

Pr₂ReC₂ and Other Ternary Rare Earth Metal Rhenium Carbides with Filled PbCl₂ (Co₂Si) Structure

W. JEITSCHKO, G. BLOCK, G. E. KAHNERT, AND R. K. BEHRENS

Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, West Germany

Received May 31, 1990

The carbides R₂ReC₂ (R = Y, Ce-Nd, Sm, Gd-Tm, Lu) were prepared by arc-melting of cold-pressed pellets of the elemental components. They crystallize with the orthorhombic space group *Pnma* and Z = 4 formula units per cell. The lattice constants for Pr₂ReC₂ are: *a* = 655.69(6) pm, *b* = 509.46(5) pm, *c* = 984.42(8) pm. The crystal structure was determined from quantitative evaluations of Guinier powder data for Y₂ReC₂ and Pr₂ReC₂, which refined to conventional residuals of *R* = 0.088 and *R* = 0.072, respectively. The structure of the isotopic carbide Er₂ReC₂ was determined from single-crystal diffractometer data: *R* = 0.032 for 842 structure factors and 26 variable parameters. The positions of the metal atoms correspond to those of the Co₂Si-branch of the "anti"-PbCl₂ structure. The carbon atoms are isolated from each other and occupy two different octahedral voids (4*R* + 2Re, 5*R* + 1Re). There are no bonding Re-Re interactions in the one-dimensionally infinite [ReC₂⁻⁶]_n polyanions. The Re-C bond lengths of between 192 pm and 203 pm suggest bond orders of about two and the rhenium atoms seem to obey the 18-electron rule. The metal atom positions of the Pr₂ReC₂ type carbides correspond to those of a distorted cubic body-centered structure, as is also found for several other complex carbides. The average valence electron number of the metal atoms is usually greater in unfilled (host) structures than in the corresponding filled (interstitial) structures. © 1990 Academic Press, Inc.

Introduction

The binary carbides of the transition metals are sometimes called "interstitial carbides" because their most frequently occurring crystal structures derive from simple close-packed metal "host" structures, where the small carbon atoms occupy interstitial octahedral voids (1). In recent years we have encountered several new examples of such filled structures in ternary lanthanoid- and actinoid-transition metal-carbon systems: LaMn₁₁C_{2-x} with filled BaCd₁₁ structure (2), Pr₂Mn₁₇C_{3-x} with filled Th₂Zn₁₇ structure (3), UCr₄C₄ with filled MoNi₄ structure (4), and Tb₂Mn₁₇C_{3-x} with filled Th₂Ni₁₇ structure (5). Here we report

on another series of interstitial carbides. Their structure was first determined from X-ray powder data of Pr₂ReC₂ and Y₂ReC₂ (6). We have now determined this structure also from single-crystal data of Er₂ReC₂, which completely confirmed the earlier results. A preliminary announcement (5) and brief reports (7, 8) of this work were given before.

Sample Preparation

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 rare earth metals (*R*) were kept under dried paraffine oil, which was washed away by repeated treatment

TABLE I

LATTICE CONSTANTS OF ORTHORHOMBIC RARE EARTH METAL RHENIUM CARBIDES $R_2\text{ReC}_2$ WITH FILLED Co_2Si STRUCTURE^a

Compound	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)
Y ₂ ReC ₂	655.69(6)	509.46(5)	984.42(8)	0.3288
Ce ₂ ReC ₂	656.9(1)	529.37(9)	1002.4(2)	0.3486
Pr ₂ ReC ₂	665.59(6)	534.54(4)	1018.35(8)	0.3623
Nd ₂ ReC ₂	665.1(1)	530.5(1)	1014.6(2)	0.3580
Sm ₂ ReC ₂	661.3(2)	522.9(2)	1001.9(3)	0.3465
Gd ₂ ReC ₂	659.27(9)	517.56(8)	994.5(1)	0.3393
Tb ₂ ReC ₂	655.85(6)	512.92(6)	986.8(1)	0.3319
Dy ₂ ReC ₂	653.65(9)	509.44(7)	982.1(1)	0.3270
Ho ₂ ReC ₂	652.11(5)	506.54(4)	978.29(8)	0.3231
Er ₂ ReC ₂	649.90(8)	503.53(2)	974.31(9)	0.3188
Tm ₂ ReC ₂	647.95(7)	500.91(7)	969.1(1)	0.3145
Lu ₂ ReC ₂	644.49(6)	496.11(6)	962.8(1)	0.3078

^a Here and in the following tables standard deviations in the positions of the least significant digits are given in parentheses.

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. For the subsequent annealing between 1 and 3 weeks at 900°C in evacuated silica tubes the samples were wrapped in tantalum foils.

Energy dispersive analyses of the ternary carbides in a scanning electron microscope were in agreement with the ideal composition. The Guinier powder patterns of samples, which were prepared with the starting ratio $R : \text{Re} : \text{C} = 3 : 2 : 3$ showed elemental

rhenium and occasionally the subcarbides $R_3\text{C}_x$ ($x \sim 1$) (9) as second and third phase products.

A well-crystallized sample of Er₂ReC₂ was obtained by first reacting the elemental components (ER : Re : C = 12 : 5.5 : 12) in an arc-melting furnace. In a second step this sample was annealed slightly below the melting point in a high-frequency furnace. The single crystals used for the structure refinement were isolated from this sample.

Properties

Compact ingots of the ternary carbides deteriorate slowly on air, powdered samples within a few hours. Freshly fractured samples have silvery grey surfaces with metallic lustre. Thus the band gaps are small or do not exist at all. However, semiconducting behavior cannot completely be ruled out, as was demonstrated recently for the carbides with similar composition LaRhC₂ and CeRhC₂ (10).

In the search for superconductivity samples of Y₂ReC₂ and Lu₂ReC₂ were placed into the coils of an *ac* inductivity apparatus. Neither compound gave an indication for a transition to a superconducting state down to 2 K.

Lattice Constants

Guinier powder patterns of the samples were recorded with α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as standard. Because

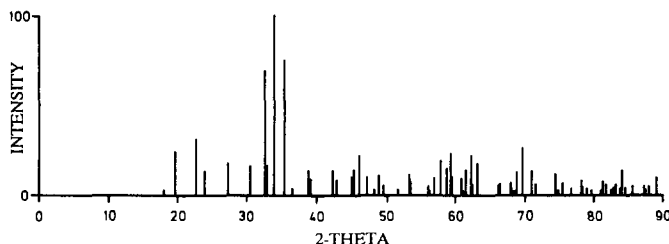


FIG. 1. Computer plot of the calculated Guinier powder pattern of Y₂ReC₂ for CuK α_1 radiation.

of their sensitivity to moist air they were sealed between foils of plastics. Using Visser's program (11) we were successful in assigning indices to the patterns on the basis of isotypic orthorhombic cells. The lattice constants (Table I) were refined by least-squares fits. To assure proper indexing at high diffraction angles, the observed intensities were compared to the intensities calculated (12) from the positional parameters of the refined structures. As an example a computer plot of the powder pattern of Y_2ReC_2 is shown in Fig. 1 and the evaluation of the pattern of Pr_2ReC_2 is listed in Table II.

Structure Determination of Y_2ReC_2 and Pr_2ReC_2 from Powder Data

The only systematic extinctions of the Guinier powder data (reflections $0kl$ observed only with $k + l = 2n$, $hk0$ only with $h = 2n$) led to the space groups $Pnma$ and $Pn2_1a$, of which the centrosymmetric group $Pnma-D_{2h}^{16}$ was found to be correct during the structure refinements. Since the crystal structures of ternary carbides frequently derive from the structures of binary intermetallic phases by filling of octahedral interstitial sites by carbon atoms (1-5, 13-15) we searched Pearson's Handbook (16) for suitable binary "host" structures. From our estimate of about 12 metal atoms per cell, the possible space groups, and the cell dimensions, we were led to the well known "anti"- $PbCl_2$ type structure, which has many representatives, e.g., Co_2P (17), Co_2Si (18), and most interesting for our problem, also the intermetallic compound La_2Au (19). A calculation (12) of the powder pattern for the metal atoms of Pr_2ReC_2 , assuming the atomic positions of La_2Au , showed good agreement with our experimental data. This encouraged us to determine the full structure of our series of isotypic ternary carbides R_2ReC_2 from powder data, although the exact carbon content of the ter-

TABLE II
GUINIER POWDER PATTERN OF Pr_2ReC_2 ^a

<i>hkl</i>	<i>I</i> _o	<i>I</i> _c	<i>F</i> _o	<i>F</i> _c	<i>Q</i> _o	<i>Q</i> _c
101	2	1	35	23	—	322
002	1	3	47	67	386	386
011	8	6	84	73	447	446
102	12	12	115	117	611	611
111	—	1	—	22	—	672
200	11	10	195	184	903	903
112	7	9	79	90	960	961
201	1	<1	47	26	—	999
103	13	16	166	185	1093	1094
013	59	63	378	391	1217	1218
210	22	22	232	234	1252	1253
202	23	24	249	252	1288	1289
211	92	100	354	369	1350	1349
020	68	71	616	631	1400	1400
113	64	68	305	315	1443	1444
004	—	<1	—	31	—	1543
212	—	<1	—	29	—	1639
121	—	<1	—	18	—	1722
104	14	13	228	216	1769	1769
203	14	9	228	180	—	1771
022	—	1	—	57	—	1786
122	7	5	123	105	2012	2011
114	—	2	—	70	—	2119
213	3	3	82	86	2124	2121
301	3	5	115	149	—	2128
220	8	6	188	164	2303	2303
221	—	<1	—	23	—	2399
302	8	8	192	196	2417	2417
204	15	14	273	267	2445	2446

^a The pattern was recorded with $CuK\alpha_1$ radiation up to a scattering angle of $2\theta = 85^\circ$. Only the evaluation of the pattern up to $2\theta = 45^\circ$ is shown here. The *Q* values are defined by $Q = 100/d^2$ [nm^{-2}].

nary compounds was not known at that time.

Intensity data for Y_2ReC_2 and Pr_2ReC_2 were obtained from optical densitometer scans of the Guinier powder patterns, which had been recorded with $CuK\alpha_1$ radiation. Overlapping reflections were not used for the structure determination. The atomic scattering factors (20) were corrected for anomalous dispersion (21). The Pr_2ReC_2 data were refined first by a full-matrix least-squares program using the positional param-

TABLE III
ATOMIC PARAMETERS OF Pr_2ReC_2 , Y_2ReC_2 ,
AND $\text{Er}_2\text{ReC}_2^a$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (10^{-2}nm^2)
Pr_2ReC_2				
Pr(1)	0.811(3)	1/4	0.048(2)	0.2
Pr(2)	0.473(3)	1/4	0.785(2)	0.2
Re	0.268(3)	1/4	0.138(1)	0.4
C(1)	0.99(5)	1/4	0.25(3)	0.6
C(2)	0.65(5)	1/4	0.56(3)	0.6
Y_2ReC_2				
Y(1)	0.819(6)	1/4	0.053(4)	0.4
Y(2)	0.465(7)	1/4	0.784(4)	0.4
Re	0.276(3)	1/4	0.132(2)	0.4
C(1)	0.02(6)	1/4	0.30(3)	0.6
C(2)	0.66(5)	1/4	0.58(3)	0.6
Er_2ReC_2				
Er(1)	0.82071(8)	1/4	0.05687(4)	0.553(6)
Er(2)	0.46535(7)	1/4	0.78329(5)	0.591(7)
Re	0.28201(6)	1/4	0.13120(4)	0.491(6)
C(1)	0.0475(17)	1/4	0.2597(10)	0.7(1)
C(2)	0.6760(16)	1/4	0.5537(9)	0.5(1)

^a All atoms are in the position 4*c* of space group *Pnma*. The last column contains the fixed (not refined) isotropic thermal parameter *B* of the atoms in Pr_2ReC_2 and Y_2ReC_2 , and the isotropic and equivalent isotropic parameter *B* of the carbon and metal atoms in Er_2ReC_2 .

eters of La_2Au (19) as starting parameters (space group *Pnma*, *Z* = 4). A difference Fourier synthesis showed as the two highest peaks positions, which also were suited for the carbon atoms from crystal chemical considerations. The same procedure with the Y_2ReC_2 data resulted in the analogous carbon positions. The isotropic thermal parameters were fixed at reasonable values. The final conventional residuals are *R* = 0.072 and *R* = 0.088 for the Pr_2ReC_2 (36 *F*-values) and Y_2ReC_2 data (32 *F*'s), respectively, with 11 variable parameters each. The positional parameters and interatomic distances are given in Tables III and IV. Listings of the structure factors can be obtained from the authors (6).

TABLE IV
INTERATOMIC DISTANCES (pm) IN THE STRUCTURES
OF $R_2\text{ReC}_2$ (*R* = Pr, Y, Er)^a

		Pr_2ReC_2	Y_2ReC_2	Er_2ReC_2	
R(1):	1C(1)	(235)	(273)	246.5	
	2C(2)	(269)	(256)	251.8	
	1C(1)	(299)	(247)	251.9	
	1C(2)	(251)	(258)	254.8	
	1Re	320	310	305.0	
	1Re	317	310	308.4	
	2Re	332	320	318.5	
	1R(2)	356	345	344.5	
	2R(2)	369	354	349.6	
	1R(2)	351	353	352.7	
	1Re	373	365	357.5	
	2R(1)	380	364	360.5	
	2R(2)	387	369	362.5	
	R(2):	1C(2)	(267)	(242)	246.2
2C(1)		(271)	(255)	252.9	
1C(2)		(261)	(242)	262.3	
2Re		328	317	311.9	
2R(2)		340	335	331.4	
2Re		345	334	333.4	
1R(1)		356	345	344.5	
2R(1)		369	354	349.6	
1R(1)		351	353	352.7	
1Re		385	365	359.3	
2R(1)		387	369	362.5	
Re:		1C(2)	(213)	(218)	192.8
		1C(1)	(218)	(234)	197.3
		1C(1)	(186)	(172)	202.6
	1R(1)	320	310	305.0	
	1R(1)	317	310	308.4	
	2R(2)	328	317	311.9	
	2R(1)	332	320	318.5	
	2R(2)	345	334	333.4	
	1R(1)	373	365	357.5	
	1R(2)	385	365	359.3	
	C(1):	1Re	(218)	(234)	197.3
		1Re	(186)	(172)	202.6
		1R(1)	(235)	(273)	246.5
		1R(1)	(299)	(247)	251.9
2R(2)		(271)	(255)	252.9	
C(2):		1Re	(213)	(218)	192.8
	1R(2)	(267)	(242)	246.2	
	2R(1)	(269)	(256)	251.8	
	1R(1)	(251)	(258)	254.8	
	1R(2)	(261)	(242)	262.3	

^a Standard deviations of the metal-metal distances in Pr_2ReC_2 and Y_2ReC_2 are all equal to or smaller than 6 pm. The metal-carbon distances of these compounds are rather large (with standard deviations of up to 40 pm) and are put in parentheses. In Er_2ReC_2 the standard deviations are all less than 0.1 pm for the metal-metal distances and equal or less than 1.0 pm for the metal-carbon distances. All distances shorter than 399 (metal-metal) and 385 pm (metal-carbon) are listed.

Structure Refinement of Er_2ReC_2 from Single-Crystal Data

The single crystal of Er_2ReC_2 used for the structure refinement was taken from the crushed sample described above. It had irregular shape with dimensions $100 \times 100 \times 20 \mu\text{m}$. All reflections within one-half of the reciprocal sphere were measured on a four-circle diffractometer up to $2\theta = 80^\circ$ with $\text{MoK}\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The scans were taken along θ with background counts at both ends of each scan. An empirical absorption correction was applied from psi scan data. Of the total of 4249 reflections 845 remained after data averaging and omission of those with intensities smaller than three standard deviations.

The structure was refined by a full-matrix least-squares program supplied by the Enraf-Nonius Company. Weights were assigned according to the counting statistics and a parameter for an isotropic secondary extinction correction was also refined. Some very strong reflections $0k0$, for which this correction was insufficient, were omitted. To check for deviations from the ideal composition one series of least-squares cycles was calculated, where all occupancy parameters (with fixed scale factor) were allowed to vary together with the isotropic thermal parameters. The results (in percentages with standard deviations in the position of the least significant digit in parentheses) were as follows: Er(1): 99.7(2), Er(2): 99.9(2), Re: 100.2(1), C(1): 106(3), C(2): 101(3). Thus, no significant deviations from the full occupancies were observed, and in the final refinement cycles the ideal occupancies were assumed. The metal atoms were refined with anisotropic, the carbon atoms with isotropic thermal parameters. In the final difference Fourier synthesis the three highest peaks were very close to the metal positions. They probably resulted from the failure to completely correct for

absorption effects. The final residual was $R = 0.032$ for 842 structure factors and 26 variable parameters. The atomic parameters and interatomic distances are listed in the Tables III and IV together with the corresponding results of Y_2ReC_2 and Pr_2ReC_2 . Listings of the anisotropic thermal parameters and the structure factors are available from the authors (22).

Discussion

The structure determinations of Y_2ReC_2 and Pr_2ReC_2 from X-ray powder data were later confirmed by the structure refinement of Er_2ReC_2 from single-crystal data. This shows that it is possible to locate the light carbon atoms from powder data in the presence of the heavy metal atoms. Further confidence in the structure refinements of the Y and the Pr compound can also be gained from the fact that the positional parameters of the metal atoms change monotonously with their size, i.e., in the sequence Pr, Y, Er. Nevertheless, the full confidence in this new structure type results from the single-crystal refinement of the Er compound. The standard deviations of this refinement are 30 to 40 times smaller than those of the powder refinements. Therefore, in the following discussion, when we quote interatomic distances, we refer to the distances in Er_2ReC_2 .

The structure and the coordination polyhedra of the Pr_2ReC_2 -type carbides $R_2\text{ReC}_2$ are shown in Fig. 2. The rare earth atoms occupy two sites with high coordination numbers. The $R(1)$ atoms have five carbon neighbors (average Er-C distance: 251.4 pm) while the $R(2)$ atoms have four (average distance: 253.6 pm). In addition, both R atoms have four Re neighbors at average (Er-Re) distances of 312.6 and 322.6 pm with a fifth Re neighbor at 357.5 and 359.3 pm, respectively. The coordination shells of both R sites are completed by eight R neighbors at (Er-Er) distances of between

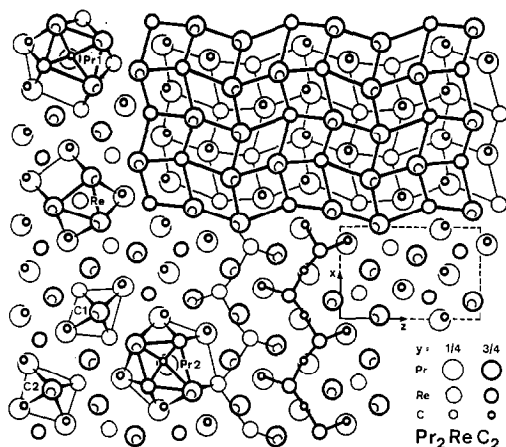


FIG. 2. Crystal structure and coordination polyhedra of Pr_2ReC_2 . In the upper right hand part of the drawing atoms at $y = 1/4$ and $y = 3/4$ are connected by thin and thick lines. In the lower middle two polyanionic chains $[\text{ReC}_2]_n$ are outlined.

331.4 and 362.5 pm with average distances of 355.3 and 348.0 pm. The Re atoms have three carbon and 10 R neighbors. There are no Re–Re and no C–C bonds. The carbon atoms occupy distorted octahedral sites formed by two Re plus four R atoms and one Re plus five R atoms, respectively.

In stressing ionicity we can write the formula $\text{Er}_2^+{}^3[\text{ReC}_2]^{-6}$, where +3 and –6 are oxidation numbers (formal charges). The Re and C atoms form a –Re–C(1)–Re–C(1)– zig-zag chain. The C(2) atoms are attached to the Re atoms with the short distance of 192.8 pm (Fig. 3a). We now want to show that the total electron count for a rhenium atom is compatible with the 18-electron rule. For this purpose we have to establish a correlation between the number of Re–C bonding electrons and the Re–C bond lengths. For the C–C, C=C, and C≡C bonds the values 154 pm, 134 pm, and 120 pm are well established (23). It is somewhat more difficult to find bond lengths for single, double, and triple Re–Re bonds. We have averaged the following literature values: for Re–Re, $\text{Re}_2(\text{CO})_{10}$ with 304.1 pm

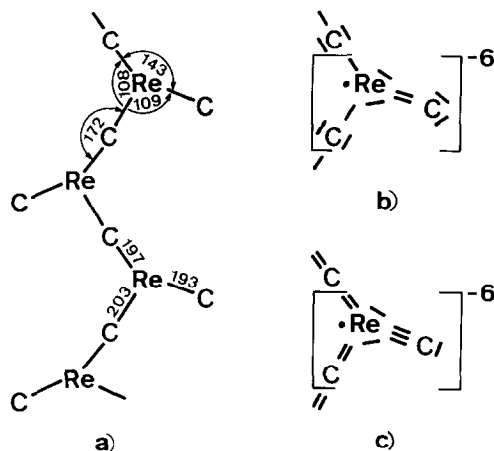


FIG. 3. The polyanion $[\text{ReC}_2]_n$ of the Pr_2ReC_2 type structure. In (a) the interatomic distances (pm) and angles ($^\circ$) are shown. In (b) and (c) we see two Lewis formulas. In (b) the Re atoms obtain 13 valence electrons, in (c) they obtain 19. A comparison of bond lengths shows that the real situation is between (b) and (c), but much closer to (c).

(24) and $(\text{Me}_3\text{SiCH}_2)_5-(\mu\text{-Cl})_3\text{Re}_3-\text{Re}_3(\mu\text{-Cl})_3\text{H}(\text{CH}_2\text{SiMe}_3)_4$ with 299.3 pm (25); for Re=Re, $\text{Re}_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$ with 255.7 pm (26), Re_2Cl_2 (bisdiphenylphosphinomethane) $_2$ and $\text{Re}_2\text{Cl}_5(\text{OC}_2\text{H}_5)$ (bisdiphenylphosphinomethane) $_2$ with 266.7 pm and 261.6 pm (27); and for Re≡Re, $\text{Re}_2\text{Cl}_5[\text{MeS}(\text{CH}_2)_2\text{SMe}]_2$ with 229 pm (28) and $\text{Re}_2(\text{C}_3\text{H}_5)_4$ with 222.5 pm (29). By halving the averages of these values and by adding the corresponding radii of the carbon atoms, we obtain the bond distances: 228 pm for Re–C, 197 pm for Re=C, and 173 pm for Re≡C.

Per $[\text{ReC}_2]^{-6}$ unit we have to account for 21 valence electrons: 7 for the rhenium atom, 8 for the two carbon atoms, and 6 for the charge (At this time it is easier to count the valence electrons of the lanthanoid atoms at the polyanion; we will come back to the partial covalent character of the lanthanoid–rhenium and lanthanoid–carbon interactions.) In (b) and (c) of Fig. 3 we show Lewis formulas for the $[\text{ReC}_2]^{-6}$ unit, where

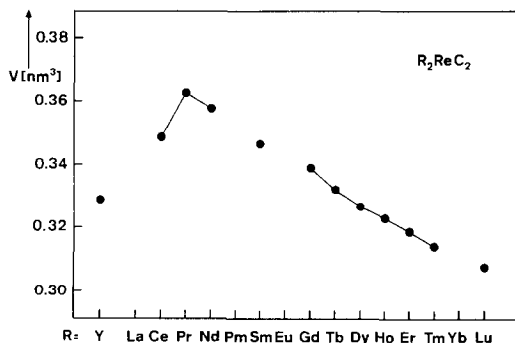


FIG. 4. Cell volumes of carbides with Pr_2ReC_2 -type structure.

each line represents two electrons. In (b) the Re atom forms two single and one double bond to the three neighboring carbon atoms; in (c) it forms two double and one triple bond. In addition, in both formulas the rhenium atoms have 5 nonbonding electrons. The carbon atoms obey the octet rule. The rhenium atoms obtain totals of 13 electrons and 19 electrons in (b) and (c), respectively. The average Re—C distance in the polyanion is 194 pm. This value is close to the Re=C distances of 197 pm established above and we can argue that the true bonding situation is in between (b) and (c), but much closer to (c). Thus, an electron count of 18 for the rhenium atoms is very plausible. The Re—C—Re angle of 172° at the bridging carbon atom is in good agreement with the formulation (c), where this carbon atom forms two double bonds like the central carbon atom of allen.

In a band structure the single electron at the rhenium atoms does not need to stay unpaired. We note that the polyanion has two ReC_2 units per the a translation period. Like the other four “nonbonding” electrons at the rhenium atoms this seemingly unpaired electron could also be involved in the bonding to the lanthanoid atoms, thus accounting for the partial covalent character of the lanthanoid–rhenium interactions. This does not change the electron count at

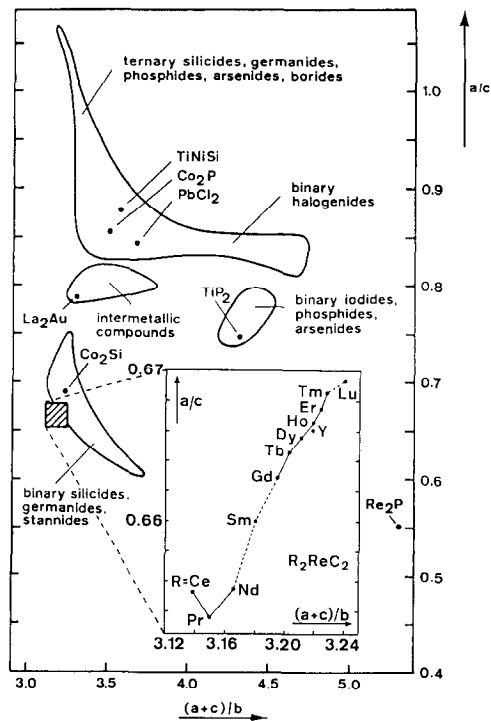


FIG. 5. Classification of some PbCl_2 -type compounds according to their axial ratios a/c and $(a+c)/b$. The axial ratios of the Pr_2ReC_2 -type carbides with “filled” PbCl_2 -type structure came close to those of Co_2Si and La_2Au .

the rhenium atoms; these electrons are then counted at both the lanthanoid and the rhenium atoms in the same way as the electrons of the Re—C interactions are counted at both the rhenium and the carbon atoms. Similarly the “lone pair” of the C(2) atoms could be involved in lanthanoid–carbon bonding. Considering the success of the 18-electron rule in the rationalization of molecular cluster compounds, we expect that this rule will also help to rationalize the structures of the ternary carbides, at least those involving the late transition metals. Here we have shown that it is compatible with the observed bond lengths. If it is obeyed, we expect diamagnetism for the polyanion, apart from the magnetism of the lanthanoid atoms and the possible Pauli paramagnetism.

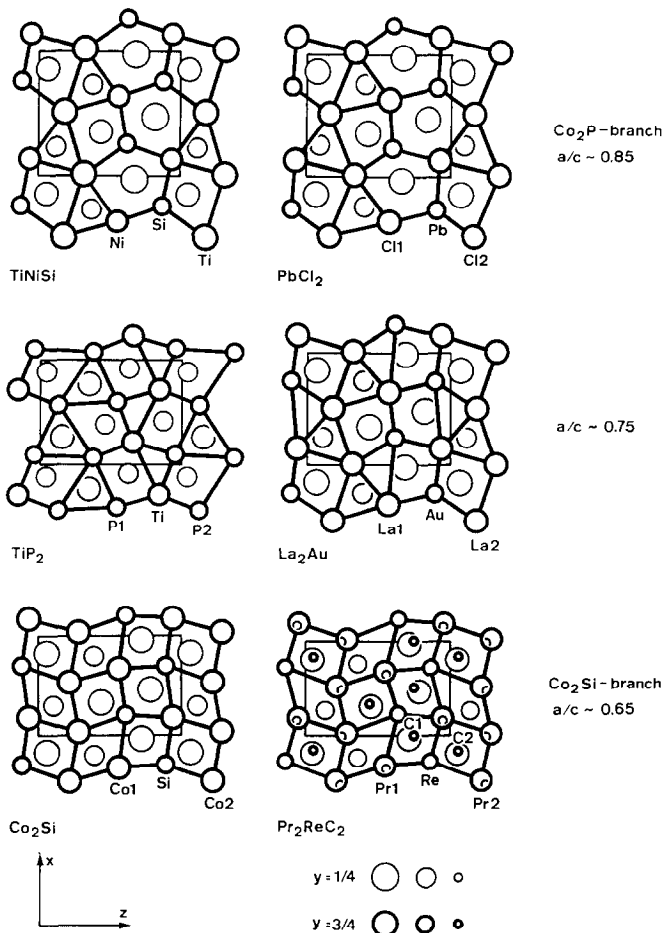


FIG. 6. Atomic positions in various compounds of different branches of the PbCl_2 -type structure. To emphasize the differences and similarities of the structures some atoms at $y = 3/4$ are connected by thick lines. These lines do not necessarily imply strong bonds. The atomic positions of Co_2Si and the metal positions of Pr_2ReC_2 correspond to the positions of a distorted cubic body-centered structure.

The volume plot of the Pr_2ReC_2 -type carbides (Fig. 4) shows the expected lanthanoid contraction. The cell volume of the cerium compound deviates from the smooth plot, indicating at least partial tetravalent character of the cerium atoms. The additional partial electrons from the cerium atoms need to be accommodated in the rhenium-carbon polyanion. Assuming that in all of these carbides the Re atoms obey the 18-electron rule, we would expect slightly longer Re-C distances in Ce_2ReC_2 than in Er_2ReC_2 .

The cell volume of the yttrium compound fits between that of the terbium and the dysprosium compounds. This is also the case for YCoC (30), $\text{Y}_2\text{Cr}_2\text{C}_3$ (31), YMoC_2 (31), and YWC_2 (31), while the volumes of other ternary yttrium carbides, e.g., $\text{Y}_8\text{Rh}_5\text{C}_{12}$ (32), $\text{Y}_2\text{Mn}_{17}\text{C}_{3-x}$ (5), Y_2FeC_4 (33), YCoC_2 (34), and YNiC_2 (34) are between those of the corresponding dysprosium and holmium compounds. In oxides the atomic radii of Y^{3+} fit between the radii of Ho^{3+} and Er^{3+} for the coordination number 6 and between

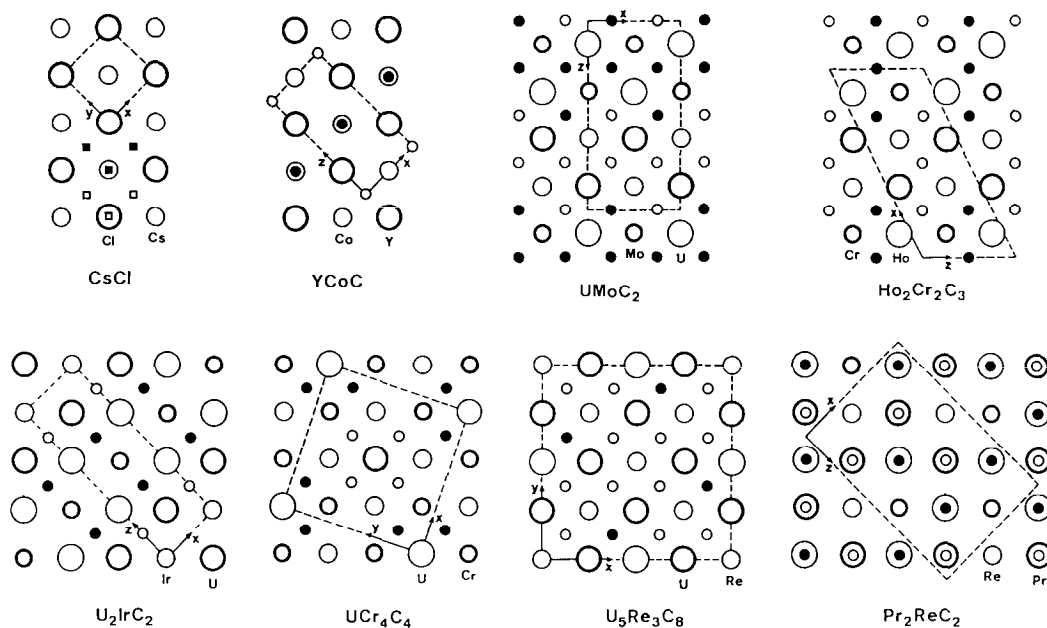


FIG. 7. Interstitial carbides derived from a cubic body-centered arrangement of metal atoms by filling of octahedral voids by carbon atoms. The rare earth and uranium atoms are shown as large circles, the transition metals as medium-sized circles, and the carbon atoms as small circles. Heavy symbols and light symbols are separated from each other by half a translation period of the projection direction. In the CsCl structure some of the (distorted) octahedral voids are indicated by squares. The structures are idealized to emphasize their correspondence.

Dy^{3+} and Ho^{3+} for the coordination numbers 8 and 9 (35).

The metal positions of the new carbides correspond to the atomic positions of PbCl_2 . This structure type occurs for some two hundred salts and intermetallics and has great flexibility, as can be seen from the widely differing axial ratios. To distinguish the Co_2P - from the Co_2Si -branch of this structure Rundqvist and Nawapong (36) classified the various compounds with this structure according to their axial ratio a/c . Later on the length of the b -axis was introduced as an additional parameter (37–42) mostly in the form of the ratio $(a + c)/b$. Such a plot is shown in Fig. 5. It can be seen that the axial ratios of the Pr_2ReC_2 type carbides are close to those of Co_2Si and La_2Au .

Similar axial ratios correspond to similar atomic positions and similar atomic coordinations. This is shown in Fig. 6 for some of these compounds with PbCl_2 type structure. It can also be seen that the atomic positions of Co_2Si and the metal positions of Pr_2ReC_2 correspond to the atomic positions of a distorted body-centered structure. In the lower right hand corner of Fig. 7 the structure of Pr_2ReC_2 is shown in an idealized form, where the metal atoms occupy the positions of an undistorted body-centered structure. As was discussed before (43) a body-centered structure of metal atoms offers three distorted octahedral voids per metal atom. Not all of these voids, however, can be occupied at the same time, because these distorted octahedra interpenetrate each other. In Fig. 7 we also show some of the octahe-

TABLE V

AVENOMA-VALUES (AVERAGE VALENCE ELECTRON NUMBER OF THE METAL ATOMS) OF UNFILLED (HOST) AND FILLED (INTERSTITIAL) STRUCTURES WITH THE SAME SPACE GROUP SYMMETRY

Host structure	Interstitial structure	Ref. ^a
La ₂ Au: 5.66	Pr ₂ ReC ₂ : 4.33	this work
MoNi ₄ : 9.2	UCr ₄ C ₄ : 6	(4)
Gd ₂ Fe ₁₇ (Th ₂ Zn ₁₇ -type): 7.5	Pr ₂ Mn ₁₇ C ₃ : 6.6	(3)
Er ₂ Fe ₁₇ (Th ₂ Ni ₁₇ -type): 7.5	Tb ₂ Mn ₁₇ C ₃ : 6.6	(5)
TbCo ₉ Si ₂ (BaCd ₁₁ -type): 7.7	LaMn ₁₁ C ₂ : 6.67	(2)
Mn ₃ Si ₃ : 5.9	Mo ₃ Si ₃ C: 5.2	(14)
Zr ₃ Co(Re ₃ B-type): 5.25	V ₃ GeC: 4.75	(46)
Cu ₃ Au: 11	Mn ₃ ZnC: 8.25	(47)
β-Mn: 7	W ₃ Re ₂ C: 6.4	(48)
Re (h.c.p.): 7; Ru: 8	W ₂ C: 6	(16)
γ-Fe (f.c.c.): 8	ZrC: 4; NbC: 5	(16)

^a References for all host structures can be found in Pearson's Handbook (16).

dral voids of the CsCl structure together with the structures of YCoC (30), Ho₂Cr₂C₃ (31), UMoC₂ (44), U₂IrC₂ (45), UCr₄C₄ (4), and U₅Re₃C₈ (43), all of which can be derived from a body-centered arrangement of metal atoms with carbon atoms filling octahedral voids.

Considering the positions of the metal atoms in the Periodic Table the compound La₂Au (19) comes closest to the metal positions of the Pr₂ReC₂ type carbides. We have recently pointed out that the average valence electron number of the metal atoms AVENOMA of the filled (interstitial) compounds is almost always lower than the AVENOMA value of the unfilled host structure, i.e., the metal components of the filled structures are usually situated in the Periodic System to the left of the elements of the corresponding host structure (4). This is demonstrated in Table V for some unfilled (host) and filled (interstitial) compounds. It was argued (4), that some orbitals of the metal atoms, which are needed in the host structure for metal-metal bonding, are utilized for metal-carbon bonding in the interstitial structure. In this context it would be interesting to explore the magnetic proper-

ties of La₂Au and the corresponding interstitial carbides of this paper.

Acknowledgments

We thank Dr. P. Seidel and Prof. Dr. W. Hoffmann (Inst. f. Mineralogie) for their hospitality and for their advice in the use of the optical densitometer. The four-circle diffractometer data were competently collected by Dr. M. H. Möller and Mrs. U. Rodewald. Dipl.-Chem. L. Boonk was so kind to check our samples for superconductivity. We are grateful to Dr. H. G. Nadler (H. C. Starck Co.), Mr. W. Kuntz (Rhône-Poulenc GmbH), and Dr. G. Höfer (Heraeus Quarzschmelze) for generous gifts of rhenium powder, rare earth metals, and silica tubes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

1. G. HÄGG, *Z. Phys. Chem. B* **12**, 33 (1931).
2. W. JEITSCHKO AND G. BLOCK, *Z. Anorg. Allg. Chem.* **528**, 61 (1985).
3. G. BLOCK AND W. JEITSCHKO, *Inorg. Chem.* **25**, 279 (1986).
4. R. K. BEHRENS AND W. JEITSCHKO, *Monatsh. Chem.* **118**, 43 (1987).
5. G. BLOCK AND W. JEITSCHKO, *J. Solid State Chem.* **70**, 271 (1987).
6. G. BLOCK, Dissertation, Universität Münster, 1987.
7. G. E. KAHNERT, G. BLOCK, R. K. BEHRENS, AND W. JEITSCHKO, *Z. Kristallogr.* **186**, 154 (1989).
8. G. E. KAHNERT, G. BLOCK, R. K. BEHRENS, AND W. JEITSCHKO, IUPAC-Conference, Stockholm, August 1989.
9. F. H. SPEDDING, K. A. GSCHNEIDNER, JR., AND A. H. DAANE, *J. Amer. Chem. Soc.* **80**, 4499 (1958).
10. R.-D. HOFFMANN, W. JEITSCHKO, AND L. BOONK, *Chem. Mater.* **1**, 580 (1989).
11. J. W. VISSER, *J. Appl. Crystallogr.* **2**, 89 (1969).
12. K. YVON, W. JEITSCHKO, AND E. PARTHÉ, *J. Appl. Crystallogr.* **10**, 73 (1977).
13. H. NOWOTNY, W. JEITSCHKO, AND F. BENESOVSKY, *Planseeber. Pulvermet.* **12**, 31 (1964).
14. E. PARTHÉ, W. JEITSCHKO, AND V. SADAGOPAN, *Acta Crystallogr.* **19**, 1031 (1965).
15. H. NOWOTNY, *Angew. Chem.* **84**, 973 (1972). *Angew. Chem., Int. Ed. Engl.* **11**, 906 (1972).
16. P. VILLARS AND L. D. CALVERT, "Pearson's Handbook of Crystallographic Data for Intermetallic Phases," American Society for Metals, Metals Park, Ohio, 1985.
17. H. NOWOTNY, *A. Anorg. Chem.* **254**, 31 (1947).

18. S. GELLER, *Acta Crystallogr.* **8**, 83 (1955).
19. O. D. McMASTERS, K. A. GSCHNEIDNER, JR., G. BRUZZONE, AND A. PALENZONA, *J. Less-Common Met.* **25**, 135 (1971).
20. D. T. CROMER AND J. B. MANN, *Acta Crystallogr. A* **24**, 321 (1968).
21. D. T. CROMER AND D. LIBERMAN, *J. Chem. Phys.* **53**, 1891 (1970).
22. G. E. KAHNERT, Diplomarbeit, Universität Münster, 1988.
23. L. PAULING, "The Chemical Bond," Cornell University Press, Ithaca, New York, 1967.
24. M. R. CHURCHILL, K. N. AMOH, AND H. J. WASERMAN, *Inorg. Chem.* **20**, 1609 (1981).
25. K. MERTIS, P. G. EDWARDS, G. WILKINSON, K. M. A. MALIK, AND M. B. HURSTHOUSE, *J. Chem. Soc., Dalton Trans.* **1981**, 705.
26. M. BOCHMANN, G. WILKINSON, A. M. R. GALAS, M. B. HURSTHOUSE, AND K. M. A. MALIK, *J. Chem. Soc., Dalton Trans.* **1980**, 1797.
27. T. J. BARDER, F. A. COTTON, D. LEWIS, W. SCHWOTZER, S. M. TETRICK, AND R. A. WALTON, *J. Amer. Chem. Soc.* **106**, 2882 (1984).
28. M. J. BENNETT, F. A. COTTON, R. A. WALTON, *J. Amer. Chem. Soc.* **88**, 3866 (1966).
29. F. A. COTTON AND M. W. EXTINE, *J. Amer. Chem. Soc.* **100**, 3788 (1978).
30. M. H. GERSS AND W. JEITSCHKO, *Z. Naturforsch.* **41b**, 946 (1986).
31. W. JEITSCHKO AND R. G. BEHRENS, *Z. Metallk.* **77**, 788 (1986).
32. R.-D. HOFFMANN, W. JEITSCHKO, M. REEHUIS, AND S. LEE, *Inorg. Chem.* **28**, 934 (1989).
33. M. H. GERSS, W. JEITSCHKO, L. BOONK, J. NIEN-TIEDT, J. GROBE, E. MÖRSEN, AND A. LESON, *J. Solid State Chem.* **70**, 19 (1987).
34. W. JEITSCHKO AND M. H. GERSS, *J. Less-Common Met.* **116**, 147 (1986).
35. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).
36. S. RUNDQVIST AND P. C. NAWAPONG, *Acta Chem. Scand.* **20**, 2250 (1966).
37. W. JEITSCHKO, *Acta Crystallogr. B* **24**, 930 (1968).
38. H. P. BECK, *Z. Anorg. Allg. Chem.* **459**, 81 (1979).
39. J. FLAHAUT AND F. THÉVET, *J. Solid State Chem.* **32**, 365 (1980).
40. D. WEBER AND H. G. V. SCHNERING, *Z. Kristallogr.* **162**, 230 (1983).
41. B. EISENMANN, H. SCHÄFER, AND K. TURBAN, *Z. Naturforsch.* **30b**, 677 (1975).
42. W. JEITSCHKO AND R. O. ALTMAYER, *Z. Naturforsch.* **45b**, 947 (1990).
43. G. BLOCK AND W. JEITSCHKO, *Monatsh. Chem.* **119**, 319 (1988).
44. D. T. CROMER, A. C. LARSON, AND R. B. ROOF, *Acta Crystallogr.* **17**, 272 (1964).
45. A. L. BOWMAN, G. P. ARNOLD, AND N. H. KRİKORIAN, *Acta Crystallogr. B* **27**, 1067 (1971).
46. H. BOLLER, *Monatsh. Chem.* **102**, 431 (1971).
47. B. N. BROCKHOUSE AND H. P. MYERS, *Canad. J. Phys.* **35**, 313 (1957).
48. J. B. KUZ'MA, V. I. LAKH, V. J. MARKIV, B. I. STADNYK, AND E. I. GLADYŠEVSKIJ, *Poroškov. Metal. Ukrain. SSR.* **4**, 286 (1963).