Structural and electronic properties of the iron pnictide compound EuFe$_2$As$_2$ from first principles

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Abstract
We report results of the electronic and mechanical structure properties of the iron pnictide compound EuFe$_2$As$_2$, at zero pressure. The open source computer code Quantum Espresso, which incorporates the Density Functional Theory (DFT), Pseudo Potentials (PP) and the Plane Wave (PW) were used to perform calculations from first principles. Projector-Augmented Wave (PAW) Pseudo Potentials were used in these calculations. The Density of States exhibits a sizeable superconducting gap and the band structure has no bandgap. Calculations were performed from scratch.

Introduction
Iron Pnictides have been studied for their potential application in technology due to their exhibition of high temperature superconductivity [1–3]. Superconductivity at high temperature has been discovered in iron-Pnictide compounds and this has ignited numerous interest and research on the properties of these compounds [4–6]. In previous studies, iron Pnictides have been seen to exhibit superconductivity up to high temperatures of \( \sim 26K \) [7–9]. Compounds based on iron are classified as ‘1111’, ‘122’, ‘111’, and ‘11’ families, depending on their structure and make up [10, 11]. In the 122 family of compounds, AFe$_2$As$_2$ (A = Ba, Ca, Sr, Eu) have stimulated high interest in research since they are easier to synthesize [11]. EuFe$_2$As$_2$ is unique in the 122 family since the Eu atom undergoes Spin Density Wave and Antiferromagnetic ordering magnetic transitions, leading to antiferromagnetic ground state [12, 13]. Other compounds in the 122 Iron Pnictide family include BaFe$_2$As$_2$ and CaFe$_2$As$_2$, which have a relatively similar structure to that of EuFe$_2$As$_2$ [14].

EuFe$_2$As$_2$ is one of the 122 iron Pnictide compounds with a Body-Centered Tetragonal crystal structure [7–9] and also exhibits superconductivity on application of pressure of up to \( \sim 2.5Gpa \) [7, 15–19]. Superconductivity in these compounds can be achieved through doping or application of pressure on the material [20], for example, application of pressure on BaFe$_2$As$_2$ and CaFe$_2$As$_2$ tunes superconductivity [7, 15] with \( T_c \) of up to 38K [21]. In this article, we report on the mechanical and electronic structure properties of EuFe$_2$As$_2$ as studied from first principles.

Computational details
In our study, we used the Plane Wave method to investigate the electronic and mechanical structure properties of EuFe$_2$As$_2$ from first principles, using the open source computer code Quantum Espresso [22–25]. Self-Consistent Calculations were run to obtain the total and Fermi energy of the system, which is a useful parameter in describing the electronic structure properties of the compound [26]. The input files were designed such that the mechanical properties including the Bulk, Shear and Young moduli, and Poisson ratio were obtained. Quantum Espresso supports the use of Projector-Augmented Wave (PAW), Ultra Soft Pseudo Potentials (USPP), which are Norm Conserving. Norm Conserving Pseudo Potentials are well normalized, a feature useful for an accurate description of bonding in the compound [27, 28]. The PAW Non Linear Correction Pseudo Potentials were used in these calculations [29–33]. Before running the Self-Consistent Calculations, the Variable
Cell relax (vc-relax) calculation was performed to obtain relaxed atomic positions and then optimization of cell dimensions, K-points, and the kinetic energy cut off was also done so as to obtain a relaxed crystal structure, to ensure that the ground state crystal structure is obtained and that the results are free from stress [8, 34–36]. The initial k-point sampling was done using $p\_a^2$, where $a$ is the lattice parameter [19]. Optimization of the K-points yielded the converged K-points, convergence ensuring a stress and strain free system [37]. The Density Functional Theory which focuses on the electron density to study the properties of a many-body system was employed.

**Results and discussion**

In this section, we report the various results obtained from the theoretical computation. Figure 1(b) shows the optimized crystal structure for EuFe$_2$As$_2$. There are three types of atoms in the crystal, namely: Europium, Iron and Arsenic. The number of atoms we considered in these calculations were five, one Europium, two iron, and two arsenic. There exists a Europium atom at the center of the structure hence the structure is Body Centered Tetragonal [7, 9], since our optimized structure had the Eu atom in the middle. Below is the crystal structure (b), obtained after vc-relax and optimization. The optimized structure has an Eu atom at the center and shows similar bonding of atoms as other iron Pnictides [13].

In this section, we present results for the optimization of K-points, cell dimensions and kinetic energy cutoff that were used throughout the calculation.

On optimization, the following curves were obtained for the cell dimensions, K-points and kinetic energy cut off. The optimized cut off kinetic energy and k-point value as from figure 2 below is $\sim$45 and $\sim$4 respectively. The optimized cell dimension as from figure 3 below is $\sim$7 Bohr units.

The optimized cell dimension three as from the optimization curve is $\sim$4.2 Bohr units.

In this section, we report on the calculations of the electronic structure properties which included the band structure calculation, Density of States and Partial Density of States.

EuFe$_2$As$_2$ in this case belongs to the 14/mmm space group [10] therefore the following high symmetry points in the Brillouin zone were used $\Gamma(0, 0, 0)$, Z(0, 1/2, 0) B(0, 0, 1/2), Y(1/2, 0, 0), C(1/2, 1/2, 0), D(0, 1/2, 1/2), A(−1/2,0,1/2), E(−1/2,1/2,1/2) [38].

There is a band gap of 0.0eV, which is in agreement with other theoretical studies on the compound [39].

The density of states curve for the compound was obtained as below.

The Density Of States with the long and sharp peaks are between energies of $\sim$7.8 eV and $\sim$10.2 eV as shown in Figure 4 above, and they represent the core electrons that have a minimal contribution to determining the properties of the electrons since they are considered to be chemically inert [42]. The Density of States between
the peaks is zero since states do not exist there as seen in Figure 4 above. A Kondo-like peak is as shown above, in agreement with results from similar iron Pnictides which show similar peaks [36].

Similar pnictide such as BaCa$_2$As$_2$ also exhibits a sizeable gap far from the Gamma-X high symmetry line [43], similar to the one present in the band structure in Figure 5 below and the Density of States.

Figure 2. Optimization curves for the kinetic energy cutoff and K-points. Both parameters exhibit convergence at $\sim$45 and $\sim$4 respectively. K-Point sampling was initially done using $2\pi/a$, $a$ being the lattice parameter. The converged k-point value agrees closely with the computed values.

Figure 3. Optimization curves for cell dimensions. Cell dimension one converges at approximately 7 Bohr units while cell dimension three shows convergence at approximately 4.5 Bohr units. The converged values correlate with the experimental values of 7.4Bohr and 5 [10].

Figure 4. There are two curves, separated by a superconducting gap of $\sim$4.5 eV, in close agreement with the results of other iron Pnictides such as BaFe$_2$As$_2$ [40] which yield coulomb parameters of $\sim$4 eV [8, 36]. It is within this gap that there exists the superconducting state of the compound. The Partial Density of States shows Europium and Iron atoms to be the major contributors to the projecting states. Other minor curves are left out in the illustration since their contribution to the Partial Density of States was minimal. The density of states of other Pnictides shows similar gaps [41].
The mechanical properties we obtained from the computation are summarized in Table 1 below. The Poisson’s ratio was found to be $\sim 0.32$ at absolute zero temperature, our result compared well to a value of 0.302 for other families of Pnictides [41], the difference may be as a result of varying atoms present in the two compounds and a slight difference in the crystal structure. This value further confirmed that EuFe$_2$As$_2$ is a stable and metallic [45,].

Other Pnictides such as SrFe$_2$As$_2$ have a Poisson’s ratio of $\sim 0.48$ upon application of pressure [47], which causes the lattice parameters to change. The Bulk modulus, Shear modulus, and Young’s modulus were found to be $\sim 346$ Gpa, $\sim 136$ Gpa and $\sim 362$ Gpa respectively, implying that the material is hard since the moduli are greater than 200 [48]. The Voigt and Reuss values for the Bulk, Shear and Young moduli values are similar to each other hence their average valid. However, there are scanty report on the structural properties of the iron Pnictide EuFe$_2$As$_2$

The Bulk, Shear and Young moduli and Poisson’s ratio we obtained are as follows:

| Property          | Voigt approximation | Reuss approximation | Voigt-Reuss-hill Average |
|-------------------|---------------------|---------------------|--------------------------|
| Bulk modulus (B)  | 3469.39040 Kbar     | 3463.52950 Kbar     | 3466.45995 Kbar          |
| Young modulus (E) | 3753.78277 Kbar     | 3502.24712 Kbar     | 3628.01495 Kbar          |
| Shear modulus (G) | 1422.24151 Kbar     | 1315.18042 Kbar     | 1368.71096 Kbar          |
| Poisson ratio (n) | 0.31967             | 0.33147             | 0.3254                   |

**Conclusion**

In this study, the electronic structure properties-Density Of States, Partial Density Of States, bands structure and structural properties including Bulk, Shear and Young’s Modulus and Poisson’s ratio of EuFe$_2$As$_2$ were investigated using the open source computer code Quantum Espresso. The compound was stable and the crystal structure was Body Centered Tetragonal, just like experimental details suggested [15]. The band structure and Density of States graph showed a sizable gap, the superconducting gap, implying that the material exhibits superconductivity, in agreement with previous studies on the material. The Poisson’s ratio of the compound implied that the compound was a stable metal.

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References

[1] Dai P, Hu J and Dagotto E 2012 Nat. Phys. 8 709
[2] Mazin I I 2010 Nature 464 183
[3] Norman M R 2008 Phys. Rev. B 78 014506
[4] Kobayashi H, Ikeda S, Sakaguchi Y, Yoda Y, Nakamura H and Machida M 2012 J. Phys. Soc. Jpn. 81 022201
[5] Johnston D C 2010 Adv. Phys. 59 803–1061
[6] Stewart G 2011 Rev. Mod. Phys. 83 1589
[7] Mahesh R and Reddy P P 2018 J. Supercond. Nov. Magn. 31 3111–7
[8] Maier T, Graser S, Scalapino D and Hirschfeld P 2009 Physical Review B 79 134520
[9] Tegel M, Rotter M, Weiss V, Schappacher F M, Potégén R and Johrendt D 2008 J. Phys. Condens. Matter 20 452201
[10] Matiti K 2015 Pramana 84 947–56
[11] Zhang S, Wang X, Sammynaiken R, Tse J, Yang L, Li Z, Liu Q, Desgreniers S, Yao Y and Liu H 2009 Physical Review B 80 014506
[12] Adhikary G, Sahadev N, Biswas D, Bindu R, Kumar N, Thamizhavew A, Dhar S and Matiti K 2013 J. Phys. Condens. Matter 25 225701
[13] Dai Y, Akrap A, Budko S, Canfield P and Homes C 2016 Physical Review B 94 195142
[14] Kobayashi H, Ikeda S, Sakaguchi Y, Yoda Y, Nakamura H and Machida M 2012 J. Phys. Condens. Matter 25 022201
[15] Alireza P L, Ko Y C, Gillett J, Petrone C M, Cole J M, Lonzarich G G and Sebastian S E 2008 J. Phys. Condens. Matter 21 012208
[16] Miciea C, Nicklas M, Jeovan H, Kasinathan D, Hossain Z, Rosner H, Gegenwart P, Geibel C and Steglich F 2009 Physical Review B 79 212509
[17] Nicklas M, Kumar M, Lengyel E, Schnelle W and Leithe-Jasper A 2011 Presented at the Journal of Physics: Conf. Series (unpublished) (https://doi.org/10.1088/1742-6596/273/1/012101)
[18] Terashima T, Kimata M, Satsukawa H, Harada A, Hazama K, Uji S, Suzuki H S, Matsumoto T and Murata K 2009 J. Phys. Soc. Jpn. 78 083701
[19] Uhoja W, Tsu O, Vohra Y K, McGuire M A, Sefat A S, Sales B C, Mandrus D and Weir S T 2010 J. Phys. Condens. Matter 22 292202
[20] Zhang Y Z, Kandpal H C, Opahle I, Teschke H O and Valenti R 2009 Physical Review B 80 094530
[21] Chen G, Li Z, Dong J, Li G, Hu W, Zhang X, Song X, Zheng P, Wang N and Luo J 2008 Physical Review B 78 224512
[22] Giannozzi P, Andreussi O, Brumme B, Bunau O, Nardelli M B, Calandra M, Car R, Cavazzoni C, Ceresoli D and Cococcioni M 2017 J. Phys. Condens. Matter 29 465901
[23] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarello G L, Cococcioni M and Dabo I 2009 J. Phys. Condens. Matter 21 395502
[24] Malakhal L, Sipunar B, Zuniga I C, Siripurapu R K and Sipunar I A 2016 International Journal of Computational Materials Science and Engineering 5 1650008
[25] Scandolo S, Giannozzi P, Cavazzoni C, de Gironcoli S, Pasquarello A and Baroni S 2005 Zeitschrift für Kristallographie-Crystalline Materials 220 574–9
[26] West D, Sun Y and Zhang S 2012 Appl. Phys. Lett. 101 082105
[27] Hamann D 1989 Physical Review B 40 2980
[28] Bettega M H, Ferreira L G and Lima M A 1993 Physical Review A 47 1111
[29] Dalgaro A, Bottcher C and Victor G 1970 Chem. Phys. Lett. 7 265–7
[30] Garrity K F, Bennett J W, Babe K M and Vanderbilt D 2014 Comput. Mater. Sci. 81 446–52
[31] Hamann D, Schlüter M and Chiang C 1979 Phys. Rev. Lett. 43 1494
[32] Kresse G and Joubert D 1999 Physical Review B 59 1758
[33] Troullier N and Martins J L 1991 Physical review. B, Condensed matter 43 993
[34] Lund A M, Orendt A M, Pagola G I, Ferraro M B and Facelli J C 2013 Crystal Growth & Design 13 2181–9
[35] Wales D J and Scheraga H A 1999 Science 285 1368–72
[36] Yang W, Sorini A, Chen C, Moritz B, Lee W S, Vernay F, Olaade-Velasco P, Denlinger J, Delley B and Chu J H 2009 Physical Review B 80 014508
[37] Brown C and Dreyer W 2003 J. Eng. Mater. Technol. 125 27–37
[38] Aroyo M I, Oroben X, de la Flor G, Taci E S, Perez-Mato J M and Wondratschek H 2014 Acta Crystallographica Section A: Foundations and Advances 70 126–37
[39] Ceder G and Persson K 2010 Physical review. B, Condensed matter (https://doi.org/10.1103/PhysRevB.82.125146)
[40] Ivanovski A 2009 J. Struct. Chem. 50 539–51
[41] Parvin F and Nabqi S 2019 J. Alloys Compd. 780 652–60
[42] Kahn I R, Bayburt P and Truhlar D G 1976 J. Chem. Phys. 65 3826–53
[43] Yi M, Lu D, Analysts J, Chu J H, Mo S K, He R H, Moore R, Zhou X, Chen G and Luo J 2009 Physical Review B 80 024515
[44] Parmanik U, Das D, Prasad R and Hossain Z 2013 J. Phys. Condens. Matter 25 265701
[45] Gereck H 2007 Int. J. Rock Mech. Min. Sci. 44 1–13
[46] Park R J T 1987 Research Report
[47] Shein I and Ivanovski A 2009 Tech. Phys. Lett. 35 961
[48] Shein I and Ivanovski A 2008 arXiv preprint at arXiv