Sc₅Re₂C₇, a Complex Carbide with C₃-Units

Rainer Pöttgen and Wolfgang Jeitschko*

Anorganisch-Chemisches Institut der Universität Münster,
Wilhelm-Klemm-Straße 8, D-W-4400 Münster

Z. Naturforsch. **47b**, 358–364 (1992); received September 2, 1991

Crystal Structure, Scandium Rhenium Carbide, 18-Electron Rule

The title compound was obtained by arc melting of the elemental components and subsequent annealing in a high frequency furnace. It crystallizes with the orthorhombic space group Cmmm, $a = 779.26(7)$ pm, $b = 1362.0(1)$ pm, $c = 320.62(3)$ pm, $V = 0.3403$ nm³, $Z = 2$. The structure was determined from single-crystal X-ray data and refined to a residual of $R = 0.021$ (692 F values and 21 variables). It is closely related to the NaCl-structure. Three of the seven carbon atoms per formula unit form linear C₃-units with C–C bond lengths of 134 pm. They are coordinated to ten Sc atoms forming bicapped quadratic prisms. Additional isolated C atoms are located in octahedral voids formed by four Sc and two Re atoms. Together with the Re atoms they form two-dimensionally infinite [Re₂C₄¹¹⁻]_n polyanions. The Re atoms have highly distorted tetrahedral carbon coordination with Re–C bond lengths of 200 and 208 pm corresponding to bond orders of about two. This coordination seems to be compatible with the 18-electron rule. The near-neighbour coordination of the Re atoms is asymmetric. It is suggested that this is due to the space requirements of nonbonding electrons. Samples of Sc₅Re₂C₇ are semiconducting and weakly paramagnetic.

Introduction

Several ternary carbides and borocarbides with scandium were found in recent years. The following crystal structures were reported: Sc₃AlC [1], ScTC₂ (T = Fe, Co, Ni) [2, 3], Sc₃TC₄ (T = Fe, Co, Ni, Ru, Rh, Os, Ir) [4, 5], ScAl₃C₃ [6], Sc₂BC₂ [7, 8], Sc₂CrC₃ [9] and ScCrC₂ [10]. Recently we reported on the crystal structure of Sc₃C₄ [11], which contains C₃-units derived from propadiene. Such units were also found in Mg₂C₃ [12], Ca₃C₃Cl₂ [13] and in Sc₅Re₂C₇ described in the present paper.

Sample Preparation and Lattice Constants

Starting materials for the preparation of Sc₅Re₂C₇ were filings of scandium (Kelpin, 40 mesh, >99.9%), rhenium powder (Starck, 400 mesh, >99.9%) and graphite flakes (Ventron, 20–60 mesh, 99.5%). The samples were prepared by arc melting of small (~300 mg) cold-pressed pellets of the elemental components with the ideal composition in an atmosphere of purified argon (99.996%). After the reaction, the samples were wrapped in tantalum foil and annealed for two weeks at 780 °C in evacuated silica tubes.

Single-crystals of Sc₅Re₂C₇ were obtained by first reacting the elemental components in an arc melting furnace. In a second step the sample was annealed slightly below the melting point (for about eight hours) in an evacuated, water-cooled silica tube in a high-frequency furnace. Energy dispersive analyses of the single-crystals and the polycrystalline samples in a scanning electron microscope did not show any impurity elements heavier than sodium.

The orthorhombic lattice constants were obtained by least-squares fits of the Guinier powder data. CuK α_1 radiation was used with α quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. The identification of the diffraction lines was facilitated by intensity calculations [14] using the positional parameters of the refined structure of Sc₅Re₂C₇. The lattice constants are $a = 779.26(7)$ pm, $b = 1362.0(1)$ pm, $c = 320.62(3)$ pm and $V = 0.3403$ nm³. The values of the lattice constants obtained on the four circle diffractometer ($a = 778.4(1)$ pm, $b = 1359.9(3)$ pm, $c = 320.3(1)$ pm, $V = 0.3390$ nm³) are slightly smaller than the values obtained from the powder data. This is due to absorption effects, which were not corrected in the least-squares calculations of the diffractometer programme.

Chemical and Physical Properties

In powdered form Sc₅Re₂C₇ is dark grey. Single crystals have metallic lustre. They are stable in air

* Reprint requests to Prof. Dr. W. Jeitschko.

over long periods of time. Powdered samples deteriorate only very slowly owing to the humidity of the air.

Magnetic susceptibility measurements of two different polycrystalline samples (~ 20 mg) of $\text{Sc}_5\text{Re}_2\text{C}_7$ with a SQUID magnetometer between 100 and 400 K with magnetic flux densities of between 1 and 5 T show nearly temperature independent weak paramagnetism. The susceptibilities were slightly field dependent, however, with different values for the two samples, indicating different amounts of a ferromagnetic impurity. This was corrected by extrapolation of the susceptibility values to an infinite magnetic field. For both samples we then obtained the same susceptibility value of $\chi = 7.5(5) \cdot 10^{-9} \text{ m}^3/\text{mol}$. The absolute value of this susceptibility is of the same order of magnitude as the diamagnetic correction and thus this weak paramagnetism could be indicative for Pauli paramagnetism. However, our electrical conductivity measurements show semiconducting behaviour.

The electrical conductivity of irregular shaped pieces (with dimensions of about $50 \cdot 50 \cdot 500 \mu\text{m}^3$) was determined with a four-probe setup. The pieces were contacted with four copper filaments by using a well-conducting silver epoxy cement. A constant alternating current was applied at two contacts, and the voltage difference was measured between the other contacts. The absolute values of the conductivities are estimated to be correct only within a factor of four because of the irregular shapes of the samples and the contact areas. The relative values for one sample at different temperatures, however, are more reliable. The electrical resistivity behaviour is that of a heavily doped semiconductor. At temperatures between 5 K and 300 K the resistivity ρ decreases as is typical for semiconductors. For the linear portion of the $\ln \rho$ vs $1/T$ plot (Fig. 1) between 100 K and 300 K an activation energy of $E_a = 0.0034(5) \text{ eV}$ was obtained by evaluation of the equation $\rho = \rho_0 \exp(E_a/2kT)$. At lower temperatures the activation energy is even smaller. These small activation energies are most likely due to impurity levels and the intrinsic band gap may be much larger. At temperatures above 300 K the resistance increases again probably for the same reason as this behaviour is rationalized in metallic conductors. A similar temperature dependence of the electrical resistivity was ob-

Fig. 1. Electrical resistivity ρ of $\text{Sc}_5\text{Re}_2\text{C}_7$ as a function of temperature (insert) and inverse temperature. The activation energy E_a was calculated from the linear portion of the ρ vs $1/T$ plot.

served recently for the carbides LaRhC_2 and CeRhC_2 [15].

Structure Determination of $\text{Sc}_5\text{Re}_2\text{C}_7$

Single-crystals of $\text{Sc}_5\text{Re}_2\text{C}_7$ were isolated from a crushed button, prepared in the high-frequency furnace. They were examined in Buerger precession cameras to establish their symmetry and suitability for intensity data collection. They showed orthorhombic symmetry, and the only systematic extinctions were those for a C centered lattice. The structure refinements eventually showed that the space group with the highest symmetry compatible with these extinctions, Cmmm-D_{2h}^{19} was the correct one.

The crystal used for the intensity data collection on an automated four-circle diffractometer had the dimensions of $20 \cdot 20 \cdot 90 \mu\text{m}^3$. Graphite monochromated $\text{MoK}\alpha$ radiation was used with a scintillation counter and a pulse-height discriminator. Background counts were taken at both ends of each scan. A total of 4040 reflections was measured in the whole reciprocal sphere up to $2\theta = 90^\circ$. An empirical absorption correction was applied from ψ -scan data. The ratio of the maximal to the minimal transmission was 1.14. The linear absorption coefficient is $\mu = 405 \text{ cm}^{-1}$. After equivalent reflections were averaged ($R_i = 0.025$) and those counts with less than three standard deviations were omitted, 692 reflections remained.

The starting atomic parameters of the metal atoms were obtained from a Patterson synthesis,

while the carbon atoms were located in difference Fourier syntheses. In the full-matrix least-squares refinements with atomic scattering factors [16], corrected for anomalous dispersion [17], a parameter correcting the secondary isotropic extinction was refined and applied to the calculated structure factors. Weights were assigned according to the counting statistics ($w = 1/\sigma^2$). The metal atoms were refined with ellipsoidal, the carbon atoms with isotropic thermal parameters. In one series of least-squares cycles the scale factor was held constant and all occupancy parameters were allowed to vary. The results – occupancy parameters (in % with standard deviations in parentheses) of 96.0(3), 96.9(6), 99.9(1), 105(2), 90(2), 100(2) and 87(3) for the Sc(1), Sc(2), Re, C(1), C(2), C(3) and C(4) positions – show mostly insignificant deviations from full occupancies with the exception of the Sc(1) position. Nevertheless, because this deviation is small, for the final least-squares cycle we assumed again the ideal occupancies. The resulting unweighted and weighted residuals are $R = 0.021$ and $R_w = 0.026$ for 21 variable parameters and 692 structure factors. A final difference Fourier synthesis gave no indication for the occupancy of additional atomic sites. Final atomic parameters and interatomic distances are listed in Tables I and II. Figures 2 and 3 show the crystal structure and near-neighbour environments. A listing of the calculated and observed structure factors is available*.

* It may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry No. CSD 55860, the names of the authors and the journal citation.

Table I. Atomic parameters of $\text{Sc}_5\text{Re}_3\text{C}_7$. Standard deviations in the positions of the least significant digits are given in parentheses. The program STRUCTURE TIDY [18] was used to standardize the positional parameters. The last column contains the isotropic B values of the carbon atoms and the equivalent isotropic B values of the anisotropic thermal parameters of the metal positions ($\times 100$, in units of nm^2).

Atom	Cmmm	x	y	z	B
Sc(1)	8q	0.2109(1)	0.12854(6)	0.5	0.34(1)
Sc(2)	2b	0.5	0	0	0.36(2)
Re	4i	0	0.28381(2)	0	0.205(3)
C(1)	4j	0	0.3816(5)	0.5	0.39(7)
C(2)	4g	0.1734(9)	0	0	0.57(8)
C(3)	4e	0.25	0.25	0	0.40(7)
C(4)	2a	0	0	0	0.5(1)

Table II. Interatomic distances (pm) in the structure of $\text{Sc}_5\text{Re}_3\text{C}_7$. All distances shorter than 400 pm (Re–Re, Sc–Sc, Sc–Re), 375 pm (Sc–C, Re–C), and 270 pm (C–C) are listed. Standard deviations are given in parentheses.

Sc(1):	1 C(1)	225.7(1)	Re:	2 C(3)	200.18(4)
	2 C(3)	232.4(1)		2 C(1)	208.4(5)
	2 C(2)	239.3(1)		1 Sc(2)	294.46(5)
	2 C(4)	288.7(1)		4 Sc(1)	301.2(1)
	2 Re	301.2(1)		4 Sc(1)	312.1(1)
	2 Re	312.1(1)		2 Re	320.62(3)
	2 Sc(1)	320.62(3)			
	2 Sc(2)	327.3(1)	C(1):	2 Re	208.4(5)
	1 Sc(1)	328.7(2)		2 Sc(1)	225.7(1)
	1 Sc(1)	336.5(2)		2 Sc(2)	227.5(6)
	1 Sc(1)	350.1(2)			
Sc(2):	4 C(1)	227.5(6)	C(2):	1 C(4)	134.4(9)
	2 C(2)	255.2(9)		4 Sc(1)	239.3(1)
	2 Re	294.46(5)		1 Sc(2)	255.2(9)
	2 Sc(2)	320.62(3)	C(3):	2 Re	200.18(4)
	8 Sc(1)	327.3(1)		4 Sc(1)	232.4(1)
			C(4):	2 C(2)	134.4(9)
				8 Sc(1)	288.7(1)

Fig. 2. The crystal structure of $\text{Sc}_5\text{Re}_3\text{C}_7$ projected along the z direction. All atoms are situated on mirror planes at $z = 0$ and $z = 1/2$ connected by thin and thick lines, respectively.

Fig. 3. Atomic environments in the structure of $\text{Sc}_5\text{Re}_2\text{C}_7$. The scandium atoms are shown as large open circles, the rhenium atoms as small open circles and the carbon atoms as filled circles. All neighbours listed in Table II are shown, even though some of these interactions might be negligible. Interatomic distances (pm) are indicated. The coordination shell of the rhenium atoms is open at the right side. It is suggested that this space is filled by nonbonding electrons (e) of the rhenium atoms.

Discussion

The crystal structure of $\text{Sc}_5\text{Re}_2\text{C}_7$ represents a new structure type. Both kinds of scandium atoms have high coordination numbers with carbon, rhenium and scandium atoms in their coordination shell. The average distances reflect the differences in the coordination numbers. The five near carbon neighbours of the Sc(1) atoms are at an average distance of 233.8 pm as compared to the six carbon neighbours of the Sc(2) atoms with an av-

erage distance of 236.7 pm. The four Re neighbours of the Sc(1) atoms have the average distance of 306.6 pm, while the two Re neighbours of the Sc(2) atoms are at the much shorter distance of 294.5 pm. Considering that the scandium atoms are by far the most electropositive components of the compound, they will largely have lost their valence electrons and thus the scandium-scandium interactions are less important. Thus, even though the shortest Sc–Sc distance of 320.6 pm is shorter

than the average Sc–Sc distance of 328.1 pm in elemental scandium [19], we will neglect these interactions in the following bonding discussion.

The Re atoms have no strong interactions with each other. They are coordinated by four carbon atoms in highly distorted tetrahedral configuration with an average distance of 204.3 pm. The nine Sc neighbours are at an average distance of 305.3 pm.

The C(1) and C(3) atoms are in distorted octahedral coordination of two Re and four Sc atoms. Octahedral coordination is most commonly found for carbon atoms in such carbides [20–22]. The two Re neighbours of the C(1) atoms are at adjacent corners of the octahedron, while they are at opposite corners for the C(3) atoms. The C(2) and C(4) atoms form linear C_3 -units, which are surrounded by ten scandium atoms forming a bicapped tetragonal prism.

Like the structure of Sc_3C_4 [11], the structure of $\text{Sc}_5\text{Re}_2\text{C}_7$ has a remarkable relation to the NaCl structure, which is also the structure of ScC_{1-x} [23]. This is demonstrated in Fig. 4. Four NaCl-like blocks may be distinguished. Some contain vacant sites. Thus, the Sc(2) atoms have 12 metal neighbours like the metal atoms in a close packed cubic structure, while the Sc(1) and Re atoms have only 10 and 11 neighbours of this coordination shell, respectively. The positions of all Sc and Re atoms correspond to the Na positions of NaCl and most carbon positions correspond to the Cl positions; only the C(4) positions correspond to Na positions of NaCl.

Chemical bonding in $\text{Sc}_5\text{Re}_2\text{C}_7$ can be rationalized to a first approximation by simple plausible assumptions. The C(2)–C(4) bond lengths of 134.4(9) pm in the linear C_3 -units correspond to double bonds and these groups may therefore be considered as derived from propadiene, where the bond lengths were found to be 131.1(6) pm by electron diffraction [24] and 133.5 pm by IR spectroscopy [25]. In Sc_3C_4 [11], Mg_2C_3 [12] and $\text{Ca}_3\text{C}_3\text{Cl}_2$ [13] these bond lengths are 134.2(3) pm, 133.2(2) pm and 134.6(4) pm, respectively; somewhat shorter than the length of 140.3 pm calculated for a C_3^{4-} species by ab initio calculations [26]. To a first approximation the isolated carbon atoms may be considered as C^{4-} anions and the scandium atoms as Sc^{3+} ions. The formula of our compound may then be written as

Fig. 4. The crystal structure of $\text{Sc}_5\text{Re}_2\text{C}_7$ and its relation to the NaCl structure. In the upper part of the drawing four NaCl-like blocks A, B, C, D of $\text{Sc}_5\text{Re}_2\text{C}_7$ and their fusion to a composite block are shown. The block B consists of 27 atoms in slightly distorted NaCl-like arrangement. The other three blocks contain vacant sites. In the lower left-hand part twelve such blocks are fused together; the four blocks A, B, C and D of the upper part are shaded. Also shown are the orthorhombic translation lengths of the $\text{Sc}_5\text{Re}_2\text{C}_7$ structure. In the lower right-hand part two layers of NaCl-like blocks are projected along the a axis.

$[5\text{Sc}^{3+}]^{15+}[2\text{Re}^{2.5+}]^{5+}[2\text{C}(1)^{4-}]^8-[2\text{C}(3)^{4-}]^8-[\text{C}(2)-\text{C}(4)-\text{C}(2)]^{4-}$, where the superscripts are oxidation numbers (formal charges). In emphasising the essentially covalent character of the rhenium-carbon interactions we can also write $[5\text{Sc}^{3+}]^{15+}[\text{Re}_2\text{C}_4]^{11-}[\text{C}_3]^{4-}$.

The $[\text{Re}_2\text{C}_4]^{11-}$ anion is polymeric and two-dimensionally infinite (Fig. 5). For Er_2ReC_2 , where the polyanion $[\text{ReC}_2^{6-}]_n$ is only one-dimensionally infinite and Re–Re interactions can be ruled out with certainty, it was argued that the Re atoms obtain a total of 18 bonding and nonbonding electrons [21]. Although we believe that the

Fig. 5. A cutout of the two-dimensionally infinite $[\text{Re}_2\text{C}_4]^{11-}$ polyanion of $\text{Sc}_5\text{Re}_2\text{C}_7$ projected along the y and z directions. Interatomic bond lengths (pm) and bond angles (degrees of arc) are indicated.

18-electron rule is likely to be obeyed also for the Re atoms in $\text{Sc}_5\text{Re}_2\text{C}_7$, the reasoning is more difficult here, because there are more possibilities depending on whether the Re–Re interactions of 320.6 pm are counted as weakly bonding or nonbonding. The Re–C bonds of 200.2 pm and 208.4 pm may be considered as being between single and double bonds, but closer to double bonds (For Re–C single and Re=C double bonds the bond lengths were estimated to be about 228 pm and 197 pm, respectively [21]). Neglecting the Re–Re interactions, two possible electron distributions for a monomeric unit $[\text{ReC}_2]^{5.5-}$ are considered in Fig. 6. In such a unit we need to account for 20.5 electrons: 7 from the Re atom, 8 from the two carbon atoms and 5.5 from the formal charge. In the forms a) and b) the Re atom obtains 12.5 and 20.5 electrons, respectively. Since the Re–C bond lengths are closer to the double than to the single bond an electron count of 18 seems to be quite plausible for the Re atom. This rationalization neglects bonding Re–Re interactions. If some bonding character is ascribed to them and if the 18-electron rule is to be obeyed, the Re–C interactions have to lose more of their double bond character.

In all of these simple models some electrons have to be accommodated in nonbonding orbitals of the Re atoms. Interestingly, the near-neighbour coordinations of the Re atoms are rather asymmetric with no close neighbours at one side. We suggest that the nonbonding electrons occupy this space, which is designated “e” in the Re coordination of Fig. 3. Similar nonbonding electrons can be “seen” at the Ni atoms in the structure of $\text{Th}_4\text{Ni}_3\text{C}_6$ [27].

We thank Dr. M. H. Möller and Dipl.-Ing. U. Rodewald for the data collection at the four-circle diffractometer, Mrs. J. Nowitzki and Dipl.-Phys. Th. Vomhof for the magnetic susceptibility measurements, Dipl.-Phys. U. Wortmann for the electrical conductivity measurements, Mrs. U. Göcke for her help with the drawings and Mr. K. Wagner for the work at the scanning electron microscope. We are also indebted to Dr. G. Höfer (Heraeus Quarzschmelze) and Dr. H. G. Nadler (H. C. Starck Co.) for generous gifts of silica tubes and rhenium powder. We also acknowledge the Fonds der Chemischen Industrie for a stipend to R. P. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Fig. 6. Two possible electron distributions for the 20.5 valence electrons in a monomeric unit $[\text{ReC}_2]^{5.5-}$ of $\text{Sc}_5\text{Re}_2\text{C}_7$. In both forms 16 electrons are shown as bonding and nonbonding electrons in the Lewis formalism. The octet rule for the carbon atoms is obeyed in both cases. In addition to these 16 electrons 4.5 electrons per monomeric unit have to be accommodated in (most likely nonbonding) Re orbitals. In this way (discounting bonding Re–Re interactions) one Re atom obtains 12.5 electrons in the form a) and 20.5 electrons in form b). A comparison of bond lengths (see text) suggests that the real situation is in between a) and b) in agreement with the 18-electron rule.

- [1] S. Rosen and P. G. Sprang, *Adv. X-Ray Analysis* **8**, 91 (1965).
- [2] E. P. Marusin, O. I. Bodak, A. O. Tsokol', and M. G. Baivel'man, *Sov. Phys. Crystallogr.* **30**, 340 (1985).
- [3] G. E. Kahnert, R. Pöttgen, G. Block, and W. Jeitschko, *Z. Kristallogr. Suppl. Issue No. 3*, 140 (1991).
- [4] A. O. Tsokol', O. I. Bodak, and E. P. Marusin, *Sov. Phys. Crystallogr.* **31**, 466 (1986).
- [5] R.-D. Hoffmann and W. Jeitschko, *Z. Kristallogr.* **186**, 133 (1989).
- [6] A. O. Tsokol', O. I. Bodak, E. P. Marusin, and M. G. Baivel'man, *Sov. Phys. Crystallogr.* **31**, 467 (1986).
- [7] J. Bauer, M. Potel, P. Gougeon, J. Padiou, and H. Noël, 9th International Conference on Solid Compounds of Transition Elements, Oxford, July 4–8 (1988).
- [8] J.-F. Halet, J.-Y. Saillard, and J. Bauer, *J. Less-Common Met.* **158**, 239 (1990).
- [9] A. O. Pecharskaya, E. P. Marusin, O. I. Bodak, and M. D. Mazus, *Sov. Phys. Crystallogr.* **35**, 25 (1990).
- [10] R. Pöttgen and W. Jeitschko, to be published.
- [11] R. Pöttgen and W. Jeitschko, *Inorg. Chem.* **30**, 427 (1991).
- [12] P. Karen and H. Fjellvåg, *Acta Crystallogr. A* **46** Supplement, C-285 (1990).
- [13] H.-J. Meyer, *Z. Anorg. Allg. Chem.* **593**, 185 (1991).
- [14] K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
- [15] R.-D. Hoffmann, W. Jeitschko, and L. Boonk, *Chem. Mater.* **1**, 580 (1989).
- [16] D. T. Cromer and J. B. Mann, *Acta Crystallogr. A* **24**, 321 (1968).
- [17] D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
- [18] L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.* **20**, 139 (1987).
- [19] J. Donohue, *The Structures of the Elements*, Wiley, New York (1974).
- [20] R. K. Behrens and W. Jeitschko, *J. Less-Common Met.* **160**, 185 (1990).
- [21] W. Jeitschko, G. Block, G. E. Kahnert, and R. K. Behrens, *J. Solid State Chem.* **89**, 191 (1990).
- [22] U. E. Musanke and W. Jeitschko, *Z. Naturforsch.* **46b**, 1177 (1991).
- [23] H. Rassaerts, H. Nowotny, G. Vinek, and F. Benesovsky, *Monatsh. Chem.* **98**, 460 (1967).
- [24] A. Almenningen, O. Bastiansen, and M. Trætteberg, *Acta Chem. Scand.* **13**, 1699 (1959).
- [25] R. C. Lord and Putcha Venkateswarlu, *J. Chem. Phys.* **20**, 1237 (1952).
- [26] P. Pykkö and Y. Zhao, *J. Phys. Chem.* **94**, 7753 (1990).
- [27] M. A. Moss and W. Jeitschko, *Z. Metallkd.* **82**, 669 (1991).