Preparation and Crystal Structure of the Carbides $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$ ($\text{Ln} = \text{Y}, \text{La}-\text{Nd}, \text{Gd}-\text{Er}$)

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Z. Naturforsch. **49b**, 1081–1088 (1994); received February 22, 1994

Crystal Structure, Lanthanoid-Rhenium-Carbides, 18-Electron Rule

The title compounds were prepared by arc-melting of the elemental components and subsequent annealing. Their crystal structure is hexagonal $\text{P}\bar{6}2\text{m}$ with one formula unit per cell. It was determined from single-crystal X-ray data of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ ($a = 1116.8(1)$ pm, $c = 545.3(1)$ pm, $R = 0.060$ for 287 structure factors and 27 variable parameters) and $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ ($a = 1066.7(1)$ pm, $c = 504.2(1)$ pm, $R = 0.018$ for 392 F's and 31 variables). The structures correspond to the formula $\text{Ln}_{12}[\text{ReC}_3]_2[\text{Re}_3\text{C}_3(\text{C}_2)_3]$, where the brackets indicate two different trigonal planar anionic rhenium-carbon groups. The coordination of the rhenium atoms in these polyanions seems to be compatible with the 18-electron rule.

Introduction

While many ternary rare-earth and actinoid transition metal carbides are known with 3d and 4d transition elements [1–7, and references cited therein], only few were reported with 5d transition metals. Of these those with rhenium are most numerous: $\text{Sc}_5\text{Re}_2\text{C}_7$ [8], Ln_2ReC_2 ($\text{Ln} = \text{Y}, \text{Ce}-\text{Nd}, \text{Sm}, \text{Gd}-\text{Tm}, \text{Lu}$) [9], UReC_2 [10], $\text{U}_2\text{Re}_2\text{C}_3$ [11] and $\text{U}_5\text{Re}_3\text{C}_8$ [12]. In the present paper we present a new series of such carbides. Some brief reports about this work were given at conferences [13–15]. The crystal structure was first determined for the lanthanum compound from an unusually small crystal and therefore it had rather large standard deviations [13]. However, the better data obtained for the holmium compound confirmed the earlier structure determination [15]. Here we give a full account of our work.

Sample Preparation and Lattice Constants

Starting materials for the preparation of the carbides were filings of the rare-earth metals (about 40 mesh, >99.9%), rhenium powder (400 mesh, >99.9%) and graphite flakes (20–60 mesh, >99.5%). The filings of the light rare-earth metals were kept under dried paraffin oil, which was washed away by repeated treatment with dried

cyclohexane prior to the reactions. Stoichiometric mixtures with a weight of about 500 mg were cold-pressed to pellets, which were reacted in an arc-melting furnace in an atmosphere of purified argon. All samples were turned over and remelted several times to ensure good homogeneity. The weight loss of the samples after several meltings was always smaller than 1%. For the subsequent annealing process in evacuated silica tubes (20 days at 900 °C) the samples were wrapped in tantalum foil. While most of the compounds were already present in the arc-melted samples, $\text{La}_{12}\text{Re}_5\text{C}_{15}$ was formed during the annealing process.

Single-crystals of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ were obtained directly from the sample annealed at 900 °C. In the case of $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ the elemental components were reacted first in an arc-melting furnace. In a second step this sample was annealed slightly below the melting point (for about two hours) in an evacuated, sealed, water-cooled silica tube in a high-frequency furnace. Energy dispersive analyses of some samples 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 α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. Indices could be assigned on the basis of the hexagonal cell found by the single-crystal investigations. The identification

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Fig. 1. Cell volumes of the carbides with $\text{La}_{12}\text{Re}_5\text{C}_{15}$ type structure.

Table I. Lattice constants of hexagonal $\text{La}_{12}\text{Re}_5\text{C}_{15}$ type carbides. Here and in the following tables standard deviations are given in parentheses.

Compound	<i>a</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> [nm ³]
$\text{Y}_{12}\text{Re}_5\text{C}_{15}$	1072.1(2)	506.7(2)	0.473	0.5044
$\text{La}_{12}\text{Re}_5\text{C}_{15}$	1116.8(1)	545.3(1)	0.488	0.5889
$\text{Ce}_{12}\text{Re}_5\text{C}_{15}$	1097.0(3)	536.9(2)	0.489	0.5596
$\text{Pr}_{12}\text{Re}_5\text{C}_{15}$	1098.6(3)	532.2(2)	0.484	0.5563
$\text{Nd}_{12}\text{Re}_5\text{C}_{15}$	1091.6(7)	530.1(4)	0.486	0.5470
$\text{Gd}_{12}\text{Re}_5\text{C}_{15}$	1080.0(3)	515.7(2)	0.478	0.5209
$\text{Tb}_{12}\text{Re}_5\text{C}_{15}$	1073.3(3)	510.5(2)	0.476	0.5093
$\text{Dy}_{12}\text{Re}_5\text{C}_{15}$	1068.3(5)	508.3(4)	0.476	0.5044
$\text{Ho}_{12}\text{Re}_5\text{C}_{15}$	1066.7(1)	504.2(1)	0.473	0.4969
$\text{Er}_{12}\text{Re}_5\text{C}_{15}$	1062.8(1)	501.0(1)	0.471	0.4900

of the diffraction lines was ensured by intensity calculations [16] using the positional parameters of the refined structures. The lattice constants (Table I) were obtained by least-squares fits of the powder data. The plot of the cell volumes of the $\text{La}_{12}\text{Re}_5\text{C}_{15}$ -type carbides (Fig. 1) shows the expected lanthanoid contraction. The small deviation of the cerium compound from the smooth plot indicates some tetravalent character of the cerium atoms in these compounds.

Properties

Compact samples of the $\text{La}_{12}\text{Re}_5\text{C}_{15}$ type compounds were all light grey with metallic luster. The powdered samples were dark grey. The carbides with the light lanthanoids are all sensitive to the humidity of the air and must therefore be kept under argon or dried paraffin oil, while the compounds with yttrium and the heavy lanthanoids are stable in air for several months.

Structure Determinations

The single-crystals of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ used for the structure determination were isolated by mechanical fragmentation of the button annealed at 900 °C. Those of the holmium compound were obtained from the sample treated in the high frequency furnace as described above. Single-crystals of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ and $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ were examined using a Buerger precession camera. They showed the hexagonal high Laue symmetry 6/mmm and the structure was eventually refined in the space group $P6_2m$ (No. 189).

Intensity data were recorded on an automated four-circle diffractometer (CAD4 turbo) with

Table II. Crystallographic data for La₁₂Re₅C₁₅ and Ho₁₂Re₅C₁₅.

	La ₁₂ Re ₅ C ₁₅	Ho ₁₂ Re ₅ C ₁₅
Lattice constants	see Table I	see Table I
Space group	P6̄2m (No. 189)	P6̄2m (No. 189)
Formula units per cell	Z = 1	Z = 1
Formula weight	2778.1	3090.4
Calculated density [g/cm ³]	d _c = 7.83	d _c = 10.33
Crystal size [μm ³]	10×12×15	22×22×66
Scan range (2θ)	60°	65°
Range in hkl	±13, ±13, 0–6	±14, ±14, ±7
Linear absorption coeff. μ(MoKα) [cm ⁻¹]	472	784
Absorption correction from	–	psi scan data
Transmission ratio (highest/lowest)	–	1.21
Total no. reflections	3137	6018
Data after averaging	413	638
Inner residual (on F values)	R _i = 0.055	R _i = 0.054
Reflections with I > nσ(I _o)	287 (1σ)	392 (3σ)
Extinction correction value, g ^a	6(2)×10 ⁻⁹	6.2(1)×10 ⁻⁸
No. of variables	27	31
Conventional residual	R = 0.060	R 0.018
Weighted residual	R _w = 0.035	R _w = 0.019
Highest residual density [e/Å ³]	9.3	3.2

^a The extinction correction value g is defined by: corr. factor = 1/(1+g·I_c).

graphite monochromated MoKα radiation and a scintillation counter with pulse-height discrimination. The crystallographic data and some results are summarized in Table II. The positions of the metal atoms were determined from a combination of a Patterson synthesis and direct methods. Those of the carbon atoms were located from subsequent difference Fourier analyses. The structures were refined by full-matrix least-squares cycles with atomic scattering factors [17], corrected for anomalous dispersion [18]. The weighting schemes included a term, which accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was refined and applied to the calculated structure factors. As checks for the ideal compositions we fixed the scale factors and varied the occupancy parameters of all atoms along with their thermal parameters (except for the carbon atoms in La₁₂Re₅C₁₅). All occupancy parameters were within four standard deviations of the ideal compositions, and thus one may assume the ideal occupancies, especially also for the carbon atoms, where a large percentage of defects was found in some structures [19–22]. In the final

Fig. 2. Crystal structure and coordination polyhedra of La₁₂Re₅C₁₅. The atoms connected by thick lines are at z = 0.

Atom	P62m	occup.	<i>x</i>	<i>y</i>	<i>z</i>	B
$\text{La}_{12}\text{Re}_5\text{C}_{15}$						
La1	6j	0.994(7)	0.2716(3)	0.4581(2)	0	0.38(6)
La2	3g	1.031(9)	0.4181(4)	0	1/2	0.34(9)
La3	3g	1.006(9)	0.7956(4)	0	1/2	0.24(9)
Re1	3f	0.986(6)	0.1518(3)	0	0	0.22(6)
Re2	2d	1.004(8)	1/3	2/3	1/2	0.39(6)
C1	6k	1.07(10)	0.286(5)	0.469(4)	1/2	0.8
C2	3f	1.13(16)	0.327(7)	0	0	0.8
C3	3f	1.00(14)	0.442(6)	0	0	0.8
C4	3f	0.88(14)	0.809(6)	0	0	0.8
$\text{Ho}_{12}\text{Re}_5\text{C}_{15}$						
Ho1	6j	0.998(2)	0.27006(8)	0.45621(7)	0	0.38(1)
Ho2	3g	0.996(3)	0.4254(1)	0	1/2	0.53(2)
Ho3	3g	1.014(4)	0.7967(1)	0	1/2	0.49(2)
Re1	3f	1.001(3)	0.1537(1)	0	0	0.43(2)
Re2	2d	0.989(4)	1/3	2/3	1/2	0.29(1)
C1	6k	1.01(5)	0.277(2)	0.470(2)	1/2	0.5(2)
C2	3f	1.09(8)	0.331(3)	0	0	1.2(5)
C3	3f	1.04(8)	0.463(3)	0	0	1.0(5)
C4	3f	1.12(7)	0.782(3)	0	0	0.9(4)

Table III. Atomic parameters of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ and $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$. The occupancy parameters were obtained in separate least-squares cycles. In the final cycles the ideal occupancies were assumed. The last column contains the isotrop B values of the carbon atoms and the equivalent isotropic thermal parameters of the metal positions ($\times 100$, in units of nm^2). The isotropic thermal parameters of the carbon atoms in $\text{La}_{12}\text{Re}_5\text{C}_{15}$ were not refined.

least-squares cycles the ideal occupancies were assumed. The metal atoms were refined with anisotropic, the carbon atoms of $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ with isotropic thermal parameters. For $\text{La}_{12}\text{Re}_5\text{C}_{15}$ even the isotropic thermal parameters of the carbon atoms could not be refined, because of the low number of structure factors. In the final difference Fourier syntheses the highest peaks (Table II) were very close to the metal positions and there were no indications for the occupancy of additional atomic sites. As a check for the absolute configuration of the $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ crystal one series of least-squares cycles was run, where all atomic positions xyz were changed to $\bar{x}\bar{y}\bar{z}$. This resulted in a residual of $R = 0.024$ as compared to $R = 0.018$ for the correct handedness. The program STRUC-TURE TIDY [23] was used to standardize the positional parameters. The final residual values, the atomic parameters and the interatomic distances are listed in Tables II–IV. A projection of the structure and the coordination polyhedra is shown

in Fig. 2. Listings of the structure factor tables and the anisotropic thermal parameters are available.*

Discussion

The ternary carbides $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$ crystallize with a new hexagonal structure type which we have first determined for the lanthanum compound. We therefore call this a $\text{La}_{12}\text{Re}_5\text{C}_{15}$ type structure. However, in the following discussion, when we quote interatomic distances we refer to the distances in $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$, since they are more accurate.

The holmium atoms occupy three different atomic sites. They have high coordination numbers with carbon, rhenium and holmium in their coordination shells. Since the holmium atoms are the most electropositive component, the holmium-carbon and holmium-rhenium interactions are more important than the holmium-holmium interactions. The Ho–C distances cover the range from 231 to 292 pm and the Ho–Re distances vary between 307 and 321 pm. Neglecting the Ho–Ho interactions and the rhenium atom at the rather long Ho2–Re1 distance of 384 pm, the coordination numbers (CN) of the holmium atoms are as follows: Ho3 with CN8 (4C+4Re), Ho1 with CN9 (6C+3Re), and Ho2 with CN10 (8C+2Re). The average Ho–C distances of 254, 255, and 270 pm

* They may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the registry no. CSD 58281, the names of the authors, and the journal citation.

Table IV. Interatomic distances (pm) in the structures of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ and $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$. All distances shorter than 500 pm (Re–Re), 420 pm (Ln–Ln, Ln–Re), 380 pm (Ln–C) and 310 pm (Re–C, C–C) are listed.

		Ln = La	Ln = Ho
Ln1:	1 C4	265(2)	231(1)
	1 C2	263(6)	250(3)
	2 C1	273.0(2)	252.5(1)
	1 C3	281(6)	253(3)
	1 C3	295(7)	292(3)
	1 Re1	324.5(2)	306.9(1)
	2 Re2	342.5(1)	321.5(1)
	1 Ln1	360.9(3)	343.9(1)
	2 Ln1	358.9(3)	345.6(1)
	2 Ln3	372.8(2)	349.6(1)
	2 Ln2	393.4(4)	371.7(7)
	2 Ln2	407.0(4)	379.5(1)
Ln2:	2 C3	273.9(7)	255.4(5)
	2 C2	291(3)	272(1)
	2 C1	289(3)	275(1)
	2 C1	295(4)	279(1)
	2 Re2	335.1(1)	318.1(1)
	4 Ln1	393.4(2)	371.7(1)
	4 Ln1	407.0(4)	379.5(1)
	2 Re1	403.5(4)	384.2(1)
	2 Ln3	404.5(6)	393.1(2)
	1 Ln3	421.5(6)	396.1(2)
Ln3:	2 C4	273.1(4)	252.6(2)
	2 C1	262(3)	255(1)
	4 Re1	341.3(2)	319.3(1)
	4 Ln1	372.8(2)	349.6(1)
	2 Ln3	395.4(5)	375.7(3)
	2 Ln2	404.5(6)	393.1(1)
	1 Ln2	421.5(6)	396.1(2)
Re1:	1 C2	195(7)	189(4)
	2 C4	195(2)	206.9(7)
	2 Re1	293.6(3)	283.9(1)
	2 Ln1	324.5(3)	306.9(1)
	4 Ln3	341.3(1)	319.3(1)
	2 Ln2	403.5(4)	384.2(1)
Re2:	3 C1	200(4)	187(1)
	3 Ln2	335.1(5)	318.1(1)
	6 Ln1	342.4(1)	321.5(1)
C1:	1 Re2	200(4)	187(1)
	2 Ln1	273.0(2)	252.5(1)
	1 Ln3	262(4)	255(1)
	1 Ln2	289(3)	275(1)
	1 Ln2	295(3)	279(1)
C2:	1 C3	129(10)	142(5)
	1 Re1	195(7)	189(4)
	2 Ln1	262.7(3)	249.7(2)
	2 Ln2	291(3)	272(1)
C3:	1 C2	129(10)	142(5)
	2 Ln1	281(5)	253(2)
	2 Ln2	273.9(7)	255.4(5)
	2 Ln1	295(3)	292(2)
C4:	2 Re1	195(5)	207(2)
	2 Ln1	265(5)	231(2)
	2 Ln3	273.1(4)	252.6(2)

appear to reflect the increasing CN, while the average Ho–Re distances of 319, 317, and 318 pm are surprisingly similar.

Both rhenium atoms have three carbon neighbors, the Re2 atoms at 187 pm, while the Re1–C distances of 189 pm and 207 pm (2×) are greater. The differences of these bond lengths can be understood only if we ascribe some bonding character to the Re1–Re1 interactions of 284 pm.

Of the four carbon atoms two have octahedral coordination. The C1 atom has one rhenium and five lanthanoid neighbors, as was found also for one carbon atom in Er_2ReC_2 [9], while the C4 atom has two rhenium (in *cis* position) and four lanthanoid neighbors, as was found for one carbon position in $\text{Sc}_5\text{Re}_2\text{C}_7$ [8]. The C2 and C3 atoms form pairs with a C–C distance of 142(5) pm. The standard deviation for this distance is rather high, however, similar C–C distances were found in many other ternary carbides of similar composition [24]. These distances are always shorter than the typical single-bond distance of 154 pm found in hydrocarbons and may be as short as the typical double-bond distance of 134 pm in olefins. The coordination shell of this C₂ pair in $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ consists of one rhenium and six holmium atoms. It can be derived from that of an octahedron, where two holmium atoms are placed at the position of one apex (Fig. 3). This coordination of a C₂ pair seems to be novel, although it shows some resemblance to that of the C₂ pair in Er_2FeC_4 [25].

Chemical bonding in $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ may be rationalized to a first approximation by simple

Fig. 3. Near-neighbor environment of the C₂ pair in $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ as compared to the polyhedron around the C₂ pair in Er_2FeC_4 .

plausible assumptions. We consider the interactions of the holmium atoms with the other atoms as predominantly ionic. Therefore, we count the valence electrons of the holmium atoms at the rhenium-carbon anions. In contrast, the rhenium-carbon interactions are certainly essentially covalent,

Fig. 4. Arrangement of the trigonal planar anionic ReC_3 and $\text{Re}_3\text{C}_3(\text{C}_2)_3$ groups in the structure of $\text{La}_{12}\text{Re}_5\text{C}_{15}$. Atoms connected by thin and thick lines are separated by half a translation period of the projection direction.

nevertheless, in order to establish oxidation numbers, we *count* the corresponding bonding electrons at the carbon atoms, assuming the octet rule for the carbon atoms to be obeyed. Through this account the number of those electrons at the rhenium atoms can be derived, which are not involved in rhenium-carbon interactions.

There are two different kinds of rhenium-carbon anions in the structure. Both are planar with trigonal symmetry. Their relative arrangements are shown in Fig. 4. In the left-hand side of Fig. 5 we show the interatomic distances within the groups, and at the right-hand side we show two extreme Lewis formulas for each of these groups together with the resulting oxidation numbers of the rhenium atoms and the electron count for each rhenium atom. Many other electron distributions are possible. However, as a first approximation and aiming for integer numbers, we considered a charge distribution corresponding to a formula $[12\text{La}^{3+}]^{36+} [2\text{ReC}_3^{9-}]^{18-} [\text{Re}_3\text{C}_3(\text{C}_2)_3]^{18-}$ as most plausible. In a thermodynamically stable solid state compound we can assume that all atomic orbitals of the rhenium atoms will either be filled with nonbonding electrons, or they will be participating in the chemical bonding unless their energy

Fig. 5. The trigonal planar anionic groups $\text{Re}_3\text{C}_3(\text{C}_2)_3$ and ReC_3 in the structure of the $\text{La}_{12}\text{Re}_5\text{C}_{15}$ type carbides. The interatomic distances as found in $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ are indicated on the left-hand side. At the right side Lewis formulas are given with the corresponding oxidation numbers and electron counts for the rhenium atoms.

is too high. This is the basis of the 18-electron rule. In the extreme Lewis formulas shown in Fig. 5 the Re1 atoms obtain between 15 and 20 electrons, while the Re2 atoms are drawn with 16 and 22 electrons, respectively. To check whether these formulas make any sense we may compare the interatomic distances given at the left-hand side of Fig. 5 with the previously estimated Re–C bond lengths of about 228, 197, and 173 pm for single, double, and triple bonds, respectively [9]. Thus, the Re1–C2 distance of 189 pm is in between a double and a triple bond, the Re1–C4 distance of 207 pm is between a single and a double bond, and the Re2–C1 distance of 187 pm is again between a double and a triple bond. Therefore, the bond lengths of both anions suggest that the real valence electron distributions are in between the extreme Lewis formulas shown in Fig. 5. These intermediate electron counts are thus compatible with the 18-electron rule.

The Re1–Re1 bond lengths of $\text{La}_{12}\text{Re}_5\text{C}_{15}$ and $\text{Ho}_{12}\text{Re}_5\text{C}_{15}$ are surprisingly different and deserve some comment. Both distances – 293.6(3) pm in the lanthanum and 283.9(1) pm in the holmium compound – are short enough to correspond to (albeit weakly) bonding interactions. There are two essential differences between lanthanum and holmium, the size and the electronegativity difference, and both may contribute to the difference of the Re1–Re1 bond lengths.

The lanthanum atoms are much larger than the holmium atoms, and this certainly results in differences of the packing in the solid. This is also evident from the different c/a -ratios (0.488 for the La and 0.473 for the Ho compound). Since the Re1–Re1 interactions are not very strong, the three-dimensional solid may compensate at these interactions any possible strain associated with the different sizes of the cations. An analysis of the packing, which in detail shows how the different sizes of the cations results in the different Re1–Re1

bond lengths, is difficult, however, and was therefore not attempted.

The other effect, resulting from the electronegativity difference, is perhaps more plausible. We have speculated above, that the $[\text{Re}_3\text{C}_3(\text{C}_2)_3]^{18-}$ polyanion may provide 18 electrons to each Re1 atom. If the electron count is less than 18, and if the Re1–Re1 bonding states are at the Fermi level, then any additional electron in the polyanion will shorten the Re1–Re1 bonds. In contrast, if the polyanion provides more than 18 electrons to each Re1 atom, and if the Fermi level cuts through the Re1–Re1 (now) *antibonding* levels, then any additional electron will lengthen the Re1–Re1 bond distances. In a band structure electron counts per atom do not need to be integers, because the electron count can change continuously as a result of differences in band width and band overlap. Since the lanthanum atoms are more electropositive than the holmium atoms, they will provide more negative charge to the polyanions. If the Re1 atoms in the holmium compound already possess 18 electrons, any additional negative charge within the polyanion originating from the more electropositive lanthanum atoms will lengthen the Re1–Re1 bonds. A sensitive band structure calculation, which reflects the electronegativity differences between lanthanum and holmium, may prove or disprove this speculation.

Acknowledgement

We thank Dr. M. H. Möller and Dipl.-Ing. U. Rodewald for the collection of the diffractometer data, Mr. K. Wagner for the work at the scanning electron microscope, and Mrs. U. Göcke for the help with the drawings. We are also grateful to Dr. H. G. Nadler (H. C. Starck Co.), Dr. G. Höfer (Heraeus Quarzschmelze) for generous gifts of rhenium powder and silica tubes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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