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

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We present a systematic study of the high-pressure FeSe phase performed by means of the first-principle electronic structure calculations. Basing on available experimental information about the unit cell geometry we calculate the band structure and characterize the related properties during their pressure driven evolution. The electronic structure including the hybrid functional B3LYP or the Hubbard parameter U for the iron d states lead to the correct semiconducting ground state for the hexagonal stoichiometric FeSe within the broad pressure range (up to 30 GPa).

The intriguing class of materials with respect to high-temperature superconductivity field is presented by iron arsenide based compounds [1–6] which exhibit the critical temperatures up to 55 K [7]. The study of these materials is complicated by the fact that their magnetic and superconducting states are competing at very similar conditions. For this reason the experiments under pressure [8] gain special importance since the magnetism is typically suppressed by decreasing the volume. In addition, the pressure is a cleanest tuning parameter that allows to study the electronic structure by *ab-initio* methods.

Probably the simplest material related to the iron arsenide family is the tetragonal (*P4/nmm*, group No. 129) β-phase of FeSe formed by 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 a crystal size and stoichiometry [9–11]. At rather ordinary temperature (~ 8 K) it becomes superconducting [12], however, with pressure the T_c raises amazingly high (up to 37 K at about 7-9 GPa) [8, 13, 14]. This important information may indicate the direction to search for the new superconductors with even higher T_c, which is the main focus of research. 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. However in contrast to these systems the vanishing of superconductivity in FeSe at very high pressure is related to a first-order structural phase transition to a hexagonal (*P6₃mmc*, 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.

The small amount of NiAs-phase appears already at ambient pressures [15, 17] and gradually substitutes the superconducting *Cmma* phase until it fully converts into NiAs-type at about 30 GPa. This indicates that at least
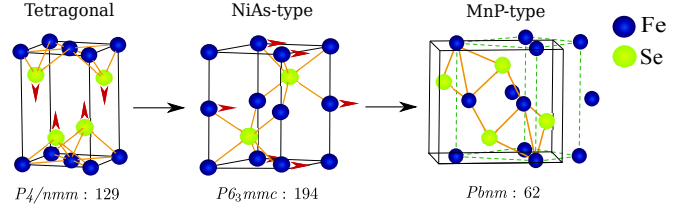

FIG. 1. Pressure driven evolution of FeSe phases: superconducting tetragonal (*Cmma*) phase is transformed to high-symmetry NiAs-type (*P6₃mmc*) structure, which in turn transforms into lower-symmetry tetragonal MnP-type (*Pbnm*) phase by little distortion.

the pressure range of superconducting dome could be extended if this structural phase transition is avoided. The central aspect in this direction is the knowledge of electronic structure of the NiAs-type phase and its related properties. Unfortunately there are no systematic studies on this system.

The crucial aspect for FeSe is the stoichiometry. Indeed, if the tetragonal low-temperature Fe$_{1.01}$Se is superconducting, the small increase of Fe amount (e. g. up to Fe$_{1.03}$Se) already leads to a strong magnetic fluctuations which destroy the superconductivity [10, 18]. The analogous situation occurs by substituting Fe with small amount of Cu [19, 20]. Many early experiments on non-stoichiometric hexagonal phases (e. g. Fe$_7$Se$_8$) 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 reveals only in a form of dynamical fluctuations, but no net magnetic state was observed.

The first-principal description of the electronic structure under pressure is a difficult task since it requires the adequate "total energy–pressure" mapping, or the so-called equation of state, based on a full structural optimization at each pressure point. This task is rather uncertain even for the high-symmetric structures with a single degree of freedom. Indeed, there are different uncontrolled sources of errors which become especially crucial for a certain pressure regime ranging from fundamen-

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tal exchange-correlation inadequacies to the insufficient non-sphericity of the one-particle potential.

Present calculations are based on the so-called CRYS-TAL06 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. As a good choice for the exchange-correlation potential within this formalism appears the so-called B3LYP functional [23] represented as the mixture of LDA [24], GGA [25] and the Hartree-Fock exact exchange. Since the Hartree-Fock method systematically overestimates the band gap and LDA symmetrically underestimates it, the mixing coefficients are found empirically in order to make use of error cancellation and to improve the approach in average for the 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 full optimization of geometry, i.e. without any constraints for the lattice parameters and internal coordinates. For the starting values we use the experimental structural data [14, 26]. Figure 2 (b) demonstrates a very close agreement of the
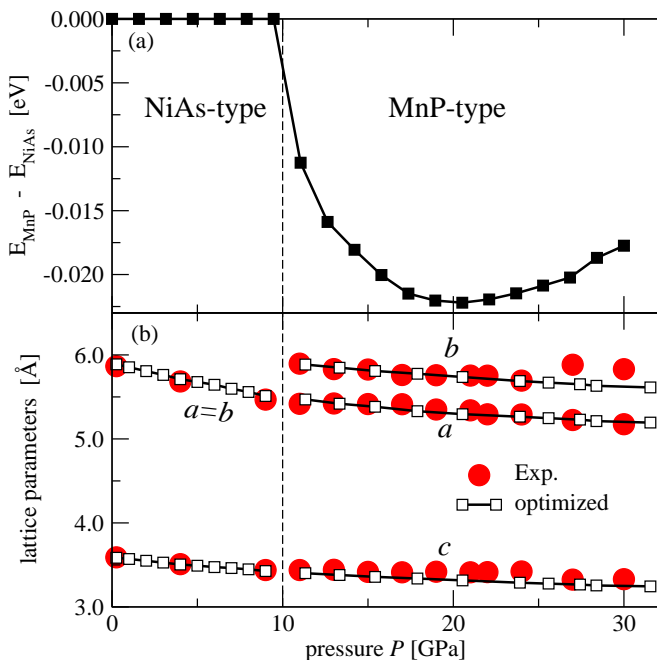

FIG. 2. (color online) (a) Difference of the total energies (per atom) of NiAs- and MnP-type structures calculated as a function of pressure. (b) The pressure driven evolution of the corresponding lattice parameters. The results of optimization are displayed by squares. Red circles mark the experimental data [14, 26].

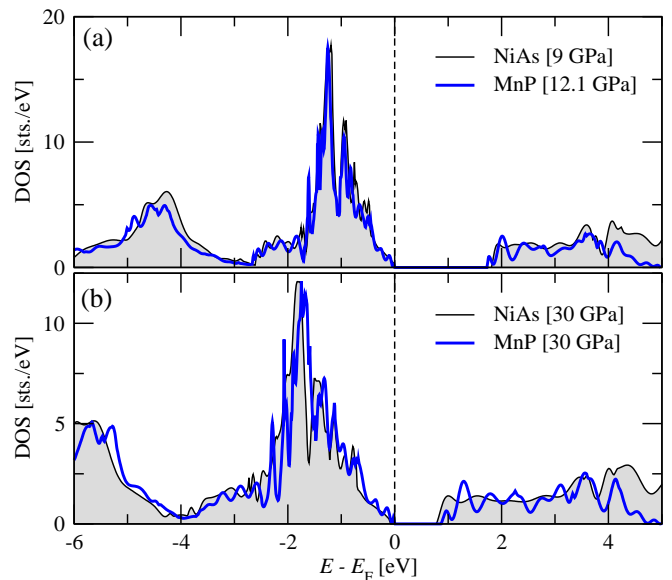optimized structures for both MnP- and NiAs-type struc-

FIG. 3. (color online) The total DOS curves calculated for the optimized NiAs-type (gray shaded area) and MnP-type (blue solid line) structures at low (a) and high (b) pressures.

tures with experiment. As it follows from comparison of total energies (Figure 2 (a)) the high-symmetric NiAs-type structure is more stable at low pressures, while at high pressures the symmetry is reduced to more general MnP case. Since this change is caused by a slight distortion (see Figure 2 (b)) it does not influence the electronic structure as indicated by comparison of the DOS curves on Figure 3. For this reason in the following we restrict the consideration to more symmetric NiAs-type structure.

As it follows from Figure 3, NiAs-type (as well as MnP-type) phase exhibits a semiconducting band gap. This finding supports the experimental reports [8]. The calculated band gap width (about 2.5 eV at ambient pressure) noticeably exceeds typical experimental values (e. g. ~ 1.2 eV for the thin films of hexagonal FeSe [27]), however such overestimation is typical of all Hartree-Fock based methods.

By increasing the pressure, the band gap gradually shrinks indicating the possibility of insulator-metal transition at very high pressures (above 30 GPa). Such behavior suggests the strongly-correlated origin of the band gap analogical to the situation encountered e. g. in transition metal oxides including the known high-T_c superconductors [28–32] which exhibit the pressure driven insulator-metal transition accompanied by competition of the localized-itinerant electron contributions.

It is also instructive to probe the correlation-induced origin of the gap by applying the alternative approaches which account for the local correlations explicitly, as e. g. LDA+U method [33]. On Figure 4 we compare the LDA and LDA+U based total DOS curves calculated by LMTO (Local Muffin-Tin Orbitals) method [34] within
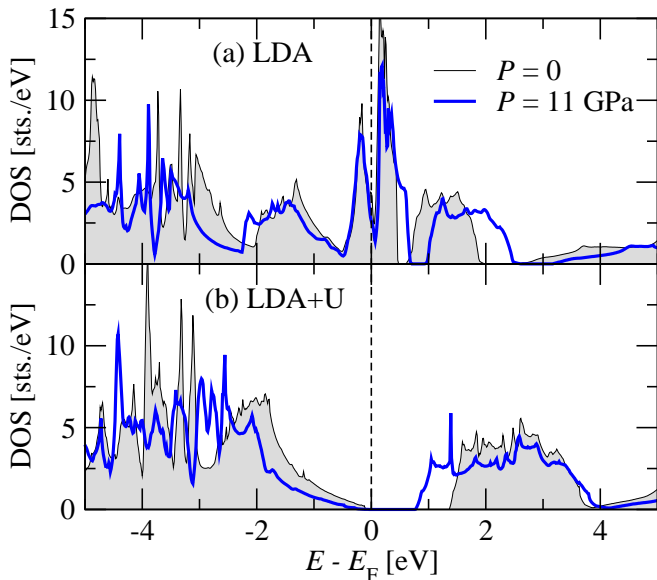
FIG. 4. (color online) DOS curves calculated at 0 (gray shaded area) and 11 GPa (blue curve) for the NiAs-type phase using LMTO method. Panels (a) and (b) compare the plain LDA and LDA+U ($U_{\text{eff}} = 7\,\text{eV}$) results, respectively.
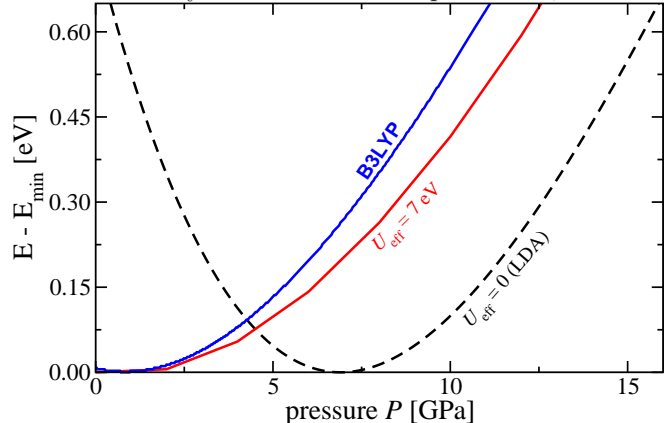

FIG. 5. (color online) Total energy of the NiAs-type phase calculated as a function of pressure within the LDA+U method for $U_{\text{eff}} = 0$ (plain LDA, dashed line) and $U_{\text{eff}} = 7\,\text{eV}$ (red solid line), compared to the B3LYP based calculation (blue solid line).

the so-called PY-LMTO package [35]. Indeed, as it follows the band gap could be explained on the basis of static approximation to the local on-site electron correlation, as provided by LDA+U. At the same time the plain LDA description which lacks the proper treatment of strong correlation delivers a metallic state in agreement with earlier calculations [36]. The latter is characterized by a high peaks of DOS at the Fermi energy, indicating the instability of the plain LDA solution. The band gap is opened due to the strong Coulomb repulsion which splits the correlated Fe d-shell into lower and upper Hubbard bands. By decreasing the volume the Hubbard bands broad, i. e. delocalize and the system metallizes.

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 easy calculated from the first principles and typically does not exceed $1\,\text{eV}$, the screened U parameter makes problems. The bare values of U can be very high (about $10\,\text{eV}$), however in metals they are substantially scaled down due to the intermediate mobile electrons. The first-principle techniques to estimate the screening of U parameter are too imprecise and computationally demanding in order to be used as practical tool. In present case, since the geometry of the system is partially known, we can estimate the adequate U_{eff} from the following fit. As it turns out from the pressure dependence of total energy (Figure 5), the plain LDA description ($U_{\text{eff}} = 0$) is indeed inadequate: the minimum of total energy is found at about $7\,\text{GPa}$. By increasing U_{eff}, the total energy minimum shifts towards lower pressures and finally riches the ambient point at $U_{\text{eff}} \approx 7\,\text{eV}$.

This huge value of U is actually not much higher than typical values needed to obtain the adequate results in similar strongly correlated systems [37, 38].

Despite the noticeable difference of the band gap values (about $1.4\,\text{eV}$ within LDA+U and $2.4\,\text{eV}$ within B3LYP), certain similarity between the Hartree-Fock and LDA+U exchange-correlation functionals lead to a similar behavior of the system under pressure which indicates the Mott insulating origin of the NiAs-type phase.

To conclude, we emphasize that the hexagonal phase of FeSe which substitutes the tetragonal superconducting phase at higher pressures is characterized as locally correlated. These local correlations lead to an insulating state which can be classified as Mott insulator. The band gap reduces due to increasing electron delocalization with pressure up to the insulator-metal transition which occurs roughly above $30\,\text{GPa}$. These results reasonably correspond to the experimental studies of FeSe and related systems under high pressure.

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