can be reached by applying even a small \( c \)-axis strain. In particular, these should occur in thin films and may also be induced by chemical pressure. At the same time, the \( ab \)-plane strains lead to opposite effects. The clear relation between the nesting features of the Fermi surface and superconducting critical temperatures, presented in this paper, indeed confirms the earlier reports that superconductivity in the FeSe-based systems is mediated by spin fluctuations.

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