Evolution of the electronic structure and structural properties of BaFe$_2$As$_2$ at the tetragonal-collapsed tetragonal phase transition

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ABSTRACT

Density functional theory generalized gradient approximation has been used to calculate the electronic and structural properties of BaFe$_2$As$_2$ compound up to 56 GPa by using Quantum Espresso code. Structural properties like bulk modulus, Fe–As bond length, and As–Fe–As bond angles have been investigated by pressure especially near the tetragonal to collapsed tetragonal (T–cT) structural phase transition. This study shows considerable changes of these parameters in the cT phase, which happens near our calculated critical pressure, $P_c = 24 \pm 2$ GPa. Electronic band structure and its orbital-resolved, total and partial density of states and Fermi surfaces have been investigated in this pressure range. The four hole- and electron-like bands have been decreased to only one electron-like band at the T–cT phase transition. The Fermi surface topology changes from two-dimensional cylinders to three-dimensional pockets in the cT phase. The sharp peaks of total and partial density of state are broadened by pressure and the width of conduction electron states increases continuously to about 2 eV at 56 GPa. The Fe3d states have the main contribution at the density of states at Fermi level, which decreases suddenly near P_c. The considerable changes in these parameters in the cT phase indicate completely different electronic properties of this compound in high pressures relative to the tetragonal phase at ambient pressure.

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1. Introduction

The FeAs superconductors with transition temperature (T_c), as high as 55 K, have been recently attracted for their many interesting physical properties and phase transitions such as structural, superconducting and magnetic transitions either by doping or pressure [1,2]. Applying pressure induces superconductivity even in the undoped systems of these compounds with high rate value of dT_c/dP [3,4], e.g. 34 K/GPa in BaFe$_2$As$_2$ [5]. This effect is much stronger than the similar effect in the high-T_c cuprates [1]. Applying pressure is a clean way to promote T_c avoiding defects or disorder which occurs by the elemental doping. So, this way could be considered as an effective way for promoting T_c by substitution of a suitable chemical doping. Also, obtained interesting correlations between the applied pressure, doping and internal ionic parameters in the superconducting state [6] help us to understand the effects of pressure on the physical properties of these systems.

One of the most interesting cases in this area is BaFe$_2$As$_2$, with having an orthorhombic–tetragonal (O–T) and antiferromagnetic–

paramagnetic phase transitions at about $T \sim 140$ K at ambient pressure [7–9]. Pressure suppresses the antiferromagnetic order and induces superconductivity with the highest T_c of about 29 K [4] or 34 K [5] in 1–4 GPa pressure range. Also, an interesting structural phase transition from tetragonal (T) to collapsed tetragonal (cT) phase, accompanied by an anomalous change of the a lattice parameter has been observed in variety of AFe$_2$As$_2$ (A = Ba, Ca, Sr, Eu) compounds near the critical pressure, P_c [2]. P_c is dependent on the chemical composition or the method of applying pressure like the degree of hydrostaticity [5,10,11], which should be considered very carefully in the result analysis. The electronic properties of the cT phase and its relation to the superconducting state have been considered by different research groups [5,12,13]. However, due to the difficulties of experimental studies in the high pressures, there is lack of transport and electronic structure data in the cT phase especially for BaFe$_2$As$_2$, which has high value of P_c [11].

In the theoretical side, however, ab-initio studies have been considered as an attractive approach to investigate the electronic structure of these systems under applying pressure. Xie et al. have calculated the electronic structure of BaFe$_2$As$_2$ up to 18 GPa by density functional theory (DFT) [14]. From this study a stable antiferromagnetic phase below 13 GPa and a Fermi surface topological

transition in about 6 GPa have been obtained. In another study, two different structural phase transitions have been obtained under hydrostatic and *c*-axis uniaxial pressures as O–T–cT for BaFe$_2$As$_2$ and O–cT for CaFe$_2$As$_2$ [15]. This study indicates a considerable reduction (about one order of magnitude) of P_c in the uniaxial pressure. The effects of in-plane uniaxial [16] and non-hydrostatic pressures [17] also have been studied on the phase transition as complementary studies. Also, the electronic structure of the BaFe$_2$As$_2$ system under high pressures has been investigated to understand the effect of pressure by molecular dynamics method in two different temperatures [18]. However, besides of these studies, there are still many open questions due to the controversy of the experimental and theoretical results and the lack of studies above T–cT phase transition. The purpose of this paper is to evaluate and validate the structural and electronic characteristics of BaFe$_2$As$_2$ in −20 to 56 GPa pressure range including both T and cT phases by ab-initio DFT approach. We especially focus on the bond lengths and angles, band structure (BS), density of states (DOS), and Fermi surface (FS) topology of this system to understand the effects of applied pressure and the T–cT phase transition on the structural and electronic properties.

2. Computational method

The ab-initio calculations have been carried out using pseudopotential Quantum Espresso code [19] with the plane wave basis sets in the generalized gradient approximation by Perdew, Burke and Ernzerhof parameterization [20]. At ambient pressure, BaFe$_2$As$_2$ has a ThCr$_2$Si$_2$-type body-centered tetragonal structure with *I4/mmm* space group (see Fig. 1(a)). Fig. 1(c) and (d) shows the *a* and *c* lattice parameters for 0 < *P* < 56 GPa have been taken from the experimental data at *T* = 300 K [11]. The total energy calculations in the non-magnetic state of this compound has been done for −20.0, −15.3, −9.8, −3.7, −1.8, 0.0, 1.8, 3.7, 9.8, 15.3, 20.0, 25.3, 27.0, 29.6, 32.1, 35.3, 39.6, 45.2, 51.3, 56.0 GPa pressures. The negative pressures have been considered for some calculations such as Murnaghan fitting of the energy–volume data to discuss the expansion effects, where their lattice parameters have been obtained from linear extrapolation of experimental data in the range of 0–10 GPa [11].

At ambient and *P* = 56 GPa pressures, the number of *k*-points in irreducible Brillioun zone (IBZ) and the cut-off energy have been determined to achieve 10^{-5} eV/unit-cell total energy convergency. For integration of the BZ, a Monkhorst–Pack uniform grid mesh of $12 \times 12 \times 4$ points was used, which equals to 115 distinguishable *k* points in the IBZ. The kinetic energy cut-offs for the wavefunctions and charge density have been determined 950 and 9500 eV, respectively. The initial *z* component of As, $z_{As} = 0.3545$ [7], has been taken from the experimental data for all the pressures and then has been relaxed by Broyden–Fletcher–Goldfarb–Shanno quasi-Newton algorithm to reach sufficient small forces as small as 10^{-4} eV/Å [21] in each pressure. For each considered pressure, the calculated pressure has been derived from the trace of the σ stress tensor as $P = Tr(\sigma)/3$ for the isotropic structural deformations from the reference structure. After finding the ground state in each pressure, the BS and its orbital-resolved have been calculated by Marzari–Vanderbilt (with broadening of 0.07 eV) method along the high-symmetry lines of the BZ: $\Gamma–X–M–\Gamma$ ($k_z = 0$) and $Z–R–A–Z$ ($k_z = 0.5$). The total and partial DOS have been calculated by tetrahedron (with finer *k*-points grid mesh, $18 \times 18 \times 6$) method. The FS calculation has been done for a grid of $24 \times 24 \times 8$ in the primitive BZ.

3. Results and discussion

3.1. Structural properties

The *a* and *c* lattice parameters have anomalous behaviors near the T–cT structural phase transition. To check this anomaly in our calculation, the pressure at each considered volume has been calculated and presented in Fig. 1(e). The non-hydrostaticity degree of pressure ($\Delta = \sigma_{zz} - \sigma_{xx}(= \sigma_{yy})$ [17]) has been calculated as small as 0.3–1.7 GPa, which indicates hydrostatic condition in this study. Comparison of the experimental [11] and calculated pressures shows a similar behavior with a negative pressure shift about 3–7 GPa in the calculated pressures. This difference could be originated from the calculation of pressure by DFT method, the experimental errors in the measured pressure or lattice parameters [2,10]. However, this difference is about 10% in the wide considered pressure range and can be neglected in this study.
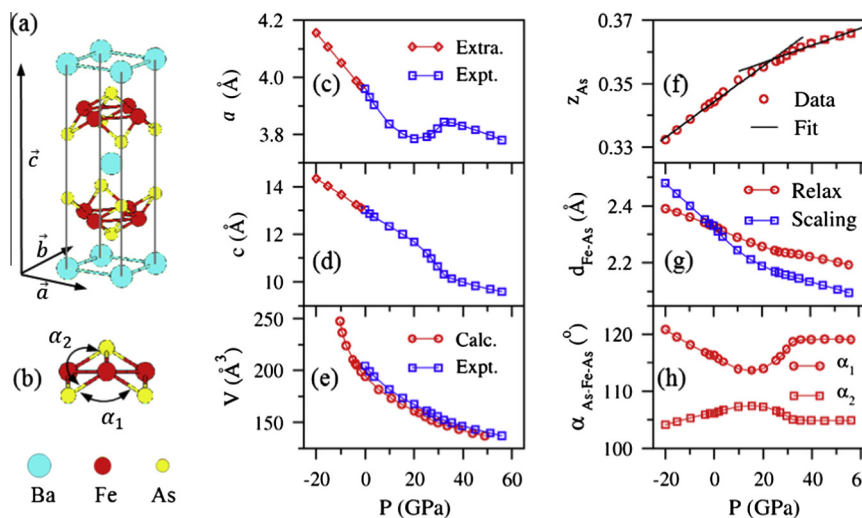

Fig. 1. (a) The body-centered tetragonal crystal structure of BaFe$_2$As$_2$ and (b) two As–Fe–As bond angles (α_1, α_2) in the Fe–As layer. (c) and (d) *a* and *c* lattice parameters for the present calculation from the experimental data (□) [11] and their extrapolation in the negative pressures *e* (e) the conventional unit cell volume versus prussure from the experimental data (□) [11] in comparison with our calculated data (○). (f) The *z* component of As after relaxation, z_{As}, (g) Fe–As bond length, d_{Fe-As}, from scaling (□) and after relaxation (○) and (h) the bond angles α_1 (○) and α_2 (□) versus pressure. The lines in (f) is the linear fitting and in other figures are guides for eyes.