Interstitial disorder in iron-based superconductor: A first-principles study

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Abstract
FeSe in bulk, film or layer form as well as its alloys have shown many intriguing magnetic and superconducting properties. In this paper, we examine the role of interstitial disorder in changing the various electronic, magnetic and superconducting properties of FeSe using ab initio method. We have studied the electronic properties of FeSe doped interstitially with the transition metal (TM) impurities, Fe(TM)₅Se (where TM = V, Mn, Co, Ni, and x = 0.0, 0.01, 0.04 and 0.10). Our results, analyzed in terms of density of states (DOS), band structure, Fermi surface (FS), and local and total magnetic moments, show that the excess of the transition-metal atoms substantially modify the Fermi surface of FeSe. We have also estimated the value of the electron-phonon mass enhancement factor, the Hopfield parameter and the superconducting transition temperature for these alloys.

1. Introduction

Iron-based superconductors have shown tremendous promise in the field of superconductivity over the past few years. Basically, iron-based chalcogenides are layered materials, which provided many interesting results in materials science and engineering. Among the layered superconductors, the ‘chalcogenides (S, Se and T)’ are one of the remarkable groups because of the variety of materials and the observation of exotic superconductivity. Moreover the presence of iron in Fe-based superconductors, which is strongly magnetic, makes their discovery completely unexpected and interesting, because superconductivity and magnetism were originally considered as mutually exclusive phenomena.

An intensive effort is being made to find new promising superconductors as well as for increasing their superconducting transition temperatures. In recent years, superconductivity has been discovered in several materials such as LaFePO in 2006 by Hosono’s group [1], and, LaFeAsO₁₋ₓFx in 2008 by Kamihara et al [2]. Researchers are continuing their efforts to increase Tc for these superconductors by way of chemical pressure, high pressure, doping, substitutional or excess impurity, or deficiency of Fe etc. This discovery of superconductivity in these materials provide a challenge to experimentalist and theoretician to understand the origin of unconventional pairing mechanism and superconducting properties in these new materials. The discovery of iron-based superconductors has led to extensive research in this area. Both experiments and theories have been used to investigate the electronic, magnetic and superconducting properties of iron-based superconductors [3–5]. Among these superconductors, FeSe (Fe-11) based superconductors have the lower Tc and the simplest crystal structure, for example, a typical 11-type superconductor β - FeSe has tetragonal (P4/nmm) structure [6].

In 2008, Hsu et al found superconductivity in Fe₁₋ₓSe with a Tc = 8.5 K, however, the concentration of Fe was small [6]. Researchers have carried out study of the effect of substitution of transition metals (Co, Ni, Cu) at Fe site in [3, 7] and Te, Si, Sb, S at the Se site in [8 – 15]. Furthermore, the effect of nominal substitution of transition metals for excess Fe in Fe₁₋ₓSe superconductor has been studied [3, 5, 16, 17]. In addition, Yadav et al have also described the enhancement of Tc by the excess Cr in β-FeSe [18, 19]. Earlier, we have studied excess Cr in FeSe and excess Mn in FeSe₀.₅Te₀.₅ in [7]. In 2012, a mono layer of FeSe deposited on a SrTiO₃ substrate was found to be superconducting. Its Tc has been raised up to 100 K [20–22]. Furthermore, it has been reported
recently that doping of Nb into FeSe enhances the $T_c$ \cite{13}. The subsequently intensive efforts to increase $T_c$ makes TM-doped FeSe interesting and it motivated us to study the physics of interstitially doped FeSe in terms of its electronic structure.

It is the first-principles density functional calculations, which have shown an important role in the study of the physical and chemical properties of iron-based chalcogenides. Therefore, in the present study FeTM$_x$Se alloys with interstitial disorder have been studied with TM $\equiv$ V, Mn, Co and Ni and the concentration $x = 0.0, 0.01, 0.04$ and 0.10, respectively. Such a study allows us to investigate the effects of interstitial disorder in these alloys by examining the changes that are brought about by disorder in DOS, band structure and Fermi surface.

To account for chemical disorder in our calculations, we have used the single-site coherent-potential approximation in the first-principles approach of Korringa–Kohn–Rostoker in the atomic sphere approximation (KKR-ASA-CPA) method. We would like to point out that within the limitations of the density-functional theory and the atomic-sphere approximations, the present work provides a reliable description of the effects of interstitial disorder. The remainder of this paper is organized as follows. In section 2, the details of the computational method are described. In section 3, we present our calculated results on electronic, magnetic and superconducting properties of FeTM$_x$Se alloys with TM doping. Finally, we give a summary in section 4.

2. Theoretical approach and computational details

We have performed the self-consistent electronic structure calculations of interstitial disorder in FeTM$_x$Se alloys by using the KKR-ASA CPA method within the local-density approximation, formulated in density functional theory. The coherent potential approximation (CPA) is used in our calculations which is considered to be a powerful tool to study random alloys. The substitution of transition-metal in FeTM$_x$Se alloys are assumed to be purely random and treated within the single-site coherent potential approximation. The atomic positions in our unit cell, given in terms of the fractional coordinates, of Fe are located at 2a site: Fe (0.75, 0.25, 0) and seat 2csite Se (0.25, 0.25, $z_{\text{Se}}$). The positions of empty spheres are located at 2c site which are E$_1$(0.25, 0.25, $z_{\text{Se}}$), and E$_2$(0.75, 0.25, 0.5), where E$_1$ and E$_2$ denote the two empty-sphere sub-lattices. The Se height above the Fe plane is given by $z_{\text{Se}} \times c$, where $a$ and $c$ are the lattice parameters of the unit cell. The unit cells for parent FeSe, including the empty sphere (E1 and E2) are shown in figure 1(a). The interstitial transition-metals (Co, Ni, Mn and V) were put at the empty sphere sites.

For both the self-consistent field and density of states calculations, a grid of $24 \times 24 \times 20$ \textbf{$k$} -points was used to perform the calculations. When integrated over the Brillouin zone, we have only 780 \textbf{$k$} -points being distributed in the irreducible BZ. The partial waves are expanded up to ($l_{\text{max}} = 3$) for each atomic sphere in our calculations. For exchange-correlation potential, the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) is used in our calculations. The band structures and Fermi surfaces for these alloys are investigated using the concept of Bloch spectral function (BSF) $A(k, E)$ \cite{23}. For BSF calculations, a small imaginary component of 2 mRy is added to the energy. The present calculations were carried out using the experimental lattice parameters \cite{24} with values for $a = 3.765$Å and $c = 5.518$Å. We took a theoretical value for $z_{\text{Se}} = 0.2343$ from \cite{4} in the calculations.
3. Results and discussions

3.1. Unpolarized calculations

In the following, we perform spin-unpolarized calculations of the electronic structure for FeVxSe, FeMnxSe, FeCoxSe and FeNixSe (x = 0.01, 0.04 and 0.10) alloys. Our results are presented in terms of calculated density of states, band structure and Fermi surfaces.

3.1.1. Density of states (DOS)

We show the calculated density of states (DOS) of pure FeSe and FeTMxSe alloys (where x = 0.0, 0.01, 0.04 and 0.10) in figures 2–5, respectively. The Fermi energy is located at E = 0 eV between the energy ranges of −6 eV to 1 eV. To carry out interstitial doping we make use of the positions of the empty spheres in the unit cell and place the excess transition metals at the empty sphere sites. For ordered FeSe, the density of states at Fermi energy is mainly composed of Fe (3d) states with small contributions from Se (4p) states as well and we find that it is similar to earlier results [3–5, 25].

It is to be noted that the excess of transition-metals (V, Mn, Co and Ni) in FeSe affects the shape of the density of states near the Fermi energy, as is shown in figures 2–5 respectively. It may be seen from these figures that there is a sharp peak around 1.2 eV below Fermi energy and this peak indicates having flat bands near EF. The peak value decreases as the concentrations of V, Mn, Co and Ni increase in parent FeSe but the overall shape of DOS does not change much as compared to FeSe. We also observe that the impurity bands get wider as x increases.

In tables 1 and 2, we have listed the total DOS at Fermi energy, which increases monotonically as the concentration of V, Mn, Co and Ni impurities increases in FeSe. We find that the most of the contribution to the total density of states at the Fermi energy comes from Fe, and the contributions from the excess transition metal and Se are relatively small. The contributions of the empty sphere sub-lattices E1 and E2 in these alloys are very small.

The increase in the concentration of excess transition metals leads to a systematic increase in the DOS at the Fermi energy for FeVxSe, FeMnxSe, FeCoxSe and FeNixSe (x = 0.01, 0.04 and 0.10) alloys. With increasing excess transition-metal concentration, the contributions of 3d and 4s states to the total DOS at EF increase in comparison to the parent alloy FeSe.
If we look at figure 6, there is a sharp peak of $d_{xy}$ orbital at Fermi energy and $d_{3z^2}-1$ orbital near Fermi energy which are the indication of magnetism in case of FeMn$_x$Se. These peaks ($d_{xy}$ and $d_{3z^2}-1$) decrease as the concentration of Mn increases in the systems. If DOS at $E_F$ is higher, then the system will lead to magnetism. According to Stoner criterion, the factors $I N(E_F)$ will be greater than unity, where $I$ is the Stoner exchange integral. Therefore, in this direction, we have also studied the magnetic properties of the Mn-doped FeSe alloys.

Figure 3. The total density of states calculated with KKR-ASA CPA method for (a) FeMn$_{0.01}$Se (b) FeMn$_{0.04}$Se and (c) FeMn$_{0.10}$Se alloys.
3.1.2. Band Structure

The band structure of FeSe, FeV\textsubscript{x}Se, FeMn\textsubscript{x}Se, FeCo\textsubscript{x}Se and FeNi\textsubscript{x}Se along the high symmetry directions (\Gamma – X – M – \Gamma – Z – R – A – M), obtained from unpolarized KKR-ASA CPA calculations, are shown in figures 7–10, respectively. With increasing concentration of excess transition metal, as expected, the bands get
more diffused due to disorder. In particular, the disorder affects the bands around $E_F$ as well as the bands which lie between $-6.0$ eV to $-4.0$ eV and they become diffused. The changes that take place in the bands are reflected in the corresponding DOS. If we see bands near $E_F$ at M point, the bands shift down as the concentration increases in case of FeV$_x$Se, FeMn$_x$Se, FeCo$_x$Se and FeNi$_x$Se. From figures 7–10 we can safely conclude that the

Figure 5. The total density of states calculated with KKR-ASA CPA method for (a) FeNi$_{0.01}$Se (b) FeNi$_{0.04}$Se and (c) FeNi$_{0.10}$Se alloys.
introduction of excess transition metals in the interstitial positions of FeSe leads to significant changes in the band structures of these alloys with respect to ordered FeSe. The excess of V, Mn, Co and Ni into FeSe make the bands diffused. From figures 7–10, it can be seen that disorder mainly affects the Fe, V, Mn, Co and Ni derived bands. It is also important to note that there are rearrangement of bands in these alloys with increasing $x$.

Figure 6. The unpolarized $d$-projected density of states of Mn in FeMnxSe alloys for $x = 0.01$ (a), 0.04 (b) and 0.10 (c).
3.1.3. Fermi surface

The Fermi surface (FS) of some metals like Fe, Mn, Co, Ni etc have been extensively investigated experimentally and theoretically. At present, their shapes of FS are well known. However, the FS of alloy is not easy to understand. The FS of parent FeSe has been studied by many researchers [3–5, 7, 26]. In the following, we investigate the changes in the FS of FeV_xSe, FeMn_xSe, FeCo_xSe and FeNi_xSe alloys with respect to the parent FeSe.

The dispersion relations of figures 7–10 along with E_F allow us to calculate the FS of these alloys. Using Fermi surface of these alloys, we can study the effects of disorder and Fermi surface nesting due to the excess of V, Mn,
Co and Ni into FeSe. From the band structure shown in figures 7–10, we find band crossing the Fermi energy in $\Gamma - X - M$ and $Z - R - A$ planes. The calculated FS of pure FeSe and FeTM$_x$Se in $\Gamma - X - M$ and $Z - R - A$ planes are shown in figures 11–15 respectively.

Our calculations of these FS lead to the following results. The Fermi surface of pure FeSe is shown in figure 11. We find that the $\Gamma$ point is surrounded by two hole-like sheets while the $M$ point has two electron-like sheets surrounding it. Our results are similar to the results obtained earlier [3–5]. The FS of FeV$_x$Se is shown in figure 12. With increasing V concentration, the size of electron-like sheets increases at M point and the size of hole-like sheets decrease at $\Gamma$ point in $\Gamma - X - M$ plane. For the present system, electron doping occurs as $x$ increases from 0 to 0.10 leading to a systematic increase in the Fermi energy. The increase in the Fermi energy reduces the hole pockets at the $\Gamma$ point. At the same time, the electron pockets at the X point become larger in case of FeV$_x$Se alloys. The adverse effects of both changing $E_F$ and the topology is to reduce the FS nesting in case of large doping [3, 27, 28]. For FeV$_{0.10}$Se, we find that electron-like sheets show the dominant nature with respect to hole-like sheets, and thus, it may be that only electron-like sheets will play a crucial role for higher
concentrations of V in these alloys. Similar behaviour can be seen in Z – R – A plane. In case of FeMn$_x$Se, it is seen that the size of electron-like sheets increase at M point and the size of hole-like sheets decrease at Γ point in Γ – X – M plane. But in Z – R – A plane, there is subtle change in the shape of hole-like sheets and disorder can be seen clearly as the the concentration of Mn increases. In case of FeCo$_x$Se, we see that there is an increase in the size of electron-like sheets but there is no significant change in the shape of hole-like sheet except for the effect of disorder. In case of FeNi$_x$Se, the FS are close to pure FeSe except small changes in the shapes of electron and hole-like sheets both in Γ – X – M and Z – R – A planes.

A schematic diagram for understanding the perfect Fermi surface nesting and superconducting gaps of Fe-based superconductor is shown in figure 16. In this diagram, there is an electron pocket around M (π, π) point, which is shown by dashed line circle and a hole pocket of roughly equal size around Γ (0, 0) point, which is shown by solid line circle. The superconducting energy gap is denoted by Δ. For optimal Fermi surface nesting, two pieces of FS should match precisely when displaced by a reciprocal space vector. In the present case, it implies that the FS pieces around Γ point and M point are connected by a reciprocal space vector. It is clear from

Figure 9. The band structure of (a) FeCo$_{0.01}$Se (b) FeCo$_{0.04}$Se and (c) FeCo$_{0.10}$Se alloys, obtained from unpolarized KKR-ASA CPA calculations.

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figure 12 to 15 that the excess of V, Mn, Co and Ni reduces the possibility of FS nesting in these alloys due to the combined effect of disorder and electron addition and hence, decreases the spin fluctuation in these systems.

3.2. Spin-Polarized calculations

The electronic and magnetic properties of FeMn$_{0.01}$Se, FeMn$_{0.04}$Se and FeMn$_{0.10}$Se alloys are obtained using total energy minimization technique to find the respective equilibrium lattice constant. We have carried out both unpolarized and spin-polarized KKR-ASA CPA calculations for these alloys. However, the energy difference between unpolarized and spin-polarized (ferromagnetic) calculations are very small. Therefore, in the following we present the calculated density of states, band structure and Fermi surface of FeMn$_{0.01}$Se, FeMn$_{0.04}$Se and FeMn$_{0.10}$Se alloys for both spin-up and spin-down electrons.
3.2.1. Density of states (DOS)

Total DOS of alloys are shown in figure 17. To illustrate the effect of disorder, the atom resolved DOS for Fe, Mn and Se are also shown in figure 17. The largest contribution coming from 3d states of Fe, with a small contribution from 3d states of Mn. It can be seen from table 3 that the density of states at EF increases to 1.222 eV/f.u. from 1.156 eV/f.u. in the FeMn_xSe alloys. We also notice in both spin-up and spin-down DOS that the DOS peak near 0.9 eV decreases as the concentration of Mn in FeMn_xSe alloys increases. We find similar behaviour between -4 eV and -5 eV. It is also clear from table 3 that both the spin up and spin down DOS as well as the total magnetic moment (TMM) and local magnetic moment (LMM) increase as x increases in FeMn_0.01Se, FeMn_0.04Se and FeMn_0.10Se, which are listed in table 3.

For a clear understanding of the evolution of magnetization in FeMn_xSe alloys, the spin-polarized, d-projected DOS of Fe and Mn are shown in figure 18. The spin-polarized, d-projected DOS of Fe, Mn in FeTM_xSe have been resolved into four non-degenerate x, y(xz) and -3z^2-12 and -x^2+y^2 symmetry components. We find that there is a degeneracy in yz and xz symmetry components. When the splitting of the d-orbital occurs, it gets divided in t_2g (the upper part with higher energy, d_3z^2 and d_yz^2) and e_g (the lower part with lower energy, d_3z^2 and d_yz^2) symmetry orbitals.

From the d-projected DOS of Fe in figures 18(a), (b), (c), we see small changes in spin-up and spin-down DOS but same is not true for Mn as shown in figures 18(d), (e), (f). We notice that the DOS at the Fermi energy decrease in the case of spin-down d_yx but for d_yx and d_yz it decreases both for spin-up and spin-down as the concentration of Mn increase in FeSe. On the other hand we find that the spin-up DOS increases in case of d_yx but it increases for both spin-up and spin-down in case of d_yz^2-1.

In case of d-projected DOS of Mn, as shown in figures 18(d), (e), (f), both spin-up and spin-down DOS have significant changes. It can be said that present system is being magnetic due to the presence of Mn in FeSe.

3.2.2. Band structure

The band structure has been calculated with the KKR-ASA CPA method using the concept of the Bloch Spectral Function (BSF) [23]. The spin-polarized band structure of FeMn_0.01Se, FeMn_0.04Se and FeMn_0.10Se alloys for both up and down spins are shown in figure 19. It can be pointed out from these figures that doping of Mn in FeSe modifies the band structure of the spin-up and spin-down states of these alloys with respect to the band structure of ordered FeSe. The reason of modifications are the Fe- and Mn-derived bands near Fermi energy and the diffused bands indicate disorder as seen in figure 19. We clearly find that the electron doping disorders the system resulting in the diffused bands as well as the lowering of Fe and Mn derived bands. The disorder is increasing with increasing x.

3.2.3. Fermi surface

For metallic systems, it is very important to study the FS. In this direction, we have carried out spin-polarized calculations of FS for these alloys in the Γ – X – M and Z – R – A planes. The calculated FS of FeMn_0.01Se, FeMn_0.04Se and FeMn_0.10Se alloys are shown in figures 20–21 for both the spin-down and spin-up bands. The FS was calculated using a two-dimensional 151 × 151 k-grid in the Γ – X – M and Z – R – A planes. By examining figures 20–21, the effects of interstitial doping of Mn on the FS of FeSe can be seen clearly in figures 20–21. The Fermi surface of these alloys show changes in terms of electron-like and hole-like sheets. If we
see the topology of these FS, we find that the electron-like pocket at M point increases in size while the size of hole-like sheets decrease as a function of $x$ increases in these alloys. It is interesting to see that the overall topology of these FS of FeMn$_{0.01}$Se, FeMn$_{0.04}$Se and FeMn$_{0.10}$Se alloys are still similar to FS of parent FeSe except disorder. From a comparison of spin up and spin down FS, it is noticed that there are notable changes in terms of disorder and FS nesting in spin-up with respect to spin-down bands.

Figure 12. The Fermi surfaces of FeV$_x$Se alloys in $\Gamma - X - M$ (a), (c), (e) and $Z - R - A$ (b), (d), (f) planes for $x = 0.01$ (a), (b), $x = 0.04$ (c), (d) and $x = 0.10$ (e), (f), as obtained from unpolarized KKR-ASA CPA calculations.
3.2.4. Sommerfeld constant and electron-phonon mass enhancement factor

To calculate the superconducting transition temperature for these alloys, we calculated bare Sommerfeld constant ($\gamma_b$) and electron-phonon mass enhancement factor ($1 + \lambda$) of FeSe and FeTM$_x$Se alloys that can be seen in table 7 and 8. We already calculated the density of states at Fermi level for these alloys and that has a direct relation to bare Sommerfeld constant. We know that the electronic heat capacity of a free-electron gas can be written as, $C_e = \gamma_b T$, where $T$ is the absolute temperature and $\gamma_b$ is the ‘bare’ Sommerfeld constant. The ‘bare’ Sommerfeld constant $\gamma_b$ is proportional to the density of states, $N(E_F)$. The details of theory and formulas that

Figure 13. The Fermi surfaces of FeMn$_x$Se alloys in $\Gamma - X - M$ (a), (c), (e) and $Z - R - A$ (b), (d), (f) planes for $x = 0.01$ (a), (b), $x = 0.04$ (c), (d) and $x = 0.10$ (e), (f), as obtained from unpolarized KKR-ASA CPA calculations.
we used here, can be seen in [3, 5, 7, 26]. In our calculations, we did not take into account the contributions of electron–electron interaction as well as contribution from spin fluctuations.

The experimentally determined value of Sommerfeld constant ($\gamma$) of FeSe is found to be 5.73 mJ mol$^{-1}$ K$^{-2}$ [29]. An enhancement of the density of states at the Fermi energy leads to an increase in $\gamma_b$. Since $N(E_F)$ increases with increase in impurity concentration, consequently, the bare Sommerfeld constant $\gamma_b$ also increases with increasing $x$. In our calculations, we find that the bare Sommerfeld constant $\gamma_b$ is enhanced with increasing

![Figure 14: The Fermi surfaces of FeCo$_x$Se alloys in $\Gamma - X - M$ (a), (c), (e) and $Z - R - A$ (b), (d), (f) planes for $x = 0.01$ (a), (b), $x = 0.04$ (c), (d) and $x = 0.10$ (e), (f), as obtained from unpolarized KKR-ASA CPA calculations.](image)
impurity concentration $x$. We also notice that the value of electron-phonon mass enhancement factor increases as the concentration of transition-metals increases.

3.2.5. *Hopfield parameter*

An accurate evaluation of the Hopfield parameter, $\eta$, electron-phonon coupling constant, $\lambda$, and the superconducting transition temperature, $T_c$, require the use of full-potential. However, within a spherically-averaged calculation carried out in atomic-sphere approximation, one can still get an approximate estimate of $\eta$.

*Figure 15.* The Fermi surfaces of FeNi$_x$Se$_{1-x}$ alloys in $\Gamma - X - M$ (a), (c), (e) and $Z - R - A$ (b), (d), (f) planes for $x = 0.01$ (a), (b), $x = 0.04$ (c), (d) and $x = 0.10$ (e), (f), as obtained from unpolarized KKR-ASA CPA calculations.
\[ \lambda = \sum_i \frac{\eta_i}{M_i w_i^2} \]  

where the sum is over the basis atoms in the primitive cell, \( M \) is the atomic mass and \( \langle w_i \rangle \) is an average phonon frequency. We used \( \langle w_i \rangle = 0.5Q_D \) formula to estimate the average phonon frequency.

From tables 4, 5 and 6, we observe that the total Hopfield parameter increases as the impurity concentration increases in FeV\textsubscript{x}Se, FeMn\textsubscript{x}Se, FeCo\textsubscript{x}Se and FeNi\textsubscript{x}Se alloys. It is clear from equation (1) that the electron-phonon coupling constant \( \lambda \) is proportional to Hopfield parameter \( h \), hence \( \lambda \) will increase for these alloys.

The calculated Hopfield parameters, associated with atoms in these alloys, given in tables 4, 5 and 6, are very small. Thus, we can say that the contributions of electron-phonon coupling to \( T_c \) is very small which suggest an unconventional mechanism for superconductivity in these alloys.

### 3.2.6. The Calculated Superconducting Transition Temperature \( T_c \)

We have used the Hopfield parameter, as listed in tables 4, 5 and 6 to calculate \( \lambda \) and then \( T_c \) of FeTM\textsubscript{x}Se alloys, with the help of MacMillan’s formula [30, 31].

\[ T_c = \frac{\Theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \]  

where \( \Theta_D \) is the Debye temperature and \( \mu^* \) is the so called pseudopotential which takes into account the Coulomb electron-electron interaction. In calculating \( T_c \) using MacMillan’s formula we have used \( \mu^* = 0.1 \) and \( \Theta_D = 210 \text{ K} \) [32]. Our results in terms of Sommerfeld constant \( (\gamma_c) \), electron-phonon coupling constant \( \lambda \) and the superconducting transition temperature \( (T_c) \) are presented in table 7 and 8 for FeTM\textsubscript{x}Se alloys. We have estimated the calculated \( T_c \) for these alloys using the experimental value for FeSe. Lack of experimental values of...
γb for alloys other than FeSe makes it difficult to carry out a systematic study of changes in Tc in other FeTMxSe alloys. Experimental values of γb for alloys would make the electron-phonon mass enhancement factor more reliable, which in turn, would give a more reliable Tc, in agreement with the experiments [19].

Figure 17. The total spin-polarized density of states calculated with KKR-ASA CPA method for (a) FeMn0.01Se, (b) FeMn0.04Se and (c) FeMn0.10Se alloys.
Figure 18. The spin-polarized d-projected density of states calculated with KKR-ASA CPA method for Fe (a), (b), (c) and Mn (d), (e), (f) in FeMn$_x$Se alloys for $x = 0.01$, 0.04 and 0.10.

Table 4. The values of the Hopfield parameters $\eta$ for FeV$_x$Se and FeMn$_x$Se alloys, obtained from 1, as described in the text.

| $x$   | $\eta_{Fe}$ | $\eta_{V}$ | $\eta_{Se}$ | $\eta_{Fe}$ | $\eta_{Mn}$ | $\eta_{Se}$ |
|-------|--------------|-------------|-------------|--------------|--------------|-------------|
| 0.0   | 0.007        | 0.0         | 0.126       | 0.0          | 0.007        | 0.126       |
| 0.01  | 0.008        | 0.007       | 0.107       | 0.01         | 0.021        | 0.284       |
| 0.04  | 0.011        | 0.009       | 0.008       | 0.04         | 0.065        | 0.559       |
| 0.10  | 0.043        | 0.027       | 0.144       | 0.10         | 0.172        | 0.938       |
Figure 19. The calculated spin polarized band structures for the spin down (a), (c), (e) and spin up (b), (d), (f) bands of FeMn$_{0.01}$Se, FeMn$_{0.04}$Se and FeMn$_{0.10}$Se alloys obtained with KKR-ASA CPA method. Fermi energy is set at 0 eV and represented by the horizontal dashed line in the figure.

Table 5. The values of the Hopfield parameters $\eta$ for FeCo$_x$Se and FeNi$_x$Se alloys, obtained from 1, as described in the text.

| $\eta$ for FeCo$_x$Se (mRy/(a.u.$^2$)) | $\eta$ for FeNi$_x$Se (mRy/(a.u.$^2$)) |
|---|---|
| $\eta_{Fe}$ | $\eta_{Co}$ | $\eta_{Se}$ | $\eta_{Fe}$ | $\eta_{Ni}$ | $\eta_{Se}$ |
| 0.01 | 0.014 | 0.001 | 0.203 | 0.01 | 0.008 | 0.021 | 0.129 |
| 0.04 | 0.004 | 0.002 | 0.401 | 0.04 | 0.010 | 0.001 | 0.146 |
| 0.10 | 0.092 | 0.006 | 0.657 | 0.10 | 0.016 | 0.043 | 0.207 |
Figure 20. The spin-polarized Fermi surfaces of spin down (a), (b), (c), (f) and spin up (c), (d), (g), (h) bands of (a), (b), (c), (d) FeMn$_{0.01}$Se (e), (f), (g), (h) FeMn$_{0.04}$Se alloys in (a), (c), (e), (g) $\Gamma - X - M$ and (b, d, f, h) $Z - R - A$ planes, as obtained with KKR-ASA CPA method.
Figure 21. The calculated spin-polarized Fermi surfaces of spin down (a), (b) and spin up (c), (d) bands of (a), (b) FeMn0.10Se alloys in (a), (c) $\Gamma - X - M$ and (b, d) $Z - R - A$ planes.

Table 6. The spin-polarized values of the Hopfield parameters $\eta_{\text{calc}}$ (calculated in mRy/(a.u.)$^2$) for FeMn$_x$Se alloys (where $x = 0.0, 0.01, 0.04, 0.10$), obtained from $1$, as described in the text.

| Alloy         | $\eta_{\text{Fe}}$ | $\eta_{\text{Mn}}$ | $\eta_{\text{Se}}$ |
|---------------|---------------------|---------------------|---------------------|
| FeMn$_{0.01}$Se | 0.008               | 0.004               | 0.123               |
| FeMn$_{0.04}$Se | 0.009               | 0.005               | 0.099               |
| FeMn$_{0.10}$Se | 0.015               | 0.008               | 0.084               |

Table 7. The calculated values of the superconducting transition temperature $T_c$(K) for FeV$_x$Se and FeMn$_x$Se alloys, obtained from MacMillan’s formula, $2$, as described in the text.

| Alloy          | $\gamma_0$ | $\lambda$ | $T_c$ | Alloy          | $\gamma_0$ | $\lambda$ | $T_c$ |
|----------------|------------|-----------|-------|----------------|------------|-----------|-------|
| FeSe           | 2.713      | 1.11      | 14.1  | FeMn$_{0.01}$Se | 2.984      | 0.92      | 10.6  |
| FeV$_{0.01}$Se | 2.713      | 1.11      | 14.1  | FeMn$_{0.04}$Se | 3.713      | 0.54      | 2.88  |
| FeV$_{0.04}$Se | 2.736      | 1.09      | 13.8  | FeMn$_{0.10}$Se | 4.953      | 0.16      | 0.00  |
| FeV$_{0.10}$Se | 2.972      | 0.93      | 10.7  |                 |            |           |       |
4. Conclusions

In conclusion, an *ab-initio* study of the electronic, magnetic and superconducting properties of FeTMₙSe alloys (where $x = 0$, 0.01, 0.04 and 0.10; TM = V, Mn, Co, Ni) has been conducted in order to understand the effects of disorder using KKR-ASA method within the CPA. We find that the excess of transition metal atoms V, Mn, Co and Ni, substantially modify the electronic structure with respect to FeSe. In fact the excess of Mn in FeSe makes FeMnₙSe alloys nearly magnetic. We also find that the excess of V, Mn, Co and Ni diminish the possibility of FS nesting in these alloys due to the combined effects of disorder and electron addition. We have estimated the $T_c$ for these alloys. Additionally, we find from the calculated Hopfield parameters that electron-phonon contribution is very small in these alloys.

Inclusion of electron correlations, a more accurate calculation of electron-phonon interactions, incorporation of spin fluctuations and the experimentally determined Sommerfeld constant for higher concentrations would make the present approach more accurate. At the present time, there are no experimental results for band structure and FS for these alloys, however, we hope that these studies of alloys will motivate relevant experiments with these systems. It is likely to require further studies, both experimental and theoretical, to resolve the origin of magnetism in these superconductors.

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Table 8. The calculated values of the superconducting transition temperature $T_c (K)$ (calculated) for FeCoₙSe and FeNiₙSe alloys, obtained from MacMillan’s formula, as described in the text.

| Alloy       | $\gamma_p$ | $\lambda$ | $T_c$ (K) | Alloy       | $\gamma_p$ | $\lambda$ | $T_c$ (K) |
|-------------|------------|-----------|-----------|-------------|------------|-----------|-----------|
| FeCo₀.₀₁Se  | 2.918      | 0.96      | 11.4      | FeNi₀.₁₀Se  | 2.781      | 1.06      | 13.2      |
| FeCo₀.₀₄Se  | 3.480      | 0.65      | 4.9       | FeNi₀.₉₄Se  | 2.998      | 0.91      | 10.4      |
| FeCo₀.₁₀Se  | 4.425      | 0.93      | 0.1       | FeNi₀.₉₆Se  | 3.41       | 0.67      | 5.6       |

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| Alloy       | $\gamma_p$ | $\lambda$ | $T_c$ (K) | Alloy       | $\gamma_p$ | $\lambda$ | $T_c$ (K) |
|-------------|------------|-----------|-----------|-------------|------------|-----------|-----------|
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| FeCo₀.₁₀Se  | 4.425      | 0.93      | 0.1       | FeNi₀.₉₆Se  | 3.41       | 0.67      | 5.6       |
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