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Magnetic Properties and Electronic Structure of ThCo$_4$B

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ABSTRACT

We present density functional theory DFT *ab initio* calculation of the electronic and magnetic properties of ThCo$_4$B compound using the self-consistent full-potential linearized augmented plane wave (FPLAPW) method as implemented in the Wien2k package. The influence of the local environment on the Co magnetic moments is discussed by comparing the magnetic and electronic properties of ThCo$_4$B to its parent ThCo$_5$ compound. The total magnetic moment in these two compounds is dominated by the Co moment. The Spin orbit interaction affects the electronic structure and spin-density maps of the p-state of Th.

1. Introduction

Several studies have been reported on substituted R-Co$_{5-x}$X$_x$ compounds (R = lanthanide, Y or Th) in order to investigate the effect of metalloids such as X = Al, Ga, Si, B on the physical properties of these systems [1-3]. In particular, there have been several studies on the structural and magnetic properties of the RCo$_4$B compounds [4-11]. The interest in these compounds was mainly because of their moderate hard magnetic properties with less content of the expensive Co than in RCo$_5$ systems.

Boron-for-cobalt substitution gives rise to new structures with general formula R$_{n+1}$Co$_{3n+5}$B$_{2n}$ derived from the CaCu$_5$ structure type. The RCo$_4$B compounds with non-magnetic R elements exhibit unique magnetic properties governed by the Co sublattice only. Their magnetic behavior differs from that of the other RCo$_4$B standards, and they exhibit large magnetocrystalline anisotropy. The RCo$_4$B structure has two R sites (1a and 1b), two others for Co atoms (2c and 6i) and one for boron (2d). It has been shown that the Co 2c site, in ThCo$_4$B is the only site, which exhibits a significant magnetic moment [12], whereas both of the Th and Co 6i sites carry a negligible magnetic moment. On the contrary, in YCo$_4$B both Co 2c and Co 6i sites do carry a magnetic moment. We present in this paper a DFT-based study on the electronic band structure, spin-density maps, magnetic moment in Th-Co$_4$B using different schemes and Brillouin-zone integration methods as implemented in the Wien2k package [13].

2. Computational Methods

The CeCo$_4$B structure can be obtained from the CaCu$_5$ structure if two different crystal lattice sites were introduced for the Ce (1a and 1b) in addition to two other sites for Co (2c and 6i) and one for B(2d), as shown in **Figure 1**. Kuzma *et al*. [14] showed that the B for Co substitution in RCo$_5$ (R is a rare earth or Y) structure leads to a series of compounds of the R$_{n+1}$Co$_{3n+5}$B$_{2n}$ type. ThCo$_4$B differs significantly from the RCo$_4$B where R is a rare earth, having much higher c lattice parameter but with the lattice parameter a close observed for PrCo$_4$B and NdCo$_4$B [2]. ThCo$_5$ crystallizes in the CaCu$_5$ structure (space groupP6/mmm, No. 191). The unit cell contains one formula unit. The experimental lattice constants used in our calculations are a = 4.75 Å and c = 3.93 Å [16]. The ThCo$_4$B has the CeCo$_4$B type of structure (space groupP6/mmm, No. 191). The unit cell contains two formula units, with the room temperature lattice parameters obtained from X-ray diffraction are a = 5.088 Å and c = 7.003 Å [17].

The Wein2K electronic structure code uses the Full-Potential Linearized Augmented Plane Wave (FPLAPW) [18] based on the Density Functional Theory (DFT) [19]. The Local Density Approximation (LDA) of Perdew and Wang [20] and the Generalized Gradient Approximation (GGA) of Perdew, Burke and Ernzerhof [21] were used for correlation and exchange potentials as implemented in the Wien2k code [13]. Both core and valence states are calculated self-consistently, the core states fully relativistically for the spherical part of the potential, and the valence
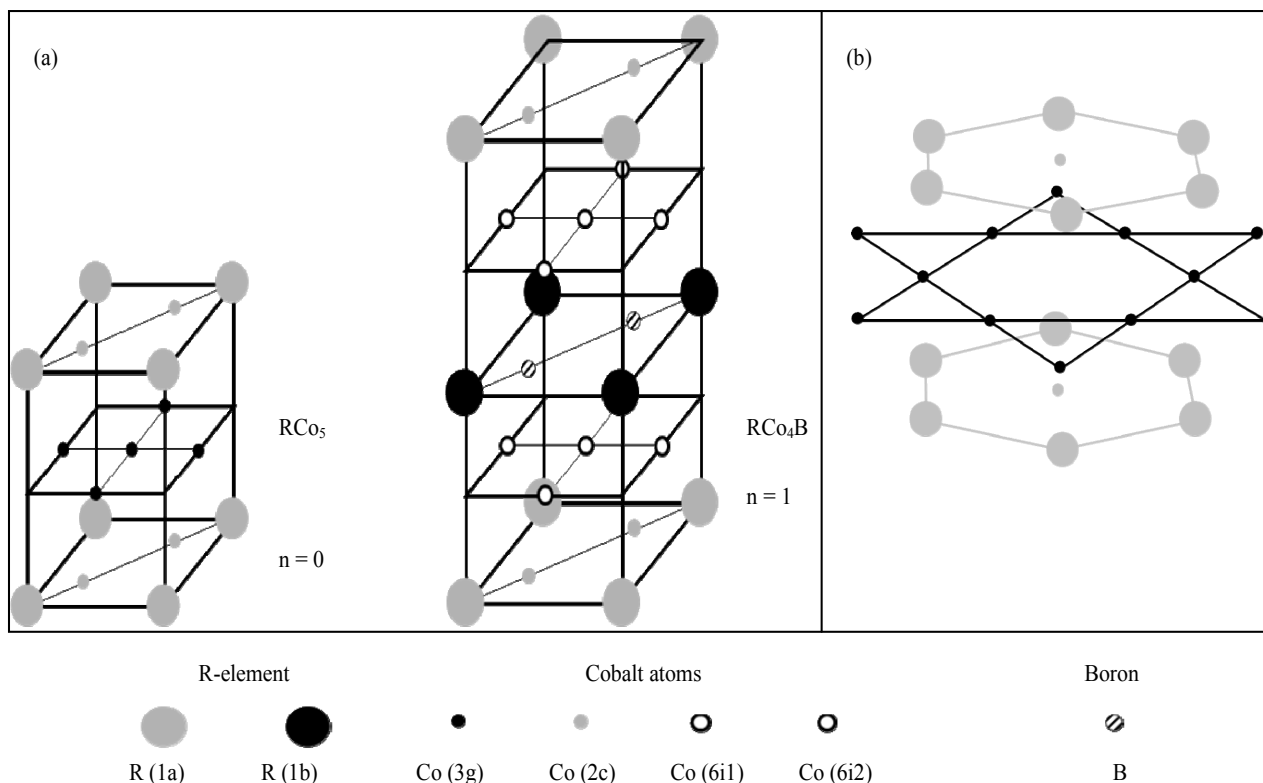
Figure 1. (a) Crystal structures of the $R_{n+1}Co_{3n+5}B_{2n}$ compounds (n = 0, and 1) [15]; (b) Crystal structure of ThCo$_5$. Shown are 2 layers of hexagonal Co (2c) with a Kagome lattice of Co (3g) atoms lying between. The Th atoms lie in the middle of the hexagons in the Co (2c) layers [14].

states using the full potential. Local orbital extensions [22] with the converged basis of approximately 1000 basis functions were used to reduce linearization errors in Th and Co spheres. For the Brillouin zone integration we used the modified tetrahedron method for the self-consistent band structure calculations. Self-consistent calculations were performed and the convergence was checked by varying the number of k points up to 64 in the irreducible Brillouin zone. In order to systematically study the effect of considering different interactions on the magnetic properties, electronic bands and spin-density structure we first performed a pure spin-polarized calculation and then subsequently incorporated SO scheme into the calculation.

The SO interaction was included using a second variational scheme [23] by taking all states below the cut off energy 1.5 Ry. The orbital moment is affected by spin orbit coupling and other correlation effects. The band structure and density of states of localized electrons are not easy to be understood using local density approximation (LDA) method. The spin orbit interaction must be considered in dealing with the 6p states of Th. The 5f states however are above Fermi energy and, unlike the 4f states in rare-earth compounds, are not considered as localized.

3. Results and Discussion

The calculated magnetic moments at each sphere and their comparison with the experimental results and other calculation are shown in **Table 1**.

In this table we present our calculated magnetic moments at different Th and Co sites in ThCo$_5$ and ThCo$_4$B structures together reported experimental and other *ab initio* results for comparison. The calculated Co magnetic moments in ThCo$_4$B at the 2c and 6i sites of Co are 1.33 and 0.28 μ_b respectively. These values are in good agreement with 1.30 and 0.26 μ_b reported by Benea *et al*. [17] using the fully relativistic SPR-KKR method. Rather different values were reported by FPLO calculations [24] namely 1.548 and 0.427 μ_b respectively. Relatively different values were reported by neutron diffraction experiments [25] namely 1.8 and 0.1 μ_b respectively. It is also evident that the magnetic moments at the non-equivalent Th (1a) and Th (1b) sites and at the B (2d) site are rather small and negative in good agreement with earlier work [17, 24].The spin and site-resolved DOS for ThCo$_4$B and ThCo$_5$ structures are shown in **Figures 2(a)** and **(b)** respectively. The main features of **Figure 2** are:

a) The f-states of Th (1a) and Th (1b) non-equivalent sites contribute significantly to the total DOS of ThCo$_4$B. These DOS states are located above E_f indicating their

Table 1. Magnetic moments in the ThCo₄B, and ThCo₅ compounds.

	Co mag. mom. (μB/atom)		Co mag. mom. (μB/atom)		Magnetic moment (μB/f.u.)		
	Calc.		Exp.[a]		Calc.	Exp.[a]	Exp.[b]
	Co 2c	Co 6i, 3g	Co 2c	Co 6i, 3g			
ThCo₄B	1.30[d] [17]	0.27[d] [17]	1.8 [12]	0.1 [12]	1.94[d] [17]	2.1 [12]	1.5 [12]
	1.548[e] [24]	0.427[e] [24]					
	1.332[c]	0.281[c]	----------	----------	2.137[c]	----------	----------
ThCo₅ (HMS)[*]	1.55[d] [17]	1.48[d] [17]	1.6 [25]	1.6 [25]	7.2[d] [17]	8.0	7.3 [26]
ThCo₅ (LMS)[**]	1.10[f] [27]	0.55[f] [27]	1.2 [25]	1.0 [25]	4.2 [27]	5.4	4.9 [26]
ThCo₅	1.201[c]	1.353[c]	----------	----------	5.857[c]	----------	----------

	Magnetic moments (μB / atom) for ThCo₄B					
	Th 1a	Th 1b	Co 2c	Co 6i	B 2d	Total
Ref.[17]	− 0.169[d]	− 0.167[d]	1.106[d]	0.252[d]	− 0.025[d]	1.670[d]
Ref.[24]	− 0.161[e]	− 0.137[e]	1.548[e]	0.427[e]	− 0.043[e]	----------
This work	− 0.152[c]	− 0.139[c]	1.332[c]	0.281[c]	− 0.022[c]	1.644[c]

[a]Neutron diffraction; [b]Magnetization measurements; [c]Current work; [d]Fully relativistic SPR-KKR calculations; [e]FPLO method; [f]Spin-orbit coupling included as perturbation. [*]High Moment Spin; [**]Low Moment Spin.

non-localized nature in these two compounds. The hybridization between the Th (1b) and B (2d) atoms results in DOS features different from those of the Th (1a) atoms. This may be attributed to the fact that Th (1a) atoms lack the presence of the B (2d) atoms in the crystal plane in which they are located;

b) The states of boron contribute but little to the total DOS. These features are generally in accord with the data reported by Benea *et al*. [17] and Szajek [24].

The calculated band structures of the two Co sites 2c and 6i have noticeable different behavior as shown in **Figure 3**. Considering the close relationship between the ThCo₄B and ThCo₅ structure types (the ordered substitution of one half of the Co 2c site in the ThCo₅ by B leads to ThCo₄B structure, with B located on the 2d site), the calculated Co contributions to DOS can be compared in mentioned compounds. Upon changing the Co by B different environment were introduced for the Co atoms and its 3g site in the ThCo₅ structure to be the 6i site in the ThCo₄B structure. The effect of the SO coupling on the 6p states of the Th (1a) and Th (1b) atoms is shown by comparing the spin-polarized Band **Figure 4(a)** to their counterparts where SO has been taken into consideration

Figure 4(b). The splitting into 6 p1/2 and 6 p3/2 is around 7 eV however it is a bit larger for the Th (1a) atom. Our calculation is consistent with the work of Szajek [24].

The spin-density maps are shown in **Figure 5**, for ThCo₄B in the (100), (001) and (002) planes using just the spin-polarized scheme. In the (100) plane nine atoms of Th and four Co (2c) are displayed. The (100) and (001) planes are boron-free. The latter one displays 5 atoms of Th and 6 Co (2c) atoms. The (002) plane, on the other hand is Co-free and has 5 Th and 6 B atoms (for the charge density maps see **Figure 6**). These spin-density maps show clearly that spin contours are concentrated mainly around the Co atoms in support to the data of **Table 1**. The effect of SO interaction on the spin density is shown in **Figure 7**. The SO effect is largely due to the p-state of the Th atoms as we have discussed earlier. We have performed similar calculation on ThCo₅ in the (100) and (001) planes. These two planes contain 9 Th + 4 Co and 5 Th + 6 Co atoms respectively. We have found that the SO effect is also strongest on the Th atoms of this system. The spin-contour maps for ThCo₅ in the (100) plane, using the bare spin-polarized approximation and in the case of incorporating the SO interaction are shown in **Figures 8(a)** and **(b)** respectively.
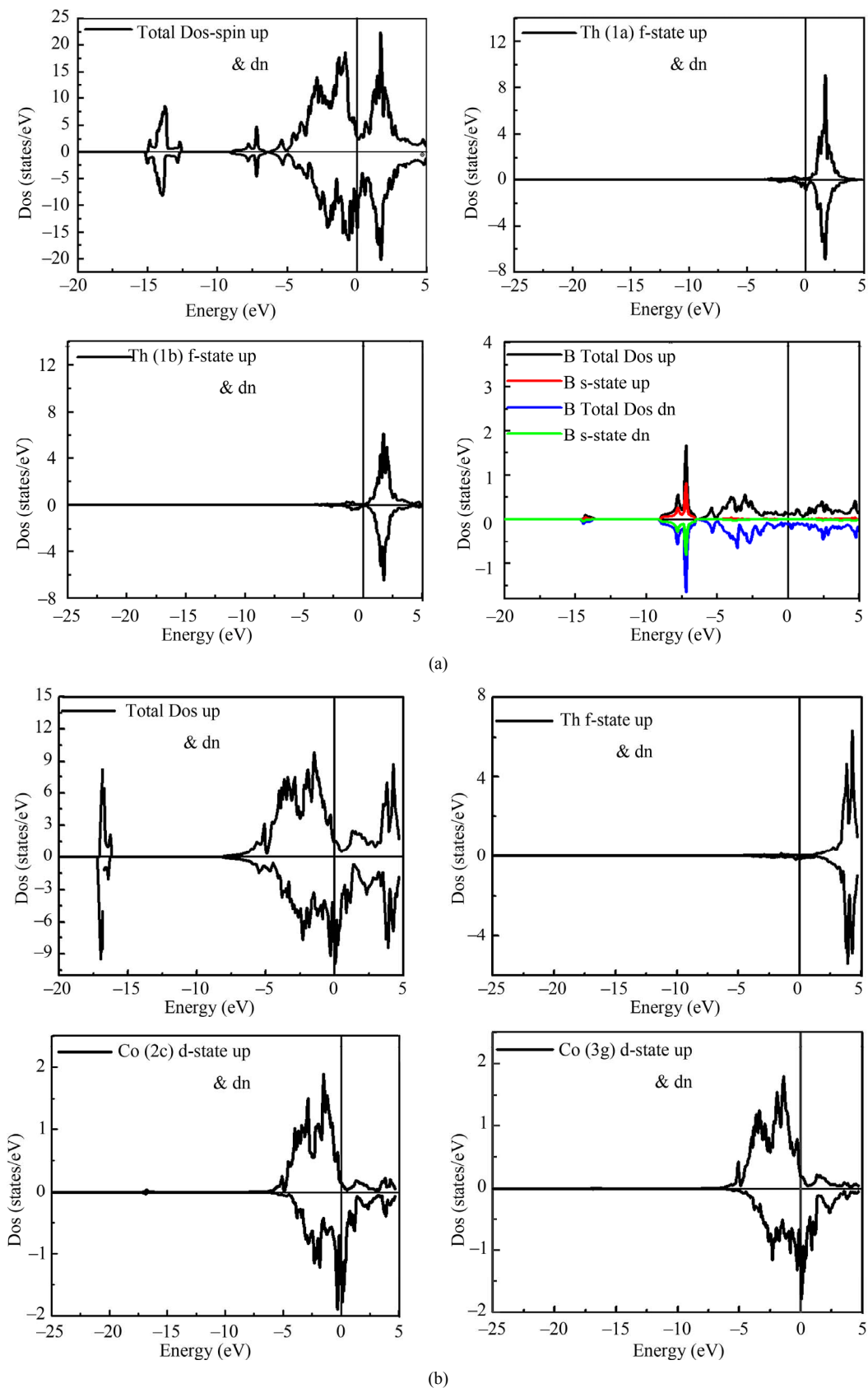
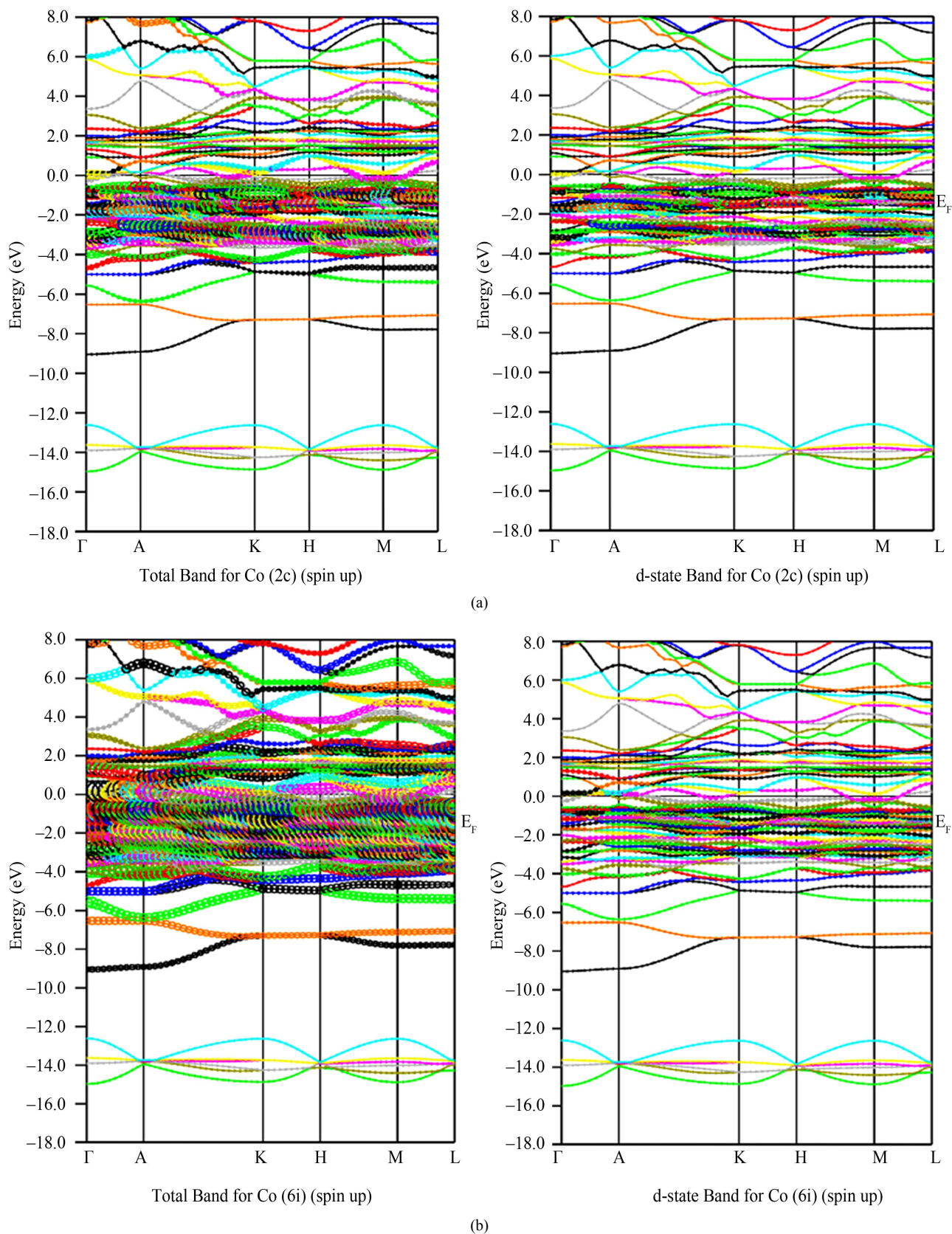Figure 2. (a) the spin polarized Dos (up + down) for ThCo$_4$B; (b) the spin polarized Dos (up + down) for ThCo$_5$.

Figure 3. (a) the spin polarized band structure (up) for the Co (2c)-atom in ThCo₄B; (b) the spin polarized band structure (up) for the Co (6i)-atom in ThCo₄B.
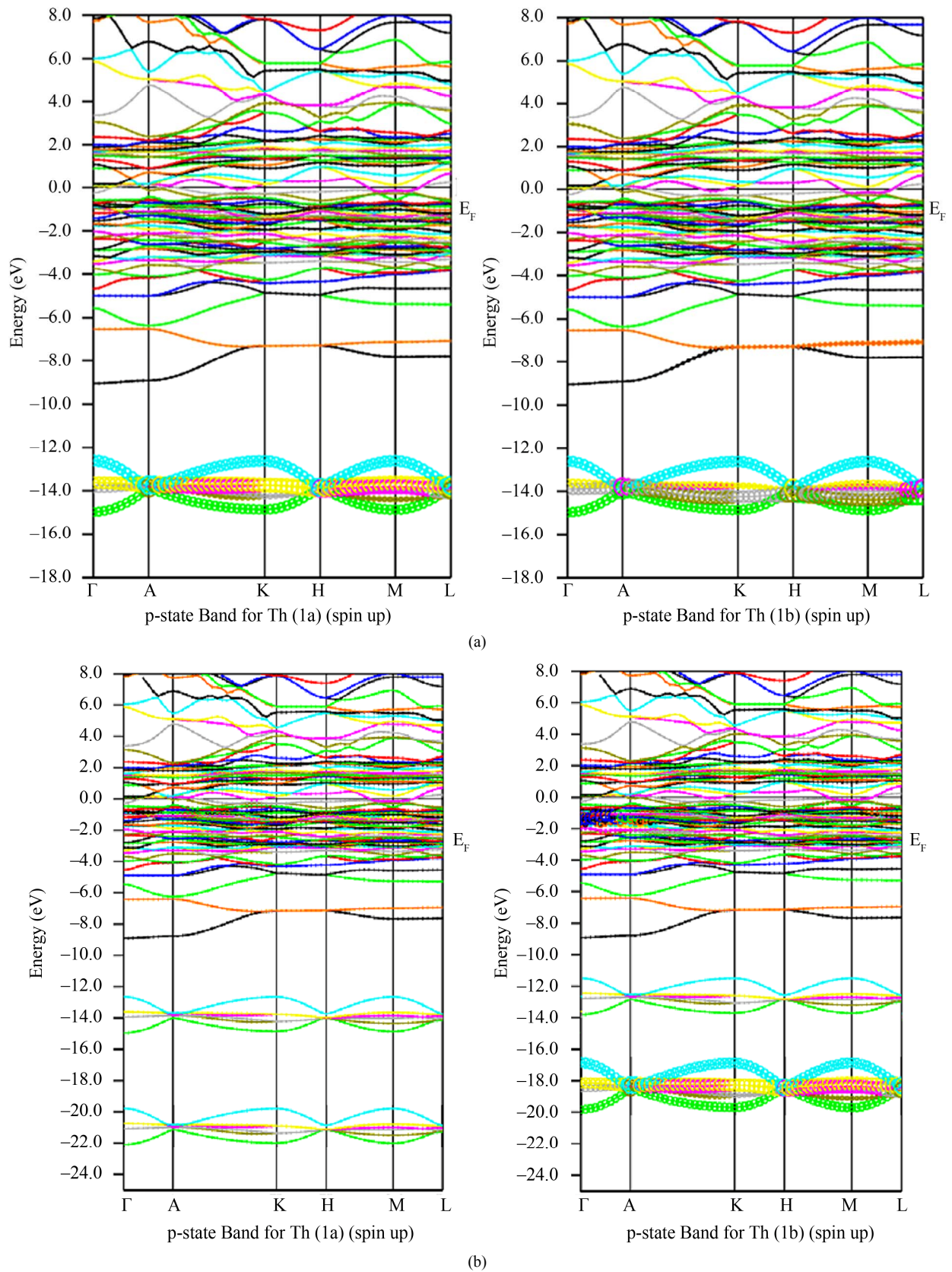
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(a)

(b)

Figure 4. (a) the spin polarized band structure (up), for Th (1a) and Th (1b) [p-state] in ThCo₄B; (b) the spin polarized band structure with So (up) for Th (1a) & Th (1b) [p-state] in ThCo₄B.
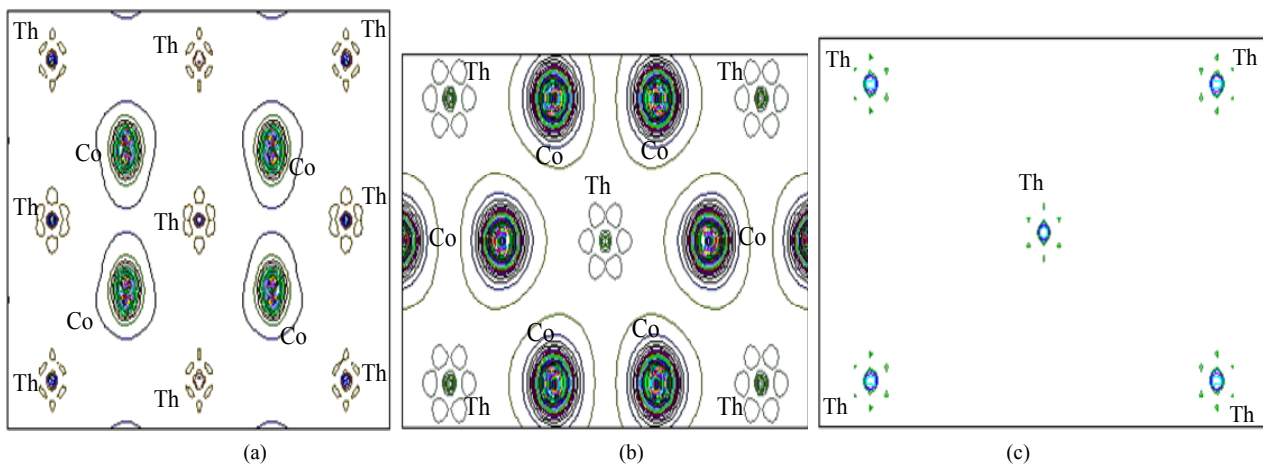
Figure 5. (a) the spin density map (spin polarized) for ThCo₄B (100-plane); (b) the spin density map (spin polarized) for ThCo₄B (001-plane); (c) the spin density map (spin polarized) for ThCo₄B (002-plane).
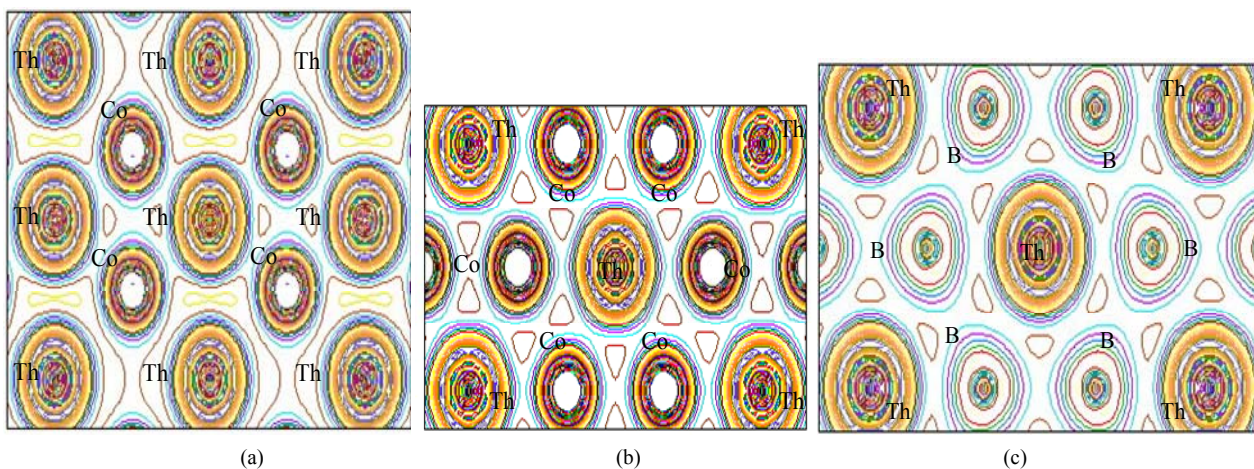

Figure 6. (a) the electronic charge density (spin polarized) for ThCo₄B (100-plane); (b) the electronic charge density (spin polarized) for ThCo₄B (001-plane); (c) the electronic charge density (spin polarized) for ThCo₄B (002-plane).
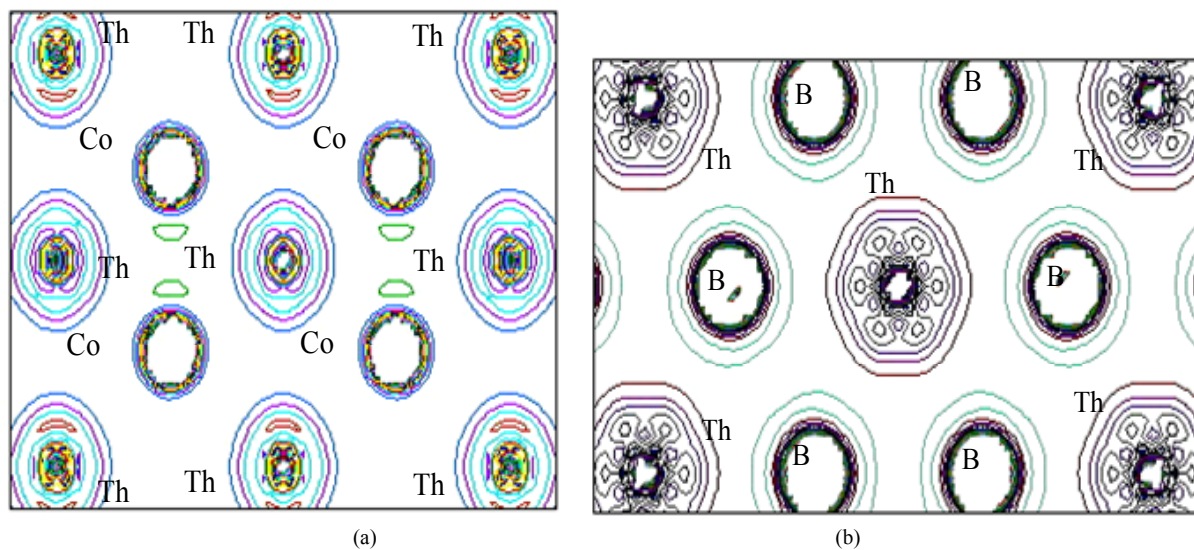

Figure 7. (a) the spin density map (spin polarized with SO) for ThCo₄B (100-plane); (b) the spin density map (spin polarized with SO) for ThCo₄B (002-plane).
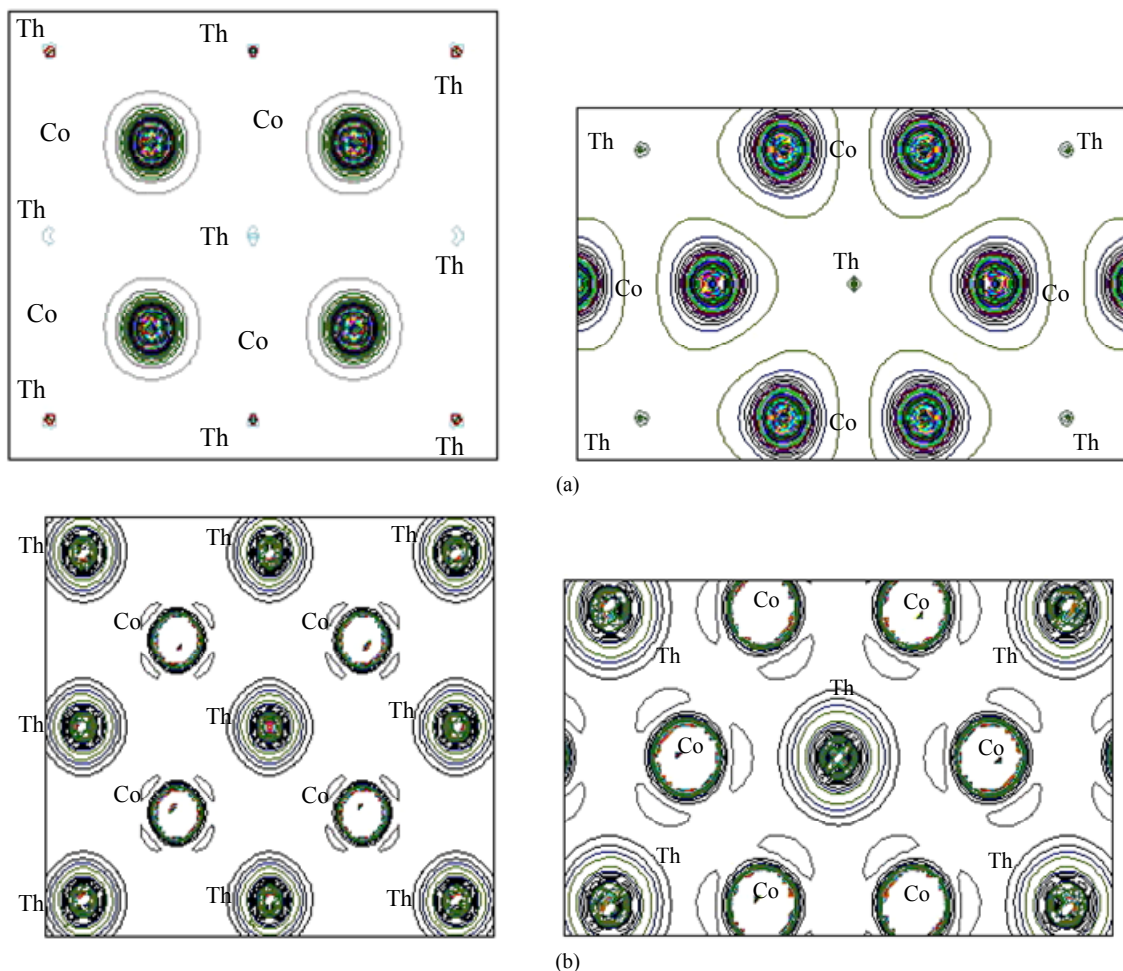
Figure 8. (a) (left) the spin density map (spin polarized) for ThCo$_5$ (100-plane). (right) the spin density map (spin polarized for) ThCo$_5$ (001-plane); (b) (left) the spin density map (spin polarized with SO) for ThCo$_5$ (100-plane). (right) the spin density map (spin polarized with SO) for ThCo$_5$ (001-plane).

4. Conclusion

The magnetic moment of ThCo$_4$B compound is largely due to cobalt atoms in particular those at the 2c sites. Spin-orbit coupling affects the p-state of Th significantly. The p$_{1/2}$-p$_{3/2}$ spin-orbit splitting of this core state is site dependent, i.e. it is not the same for the Th (1a) and (1b) sites. Spin-polarized and spin-polarized calculation with SO interaction included, demonstrate the effect of SO on the spin density maps in ThCo$_4$B and its parent compound ThCo$_5$.

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