Inorg. Chem. **1986**, *25*, 279-282

Contribution from the Institute for Inorganic Chemistry,
University of Münster, D-4400 Münster, West Germany

Ternary Carbides $Ln_2Mn_{17}C_{3-x}$ (Ln = La, Ce, Pr, Nd, Sm) with Filled Th_2Zn_{17} Type Structure

Günter Block and Wolfgang Jeitschko*

Received June 19, 1985

The new title compounds were prepared by reaction of the elemental components at high temperatures. They crystallize with a rhombohedral cell in space group $R\bar{3}m$. The structure was determined for $Pr_2Mn_{17}C_{3-x}$ ($x = 1.23$), which has the lattice constants $a = 8.8714$ (7) Å and $c = 12.783$ (2) Å with $Z = 3$ formula units in the hexagonal setting of the cell. The structure refinement from single-crystal X-ray data resulted in a residual of $R = 0.023$ for 25 variable parameters and 414 unique structure factors. The Pr and Mn positions correspond to those of the Th and Zn positions in Th_2Zn_{17}. The carbon atoms fill voids of nearly octahedral shape formed by a rectangle of Mn atoms (Mn–C distances 1.94 and 1.95 Å) and two Pr atoms at 2.57 Å. The idealized composition with all octahedral voids filled is $Pr_2Mn_{17}C_3$. The refinement of the occupancy parameter for this position resulted in a value of 59 ± 3% for the crystal used for the structure determination. The discussion reviews the correspondence of binary intermetallic and ternary complex carbide phases.

Introduction

Many ternary compounds are known in the systems lanthanoid (Ln)–transition metal (T)–boron,[1,2] Ln–T–silicon,[2,3] and Ln–T–phosphorus.[4] When we started investigations of the corresponding ternary systems Ln–T–carbon, only very few reports of such studies were available. Holleck[5] had reported a series of ternary carbides LnT_3C_{1-x} with the "filled" Cu_3Au structure, and Bodak et al. had described[6] a series of compounds with the composition $LnCoC_2$. In the meantime, phase-diagram determinations of the ternary systems Gd–Fe–C,[7] Ce–Fe–C,[8] and Ce–Ni–C[9] indicated that such systems may contain as many ternary carbides as the corresponding systems with boron, silicon, and phosphorus.

We started our investigations with manganese as the transition-metal component, having reported[10] already on $LaMn_{11}C_{2-x}$ and $PrMn_{11}C_{2-x}$, where the positions of the metal atoms correspond to those of the binary compound $BaCd_{11}$ and the carbon atoms fill octahedral voids formed by the metal atoms. The structure of the presently reported compounds derives in a similar way from the structure of the binary compound Th_2Zn_{17}. Some of these compounds had been briefly introduced.[11]

Preparation and Characterization

Samples of the ternary carbides were prepared by reaction of the elemental components in a high-frequency furnace ($La_2Mn_{17}C_{3-x}$) and an arc-melting furnace (the Ce, Pr, Nd, and Sm compounds). The reactions are exothermic. Subsequent annealing at temperatures between 400 °C (5 weeks) and 900 °C (2 weeks) showed that the Ce, Pr, and Nd compounds are stable at these temperatures whereas $La_2Mn_{17}C_{3-x}$ was observed only in the quenched samples. Annealing of the $La_2Mn_{17}C_{3-x}$ samples at temperatures between 400 and 900 °C resulted in the formation of $LaMn_{11}C_{2-x}$.[10] Annealing temperatures of $Sm_2Mn_{17}C_{3-x}$ samples were between 800 and 900 °C.

Table I. Hexagonal Lattice Constants of Carbides with Filled Th_2Zn_{17} Structure[a]

compd	*a*, Å	*c*, Å	*c/a*	*V*, Å^3
$La_2Mn_{17}C_{3-x}$	8.983 (1)	12.940 (3)	1.4405	904.3 (2)
$Ce_2Mn_{17}C_{3-x}$	8.785 (2)	12.683 (3)	1.4437	847.7 (3)
$Pr_2Mn_{17}C_{3-x}$	8.8714 (7)	12.783 (2)	1.4409	871.3 (1)
$Nd_2Mn_{17}C_{3-x}$	8.847 (1)	12.750 (3)	1.4412	864.2 (2)
$Sm_2Mn_{17}C_{3-x}$	8.8100 (7)	12.777 (2)	1.4503	858.9 (1)

[a] Standard deviations in the least significant digits are given in parentheses. They do not reflect the homogeneity ranges of the compounds, which were not investigated in detail; however, in different samples differing lattice constants were observed. Thus for instance the cell volumes obtained from different samples of one compound differed up to 3 Å^3.

Starting materials were ingots of the rare-earth metals with a nominal purity of better than 99.9%, chips of manganese (99.97%), and graphite powder (99.5%). Filings of the rare-earth metals were prepared and kept under dried paraffin oil. Adherent iron particles were removed by a magnet. Prior to the reactions the paraffin oil was washed away by repeated treatment with dried methylene chloride under argon. Stoichiometric mixtures of the elements with a total weight of about 1 g were reacted in an arc-melting or a high-frequency furnace. To prevent reaction with the silica tubes, the samples were wrapped in tantalum foil for the annealing process.

Because of incomplete reactions stoichiometric samples generally are contaminated by second- and third-phase impurities (mainly the binary carbides Ln_2C_3 and two different ternary phases of as yet unknown structures). Single-phase products were obtained from samples with starting ratios varying between Ln:Mn:C = 5:12:3 and 3:15:2. After annealing, the samples were crushed and kept under moist ethanol for a few hours or a day. This treatment decomposes the impurity phases while the crystals of the new compounds are not visibly attacked. The crystals can then be separated mechanically from the poorly crystallized residue, mainly $La(OH)_3$.

The crystals of the new compounds have the habit of triangular plates; they show metallic luster and do not react with air at room temperature. Energy dispersive analyses in a scanning electron microscope did not show any impurity elements heavier than magnesium.

The powdered samples were characterized by the Guinier technique using α-quartz ($a = 4.9130$ Å, $c = 5.4046$ Å) as a standard. The patterns could be indexed on the basis of the hexagonal cell obtained from the single-crystal diffraction patterns. The identification of the diffraction lines was facilitated by intensity calculations[12] using the positional parameters of the refined structure of $Pr_2Mn_{17}C_{3-x}$. Least-squares refine-

---

(1) Parthé, E.; Chabot, B. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1984; Vol. 6, pp 113–334.

(2) Rogl, P. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1984; Vol. 6, pp 335–523.

(3) Gladyshevskii, E. I.; Bodak, O. I. "Crystal Chemistry of Intermetallic Compounds of the Rare Earth Metals" (in Russian); Vishcha Shkola: Lvov, 1982.

(4) Hofmann, W. K.; Jeitschko, W. *J. Solid State Chem.* **1984**, *51*, 152. Grandjean, F.; Gérard, A.; Braun, D. J.; Jeitschko, W. *J. Phys. Chem. Solids* **1984**, *45*, 877. Meisen, W.; Jeitschko, W. *J. Less-Common Met.* **1984**, *102*, 127. Meisen, U.; Jeitschko, W. *Z. Kristallogr.* **1984**, *167*, 135. Jeitschko, W.; Meisen, U.; Scholz, U. D. *J. Solid State Chem.* **1984**, *55*, 331. Jeitschko, W.; Meisen, U., Möller, M. H.; Reehuis, M. *Z. Anorg. Allg. Chem.* **1985**, *527*, 73. Jeitschko, W.; Reinbold, E. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 900. Jeitschko, W.; Jakubowski, U.; *J. Less-Common Met.* **1985**, *110*, 339 and references therein.

(5) Holleck, H. *J. Nucl. Mater.* **1972**, *42*, 278.

(6) Bodak, O. I.; Marusin, E. P.; Bruskov, V. A. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1980**, *25*, 355.

(7) Stadelmaier, H.-H.; Park, H. K. *Z. Metallkd.* **1981**, *72*, 417.

(8) Park, H. K.; Stadelmaier, H.-H.; Jordan, L. T. *Z. Metallkd.* **1982**, *73*, 399.

(9) Bodak, O. I.; Marusin, E. P.; Fundamenskii, V. S.; Bruskov, V. A. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1982**, *27*, 657.

(10) Jeitschko, W.; Block, G. *Z. Anorg. Allg. Chem.* **1985**, *528*, 61.

(11) Block, G.; Jeitschko, W. Abstracts, 13th International Congress on Crystallography, Hamburg, Aug 9–14, 1984; p 239.

(12) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.

0020-1669/86/1325-0279$01.50/0 © 1986 American Chemical Society

Table II. X-ray Powder Pattern of $La_2Mn_{17}C_{3-x}$[a]

hkl	Q_o	Q_c	I_o	I_c	*hkl*	Q_o	Q_c	I_o	I_c
101		225		<1	223	2524	2520	5	20
012		404		1	116	2648	2646	5	4
110		486		3	125		2650		7
003		537		4	401		2703		5
021	720	721	5	5	042		2883		7
202		900		1	107		3092		5
113	1033	1033	20	38	134		3104		3
104	1121	1121	5	12	321		3199		4
211	1218	1216	5	15	232		3378		9
122		1396		7	140		3470		4
300	1487	1487	40	38	027		3587		3
024	1615	1616	40	34	404		3599		<1
015		1658		<1	306		3637		6
220	1983	1983	100	81	315		3641		<1
303	2025	2025	100	100	018		3987		0
214	2112	2112	5	23	143	4007	4007	5	25
006	2151	2150	10	35	217		4083		17
205		2154		16	324	4092	4095	5	17
131		2208		<1	226	4134	4133	5	22
312		2387		<1	045		4137		<1

[a] The *Q* values are defined by $Q = 10^4/d^2$ ($Å^{-2}$). Cu $K\alpha_1$ radiation; Guinier camera.

Table III. Positional and Thermal Parameters of $Pr_2Mn_{17}C_{3-x}$[a]

atom	$R\bar{3}m$	occup	*x*	*y*	*z*	*B*, $Å^2$
Pr	6c	1	0	0	0.34548 (4)	0.414 (5)
Mn(1)	9d	1	$^1/_2$	0	$^1/_2$	0.50 (2)
Mn(2)	18f	1	0.2807 (1)	0	0	0.49 (1)
Mn(3)	18h	1	0.50536 (7)	0.49464	0.15126 (6)	0.63 (1)
Mn(4)	6c	1	0	0	0.0954 (1)	0.48 (2)
C	9e	0.59 (3)	$^1/_2$	0	0	1.0 (2)

[a] Numbers in parentheses are esd's in the least significant digits. The last column contains the isotropic *B* value of the carbon position and the equivalent isotropic *B* values of the anisotropic temperature parameters of the other positions.

ments of the lattice constants resulted in the values listed in Table I. As an example, the evaluation of the powder pattern of $La_2Mn_{17}C_{3-x}$ is shown in Table II.

Structure Determination of $Pr_2Mn_{17}C_{3-x}$

A crystal of $Pr_2Mn_{17}C_{3-x}$ was examined in a Buerger camera with Mo $K\alpha$ radiation. It showed the Laue symmetry $6/mmm$ and at the same time the extinction condition that reflections *hhl* were only observed with $l = 3n$. Since these two observations are incompatible with each other, twinning was suspected. This was proven to be correct by another crystal that had the Laue symmetry $\bar{3}m$ and the rhombohedral extinction condition with reflections *hkil* observed only with $-h + k + l = 3n$. This leads to the possible space groups $R\bar{3}m$, $R3m$, $R32$, $R\bar{3}$, and $R3$. Of these, the group with the highest symmetry $R\bar{3}m$ was found to be correct during the structure refinements. The twinning of the specimen with $6/mmm$ symmetry was also proven by a comparison of the reflection intensities.

Intensity data were recorded at 20 °C form a single-crystal of maximal and minimal extensions of 45 and 33 μm in a four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The scans were taken along 2θ with scanning rates varying between 0.9 and 3.3° 2θ/min optimized by fast prescans. The scan widths were 1.3° of 2θ plus the angular separations of the $K\alpha$ doublets. Background counts were taken at both ends of each scan. A total of 3656 reflections was measured within half of the reciprocal sphere up to $2\theta = 80°$. An empirical absorption correction was applied from ψ-scan data. The ratio of the maximal to the minimal transmission was 1.35. The linear absorption coefficient is $\mu = 252$ cm^{-1}. After equivalent reflections were averaged (internal $R = 0.044$) and those counts with less than three standard deviations were omitted, 414 reflections remained.

The structure was determined and refined by a program system supplied by the Enraf-Nonius Co. At an early stage of the structure determination we recognized the similarities in the symmetry, cell content ($Z = 3$ formula units/hexagonal cell; X-ray density 7.07 g/cm³ for the composition $Pr_2Mn_{17}C_{1.77}$ found during the structure refinement), and the calculated powder patterns of the new carbide structure to those of the Th_2Zn_{17} structure.[13] The first series of least-squares cycles with the Pr and Mn atoms placed on the positions of the Th and Zn atoms of the Th_2Zn_{17} structure already resulted in a residual of 0.038. The positions of the carbon atoms were obtained from a difference Fourier synthesis. In the full-matrix least-squares refinements with atomic scattering factors[14] corrected for anomalous dispersion,[15] a parameter for the isotropic

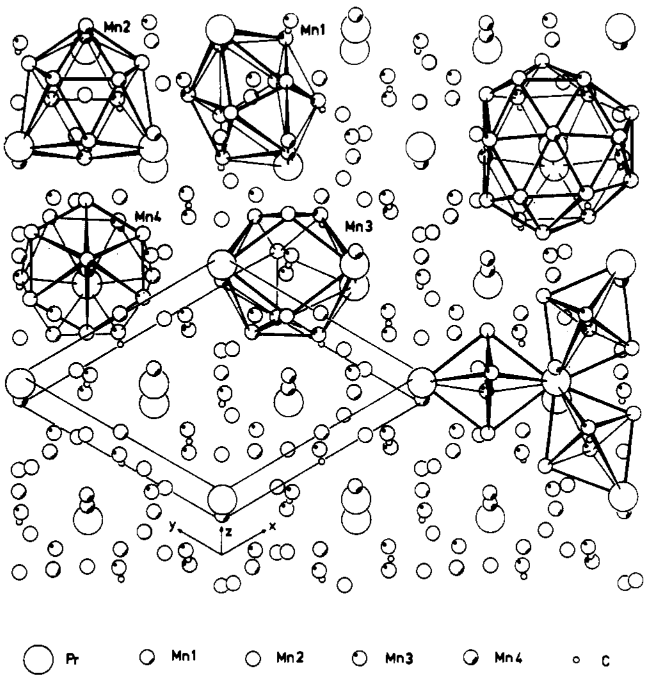

Figure 1. Coordination polyhedra in the structure of $Pr_2Mn_{17}C_{3-x}$. Only half of the structure between $z = 0$ and $z = {}^1/_2$ is shown. The three carbon atoms of the polyhedron around the Pr atom are situated in the centers of planes formed by four Mn atoms. The carbon atoms of the coordination polyhedra of the Mn(2) and Mn(3) atoms are positioned in the centers of parallelograms formed by two Pr and two Mn atoms.

---

(13) Makarov, E. S.; Vinogradov, S. I. *Sov. Phys.—Crystallogr.* (*Engl. Trans.*) **1956**, *1*, 499.

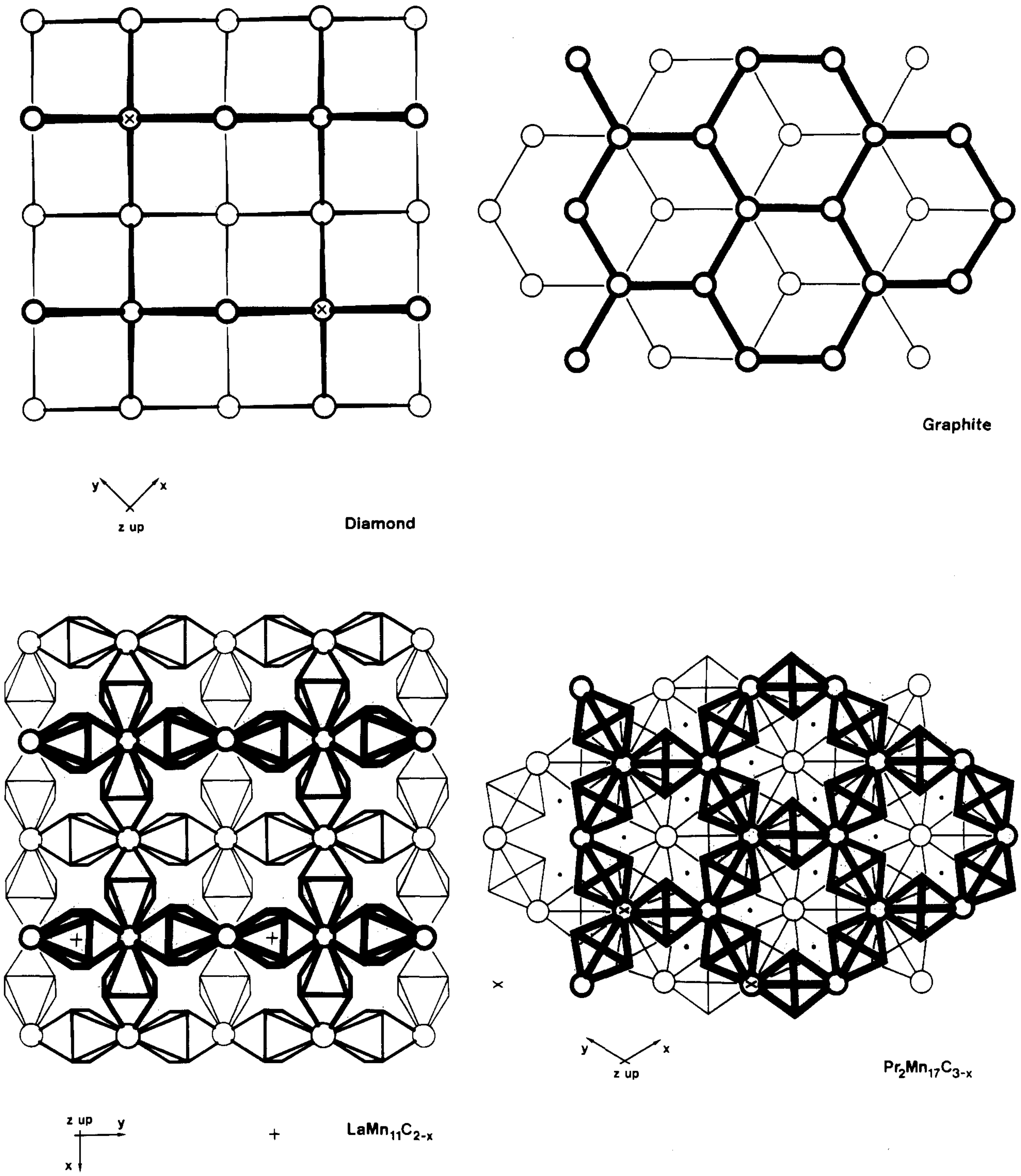

Figure 2. Linkages of the Ln_2Mn_4 coordination octahedra of the carbon atoms in $LaMn_{11}C_{2-x}$ and $Pr_2Mn_{17}C_{3-x}$ and topological relationship of these structures to those of diamond and graphite. The positions of the lanthanoid atoms (large circles) in the complex carbides correspond to the positions of the carbon atoms in diamond and graphite. The Ln_2Mn_4C octahedra of the complex carbides correspond to the bonds between the carbon atoms in the two carbon modifications. In the drawing of the $Pr_2Mn_{17}C_{3-x}$ structure octahedra drawn with thin and thick lines are at about $z = 0$ and $z = {}^1/_3$. In the structure of $LaMn_{11}C_{2-x}$ manganese atoms with no carbon neighbors are omitted. In the drawing of the $Pr_2Mn_{17}C_{3-x}$ structure the positions of the Mn(1) atoms are indicated by dots; the Mn(4) atoms (not shown) are positioned above and below the Pr atoms.

correction of the secondary extinction was refined and applied to the calculated structure factors. Weights were assigned according to the counting statistics ($w = 1/\sigma_F^2$). In the final cycles parameters for ellipsoidal thermal motion of the metal atoms and a parameter allowing a deviation from the full occupancy of the carbon position were refined. The final R value is 0.023 ($R_w = 0.018$) for 25 variable parameters and 414 structure factors. A listing of the atomic parameters is given in Table III, and interatomic distances are listed in Table IV. The coordination polyhedra are shown in Figure 1. Listings of anisotropic thermal parameters and of calculated and observed structure factors are available as supplementary material.

As a check for the composition, we have also refined in one series of least-squares cycles the occupancy parameters of all atom positions with the exception of the Pr position, which was kept at the ideal value to fix the scale factor. The R value was slightly lowered to 0.022, and the following occupancies (in percent; standard deviations in parentheses) were obtained: Mn(1), 98.3 (0.3); Mn(2), 98.1 (0.2); Mn(3), 96.3 (0.2); Mn(4), 101.3 (0.4); C, 56.2 (3.0). A similar result was obtained[10] in the structure refinement of $LaMn_{11}C_{2-x}$. Thus there is some indication that the Mn positions might not be fully occupied in these structures (assuming that the calculated scattering factors are sufficiently accurate).

---

(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(15) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table IV. Interatomic Distances (Å) in the Structure of $Pr_2Mn_{17}C_{3-x}$[a]

Pr	3 C	2.566	Mn(3)	1 C	1.935
	3 Mn(3)	3.186		2 Mn (1)	2.528
	1 Mn(4)	3.197		2 Mn(2)	2.659
	6 Mn(2)	3.220		2 Mn(3)	2.672
	3 Mn(3)	3.241		1 Mn(4)	2.715
	3 Mn(3)	3.421		2 Mn(2)	2.744
	3 Mn(1)	3.433		1 Pr	3.186
	1 Pr	3.950		1 Pr	3.241
				1 Pr	3.421
Mn(1)	4 Mn(2)	2.501		(2 C	3.492)
	4 Mn(3)	2.528			
	2 Mn(4)	2.718	Mn(4)	1 Mn(4)	2.438
	(4 C	3.331)		3 Mn(3)	2.715
	2 Pr	3.433		3 Mn(1)	2.718
				6 Mn(2)	2.773
Mn(2)	1 C	1.946		1 Pr	3.197
	2 Mn(2)	2.490			
	2 Mn(1)	2.501	C	2 Mn(3)	1.935
	2 Mn(3)	2.659		2 Mn(2)	1.946
	2 Mn(3)	2.744		2 Pr	2.566
	2 Mn(4)	2.773			
	2 Pr	3.220			

[a] All distances shorter than 4.0 Å (Pr atoms), 3.8 Å (Mn atoms), and 3.3 Å (environment of the C atoms) are listed. Standard deviations are all less than 0.002 Å.

However, since the deviations from the ideal occupancies are not great (positional parameters are the same within one standard deviation; thermal parameters differ by at most six standard deviations), we have preferred to consider the refinements with full occupancy of all metal positions as the final one.

Discussion

The positions of the metal atoms in $Pr_2Mn_{17}C_{3-x}$ correspond to those of the binary compound Th_2Zn_{17}.[13] The carbon atoms fill voids of approximately octahedral shape formed by four Mn atoms and two Pr atoms at opposite corners. Thus the carbon coordination is very similar to that in $LnMn_{11}C_{2-x}$.[10] The deviations from the ideal octahedral shape are essentially due to the larger size of the lanthanoid atoms (Mn–C distances 1.935 and 1.946 Å in $Pr_2Mn_{17}C_{3-x}$ and 1.914 Å in $LaMn_{11}C_{2-x}$; Pr–C = 2.566 Å; La–C = 2.736 Å). The Pr_2Mn_4C octahedra are linked via common Pr atoms. Each Pr atom belongs to three octahedra. In this way the nets of the linked octahedra form networks resembling the nets in the rhombohedral modification of graphite,[16] whereas the corresponding network in the structure of $LaMn_{11}C_{2-x}$ is analogous to that of a diamond structure that is compressed along one of the fourfold axes (Figure 2).

The coordination numbers of the metal atoms are all high, as is typical for intermetallic phases. The Pr atom has 19 Mn neighbors at distances varying from 3.186 to 3.433 Å, 1 Pr neighbor (3.950 Å), and 3 almost coplanar (C–Pr–C angles of 119.64° instead of 120°) C neighbors. The Mn(2) and Mn(3) atoms have a coordination of 1 carbon and 12 metal atoms [10 Mn plus 2 Pr neighbors for Mn(2); 9 Mn plus 3 Pr neighbors for Mn(3)]. The Mn(1) and Mn(4) atoms have no C neighbors. The Mn(1) atom is situated in the center of an icosahedron that is distorted due to the large size of the two Pr neighbors. The coordination of the Mn(4) atom is that of the Frank–Kasper polyhedron[17] for the coordination number 14 with its one Pr neighbor and one Mn(4) neighbor at the (nearly) sixfold vertices. This Mn(4)–Mn(4) distance of 2.438 Å is the shortest in the structure; the longest bonding Mn–Mn distance is 2.773 Å.

The carbon positions in the crystal of $Pr_2Mn_{17}C_{3-x}$ used for the structure determination are filled to only 59 ± 3% ($x = 1.23$), the ideal composition being $Pr_2Mn_{17}C_3$. In $LaMn_{11}C_{2-x}$, the occupancy of the carbon position was found[10] to be 76 ± 1%. Partially filled carbon positions are frequently observed in transition-metal carbides. The best known example is probably NaCl type TiC_{1-x}, which has a homogeneity range from $x \sim 0$ to $x \sim 0.4$. We have not investigated the homogeneity ranges of the $Ln_2Mn_{17}C_{3-x}$ carbides. This certainly would be an experimentally difficult and time-consuming undertaking. Thus we do not know whether the ideal composition is within the homogeneity range. However, the systems lanthanum–manganese[18] and cerium–manganese[19] do not contain any binary phases (they have miscibility gaps even in the liquid!), and thus the relatively small carbon content is needed for the formation of the compounds. It can be rationalized that through the addition of the carbon atoms electrons are accommodated in bonding metal–carbon states that would fill antibonding states in a binary La–Mn compound.[10]

Table V. Interstitial Compounds That Derive from Elemental or Binary Structure Types of the Same Symmetry by Filling of Octahedral Voids

elemental or binary structure type	examples of "filled" ternary structures	ref
Cu	TiC_{1-x}	22
Mg	δ-NbN	22
Cu_3Au	Mn_3CuN, Mn_3AlC, Ti_3AlC, Ce_3InC_{1-x}	23
Mn_5Si_3	$Mo_5Si_3C_{1-x}$, $Nb_5Ga_3C_{1-x}$	24
β-Mn	Mo_3Al_2C, V_3Zn_2N	25
Ti_2Ni	Ti_4Ni_2O, W_6Fe_6C, $Nb_8Zn_4C_{3-x}$	26
Re_3B	V_3AsC	27
U_3Si	Cr_3AsN, Mn_3GeC	28
$BaCd_{11}$	$LaMn_{11}C_{2-x}$	10
Th_2Zn_{17}	$Pr_2Mn_{17}C_{3-x}$	this work
Th_2Ni_{17}	$Tb_2Mn_{17}C_{3-x}$	20

The structures of $LaMn_{11}C_{2-x}$ and $Pr_2Mn_{17}C_{3-x}$ derive from the binary structure types $BaCd_{11}$ and Th_2Zn_{17} by filling of the octahedral voids with carbon atoms. Other "interstitial" compounds that can be derived from elementary or binary structure types of the same space group symmetry by filling of octahedral voids are listed in Table V. Very recently we have also obtained ternary carbides $Ln_2Mn_{17}C_{3-x}$ (with all the lanthanoids from Gd to Lu with the exception of Yb), which crystallize with a "filled-up" Th_2Ni_{17} type structure.[20] The Th_2Zn_{17} and Th_2Ni_{17} structures may be considered as stacking variants of each other.[21] A corresponding stacking fault was probably responsible for the twinning of one of the crystals of $Pr_2Mn_{17}C_{3-x}$ investigated during this work.

Acknowledgment. We wish to thank Dr. M. H. Möller for the competent collection of the single-crystal diffractometer data and H. J. Göcke for work on the scanning electron microscope. W. Kuntz (Rhône-Poulenc GmbH, Frankfurt) and Dr. G. Höfer (Heraeus Quarzschmelze, Hanau) are thanked for generous gifts of rare-earth metals and silica tubes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factors of $Pr_2Mn_{17}C_{3-x}$ (6 pages). Ordering information is given on any current masthead page.

---

(16) Donohue, J. "The Structures of the Elements"; Wiley: New York, 1974.

(17) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1958**, *11*, 184.

(18) Rolla, L.; Iandelli, A. *Ber. Dtsch. Chem. Ges. B* **1942**, *75*, 2091.

(19) Iandelli, A. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1952**, *13*, 265.

(20) Block, G.; Jeitschko, W., to be submitted for publication.

(21) Iandelli, A.; Palenzona, A. *J. Less-Common Met.* **1967**, *12*, 333.

(22) Pearson, W. B. "A Handbook of Lattice Spacings and Structures of Metals and Alloys"; Pergamon Press: Oxford, 1958.

(23) Juza, R.; Puff, H. *Z. Elektrochem.* **1957**, *61*, 810. Stadelmaier, H. H. *Z. Metallkd.* **1961**, *52*, 758. Jeitschko, W.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1964**, *95*, 319. Stadelmaier, H. H. In "Developments in the Structural Chemistry of Alloy Phases"; Giessen, B. C., Ed.; Plenum Press: New York, 1969.

(24) Parthé, E.; Jeitschko, W.; Sadagopan, V. *Acta Crystallogr.* **1965**, *19*, 1031. Nowotny, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *20*, 906.

(25) Jeitschko, W.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1964**, *95*, 1212.

(26) Mueller, M. H.; Knott, H. W. *Trans. Soc. Min. Eng. AIME* **1963**, *227*, 674. Leciejewicz, J. *J. Less-Common Met.* **1964**, *7*, 318. Jeitschko, W.; Holleck, H.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1964**, *95*, 1004.

(27) Boller, H.; Nowotny, H. *Monatsh. Chem.* **1967**, *98*, 2127.

(28) Boller, H. *Monatsh. Chem.* **1968** *99*, 2444.