Electronic and Magnetic Properties of ThCo$_4$B

A. Szajek

Institute of Molecular Physics, Polish Academy of Sciences

M. Smoluchowskiego 17, 60-179 Poznań, Poland

ThCo$_4$B compound crystallizes in the hexagonal CeCo$_4$B type structure. The electronic structure is calculated based on full-potential local-orbital full-relativistic method. The *ab initio* calculations showed that small magnetic moments ($\approx 0.1\ \mu_{\rm B}$/atom) are formed on Th and B atoms, antiparallel to the moments on Co atoms equal to 1.55 and 0.43 $\mu_{\rm B}$/atom for Co(2c) and Co(6i), respectively. The densities of states at the Fermi level are equal to 1.3 and 5.4 states/(eV spin f.u.) for spin up and down, respectively. These values are predominated by Co(3d) electrons.

PACS numbers: 71.20.–b, 75.20.Hr

1. Introduction

Recently uranium compounds have attracted interest because of many interesting properties such as the Pauli paramagnetism, spin fluctuations, heavy fermions, magnetic ordering, or superconductivity [1, 2]. Wide range of properties in these compounds is caused by the uranium 5f electrons, which show an intermediate character between the localized 4f electron system and itinerant character of 3d electrons. The role of 5f electrons is important in actinides and the question is if they are localized or itinerant or perhaps the two situations coexist giving rise to a new character of the electronic structure, referred to as the duality of the behavior of 5f electrons [3]. It is very useful to compare properties of isostructural systems with and without 5f electrons treating the systems with thorium as reference ones. The ThCo$_4$B phase crystallizes in a hexagonal CeCo$_4$B type structure and orders ferromagnetically at 303 K [4]. Investigations by high resolution neutron diffraction gave magnetic moments on Co atoms equal to 1.2 and 0.2 $\mu_{\rm B}$/atom for 2c and 6i site, respectively [4]. In isostructural UCo$_4$B no magnetic order was observed [5].

The aim of this paper is to calculate electronic structure of the ThCo$_4$B compound based on a spin-polarized *ab initio* method.

2. Computational details

In order to study electronic structure of the ThCo$_4$B compound we used the full-potential local-orbital (FPLO) method [6, 7] based on the local spin density approximation (LSDA) [8]. The fully-relativistic mode was used in the calculations.

The calculations were carried out for the hexagonal structure with 12 atoms per unit cell (two formula units) and experimental values of the lattice constants [4]. We assumed the following electron configurations of atoms: core + semi core electrons ($5d6s$) + valence electrons ($6p7s7p6d5f$) for Th atoms, core + semi core electrons ($3s3p$) + valence electrons ($4s4p3d$) for Co atoms, and finally on B atom $1s$ electrons were treated as semi core, and ($2s2p3d$) electrons as valence ones. The calculations were performed for the reciprocal space mesh containing 1456 points within the irreducible wedge of the Brillouin zone using the tetrahedron method [9] for integrations. The LSDA exchange-correlation potential was assumed in the form proposed by Perdew and Wang [10]. The self-consistent criterion was equal to 10^{-8} Ry for the total energy.

3. Results and discussion

The spin resolved densities of states (DOSs) are presented in Fig. 1 (total and partial DOSs in (A) and site projected ones in (B)). The presented spectrum of electronic states can be divided into two parts. The first part is formed by $6p$ electrons located on Th atoms. The Th($6p_{1/2}$) and Th($6p_{3/2}$) peaks, split by the spin–orbit interactions, are located about 22 and 15 eV below the Fermi level (E_F), respectively. The second part, the valence band, is formed by electrons from the B and Co atoms as well as the Th($6d7s$) electrons. The Th($5f$) states are not occupied by electrons and they are well above the Fermi level. The large number of Co atoms causes that the valence band is dominated by $3d$ electrons. The values of DOS at the Fermi level are equal to about 1.3 and 5.4 states/(eV f.u. spin) for spin up and down, respectively. Particular partial and local contributions are collected in Table. The total value of DOS ($E = E_F$) corresponds to the value of 15.79 mJ/(mol K^2) of the calculated coefficient γ_0 in the linear term of the specific heat. The Co atoms provide above 80 and 90% contributions to the total DOS at the Fermi level for spin up and down, respectively. ThCo$_4$B, contrary to isostructural UCo$_4$B compound [5], is magnetically ordered below 303 K [4], and the saturation magnetization obtained from the 4 K isothermal magnetization curve is equal to 1.5±0.1 μ_B/f.u. Neutron diffraction measurements gave magnetic moments aligned along the c-axis of the hexagonal structure in the whole ordered temperature region [4]. At 2 K a substantial magnetic moment of 1.8 ± 0.1 μ_B was observed on the Co(2c) site whereas a nearly zero moment was found on the Co(6i) site.

A similar behaviour was also found at room temperature, 1.2 ± 0.2 μ_B on the Co(2c) site and a nearly zero μ_B on the Co(6i) site. The calculated values of the magnetic moments are collected in Table. The value for Co(2c) atom is equal to 1.55 μ_B with 0.19 μ_B of orbital contribution. This value is less than the experimental value, but close to the magnetic moment calculated in the case of RCo$_4$B (R = Y [11], R = Gd, Tb [12]). The total moment calculated per formula unit is overestimated first of all by the moment obtained for Co(6i) atoms,
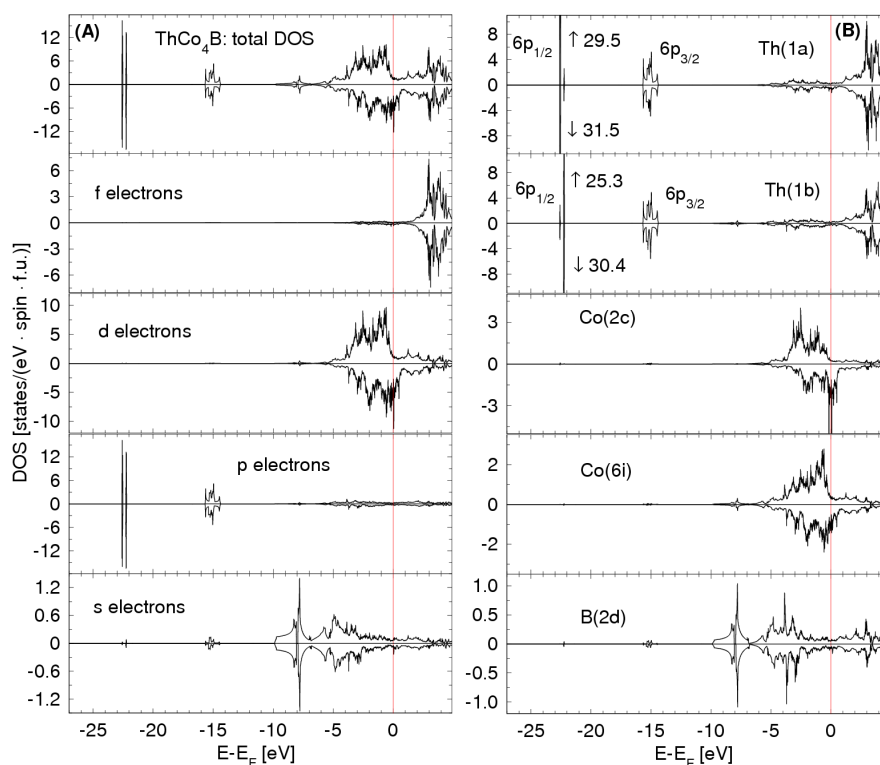
Fig. 1.   (A) total and partial DOS plots, (B) site projected DOS plots.

0.43 μ_B with orbital contribution below 0.01 μ_B. This moment is much reduced comparing with mentioned earlier RCo$_4$B compounds (about 0.7–0.8 μ_B) [11, 12] but experimental value is nearly equal to zero. Small moments are induced on Th and B atoms, about 0.16, 0.14, and 0.04 μ_B for 1a, 1b, and 2d sites, respectively. These moments are antiparallel to the Co ones. In comparison with nonmagnetic UCo$_4$B, ThCo$_4$B has larger lattice constants, especially the a one. It results in larger interatomic distances in xy planes and weaker hybridization. The latter is additionally weakened by lack of $5f$ electrons in Th atoms. Usually the $5f$ electrons, in the case of light actinides, have delocalized character, which leads to stronger hybridization.

Concluding, one can state, based on band structure calculations, that the ThCo$_4$B is magnetically ordered compound with main contribution to the total magnetic moment provided by $3d$ electrons of both types of Co atoms. The moment for Co(6i) is about twice smaller than in the case of RCo$_4$B systems (R = Y, Gd, Tb) but still too high comparing with neutron experiment. The calculated Sommerfeld coefficient from the linear term in the specific heat is lower than for UCo$_4$B because of absence of $5f$ states on Th atoms and is equal to about 16 mJ/(mol K^2). This value is provided mainly by Co($3d$) electrons.

TABLE

The values of DOS ($E = E_\mathrm{F}$) [states/(eV spin (f.u. or atom))] and local magnetic moments m. The signs ↑ and ↓ describe spin directions up and down, respectively.

Type of DOS	Spin	Total and partial DOS [per f.u.]	Atom (position)	Site-projected DOS [per atom]	m [μ_B/atom]
Total	↑	1.312	Th(1a)	0.191	−0.161
	↓	5.435		0.524	
Total for s electrons	↑	0.060	Th(1b)	0.151	−0.137
	↓	0.068		0.212	
Total for p electrons	↑	0.192	Co(2c)	0.231	1.548
	↓	0.248		1.954	
Total for d electrons	↑	1.024	Co(6i)	0.286	0.427
	↓	5.011		1.014	
Total for f electrons	↑	0.036	B(2d)	0.052	−0.043
	↓	0.108		0.071	

Acknowledgments

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