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The Rare Earth Osmium Carbides $Ln_5Os_3C_{4-x}$ (Ln = La–Nd, Sm) with a New Type of Filled Mn_3Si_3 Structure

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The five compounds $Ln_5Os_3C_{4-x}$ (Ln = La–Nd, Sm) have been prepared by arc-melting cold-pressed pellets of the elemental components and subsequent annealing. They crystallize with a new hexagonal structure type ($P6_3/mcm$, $Z = 2$), which has been determined from single-crystal X-ray data of $Ln_5Os_3C_{3.25(4)}$ ($a = 919.57(8)$ pm, $c = 673.86(4)$ pm, $R = 0.015$ for 293 structure factors and 14 variable parameters) and also refined for $Nd_5Os_3C_{3.17(7)}$ ($a = 897.8(1)$ pm, $c = 667.42(9)$ pm, $R = 0.028$, 440 F values, 14 variables). The metal positions correspond to the positions of the Mn_5Si_3 structure. The carbon position of the $Mo_5Si_3C_{1-x}$ structure is partially filled. The three additional carbon atoms of the formula $La_5Os_3C_{4-x}$ occupy distorted octahedral La_4Os_2 voids. The linear Os–C–Os units of these La_4Os_2C octahedra have Os–C bond lengths of 191 pm. They are linked via common osmium atoms, thus forming a new kind of zig-zag-shaped polyanion. Using oxidation numbers the compound may be rationalized with the formula $(5La^{+3})^{+15}(Os_3C_3)^{-14}(0.25C^{-4})^{-1}$. © 1997 Academic Press

INTRODUCTION

Ternary lanthanoid transition metal carbides with ruthenium as transition metal component have been known for some time, e.g., the perovskite carbide $CeRu_3C$ (1) and the corresponding series of isotypic carbides $LnRu_3C$ (2), as well as the series $Ln_7Ru_2C_{11}$ (3) and $Ln_{3.67}RuC_6$ (4). Only one representative is known with the filled NiAs-type structure of $GdRuC_2$ (5). In contrast, no ternary carbides with the homologous element osmium have been reported with the exception of a preliminary account of the present work (6).

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

Starting materials were filings of the rare-earth metals (>99.9%), osmium powder (Degussa, 99.9%, 300 mesh) and graphite flakes (Alpha, >99.5%, 20 mesh). The samples were prepared by arc-melting of small (about 400 mg) cold-pressed pellets of the elemental components of the ideal compositions in an atmosphere of purified argon. The samples were melted from both sides to enhance their homogeneity. They were then wrapped in tantalum foil and annealed in evacuated silica tubes for 30 days at 900°C.

The ternary carbides are all stable in air for long periods of time. Well-crystallized samples have a light-gray color with metallic luster; the powders are dark gray. Energy dispersive analyses of the ternary osmium carbides in a scanning electron microscope were in agreement with the ideal composition and did not reveal any impurity elements heavier than sodium.

Guinier powder diagrams of the samples were recorded with $CuK\alpha_1$ radiation and α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. Indices were assigned on the basis of the hexagonal cell found by the single-crystal investigation. The identification of the diffraction lines was facilitated by intensity calculations (7) using the positional parameters of the refined structures. The lattice constants, obtained by least-squares fits, are listed in Table 1. The cell volumes (Fig. 1) reflect the lanthanoid contraction.

STRUCTURE DETERMINATION AND REFINEMENTS

Single-crystals of $La_5Os_3C_{4-x}$ and $Nd_5Os_3C_{4-x}$ were investigated in a Buerger precession camera to establish their symmetry and suitability for the data collections. The intensity data were recorded on an Enraf Nonius CAD4 diffractometer with graphite-monochromated $MoK\alpha$ radiation and a scintillation counter with pulse-height discrimination. The crystallographic data and some results are summarized in Table 2.

The positions of the metal atoms were determined from a combination of a Patterson synthesis and direct methods, while the carbon atoms were located by difference Fourier syntheses. Both structures were refined by a full-matrix least-squares program with atomic scattering factors (8)

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TABLE 1
Lattice Constants of Carbides with the Hexagonal $La_5Os_3C_{4-x}$-Type Structure[a]

Compound	*a* (pm)	*c* (pm)	*c*/*a*	*V* (nm^3)
$La_5Os_3C_{4-x}$	919.57(8)	673.86(4)	0.7328	0.4935
$Ce_5Os_3C_{4-x}$	905.5(1)	666.20(7)	0.7357	0.4730
$Pr_5Os_3C_{4-x}$	900.5(1)	667.83(6)	0.7416	0.4690
$Nd_5Os_3C_{4-x}$	897.8(1)	667.42(9)	0.7434	0.4659
$Sm_5Os_3C_{4-x}$	893.0(2)	664.4(2)	0.7440	0.4589

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

corrected for anomalous dispersion (9). The weighting schemes included a term, which accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was optimized. The metal atoms were refined with anisotropic, the carbon atoms with isotropic displacement parameters. To check for deviations from the ideal compositions, the scale factor was held constant in one series of least-squares cycles, and all occupancy parameters were allowed to vary along with the thermal parameters. The results showed no significant deviations from the full occupancies for most atomic sites, and in the final least-squares cycles the ideal occupancies were assumed, with the exception of the C2 position. In the final difference Fourier synthesis there were no indications for the occupancy of additional atomic sites. The highest residual electron densities were all at locations too close to the metal positions to be suited for additional atomic sites.

The atomic parameters and the interatomic distances of both structures are listed in Tables 3 and 4. The structure factor tables and the anisotropic thermal parameters of the two structures are available from the authors (10, 11).

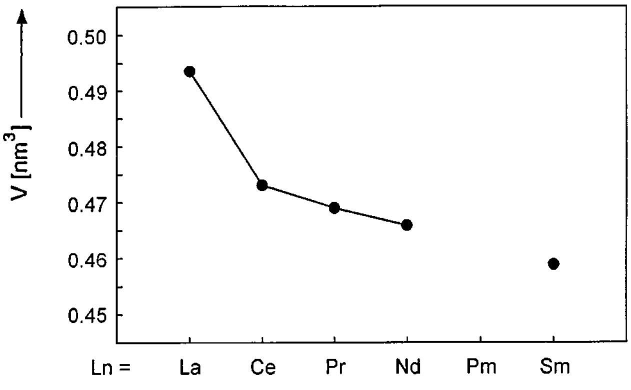

FIG. 1. Cell volumes of $La_5Os_3C_{4-x}$-type carbides.

TABLE 2
Crystallographic Data for $La_5Os_3C_{4-x}$ and $Nd_5Os_3C_{4-x}$

Compound	$La_5Os_3C_{3.25(4)}$	$Nd_5Os_3C_{3.17(7)}$
Lattice constants	Table 1	Table 1
Formula units/cell	$Z = 2$	$Z = 2$
Space group	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)
Formula mass	1304.2	1329.9
Calculated density (g/cm^3)	8.78	9.48
Crystal dimensions (μm^3)	$30 \times 30 \times 50$	$40 \times 40 \times 60$
$\theta/2\theta$ scans up to	$2\theta = 74°$	$2\theta = 90°$
Range in *hkl*	±12, ±12, 0–11	±15, ±15, 0–13
Total no. of reflections	5303	8780
Absorption correction	from psi scans	from psi scans
Transmission (highest/lowest)	1.22	2.10
Unique reflections	547	804
Inner residual	$R_i = 0.042$	$R_i = 0.052$
Reflections with $I > 3\sigma(I)$	293	440
No. of variables	14	14
Highest residual electron density (e/Å^3)	1.6	5.5
Conventional residual (on *F* values)	$R = 0.015$	$R = 0.028$
Weighted residual	$R_w = 0.016$	$R_w = 0.030$

DISCUSSION

The structure of $Ln_5Os_3C_{4-x}$ represents a new structure type which, however, is closely related to the Mn_5Si_3 ($D8_8$) structure (Fig. 2), where the metal positions of $Ln_5Os_3C_{4-x}$ correspond to the positions of the manganese and silicon atoms (12–14). The Mn_5Si_3 structure type has been reported for many binary compounds, e.g., the series of rare earth (*Ln*) silicides, germanides, stannides, and plumbides Ln_5Si_3, Ln_5Ge_3, Ln_5Sn_3, and Ln_5Pb_3 (15). The rare-earth atoms of the Wykoff position 6*g* form octahedral voids, which are known to be suited for the accommodation of interstitial

TABLE 3
Atomic Parameters of $La_5Os_3C_{4-x}$ and $Nd_5Os_3C_{4-x}$[a]

Atom	$P6_3/mcm$	Occupancy	*x*	*y*	*z*	*B*
$La_5Os_3C_{3.25(4)}$						
La1	6*g*	0.999(2)	0.24762(8)	0	1/4	1.01(1)
La2	4*d*	1.001(2)	1/3	2/3	0	0.679(7)
Os	6*g*	1.002(1)	0.59867(5)	0	1/4	0.674(7)
C1	6*f*	0.96(2)	1/2	0	0	0.8(1)
C2	2*b*	0.25(4)	0	0	0	0.8[b]
$Nd_5Os_3C_{3.17(7)}$						
Nd1	6*g*	0.991(2)	0.2469(1)	0	1/4	0.78(1)
Nd2	4*d*	1.003(3)	1/3	2/3	0	0.583(8)
Os	6*g*	0.999(2)	0.60197(7)	0	1/4	0.562(8)
C1	6*f*	1.05(4)	1/2	0	0	1.1(2)
C2	2*b*	0.17(7)	0	0	0	1.1[b]

[a] The last column contains the isotropic thermal parameters of the carbon atoms and the equivalent isotropic thermal parameters ($\times 10^4$, in units of pm^2) of the metal atoms. The occupancy parameters were refined in separate least-squares cycles. In the final cycles the ideal occupancies were assumed except for the C2 position.

[b] The *B* values of the C1 and C2 positions were constrained to be equal.

TABLE 4
Interatomic Distances in the Structures of $La_5Os_3C_{4-x}$ and $Nd_5Os_3C_{4-x}$[a]

		$La_5Os_3C_{4-x}$	$Nd_5Os_3C_{4-x}$
*Ln*1:	2C2	283.3	277.5
	2C1	286.8	281.9
	2Os	322.5	312.5
	1Os	322.8	318.8
	2Os	365.4	360.2
	4*Ln*2	390.8	382.9
	2*Ln*1	394.4	384.0
	4*Ln*1	406.7	400.6
*Ln*2:	3C1	265.5	259.2
	6Os	327.2	321.5
	2*Ln*2	336.9	333.7
	6*Ln*1	390.8	382.9
Os:	2C1	191.4	190.3
	2*Ln*1	322.5	312.5
	1*Ln*1	322.8	318.8
	4*Ln*2	327.2	321.6
	2*Ln*1	365.4	360.2
	2Os	382.7	380.6
	2C2	405.7	394.4
C1:	2Os	191.4	190.3
	2*Ln*2	265.5	259.2
	2*Ln*1	286.8	281.9
C2:	6*Ln*1	283.3	277.5

[a] All distances shorter than 420 pm (metal–metal, metal–C) and 300 pm (C–C) are listed. The standard deviations are all 0.1 pm or less.

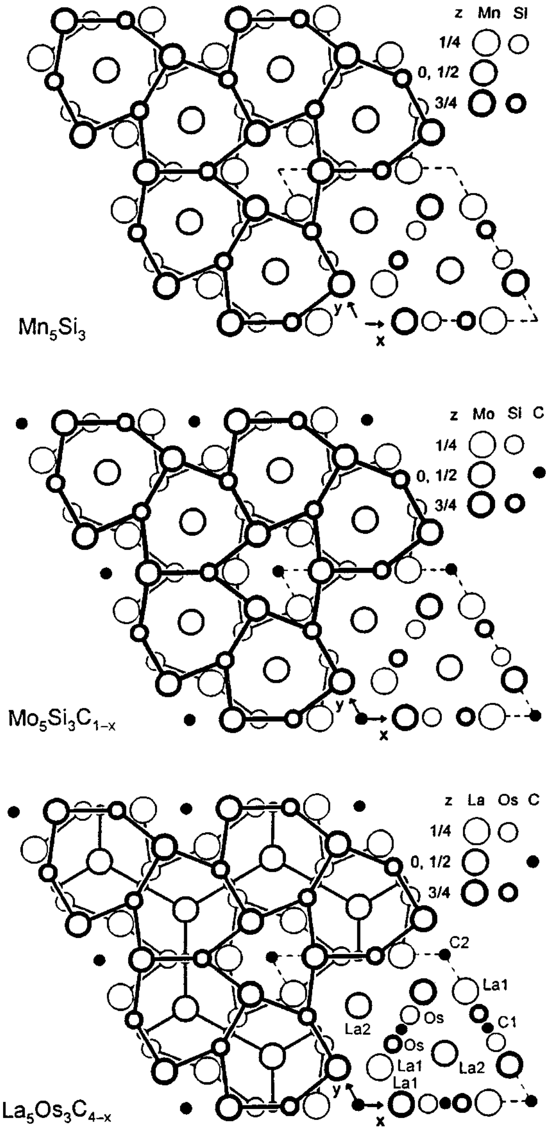

FIG. 2. The crystal structure of $La_5Os_3C_{4-x}$ as compared to the closely related structures of Mn_5Si_3 and $Mo_5Si_3C_{1-x}$. Atoms connected by thick and thin lines are situated at two different heights of the projection direction. These lines do not necessarily represent strong bonds.

atoms like carbon or nitrogen. These ternary $D8_8$ phases have been called Nowotny phases. Their structure has been established for $Mo_5Si_3C_{0.6}$ by neutron diffraction (16). The molybdenum octahedra, which accommodate the carbon atoms of $Mo_5Si_3C_{0.6}$ are sharing faces, and as a rule, in carbides face-shared metal octahedra are never fully occupied by carbon atoms (17). This is also the case for the carbon atoms in $Mo_5Si_3C_{0.6}$, where the composition with the full occupancy would be $Mo_5Si_3C_{1.0}$. The corresponding carbon atoms C2 of $La_5Os_3C_{4-x}$ and $Nd_5Os_3C_{4-x}$ show a similar behavior, the C2 sites are occupied to only 25(4) and 17(7)%, respectively; i.e., these carbides have the compositions $La_5Os_3C_{3.25(4)}$ and $Nd_5Os_3C_{3.17(7)}$.

The C1 atoms of $La_5Os_3C_{4-x}$ occupy a site, which never has been found to be occupied in compounds with a Mn_5Si_3- or Mo_5Si_3C-related structure, and in that sense the present carbides crystallize with a new structure type. Again these carbon atoms occupy octahedral voids; however, in contrast to the C2 atoms, which occupy octahedral voids formed only by lanthanoid atoms, the C1 atoms are situated in distorted La_4Os_2 octahedra. These octahedra do not share faces, and consequently these carbon positions are fully occupied. The La_4Os_2 octahedra are linked via common edges thereby forming chains, which extend along the *c* axis. These chains are interconnected via common corners formed by the La2 atoms. They are also connected to the chains of the face sharing lanthanum octahedra around the C2 atoms via common La1 atoms (Fig. 3).

The *Ln*1 atoms in $La_5Os_3C_{4-x}$ (and $Nd_5Os_3C_{4-x}$, respectively) are surrounded by four carbon atoms in almost square–planar coordination (Fig. 4) at an average distance of 285.0 (279.7) pm. The *Ln*2 atoms have only three C neighbors in coplanar arrangement and since they have fewer carbon neighbors than the *Ln*1 atoms, the *Ln*2–C1 distances are shorter: 265.5 (259.2) pm. These coordinations are augmented by 5 Os and 10 *Ln* neighbors for the *Ln*1 atoms and

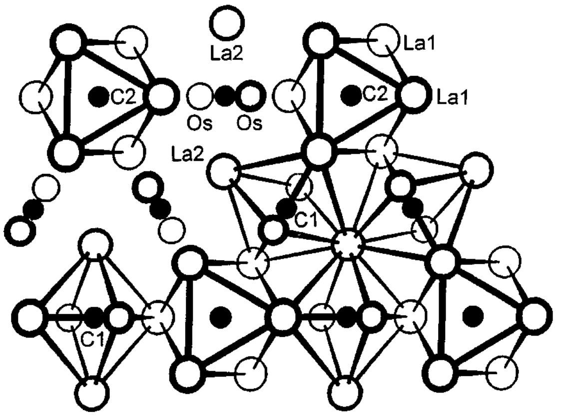

FIG. 3. The structure of $La_5Os_3C_{4-x}$ emphasizing the octahedral metal environments of the carbon atoms. The $(La1)_6$ octahedra around the C2 atoms share those common faces, which are oriented perpendicular to the hexagonal *c* axis. The $(La1)_2(La2)_2Os_2$ octahedra containing the C1 atoms are connected via common La1–Os edges. The thus formed infinite $[(La1)_{6/2}C2]_n$ and $[(La1)_2(La2)_{2/2}Os_{2/2}C1]_n$ chains extend along the *c* direction. They are further linked to each other in the *ab* plane via common lanthanum (both La1 and La2) atoms. This is emphasized in the lower right-hand part of the figure.

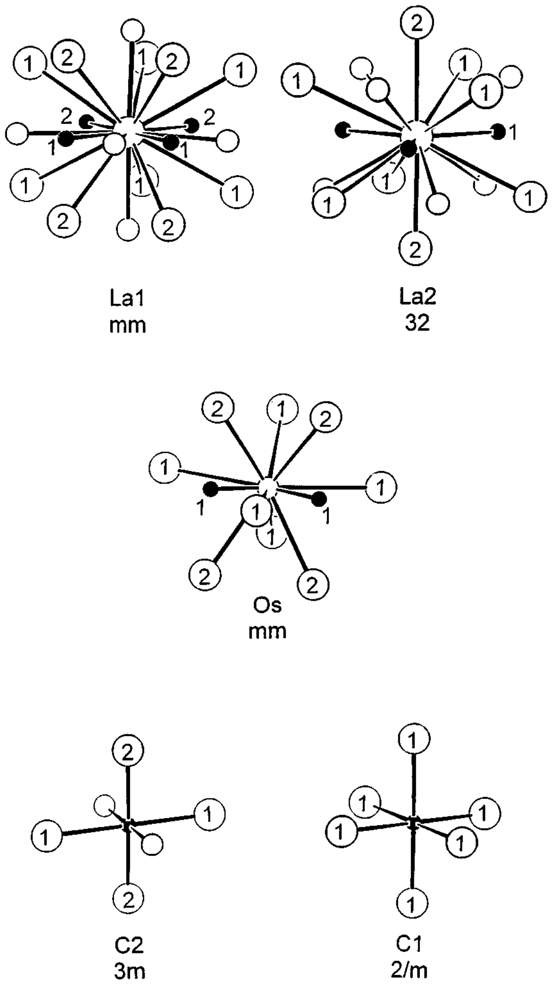

FIG. 4. Near-neighbor environments in the structure of $La_5Os_3C_{4-x}$. The site symmetries of the central atoms are indicated.

by 6 Os and 8 *Ln* neighbors for the *Ln*2 atoms. The bonding character of the metal–metal interactions is certainly less important; however, in view of the large metal content of the compounds, we believe it should not be neglected entirely.

Each osmium atom has two carbon neighbors at the rather short distance of 191.4 pm (190.3 pm in the neodymium compound). In addition, each osmium atom has 9 *Ln* neighbors at distances covering the range from 322.5 to 365.4 pm (312.5 to 360.2 pm). The shortest Os–Os distance of 382.7 (380.6) pm is outside the range to be considered for bonding.

Chemical bonding in $La_5Os_3C_{4-x}$ can to a first approximation be rationalized on the basis of simple assumptions. Using oxidation numbers (formal charges), where the bonding electrons are counted at the atoms with the higher electronegativity, we obtain the formula $(3La1^{+3})^{+9}(2La2^{+3})^{+6}(3Os^{-2/3})^{-2}(3C1^{-4})^{-12}(0.25C2^{-4})^{-1}$. This formula accounts for the fact that the lanthanum atoms have largely transferred their valence electrons to the osmium and carbon atoms, and it is in agreement with the octet rule for the carbon atoms. The negative oxidation number of $-2/3$ for the osmium atoms results from the charge balancing. The C2 atoms are surrounded only by lanthanum atoms and they may therefore well be considered as C^{4-} ions. In contrast, the C1 atoms have two close osmium neighbors in linear arrangement and together with these osmium atoms they form a one-dimensionally infinite –Os–C–Os–C– zig-zag chain (Fig. 5). In deemphasizing the partially ionic character of the Os–C1 bonds we may also write the formula $(5La^{+3})^{+15}(3Os3C1)^{-14}(0.25C2)^{-1}$; i.e., one (OsC1) unit carries a formal charge of $-\frac{14}{3} = -4\frac{2}{3}$. Thus, each (OsC1) unit contains $16\frac{2}{3}$ valence electrons: eight from the osmium atom, four from the carbon atom, and $4\frac{2}{3}$ from the formal charge. If we assume all valence orbitals of the carbon atoms to be involved in bonding toward the osmium atoms, the osmium atoms attain an electron count of $16\frac{2}{3}$: 8 electrons from the two double-bonds to the neighboring carbon atoms, plus $8\frac{2}{3}$ nonbonding electrons, which are accommodated in nonbonding orbitals of the osmium atoms. The fractional electron count per osmium atom or per (OsC1) unit is not a problem in a band structure, where the electrons at the Fermi level are delocalized. Since the osmium atoms have not reached the inert gas shell (the magic electron count of 18), it might be possible to synthesize isotypic compounds with iridium as transition metal component. However, the problem with such predictions is always that other competing structures (including the ones with different stoichiometry) might be thermodynamically more stable.

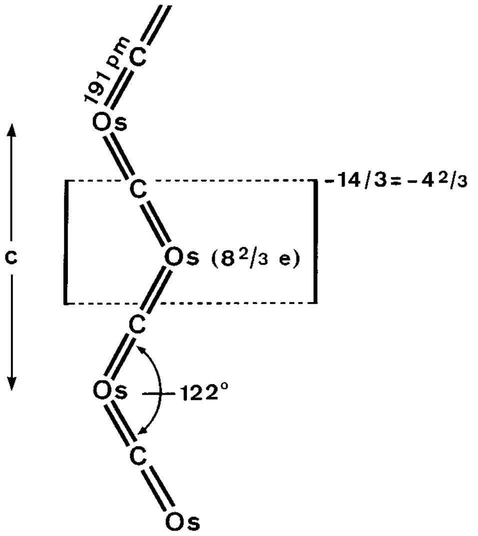

FIG. 5. A cut-out of the infinite $[(Os_3C_3)^{-14}]_n$ zig-zag chain formed by osmium and the C1 atoms. The OsC monomer has an oxidation number (formal charge) of $-\frac{14}{3}$, and assuming a double bond for each Os–C interaction the osmium atoms attain an electron count of $16\frac{2}{3}$; i.e., 8 electrons are involved in bonding toward the two adjacent carbon atoms and $8\frac{2}{3}$ electrons per (OsC) unit are accommodated in nonbonding orbitals of the osmium atoms.

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