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Ab initio studies of the electronic structure and magnetic properties of bulk and nano-particle $CeCo_2$

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Abstract

We have carried out a theoretical study of the electronic structure and magnetic properties of both bulk and supercell slab $CeCo_2$. The calculations are based on first-principles density functional theory with generalized gradient approximation (GGA) and also with the GGA + U scheme. Both GGA and GGA + U calculations predict bulk $CeCo_2$ to be nonmagnetic, in agreement with experiments. However, calculations for a supercell slab with a 14 Å thickness, show that the system becomes ferrimagnetic. In particular, the local magnetic moments on all the Ce and Co atoms in the thin film are pronounced. This suggests that surface effect may play a significant role in the magnetism observed in nano-particle $CeCo_2$.

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Bulk $CeCo_2$ crystallizes in cubic A15 structure and undergoes a superconducting transition near 1 K. It is non-magnetic or Pauli-paramagnetic at best [1]. However, nano-particles $CeCo_2$ show transitions to magnetic states at low temperatures [2]. It is speculated that the magnetism in the particles would be caused by either quantum size effect or surface effect or both. As a first step to gain a full microscopic understanding of this interesting phenomenon, we have performed a first principles density functional theoretical study of the electronic structure and magnetic properties of bulk and supercell slab $CeCo_2$ within the generalized gradient approximation (GGA) and also the GGA + U scheme.

Highly accurate all-electron full-potential linearized augmented plane wave (FLAPW) method [3] has been used to calculate the electronic structure and magnetic properties of the $CeCo_2$ systems. We consider bulk cubic A15 structure as well as a thin film with a slab width of two cubic cells (14.3 Å). The thin film is used to model the surface effects on the magnetic properties of nanoparticles $CeCo_2$ because nanoparticles have a high surface-to-volume ratio. A large number of augmented plane waves are used, about 90/atom for the thin film and 130/atom for the bulk. The number of k-points in the irreducible Brillouin zone wedge used are 56 and 286 for the thin film and the bulk, respectively. The muffin-tin sphere radii used are 2.5 and 2.2 a.u. for Ce and Co, respectively. In the GGA + U calculations, the on-site Coulomb energy U and exchange parameter J applied to Ce 4f-orbitals are 6 and 0.6 eV, respectively.

We first performed the spin-polarized GGA calculations for bulk $CeCo_2$ at a number of lattice constants to determine the theoretical lattice constant. The calculated theoretical lattice constant is 7.08 Å, being in good agreement with the experimental value (7.16 Å) [2]. The calculated bulk modulus is 1.45 Mbar. Bulk $CeCo_2$ is predicted to be nonmagnetic in the whole volume range studied, in good agreement with experiments [1,2]. This finding is not changed in our subsequent spin-polarized calculations within the GGA + U scheme. The total, Co- and Ce-site decomposed density of states (DOS) from a GGA + U calculation at the experimental lattice

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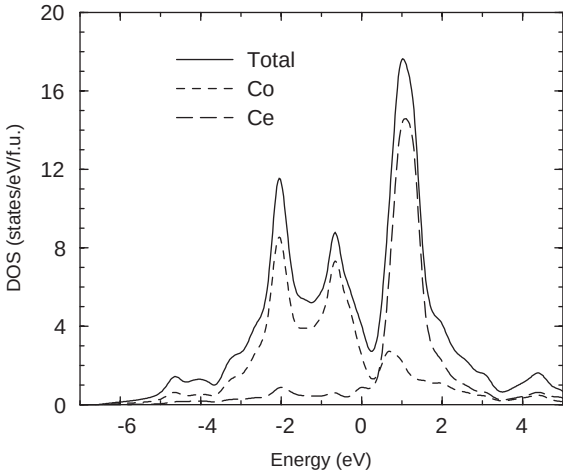

Fig. 1. The GGA + U density of states of bulk $CeCo_2$. The zero energy denotes the Fermi level.

constant is displayed in Fig. 1. It is seen from Fig. 1 that the valence band is Co-dominant, consisting of two pronounced peaks at 0.7 and 2.0 eV below the Fermi level (E_F), respectively. There is a sharp Ce 4f-dominant peak in the conduction band at 1.0 eV above the E_F. Strikingly, the E_F falls in the valley between the Ce 4f peak and the upper Co-dominant valence peak, resulting in a low DOS at the E_F (4.1 states/eV/f.u.)(f.u. denotes formula unit). This explains why the bulk $CeCo_2$ is nonmagnetic. We note that the calculated DOS in Fig. 1 is similar to that of a previous calculation using relativistic linearized augmented plane wave method with the muffin-tin potential approximation [4].

We then performed self-consistent spin-polarized calculations for the $CeCo_2$ thin film at the experimental lattice constant. The ideal surface structure is assumed, i.e., no atomic relaxation is taken into account. We also neglect the surface oxidation since CeO_2 is a nonmagnetic insulator. The slabs are separated by a vacuum layer of one cubic layer (7 Å). Remarkably, both the GGA and GGA + U calculations predict that the thin film is a ferrimagnet. Since Ce 4f-orbitals are rather localized, the 4f-electron correlations are expected to be strong. Consequently, the GGA + U calculations are more appropriate and thus we only display and discuss the results from the GGA + U calculations below. The calculated spin magnetic moments are listed in Table 1. Table 1 demonstrates that the surface effect on the magnetic properties of nanoparticles $CeCo_2$ would be strong. Total magnetization increases from zero in the bulk to 0.35 μ_B/atom (or 1.05 μ_B/f.u.) in the 14.3 Å thick thin film. Even the Co atoms on the central layers away from the surface have a magnetic moment of $\sim$0.6 μ_B/atom, suggesting that the surface magnetic layer would be rather thick, at least on the order of one nanometer.

Table 1
Calculated total and atom-decomposed spin magnetic moments (m_s) (in units of μ_B/atom) in the thin film of $CeCo_2$ from the GGA + U calculation

	1	2	3	4	5	Total
m_s Co	0.56	0.62	0.73	0.75	—	0.35
Ce	−0.31	−0.56	0.63	0.84	−0.71	

The numbers denote the atomic layers from the center to the surface.

The spin magnetic moments of Ce atoms are also sizeable (Table 1). However, some Ce magnetic moments are aligned parallel to that of the Co atoms but others are antiparallel to that of the Co atoms. Thus, the $CeCo_2$ thin film is a ferrimagnet. To understand the origin of the magnetism in the $CeCo_2$ thin film, we have calculated site-decomposed DOS (not shown here). We find that the Co-dominant valence band on the outer Co layers (e.g., Co3 and Co4) becomes narrower and moves up slightly towards the E_F with respect to the bulk Co band (Fig. 1). As a result, the local DOS at the E_F on the outer Co atoms becomes larger than that in the bulk, causing the formation of the spin magnetic moments. Interestingly, the Ce 4f-dominant conduction band peak from the outer Ce layers (e.g., Ce4 and Ce5) is shifted away from the E_F by as much as 2 eV.

Experimentally, the nanoparticles $CeCo_2$ have a mean diameter of 68 Å with a thin layer of CeO_2 on surface [2]. At temperatures above 100 K, they show a Curie–Weiss behavior with an effective magnetic moment of 6.1 μ_B/f.u. At $T \sim 30$ K, the effective moment is reduced to about 2.5 μ_B/f.u. [2]. The calculated magnetic moment (1.05 μ_B/f.u.) from the GGA + U appears to be qualitatively consistent with the low-temperature effective moment. Of course, the nanoparticles $CeCo_2$ are more complex than the present theoretical model. In particular, the effects of the oxide layer and surface relaxation have not been considered, the thin films have much less surface area than the nanoparticles, and the spin–orbit coupling has not been account into account. Nonetheless, the present calculations do show that the surface magnetism would play a significant role in the formation of the magnetic moments observed in the nanoparticles $CeCo_2$.

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