First-principles calculations of electronic and magnetic properties of CeN: The LDA + U method*

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Electronic and magnetic properties of CeN are investigated using first-principles calculations based on density functional theory (DFT) with the LDA + U method. Our results show that CeN is a half-metal. The majority-spin electron band structure has metallic intersections, whereas the minority-spin electron band structure has a semiconducting gap straddling the Fermi level. A small indirect energy gap occurs between X and W. The calculated magnetic moment is 0.99 μ_B per unit cell.

Keywords: first-principles calculations, strongly correlated system, electronic structure, magnetic properties

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1. Introduction

The rare-earth mononitrides (RENs) are a family of NaCl-type structure compounds. They have recently received renewed attention in both theoretical and experimental aspects due to their peculiar electronic, magnetic properties, and their potential application in spintronics.[1–3] The valency instabilities in some rare-earth metals and their compounds was one of the most interesting puzzles in the 1970s. When inter-configuration fluctuations occur, the "valency" loses the traditional precise meaning. Olcese[4] found an ionic radius lower than that expected for Ce^{3+}, indicating the possible occurrence of interconfiguration fluctuation between the Ce^{3+} and Ce^{4+} states. The average valency of Ce in CeN appears to be 3.85 under standard conditions.

The electronic structure of REN is studied systematically using *ab-initio* self-interaction corrected local-spin-density approximation.[5] The result shows that CeN exhibits mixed valence behavior and rather unusual properties compared with the other REN. Its lattice constants are anomalously smaller than those of the other REN. A jump in lattice constants from CeN to PrN is due to the fact that the ground state of Ce in CeN is tetravalent instead of trivalent. In the mixed-valency picture, the localized f electrons hybridize weakly with the conduction electrons, leading to an effective Ce valence in CeN between 3 and 4.[6] However, the analyses of photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) spectra suggest that CeN does not have a mixed valency in fact.[7] Delin *et al.*[8] reported on *ab-initio* calculations of the ground state and optical properties of CeN. Their results show that 4f electrons in CeN are itinerant and the necessary precondition for mixed valency is not supported by their calculations.

Polycrystalline CeN has been reported by several groups to be both a wide band-gap semiconductor and a conductor. Sclar[9] predicted that CeN is a semiconductor with an estimated band gap of 1.8 eV. Xiao and Takai[10] reported that CeN is a p-type semiconductor with a direct optical band gap of 1.76 eV by optical absorption experiments. Lee *et al.*[11] determined experimentally that CeN is a metal rather than a wide band-gap semiconductor.

To address some of these controversies, we investigate the electronic structure of CeN using first-principles calculations based on density functional theory with the LDA + U method, and the magnetic property of CeN is calculated for the potential application in the spintronics.

2. Computational details

The calculations were performed using the plane-wave pseudopotential density functional theory (DFT) method as implemented in the CASTEP simulation package.[12] The ultrasoft pseudopotential with the LDA + U method was employed to model the ion–electron interaction.

The LDA + U theory is designed to give the self-energy correction to localized states embedded in delocalized states. The localized states have a large Coulomb correlation which is accounted for by the U-term whereas the delocalized states are well described by the LDA.[13,14] The advantage of the LDA + U method is the ability to treat simultaneously delocalized conduction band electrons and localized 4f electrons in the same computational scheme. The LDA + U method was proved to be a very efficient and reliable tool in calculating the electronic structure of systems where the Coulomb interaction is strong enough to cause the localization of the electrons.

The convergence criteria for structure optimization and

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energy calculation were set to ultrafine quality with a kinetic energy cutoff of 770 eV and k-point meshes of 6×6×6. The self-consistent convergence accuracy was set to be 5.0×10^{-6} eV/atom. The convergence criterion for the maximal force between atoms was 0.01 eV/Å. The maximum displacement was 5.0×10^{-4} Å, and the stress was set to be 0.02 GPa.

3. Results and discussion

3.1. Electronic structure

CeN is a strongly correlated system with 4f electrons. 4f bands are generally very narrow, significantly different from the bands dominated by s, p, and d states. Therefore there exist strong on-site Coulomb repulsions between the highly localized f electrons.[15]

The LDA + U method takes into account the orbital dependence of the Coulomb. Applied to the rare-earth metal compounds, the LDA + U method gives a qualitative improvement not only on excited-state properties such as energy gaps but also on ground-state properties such as magnetic moments. The U parameter for Ce 4f state is determined empirically and there are several studies in which how the value of U is fitted against the experimental results was described.[16–18] In the present study, the LDA + U method ($U = 6$ eV) is used to correct the strong on-site Coulomb repulsion of Ce 4f states.

We have carried out spin-polarized electronic band structure calculations of CeN, and the results are shown in Fig. 1. From Fig. 1, one can see that a striking feature is the majority-spin electron band structure with metallic intersections, whereas the minority-spin electron band structure has a semiconducting gap straddling the Fermi level. A small indirect energy gap occurs between X and W. These characteristics indicate that CeN is a half metal. A half-metal is any substance that acts both as a conductor for electrons of one spin orientation and as an insulator for the electrons of the opposite spin orientation.[19] In a half-metal, the valence band related to one type of these electrons is fully filled and the other is partially filled.[20] Our result is consistent with that given by Larson *et al.*[2]

Partial density of states of N-sp and Ce-spdf electrons of CeN are shown in Figs. 2–4, respectively. From Fig. 2, it can be seen that around −11 eV are the N 2s bands in both of the spin channels without any splitting. Just below the Fermi energy, the states are predominantly due to the contributions of N 2p electrons in both of the spin channels. The nitrogen p bands are close enough to the Fermi surface to hybridize slightly with the low-energy tail of Ce s–d bands, causing the material to be metallic.

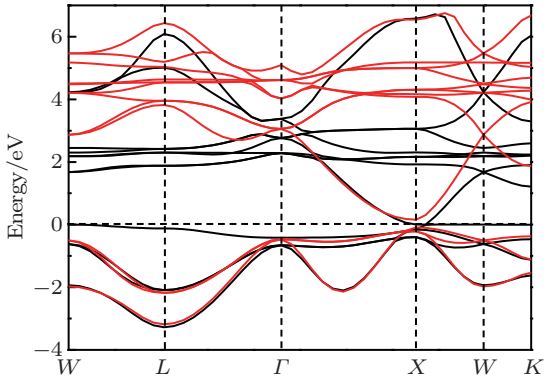


Fig. 1. (color online) Band structure of CeN at zero pressure. The black and red lines represent majority- and minority-spin states, respectively.

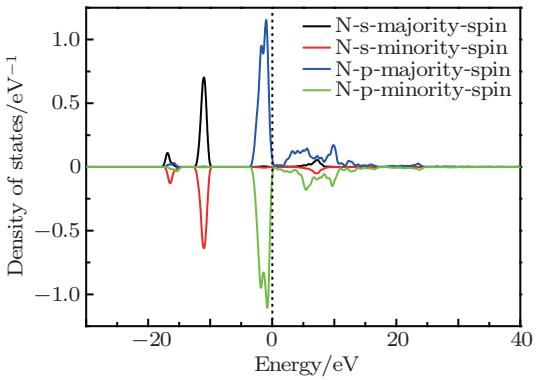


Fig. 2. (color online) Partial densities of states of N-s and N-p electrons of CeN.

From Fig. 3, we see that the lowest-lying states stem from Ce-s states in both of the spin channels with a small exchange splitting. Above these, around −16 eV are Ce-p bands in both spin channels.

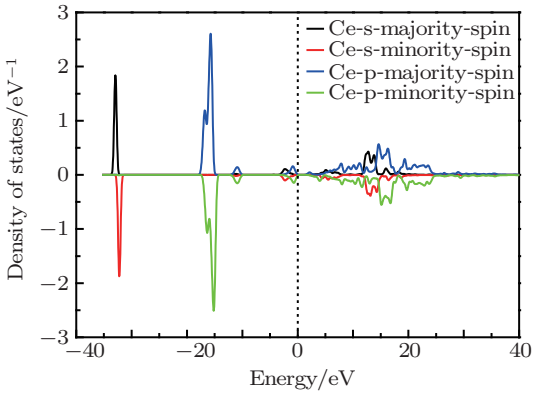


Fig. 3. (color online) Partial densities of states of Ce-s and Ce-p electrons of CeN.

From Fig. 4, it can be clearly seen that some of the 4f bands from the majority-spin cross the Fermi level. Above E_f are mainly the Ce 4f bands with some hybridization yielding small contributions from Ce s–d electrons and N p states. Above the Fermi level there are two peaks. The first one is from the unoccupied majority-spin f bands, and the other

is from the completely unoccupied minority-spin f bands. There exists a separation between the majority-spin peak and the minority-spin peak. A similar behavior was observed in PmN.[20] The exchange splitting is a necessary condition for half-metallicity.[1]

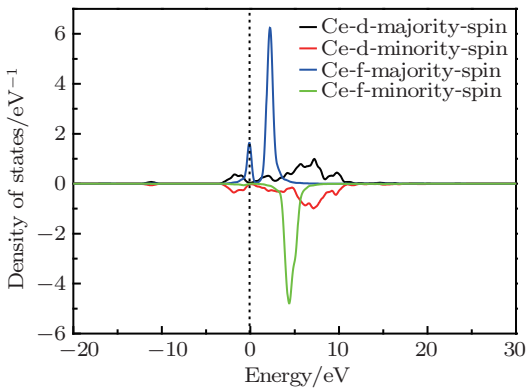


Fig. 4. (color online) Partial densities of states of Ce-d and Ce-f electrons of CeN.

3.2. Magnetic property

The rare-earth materials have high magnetic moments and form a wide range of magnetic structures. It is the occupancy of the highly localized 4f states that determines the magnetic properties while the other electronic properties are determined principally by the itinerant s–d electrons.[21] The spin magnetic moment is dominated by the rare-earth f electrons, with some hybridization yielding small contributions from the rare-earth s–d electrons and the nitrogen p states.

CeN would have a single 4f electron if Ce were trivalent, but zero 4f electrons if it were tetravalent. The three valence electrons of Ce can fill the three holes of the N p band and create a full p band. The calculated magnetic moment is 0.99 μ_B. The spin magnetic moment is nearly integer, defined by the number of filled 4f states.[2] So we conclude that Ce ion is trivalent in CeN. This result does not accord with that of Larson *et al*. in Ref. [2]. They found zero magnetic moment in CeN, which is consistent with the tetravalent situation.

As is well known, the first-principles description of f-electreon systems is a considerable challenge and a highly debated topic in condensed matter physics. The coexistence of itinerant spd states and localized partially occupied f states and their mutual interaction in rare-earth material gives rise to a rich variety of physical phenomena that continue to be a testing ground for electronic structure theories.[22] CeN has been widely used as a testing ground for the theoretical models and also for the development of new magnetic systems. For CeN very little experimental data appear to be available. We hope that the future experiments could test these theoretically conflicting results.

4. Conclusions

In this study, first-principles calculations are used to investigate the electronic structures and magnetic properties of CeN. Our result shows that CeN is a ferromagnetic half-metal with a magnetic moment of 0.99 μ_B.

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