Effects of disorder in FeSe: an ab initio study

Prabhakar P Singh

Department of Physics, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

E-mail: ppsingh@phy.iitb.ac.in

Received 30 December 2009, in final form 30 January 2010
Published 17 March 2010
Online at stacks.iop.org/JPhysCM/22/135501

Abstract
Using the coherent-potential approximation, we have studied the effects of excess Fe, Se deficiency and substitutions of S and Te on the Se sub-lattice and Co, Ni and Cu on the Fe sub-lattice in FeSe. Our results show that (i) a small amount of excess Fe substantially disorders the Fe-derived bands while an Se deficiency affects mainly the Se-derived bands, (ii) the substitution of S or Te enhances the possibility of Fermi surface nesting, especially in FeSe$_{0.5}$Te$_{0.5}$, in spite of disordering the Se-derived bands and (iii) the electron doping through Co, Ni or Cu disorders the system and pushes down the Fe-derived bands, thereby destroying the possibility of Fermi surface nesting. A comparison of these results with the rigid-band, virtual-crystal and supercell approximations reveals the importance of describing disorder with the coherent-potential approximation.

1. Introduction
The superconductivity in iron pnictides [1, 2] and chalcogenides [3], with the interactions resulting from charge and spin degrees of freedom of electrons delicately balanced [4–6], provides a unique opportunity to unravel the mystery of unconventional superconductivity [7–10]. From the experimental characterizations [11] of the superconducting state of the iron pnictides and chalcogenides as well as theoretical calculations [12], it seems clear that the superconductivity in these alloys is not mediated by the phonons [13]. Therefore, attempts are being made to understand the superconductivity in iron pnictides and chalcogenides in terms of spin fluctuations and related theories [14].

In spin-fluctuation theories [9, 10, 14], in addition to the proximity of the system to a magnetic instability, its Fermi surface (FS) and, in particular, the FS nesting plays a crucial role in enhancing the magnetic interactions. In turn, by tuning the magnetic properties and the FS of the system by chemical substitutions, or electron or hole doping, one can bring out the details of the superconducting properties of the system and thereby close in on the exact nature of the interaction responsible for superconductivity. Out of all the recently discovered superconducting iron pnictides and chalcogenides, FeSe and its alloys with one of the simplest crystal structures are well suited for such a study.

In FeSe, the superconducting transition temperature $T_c$ of $\approx 8$ K [3] increases up to 15 K with S and Te substitutions [15] but decreases rapidly with electron doping using Co, Ni or Cu substitutions [15–17]. The presence of excess Fe as well as the Se deficiency in FeSe is known to affect its superconducting properties [18]. In addition, with an increase in pressure up to 8.9 GPa, the $T_c$ of FeSe increases to 36.7 K [19–21].

Previous theoretical attempts [22–26] at understanding the changes in the normal state electronic properties, as a prelude to understanding the changes in their superconducting properties, of several of the pnictides and chalcogenides upon alloying have used either the virtual-crystal or the supercell or a series of ordered alloys or parameterized model Hamiltonian approaches. The virtual-crystal and the supercell approaches are known to be quite inadequate to describe the effects of disorder in metallic alloys, especially in d-band metals [27]. In addition, an ab initio study of the effects of alloying in FeSe has been lacking so far.

In an attempt to understand the changes in the normal state electronic properties of FeSe upon alloying, which may, in turn, provide some understanding of the changes in its superconducting properties, we have used the Korringa–Kohn–Rostoker coherent-potential approximation method [27] in the atomic-sphere approximation (KKR-ASA CPA) [28] to carry out charge, self-consistent electronic structure calculations of FeSe and its alloys with S, Te, Co, Ni and Cu, including the
presence of excess Fe and the deficiency of Se. We have also carried out a detailed comparison of these results with the rigid-band, virtual-crystal and supercell approximations.

Based on our calculations, we find that (i) a small amount of excess Fe substantially disorders the Fe-derived bands near the Fermi energy ($E_F$) while Se deficiency affects mainly the Se-derived bands away from $E_F$, (ii) the substitution of S or Te on the Se sub-lattice enhances the possibility of FS nesting in spite of disordering the Se-derived bands, especially in the FeSe$_{0.5}$Te$_{0.5}$ alloy and (iii) the substitution of Co, Ni or Cu on the Fe sub-lattice disorders the system and pushes down the Fe-derived bands, thereby destroying the possibility of FS nesting. We also find that, for descriptive substitutional disorder, the coherent-potential approximation is more reliable than the rigid-band, virtual-crystal or supercell approximation.

2. Computational method

We have studied Fe$_{1+x}$Se with $\delta = 0.0, 0.01, 0.03$ and 0.06, FeSe$_{1-x}$ with $\chi = 0.01, 0.03, 0.06$, 0.12 and 0.18, FeSe$_{1-y}$Te$_{y}$ with $y = 0.25$ and 0.5, FeSe$_{0.9}$S$_{0.1}$, Fe$_{0.9}$Co$_{0.1}$Se, Fe$_{0.9}$Ni$_{0.1}$Se and Fe$_{0.9}$Cu$_{0.1}$Se in the tetragonal ($P4/nmm$) crystal structure, while Fe$_{1.01}$Se has been studied in the orthorhombic structure as well. The substitution of 10% Cu on the Fe sub-lattice in Fe$_{1.01}$Se results in the composition Fe$_{0.91}$Cu$_{0.09}$Se$_{1}$, used in the cited experiment [17] and hence in our calculations. To reduce the errors due to the ASA, we have introduced four empty spheres in the unit cell containing two Fe and two Se atoms. The atomic as well as the empty-sphere positions in the unit cell are: Fe(3/4, 1/4, 0; 2a), Se(1/4, 1/4, $z_{Se}$; 2c), E1(1/4, 1/4, $z = -z_{Se}$; 2c) and E2(3/4, 1/4, 0.5; 2c), where E1 and E2 denote the two empty-sphere sub-lattices. The E1 empty-sphere layer, in the same plane as the Se layer, was used to accommodate the excess Fe in the calculations of Fe$_{1+x}$Se and Fe$_{0.91}$Cu$_{0.09}$Se. To see the effects of incorporating the excess Fe in other interstitial regions, we have also used the E2 empty-sphere site for the excess Fe in Fe$_{1.01}$Se and sites just below the Se plane.

To model the effects of disorder, we have used the CPA [29, 27] rather than a rigid-band, virtual-crystal or supercell method because CPA has been found to reliably describe the effects of disorder in metallic alloys [28, 27]. We used the Barth and Hedin [30] exchange–correlation potential. The Brillouin zone (BZ) integration during self-consistency was carried out using a grid of $24 \times 24 \times 20$ points in the BZ. The density of states (DOS) was calculated with a grid of $28 \times 28 \times 24$ points in the BZ except for the pure FeSe and FeTe, where a grid of $36 \times 36 \times 32$ points was used. For both DOS and spectral function calculations, we have added a small imaginary component of 1 mRyd (1.5 mRyd for FeSe and FeTe) to the energy. In the following figures the Se-derived s-band is not shown. In our calculations, the lattice parameters $a$ and $c$ were taken from experiments [15, 18, 16, 17] while the theoretically relaxed $z$ values were taken from [13]. For some of the intermediate alloys, we used the concentration-weighted average of the $z$ values. The lattice parameters of FeSe, FeTe and their alloys, used in the present calculations, are listed in table 1.

We have analyzed our results using the Bloch spectral function [27] $A(k, E)$, defined by

$$A(k, E) = -\frac{1}{\pi} G(k, E),$$  

(1)

where $G(k, E)$ is the k-space coherent-potential Green’s function, and $k$ and $E$ represent the wavevector and the energy, respectively, of the electron. The band structure along the BZ symmetry directions was calculated by evaluating equation (1) for the given $k$ points and the energy $E$ in the given range. The Fermi surface in a given $k$-space plane was mapped by evaluating equation (1) over a two-dimensional grid of 151 × 151 $k$ points in the plane at the Fermi energy $E = E_F$. The peaks in the spectral function $A(k, E)$ form the Fermi surface of the alloy. All the plots of the band structures and the Fermi surfaces were carried out with the same value for the color map in the range of 0–30 (15 for the Fermi surface) with the minimum and maximum values represented by blue and red, and the intermediate values assigned colors varying from blue, light blue, green, yellow, orange to then red. Thus, a movement away from red and towards blue in the band structure and Fermi surface plots indicates a reduction in the peak value of $A(k, E)$.

The formation energy, $E_{\text{form}}$, of excess Fe in Fe$_{1+x}$Se and the Se vacancy in FeSe$_{1-x}$ alloys has been calculated as

$$E_{\text{form}} = E_{\text{FeSe}} + E_{\text{Se}} - \delta E_{\text{Fe}}$$  

(2)

$$E_{\text{form}} = E_{\text{FeSe},\text{vac}} - E_{\text{FeSe}} + \delta E_{\text{Se}},$$  

(3)

where the superscripts e and v correspond to the formation energy of FeSe with excess Fe or with Se vacancy, respectively. The subscripts on the right-hand side of equations (2) and (3) denote the calculated total energies of the corresponding alloys except for $E_{\text{Fe}}$ and $E_{\text{Se}}$, which represent the corresponding free atom energy.

The rigid-band calculations were carried out by first determining the amount of shift in Fermi energy required to either accommodate or remove a given number of electrons from the self-consistent potential of the ordered FeSe. The Fermi surface in the rigid-band was then evaluated by the KKR-ASA CPA method at the shifted Fermi energy and using the self-consistent potential of ordered FeSe.

For the virtual-crystal approximation [31], we replaced the disordered sub-lattice by an ordered sub-lattice containing

| Table 1. The experimental lattice parameters $a$ and $c$ of FeSe, FeTe and their alloys used in the present calculations. |
|---|---|---|---|---|---|
| Alloy | $a$ (Å) | $c$ (Å) | Alloy | $a$ (Å) | $c$ (Å) |
| FeSe | 3.765 | 5.518 | Fe$_{0.96}$Co$_{0.04}$Te$_{0.5}$ | 3.7637 | 5.5043 |
| Fe$_{0.01}$Se | 3.7734 | 5.5258 | Fe$_{0.96}$Ni$_{0.04}$Te$_{0.5}$ | 3.7713 | 5.503 |
| FeSe$_{0.99}$ | 3.7787 | 5.5208 | Fe$_{0.96}$Cu$_{0.04}$Te$_{0.5}$ | 3.807 | 5.495 |
| Fe$_{1.01}$Se | 3.7747 | 5.5229 | Fe$_{0.96}$Co$_{0.04}$Te$_{0.5}$ | 3.763 | 5.503 |
| FeSe$_{0.97}$ | 3.7747 | 5.5229 | Fe$_{0.96}$Ni$_{0.04}$Te$_{0.5}$ | 3.7989 | 5.9685 |
| Fe$_{1.03}$Se | 3.7693 | 5.4861 | Fe$_{0.96}$Cu$_{0.04}$Te$_{0.5}$ | 3.7909 | 5.9570 |
| Fe$_{0.87}$ | 3.7676 | 5.4847 | FeTe | 3.8215 | 6.2695 |

---

J. Phys.: Condens. Matter 22 (2010) 135501 P P Singh
Figure 1. The unit cell of (a) tetragonal FeSe and the $2 \times 2 \times 1$ supercells used for (b) Fe$_9$Se$_8$ and (c) Fe$_8$Se$_7$ calculations. The large spheres represent Fe (red/black) and Se atoms (yellow/gray), and the smaller spheres represent empty spheres (gray). The excess Fe in Fe$_9$Se$_8$ is placed at an empty-sphere site while the vacancy in Fe$_8$Se$_7$ is formed by replacing an Se atom by an empty sphere.

Figure 2. (a) The band structure of tetragonal FeSe (top) and FeTe (bottom) along the BZ symmetry directions using experimental lattice parameters and theoretically relaxed $z_{Se}$. The Fermi energy is indicated by the horizontal line at 0 eV. (b) The color map used for all the band structure and Fermi surface plots as described in the text.

3. Ordered FeSe and FeTe in the atomic-sphere approximation

To be able to separate out the effects of disorder from the atomic-sphere-approximation-related changes, in this section we compare the electronic structure of ordered FeSe and FeTe alloys with the more accurate full-potential results. In figures 2–4, we show the band structure, the density of states and the Fermi surface of FeSe and FeTe alloys, which are similar to those of [13] except for the gap between Se- and Fe-derived bands around 2.5 eV below $E_F$ in FeSe. Since it is already known that electronic structure calculations of FeSe are very sensitive to the height of the Se layer above the Fe plane, we have carried out full-potential, linear muffin-tin orbital (FP-LMTO) calculations for FeSe using the lattice parameters as above. We find that the gap predicted by FP-LMTO is $\approx 0.3$ eV, which increases to $\approx 0.4$ eV if the muffin-tin spheres are enlarged to atomic spheres within the full-potential approach. In the atomic-sphere approximation, which uses additional approximations, including that of making the potential spherical, the gap is found to be $\approx 0.8$ eV. However, the Fe-derived bands, which are responsible for superconductivity in these alloys, compare well with the more accurate FP-LMTO calculations as well as with that of [13].

Using the idea of FS nesting, it is possible to get some quantitative measure of the response of the system without evaluating the susceptibility. For example, if the FS around the $\Gamma$ point matches exactly with the FS around the M point when displaced by a reciprocal space vector then the nesting is optimal. In the present context, the optimal nesting corresponds to FS at $\Gamma$ and M points having matching radii and sharp Fermi surfaces (reflected by thin red lines in the figures). Any deviation, either from the matching radii or sharpness of the Fermi surfaces (reflected by diffused and/or broadened lines in the figures), generally reduces the effect of nesting.

The FS of FeSe, shown in figure 4, consists of two hole-like sheets around the $\Gamma$ point and two electron-like sheets around the M point, both sheets being derived from the $xz$ ($yz$) and $xy$ bands of Fe. In FeTe, there are three hole-like sheets...
Figure 3. The total (black, solid) and the sub-lattice-resolved DOS of tetragonal FeSe (top) and FeTe (bottom) obtained using experimental lattice parameters and theoretically relaxed $z_{Se}$. The contributions from the Fe (red, dashed) and the Se/Te (blue, dotted-dashed) sub-lattices as well as from the empty-sphere sub-lattices E1 (green, dotted) and E2 (violet, double-dashed-dotted) are shown. The vertical, dashed line denotes the Fermi energy. Note that the total DOS in the figure corresponds to per two atoms.

Figure 4. The Fermi surface of FeSe (top) and FeTe (bottom) in $\Gamma$–X–M and Z–R–A planes obtained using experimental lattice parameters and theoretically relaxed $z_{Se}$. Around the $\Gamma$ point and only two sheets around the M point as shown in figure 4. The Fermi surfaces shown in figure 2 reveal enhanced FS nesting at the $\Gamma$–X–M plane in FeSe rather than in FeTe. Note that the two bands around the M point in FeSe are not resolved in figure 2. In the following, we will see if the changes in the shape and the nesting of the FS of FeSe induced upon alloying can be used to understand the changes in the superconducting properties of these alloys within the framework of the spin-fluctuation theories.

4. Effects of theoretical versus experimental $z_{Se}$

The role of Se height above the Fe plane, given by $z_{Se}$, plays a crucial role in determining the electronic properties, especially the magnetic properties [32], of FeSe and its alloys. It is not surprising that $z_{Se}$ plays such an important role in deciding the electronic properties of FeSe because a change in $z_{Se}$ directly impacts the Fe d-orbitals which, in turn, affect the Fe-derived d-bands around $E_F$. Most of the theoretical work on FeSe has used the experimental values of the lattice parameters $a$ and $c$, and the theoretically relaxed value for $z_{Se}$. To see what role $z_{Se}$ plays in the present context, we have studied FeSe and its alloys using the experimental value of $z_{Se} = 0.266$ and the theoretically relaxed value of $z_{Se} = 0.2343$ [13].

In figure 5, we show the band structure of FeSe calculated with the experimental as well as the theoretically relaxed value...
of $z_{\text{Se}}$. In both cases, the experimental values of the lattice parameters $a$ and $c$ were used, and the exchange–correlation potential was parameterized using the generalized-gradient approximation of Perdew et al [33]. The use of experimental $z_{\text{Se}}$, which is larger than the theoretical value, allows most of the bands, including the Se-derived bands, to move up with respect to $E_F$. Such a movement results in three bands crossing $E_F$ along $\Gamma$–X, M–$\Gamma$ and $Z$–R. The use of theoretical $z_{\text{Se}}$, which reduces the Se height above the Fe plane, affects the individual Fe-derived d-bands around $E_F$ differently due to the orientation of the d-orbitals. In particular, we find that the $3z^2-1$-derived band along $\Gamma$–X and $\Gamma$–Z is suppressed more than the other two bands, resulting in only two bands crossing $E_F$ along $\Gamma$–X, M–$\Gamma$ and $Z$–R for theoretically relaxed $z_{\text{Se}}$.

The effects of using experimental or theoretical $z_{\text{Se}}$ get amplified in the total DOS as shown in figure 6. The higher value of $z_{\text{Se}}$ shifts the DOS towards $E_F$ as well as redistributes some of the electronic states between 0 and $-2$ eV. The Fe peak in the DOS is closer to $E_F$ for the experimental $z_{\text{Se}}$ than for the theoretical $z_{\text{Se}}$. From figure 6, we also find that the DOS of FeSe obtained with the Barth–Hedin exchange–correlation potential is essentially identical to the DOS obtained with the Perdew–Wang [34] exchange–correlation potential within the local-density approximation.

We have also calculated the Fermi surface of FeSe with experimental and theoretical $z_{\text{Se}}$. As discussed above, in the context of the band structure of FeSe, we find three bands around the $\Gamma$ and $Z$ points for experimental $z_{\text{Se}}$.

5. Electronic structure of disordered Fe$_{1+\delta}$Se and FeSe$_{1-x}$ alloys

Generally, the synthesis of FeSe results in an alloy with either excess of Fe or deficiency in Se [18, 35, 17]. Measurements on such alloys have shown that Fe$_{1+\delta}$Se is superconducting only when $\delta \leq 0.01$ and the underlying lattice is orthorhombic [16]. On the other hand, Se-deficient alloys FeSe$_{1-x}$ remain superconducting for $x \leq 0.18$ in the tetragonal structure [3, 18]. In order to understand the contrasting superconducting properties of Fe$_{1+\delta}$Se and FeSe$_{1-x}$ alloys, we have studied their normal state electronic structure as a function of $\delta$ and $x$ with $0 \leq \delta \leq 0.06$ and $0 \leq x \leq 0.18$.

The changes in the band structure, the density of states and the FS in Fe$_{1+\delta}$Se and FeSe$_{1-x}$ alloys with increasing $\delta$ and $x$ are shown in figures 7–10. In the unit cell, the excess Fe atom, denoted by Fe(2) (the Fe at the stoichiometric site is denoted by Fe(1)), is kept in the Se plane with $z_{\text{Fe}} = -z_{\text{Se}}$, which is one of the two inequivalent sub-lattices containing empty
Figure 8. The total and the sub-lattice-resolved DOS of (a) Fe$_{1+\delta}$Se and (b) FeSe$_{1-x}$ with $\delta$ and $x$ = 0.01 (black, solid), 0.03 (blue, dotted) and 0.06 (red, dashed). For FeSe$_{1-x}$, the DOS corresponding to $x$ = 0.12 (magenta, double-dotted–dashed) and 0.18 (green, double-dashed–dotted) are also shown. The vertical, dashed line denotes the Fermi energy. The atom-resolved DOS at (c) the E1 site of Fe$_{1+\delta}$Se and (d) the Se site of FeSe$_{1-x}$ are also shown.

Figure 9. The d-resolved DOS at the Fe(1) (left panel) and Fe(2) (right panel) sites in Fe$_{1+\delta}$Se with $\delta$ = 0.01 (black, solid), 0.03 (blue, dotted) and 0.06 (red, dashed). The vertical, dashed line denotes the Fermi energy.

spheres. Our main conclusions are independent of the possible locations of the excess Fe atoms within the FeSe lattice, as was found in [18]. The increase in disorder induced by the presence of excess Fe can be clearly seen, as indicated by the diffused intensity, in the Fe-derived bands in figure 7(a). The Se-derived bands are left relatively untouched by the excess Fe. From the DOS of Fe$_{1+\delta}$Se alloys, shown in figures 8(a) and (c), and 9, we find that the excess Fe kept on the E1 sub-lattice creates states around $E_F$ and around $-2$ eV. The possibility of the excess Fe becoming magnetic due to the increased local density of states at $E_F$ can be clearly seen in the d-resolved DOS of Fe(1) and Fe(2) in figure 9. On the other hand, the increase in excess Fe quickly destroys the FS nesting as seen from figure 10(a). Note that, even for $\delta$ = 0.01, the nesting is not optimal.

For Fe$_{1.01}$Se in the orthorhombic structure, the overall change in electronic structure with respect to the tetragonal structure is symmetry-induced and minimal. There are three bands crossing $E_F$ around the $\Gamma$ point instead of two bands, as is the case in the tetragonal structure, leading to some changes in the FS around the $\Gamma$ point. The DOS remains essentially unchanged with respect to the tetragonal case.

The FeSe$_{1-x}$ alloys remain superconducting over a wide range of $x$ values, indicating an unusually small impact on the bands around $E_F$ due to vacancies in the alloy. Our results for FeSe$_{1-x}$ alloys, shown in figures 7–10, seem to confirm it. The vacancies on the Se sub-lattice affect the Se-derived bands which are away from $E_F$, leaving the bands around $E_F$ essentially untouched for small $x$. In addition to the lowering of $E_F$ due to electron loss, for $x \geq 0.06$ the bands around $E_F$ begin to get affected by disorder. For example, for $x \geq 0.12$, we find that the Se-derived bands have been substantially diffused. The loss of electrons due to increasing Se vacancy moves $E_F$ inward, seen clearly in figure 8(b), bringing the peak in DOS due to the stoichiometric Fe closer to $E_F$ as shown in figure 8(d), and thereby increasing
Figure 10. The Fermi surface of (a) Fe$_{1+\delta}$Se and (b) FeSe$_{1-x}$ with $\delta$ and $x = 0.01$ (top), 0.03 (middle) and 0.06 (bottom) in $\Gamma$–X–M and Z–R–A planes.

the total DOS at $E_F$. The largest contribution to the DOS at $E_F$ comes from the states of Fe(1) having $x^2 - y^2$ and $xy$ symmetries. Such an increase in the DOS at $E_F$ may lead to magnetism in the alloy [23]. We emphasize that Fe(2) atoms are responsible for possible magnetism in Fe$_{1+\delta}$Se, while Fe(1) atoms may lead to magnetic behavior in FeSe$_{1-x}$. With increasing $x$, the gradual loss of possible FS nesting in Fe$_{1+\delta}$Se and FeSe$_{1-x}$ can also be seen in figure 10. If FS nesting is crucial for superconductivity in FeSe$_{1-x}$ alloys then clearly the possibility of superconductivity is diminished for large $x$ as the nesting is essentially destroyed as shown in figure 10. However, experiments [35, 17] have shown that FeSe$_{1-x}$ for large $x$, contain impurity phases such as elemental Fe, leading to incorrect determination of Se content. Therefore, the Se content in superconducting FeSe$_{1-x}$ alloys must be determined carefully.

In both Fe$_{1+\delta}$Se and FeSe$_{1-x}$, our results clearly show that the effects of excess Fe or Se deficiency on the electronic structure of FeSe are very different, and that for $x \geq 0.06$ the FS nesting is essentially destroyed.

6. Energetics of excess Fe and Se deficiency in FeSe

To get an estimate of the energetics involved in the formation of FeSe alloys with either excess Fe or Se deficiency, we have calculated the formation energy of Fe$_{1+\delta}$Se and FeSe$_{1-x}$ alloys as described in section 2. In Fe$_{1+\delta}$Se, we find that the formation energy $E_{\text{form}}^F = -98, -94$ and $-87$ meV/atom for $\delta = 0.01, 0.03$ and 0.06, respectively. The vacancy formation energy in FeSe$_{1-x}$ alloys is found to be $E_{\text{form}}^V = 115, 126, 132, 134$ and 136 meV/atom for $x = 0.01, 0.03, 0.06, 0.12$ and 0.18, respectively. As our calculations are done within the atomic-sphere approximation and without taking relaxation into account, these results are expected to change with the incorporation of full-potential and relaxation effects [23].

In order to check the effects of keeping the excess Fe in Fe$_{1+\delta}$Se at the various interstitial regions, we have studied the Fe$_{1.06}$Se alloy keeping the excess Fe (Fe(2)) in the Se plane with $z_{\text{Fe}} = -z_{\text{Se}}$, slightly below the Se plane with $z_{\text{Fe}} = 0.7755$ and in the middle of the two Se planes with $z_{\text{Fe}} = 0.5$ for theoretically relaxed $z_{\text{Se}}$ as well as experimental $z_{\text{Se}}$. As noted in section 4, the DOS of FeSe and its alloys are expected to be different for theoretically relaxed $z_{\text{Se}}$ and experimental $z_{\text{Se}}$, as is the case for Fe$_{1.06}$Se in figure 11. Not surprisingly, the DOS corresponding to $z_{\text{Fe}} = -z_{\text{Se}}$ and $z_{\text{Fe}} = 0.7755$ are essentially identical for theoretically relaxed $z_{\text{Se}}$. 

Figure 11. The total and the Fe(1) and Fe(2) DOS in Fe$_{1.06}$Se with theoretically relaxed $z_{\text{Se}}$ (left panel) and experimental $z_{\text{Se}}$ (right panel). The DOS correspond to different positions of the excess Fe (Fe(2)) given by $z_{\text{Fe}} = -z_{\text{Se}}$ (black, solid) with Fe(2) in the Se plane, $z_{\text{Fe}} = 0.7755$ (blue, dotted) with Fe(2) slightly below the Se plane and $z_{\text{Fe}} = 0.5$ (red, dashed) with Fe(2) in the middle of the two Se planes. The vertical, dashed line denotes the Fermi energy.
However, when the excess Fe is placed in between the two Se planes instead of in the Se plane, the resulting Fe(2) DOS’s are somewhat different from each other, as shown in the bottom panel of figure 11. These differences arise due to the relatively free space available to Fe(2) when $z_{Fe} = 0.5$. We also find that it is only with the inclusion of the Madelung potential in the muffin-tin-corrected total energy that Fe(2) prefers to go to $z_{Fe} = -z_{Se}$ instead of $z_{Fe} = 0.5$ by 11 meV/atom for experimental $z_{Se}$. We must point out that a more reliable way of calculating the site preference involving different structures is through the full-potential approach with relaxation included.

7. Electronic structure of disordered FeSe$_{0.9}S_{0.1}$, FeSe$_{1-y}Te_{y}$, Fe$_{0.9}Co_{0.1}Se$, Fe$_{0.9}Ni_{0.1}Se$ and Fe$_{0.91}Cu_{0.1}Se$ alloys

To understand the changes in the superconducting properties of FeSe upon substitution of impurities through the changes in the normal state electronic properties, we have studied the effects of substituting S and Te on the Se sub-lattice and Co, Ni and Cu on the Fe sub-lattice. In figures 12–14, we show our results for the band structure, density of states and FS of FeSe$_{0.9}S_{0.1}$, FeSe$_{0.75}Te_{0.25}$, FeSe$_{0.5}Te_{0.5}$, Fe$_{0.9}Co_{0.1}Se$, Fe$_{0.9}Ni_{0.1}Se$ and Fe$_{0.9}Cu_{0.1}Se$ alloys. Based on the atomic-size mismatch, it is expected that the substitution of Te would lead to more disorder than the substitution of S on the Se sub-lattice in FeSe. Indeed, we find that the effects of disorder are minimal due to S but substitution of Te creates states in the gap region with substantial disorder in the Se-derived bands. The states created in the gap between Se- and Fe-derived bands can be clearly seen in figures 12(a) and (c). Surprisingly, for the FeSe$_{0.5}Te_{0.5}$ alloy, we find that the substitution of Te has rearranged the bands around $E_F$ such that the possibility of FS nesting is maximized as shown in the bottom panel of figure 14(a).

The presence of Co, Ni and Cu in the Fe sub-lattice of FeSe is expected to affect the bands around $E_F$ as well as move $E_F$ up due to disorder and electron doping, thereby significantly changing its superconducting properties. As shown in figure 12(b), a 10% addition of Ni or Cu moves $E_F$ above the two bands around the $\Gamma$ point. The substitution of Cu seems to disorder both the Fe-and the Se-derived bands, as can be seen from the diffused intensity of the bands in figure 12(b). The addition of Co, Ni or Cu creates states in the gap region around $-2$ eV as seen from figures 13(b) and (d). The combined effect of disorder and electron addition diminishes the possibility of FS nesting in Fe$_{0.9}Co_{0.1}Se$ and destroys it in Fe$_{0.9}Ni_{0.1}Se$ and Fe$_{0.91}Cu_{0.1}Se$, as seen in figure 14(b).

8. Describing disorder: rigid-band, virtual-crystal, supercell and coherent-potential approximations

In order to emphasize the importance of describing the effects of substitutional disorder accurately and reliably in
Figure 13. The total and the sub-lattice-resolved DOS of (a) S and Te substitutions on Se sub-lattice and (b) Co, Ni and Cu substitutions on Fe sub-lattice. The DOS in (a) correspond to FeSe$_0.9$S$_{0.1}$ (black, solid), FeSe$_0.75$Te$_{0.25}$ (blue, dotted) and FeSe$_0.5$Te$_{0.5}$ (red, dashed), and in (b) Fe$_0.9$Co$_{0.1}$Se (black, solid), Fe$_0.9$Ni$_{0.1}$Se (blue, dotted) and Fe$_0.9$Cu$_{0.1}$Se (red, dashed). The vertical, dashed line denotes the Fermi energy. The atom-resolved, DOS of S and Te substitutions at the Se sub-lattice and Co, Ni and Cu substitutions at the Fe sub-lattice are shown in (c) and (d), respectively.

Figure 14. The Fermi surface of (a) FeSe$_0.9$S$_{0.1}$ (top), FeSe$_0.75$Te$_{0.25}$ (middle) and FeSe$_0.5$Te$_{0.5}$ (bottom), and (b) Fe$_0.9$Co$_{0.1}$Se (top), Fe$_0.9$Ni$_{0.1}$Se (middle) and Fe$_0.9$Cu$_{0.1}$Se (bottom) in $\Gamma$–X–M and Z–R–A planes.

metals, in general, and in FeSe and its alloys, in particular, we have studied selected FeSe alloys using the rigid-band approximation, the virtual-crystal approximation and the supercell approximation. In this section, we describe and compare our results, in terms of DOS and Fermi surface, of the rigid-band approximation, the virtual-crystal approximation
Figure 15. The total DOS of Fe\(_{1+\delta}\)Se (left panel) and FeSe\(_{1-\delta}\) (right panel) with \(\delta\) and \(x = 0.01\) (top), 0.06 (middle) and 0.125 (bottom) calculated in the rigid-band approximation (blue, dotted), the virtual-crystal approximation (red, dashed) and the coherent-potential approximation (black, solid). In the bottom panel, the total DOS obtained in the supercell approximation (green, double-dashed–dotted) using Fe\(_9\)Se\(_8\) (left) and Fe\(_8\)Se\(_7\) (right) are also shown. The vertical, dashed line denotes the Fermi energy.

Figure 16. The total and the virtual-atom-site DOS of Fe\(_{0+\delta}\)Ni\(_{0.8}\)Se (red, dashed), calculated in the virtual-crystal approximation as described in the text. The corresponding DOS in the rigid-band approximation (blue, dotted) and the coherent-potential approximation (black, solid) are also shown. The vertical, dashed line denotes the Fermi energy.

and the supercell approximation with that of the coherent-potential approximation for the selected FeSe alloys.

We have studied Fe\(_{1+\delta}\)Se and FeSe\(_{1-\delta}\) with \(\delta\) and \(x = 0.01, 0.06\) and 0.125, and Fe\(_{0.9}\)Ni\(_{0.1}\)Se alloys in both the rigid-band approximation and the virtual-crystal approximation. For \(\delta\) and \(x = 0.125\), studied for comparison with the supercell approximation, we have used the lattice parameters corresponding to \(\delta = 0.06\) and \(x = 0.12\), respectively. We have also studied Fe\(_5\)Se\(_8\) and Fe\(_8\)Se\(_7\) as well as Fe\(_9\)Se\(_8\) in the supercell approximation. The selected alloys cover a wide range of systems with effects due to disorder involving addition of \(d\) electrons in Fe\(_{1+\delta}\)Se, removal of \(s\) and \(p\) electrons in FeSe\(_{1-\delta}\) and similar atoms in Fe\(_{0.9}\)Ni\(_{0.1}\)Se. Generally, one expects the rigid-band approximation to work well for free-electron-like systems or systems consisting of similar atoms. On the other hand, the virtual-crystal approximation is expected to work well for systems consisting of atoms from nearby columns of the periodic table such as Fe\(_{0.9}\)Ni\(_{0.1}\)Se. The supercell approximation or its more efficient version known as the special quasi-random structure [36] for describing the disordered alloy can be used to extract many properties of alloys such as the density of states and phase stability.

In figure 15, we compare the total DOS of Fe\(_{1+\delta}\)Se and FeSe\(_{1-\delta}\) with \(\delta\) and \(x = 0.01, 0.06\) and 0.125 calculated in the rigid-band and virtual-crystal approximations with that of the coherent-potential approximation. For \(\delta\) and \(x = 0.01\), we find that the total DOS obtained in the rigid-band approximation is close to that of the coherent-potential approximation. For higher concentrations, the rigid-band DOS begins to differ substantially from the CPA DOS for Fe\(_{1+\delta}\)Se. Not surprisingly, in FeSe\(_{1-\delta}\) the Se vacancy, involving the absence of \(s\) and \(p\) electrons, leads to a relatively small disagreement up to \(x = 0.06\).

For both Fe\(_{1+\delta}\)Se and FeSe\(_{1-\delta}\), the DOS calculated with the virtual-crystal approximation differs substantially with the CPA DOS for \(\delta\) and \(x \geq 0.06\), as can be seen from figure 15. Note that, for \(x = 0.125\), the virtual-crystal approximation replaces the Se atom on the Se sub-lattice in FeSe\(_{1-\delta}\) by a virtual atom with atomic number equal to 33.25. Thus, we find that the virtual-crystal approximation essentially fails to describe accurately the effects of disorder in the DOS of either Fe\(_{1+\delta}\)Se or FeSe\(_{1-\delta}\) for \(\delta\) and \(x \geq 0.06\). However, the virtual-crystal approximation is expected to work better if the virtual atom is made out of atoms with similar atomic numbers, as in Fe\(_{0.9}\)Ni\(_{0.1}\)Se. In figure 16, we compare the total and the Fe sub-lattice DOS in Fe\(_{0.9}\)Ni\(_{0.1}\)Se in the virtual-crystal approximation with the corresponding CPA DOS. Indeed, we find a good agreement in the DOS of Fe\(_{0.9}\)Ni\(_{0.1}\)Se. Some of the differences in the DOS of Fe\(_{0.9}\)Ni\(_{0.1}\)Se around \(-1.9\) and \(-1.0\) eV highlight one of the shortcomings of the virtual-crystal approximation (as well as that of the supercell approximation) in assuming a periodic lattice with no energy-dependent electron scattering. The virtual-crystal approximation, as implemented here, cannot be applied to FeSe\(_{0.5}\)Te\(_{0.5}\). A more appropriate approach for implementing the virtual-crystal approximation in alloys may be through the use of pseudopotentials [37].

In figure 15, the total DOS obtained for Fe\(_5\)Se\(_8\) and Fe\(_8\)Se\(_7\), corresponding to the supercell approximation for 0.125 of excess Fe and 0.125 of Se vacancy per atom in FeSe, respectively, are also shown. The total DOS for Fe\(_5\)Se\(_7\) is in overall agreement with the corresponding CPA DOS of Fe\(_{1.125}\)Se. For the Se vacancy, the total DOS of Fe\(_5\)Se\(_7\) is very close to the fully relaxed, full-potential supercell result of [23], as shown in their figure 2. A comparison of the supercell DOS of Fe\(_5\)Se\(_7\) with the CPA DOS of Fe\(_{0.875}\)Se\(_{0.125}\) shows some differences around the Se region and around \(E_F\). In particular, the sharp peak close to \(E_F\) is missing in the CPA DOS. If the presence of the peak is confirmed by experiment, then it would indicate the need to go beyond the single-site CPA. The supercell approximation does provide the possibility of including several atomic environments: however, its inherent flaw of not including energy-dependent electron scattering limits its applicability.

The \(k\)-resolved properties of alloys provide a more stringent test for the accuracy and the reliability of the various approximations for describing disorder that we have discussed.
so far. Therefore, we have calculated the Fermi surface of the selected alloys in the $\Gamma$–X–M and Z–R–A planes in the rigid-band, virtual-crystal and supercell approximations, and the results are shown in figures 17–19. The Fermi surface of Fe$_{1+\delta}$Se and FeSe$_{1-x}$ obtained in the rigid-band approximation, figure 17, agrees with the corresponding CPA Fermi surface, figure 10, for $\delta$ and $x = 0.01$ only. The Fermi surface obtained in the virtual-crystal approximation, shown in figure 18, disagrees with both the rigid-band, figure 17, and the CPA, figure 10, results for $\delta$ and $x \geq 0.06$. Similarly, for Fe$_{0.9}$Ni$_{0.1}$Se the Fermi surface in the rigid-band approximation is closer to the corresponding CPA Fermi surface than the Fermi surface obtained in the virtual-crystal approximation as shown in figure 19(a). Finally, we show the Fermi surface of Fe$_8$Se$_8$, Fe$_9$Se$_8$ and Fe$_8$Se$_7$ in figure 19(b), obtained in the supercell approximation. Due to the folding in $k_x$ and $k_y$ directions, the Fermi surface of Fe$_8$Se$_8$ and Fe$_8$Se$_7$ cannot be compared directly with the CPA Fermi surface obtained using the primitive cell. Therefore, we also show in figure 19(b) the Fermi surface of Fe$_8$Se$_8$. We find that the supercell approximation of Fe$_8$Se$_8$ and Fe$_8$Se$_7$ predicts a very different Fermi surface of disordered FeSe alloys than the coherent-potential approximation.

9. Conclusions

In conclusion, we have studied the electronic structure of Fe$_{1+\delta}$Se, FeSe$_{1-x}$ and FeSe$_{1-y}$Te$_y$ as a function of $\delta$, $x$ and $y$ as well as FeSe$_{0.9}$S$_{0.1}$, Fe$_{0.9}$Co$_{0.1}$Se, Fe$_{0.9}$Ni$_{0.1}$Se and
Fe$_{0.93}$Cu$_{0.1}$Se alloys, our results show that (i) a small amount of excess Fe substantially disorders the Fe-derived bands near $E_F$ while the Se deficiency affects mainly the Se-derived bands away from $E_F$, (ii) the substitution of S and Te enhances the possibility of FS nesting in spite of disordering the Se-derived bands, especially in the FeSe$_{0.75}$Te$_{0.25}$ alloy and (iii) the substitution of Co, Ni or Cu disorders and pushes down the Fe-derived bands, thereby destroying the possibility of FS nesting. We also find that the coherent-potential approximation is more reliable than the rigid-band, virtual-crystal or supercell approximations for describing substitutional disorder in FeSe alloys. Thus, within the framework of spin-fluctuation theories, our results provide a consistent basis for understanding the superconducting properties of FeSe alloys.

**Acknowledgment**

We would like to thank A V Mahajan for helpful discussion.

**References**

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. **130** 3296
[2] Ren Z-A et al 2008 Chin. Phys. Lett. **25** 2215
[3] Hsu F-C, Luo J-Y, Yeh K-W, Huang T-W, Wu P M and Lee Y-C 2008 Proc. Natl Acad. Sci. USA **105** 14262
[4] Drew A J et al 2008 Phys. Rev. Lett. **101** 097010
[5] Bao W et al 2009 Phys. Rev. Lett. **102** 247001
[6] Han M J, Yin Q, Pickett W E and Savrasov S Y 2009 Phys. Rev. Lett. **102** 107003
[7] Berk N F and Schrieffer J R 1966 Phys. Rev. Lett. **17** 433
[8] Monthoux P, Pines D and Lonzarich G G 2007 Nature **450** 1177
[9] Moriya T, Takahashi T and Ueda K 1990 J. Phys. Soc. Japan **59** 2905
[10] Moriya T 1985 *Spin Fluctuations in Itinerant Magnetism* (Berlin: Springer)
[11] Ishida K, Nakai Y and Hosono H 2009 J. Phys. Soc. Japan **78** 062001
[12] Mazin I I and Schmalian J 2009 arXiv:0901.4790
[13] Subedi A, Zhang L, Singh D J and Du M H 2008 Phys. Rev. B **78** 134514
[14] Mazin I I, Singh D J, Johannes M D and Du M H 2008 Phys. Rev. Lett. **101** 057003
[15] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2009 J. Phys. Soc. Japan **78** 074712
[16] McQueen T M, Williams A J, Stephens P W, Tao J, Zhu Y, Ksenofontov V, Casper F, Felser C and Cava R J 2009 Phys. Rev. Lett. **103** 057002
[17] Williams A J, McQueen T M and Cava R J 2009 *Solid State Commun.* **149** 1507–9
[18] McQueen T M et al 2009 Phys. Rev. B **79** 014522
[19] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. **93** 152505
[20] Margadonna S, Takabayashi Y, Ohishi Y, Mizuguchi Y, Takano Y, Kagayama T, Nakagawa T, Takata M and Prassides K 2009 arXiv:0903.2204
[21] Medvedev S et al 2009 Nat. Mater. **8** 630
[22] Yaresko A N, Liu G Q, Antonov V N and Andersson O K 2009 Phys. Rev. B **79** 144421
[23] Lee K W, Pardo V and Pickett W E 2008 Phys. Rev. B **78** 174502
[24] Zhang L, Singh D J and Du M H 2009 Phys. Rev. B **79** 012506
[25] Xu G, Ming W, Yao Y, Dai X, Zhang S-C and Fang Z 2008 Eur. Phys. Lett. **82** 67002
[26] Yu S-L, Kang J and Li J-X 2009 Phys. Rev. B **79** 064517
[27] Faulkner J S 1982 *Prog. Mater. Sci.* **27** 1
[28] Singh P P and Gonis A 1994 Phys. Rev. B **49** 1642
[29] Soven P 1967 Phys. Rev. **156** 809
[30] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[31] Kubler J 1980 *J. Magn. Magn. Mater.* **15–18** 859
[32] Yin Z P, Lebegue S, Han M J, Neal B, Savrasov S Y and Pickett W E 2008 Phys. Rev. Lett. **101** 047001
[33] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. **77** 3865
[34] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
[35] Ponomarenko L I, Conder K, Ponomarenko V, Bendele M and Khasanov R 2009 arXiv:0905.2115
[36] Zunger A, Wei S-H, Ferreira I G and Bernard J E 1990 Phys. Rev. Lett. **65** 353
[37] Bellaiche L and Vanderbilt D 2000 Phys. Rev. B **61** 7877