

Tb₂Mn₁₇C_{3-x} with Filled Th₂Ni₁₇-Type Structure and Some Structural and Magnetic Properties of Related Compounds*

G. BLOCK AND W. JEITSCHKO

Anorganisch-Chemisches Institut, Universität Münster, Corrensstrasse 36, D-4400 Münster, Federal Republic of Germany

Received January 14, 1987

The new compounds $R_2Mn_{17}C_{3-x}$ ($R = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu$) were prepared by reacting the elemental components in an arc-melting furnace with subsequent annealing at temperatures between 400 and 900°C. Their crystal structures were determined from single-crystal X-ray diffractometer data of $Tb_2Mn_{17}C_{3-x}$ and refined to a residual of $R = 0.035$ for 27 variable parameters and 588 structure factors. It is hexagonal, space group $P6_3/mmc$ with the lattice constants $a = 873.8(1)$ pm, $c = 851.1(1)$ pm and $Z = 2$ formula units per cell. The positions of the metal atoms correspond to those of Th_2Ni_{17} . The carbon atoms are situated in approximately octahedral voids formed by two Tb and a rectangle of Mn atoms. Of these carbon positions 81 (4)% are occupied in the crystal investigated; this corresponds to the composition $Tb_2Mn_{17}C_{2.43}$. The new carbides $CeMn_{11}C_{2-x}$, $NdMn_{11}C_{2-x}$, and $ThMn_{11}C_{2-x}$ crystallize with $LaMn_{11}C_{2-x}$ (filled $BaCd_{11}$) structure; $Th_2Mn_{17}C_{3-x}$ has $Pr_2Mn_{17}C_{3-x}$ (filled Th_2Zn_{17}) structure. The crystal chemistry of these and other interstitial carbides is discussed. The compounds $LaMn_{11}C_{2-x}$, $CeMn_{11}C_{2-x}$, $Pr_2Mn_{17}C_{3-x}$, and $Tb_2Mn_{17}C_{3-x}$ are paramagnetic with Curie-Weiss behavior at high temperature and no magnetic order at least above about 100 K. The Mn atoms carry magnetic moments in all four compounds. Down to 1.9 K no transition to a superconducting state could be observed for $LaMn_{11}C_{2-x}$, $La_2Mn_{17}C_{3-x}$, $Y_2Mn_{17}C_{3-x}$, or $Lu_2Mn_{17}C_{3-x}$. © 1987 Academic Press, Inc.

Introduction

The crystal structures of binary and ternary carbides frequently derive from "host" structures by filling their interstitial sites with the relatively small carbon atoms. For this reason such carbides together with nitrides and some suboxides are frequently called "interstitial compounds" (1), although there is agreement today that geometrical considerations are only a prerequisite for the formation of the carbide and strong covalent bonds are formed be-

tween the metal and the carbon atoms, which benefit the stability of the whole structure (2, 3). Nowotny and his co-workers have synthesized and characterized numerous ternary carbides, where the metal host lattice corresponds to a simple elemental or binary structure type (4-7). We report here on another series of ternary carbides, whose structure derives from that of the binary compound Th_2Ni_{17} (8). A preliminary account of this work has been given before (9). We also report on new carbides with $LaMn_{11}C_{2-x}$ (10) and $Pr_2Mn_{17}C_{3-x}$ (11) structure, which derive from those of the binary compounds $BaCd_{11}$ (12) and Th_2Zn_{17} (13).

* Dedicated to Dr. H. Nowotny.

Sample Preparation and Properties

Starting materials were the elements in the form of powders with nominal purities of >99.9% (metals) and >99.5% (graphite). The powders of the early, air-sensitive rare-earth metals (*R*) were kept under dried paraffin oil, which was washed away by repeated treatment with dried methylene chloride prior to the reactions. Stoichiometric mixtures of the elements were cold-pressed to pellets (300 mg) under argon and reacted in an arc-melting furnace. The new compounds with $Tb_2Mn_{17}C_{3-x}$ structure were present in the as cast alloys as well as after annealing at 900°C (9 days) and 800°C (10 days). The compounds $Ln_2Mn_{17}C_{3-x}$ ($Ln = Gd, Tb, Dy$) were also observed after a heat treatment at 700°C (20 days) and 400°C (34 days). $Th_2Mn_{17}C_{3-x}$ was observed in the as cast condition as well as after annealing at 900°C. The compounds $CeMn_{11}C_{2-x}$, $NdMn_{11}C_{2-x}$, and $ThMn_{11}C_{2-x}$ were prepared in a high-frequency furnace with subsequent annealing at 900°C. For these heating processes in evacuated silica tubes most samples were wrapped in tantalum foils.

TABLE I

LATTICE CONSTANTS OF COMPOUNDS WITH HEXAGONAL $Tb_2Mn_{17}C_{3-x}$ STRUCTURE AND OF OTHER NEW COMPLEX CARBIDES WITH HEXAGONAL ($R\bar{3}m$) $Pr_2Mn_{17}C_{3-x}$ AND TETRAGONAL $LaMn_{11}C_{2-x}$ -TYPE STRUCTURE^a

Compound	Structure type	<i>a</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)
$Y_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	869.89(7)	852.7(1)	0.5588(1)
$Gd_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	876.0(2)	850.4(2)	0.5652(2)
$Tb_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	873.8(1)	851.1(2)	0.5628(1)
$Dy_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	871.5(2)	851.5(3)	0.5600(2)
$Ho_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	870.04(8)	851.5(1)	0.5582(1)
$Er_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	867.81(8)	850.6(1)	0.5548(1)
$Tm_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	865.8(2)	850.0(2)	0.5518(2)
$Lu_2Mn_{17}C_{3-x}$	$Tb_2Mn_{17}C_{3-x}$	865.7(2)	851.8(2)	0.5528(2)
$Th_2Mn_{17}C_{3-x}$	$Pr_2Mn_{17}C_{3-x}$	878.61(7)	1264.9(2)	0.8456(1)
$CeMn_{11}C_{2-x}$	$LaMn_{11}C_{2-x}$	1031.9(3)	669.6(3)	0.7131(4)
$NdMn_{11}C_{2-x}$	$LaMn_{11}C_{2-x}$	1033.69(8)	670.6(1)	0.7165(1)
$ThMn_{11}C_{2-x}$	$LaMn_{11}C_{2-x}$	1032.94(6)	669.62(7)	0.7145(1)

^a Standard deviations in the least significant digits (in all tables) are given in parentheses. They do not reflect the large homogeneity ranges (see text).

For none of the samples, which had been annealed at different temperatures, did we observe significant differences in the X-ray powder patterns, except for some variations of lattice constants.

The new compounds show metallic luster and do not react with air at room temperature. Energy dispersive analyses of the ternary carbides in a scanning electron microscope did not show any impurity elements heavier than magnesium.

To search for superconductivity, the *ac* inductivities of $LaMn_{11}C_{2-x}$ (*I0*), $La_2Mn_{17}C_{3-x}$ (*I1*), $Y_2Mn_{17}C_{3-x}$, and $Lu_2Mn_{17}C_{3-x}$ were determined at low temperatures. No transition to a superconducting state was observed for either compound down to about 1.9 K.

Lattice Constants

Guinier powder patterns of the samples were recorded with α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as standard. Indices could be assigned on the basis of the hexagonal $Tb_2Mn_{17}C_{3-x}$ structure, the tetragonal $LaMn_{11}C_{2-x}$ (*I0*), and the rhombohedral $Pr_2Mn_{17}C_{3-x}$ (*I1*) structure, respectively. To assure proper indexing, the observed patterns were compared with the calculated ones (*I4*), assuming the positional parameters as obtained in the respective structure determinations. The lattice constants (Table I) were refined by least-squares treatments of the data. As an example the evaluation of a powder pattern of $Tb_2Mn_{17}C_{3-x}$ is shown in Table II.

Most compounds $R_2Mn_{17}C_{3-x}$ were prepared also with a variety of slightly differing starting compositions and annealing temperatures. In these samples relatively large variations in the lattice constants were observed. For example a multiple-phase sample with the overall composition $Gd : Mn : C = 1 : 11 : 1$ showed the following lattice constants for the compound $Gd_2Mn_{17}C_{3-x}$ in the as cast (high-frequency furnace)

TABLE II
POWDER PATTERN OF $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ ^a

<i>hkl</i>	<i>Q</i> _o	<i>Q</i> _c	<i>I</i> _o	<i>I</i> _c
102	727	727	10	4
201	835	837	10	5
112	1075	1076	50	40
202	1252	1251	10	4
211	1360	1360	30	16
103	1416	1417	10	5
300	1571	1572	50	37
212	1778	1775	10	8
203	1940	1941	70	44
220	2095	2095	100	79
302	2124	2124	100	100
004	2209	2209	50	37
213	2465	2465	20	20
222	2649	2648	20	20
401	2934	2932	10	9
214	—	3431	—	6
321	3458	3456	10	10
304	3779	3780	10	7
322	—	3870	—	5
412	4216	4219	30	25
224	4304	4304	30	23
323	4561	4560	20	14

^a The pattern was recorded in a Guinier camera with $\text{CuK}\alpha_1$ radiation. All observed reflections and all calculated reflections with $I_c > 4$ are listed. The *Q* values are defined by $Q = 100/d^2$ (nm^{-2}).

condition: $a = 877.5(1)$ pm, $c = 855.7(1)$ pm, $V = 0.5706(1)$ nm³. After annealing at 800°C the lattice constants had decreased to $a = 872.8(2)$ pm, $c = 854.5(3)$ pm, $V = 0.5637(3)$ nm³. Smaller homogeneity ranges were observed by comparing the lattice constants of various samples of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ (from $V = 0.5612(1)$ nm³ to $0.5642(2)$ nm³) and $\text{Ho}_2\text{Mn}_{17}\text{C}_{3-x}$ (from $V = 0.5582(1)$ nm³ to $0.5611(2)$ nm³). They are most likely not only due to differing carbon contents of the compounds. A partial exchange of two Mn atoms for one Ln atom and vice versa is equally probable. On a larger scale and in a regular way such substitutions are well known to give rise to a whole family of related structures, which

are closely related to the CaZn_5 (CaCu_5)-type structure (15–17).

Magnetic Susceptibilities

The magnetic properties of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ and the earlier reported compound $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$, which has a different structure (11), were determined with a Faraday balance for samples of about 5 to 10 mg in a magnetic field of 1 T. The absence of ferromagnetic impurities was ascertained by the lack of a magnetic field dependence of the susceptibilities. The results of these measurements are shown in Figs. 1 and 2.

Within the investigated temperature range of about 80 to 300 K both compounds are paramagnetic and show Curie–Weiss behavior with slight deviations from a straight line at lower temperatures. The effective magnetic moments were determined from the linear portions of the $1/\chi$ vs T plots between 200 and 300 K. They are $\mu_{\text{exp}} = 5.46 \mu_B$ and $\mu_{\text{exp}} = 11.62 \mu_B$ per half formula unit of $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ and $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$, respectively. These values may be compared with the effective magnetic moments of the free rare-earth ions $\mu_{\text{eff}} = 3.58 \mu_B$ for Pr^{3+} and $\mu_{\text{eff}} = 9.72 \mu_B$ for Tb^{3+} , calculated according to the relation $\mu_{\text{eff}} =$

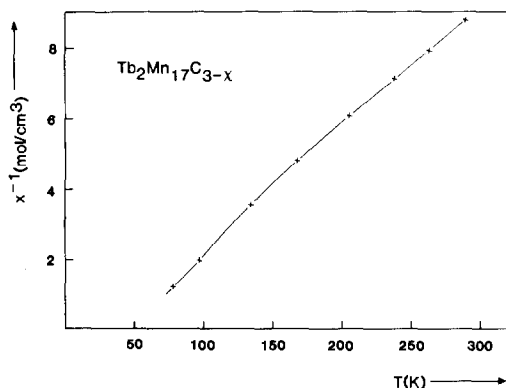


FIG. 1. Reciprocal magnetic susceptibility of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ as a function of temperature.

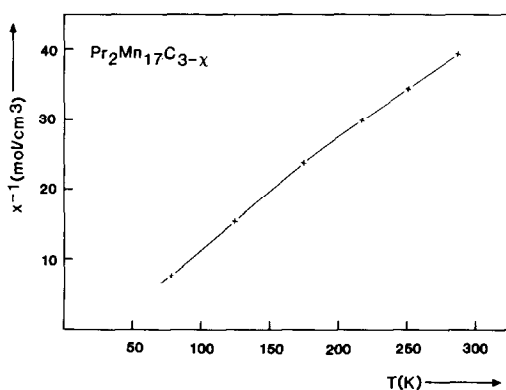


FIG. 2. Reciprocal magnetic susceptibility of $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$.

$g[J(J + 1)]^{1/2}$ (18). In subtracting these values from the experimentally determined ones, we obtain the differences $\Delta\mu = 1.88 \mu_B$ and $\Delta\mu = 1.90 \mu_B$ per half formula unit of $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ and $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$. Within the error limits of about $\pm 0.1 \mu_B$ these differences (which may be attributed to the manganese atoms) are the same, although the compounds are not isotypic (They are stacking variants of each other).

The magnetic susceptibilities of the earlier reported compound $\text{LaMn}_{11}\text{C}_{2-x}$ (10) and of the new compound $\text{CeMn}_{11}\text{C}_{2-x}$ were measured with a Gouy balance at three temperatures (boiling point of O_2 , solid CO_2 in methanol, and room temperature), each with varying field strengths for samples of about 0.15 g. The susceptibilities of both compounds were essentially independent of the magnetic field strengths. The results are shown in Fig. 3.

Both compounds are paramagnetic and follow the Curie-Weiss law. From the slopes of the $1/\chi$ vs T plots the effective magnetic moments of $\mu_{\text{exp}} = 1.7 \mu_B$ and $\mu_{\text{exp}} = 1.6 \mu_B$ per manganese atom (error limits of about $\pm 0.1 \mu_B$) in $\text{LaMn}_{11}\text{C}_{2-x}$ and $\text{CeMn}_{11}\text{C}_{2-x}$, respectively, were obtained. Although the cell volume of $\text{CeMn}_{11}\text{C}_{2-x}$ is smaller than that of $\text{NdMn}_{11}\text{C}_{2-x}$ (Table I), indicating nonmagnetic Ce^{4+} , the similarity

of the magnetic moments of the La and Ce compounds does not fully exclude the possibility of a mixed or intermediate valence for cerium because of the small cerium/manganese ratio in $\text{CeMn}_{11}\text{C}_{2-x}$.

Crystal Structure of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$

The single crystal ($25 \times 50 \times 63 \mu\text{m}^3$) of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ used for the structure determination was isolated from a sample with the starting composition $\text{Tb} : \text{Mn} : \text{C} = 3 : 15 : 2$, which had been annealed at 900°C . Precession diagrams indicated hexagonal symmetry and the only systematic extinctions—reflections hhl were observed only with $l = 2n$ —were compatible with the high-symmetry space group $P6_3/mmc$, already arrived at in the structure refinement of the binary “host” structure $\text{Th}_2\text{Ni}_{17}$ (8).

Intensity data were recorded in a four-circle diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. A total of 12,210 intensity values were recorded within one-half of the reciprocal sphere up to $2\theta = 100^\circ$ with $\theta/2\theta$ scans. Background counts were taken at both ends of each scan. An empirical absorption correction was applied from ψ -scan data with a ratio of the maximal to the minimal trans-

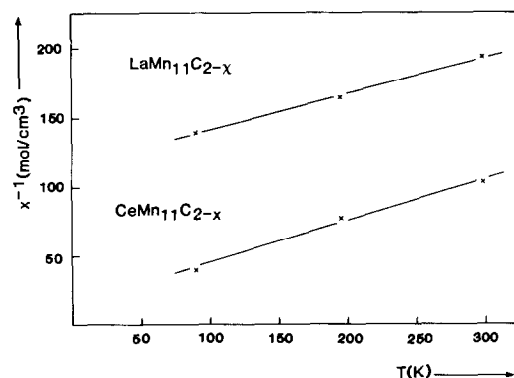


FIG. 3. Reciprocal magnetic susceptibilities of $\text{LaMn}_{11}\text{C}_{2-x}$ and $\text{CeMn}_{11}\text{C}_{2-x}$.

mission of 1.31. After averaging of equivalent reflections (internal $R = 0.063$) 1218 intensity values were obtained.

The similarity of the structure to that of $\text{Th}_2\text{Ni}_{17}$ (8) had been recognized at an early stage of our investigation from the cell dimensions and the estimated cell content. A full-matrix least-squares refinement with atomic scattering factors (19), corrected for anomalous dispersion (20) for the 428 structure factors greater than three standard deviations for the corresponding metal positions $\text{Tb}_2\text{Mn}_{17}$ resulted in a residual of $R = 0.045$. The subsequently computed difference Fourier analysis clearly revealed the carbon positions with an electron density of $18 \times 10^3 \text{ e/nm}^3$. In the last least-squares cycles ellipsoidal thermal parameters for the metal atoms, an occupancy factor for the carbon position, and one parameter accounting for isotropic secondary extinction were refined. Weights were assigned according to the counting statistics. A final residual of $R = 0.035$ was obtained for 27 variable parameters and 588 structure fac-

tors greater than one standard deviation. The positional parameters are listed in Table III and interatomic distances in Table IV. A listing of the observed and calculated structure factors can be obtained from the authors. A projection of the structure and the coordination polyhedra is shown in Fig. 4.

Discussion

The crystal structure of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ is of a new type which can be derived from that of the binary compound $\text{Th}_2\text{Ni}_{17}$ (8) where the atomic positions correspond to those of the Tb and Mn positions in $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$. The carbon atoms occupy one interstitial site of the metal positions. As was already discussed above, ternary carbides, nitrides, and suboxides frequently adopt structures where the metal positions correspond to those of elemental or binary structure types. In Table V we give a listing of such corresponding structures with the restriction that the host structure and the struc-

TABLE III
ATOM PARAMETERS OF $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ ^a

	Atom						
	Tb(1)	Tb(2)	Mn(1)	Mn(2)	Mn(3)	Mn(4)	C
$P6_3/mmc$	2(b)	2(d)	6(g)	12(j)	12(k)	4f	6(h)
Occupancy	1	1	1	1	1	1	0.81(4)
x	0	$\frac{1}{4}$	$\frac{1}{2}$	0.3279(2)	0.1687(2)	$\frac{1}{4}$	0.835(2)
y	0	$\frac{3}{8}$	0	0.9450(2)	2x	$\frac{3}{8}$	2x
z	$\frac{1}{4}$	$\frac{3}{4}$	0	$\frac{1}{4}$	0.9761(1)	0.1077(3)	$\frac{1}{4}$
U_{11}	47(3)	30(2)	39(6)	58(5)	40(4)	51(5)	—
U_{22}	U_{11}	U_{11}	68(9)	55(4)	78(5)	U_{11}	—
U_{33}	102(5)	29(3)	44(6)	32(4)	43(4)	19(8)	—
U_{12}	$U_{11}/2$	$U_{11}/2$	$U_{22}/2$	18(4)	$U_{22}/2$	$U_{11}/2$	—
U_{13}	0	0	$U_{23}/2$	0	$U_{23}/2$	0	—
U_{23}	0	0	9(9)	0	-2(9)	0	—
B	0.56(1)	0.26(1)	0.43(4)	0.42(2)	0.46(2)	0.37(2)	0.5(2)

^a The last line contains the isotropic thermal parameter of the carbon position and the equivalent isotropic thermal parameters of the metal atoms in units of \AA^2 ($=10^{-2} \text{ nm}^2$). The anisotropic thermal parameters U ($\times 10^4$) are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{13} + \dots)]$.

TABLE IV
INTERATOMIC DISTANCES (pm) IN $Tb_2Mn_{17}C_{3-x}$ ^a

Tb(1)	3 C	249	Mn(3)	1 C	193
	6 Mn(2)	313.4		2 Mn(1)	251.6
	6 Mn(3)	319.7		2 Mn(3)	258.5
	6 Mn(3)	345.7		2 Mn(2)	264.1
	2 Tb(1)	425.6		2 Mn(2)	271.5
Tb(2)	3 C	255	Mn(4)	1 Mn(4)	273.2
	2 Mn(4)	304.4		1 Tb(2)	314.9
	6 Mn(3)	314.9		1 Tb(1)	319.7
	6 Mn(2)	319.9		(2 C	344)
	6 Mn(1)	330.0		1 Tb(1)	345.7
Mn(1)	4 Mn(2)	250.9	C	2 Mn(2)	191
	4 Mn(3)	251.6		2 Mn(3)	193
	2 Mn(4)	268.4		1 Tb(1)	249
	2 Tb(2)	330.0		1 Tb(2)	255
	(4 C	331)			
Mn(2)	1 C	191			
	1 Mn(2)	238.5			
	2 Mn(1)	250.9			
	1 Mn(2)	252.6			
	2 Mn(3)	264.1			
	2 Mn(3)	271.5			
	2 Mn(4)	273.8			
	1 Tb(1)	313.4			
	1 Tb(2)	319.9			
(1 C	374)				

^a All distances are shorter than 440 pm (for Tb atoms), 380 pm (Mn), and 330 pm (C) are listed. The standard deviations, computed from those of the positional parameters and the lattice constants, are all less than 0.2 pm for metal-metal distances and less than 2 pm for the metal-carbon distances with the exception of the Mn(4)-Mn(4) distance, which has a standard deviation of 0.4 pm.

ture of the interstitial compound are of the same space group symmetry.

The environment of the carbon atoms in $Tb_2Mn_{17}C_{3-x}$ is about octahedral with four Mn atoms approximately forming a square and two terbium atoms completing the (distorted) octahedron. Corresponding octahedral environments were also found for the carbon atoms in $LaMn_{11}C_{2-x}$ (10) and $Pr_2Mn_{17}C_{3-x}$ (11). The Tb_2Mn_4C octahedra are connected by common Tb atoms. Each Tb

atom belongs to three octahedra. It was discussed before (11) that the network of linked octahedra in $LaMn_{11}C_{2-x}$ corresponds to the interatomic bonds in the diamond structure, while the nets of octahedra in $Pr_2Mn_{17}C_{3-x}$ correspond to the rhombohedral graphite structure (stacking *ABC, ABC*). The nets formed by the linked octahedra in $Tb_2Mn_{17}C_{3-x}$ corresponds to the hexagonal graphite structure (stacking *AB, AB*). Thus, like the binary host structures Th_2Zn_{17} (13) and Th_2Ni_{17} (8), the structures of the corresponding carbides $Pr_2Mn_{17}C_{3-x}$ and $Tb_2Mn_{17}C_{3-x}$ are stacking variants of each other (Fig. 5).

Apparently the stabilities of both structure types depend on the size of the lanthanoid components. Since the space requirements of the atoms change with temperature, we considered possible phase transitions for the cerium, samarium, and gadolinium compounds, with the $Tb_2Mn_{17}C_{3-x}$ -type structure being stable at low temperatures and the $Pr_2Mn_{17}C_{3-x}$ -type structure being preferred at higher temperatures. Similar transitions between the corresponding Th_2Ni_{17} - and Th_2Zn_{17} -type structures

TABLE V
ELEMENTAL OR BINARY STRUCTURE TYPES AND THE CORRESPONDING INTERSTITIAL STRUCTURES OF THE SAME SPACE GROUP SYMMETRY

Elemental or binary structure type	Corresponding interstitial compounds	Ref.
Cu	ScN, TiC_{1-x} , VN_{1-x}	21
Mg	δ' -NbN	22
Cu ₃ Au	Mn_3CuNi_{1-x} , Mn_3ZnC , Ti_3AlC , Ce_3TiC_{1-x}	23-26
Ti_2Ni	Ti_4Ni_2O , W_6Fe_6C , $Nb_8Zn_4C_{3-x}$	27-29
Mn_5Si_3	$Nb_5Ga_3N_{1-x}$, $Mo_5Si_3C_{1-x}$	30, 31
β -Mn	$Mo_{13}Fe_7N_4$, Mo_3Al_2C , W_3Re_2C , V_3Zn_2N	32-35
Re_3B	V_3AsC	36
U_3Si	Cr_3AsN , Mn_3GeC	37
$BaCd_{11}$	$LaMn_{11}C_{2-x}$	10
Th_2Zn_{17}	$Pr_2Mn_{17}C_{3-x}$	11
$MoNi_4$	UCr_4C_4	38
Th_2Ni_{17}	$Tb_2Mn_{17}C_{3-x}$	This work
$PbCl_2$ (La_2Au)	Pr_2ReC_{2-x}	39

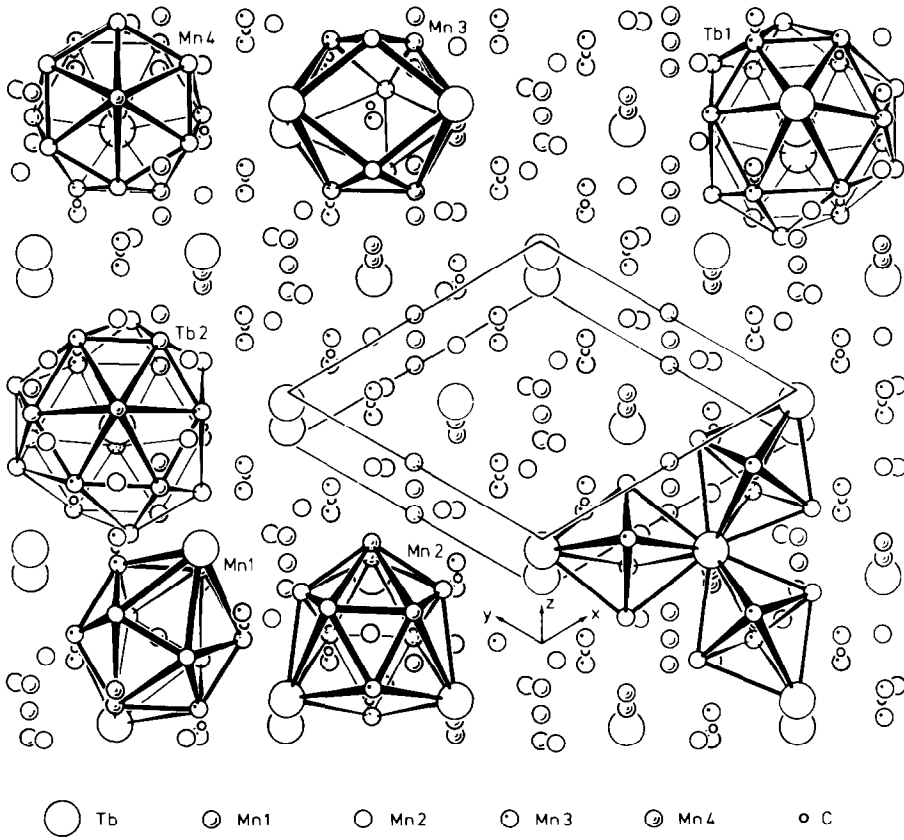


FIG. 4. Projection of the crystal structure and the coordination polyhedra of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ along a direction close to the hexagonal c axis.

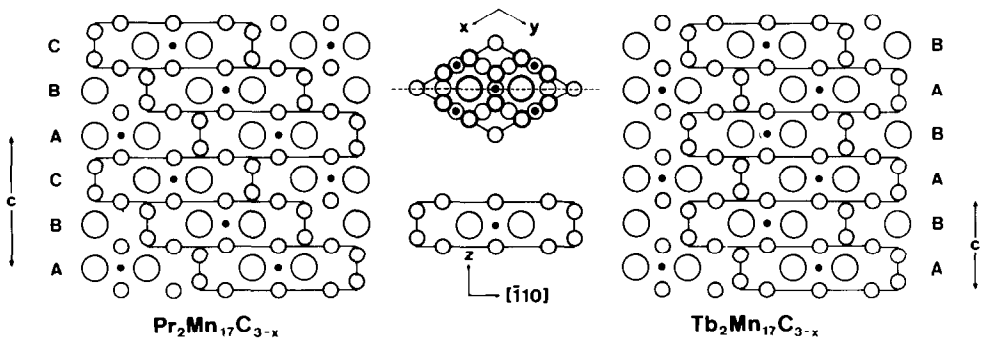


FIG. 5. Comparison of the slightly idealized crystal structures of $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ (space group $R\bar{3}m$) and $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ ($P6_3/mmc$). On the left and right side, cuts along the (110) planes of the hexagonal cells are shown. Large and small circles represent the lanthanoid and manganese atoms. The positions of the carbon atoms are indicated by dots. In the middle a $[001]$ projection of a building element (slab) is shown with the corresponding (110) cut. The $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ structure is generated by the stacking sequence ABC, ABC of such slabs, while the $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ structure corresponds to the stacking AB, AB .

were observed before for compounds $\text{Ln}_2\text{Zn}_{17}$ (40).

For this reason we have annealed samples of $\text{Ce}_2\text{Mn}_{17}\text{C}_{3-x}$ and $\text{Sm}_2\text{Mn}_{17}\text{C}_{3-x}$ at low temperatures (400°C for 39 days and 500°C for 39 days respectively); however, the Guinier diagrams remained unchanged. Similarly the Guinier diagrams of the as cast (after arc-melting) alloys of $\text{Gd}_2\text{Mn}_{17}\text{C}_{3-x}$ did not reveal a definite phase transition to a $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ -type structure. In this context it should be mentioned, however, that the unannealed samples generally had Guinier patterns with some diffraction lines (especially reflections with $l \neq 0$) being more diffuse than others, thus indicating a large number of stacking faults in the as cast samples.

Makarov and Vinogradov (13) have described another stacking variant for the binary compound U_2Zn_{17} with a stacking sequence $ABCACB, ABCACB$, thus requiring a doubling of the c axis of the $\text{Th}_2\text{Zn}_{17}$ -type structure. In our Guinier patterns we have not observed reflections which require such a large c axis; however, a corresponding carbide structure seems possible. It

may be stable for one or the other composition at different annealing temperatures.

The cell volumes of the $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ -type carbides are plotted in Fig. 6 together with those of $\text{Th}_2\text{Mn}_{17}\text{C}_{3-x}$ and the other $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ -type carbides reported earlier (11). While we have not attempted to synthesize any compounds with the radioactive element promethium, we were not successful in preparing the corresponding europium and ytterbium carbides, apparently because other compounds, where these elements are divalent, have higher thermodynamic stability. The cell volume of the cerium compound is smaller than that of $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$. This indicates that cerium is, at least partially, tetravalent in that compound.

The cell volume of the lutetium compound is greater than that of the thulium compound, although lutetium is not known to have a tendency for a lower valence state. This anomalous behavior is probably due to a slight deviation from the ideal Lu/Mn ratio. Apparently the cell volume is becoming too small for the lutetium compound to form a thermodynamically stable

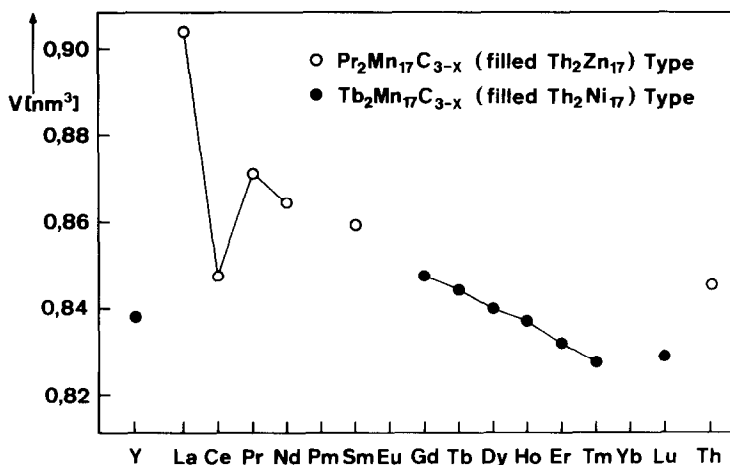


FIG. 6. Cell volumes of ternary rare-earth and thorium manganese carbides with $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ - and $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ -type structure. To facilitate comparisons the cell volumes for three layers (Fig. 5) of each structure are shown. Thus the cell volumes of the $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ -type compounds are multiplied by 1.5.

$\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ -type compound with ideal composition. Similar upturns in the cell volume of the last compound (the one with the heaviest lanthanoid) of an isotopic series of rare-earth compounds were observed for TmNi_2P_2 (41), ErPd_2P_2 (42), LuCo_5P_3 (43), LuCo_3P_2 (44), and Lu_2FeC_4 (45).

The structure refinement of $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ showed that only $81 \pm 4\%$ of the carbon positions are occupied. This corresponds to the composition $\text{Tb}_2\text{Mn}_{17}\text{C}_{2.43}$ ($x = 0.57$). Similar carbon defects were observed in the structure refinements of $\text{LaMn}_{11}\text{C}_{2-x}$ ($x = 0.48$) and $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ ($x = 1.23$). Although we cannot fully exclude that samples with 100% occupancy of the carbon positions could be prepared, we consider this at least as difficult. Our attempts to determine the homogeneity ranges of this structure with respect to the carbon positions in the systems Sm-Mn-C and Ho-Mn-C indicated that the thermodynamically stable compositions are carbon deficient.

The average Mn-C distance of 192 pm in $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ is in good agreement with the corresponding distances of 191.4 pm in $\text{LaMn}_{11}\text{C}_{2-x}$ and 194.0 pm in $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$. The average Tb-C distance of 252 pm in $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ compares very favorably with the Pr-C distance of 256.6 pm in $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ considering the lanthanoid contraction.

A comparison of the coordination polyhedra and interatomic distances of the two stacking variants $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ and $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ does not clearly reveal why the $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ structure is preferred by the large and the $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ structure by the small lanthanoids. The coordination polyhedra of the manganese and carbon atoms in the two structures correspond completely. It is interesting, however, that almost all Mn-Mn distances are larger in $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ (average Mn-Mn distance 264.7 pm) than in $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$ (average Mn-Mn distance 262.7 pm). On the other hand, considering the metallic radii for Pr

(182.8 pm) and Tb (178.2 pm) (46), the average Mn-Pr distance of 328.2 pm is in good agreement with the average Mn-Tb distance of 322.9 pm. The main difference between the two structures results from the splitting of the uniform coordination of the Pr atoms in $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$ to two different coordinations for the Tb atoms in $\text{Tb}_2\text{Mn}_{17}\text{C}_{3-x}$. While the Pr atoms have 3 C (256.6 pm), 1 Pr (395.0 pm), and 19 Mn (average distance 328.2 pm) neighbors, the Tb(1) atoms have 3 C (249 pm), 2 Tb (425.6 pm), and 18 Mn (average distance 326.3 pm) neighbors and the Tb(2) atoms 3 C (255 pm), no Tb, and 20 Mn (average distance 319.9 pm) neighbors. Thus, although the coordination numbers of the lanthanoid atoms are essentially the same in the two structures, the Tb(2) atom has the large lanthanoid neighbor replaced by a smaller manganese neighbor, and the two Tb neighbors of Tb(1) are at a rather large distance and do not need to be completely counted to the coordination sphere. One might thus conclude that the relatively smaller Tb atoms have a smaller effective coordination number than the Pr atoms.

Acknowledgments

We thank Dipl.-Chem. M. Reehuis and Mrs. I. Brendel for magnetic susceptibility measurements. Dr. M. H. Möller collected the single-crystal diffractometer data and Dipl.-Chem. L. Boonk checked our samples for superconductivity. We also acknowledge Dr. G. Höfer (Heraeus Quarzschmelze) for a donation of silica tubes. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

References

1. G. HÄGG, *Z. Phys. Chem. B* **12**, 33 (1931).
2. A. NECKEL, K. SCHWARZ, R. EIBLER, P. WEINBERGER, AND P. RASTL, *Ber. Bunsenges. Phys. Chem.* **79**, 1053 (1975).
3. S. D. WIEYESEKERA AND R. HOFFMANN, *Organometallics* **3**, 949 (1984).
4. H. NOWOTNY, W. JEITSCHKO, AND F. BENEVOVSKY, *Planseeber. Pulvermet.* **12**, 31 (1964).

5. H. NOWOTNY AND F. BENESOVSKY in "Phase Stability in Metals and Alloys" (P. S. Rudmann, J. Stringer, and R. I. Jaffee, Eds.), McGraw-Hill, New York (1967).
6. H. NOWOTNY, H. BOLLER, AND O. BECKMANN, *J. Solid State Chem.* **2**, 462 (1970).
7. H. NOWOTNY, *Angew. Chem.* **84**, 973 (1972); *Angew. Chem. Int. Ed. Engl.* **11**, 906 (1972).
8. J. V. FLORIO, N. C. BAENZIGER, AND R. E. RUNDLE, *Acta Crystallogr.* **9**, 367 (1956).
9. G. BLOCK AND W. JEITSCHKO, *Z. Kristallogr.* **174**, 19 (1986).
10. W. JEITSCHKO AND G. BLOCK, *Z. Anorg. Allg. Chem.* **528**, 61 (1985).
11. G. BLOCK AND W. JEITSCHKO, *Inorg. Chem.* **25**, 279 (1986).
12. M. J. SANDERSON AND N. C. BAENZIGER, *Acta Crystallogr.* **6**, 627 (1953).
13. E. S. MAKAROV AND S. I. VINOGRADOV, *Sov. Phys. Crystallogr.* **1**, 499 (1956).
14. K. YVON, W. JEITSCHKO, AND E. PARTHÉ, *J. Appl. Crystallogr.* **10**, 73 (1977).
15. K. SCHUBERT, "Kristallstrukturen zweikomponentiger Phasen," Springer, Berlin (1964).
16. W. B. PEARSON, "The Crystal Chemistry and Physics of Metals and Alloys," Wiley, New York (1972).
17. E. PARTHÉ AND R. LEMAIRE, *Acta Crystallogr. B* **31**, 1879 (1975).
18. S. LEGVOLD in "Ferromagnetic Materials" (E. P. Wohlfarth, Ed.), Vol. 1, North-Holland, Amsterdam (1980).
19. D. T. CROMER AND J. B. MANN, *Acta Crystallogr. A* **24**, 321 (1968).
20. D. T. CROMER AND D. LIBERMAN, *J. Chem. Phys.* **53**, 1891 (1970).
21. P. VILLARS AND L. D. CALVERT, "Pearson's Handbook of Crystallographic Data for Intermetallic Phases," American Society for Metals, Metals Park, Ohio (1985).
22. G. BRAUER AND J. JANDER, *Z. Anorg. Allg. Chem.* **270**, 160 (1952).
23. R. JUZA AND H. PUFF, *Z. Elektrochem.* **61**, 810 (1957).
24. R. G. BUTTERS AND H. P. MYERS, *Philos. Mag.* **46**, 132 (1955).
25. H. H. STADELMAIER, *Z. Metallkd.* **52**, 758 (1961).
26. W. JEITSCHKO, H. NOWOTNY, AND F. BENESOVSKY, *Monatsh. Chem.* **95**, 319 (1964).
27. M. H. MUELLER AND H. W. KNOTT, *Trans. Soc. Min. Eng. AIME* **227**, 674 (1963).
28. J. LECIEJEWICZ, *J. Less-Common Met.* **7**, 318 (1964).
29. W. JEITSCHKO, H. HOLLECK, H. NOWOTNY, AND F. BENESOVSKY, *Monatsh. Chem.* **95**, 1004 (1964).
30. W. JEITSCHKO, H. NOWOTNY, AND F. BENESOVSKY, *Monatsh. Chem.* **95**, 1242 (1964).
31. E. PARTHÉ, W. JEITSCHKO, AND V. SADAGOPAN, *Acta Crystallogr.* **19**, 1031 (1965).
32. D. A. EVANS AND K. H. JACK, *Acta Crystallogr.* **10**, 769 (1957).
33. W. JEITSCHKO, H. NOWOTNY, AND F. BENESOVSKY, *Monatsh. Chem.* **94**, 247 (1963).
34. JU. B. KUZ'MA, V. I. LAKH, V. JA. MARKIV, B. I. STADNYK, AND E. I. GLADYŠEVSKII, *Poroškov. Metal. Ukrain., SSR* **4**, 40 (1963).
35. W. JEITSCHKO, H. NOWOTNY, AND F. BENESOVSKY, *Monatsh. Chem.* **95**, 1212 (1964).
36. H. BOLLER AND H. NOWOTNY, *Monatsh. Chem.* **98**, 2127 (1967).
37. H. BOLLER, *Monatsh. Chem.* **99**, 2444 (1968).
38. R. K. BEHRENS AND W. JEITSCHKO, *Monatsh. Chem.* **118**, 43 (1987).
39. G. BLOCK AND W. JEITSCHKO, unpublished results.
40. A. IANDELLI AND A. PALENZONA, *J. Less-Common Met.* **12**, 333 (1967).
41. W. JEITSCHKO AND B. JABERG, *J. Solid State Chem.* **35**, 312 (1980).
42. W. JEITSCHKO AND W. K. HOFMANN, *J. Less-Common Met.* **95**, 317 (1983).
43. U. MEISEN AND W. JEITSCHKO, *J. Less-Common Met.* **102**, 127 (1984).
44. W. JEITSCHKO AND U. JAKUBOWSKI, *J. Less-Common Met.* **110**, 339 (1985).
45. M. H. GERSS, W. JEITSCHKO, L. BOONK, J. NIEN-TIEDT, J. GROBE, E. MÖRSEN, AND A. LESON, *J. Solid State Chem.* **70**, 19 (1987).
46. E. TEATUM, K. GSCHNEIDNER, JR., AND J. WABER, LA-2345, U.S. Department of Commerce, Washington, DC. (1960).