The role of correlations in the high-pressure phase of FeSe

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Abstract
This study addresses the structural and electronic properties of the NiAs- and MnP-type phases dominating in FeSe at high pressures. The analysis is performed using first-principle band structure calculations within the framework of the B3LYP hybrid exchange–correlation functional. Based on the volume–pressure relation deduced from the available experimental data, we optimize the form and internal coordinates of the unit cell, which agree reasonably well with experiment. In particular, the present calculations resolve the structural NiAs–MnP phase transition which occurs at about 10 GPa. Both structures are found to be semiconducting at low pressures and metallizing at about 80–90 GPa. Using the complementary LDA + U approach the semiconducting state can be explained as the result of the strong local correlations within the Fe d-shell.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
New perspectives for understanding the high-\(T_c\) superconducting mechanisms are closely connected with the recently proposed group of iron arsenide based compounds [1–6], which exhibit critical temperatures up to 55 K [7]. The superconducting state of these materials is often found in close proximity to the magnetic transition. In turn, such a situation makes the experiments under pressure [8] of special importance since the magnetism is typically suppressed by decreasing the volume. In addition, the pressure is the cleanest tuning parameter that allows us to apply the full power of \textit{ab initio} electronic structure methods.

One of the simplest materials related to the iron arsenide family is the tetragonal (\(P4/nmm\), group no. 129) \(\beta\)-phase of FeSe formed by the layers of edge-sharing tetrahedrons. Upon cooling, the tetragonal phase undergoes a slight orthorhombic distortion by lowering its symmetry down to \(Cmma\) (group no. 67) [9, 10]. This phase transition takes place within a broad temperature range centered at about 100 K, depending on the crystal size and stoichiometry [9–11]. At rather ordinary temperatures (\(\sim 8\) K) it becomes superconducting [12], however by applying pressure the \(T_c\) rises amazingly high (up to 37 K at about 7–9 GPa) [8, 13, 14]. This important information may indicate the direction in which to search for new superconductors with even higher \(T_c\). At first glance, the pressure dependence of the \(T_c\) in FeSe is reminiscent of the superconducting dome observed in many unconventional superconductors, such as cuprates, heavy fermions and pnictides. In contrast to these systems, vanishing superconductivity in FeSe at very high pressure is related to the first-order structural transition into a hexagonal (\(P6_3mmc\), NiAs-type) more densely packed phase [8, 15, 16] or its very similar low-temperature orthorhombic modification (\(Pbnm\), MnP-type) [8, 16]. The corresponding structures are shown in figure 1.

Small amounts of NiAs-phase appear already at ambient pressures [15, 17] and gradually substitute the superconducting \(Cmma\) phase until it fully converts into NiAs-type (or MnP-type) at about 30 GPa. This indicates that at least the pressure range of the superconducting dome could be extended if this structural phase transition were avoided. The central aspect in this direction is the knowledge of the electronic structure of the NiAs-type phase and its related properties. Unfortunately there are no systematic studies on this system.

The crucial issue for FeSe is the stoichiometry. Indeed, whereas the tetragonal low-temperature Fe\(_{1.0}\)Se is superconducting, a small increase of Fe amount (e.g. up to Fe\(_{1.0}\)Se) leads to strong magnetic fluctuations which destroy the superconductivity [10, 18]. An analogous situation occurs
by substituting Fe with a small amount of Cu [19, 20].

The early experimental studies on the non-stoichiometric hexagonal phases (e.g. Fe$_2$Se$_3$) performed at the ambient pressure report an antiferromagnetic order [15, 17]. For thin films the ferromagnetic order was reported as well [21]. On the other hand, the stoichiometric hexagonal phase is unstable at ambient conditions; however, even for the lowest pressures the magnetism was revealed only in the form of dynamical fluctuations, but no net magnetic state was observed.

### 2. Structural optimization

The first-principles description of the electronic structure under pressure is a complicated problem since it requires an adequate ‘enthalpy–pressure’ mapping, the so-called equation of state, based on a full structural optimization at each pressure. This task often becomes complicated even for the high-symmetric structures with a single degree of freedom. Indeed, there are different uncontrolled sources of errors ranging from fundamental exchange–correlation inadequacies to the insufficient non-sphericity of the one-particle potential, which might become especially crucial for certain pressure regimes.

The present calculations are based on the so-called CRYSTAL06 code [22] which utilizes the local Gaussian basis well suited for the description of the localized electrons in molecules. This formalism can be also applied to describe the solid state systems, in particular locally correlated insulators and semiconductors. A good choice for the exchange–correlation potential within this formalism is the so-called B3LYP functional [23] which is a mixture of the local density approximation (LDA) [24], the generalized gradient approximation (GGA) [25] and the Hartree–Fock exact exchange. Since the Hartree–Fock method systematically overestimates the band gap and LDA underestimates it, the mixing coefficients are found empirically in order to make use of error cancelation and to improve the approach on average for a wide range of systems. Since the B3LYP approach typically fails to describe itinerant magnetism, our calculations refer to the non-magnetic case. Fortunately this corresponds to the experimental evidence which reports the absence of magnetic order for the stoichiometric FeSe.

In the following we perform the geometrical optimization at each pressure point, i.e. we minimize the enthalpy in terms of the lattice parameters and internal coordinates. The only applied constraint is the fixed volume deduced from exponential interpolation of the experimental volume–pressure relation [14, 26]. This prevents us from making additional errors when using the equation of state, which can become significant at high pressures. Note, that by comparing the optimized MnP- and NiAs-type structures at the same volume, the relevant criterion reduces to the total energy difference. As the starting values, we use the experimental structural data.

Figure 2(b) demonstrates the close agreement with experiment of both optimized MnP- and NiAs-type structures. As follows from the enthalpy differences shown in figure 2(a), the high-symmetric NiAs-type structure is more stable at low pressures, while at high pressures the symmetry is reduced and the MnP-type structure becomes more stable. The zero values of the enthalpy differences within the low-pressure regime
mean that the optimization of MnP-type results in the higher-symmetric NiAs-type. Since the difference between MnP- and NiAs-types is caused by a slight distortion (see figure 2(b)) this does not influence the electronic structure substantially, as indicated by comparison of the density of state (DOS) curves in figure 3. It follows that both phases exhibit a semiconducting band gap. This finding supports the earlier experimental reports [8]. The calculated band gap width (about 2.5 eV at ambient pressure) noticeably exceeds typical experimental values (e.g. $\sim 1.2$ eV for the thin films of hexagonal FeSe [27]), however such an overestimation is typical of all Hartree–Fock based methods.

By increasing the pressure, the band gap gradually shrinks, indicating the possibility of an insulator–metal transition at very high pressures (above 80 GPa). Such behavior suggests the strongly correlated origin of the band gap analogous to the situation encountered, for example, in transition metal oxides including the known high-$T_c$ superconductors [28–32] which exhibit a pressure driven insulator–metal transition accompanied by competition from the localized-itinerant electron contributions.

3. Correlation effects

It is instructive to probe the origin of the band gap by applying alternative approaches which account for the local correlations explicitly, such as the LDA + $U$ method [33]. In figure 4 we compare the LDA and LDA+$U$ derived DOS curves calculated by the linear muffin tin orbital (LMTO) method within the PY-LMTO package [35]. Indeed, it follows that the band gap could be explained on the basis of a static approximation to the local on-site electron correlation, as provided by LDA+$U$.

Figure 3. The total DOS curves calculated using the B3LYP approach for the optimized NiAs-type (gray shaded area) and MnP-type (blue solid line) structures at (a) 9 GPa (NiAs) and 12.1 GPa (MnP), (b) 30 GPa, (c) 80 GPa and (d) 90 GPa.

Figure 4. DOS curves calculated at 0 (gray shaded area) and 11.25 GPa (red solid line) for the NiAs-type phase using the LMTO method. Panels (a) and (b) compare the plain LDA and LDA+$U$ ($U_{\text{eff}} = 7$ eV) results, respectively.

The central parameter of the theory is $U_{\text{eff}} = U - J$, where $U$ and $J$ are the effective (screened) Coulomb direct and exchange interaction potentials. If the $J$ value can be relatively easily calculated from first principles and typically does not exceed 1 eV, the estimation of the screened $U$ parameter is not so straightforward. The bare values of $U$ can be very high (about 10 eV), however in metals they are substantially scaled down due to the intermediate mobile electrons. The first-principles techniques to estimate the screening of the $U$ parameter are too imprecise and computationally demanding to be used as a practical tool. In the present case, since the geometry of the system is known, we can estimate an adequate $U_{\text{eff}}$ from the following fit. As it turns out from the pressure dependence of the total energy (figure 5), the plain LDA description ($U_{\text{eff}} = 0$) is indeed inadequate; the minimum of total energy is found at about 7 GPa (i.e. for the smaller volume). By increasing $U_{\text{eff}}$, the total energy minimum shifts towards lower pressures and finally reaches the ambient point at $U_{\text{eff}} \approx 7$ eV. This huge value of $U$ is not much different...
from typical values needed to obtain adequate results in similar strongly correlated systems [36, 37].

Despite the noticeable difference in the band gap values (about 1.4 eV within LDA + U and 2.4 eV within B3LYP), a certain similarity between the Hartree–Fock and the LDA + U exchange–correlation functionals leads to a qualitatively similar behavior under pressure.

4. Summary

To summarize, we emphasize two important issues addressed within the present work. First, the consistent picture of the FeSe structural phase evolution with pressure is presented. The optimization by the B3LYP functional delivers lattice parameters that agree reasonably well with experiment. In particular, the experimentally observed hexagonal–orthorhombic phase transition which occurs at about 10 GPa is also reproduced in calculations. The second important point concerns the electronic structure, which is qualitatively different from previous numerical studies. Namely, both orthorhombic and hexagonal phases are found to be semiconducting in contrast to the plain LDA/GGA calculations which deliver the metallic state. Also it is shown by the complementary LDA + U calculations that the band gap originates from the strong local correlations in the d–shell of Fe. The band gap reduces with pressure due to the increasing electron delocalization up to the insulator–metal transition which occurs roughly above 80 GPa.

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