Structural transition of FeSe under high pressure*

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(Received 25 July 2010; revised manuscript received 25 September 2010)

The density functional calculations of the energy band structure and density of state for the tetragonal PbO-type phase α-FeSe and hexagonal NiAs-type phase β-FeSe are reported in this paper. The structural phase transition from tetragonal to hexagonal FeSe under high pressure is investigated, it is found that the calculated transition pressure for the $\alpha \rightarrow \beta$ phase transformation is 8.5 GPa. Some fluctuations in the transition pressure maybe occurred by different external factors such as temperature and stress condition. There is about 17% volume collapse accompanying the $\alpha \rightarrow \beta$ phase transformation.

Keywords: FeSe, density functional calculations, phase transition

PACS: 61.50.Ks, 71.15.Mb, 81.30.–t **DOI:** 10.1088/1674-1056/20/2/026101

The discovery of superconductivity in the iron selenide with tetragonal PbO structure has aroused a wide scope of exploration related to FeS.[1−14] Because of the pressure dependence of the superconducting transition temperature of FeSe, many investigations on press-induced structural transition of FeSe were made. D Braithwaite performed a room temperature high pressure x-ray diffraction study up to 12 GPa on an FeSe sample, and found that the tetragonal PbO structure undergoes a structural transition to a hexagonal structure between 8.5 GPa and 12 GPa.[15−19] However, no theoretical study on press-induced structural transition of FeSe was carried out.

According to Ref. [20], FeSe mainly exists with several phases: 1) a tetragonal PbO-type phase α-FeSe; 2) a hexagonal NiAs-type phase β-FeSe with a wide range of homogeneity; 3) an $FeSe_2$ phase which has the orthorhombic structure. When the temperature is higher than 650 °C, α-FeSe transforms completely to β-FeSe. The structural phase transition from tetragonal to hexagonal FeSe under high pressure was investigated using first-principles calculations in our work.

The first-principles calculations presented here were performed based on density functional theory using a plane-wave basis set for the expansion of the wave functions.[21−24] Non-local ultra-soft pseudopotentials were used to describe the interaction of core and valence electrons.

Generalized gradient approximation (GGA) with the Perdrew–Burke–Ernzerhof (PBE) scheme was adopted to evaluate exchange–correlation energy. Monk horse-pack mesh was used to select 56 k-points for bulk calculation. A plane-wave cutoff energy of 340 eV was employed throughout. It was shown that the results are well converged at this cutoff.

The Fe (3d 4s) and Se (4s 4p) were treated as valence state. The geometries for all the systems were optimized. The minimum total energy of the structure was achieved by relaxing the internal coordinates using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The following thresholds for converged structures were employed: energy change per atom less than 2×10^{-6} eV, residual force less than 0.5 eV/nm, stress below 0.05 GPa and the displacement of atoms during the geometry optimization less than 0.001 nm.

The tetragonal α-FeSe was selected, and the lattice parameters, $a = b = 0.377$ nm, $c = 0.552$ nm were taken as a starting point for geometry optimization. The hexagonal β-FeSe was also selected, and the lattice parameters, $a = b = 0.362$ nm, $c = 0.592$ nm were

*Project supported by the National Natural Science Foundation of China (Grant No. 61072028), the Key Science and Technology Program of Guangdong Province of China (Grant No. 2010B010800028), the Natural Science Foundation of Guangdong Province of China (Grant No. 10151063101000048).

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taken as a starting point for geometry optimization.

The energy band structures and density of state (DOS) of FeSe at 0 GPa were obtained. Figure 1 shows the density of state (DOS) of two structure of FeSe at 0 GPa. The DOS of tetragonal α-FeSe is shown in Fig. 1(a), which is basically consistent with the reports of Alaska Subedi.[3] However, the peak near the Fermi level moves left a little bit compared to Ref. [3], since we have chosen GGA rather than LDA. The DOS of hexagonal β-FeSe is shown in Fig. 1(b). There are four main regions (A, B, C and D) in the DOS curve of β-FeSe. The region A in the lower energy part of the DOS curve is mainly derived from Fe (4s) states with less contribution from Se (4s) states, which are localized and contribute little to the bonding of Fe–Se. For the region B, the DOS mainly originates from Se (4p) and Fe (3d) states. For the region C around the Fermi level, the DOS mainly originates from hybridized state of Fe (3d) and Se (4p) states with less contribution from Fe (4s) states. The region D in the lower energy part of the DOS curve is mainly derived from Se (4p) states and Fe (4s) with less contribution from Fe (3d) states. We find that the region D split into two similar peaks in the DOS curve of α-FeSe. This reflects that the Fe layer is sandwiched by the selenium atoms in the tetragonal α-FeSe, and the Fe atoms surrounded by the Se atoms in the hexagonal β-FeSe. The energy band structures and density of state (DOS) of FeSe at 9 GPa were also obtained. For the tetragonal α-FeSe, the DOS curve moves left a little bit while the pressure is increased. However, for the hexagonal β-FeSe, there is almost no change in the DOS curve compared with that of 0 GPa. We think that the electronic structure of the hexagonal β-FeSe is more stable under high pressure than that of the tetragonal α-FeSe.

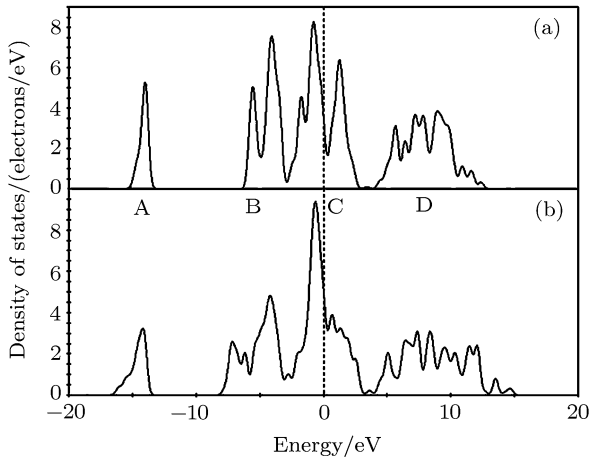


Fig. 1. DOS of FeSe. (a) α-FeSe. (b) β-FeSe.

In order to study the press-induced structural transition of FeSe, we set hydrostatic pressure to FeSe solids with two possible types of structural phases (α and β) and fully optimized both the lattice parameters and atomic positions. The calculated relative enthalpy versus pressure curves for two phases are shown in Fig. 2. The transition pressure is the pressure at which the relative enthalpy curves for two phases will cross. From Fig. 2, we find that the calculated transition pressure for the $\alpha \rightarrow \beta$ phase transformation is 8.5 GPa. We also can see that the enthalpies of α-FeSe and β-FeSe are very close to each other around the transition pressure. It suggests that the relative stability of two phases may be sensitive to external factor. So, some fluctuations in the transition pressure may be occurred by different external factors such as temperature and stress condition. From the calculation we find that there is about 17% volume collapse accompanying the $\alpha \rightarrow \beta$ phase transformation. This is well close to the experimental result of 16% volume collapse.[15]

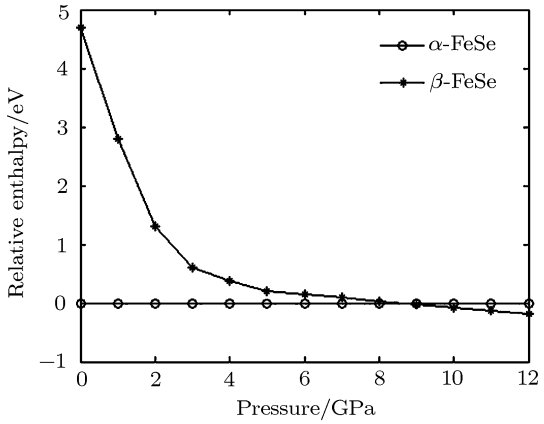


Fig. 2. The calculated relative enthalpy versus pressure.

While the pressure increases, the tetrahedral in the tetragonal α-FeSe actually becomes even more distorted as the deviation of angle becomes even larger.[18] As the pressure rises, the compression is larger along the c axis than along the a or b axis due to the layering of the crystal structure, which is in agreement with the reports of S. Margadonna and Jasmine N. Millican.[16–18] Pressure leads to a rapid decrease in α-phase Se–Se interlayer contacts. As a result the sign of the compressibility along c axis changes and the interlayer spacing begins to increase upon a further increase in pressure. In addition, the three-dimensional β-FeSe is more densely packed than the quasi-two-dimensional structure of α-FeSe.[16] The x-ray and DTA measurements indicated that the transition temperature for $\alpha \rightarrow \beta$ phase is 650 °C,[20] which

is high enough to make the kinetic energy of atoms increase to drive the phase transformation. We think that applying high pressure can also play a similar role to drive the phase transformation through increasing the kinetic energy of atoms.

As mentioned above D. Braithwaite reported the structural of FeSe between 8.5 GPa and 12 GPa, which results in a volume decrease of about 16%.[15] These are in agreement with our calculated results. He found a more complicated structure, which can be indexed best as a mixture of the hexagonal and tetragonal phases, with an additional orthorhombic ($Cmcm$) phase. This orthorhombic ($Cmcm$) phase can be understood as a necessary intermediate phase to allow the transition from tetragonal to hexagonal. We did not calculate the relevant electronic properties of this orthorhombic phase because we lack concrete structure parameters. Medvedev also showed a wide pressure range (7–35 GPa) for phase transition from the tetragonal to hexagonal phase.[19]

In the present work, the energy band structure and density of state (DOS) of FeSe were calculated, and the structural phase transition from tetragonal to hexagonal FeSe under high pressure was investigated by using first-principles calculations. The calculated transition pressure for the $\alpha \rightarrow \beta$ phase transformation is 8.5 GPa. There is about 17% volume collapse accompanying the $\alpha \rightarrow \beta$ phase transformation. We consider that some fluctuations in the transition pressure maybe occurred with different external factors such as temperature and stress condition.

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