Introduction to Density Functional Theory Calculations

COMPUTATIONAL ACTIVITY 3

UNIVERSITY of SAN CARLOS
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Density of States and Band Structures

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The density of states and band structures are two of the most common calculations which are done in studying the elctronic properties of a material. In this study, first-principle calculations based on the density functional theory (DFT) were employed to solve the DOS and band structures of BCC Fe, FCC Au and diamond Si systems. The calculations were implemented in Quantum Espresso. The DOS results show that Fe is magnetic while Au and Si are both nonmagnetic. Furthermore, the band structure reveal that Fe and Au are both conductors while Si is an semiconductor.

1. Introduction

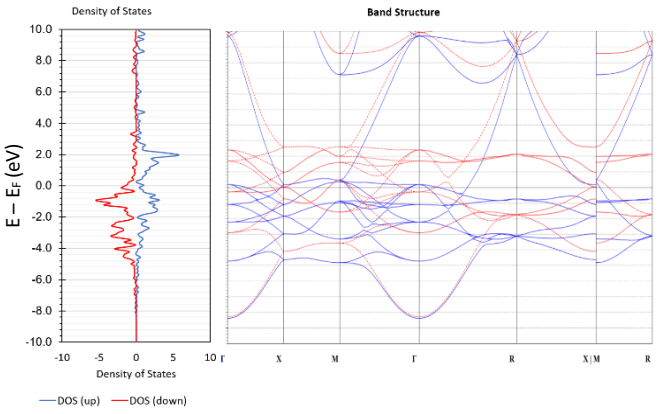
In solid state physics and condensed matter physics, the electronic state of a material is commonly described using the density of states (DOS) and the band structure. In this study, the DOS and the band structures of three systems were calculated. These systems include a body-centered cubic (BCC) Fe, face-centered cubic (FCC) Au, and a diamond Si.

The density of states of a certain system refer to the number of states that are available to be occupied by the system at each energy level in the interval E and E + dE. Mathematically, DOS is represented as a probability density distribution and is generally averaged over the space and time domains of the various states occupied by the system. The DOS may be an atom-projected or orbital-projected. In calculating the DOS, there are several factors that need to be considered. Firstly, a large number of k points is necessary to obtain more accurate results. Secondly, DOS must be plotted with respect to the Fermi energy E_F which is the energy of the highest occupied electronic state. The DOS can be used in characterization of a material whether it is metallic, semiconductor, or insulator. Aside from this, the DOS can also give important information such as the hybridization of the orbitals and the nature of bonding between the atoms.

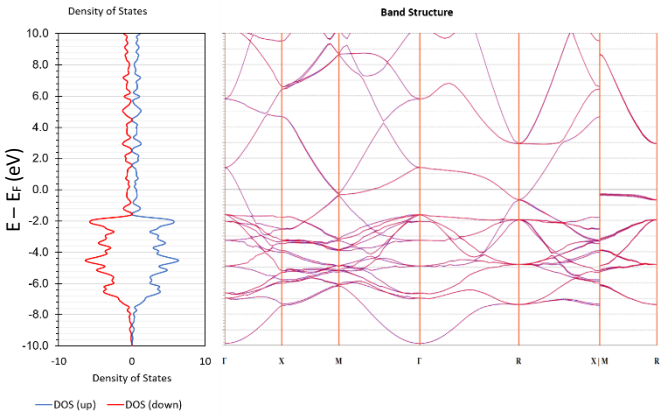
The electronic band structure on the other hand, describes range of energies that an electron within the solid can or cannot have. The range of energies that the electron can have is referred to as the energy bands or the allowed bands while the energies that the electron cannot have is referred to as the band gaps or the forbidden bands. The band structure is given as a function of the of the wave vector k in the reciprocal space. The band structure can be used in identifying the bands that crosses the Fermi level to determine if the material is metallic or not. Moreover, the band structure is also a helpful tool in calculating the direct and indirect band gap in characterization of the electrical conductivity of the solid. Generally, substances with large bandgaps are insulators, those with smaller bandgaps are semiconductors and those that have either very small or no bandgaps are conductors.

2. Results and Discussion

Figure 1. show the calculated atom-projected (total) DOS and band structure of the three (a) BCC Fe, (b)FCC Au and (c) diamond Si systems, respectively.

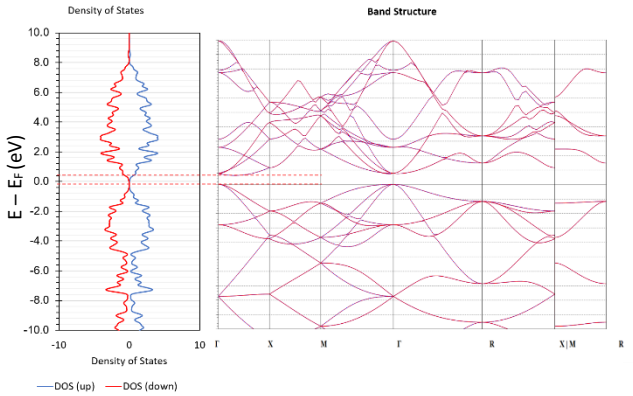


(a)



(b)

In the DOS plots, high DOS at specific energy levels means that more states are available for occupation. The



(c)

Figure 1. Calculated density of states (DOS) and band structures of (a) BCC Fe, (b)FCC Au and (c) diamond Si systems. *(Note: The red broken lines in (c) mark the bandgap.)*

states having negative energies are occupied states while states having positive energies are unoccupied or available states. For instance, it can be observed that Fe and Au have more occupied states while Si has comparable occupied and unoccupied states. Furthermore, the symmetry of the spin up and spin down density of states describes the magnetic state of the material. In this case, the DOS for the Fe system is not symmetric indicating that this material has a net magnetization implying that this material is magnetic. For the Au and Si, the DOS are symmetric about the vertical axis. This means that these two materials are nonmagnetic.

For the band structures, the graphs reveal that several bands for the Fe system and a few bands for the Au system cross the Fermi level. These bands crossing the Fermi level indicate partially filled bands implying that both Si and Au are metals. Due to these overlapping bands, electrons in the conducting band are free to move within the crystal lattice serving as charge carriers to conduct electric current. Hence, these two materials are classified as conductors. On the other hand, the Si system don't have these crossing bands but rather an energy gap or bandgap about the Fermi level where no electron states can exist. In the electronic band structure shown in Figure 1 (c), the bandgap refers to the indirect gap between the valence band maximum or the highest occupied molecular orbital (HOMO) and the conduction band minimum or the lowest unoccupied molecular orbital (LUMO) near the Γ symmetry. The bandgap is the required energy to promote a valence electron to the conduction band. In this case, the band gap is ~0.6 eV implying that Si is a semiconductor. This small indirect bandgap value is only about half the known values reported in [1,2,3]. This great discrepancy may be due to the so-called 'bandgap problem', in which DFT in LDA/GGA fails to correctly predict the energy gaps between occupied and unoccupied states as mentioned in [4].

3. Conclusion

The DOS and band structures of BCC Fe, FCC Au, and diamond Si systems were calculated using DFT method implemented in Quantum Espresso. Results from these calculations are used to describe the electronic and magnetic properties of each system. The DOS calculations reveal that Fe is magnetic while Au and Si are both nonmagnetic. Furthermore, the band structures show that Fe and Au are both conductors while Si is a semiconductor.

Computational Model

DFT calculations were implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons was described using the projector augmented wave (PAW) method. Plane wave basis sets were employed with an energy cut-off of 600 eV. The surface Brillouin zone integrations was performed on a grid of 8×8×8 Monkhorst-Pack k-points using Methfessel-Paxton smearing of σ=0.2 eV.

Notes and references

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