Magnetic characterization and structural study of new ternary carbides: $ThFe_{11}C_x(1.5 \leqslant x \leqslant 2)$

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Abstract. We report on the crystal and magnetic structure determination of $ThFe_{11}C_x$. The positions of the metal atoms correspond to the $BaCd_{11}$ type of structure. The carbon atoms occupy octahedral sites formed by four iron and two thorium atoms. Compounds having carbon concentrations $x = 1.5$ and 2 were found to order magnetically between 400 and 500 K. Low-temeperature neutron diffraction experiments provide evidence of a ferromagnetic structure with moments oriented perpendicular to the c axis whereas at room temperature the magnetic moments appear to be aligned parallel to the c axis of the tetragonal structure.

1. Introduction

Recently, in the ternary system Th–Fe–C a new phase derived from the $BaCd_{11}$ type was evidenced [1]. This carbon-stabilized type of interstitial alloy is isotypic with the manganese-based series $LaMn_{11}C_{2-x}$ [2] and with the pseudo-ternary $RFe_{10}SiC_{0.5}$ (R ≡ Ce, Pr, Nd, Sm) [3]. With thorium, it was found that no Si substitution was required to stabilize the $BaCd_{11}$ type.

This paper deals with neutron diffraction studies of both the crystal and the magnetic structures of $ThFe_{11}C_x$ for $x = 1.5$ and 2. The magnetic properties [1] are discussed in the light of the present results.

2. Experimental details

2.1. Synthesis

The samples were synthesized using the arc melting technique from elements of at least 99.9% purity. After combination of the elements, the samples were wrapped into tantalum foils and sealed into evacuated quartz tubes. The ingots were annealed at 1100 °C for about 2 weeks and then water quenched.

The purity of the samples was checked by x-ray analysis, using a conventional diffractometer (Cu Kα radiation) equipped with a graphite back-scattering monochromator. The compounds were found to be single phase and the diagrams were indexed using the $BaCd_{11}$ type of structure.

2.2. Neutron diffraction experiments

The structural investigations have been carried out using the high-flux powder neutron diffractometer DN5 of the Siloe reactor at the Centre d'Etudes Nucléaires de Grenoble (CENG).

Two different wavelengths $\lambda = 2.478$ Å and 1.522 Å were used when operating at 300 K and 2 K, respectively. The diffraction data were analysed using a modified Rietveld program (Fullprof) [4]. Figures 1(*a*) and 1(*b*) represent the diffraction patterns of $ThFe_{11}C_{1.5}$ at 300 K and $ThFe_{11}C_2$ at 2 K, respectively.

3. Crystal structure refinements

The x-ray diffraction patterns of $ThFe_{11}C_x$ have revealed a $BaCd_{11}$-type phase; hence the crystal structure has been refined using the model previously reported for isotypic ternaries [2, 3]. Our data confirm that the metal positions correspond to those found for the $BaCd_{11}$ structure type (table 1, figure 2). The carbon atoms are located within the interstitial sites on the axis between two Th atoms and at equal distances from four Fe(3) atoms. The refined structure parameters for both $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_2$ are reported in table 2 using the notation of [2]. The interatomic distances are listed in table 3.

Table 1. Lattice parameters and reliability factors from the $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_2$ structure refinements.

Compound	λ (Å)	T (K)	a (Å)	c (Å)	V (Å^3)	R_{exp} (%)	R_{mag} (%)	R_p (%)
$ThFe_{11}C_2$	2.478	300	10.249(1)	6.649	698	0.73	5.56	4.36
$ThFe_{11}C_2$	1.522	2	10.262(1)	6.656(1)	701	1.03	12.5	3.63
$ThFe_{11}C_{1.5}$	2.478	300	10.203(1)	6.611(1)	688	3.53	5.64	3.53
$ThFe_{11}C_{1.5}$	1.522	2	10.190(1)	6.592(1)	684	1.28	15.5	4.52
$ThFe_{11}C_{1.35}$	2.478	300	10.191(1)	6.609(1)	686	2.03	9.87	4.88
$ThFe_{11}C_{1.35}$	1.522	2	10.174(1)	6.581(1)	681	1.40	9.23	4.00

4. Discussion of the crystal structure

In the $R_2Fe_{17}C_x$ compounds, the coordination number and the nature of the carbon site are the same as reported here for $ThFe_{11}C_x$. However, in this series, two different values correspond to the Fe–C distances. Accordingly the Th–C bond is significantly shorter [5]. From preliminary studies of the Th–Fe–C phase diagram [1], it became evident that both the $Th_2Fe_{17}C_x$ and the $ThFe_{11}C_x$ crystal structures can be stabilized, depending on the carbon concentration. Refinement of the nominal composition $Th_2Fe_{17}C_{1.5}$ reveals two phases in equilibrium: $Th_2Fe_{17}C_{1.25}$ and $ThFe_{11}C_{1.35}$. Thus the lower limit of the stability of $ThFe_{11}C_x$ can be estimated to correspond to about $x = 1.35$. The $ThFe_{11}C_x$ crystal structure can be stabilized for carbon concentrations between $x = 1.35$ and $x = 2$. The compound richest in iron has the highest maximum carbon content.
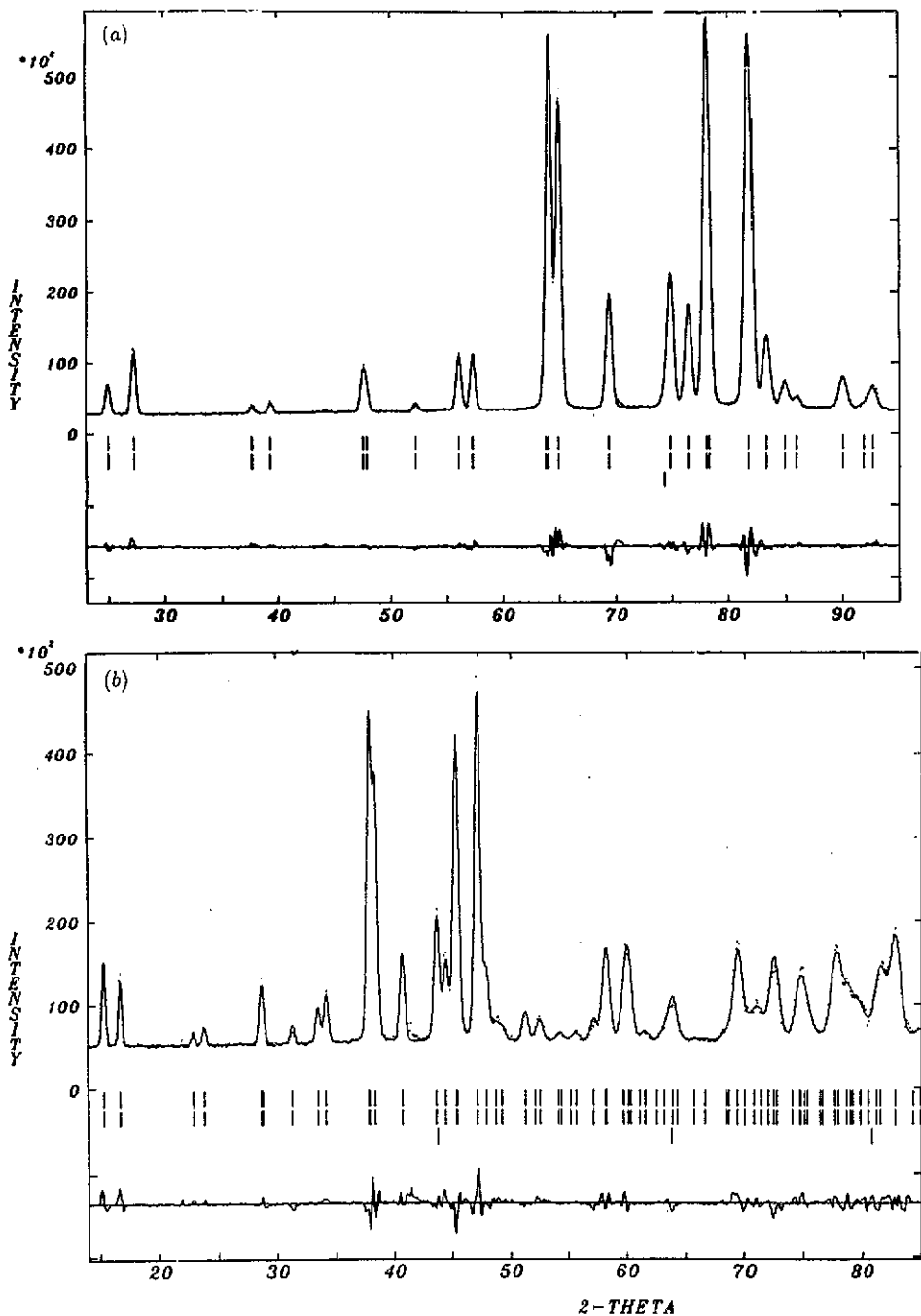
Figure 1. (a) Neutron powder diffraction pattern of ThFe₁₁C₁.₅ at 300 K. The dots and the full curve refer to the recorded pattern and the calculated fit, respectively. The difference pattern is plotted in the lower part of the figure on the same scale. The first and second sets of bars refer to the nuclear and magnetic diffraction lines, respectively, of ThFe₁₁C₁.₅. The third set refers to α-iron present as an impurity. (b) Neutron powder diffraction pattern of ThFe₁₁C₂ at 2 K. The dots and the full curve refer to the recorded pattern and the calculated fit, respectively. The difference pattern is plotted in the lower part of the figure on the same scale. The first and second sets of bars refer to the nuclear and magnetic diffraction lines, respectively, of ThFe₁₁C₂. The third set refers to α-iron present as an impurity.

Table 2. Refined structural parameters for $ThFe_{11}C_2$, $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_{1.35}$ and the magnetic moments measured on the Fe sites (the mean magnetic moment per Fe atom is refined to be along the c or a axis as indicated), n is the occupancy and $B_{overall}$ is the overall Debye–Waller factor. In all cases, Th is located in 4a ($x = 0$, $y = \frac{3}{4}$, $z = \frac{1}{8}$) with $n = 0.125$, Fe(1) is located in 4b ($x = 0$, $y = \frac{1}{4}$, $z = \frac{3}{8}$) with $n = 0.125$, and Fe(2) is located in 8d ($x = 0$, $y = 0$, $z = \frac{1}{2}$) with $n = 0.25$. The notation is taken from [2].

Atom	Site	x	y	z	n	$\langle m \rangle$ (μ_B)
$ThFe_{11}C_{1.5}$ (room temperature; $B_{overall} = 0.8$ Å^2; along c axis)						
Fe(3)	32i	0.1276(2)	0.0456(2)	0.1905(3)	1	1.78(8)
C	8c	0	0	0	0.173(1)	0
$ThFe_{11}C_2$ (room temperature; $B_{overall} = 0.8$ Å^2; along c axis)						
Fe(3)	32i	0.1283(2)	0.0463(2)	0.1935(3)	1	2.32(9)
C	8c	0	0	0	0.223(2)	0
$ThFe_{11}C_{1.35}$ (room temperature; $B_{overall} = 0.8$ Å^2; along c axis)						
Fe(3)	32i	0.1263(1)	0.0460(1)	0.1911(1)	1	1.28(4)
C	8c	0	0	0	0.161(1)	0
$ThFe_{11}C_{1.5}$ (2 K; along a axis)						
Fe(3)	32i	0.1274(3)	0.0460(3)	0.1924(6)	1	2.44(9)
C	8c	0	0	0	0.157(4)	0
$ThFe_{11}C_2$ (2 K; along a axis)						
Fe(3)	32i	0.1284(2)	0.0464(2)	0.1935(4)	1	2.53(6)
C	8c	0	0	0	0.221(2)	0
$ThFe_{11}C_{1.35}$ (2 K; along a axis)						
Fe(3)	32i	0.1269(1)	0.0411(1)	0.1946(2)	1	2.7(3)
C	8c	0	0	0	0.167(2)	0

Pearson [6] has pointed out the major role played by the 32i sites occupied by Cd(3) atoms in the $BaCd_{11}$ type of structure. He shows that the unit-cell parameters of this structure are weakly dependent on the size of the atoms occupying the Ba positions. He attributes this effect to the particularity of the 32i site which has three variable position parameters, allowing the atom occupying this site to adjust its position according to the size of the atom at the Ba site without significant change in the cell dimensions. It is worth noting that the carbon atoms which stabilize this $BaCd_{11}$ structure type for $ThFe_{11}$ are located at the centres of the four Fe(3) atoms. It seems reasonable to assume that it is this very property of the 32i atoms to adjust their position without major lattice expansion which makes it possible to take up C atoms with only minor expenditures in elastic energy of the lattice, thereby increasing the stability due to the additional carbon–metal atom bonds.

Inspection of the interatomic distances between carbon and the nearest Fe(3) atoms in the $ThFe_{11}C_x$ structure reveals that the Fe(3)–C bond is about 1.90 Å, which is significantly lower than that observed [7, 8] in Fe_3C (1.988 Å and 2.04 Å) where the C atoms have the same metal coordination. The shorter Fe–C distance in $ThFe_{11}C_x$ is probably due to a stronger bond with iron. The Th–C distance has the values 2.68 Å and 2.69 Å in $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_2$, respectively. They have to be compared with the Th–C distance of 2.52 Å found for $Th_2Fe_{17}C_{1.25}$, being of
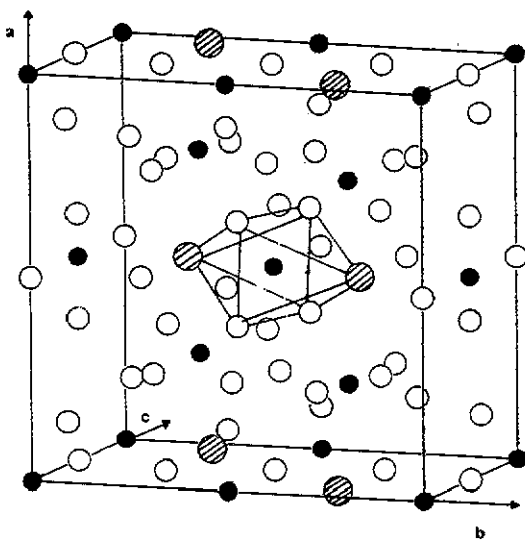
Figure 2. Schematic representation of the $ThFe_{11}C_x$ tetragonal structure (space group, I4/amd). The shaded and open circles represent the thorium and iron atoms, respectively. The full circles represent the carbon atoms. The octahedral environment of the carbon atom is drawn in the centre of the diagram.

the same order of magnitude as that encountered for ThC. The environment of the carbon atom is more symmetrical in $ThFe_{11}C_x$ than in $Th_2Fe_{17}C_x$, since the four nearest-neighbour iron atoms are located at the same distance to the carbon atom. Unlike the Fe–C bonds, the Th–C bonds are larger in the $ThFe_{11}C_x$-type phase than in the $Th_2Fe_{17}C_x$-type phase.

The relative stability of the two ternary carbides $Th_2Fe_{17}C_x$ $(0 < x < 1.25)$ and $ThFe_{11}C_x$ $(1.35 < x < 2)$ corresponds to a reverse bonding effect; the Fe–C distances decrease from 1.99 and 1.90 Å in the former to 1.87 Å in the latter whereas the Th–C distances increase from 2.52 to 2.68 Å. Consequently the Fe–Fe distances within the polyhedra around the C atoms decrease somewhat from 2.75 Å ($Th_2Fe_{17}C_{1.25}$ rhombus) to 2.69 and 2.60 Å ($ThFe_{11}C_{1.5}$ rectangle).

In the case of $ThFe_{11}C_x$, the carbon atom has to be taken as an alloying element as in the case of $Nd_2Fe_{14}C$ or $Nd_2Fe_{14}B$. The $ThFe_{11}C_x$ compounds are true ternaries since no binary alloy of the type $ThFe_{11}$ is stable; the C atoms must not be regarded as interstitial atoms but they play a major role in the stability of the phase. For the carbides of Th_2Fe_{17}, it has been shown that carbon is a real interstitial atom and the 2:17 hydrides, carbides or nitrides can be looked upon as pseudo-binary alloys with H, C and N as interstitial elements rather than as true ternaries.

5. Magnetic properties

The saturation magnetization was measured by means of a quantum design (SQUID) magnetometer at 5 K in a field of up to 4400 kA m^{-1} (55 kOe). Magnetization measurements performed on non-oriented samples lead to the following values at 5 K: $ThFe_{11}C_{1.5}$, $26.9\mu_B$ per formula unit; $ThFe_{11}C_2$, $26.1\mu_B$ per formula unit. The average iron moments corresponding to these values are $\langle m_{Fe} \rangle = 2.45\mu_B$ and $\langle m_{Fe} \rangle = 2.37\mu_B$, respectively.

Table 3. Relevant bond distances in $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_2$ refined at 2 and 300 K.

| | Bond distance (Å) | | | |
| | $ThFe_{11}C_{1.5}$ | | $ThFe_{11}C_2$ | |
Atomic bond	$T = 2$ K	$T = 300$ K	$T = 2$ K	$T = 300$ K
Th–4C	2.68	2.68	2.70	2.69
Th–8Fe(3)	3.22	3.22	3.25	3.25
Th–8Fe(3)	3.32	3.31	3.34	3.34
Th–2Fe(1)	3.30	3.31	3.33	3.33
Th–4Fe(2)	3.55	3.56	3.58	3.57
Fe(1)–4Fe(2)	2.68	2.68	2.70	2.69
Fe(1)–8Fe(3)	2.73	2.74	2.75	2.74
Fe(1)–2Th	3.30	3.31	3.33	3.33
Fe(3)–C	1.88	1.87	1.90	1.90
Fe(3)–Fe(2)	2.46	2.46	2.47	2.46
Fe(3)–Fe(2)	2.46	2.47	2.47	2.47
Fe(3)–2Fe(3)	2.51	2.51	2.53	2.52
Fe(3)–Fe(3)	2.60	2.60	2.62	2.62
Fe(3)–Fe(3)	2.61	2.62	2.63	2.61
Fe(3)–Fe(3)	2.59	2.59	2.62	2.61
Fe(3)–Fe(3)	2.70	2.69	2.75	2.75
Fe(3)–Fe(3)	2.65	2.68	2.66	2.65
Fe(3)–Th	3.22	3.22	3.25	3.25
Fe(3)–Th	3.32	3.31	3.34	3.34
Fe(2)–4Fe(3)	2.46	2.46	2.47	2.46
Fe(2)–4Fe(3)	2.46	2.47	2.47	2.47
Fe(2)–2Fe(1)	2.68	2.68	2.70	2.69
Fe(2)–2Th	3.55	3.56	3.58	3.58
C–4Fe(3)	1.88	1.87	1.90	1.90
C–2Th	2.68	2.68	2.70	2.69

The temperature dependence of magnetization was measured in a low field (0.5 kOe) by means of an automatic $(\sigma-T)$ recorder based on the Faraday method using polycrystalline powder samples. The results of these measurements are shown in figure 3. The Curie temperatures are $T_C = 411$ K and 501 K for $x = 1.5$ and $x = 2$, respectively. A kink is observed on each of the curves at about $T_k = 200$ K and 260 K. Carbon insertion leads to an increase in the Curie temperature but to lower T_k-values. Similar kinks have also been observed for the $R_2Fe_{14}C$ series [9] and ascribed to the spin reorientation phenomena.

X-ray diffraction measurements have been performed parallel and perpendicular to the easy axis on field-aligned powders (fixed with glue). Inspection of the x-ray patterns of the aligned samples reveals that at room temperature the Bragg peaks with high l indices are reinforced where the measurements were performed parallel to the easy axis, indicating that the easy-magnetization direction is along the c axis.

The neutron diffraction experiments performed at room temperature have been interpreted by assuming a ferromagnetic alignment of the moments along the c axis of the tetragonal structure. The refined values are $\langle m_{Fe} \rangle = (1.8 \pm 0.1)\mu_B$ and
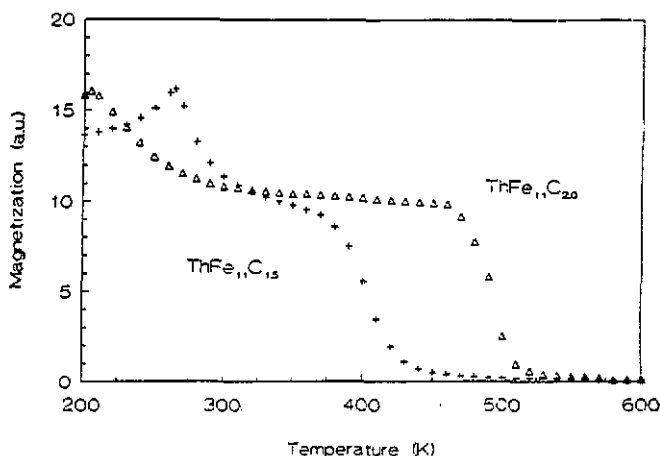
Figure 3. Temperature dependence of magnetization of $ThFe_{11}C_{1.5}$ (+) and $ThFe_{11}C_2$ ($\triangle$).

$(2.2\pm0.1)\mu_B$ for $x = 1.5$ and 2, respectively. No magnetic moment has been refined on the Th site since it is assumed to be tetravalent in intermetallic compounds (despite the possibility of a very low induced moment value, less than $0.2\mu_B$, which cannot be taken into account in neutron powder experiments).

At 2 K the refinements have been performed assuming a ferromagnetic alignment of the moment either along the c axis or within the basal plane. The agreement factors obtained in both cases do not differ much. The magnetic moments refined parallel to the c axis are found to be equal to $(3.4\pm0.1)\mu_B$ and $(3.0\pm0.1)\mu_B$ per iron atom. The values obtained for a refinement within the basal plane are $(2.53\pm0.1)\mu_B$ and $(2.4\pm0.1)\mu_B$ for $ThFe_{11}C_2$ and $ThFe_{11}C_{1.5}$, respectively; the latter values are in good agreement with the magnetization measurement performed at 55 kOe.

All these results are consistent with the occurrence at T_k of a spin reorientation process from a high-temperature easy-axis structure to a low-temperature easy-plane structure.

Assuming that there is no magnetic anisotropy contribution from the thorium site, we conclude that carbon insertion plays a significant role in the different terms of anisotropy of the iron sites. The main result is the increase in the temperature range of the easy-axis behaviour; T_C increases and T_k decreases when the carbon concentration is increased. Since no significant increase in the mean Fe moment has been measured, one has to assume that C insertion significantly increases the Fe–Fe exchange interactions from $x = 1.5$ to 2, leading to a relative increase in T_C by 25% when going from $x = 1.5$ to $x = 2$.

6. Conclusion

The crystal and magnetic structures of a new iron-rich ternary compound have been determined by means of neutron diffraction. Analysis of the structural results reveals that strong Fe–C bonds (short distances) are found in these $ThFe_{11}C_x$ compounds. The carbon atom seems to play a major role in stabilizing the $BaCd_{11}$ phase which only exists in a small composition range having between 1.35 and 2 C atoms per formula unit. These compounds have to be regarded as true ternaries. The carbon

atoms do not give rise to a simple interstitial solution since, to our knowledge, the pure $ThFe_{11}$ phase is not stable. Significant effects of carbon atoms on the crystal parameters, as well as on the magnetic moments, have been demonstrated. The results of the refinements of the neutron data as well as the results of the magnetization measurements led us to propose that a spin reorientation transition occurs at around 275 K and around 200 K in $ThFe_{11}C_{1.5}$ and $ThFe_{11}C_2$, respectively. The easy-magnetization direction is found to be perpendicular to the c axis at low temperatures and parallel to the c axis at higher temperatures. In such a series, iron fundamental characteristics such as exchange interactions and magnetocrystalline anisotropy appear to be very sensitive to the carbon concentration in $ThFe_{11}C_x$. Mössbauer as well as AC susceptibility experiments are in progress in order to confirm the spin reorientation behaviour.

Acknowledgments

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