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Neutron diffraction investigation of the crystal and magnetic structure of the new ThCo_4B compound

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Abstract

The crystal and magnetic structures of a new ternary phase in the Th–Co–B system have been investigated by high resolution neutron diffraction. The spontaneous magnetization and Curie temperature were determined by magnetic measurements. The ThCo_4B phase crystallizes in a hexagonal crystal structure, space group $P6/mmm$ with $a = 5.088 \text{ \AA}$ and $c = 7.003 \text{ \AA}$. ThCo_4B orders ferromagnetically at 303 K, a temperature much smaller than that of the isotopic RCo_4B where R is a rare-earth element or yttrium. The Co magnetic moments are found to be aligned along the c -axis of the hexagonal structure in the whole ordered temperature region. The two inequivalent Co crystal sites are found to exhibit different magnetic behaviours. At 2 K a substantial magnetic moment of $1.8 \pm 0.1 \mu_B$ is observed on the Co 2c site whereas a nearly zero magnetic moment is found on the Co 6i site. A similar behaviour was also found at room temperature, $1.2 \pm 0.2 \mu_B$ on the Co 2c site and zero μ_B on the Co 6i site. The influence of the local environment on the magnitude of the Co moments in ThCo_4B is discussed. The magnetic properties of ThCo_4B are compared to that of isotypic YCo_4B .

1. Introduction

The search for new thorium containing intermetallic phases is an active field of research [1–4]. These last ten years, the study of thorium–transition metal intermetallic phases has led to the discovery of many new phases such as the $\text{ThFe}_{0.22}\text{Sn}_2$ and $\text{Th}_4\text{Fe}_{13}\text{Sn}_5$ [2, 3] ternary phases. Among these new phases, the $\text{ThFe}_{11}\text{C}_x$ compounds have been discovered by Jacobs and co-workers [5]. The magnetic properties have been reported in detail [6, 7]. In their pioneer

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studies, Buschow *et al* [8, 9] have evidenced that four intermetallic compounds occur in the Th–Co system. A large homogeneity region has been observed [9] for the ThCo₅ phase which is stabilized from ThCo₅ up to a stoichiometry of ThCo_{5.7}. This large homogeneity range was found to lead to different magnetic behaviour [10] and even to a magnetic transition for some cobalt concentrations. In compounds where the Co content is larger than ThCo_{5.1} a normal ferromagnetic behaviour is observed. In contrast, a metamagnetic transition is observed at about 10 T in ThCo₅ [10], a transition which has been attributed to the 3d band on the 3g site. The Co 3g site changes its magnetic moment from 1.1 to 1.4 μ_B . Here we report on a new phase of the Th–Co–B ternary phase diagram which can be described as deriving from the ThCo₅ crystal structure. The crystal structure as well as the magnetic structure of ThCo₄B are investigated from Rietveld refinements of the observed neutron intensities.

2. Experimental details

The alloys were prepared from commercially supplied metals: thorium (99.8 wt% purity) from Metals Crystals and Oxides Ltd, UK, cobalt (99.95% purity) from Aldrich Chemical Company USA and isotopic ¹¹B from Eurisotop, France. We have chosen to use ¹¹B instead of ¹⁰B in order to lower the neutron absorption cross section. Polycrystalline samples were prepared by melting starting elements using an arc furnace and subsequently re-melted in a high frequency induction furnace under a purified argon gas atmosphere. For better homogeneity the sample was wrapped in a Ta foil and subsequently annealed at 1173 K for a week in an evacuated quartz tube. The purity of phases was checked by x-ray diffraction using a Siemens D500 powder diffractometer with the $K\alpha_1$ radiation of copper ($\lambda = 1.5406 \text{ \AA}$). A precise determination of the lattice parameters was obtained by a least squares refinement method.

In order to determine the easy magnetization direction (EMD), the x-ray diffraction investigations were performed on field-oriented samples, prepared at room temperature, by solidifying the mixture of epoxy resin and the powder specimen (grain size $\leq 50 \mu\text{m}$) in a magnetic field of about 1 T. For these experiments a Philips PW1050 $\theta/2\theta$ diffractometer operating at a wavelength of 1.9373 \AA was used. The same procedure is also used to prepare field-aligned samples for the magnetic anisotropy measurements.

The alloy purity has been checked by using a JEOL 840A scanning electron microscope equipped with an KEVEX energy dispersive x-ray EDX microprobe.

The magnetic ordering temperature has been determined with a Faraday type balance at heating and cooling rates of 5 K min⁻¹. A sample of about 50–100 mg was sealed under vacuum in a small silica tube in order to prevent oxidization of the sample during heating. The magnetization curve of ThCo₄B was recorded at 4 K by the extraction method [11] in a continuous field up to 10 T. The saturation magnetization values have been derived from an extrapolation to zero field of the magnetization obtained in fields higher than 4 T. A detailed description of the experimental set-up can be found elsewhere [11].

The neutron diffraction experiments have been performed at the Institut Laue Langevin (ILL) at Grenoble, France, on the *D1B* and *D1A* instruments whose detailed description can be found elsewhere [12]. *D1A* is a very high resolution powder diffractometer operating with a take-off angle of the monochromator of 122°. In the configuration used the resolution of *D1A* is about 0.3° (full width at half maximum) at 90°. The measurement recorded at 2 K was carried out at a wavelength of $\lambda = 1.911 \text{ \AA}$. During the neutron diffraction measurements a cylindrical vanadium sample holder of 6 mm inner diameter was used. The neutron detection is performed with ³He counting tubes spaced at 6°. The complete diffraction pattern is obtained by scanning over the whole 2θ range. The room temperature diffraction pattern has been measured on the instrument *D1B* operated by the CNRS at the ILL. On the *D1B* instrument the diffraction

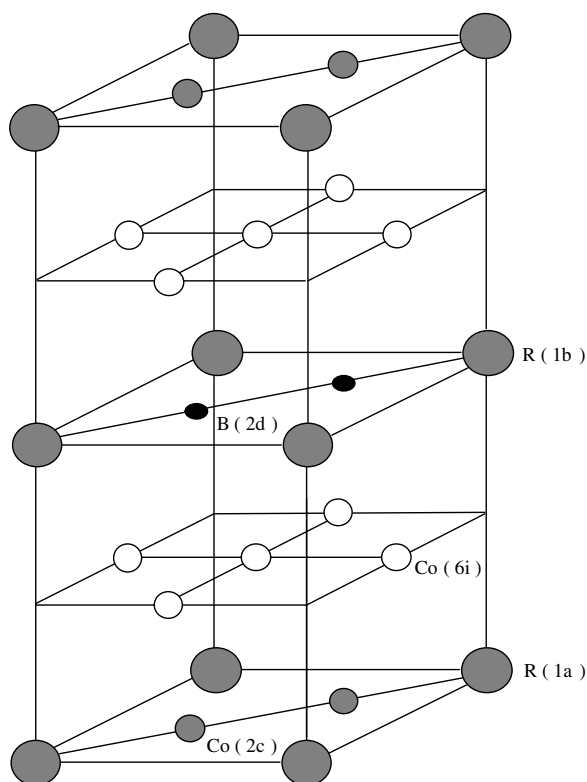


Figure 1. Crystal structure of ThCo₄B comprising two types of Co site (6i and 2c), one for B (2d) and two for Th (1a, 1b). The Th atoms are occupying the sites labelled R.

patterns have been recorded over an angular range of 80° (2θ) using a multidetector with a step of 0.2° between each of the 400 ^3He detection cells. In this configuration *D1B* is operating with a wavelength of $\lambda = 1.28 \text{ \AA}$ selected by a (311) Bragg reflection of a Ge monochromator, the take-off angle being 44.2° in 2θ .

The data were analysed with the Rietveld structure refinement program FULLPROF [13]. Definition of the Rietveld refinement agreement factors used here can be found elsewhere [14]. The neutron scattering lengths used were $b_{\text{Co}} = 0.249 \times 10^{-14} \text{ m}$, $b_{\text{Th}} = 1.031 \times 10^{-14} \text{ m}$ and $b_{\text{B}} = 0.530 \times 10^{-14} \text{ m}$, values taken from [15].

The problem of the neutron absorption has been taken into account according to [16]. The transmission factor A_{hkl} has been calculated according to the formula proposed by Hewat [17] and this leads to adjustments of the isotropic Debye–Waller factors (B) also often referred to as atomic displacement parameters. The correction to the isotropic atomic displacement parameters is calculated to be $\Delta B = 0.25 \text{ \AA}^2$ for ThCo₄B.

3. Results and discussion

The x-ray diffraction analysis confirms that the compound is single phase with the CeCo₄B structure [18] of space group $P6/mmm$ (191). The CeCo₄B type structure can be derived from the CaCu₅ structure and has two different crystallographic sites for cerium (1a and 1b), two other sites for cobalt (2c and 6i) and one site for the boron atom (2d), figure 1. This structure type

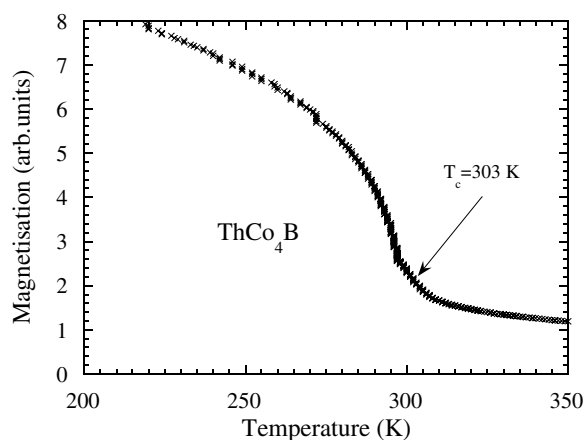


Figure 2. Thermomagnetic investigation of ThCo_4B , showing the Curie temperature at 303 K.

Table 1. Room temperature lattice parameters obtained from x-ray diffraction and magnetic properties of ThCo_4B (this work), CeCo_4B and YCo_4B [18, 19, 25].

	a (Å)	c (Å)	V (Å ³)	T_C (K)	M_S (μ_B/fu)
ThCo_4B	5.088(1)	7.003(1)	157.0	303(4)	1.5(1)
CeCo_4B	5.005	6.932	150.4	297	—
YCo_4B	5.020(1)	6.891(2)	150.4	380(4)	2.9(1)

was first reported by Kuz'ma and Bilonizhko [18] who observed that a limited substitution of boron for cobalt is possible in the RCO_5 structure, leading to a series of compounds of formula $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$. Since then several studies have been focused on the investigation of the structural and magnetic properties of these phases either by neutron diffraction [19–21], nuclear magnetic resonance (NMR) spectroscopy [22–24], magnetic measurements [25] or band structure calculations [26, 27]. To our best knowledge the formation of the ThCo_4B phase has not been reported until now. The lattice parameters of the ThCo_4B phase are summarized in table 1. It has been shown that in the RCO_4B compounds [25] the c parameter remains constant at about 6.889(2) Å, whatever the rare-earth element is, whereas a significant dependence of the a parameter on R element is observed. It is worth noting that in ThCo_4B , the c lattice parameter differs significantly from that of RCO_4B . Table 1 gives a comparison between the lattice parameters of ThCo_4B and those of YCo_4B , for instance. For ThCo_4B a significantly higher value is obtained: 7.003(1) Å. In the RCO_4B phase the c parameters were found to be determined by the Co (2c)–Co (6i) and Co (6i)–B (2b) exclusively [25]. CeCo_4B is the only compound exhibiting c parameter significantly larger than that reported for the other rare-earth elements as a result of the tetravalent nonmagnetic state of Ce [18]. In ThCo_4B the c parameter is also large and could result from the non-trivalent state of Th. The a lattice parameter of ThCo_4B is close to that observed for PrCo_4B and NdCo_4B . Because, in most Th transition metal compounds, Th does not carry any magnetic moment [2, 5, 8, 9], the magnetic properties of ThCo_4B will be compared to that of the YCo_4B isotypic phase. In spite of no significant magnetic moment on Y and Th, table 1, YCo_4B and ThCo_4B have different ordering temperatures of 380 and 303 K respectively as shown by the temperature dependence of the magnetization in ThCo_4B in figure 2. In CeCo_4B the ordering temperature is 297 K, a value much closer to that of ThCo_4B .

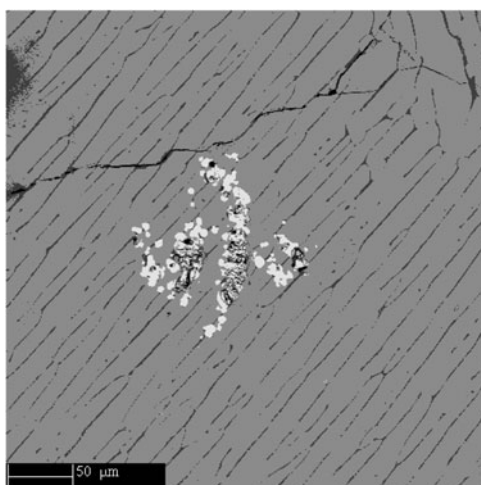


Figure 3. Back-scattered electron image recorded using a JEOL 840A scanning electron microscope. The grey and white phases correspond to ThCo_4B and ThO_2 respectively.

In addition to x-ray diffraction analysis, scanning electron microscopy (SEM) has been used to analyse the phase purity of the sample. According to the quantitative EDX analysis, the main phase observed in figure 3 is found to correspond to the ThCo_4B phase. The Th and Co concentrations obtained by the EDX analysis are in good agreement with the composition expected for ThCo_4B . Light elements such as boron cannot be quantified accurately by EDX analysis, consequently boron concentration will be determined by neutron diffraction experiment. As can be seen from figure 3, traces of an impurity have been observed. This impurity phase appears in white in the picture recorded with back-scattered electrons. This implies that this phase is richer in Th atoms than the matrix ThCo_4B . EDX microprobe analysis reveals that this minor impurity phase contains oxygen and thorium. As will be seen later on, this impurity phase corresponds to ThO_2 .

In order to go further in the analysis of the ThCo_4B compound and compare it with YCo_4B , we have performed neutron powder diffraction investigations. The data recorded have been analysed with the Rietveld method, results of which can be seen in figures 4 and 5. The structural and magnetic feature of ThCo_4B are summarized in table 2. At room temperature, the atomic displacement parameters, also often referred to as Debye–Waller thermal parameters, are found to be 0.45, 0.25 and 0.6 Å for the Co, Th and B atoms respectively. As can be seen from figures 4 and 5 a small amount of 2 vol% of ThO_2 as impurity was detected. In spite of the fact that the Curie temperature is very close to room temperature, a significant magnetic scattering was evidenced for the neutron diffraction investigation performed on the *D1B* instrument. Since YCo_4B is well known to exhibit a spin reorientation phenomenon between the basal plane and the *c* axis of the hexagonal structure a question is ‘what is the orientation of the magnetic moments in ThCo_4B ?’. To answer this, x-ray diffraction has been performed on a sample oriented in an external magnetic field. The corresponding diffraction pattern is represented in figure 6. In the case of ThCo_4B , the effects of the orientation by a magnetic field on the x-ray diffraction pattern are an increase of the Bragg peaks corresponding to (00*l*) planes. Some other Bragg peaks disappear, even the most intense ones observed in the conventional diffraction pattern. This is a clear indication that, at room temperature, the EMD of ThCo_4B is along the *c* axis of the crystal structure. Hence, the refinement of the magnetic

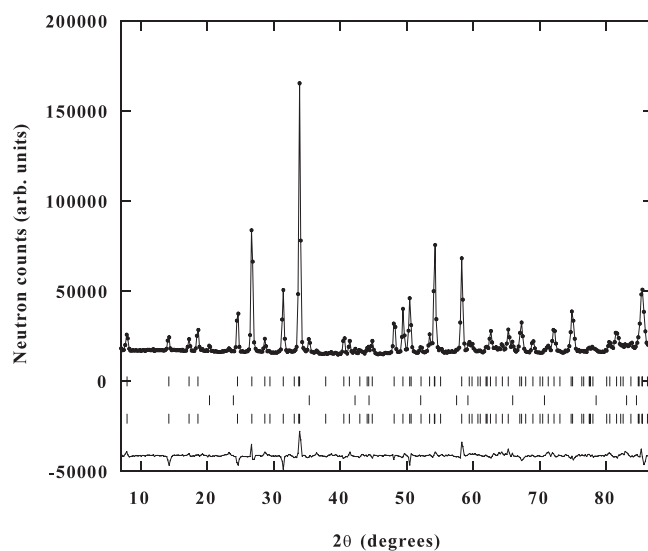


Figure 4. Neutron powder diffraction pattern for ThCo_4B at 300 K ($\lambda = 1.28 \text{ \AA}$). The dots represent the experimental data. The difference between the experimental data and the calculated fit is plotted in the lower part of the figure. Vertical bars indicate calculated Bragg peak positions for both nuclear (first row) and magnetic structures (third row). The second row of bars corresponds to the Bragg peak positions of the impurity ThO_2 .

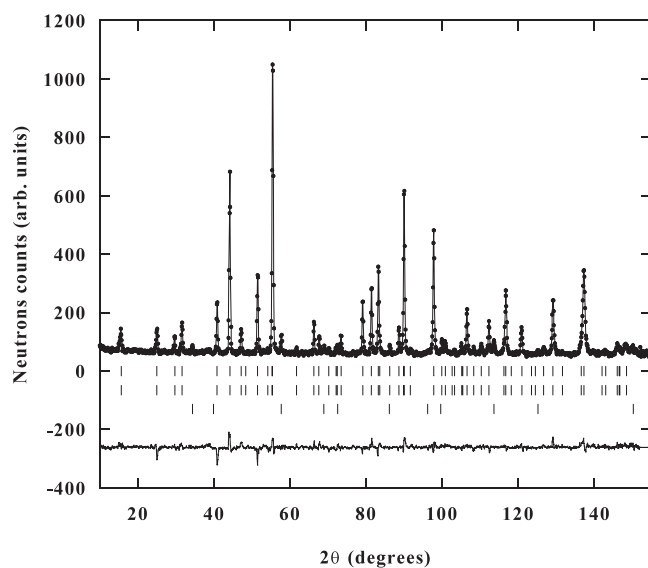


Figure 5. Neutron powder diffraction pattern for ThCo_4B at 2 K ($\lambda = 1.91 \text{ \AA}$). The dots represent the experimental data. The difference between the experimental data and the calculated fit is plotted in the lower part of the figure. Vertical bars indicate calculated Bragg peak positions for both nuclear (first row) and magnetic structures (second row). The third row of bars corresponds to the Bragg peak positions of the impurity ThO_2 .

structure has been carried out assuming that the Co magnetic moments are aligned along the c axis of the unit cell, in agreement with the RT alignment in YCo_4B [19–21, 25]. Refinement of

Table 2. Rietveld analysis results of the neutron powder diffraction data recorded at 2 and 300 K for ThCo₄B. The investigations were performed on *D1A* ($\lambda = 1.911$ Å) and *D1B* ($\lambda = 1.28$ Å) instruments at the ILL.

Parameter	290 K	2 K
Instrument	<i>D1B</i>	<i>D1A</i>
Wavelength (Å)	1.28	1.911
Th 1a (<i>x, y, z</i>)	(0, 0, 0)	(0, 0, 0)
Th 1b (<i>x, y, z</i>)	(0, 0, 0.5)	(0, 0, 0.5)
Co 2c (<i>x, y, z</i>)	(1/3, 2/3, 0)	(1/3, 2/3, 0)
Co 6i (<i>x, y, z</i>)	(0.5, 0, 0.2946)	(0.5, 0, 0.2935)
B 2d (<i>x, y, z</i>)	(1/3, 2/3, 0.5)	(1/3, 2/3, 0.5)
$M_{\text{Co}}(2c)$ (μ_B)	1.2(2)	1.8(1)
$M_{\text{Co}}(6i)$ (μ_B)	0.2(2)	0.1(1)
<i>a</i> (Å)	5.083(1)	5.070(1)
<i>c</i> (Å)	7.001(1)	6.981(1)
R_{Bragg} (%)	8.6	8.8
R_{wp} (%)	4.86	7.46
R_{exp} (%)	0.68	4.61
R_{mag} (%)	24.7	19
χ^2	50.4	2.61

the magnetic moment leads to a substantial moment of $1.2 \pm 0.2 \mu_B$ on the Co 2c crystal site and, most interesting, results in a nearly zero magnetic moment on the Co 6i site, see table 2.

It is worth mentioning that the rather high value obtained for the magnetic Rietveld agreement factor is due to the small intensity of the magnetic scattering comparison to the nuclear scattering in ThCo₄B. This is a general feature of the RCo₄B phase and has already been mentioned elsewhere [21]. This is even more important here since Th does not carry any localized magnetic moment. In order to investigate the magnetic structure at low temperature, high resolution powder diffraction investigation has been performed on *D1A*. As expected the refined Co 2c site magnetic moment is found to be larger at $1.8 \pm 0.1 \mu_B$, a value which is slightly larger than the saturation magnetization. This can be easily explained by the negative polarization of the conduction electrons. At low temperature, the magnetic moment is also found to be aligned along the *c* axis of the structure. The magnitude of the magnetic moments on the Co 2c site is very close to that observed on elemental Co ($1.7 \mu_B/\text{Co atom}$), or that earlier reported for YCo₅ ($1.8 \mu_B/\text{Co atom}$) [28, 29] or that found on the same position in YCo₄B phases [19–21]. In the case of the Co 6i site, the situation is very peculiar since no significant magnetic moment is observed even at 2 K. In the isotypic RCo₄B phases [30, 31] a small but significant magnetic moment of about $0.7 \mu_B/\text{atom}$ is measured on this site. In ThCo₄B the Co magnetic moment on the Co 6i must be less than $0.1 \mu_B$. It is worth stressing that a unusual magnetic behaviour has also been reported in the ThCo₅ type phase [10, 32]. A detailed investigation of the magnetic properties of ThCo₄B is in progress and will be reported elsewhere [33].

The absence of significant magnetic moment on the Co 6i site results from the strong electronic hybridization of this site with the surrounding boron and thorium atoms. Indeed, particularly short inter-atomic Co–B distance is observed: $d_{\text{Co6i-B}} = 2.06(1)$ Å. The Co 2c–B distance is longer at $3.50(1)$ Å and hence Co 2c is not influenced by boron. In the R_{*n*+1}Co_{3*n*+5}B_{2*n*} structures, the hybridization of the cobalt 3d electronic states with the boron 2p states has been found to play a major role in the determination of the magnitude of the Co magnetic moment [21, 31]. The second factor influencing the Co magnetic moment may be the bonding between the Co and the neighbouring Th atoms. Indeed, the Co 6i site is

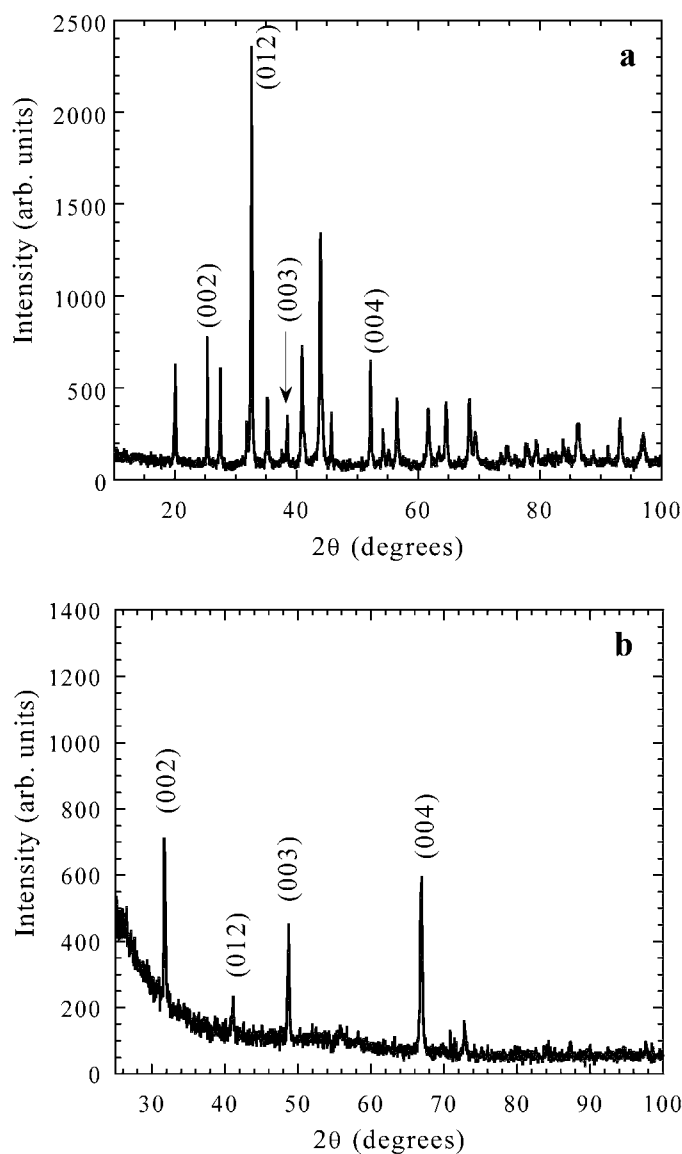


Figure 6. Comparison between the x-ray diffraction patterns obtained on a free powder (a) and that recorded on a field-oriented sample (b) of ThCo_4B at room temperature with $\lambda = 1.5418$ and 1.9373 \AA respectively. The corresponding (hkl) values are given in both parts for clarity.

characterized by both the shorter Co–Th bond lengths and the larger number of Th atoms in its environment, see table 3. The Co 6i site has two Th 1a and Th 1b neighbours located at 3.26 and 2.92 \AA respectively. An electronic transfer from the Th atoms onto the Co electronic orbitals may explain the dramatic decrease of the magnetic moment on the Co 6i site, in comparison with the isotopic RCo_4B phases. Indeed, the absence of magnetic moment on the Th atom indicates an empty 5f electronic shell and consequently an excess of valence electrons in the 6d and 7s shells. The magnetism of Co atoms is well known to be very sensitive to the number of valence electrons in its neighbourhood since no Co magnetic moments are observed for the

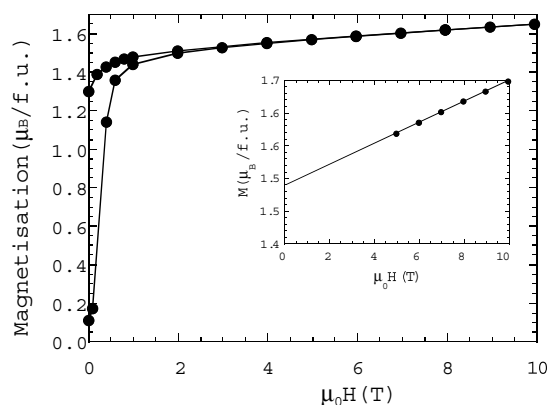


Figure 7. Isothermal magnetization curve recorded at 4 K for ThCo₄B. Inset: determination of the saturation magnetization by extrapolation to zero field of the magnetization curve recorded above 4 T.

Table 3. Shorter inter-atomic distances at room temperature in ThCo₄B.

Distances (Å)	Th 1a	Th 1b	Co 2c	Co 6i	B
Th 1a	—	3.50	2.93	3.26	—
Th 1b	3.50	—	—	2.92	2.93
Co 2c	2.93	—	2.93	2.52	3.50
Co 6i	3.26	2.92	2.52	2.54	2.06
B	—	2.93	3.50	2.06	2.93

rare-earth rich R–Co intermetallic compounds [34]. In contrast, the Co 2c site keeps the same magnetic moment as observed in the other RCo₄B compounds, because first the Co has no direct bonds with boron and second has only three Th atoms in its environment.

The absence of Co 6i site magnetic moment induced by the presence of Th neighbours is a further indication of the sensitivity of the cobalt magnetism to its local environment. The iron moment has also been observed to be very sensitive to its environment; an extensive discussion of this can be found elsewhere [35].

We have seen that unlike YCo₄B, ThCo₄B does not exhibit any spin reorientation phenomenon of its easy magnetization direction. According to the present neutron diffraction investigation, this can be explained by the fact that in YCo₄B the spin reorientation phenomenon results from a competition between the preferential anisotropy direction of the two different Co crystal sites. In ThCo₄B, only the Co 2c site is magnetic and consequently this site imposes its easy magnetization direction in the whole ordered temperature range.

The 4 K isothermal magnetization curve of ThCo₄B is plotted in figure 7. According to the inset of figure 7, the saturation magnetization is $1.5 \pm 0.1 \mu_B/\text{fu}$. When decreasing the external field to zero, a remanent magnetization of $1.3 \mu_B/\text{fu}$ is observed.

4. Conclusion

A new ThCo₄B phase has been synthesized and was found to crystallize in the CeCo₄B structure type, space group *P6/mmm*, which is an ordered superstructure of the CaCu₅ structure type. In spite of the fact that ThCo₄B retains the same crystal type as the RCo₄B phases both its structural properties and magnetic behaviour present peculiarities. The *c* lattice parameter of

ThCo₄B is larger than that of the RCo₄B one. ThCo₄B orders ferromagnetically below 303 K, a temperature which is a much smaller than those of the RCo₄B isotypic compounds, as a result of the much smaller cobalt magnetization. Indeed, in ThCo₄B, the Co 2c site is found to carry most of the magnetic moment, similar to that observed on the 2c site in the other RCo₄B, whereas the Co 6i site carries a negligible magnetic moment. In RCo₄B isotypic compounds, the Co 6i site is known to carry a significantly reduced magnetic moment because of its strong bond with the boron near neighbours; furthermore, the progressive filling of the 3d band by the Th valence electrons may be at the origin of the observed collapse of the Co 6i magnetic moment. The possible influence of the Co–Th and Co–B bonds on the magnitude of the Co magnetic moment seems to be determinant. The magnitude of the Co 2c site magnetic moment is not affected by the replacement of Y by Th, whereas the Co 6i site magnetic moment is much more sensitive and even disappears after this replacement. The absence of magnetic moment on the Co 6i site is probably at the origin of the dramatic decrease of the Curie temperature from YCo₄B to ThCo₄B.

According to the neutron diffraction investigation, the Co magnetic moments are aligned along the *c* axis of the crystal structure from 2 K up to the Curie temperature. Further studies have to be carried out in order to find whether other Th_{*n*+1}Co_{3*n*+5}B_{2*n*} phases such as ThCo₃B₂ or Th₃Co₁₁B₄ can be stabilized in the Th–Co–B ternary phase diagram.

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References

- [1] Manfrinetti P, Palenzona A, Dhar S K and Mitra C 1999 *Intermetallics* **7** 1291
- [2] Moze O, Manfrinetti P, Canepa F, Palenzona A, Fornasini M L and Rodriguez-Carvajal J R 2000 *Intermetallics* **8** 273
- [3] Manfrinetti P, Canepa F, Palenzona A, Fornasini M L and Giannini E 1997 *J. Alloys Compounds* **247** 109
- [4] Jacobs T H, Long G J, Pringle A O, Grandjean F and Buschow K H J 1991 *J. Appl. Phys.* **70** 5983
- [5] Isnard O, Soubeyroux J L, Fruchart D, Jacobs T H and Buschow K H J 1992 *J. Phys.: Condens. Matter* **4** 6367
- [6] Le Caer G, Malaman B, Isnard O, Soubeyroux J L, Fruchart D, Jacobs T H and Buschow K H J 1993 *Hyperfine Interact.* **77** 221
- [7] Isnard O, Pop V and Buschow K H J 2002 *J. Magn. Magn. Mater.* at press
- [8] Buschow K H J 1971 *J. Appl. Phys.* **42** 3433
- [9] van der Groot A S and Buschow K H J 1971 *Phys. Status Solidi* **5** 665
- [10] Givord D, Laforest J and Lemaire R 1977 *Physica B* **86–88** 204
- [11] Barlet A, Genna J C and Lethuillier P 1991 *Cryogenics* **31** 801
- [12] *Yellow Book* www.ill.fr
- [13] Rodriguez Carjaval J 1993 *Physica B* **192** 55
- [14] McCusker L B, Von Dreele R B, Cox D E, Louer D and Scardi P 1999 *J. Appl. Crystallogr.* **32** 36
- [15] Sears V F 1992 *Neutron News* **3** 26
- [16] Rouse K D and Cooper M J 1970 *Acta Crystallogr. A* **26** 682
- [17] Hewat A W 1979 *Acta Crystallogr. A* **35** 248
- [18] Kuz'ma Yu B and Bilonizhko N S 1974 *Sov. Phys.–Crystallogr.* **18** 447
- [19] Chacon C and Isnard O 2001 *J. Appl. Phys.* **88** 3570
- [20] Chacon C and Isnard O 2001 *J. Appl. Phys.* **89** 71
- [21] Chacon C and Isnard O 2001 *J. Phys.: Condens. Matter* **13** 5841

- [22] Maryama F, Nagai H, Amako Y, Yoshie H and Adachi K 1998 *Japan. J. Appl. Phys.* **37** 2492
- [23] Kapusta Cz, Spiridis N and Figiel H 1990 *J. Magn. Magn. Mater.* **83** 153
- [24] Kapusta Cz, Rosenberg M and Buschow K H J 1992 *J. Alloys Compounds* **187** 409
- [25] Chacon C and Isnard O 2000 *J. Solid State Chem.* **154** 242
- [26] Yamada H, Terao K, Nakazawa H, Kitagawa I, Susuki N and Ido H 1998 *J. Magn. Magn. Mater.* **183** 94
- [27] Jezierski A, Kowalczyk A, Mähl S, Neumann M and Borstel G 1998 *J. Phys.: Condens. Matter* **10** 6277
- [28] Tasset F 1975 *PhD Thesis* Université de Grenoble
- [29] Schweitzer J and Tasset F 1980 *J. Phys. F: Met. Phys.* **10** 2799
- [30] Zlotea C, Chacon C and Isnard O 2003 *J. Appl. Phys.* **92** 7382
- [31] Chacon C and Isnard O 2003 *Appl. Phys. A* at press
- [32] Laforest J 1981 *PhD Thesis* University of Grenoble
- [33] Pop V, Toussaint J C and Isnard O 2003 at press
- [34] Burzo E, Chelkowski A and Kirchmayr HR 1990 *Landolt–Börnstein New Series: Magnetic Properties of Metals* vol 19d2 (Berlin: Springer)
- [35] Isnard O and Fruchart D 1994 *J. Alloys Compounds* **205** 1