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DENSITY FUNCTIONAL THEORY STUDY OF ELECTRONIC AND STRUCTURAL PROPERTIES OF $CeCo_2$

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Abstract

Electronic and structural properties of bulk-non-superconducting $CeCo_2$ are investigated using density functional based technique. The calculated band structure has been found to show overlapping of Ce 4f and Co 3d states pointing towards metallic nature of the material. Moreover, our results illustrate that the material is non-magnetic because no spin polarization is available. The total and partial DOS (Density of States) of $CeCo_2$ suggests that properties of $CeCo_2$ are highly dependent upon the localized 4f states of Ce. The calculated results are found to be in good agreement with experimental results available in the literature.

Keywords: $CeCo_2$, Bulk, Density Functional Theory, Electronic Properties.

Introduction

Among rare-earth based inter-metallic compounds, Ce based systems fascinate the material scientists because of their puzzling electronic properties such as Kondo effects, long range ordering, coexistence of heavy fermionic behavior and superconductivity (Dong et al., 2009). These extra ordinary electronic and magnetic properties of rare earth compounds are due to the unique nature of f electrons, which can possess both localized and band like character. Moreover, $CeCo_2$ owns intermediate valence behavior which provides a probe to explore its magnetic and/or non-magnetic properties. One more interesting property of $CeCo_2$ is the loss of the magnetic moments in the 4f shell under pressure (Dong et al., 2007; Panfilov et al., 2002). This important and significant feature of the Ce based materials is exposed to the scientists by the recent size for dependent study of the bulk and nano $CeAl_2$, Ce_3Al. This study of fermion compounds $CeAl_2$ has demonstrated that the bulk $CeAl_2$ exhibits magnetic ordering, while the nano-particles of the same compound show non-metallic nature (Chen et al., 2005). These properties of $CeAl_2$ motivated the scientists to investigate other Ce based materials like $CeFe_2$, $CeNi_2$ (Panfilov et al., 2002). One more important Ce based material which inspires to the workers is $CeCo_2$ which is found in bulk form and usually available in well-known cubic Laves phase lattice C15. It undergoes superconducting transitions near Tc = 0.9-1.5 K (Panfilov et al., 2002; Guo et al., 2004).

The magnetic measurements carried out on $CeCo_2$ described precisely curie-Weiss behavior by measuring the magnetic susceptibility in the temperature range 4.5-300K (Seixas et al., 1999). The value magnetic susceptibility for $CeCo_2$ was found very low which indicates that both Ce and Co are essentially in non-magnetic state. It is also known that Ce is likely to have an intermediate valence state (Wang et al., 2002). This intermediate valence state is actually due to the collapsed volume of the compound and is responsible for the observed volume dependent trends in the series of cobalt based compounds (Panfilov et al., 2002). $CeCo_2$ is usually characterized as pauli-paramagnetic material and undergoes the transition from magnetic to non-magnetic phase when the bulk size is reduced up to nano-scale (Guo et al., 2004). In addition, to study the compounds many groups are now using computational methods instead of experimental techniques. We report electronic properties of $CeCo_2$ using density functional theory thereby discussing results of band structure and density of states.

Results and Discussions

1. Computational Details

The calculations were performed using density functional theory (DFT) based package

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ADF (Amsterdam Density Functional) under generalized gradient approximation (GGA) correlation. $CeCo_2$ is a prominent and effective material that can reveals a superconducting as well as magnetic and non-magnetic (metallic in bulk form) behavior under the constraints of temperature (Wang et al., 2002). In the present study, we have used the non-super conducting temperature of about 300 K. The crystal of $CeCo_2$ usually grows in the form of zinc blend structure. We employed 6 atoms unit cell made for $CeCo_2$ in which cerium and cobalt have the distribution of atoms as 2 and 4, respectively. This ratio of cerium and cobalt atoms tells us that we require 12, 24, 36, 48 and so on,… atoms to maintain the symmetry of crystal structure (periodicity of crystal structure). We used six atoms unit cell of $CeCo_2$ due to the high symmetry configuration with these numbers of atoms. The periodicity of the large and dispersed crystal structure is maintained by the mentioned number of atoms in each unit cell of $CeCo_2$. The calculations were performed to explore some peculiar electronic and structural properties of $CeCo_2$ illustrated by its density of states and band structure. The calculations of the band structure of $CeCo_2$ are carried out for 3×3×3 K-mesh. Although, it is a very condensed form of the material but it does not have the effect to our energy states at room temperature.

2. Density of states

The calculated density of states of subatomic levels and total density of states for face centered cubic structure $CeCo_2$ are shown in Figure 1.

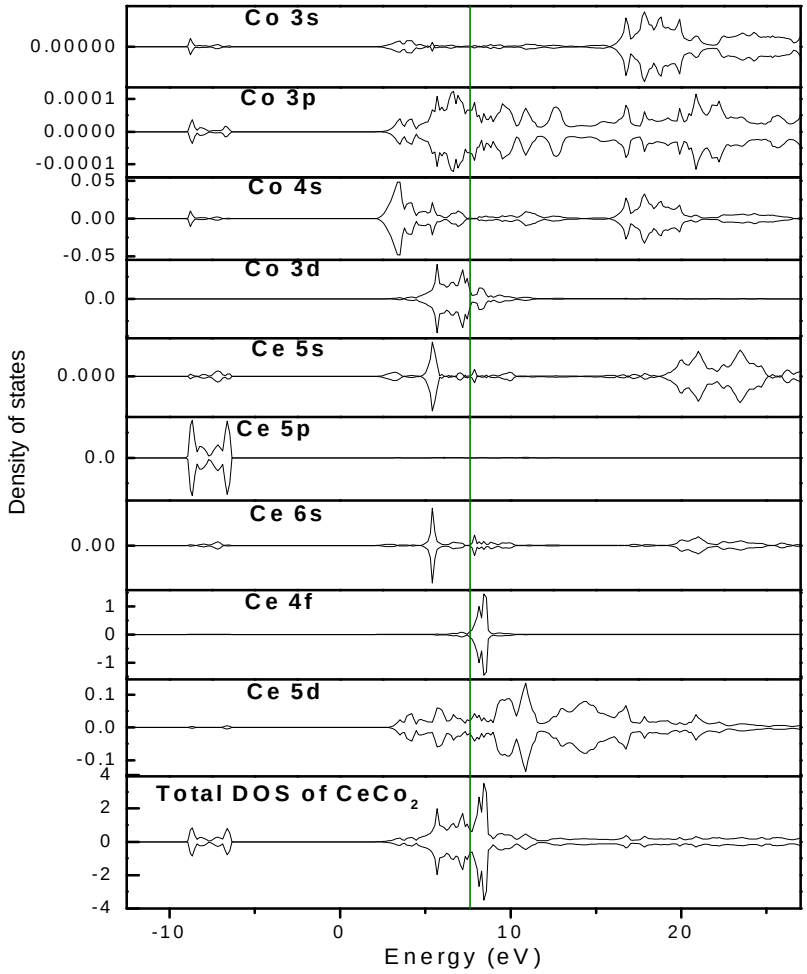

Figure 1. Partial and total DOS of $CeCo_2$

These DOS are clearly describing the metallic properties of the material by having the overlapping in 3d states of cobalt and 4f states of cerium. Overlapping, in these significant states, tells us that conduction band and valence band of $CeCo_2$ are merged with each other by containing maximum contribution from Co 3d state with Ce-5s and 6s states at energy of 5.67eV. In Figure 1, total density of states is also represented at the tail in which maximum value of DOS is available at the energy of 8.42eV. It also shows that total density of states of $CeCo_2$ shows three peaks at the energy value of 5.67eV, 7.11eV and 8.42eV. In the first peak starting from left at energy of 5.67eV, the TDOS of $CeCo_2$ gets maximum contribution from Ce-6s, 5s and Co-3d, 3p while the second peak appearing at energy of 7.11eV is due to the maximum contribution of Co-3d, 3p states and Ce-5d whereas a prominent peak arrives at energy of 8.42eV which carries an extra ordinary contribution from Ce-4f and Co-3d, 3p states. It can also be observed from the partial as well as total DOS of $CeCo_2$ that it shows no kind of spin polarization (that is spin up and spin down states are truly identical) available in any of the orbital. This is a solid evidence for a non-magnetic behavior of $CeCo_2$ at room temperature.

Due to the local crystal symmetry, Co-3d levels split into five degenerate levels as shown in Figure 2, while Ce-4f levels split into seven degenerate energy levels given in Figure 3. Five and seven degenerate levels of Co-3d and Ce-4f are $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$ and $4f_{xyz}$, $4f_{y^3-3yx^2}$, $4f_{xz^2}$, $4f_{z^3}$, $4f_{yz^2}$, $4f_{zx^2-zy^2}$, $4f_{x^3-3xy^2}$.

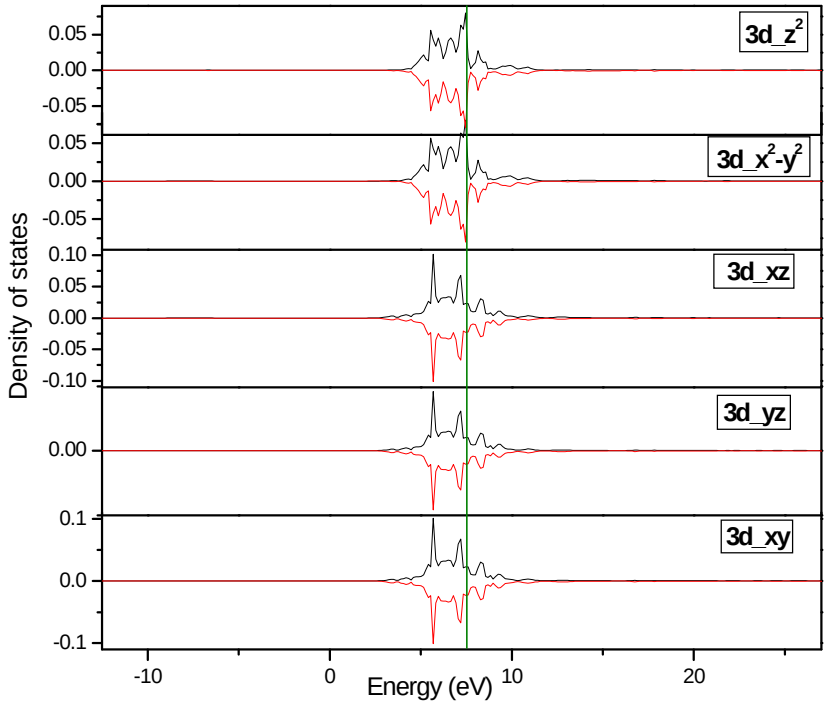

Figure 2. DOS of doubly and triply degenerate states of Co-3d

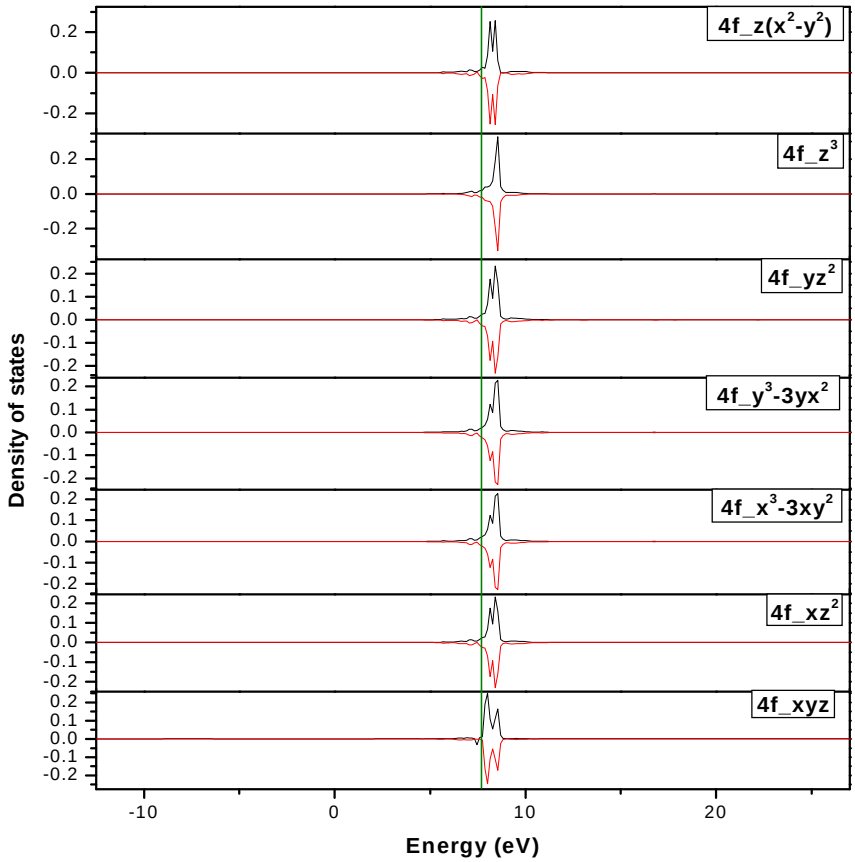

Figure 3. DOS of degenerate states of Ce-4f

In tetrahedral structures, the three fold degenerate levels lie at high energy than that of two fold degenerate levels (Blundel et al., 2004). Moreover, these doubly and triply degenerate states are separated into bonding, non-bonding and anti-bonding states in a tetrahedral crystal structure. In these 3d and 4f orbitals, there is an important mechanism of direct exchange is available which is controlling the magnetic properties. From Figure 2 and Figure 3, it is easy to view that doubly degenerate states of cobalt are coupled with degenerate 4f states of cerium and providing an effective exchange scenario. But the triply degenerate states of cobalt are not coupled with 4f degenerate states of cerium due to the energy difference. In rare earths, 4f electrons are strongly localized and present closer to the nucleus. It gives result to us that direct exchange is very effective in rare earths. In transition metals like iron, cobalt and nickel, 3d orbitals are extended further from nucleus. Since direct overlap is available in the $CeCo_2$ this reveals that the material is metallic in nature. But this information is not sufficient to demonstrate clearly the magnetic or non-magnetic behavior of $CeCo_2$. Since, it can be observed clearly from the Figures 1, 2 and 3, that there is not available a single spin polarized state that can provide a manifestation of non-magnetic behavior of $CeCo_2$. If we want to study the magnetic behavior of $CeCo_2$ then both localized as well as band character of electron is needed to be taken into account (Blundel et al., 2004).

3. Band structure

The calculated band structure for face centered cubic $CeCo_2$ in the high symmetry directions is shown in the brillion zones.

Band diagram of $CeCo_2$ in bulk form is shown in Figure 4, with net spin configuration. The Fermi energy of $CeCo_2$ is 7.68 eV clearly highlighted in the band diagram with the help of solid green line. K-points representation of material with spin configuration is also illustrated in Figure 4.

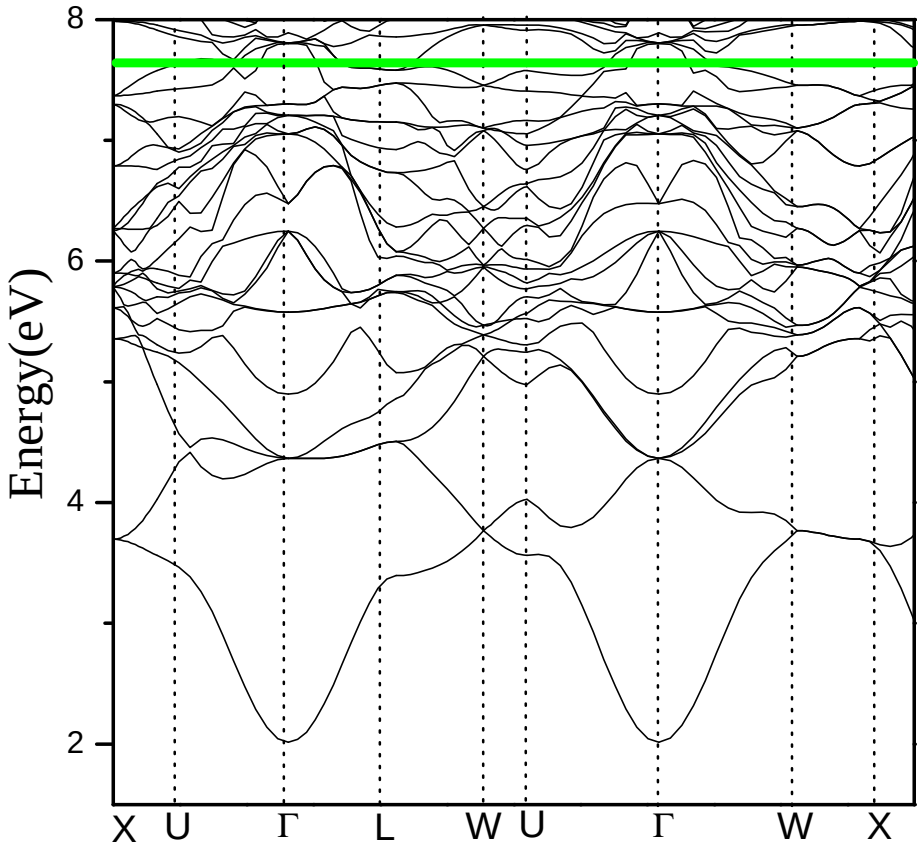

Fig. 4. Band structure diagram of $CeCo_2$

As it has been observed that the Fermi energy appears at the value of 7.68eV which is just closer to the experimentally found value of E_f (Panfilov et al., 2002). The peaks in Figure 4, between the energy range 4-5 eV are found to clearly describe the metallic nature of bulk form $CeCo_2$.

Conclusion

We have studied the density of states and band structure of $CeCo_2$ theoretically. The plotted diagrams of DOS and band structure are for 6 atoms unit cell. This study demonstrates that localized Ce-4f states and Co-3d states are overlapped. This overlapping of magnetic orbitals results in the metallic nature of the material. And it has also been observed in DOS of the non-superconducting bulk $CeCo_2$ that there is no spin polarization available for this material which provides a clear cut evidence for the non-magnetic behavior of the material. So, at the end of this thorough and comprehensive discussion about the doubly and triply degenerate states of Co-3d, we have concluded that the $CeCo_2$ is metallic and ultimately non-magnetic in nature.

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